

Title: Determination of Organic Carbon and Elemental Carbon (OC/EC) in Particulate Matter Collected on Quartz Filters		Copy No: ##
Method No.: 1.03/1.7/M	Effective Date: September 11, 2013	Location: ###

QSM Approval: _____

Determination of Organic Carbon and Elemental Carbon (OC/EC) in Particulate Matter Collected on Quartz Filters

1. INTRODUCTION AND SCOPE

- 1.1. This methodology provides procedures for the determination of organic carbon and elemental carbon in particulate matters in the ambient air collected on Tissuquartz filters using a thermal/optical carbon analyzer.
- 1.2. This methodology is used in the following projects: National Air Pollution Surveillance Network - PM2.5 Speciation project.
- 1.3. This methodology is recommended for use only by or under the supervision of analysts experienced in the use of carbon analyzer and in the interpretation of OC/EC results.

2. SUMMARY OF METHOD

- 2.1. The thermal/optical carbon analysis method is based on the preferential oxidation of organic carbon (OC) and elemental carbon (EC) compounds at different temperatures. It relies on the fact that organic compounds can be volatilized from the sample deposit in helium (He) atmosphere at low temperatures, while elemental carbon is subsequently oxidized and removed in 2% O₂ / 98% He atmosphere at higher temperature. The carbon analyzer operates by:
 - 2.1.1. Liberating carbon compounds under different temperatures and oxidation environments (see Table 1) from a small sample punch (about 0.5 cm²) taken from a quartz fiber filter.
 - 2.1.2. Converting these compounds to carbon dioxide (CO₂) by passing the volatilized compounds through an oxidizer (heated manganese dioxide, MnO₂).
 - 2.1.3. Reduction of CO₂ to methane (CH₄) by passing the flow through a methanator (Hydrogen-enriched nickel catalyst).
 - 2.1.4. Quantification of CH₄ equivalents by a flame ionization detector (FID).
 - 2.1.5. Correction for pyrolysis of organic carbon compounds to elemental carbon is accomplished by an optical manner to avoid underestimation of OC and overestimation of EC due to inclusion of pyrolyzed organic carbon. Both light reflectance from sample filter and transmission through filter are continuously monitored via a helium-neon laser and two photodetectors throughout an analysis cycle. As pyrolysis takes place there is an increase in light absorption,

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resulting in a decrease in reflectance and transmission. By monitoring the reflectance/transmission, the portion of the elemental carbon peak corresponding to pyrolyzed organic carbon can be accurately assigned to the organic fraction.

- 2.1.6. Seven carbon fractions (OC1, OC2, OC3, OC4 and EC1, EC2, EC3) as well as the pyrolyzed organic carbon (POC) are individually determined. The total OC is reported as OC1 + OC2 + OC3 + OC4 + POC and total EC as EC1 + EC2 + EC3 – POC.
- 2.2. The *DriCarb* (V6182004) program is currently used to run the analyzer. The following methods are executed during the procedure of sample analysis:
 - 2.2.1. *cmdBakeOven*: for oven bake to clean up the system free from carbon contamination.
 - 2.2.2. *cmdCalib-HeO₂* and *cmdCalib-HeOnly*: for daily system calibration with CH₄ or CO₂.
 - 2.2.3. *cmdImprove*: for routine OC/EC analysis.

TABLE 1. Experimental Conditions

Parameters	Carbon Fraction						
	OC1	OC2	OC3	OC4	EC1	EC2	EC3
Carbon fraction	OC1	OC2	OC3	OC4	EC1	EC2	EC3
Oven Temperature Range (°C)	50-120	120-250	250-450	450-550	550-550	550-700	700-800
Duration Time	Minimum 150 seconds at each fraction						
Carrier Gas	Helium				2% Oxygen in Helium		
Gas Flow Rate	50 mL/min						
Oxygenator Temperature	900 °C						
Methanator Temperature	420 °C						
FID Temperature	125 °C						

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3. METHOD DETECTION LIMIT, PRECISION and ACCURACY

- 3.1. Typical carbon values range between 5 and 100µg carbon/cm² for ambient samples. The distribution between organic and elemental carbon depends on the particulate source types, and range from no elemental carbon (e.g., hot gasoline exhaust) to 80% or more elemental carbon (e.g., wood smoke and diesel exhaust).
- 3.2. The method detection limit (MDL) is estimated from 303 lab-blank filter punches run on the instrument in 2012, and defined as three times the standard deviation of their measured results.

	TC	OC	EC
MDL (µg/cm ²)	0.55	0.53	0.04

The procedure described above provides estimates of detection limits. Sample detection limits may be better or worse than these values, depending upon a variety of sample-specific, upon the variable carbon content of the blank quartz filters as well as system performance factors. For better MDL, the unexposed filters should be pre-fired in an oven at high temperatures for several hours to remove any residual carbon contamination. Because even pre-fired filters can absorb organic vapors during shipping and storage, the MDL of analysis on a particular set filters depends on the number of field blanks analyzed and the variability in the results from those blanks.

- 3.3. The precision of this analysis ranges from 2 to 30%. Analysis of actual ambient and source filters, homogeneity of the deposit is most important for reproducible results. For homogeneous deposits containing >5 µg/cm² of total carbon, precision is generally 10% or less; for inhomogeneous deposits replicates may deviate by as much as 30%.
- 3.4. The accuracy of the method for total carbon determined by analyzing a known amount of carbon in sucrose and KHP is average 3.5%, and in NIST1649b is average 12%.
- 3.5. The method is fit for the intended use.

4. INTERFERENCES

- 4.1. Interferences in carbon analysis can be caused by the presence of carbonate carbon if it constitutes more than 5% of total carbon in the ambient sample, as it is measured as both organic and elemental carbon during thermal/optical carbon analysis. Acid pretreatment of the filter samples can eliminate the carbonate interference.

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Carbonate carbon can also be determined, if necessary, by measuring the CO₂ evolved upon acidification of the sample punch before the normal carbon analysis procedure.

A small quantity of carbonates (e.g., CaCO₃) is found in some fine particulate samples, but this is rarely comparable to the EC content.

- 4.2. The presence of some minerals can affect the laser correction for pyrolysis by changing color or changing the surface texture of the deposit residue as the sample punch is heated. In this case, the split between organic and elemental carbon should be examined manually.
- 4.3. Some colored organic compounds can affect the laser correction causing increased reflectance as these compounds are removed. This effect is readily ascertained by examining the laser response during the organic portion of the analysis. The split between organic and elemental carbon should be examined manually if the effect is large.
- 4.4. The presence of certain elements (Na, K, Pb, Mn, V, Cu, Ni, Co, and Cr), existing either as contaminants on the filters or as part of the deposit material has been shown to catalyze the removal of elemental carbon at lower temperatures. Such catalysis would affect the distribution of carbon peaks during the analysis.
- 4.5. Water vapor either contained in the deposit or remaining after acidification of the sample punch can shift the FID baseline. Allowing the sample punch to dry in the analyzer by passing carrier gases over it will eliminate this effect.

5. SAMPLE REQUIREMENT, PREPARATION and STORAGE

5.1. Filter preparation:

- 5.1.1. Tissuquartz filter papers (8" x 10") are purchased from PALL Inc. (Mississauga, ON) or equivalent suppliers
- 5.1.2. About 20 filter punches (47 mm in diameter) can be taken from each sheet of filter paper.
- 5.1.3. A batch of about 100 filters is pre-fired at 900°C for a minimum of 5 hours to remove any residual carbon contamination.
- 5.1.4. Two pre-fired filters are randomly selected and checked on the OC/EC analyzer. The pre-fired filters are accepted if the amount of total carbon residue is 15 µg / filter or less.
- 5.1.5. The pre-fired filters are wrapped (divided into a small amount, usually 4 to 5 pre-fired filters per envelop) in cleaned aluminum foil (bake in oven at 230°C

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for 5 hr) and put in sealed Whirlpak bags, labeled “PREFIRED”, the filter type, the batch, the date, and analyst initial, and distributed to the groups which are responsible for the sample collection.

5.2. Sample preparation:

- 5.2.1. The cleaned filters are loaded to a sampling cartridges and sent to field by the sample preparation lab, see “SOP 6.10/*.*S: Preparation, Shipping and Unloading of HoneyComb Cartridges” and “SOP 6.01/*.*S: Sample Management”.
- 5.2.2. The sample filters unloaded from cartridges upon receiving are stored in Petri dish at temperature between -20°C to -5°C (consult SOP 2.06/*.*S) before analysis.
- 5.2.3. One 0.5 cm² sample punch taken from a sampled filter is analyzed. The remaining filter is restored in a freezer (-20°C to -5°C) for a period of at least six months.

6. EQUIPMENT and SUPPLIES

- 6.1. DRI Model 2001 Thermal/Optical OC/EC Carbon Analyzer from Atmoslytic Inc Calabasas, CA, USA.
- 6.2. METTLER XP205 analytical balance, display to 0.01mg, for weighing samples and reagents.
- 6.3. VWR Muffle Furnace 1300GM Series, for pre-baking filters.
- 6.4. Stainless steel punching tool: ⁵/₁₆-inch diameter. This punching tool must be kept clean and sharp. The punch size should be determined when new, and whenever the punch is sharpened. Verification is performed by removing at least 7 punches from a 47-mm od quartz fiber filter (17.35 cm²). Then use ¹/₇ of the weight loss of the filter to determine the punch area, assuming that weight is proportional to area.
- 6.5. Syringes: gas-tight 100, 250, 500 and 1000 microliter (µL) syringes for instrument calibration with primary gas injections.
- 6.6. Micropipettes: 20µL and 10µL for instrument calibration with solution.
- 6.7. Tweezers (flat tip), Glass Petri dish and Kimwipes.
- 6.8. Small cooler and blue ice packs.

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6.9. Butane lighter to light the FID.

7. REAGENTS, GASES and CALIBRATION STANDARDS

7.1. The following chemicals should be analytical reagent grade or better:

- 7.1.1. Potassium hydrogen phthalate (KHP) (analytical grade), for calibration use
- 7.1.2. Sucrose (analytical grade), for calibration uses.
- 7.1.3. Manganese dioxide (MnO₂) (analytical grade), crystalline, as an oxidizer in the oxygen oven.
- 7.1.4. Nickelous Nitrate [Ni (NO₃)₂ • 6H₂O] (crystalline, analytical grade), used as a reducer in the methanator.
- 7.1.5. Chromosorb G, 60/80 mesh, used as a support for nickel catalyst in methanator. Both nickelous nitrate and this support are for preparing the reduction catalyst in the methanator.
- 7.1.6. Hydrochloric acid (HCl), 0.4 M solution (diluted from a concentrated solution, analytical grade), for use in cleaning punch and for use in carbonate analysis.
- 7.1.7. Deionized water (Milli-Q grade or equivalent).

7.2. Gases:

- 7.2.1. Helium (ultra high purity 5.0).
- 7.2.2. 5% ± 0.02% nominal Methane in Helium (primary standard).
- 7.2.3. 5% ± 0.02% nominal Carbon dioxide in Helium (primary standard).
- 7.2.4. 10% ± 0.02% nominal Oxygen in Helium (primary standard).
- 7.2.5. Hydrogen (300 cc/min, HOGEN GC300 hydrogen generator or equivalent).
- 7.2.6. Compressed air (30-lpm, AADCO737-12 pure air generator or equivalent).

7.3. Calibration standards:

- 7.3.1. 5% nominal CH₄ in He and 5% nominal CO₂ in He are used for daily instrument calibration.

The calibration gases are traceable to NIST standards. The gas is assayed for exact concentrations by the gas supplier to two decimal places. The assay value is obtained from the tag on the cylinders. For the best of accuracy, the temperature and pressure at the time of analysis need to be taken into account. For a 5% standard, it will be 0.0268 µg C per µL at STP (the Standard Temperature and Pressure).

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7.3.2. KHP and sucrose are used to check the recovery of OC when comparing to the response of CH₄ or CO₂.

To make a 1800 ppm KHP solution, the KHP is dried at 110°C for two hours before dispensing. Transfer 0.3826 g of KHP into a 100-mL volumetric flask after the KHP has come to room temperature. Refer to “SOP 2.01/.*S: Gravimetric Measurements”. Add sufficient deionized water (DIW) to the flask to dissolve the KHP. Add 0.2mL of concentrated HCl and dilute to volume with DIW. Mix the KHP thoroughly. Store this solution in a refrigerator until it is used for calibration purposes. Label the flask with the chemical name, the date of preparation, the name of the chemist preparing the solution, and the exact concentration. This solution is good for 3 months. The exact concentration can be determined by using the following relationship:*

$$\left(\frac{\text{Actual g KHP}}{100 \text{ mL}} \right) \left(\frac{96 \text{ Carbon}}{204.23 \text{ g KHP}} \right) \left(\frac{10^{-3} \text{ mL}}{\mu\text{L}} \right) \left(\frac{10^6 \mu\text{g}}{\text{g}} \right) = \frac{\mu\text{g Carbon}}{\mu\text{L Solution}}$$

The nominal 1800 ppm sucrose solution is prepared by transferring 0.428 g of sucrose into a 100 mL volumetric flask. Dilute to volume with DIW. Mix the sucrose thoroughly. Store this solution in a refrigerator until it is used for calibration purposes. Label the flask with the chemical name, the date of preparation, the name of the chemist preparing the solution, and the exact concentration. This solution is good for 3 months. The concentration is calculated by using the following relationship:

$$\left(\frac{\text{Actual g Sucrose}}{100 \text{ mL}} \right) \left(\frac{144 \text{ Carbon}}{342.31 \text{ g KHP}} \right) \left(\frac{10^{-3} \text{ mL}}{\mu\text{L}} \right) \left(\frac{10^6 \mu\text{g}}{\text{g}} \right) = \frac{\mu\text{g Carbon}}{\mu\text{L Solution}}$$

To prepare a blank solution, add 0.2 mL of concentrated HCl to a 100 mL volumetric flask and dilute to volume with DIW. This acidified DIW is made fresh each time 1800 ppm KHP stock solution is prepared.

8. CALIBRATION AND STANDARDIZATION

8.1. Analyzer Calibration:

8.1.1. Currently no primary standard (NIST traceable) exist for carbon analysis. Two solutions (KHP and sucrose) and two gases (CH₄/He and CO₂/He) are used for calibration and system audit purposes.

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- 8.1.2. Full scale calibration using both gas and solution is performed every six month or whenever necessary to ensure the efficiency of the system. Single point solution calibration (KHP-5 µL or sucrose-5 µL) is performed every week. One point gas calibration (1000 µL 5% CH₄/He or 5% CO₂/He) is performed at the beginning of the day and at the end of day.
- 8.1.3. A 1000 µL 5% CH₄/He standard is injected by instrument program automatically at the end of each sample run. This acts as an internal standard to check any drift that may be with the FID response and for the conversion of integrated peak counts to µg of carbon for each peak in the thermogram. All FID readings during the analysis run are normalized to this peak to minimize the effects of FID performance and electronic drift over time. Integrated calibration peak counts should be checked by the operator immediately after each run and make sure the calibration peak area counts are greater than 20,000.
- 8.1.4. To perform full scale calibration using gas standard - Execute *cmdCalib* protocol from the analysis screen. Inject known volumes of CH₄/He or CO₂/He standard with a gastight syringe. Volume of injection depends on the range of carbon desired relative to the sample carbon. Injection volumes are 100, 250, 500, 750 and 1000 µL. At the end of the run, note the peak area counts. Regress the ratio of the integrated sample peak counts to the internal calibration peak counts against microgram of carbon to obtain the calibration slope and intercept. For the best accuracy, the temperature and pressure at the time of calibration need to be taken into account. For a 100% CH₄ or CO₂ standard at 760 mmHg at 20°C, each µL = 0.499 µg carbon. For a 5% standard, it will be 0.02495 µg carbon/µL at standard temperature and pressure (STP; 20°C, 760 mm Hg). The Ideal Gas Law should be used to correct for the temperature and pressure of the laboratory.

$$\text{Actual } \mu\text{g C per } \mu\text{L} = \left(\frac{P}{760}\right) \left(\frac{1}{T + 273.15}\right) \left(\frac{1}{0.08206}\right) \times \% \text{ of cal gas} \times 12$$

where P is pressure in mmHg, T is ambient temperature.

- 8.1.5. To perform full scale calibration using KHP and sucrose standard solutions – Execute *cmdOvenBake* protocol with the filter disc in the oven to ensure that a clean disc will be used for loading the standard solution. Then execute the *cmdImprove* protocol. First, test the blank solution (5 µL dilute HCl which is used to make up the KHP solution), then load the calibration solutions (volumes loaded onto the filter disc for calibration are 5, 10, 15 and 20 µL). Execute a purge step at a rate of 1 min for every microliter solution loaded. Regress the ratio of the integrated sample peak counts to the internal calibration peak counts against microgram of carbon to obtain the calibration slope and intercept which

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should match up with the gas calibration closely. Significant deviation will indicate problem with the catalysts or a deteriorated standard.

- 8.1.6. The calibration slopes derived from the two gases and KHP- and sucrose-spiked filter punches are averaged together to yield a single calibration slope for a given analyzer. Calibration values are plotted as actual µg carbon vs. the ratio of the integrated sample peak counts to the calibration peak counts. Obvious outliers are identified and rerun. Linear regression is performed on each set of calibration data (separate calculations for KHP, sucrose, CH₄/He, and CO₂/He).

The slope (m) is calculated from:
$$m = \frac{\sum(y_i x_i)}{\sum(x_i)^2}$$

Where: x_i = ratio of (injected carbon peak area) to (calibration peak area)
 y_i = calculated carbon in spiked filter or manual injection (µg)

The correlation coefficient (r²) of the regression line for calibration curve must be greater than 0.98. The calibration slopes determined by these four compounds historically differ by less than 5% on a given analyzer if sufficient care is taken during the calibration procedure.

- 8.1.7. *Note that the current calibration procedure is based only on the total carbon; currently no routine procedure exists to check the accuracy of the OC/EC split.*

8.2. Typical Accuracy of Calibration Standards:

- 8.2.1. The accuracy of the calibration standards is primarily limited by the accuracy of the calibration gas assays and by the accuracy of the preparation of the KHP and sucrose solutions. The resulting calibration slopes determined by these four materials is compared to previous calibration results. New values should be no more than ±10% different than previous calibrations if no major analyzer changes have been made. If variation is >10%, calibration must be redone to verify values.
- 8.2.2. One point gas calibration (1000 µL 5% CH₄/He or 5% CO₂/He) is performed at the beginning of the day and at the end of day. The manual calibration injections serve to verify proper analyzer performance. The procedure for manual injections is described in Section 9.2. The calibration peak counts should be above 80% of the peak counts from end-of-run internal calibration, If the calibration result is unsatisfactory, follow the steps below until a satisfactory result is obtained:
1. Repeat the calibration using the same calibration gas under a He only atmosphere.
 2. Perform a full “Leak Test” as described in Section 9.1 in order to determine if a gas leak exists.

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3. Repeat the calibration using the same calibration gas but under a He/O₂ atmosphere.
4. Repeat the calibration using the other calibration gas under a He/O₂ atmosphere.
5. If the calibration still does not pass, consult the laboratory supervisor for instructions.

9. ANALYSIS

9.1. Analyzer Start-Up

- 9.1.1. Check pressures of all the gas cylinders; cylinders with gas pressure less than 300 psi should be replaced before beginning the day's analysis.
- 9.1.2. Check that all gas delivery pressures are correct.
- 9.1.3. If the instrument was shut down, increase the H₂ flow to the higher setting posted on the rotameter (~4.4). Wait for several minutes for the adjustment to be stabilized. Ignite the flame with a butane lighter. A light pop indicates that the flame is lit. Check that the FID is lit by holding a pair of tweezers over the FID exhaust stack and watching for condensation. Allow at least 10 minutes at the high gas flow to pass before returning the H₂ rotameter to its correct (lower) rotameter setting.
- 9.1.4. Check all gas flows at the analyzer. The correct readings are posted on each rotameter. Read through the center of the ball. If drastic deviations are noted, momentarily stop the flow by closing the shut-off toggle to check if the ball is stuck. Otherwise, verify that the delivery pressure is correct. A significant drop in the rotameter ball reading may be due to a leak ahead of the rotameter inlet, or a restriction downstream of the outlet. In either case, the problem will appear as a failure to increase the flow rate at the rotameter.
- 9.1.5. Click the *DriCarb* shortcut icon to begin the carbon program. Make sure that the analyzer's multi-function *switch* (at the left of the front panel) is at 'auto'.
- 9.1.6. Perform a leak test on the system. Be sure the breech is closed before performing test. Flip down Outlet Furnace Oven Toggle Valve, wait until pressure in the oven raises up to ~5 psi, flip down Inlet Oven Toggle Valve, observe the oven pressure (no changes in pressure value has to be occurring during 30 sec.). When the system leak checks are satisfactory; open the oven outlet toggle valve then inlet toggle valve to re-establish gas flow (at least 2 min).
- 9.1.7. Execute an oven bake procedure by selecting *cmdOvenBake* command and hit the *Run* button. Repeat the procedure until the calculated carbon concentrations is no more than 0.2 µg total carbon for system blank.

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9.2. Routine (Every Day) OC/EC Analysis

- 9.2.1. Select *cmdCalib-HeO₂* to begin morning calibration. Select either CH₄/He or CO₂/He calibration gas type as the same gas used the previous afternoon (check the analyzer logbook). For any given day, one gas will be used in the morning and the other in the afternoon. By using the same gas in the morning as was used the previous afternoon, the calibration gas used in the morning will be rotated on a regular schedule.
- 9.2.2. Inject 1000 µL of calibration gas. When the analysis is complete, check the tabular and graphical printouts and record calibration peak count in the logbook. If the calibration result is satisfactory, proceed with sample analysis.
- 9.2.3. Take out samples to be analyzed from freezer and store in a Styrofoam cooler with blue ice packs. Record the sample ID in the logbook.
- 9.2.4. Select the analysis protocol such as *cmdImprove* from the main screen and enter the information fields such as sample ID, etc. Enter any analysis flag options. A list of valid choices is presented on screen. Answer the purge question. The sample oven must be purged with He for at least 90 seconds to remove all oxygen before the analysis begins.
- 9.2.5. You will be prompted on loading a sample punch and subsequent steps.
- 9.2.6. Ensure that the glass petri dish, tweezers, and punching tool are thoroughly wiped clean with clean KimWipes.
- 9.2.7. Remove the filter from the PetriSlide or petri dish with tweezers, handling the filter only by the edge. Place the filter on the glass petri dish and remove a sample punch by pushing down gently on the punching tool. Rocking the punching tool slightly will ensure that the punch is completely severed. Try to remove the punch from the edge of the deposit to avoid wasting the filter, but try to avoid areas of non-uniform deposits. Leaving the sample punch in the punching tool, place the punching tool on a clean Kimwipe. Return the filter to the PetriSlide or petri dish.
- 9.2.8. Remove the sample disc from the punching tool by grasping the bottom edge with the tweezers. Place the punch in the sample boat, and gently push the edge of the sample disc until it is seated in the well of the boat.
- 9.2.9. Reply the prompts in the analysis screen and analysis will proceed automatically.
- 9.2.10. Wipe the tweezers, glass petri dish, and punching tool with clean Kimwipes.
- 9.2.11. Return the sample PetriSlide or petri dish into the Styrofoam cooler.
- 9.2.12. At the end of the program, data is saved to the hard drive, split times are calculated, carbon peaks are integrated and tabulated and graphical printouts are produced. The sample boat will retract to the 'Calibrate' position when it is sufficiently cooled by the fan.

9.3. Analysis with Carbonate Removal (by request)

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- 9.3.1. Routine analysis procedures depend on whether or not carbonate carbon will be determined before OC/EC analysis. The procedures are different for these two options. Currently, routine analysis does not involve carbonate analysis unless requested by the client.
- 9.3.2. The analysis with carbonate removal is identical to the routine procedure except that the sample disc will be acidified with 20 µL of 0.4N HCl injected through the septum port when the boat is in the 'Calibrate' position. You need to execute a Purge time of ~20 min. (1 min or more for every microliter of liquid) to allow the sample to dry before the run starts.

9.4. Analyzer Shut-Down

- 9.4.1. Leave the last analyzed punch in the boat with the boat in the 'Calibrate' position (use for system blank checking or solution calibration next time).
- 9.4.2. Perform end of the day calibration gas injection routine.
- 9.4.3. When the analysis is completed, record the calibration peak counts. Any values outside the ranges should be investigated and rerun. Because low values from the end-of-day calibration could potentially invalidate the entire day's runs, any deviation (for example: calibration peak area < 20000 µV/sec; Internal calibration peak smaller than calibration peak of manually injection of calibration gas) from the accepted ranges must be noted and must identify the cause.
- 9.4.4. Turn off the following gases: He1, He3 and Cal gas in order to minimize the operation cost.
- 9.4.5. Close the software program.

9.5. Data Processing

- 9.5.1. At the end of the run, both tabular (carbon concentration) and graphical (thermogram) printouts will be saved in *output* data directory which is in D drive of the computer. The raw data will be also saved in D drive under the directory *rawData*.
- 9.5.2. Examine the tabular to insure the calibration peak counts are within specifications. The calibration peak counts should be consistent throughout the same batch.
- 9.5.3. Examine the *thermogram* for proper laser response, temperature profiles, realistic carbon peaks, and the presence of the calibration peak at the end of the analysis.
- 9.5.4. Mark the analysis date on the sample analysis list.
- 9.5.5. If a problem is found, indicate the problem in the analyzer logbook and rerun the sample. Repeat the above steps for additional sample run.

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9.6. Data Storage and Handling

- 9.6.1. After the measurements and reprocessing of the samples are completed, back up all data files from the laboratory computer to sever computer "LabOCEC\$ on ncr.int.ec.gc.ca\lab\riv\atsdata".
- 9.6.2. Make sure all the files are copied properly
- 9.6.3. Use Excel to prepare a final report. After approval of results by lab supervisor, send the data report to sever computer "Fin_rep_atu on Ncr.int.ec.gc.ca\Lab\Riv".

10. CALCULATION OF RESULTS

10.1. The results of carbon analysis are calculated from the area count of each peak (mv-secs) and then converted to the mass of carbon using the calibration slope and the internal calibration counts. This process is performed by the computer at the end of the analysis program. The units in the output file are given in $\mu\text{g C/ cm}^2$ and/or $\mu\text{g C/ filter}$. The $\mu\text{g C/ filter}$ unit is used in the client report.

10.2. The equations used are the following:

$$\mu\text{g C/cm}^2 = \left(\frac{\text{Integrated Peak Area}}{\text{Internal Calibration Peak Area}} \right) \left(\frac{\text{Calibration Slope}}{\text{Punch Area}} \right)$$

$$\mu\text{g C/ filter} = (\mu\text{g C/cm}^2) (\text{Filter Deposit Area})$$

where
 Peak Area is in mv-secs
 Calibration Slope is ($\mu\text{g C / peak ratio}$)
 Punch Area is in cm^2 (0.526 cm^2)
 Deposit Area is in cm^2 (10.752 cm^2)

11. QUALITY CONTROL

11.1. Performance Test

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- 11.1.1. System blanks are tested at the beginning of sample analysis every day to ensure the system is not introducing bias in the carbon results and to ensure that the laser signals are not temperature dependent.
- 11.1.2. Lab blanks are tested for every batch.
- 11.1.3. Field blank are tested when received from sample preparation lab.
- 11.1.4. The calibration peak at the end of each analysis run serves as a regular standard and the integrated area under the calibration peak serves as a measure of analyzer performance. In addition, the daily injections of two calibration gases further serve as standards. Finally, weekly 1-point check (solution standard) and semi yearly full scale calibration (both gas and solution standards) are executed to ensure that the instrument is in good condition.
- 11.1.5. Primary standards in the form of NIST-traceable spiked filter punches do not exist.
- 11.1.6. Syringe used for gas calibration and micropipette used for solution calibration are validated every year. Refer to "SOP 19.02/*.*S: Volumetric Measurement - Micropipettes and Bottle-top Dispensers". The % uncertainty for 1.0 mL syringe (Pressure Lok Series A) is estimated as 0.82%, while the % uncertainty for the micropipette (Eppendorf 2-20 µL) is 2.85% and for the micropipette (Eppendorf 0.5-10 µL) is 2.77% .
- 11.1.7. Proficiency test is carried out twice a year by executing intra-lab comparison both between technicians and between instruments.

11.2. Reproducibility Test

- 11.2.1. At least one duplicate is performed per sample sequence. The duplicate is selected randomly and run as the last sample of the day. The µg/filter values for OC, EC, and TC are compared with the original run. The values should fall into the following criteria:

For homogeneous deposits containing >5 µg/cm²

- TC < 20% of average of the 2 values
- OC < 20% of average of the 2 values
- EC < 30% of average of the 2 values

For inhomogeneous deposits replicates may deviate by as much as 30%. This precision is also influenced by the filter loading and source type.

- 11.2.2. Cross instrument testing is carried out once every week. At the end of the sequence, instead of running a duplicate on the same instrument, the duplicate is performed on the other instrument.

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12. MEASUREMENT UNCERTAINTY

12.1. Estimation of Measurement Uncertainty

12.1.1. Refer to SOP 2.10/*.*/*S for the detailed estimation approach.

12.1.2. The uncertainty sources of method and QC data used for uncertainty estimation are sample deposit homogeneity and precision of duplicate runs.

12.1.3. The estimated uncertainty (expended %RSD of duplicates) of the measurement:

	TC	OC	EC
U%	20	20	30

13. MAINTENANCE

13.1. Regular maintenance for the analyzer includes daily checking of compressed gas supplies, cleaning the punching tool and tweezers between each sample with clean KimWipes (Kimberly-Clark Corporation), and backing up data files on a daily basis. Check and clean O-rings and joints if required. Replace push-rod ferrule if necessary. Checks of laser adjustments (physical and electrical) are made if necessary. Calibrate instrument as required. All calibrations and repairs must be recorded in the logbook.

14. APPLICABLE SOPs

SOP 2.01/*.*/*S	Gravimetric Measurements
SOP 2.06/*.*/*S	Laboratory Refrigerators
SOP 2.10/*.*/*S	Estimation of Uncertainty in Chemical Analysis
SOP 6.01/*.*/*S	Sample Management
SOP 6.10/*.*/*S	Preparation, Shipping and Unloading of HoneyComb Cartridges
SOP 19.02/*.*/*S	Volumetric Measurement, Micropipettes and Bottle-Top Dispensers

15. REFERENCE

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DRI Model 2001 OC/EC Carbon Analyzer Instruction Manual, Atmoslytic Inc., 2002

DRI SOP for “Thermal/Optical Reflectance Carbon Analysis of Aerosol Filter Samples”, Desert Research Institute, 2000

“The DRI Thermal/Optical Reflectance Carbon Analysis System Description, Evaluation and Applications in U.S. Air Quality Studies”, Chow, J.C., Watson, J. G., Pritchett, L. C., Pierson, W. R., Frazier, C. A., and Purcell, R. G. *Atmos. Environ.* 27A:1185–1201, 1993

16. REVISIONS

Nov. 2005: Author: Luyi Ding; New document

March 2006: A new Section 8.2.2 is added.

May 2006: In 5.2.1, added “ and SOP 6.01/*.*S: Sample Management”.
 In 7.3.2, added “Refer to “SOP 2.01/*.*S: Gravimetric Measurements”.
 In 8.1.2, added “or sucrose-5µL”.
 Added two new sections: “11.1.6” and “11.1.7”.
 In section 14, added “SOP 2.10/*.*S: Estimation of Uncertainty in Chemical Analysis”.

Nov. 2007: In section 2, table1, changed fraction temperature from value to range;
 In 7.3.2, added “To make a 1800 ppm KHP solution,”;
 In 6.2, balance changed to “XP205 analytical balance”;
 Rewording 8.1.3, 8.1.4, 8.1.5, 8.2.1 and 8.2.2 to better suit application;
 In 9.6.1, added “and sever computer LabOCEC\$ on etc08;
 In 10.1, added “This process is performed by the computer at the end of the analysis program.”;
 In 11.1.1, added “System blanks are tested at the beginning of sample analysis every day”;
 In 11.1.6, added “and for the micropipette (BIOHIT 0.5-10 µL) is 6.29% at 95% CL
 In 11.2.1, added “For homogeneous deposits containing >5 µg/cm²” and “For inhomogeneous deposits replicates may deviate by as much as 30%. This precision is also influenced by the filter loading and source type”;
 In 13.1, deleted “Additionally, all repairs must be recorded in the maintenance logbook.”.

Dec. 2007: Modified sections 8.1.4, 8.1.6 and 8.2.1 to include the fit acceptance criteria for the calibration curve.

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Updated references to SOP 2.02/*.*S to 19.02/*.*S.

- Dec. 2009: In section 5.1.1, added “or equivalent suppliers”.
 In section 5.1.3 changed “900°C” to “500°C”.
 In sections 6.5, 6.6, 7.1, and 7.2, removed references to specific suppliers and added detailed specifications for chemical and gas requirements.
- Sep. 2011: In section 3.2, MDL was reassessed using 366 lab-blanks ran in 2010.
 In section 3.2, accuracy was reassessed using sucrose, KHP and NIST1649.
 In section 5.1.3, changed “500°C” to “900°C”.
 In sections 6.3, replaced furnace brand to VWR Muffle Furnace 1300GM.
 In section 6.5, added 100, 250 and removed 2500.
 In section 7.2.5, replaced hydrogen generator brand to HOGEN GC300.
 In section 8.1.4, injection volumes changed to 100, 250, 500, 750, 1000 µL.
 In section 11.1.6, reassessed uncertainty of syringe and micropipette.
- Aug. 2013: In section 2.1.6, added “The total OC is reported as OC1 + OC2 + OC3 + OC4 + POC and total EC as EC1 + EC2 + EC3 – POC”.
 In section 3.2, MDL was reassessed using 303 lab-blanks ran in 2012.
 In section 7.3.2, added “This solution is good for 3 months”
 In section 8.1.6, added “The calibration slopes determined by these four compounds historically differ by less than 5% on a given analyzer if sufficient care is taken during the calibration procedure.
 In sections 9.6.1, removed “analyst’s computer and DVD backup”.

Reviewer: Luyi Ding **Date:**
Title: Chemist, Air Toxics Unit, AAQS, AQRD

Approved By: Daniel Wang **Date:**
Title: Project Scientist, Air Toxics Unit, AAQS, AQRD

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