Standard Operating Procedure (SOP) For the Analysis of Organic and Elemental Carbon (OC/EC) Using the Sunset Laboratory Semi-Continuous Carbon Aerosol Analyzer

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Sunset Laboratory Inc.

Sunset Laboratory Inc.

10160 SW Nimbus Avenue
Suite F-8
Portland, Oregon 97223

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I Scope and Applicability

This SOP describes the analytical method to determine the levels of organic and elemental carbon in particulates collected using the Sunset Laboratory semi-continuous carbon aerosol analyzer (RT-OCEC). The particulate samples are collected by the instrument using a predetermined sample schedule and analyzed by a thermal/optical method. Time resolution of 30 minutes to 8 + hours are possible.

II Summary of Method

A quartz filter is mounted in the quartz oven and samples are collected for the specified time. After the sample is collected, the system closes off the sample port, purges the analytical flowpath with helium and performs the thermal/optical analysis. The thermally removed carbon components are converted to CO_2 which is subsequently measured by non-dispersive infrared (NDIR). External sucrose solution and methane gas carbon standards are used for NDIR calibration. Correction for the pyrolytically generated carbon (char) that sometimes forms during the first stage of the analysis is based on filter absorbance measurements. The pyrolysis step is facilitated using a laser absorbance technique.

III Working Definitions

Organic Carbon (OC) - Optically transparent carbon removed (through thermal desorption or pyrolysis) and char deposited when heating a filter sample to a preset maximum (840 °C) in a non-oxidizing (helium) carrier gas.

Elemental Carbon (EC) - Carbon (e.g., in soot particle cores) that can only be removed from the filter under an oxidizing carrier gas (He/O_2). Optically absorbing carbon removed at high temperatures (e.g. 850 °C) in a non-oxidizing carrier gas when internal (sample matrix) oxidants are present.

IV Health and Safety Warnings

The Sunset Laboratory Thermal/Optical Carbon Analyzer uses high temperatures (up to 870°C) and laser radiation to perform the required steps in this analytical procedure. Under normal operation, the analyst is protected from exposure to these energy sources. However, during repair or trouble shooting, when the instrument cover is removed, the analyst must take the following precautions:

a) Before attempting any repairs, turn off the power and wait for all heated zones to cool.

b) For most repair work, unplug power to the ovens and avoid contact with any power sources in the oven cabinet.

c) Although the laser source has an interlock protection system, if the interlock is overridden, direct exposure to the laser can occur under certain conditions. Do not look directly at the laser source as permanent eye damage can occur.

d) Use caution when handling all support gas cylinders and regulators. Always have cylinders properly chained to a safety rack.

V Procedure

a) General Instructions

See the attachment – "Installation Notes" for basic installation and operation procedures

b) Samples

The analyzer is deployed to the field site. It collects airborne particulate samples on an internally mounted filter and analyzes the sample on a semi-continuous basis. There is no option for replicates without a second sampler. Sample data are stored in raw data files. Additionally, a short result file is printed to a file at the end of each analysis. An optional output can also be transmitted to a data logger equipped with a serial input. The data should be considered irreplaceable and should be backed up on a frequent basis to some sort of permanent media such a CD rom or tape.

c) Materials

See Table 1 for all required reagents and gases. Check the labels carefully to ensure that they are not expired and are of the proper purity/grade. Document the supplier, grade/purity and Lot No. as appropriate on the Analysis Data Form.

Table 1. Materials

Material	Use
UHP Helium (99.999%)	Carrier gas
Helium/Oxygen Mix (10% O_2; balance UHP He)	EC oxidant carrier gas
Helium/Methane (5.0% methane; UHP He balance)	External standard gas
Sucrose (99.9% reagent grade)	Analytical standard

d) Equipment

See Table 2 for all required major pieces of equipment. Check calibration of all equipment requiring calibration to ensure that it is current.

Table 2. Equipment

Equipment	Use
Forceps	Filter installation
Clean quartz filters	Work area preparation
Filter punch tool (1.6 cm diameter circle)	Preparing sample filters
Filter removal tool	Periodic replacement of filters
10 µl analytical syringe	Calibration
Volumetric Flasks, Class A.	Standard preparation
Analytical balance	Standard preparation

e) Sample Collection and Analysis Procedure

This procedure includes default instrument setup, standards preparation as well as general operation of the Sunset Laboratory RT-OCEC analyzer. It is assumed that the analyst has experience with the routine operation of the instrument.

i) OC/EC instrument startup - Setting up for data collection

(1) Check cylinders for sufficient volume and pressure.
(2) Turn ON computer be sure that the serial port cables are installed correctly and the software configured correctly.
(3) Turn on both switches on the back of the instrument.
(4) Start the RT Program by double clicking
(5) Make sure the computer and instrument CPU link up. Note the temperature boxes and the flows on the flow table. They should start changing as the instrument stabilizes after startup.
(6) Check the instrument gas flows on the table to be sure they are stable.
(7) Check the instrument pressure to be sure it is normal (0.5 to 1.5 psi; instrument dependent)
(8) Install new filters if necessary.
(9) Run a “CLEAN OVEN” procedure from the Pull down menu if a new filter has been installed.
(10) Enter a sample name.

(11) Select the proper parameter file to be used for analysis. By default it is "rtquartz.par".

(12) If you desire the raw data to go into an automatically generated file each day, the default ending of "\" is already selected. To have the data go into a file of another name, type the name of the file after the "\" already there. Be sure and end the filename with the extension "txt"(example: yourfilename.txt)

(13) Determine how the instrument will be cycled; either by sampling for a fixed time followed by the analysis; or by starting sampling times and pre-determined times and lengths from an external file.

(14) Make sure the Cycle Box is checked for continuous operation.

(15) Click on "Start"

VI Calibration and Audit Procedures

Calibration and Audit procedures are related in that each is designed to check the instrument performance. Calibration measurements are performed to set up critical instrument performance parameters while Audit measurements are more routine measurements performed to assure the instrument is operating within a desired specification. Many of the techniques and procedures are similar.

i) Test Equipment and Materials

(1) Preparation of Carbon Standard Stock Solution

(a) Weigh 10.00 ± 0.01 g of sucrose on the analytical balance and quantitatively transfer it into a 1 liter volumetric flask. Dissolve in and dilute to volume with DDi H_2O. Record in the laboratory notebook. This will serve as the general QA/QC performance standard. Concentration = 4.207 µg C/µl solution. Note the date and replace every 6 months. Pour about 20 mL of the standard into a clean glass vial (with Teflon cap liner) and place the rest in the refrigerator.

(b) For a "low-level" working standard, make a 1 to 4 dilution in a volumetric flask with DDI H_2O. This solution has 1.05 µgC/µl of solution and is used for the lowest concentration standard of a multi-point calibration. Note the date and replace every 6 months. Pour about 20 mL of the standard into a clean glass vial (with Teflon cap liner) and place the rest in the refrigerator.

(2) External Standard

The external standard is the mixed helium/methane cylinder noted in Table 1. Methane in a sample loop is automatically injected at the end of every analysis. The analytical result is normalized to the response of the methane standard to adjust for slight variations in flow rates that might occur during the day. At 760 torr and 298 K, a 5.00% methane in helium mixture contains 24.54 µg of carbon per ml of gas.

(3) Basic Performance Calibrations

The Sunset Laboratory OC/EC instrument is calibrated during the initial installation using a multipoint external standard calibration. The external standard calibration is used to determine the carbon in the external standard gas loop. The external standard carbon content is dependent on the volume of the loop (nominally 0.8 ml) and the concentration of methane in the methane/helium tank standard. Once the standard loop carbon in determined, a parameter file is set up containing (among others) three calibration parameters; 1) the measured deposit area, 2) the calibration constant which is the number of µg carbon in the loop specific to the cylinder of helium/methane mix provided at the site, and 3) the transit time which is the time required for methane generated from a sample to reach the NDIR. These parameters are often stable for many months. External standards should be run according to program requirements with results monitored on a control chart. See sections on Acceptance Criteria and Remedial Action when the external standard responses fall out of accepted range.

(a) External Standard Loop Calibration using the stock sucrose solution

(i) Punch out three new, clean 16 mm diameter filter sections of quartz filter with the circular filter punch.

(ii) Insert 2 of the filters in the oven as required for a normal analysis cycle. Place the third filter horizontally in the quartz tube insert as close to the end as possible so that it will be in close proximity to the 2 vertically mounted filters. Re-install the insert and photodetector as required for a normal analysis.

(iii) Go to the “Run” Pull-down Menu and left-click on the Clean Oven cycle to completely clean the filter punches.

(iv) Wait for the instrument to complete the clean cycle and the status window to read “Safe the put in a new Sample”

(v) Expand the lower status window to full screen and check the “QAQC Peak Performance” Box. This will set the back oven to a constant value during the calibration testing. You will be asked to verify this setting each time you run a sample.

(vi) Go to the top Start Window and un-check the “Cycle” box and set the sample time to “0”.

(vii) Go to the “Parameter File” field and select sucrose-TC.par from the PAR folder.

(viii) Using the precision syringe, measure a sample volume of from 5 - 10 µl of the standard carbon (sucrose) solution.

(ix) Remove the photodetector head and slide out the quartz insert.

(x) Carefully apply the solution on the filter suspended in the quartz insert. Re-install the quartz insert and photodetector promptly. Use caution so as not to contaminate the insert or quartz filter. Record the exact volume of the aliquot in the log book.

(xi) Go to the user interface field that is labeled “Output Raw Data file” and type a new name for the raw data file.

(xii) In the "Sample ID" field in the top "Start" window, type in the expected carbon loading.

(xiii) Start the analysis. Wait for the instrument to run through its analysis protocol and return to the Idle mode and safe to put in a new sample.

(xiv) Analyze a range of samples as required for the calibration. A typical multi-point calibration for ambient filters would include;

1. A 10 µl sample from the "low-level" working standard yielding 10.5 µg carbon.
2. A 5 µl sample from the standard carbon stock solution yielding 21.03 µg carbon.
3. A 10 µl sample from the standard carbon stock solution yielding 42.07 µg carbon.

(b) **External Standard analysis using a fix volume standard gas injection.**

(i) Check the OC/EC oven to determine if the temperature is cool enough to insert a sample. (Flashing green screen section on the computer monitor).

(ii) Expand the lower status window to full screen and check the "QAQC Peak Performance" Box. This will set the back oven to a constant value during the calibration testing. You will be asked to verify this setting each time you run a sample.

(iii) Go to the top Start Window and un-check the "Cycle" box and set the sample time to "0".

(iv) Go to the "Parameter File" field and select cal-injection.par from the PAR folder.

(v) Go to the "Sample ID" field in the top and type in 1.0 ml cal gas sample.

(vi) Go to the lower status window and check the "Valve Values Table" checkbox.

(vii) A new window will pop up with the gas flow controls present. Check the "Override flows" box at the lower right of the panel. Highlight the bottom right number (Default = 5) for the flow rate of the Cal Gas. Change the value to 25 and wait for the new flow setting to stabilize.

(viii) Using a 1.0 ml gas tight syringe, collect a cal gas sample from the back "Cal Gas Vent" port.

(ix) Start the analysis. Wait for the Analyze mode and the temperature to stabilize. Inject the gas sample in a steady single motion in 1 – 2 seconds. Leave the syringe in the septum until the peak has finished eluting then remove the syringe and wait for the analysis to finish.

(x) Calculate the result and verify that the carbon measured is within (±) 5.0% of the expected total carbon.

(xi) Calculations:

Total Carbon (ugC) = (mls inj) x (% methane/100) x 12 x (P/RT)

Where: P/RT = pressure (atm) / (.082 x Temp (K)

VII Data Analysis - Calculations

a) The Sunset Laboratory OC/EC Analysis Program is used to calculate the results from a sample set after the data are stored under the base file name. The OC/EC calculation program is initiated by clicking on the icon. The program then asks for the file name to perform calculations. In general, the following software parameters apply to all calculations;

b) The overall carbon response is based on a multi-point external calibration.

c) The external methane standard for every cylinder is calibrated against the external multi-point calibration.

d) The external methane standard is run at the end of every sample. This known amount is used to normalize the response factor for each sample. This essentially cancels out small drifts in detector response over time.

e) The software determines an initial NDIR response baseline prior to the desorption. The area at each point along the thermogram curve minus the baseline is multiplied against the calibration response to determine the carbon. The data are summed over the range to yield the total carbon results.

f) The automated OC/EC split point is calculated from where the laser absorbance in the oxidizing phase of the EC analysis matches the initial absorbance measured when the sample was first inserted into the oven. Carbon observed before the split point is considered oganic carbon and carbon after the split is considered elemental carbon.

g) The analyst has several options in computing the results from a set of experiments. These should be exercised with caution based on the extent of the analyst's experience.

h) The analysis program can batch process all of the sample data sets in a file without further review. It is recommended that the analyst study each individual data set as it is processed to look for any anomalies.

i) During the processing, the analyst can calculate carbonate (if evolved as a single peak) by using the manual integration feature in the program. This must be performed by setting the left and right cursors on the beginning and ending points of the carbonate peak. When re-integrating, the program draws a baseline between the designated points and calculates the peak area. The program will then automatically call this area carbonate and subtract it from the initial area for organic carbon (which includes carbonate, if present). There is no option for validating the presence of carbonate (as there is with integrated sample filters) because all of the sample is consumed during the analysis.

j) If necessary, the OC/EC split point can be manually set (reassigned) by moving the cursor to the desired point. The software will calculate the split based on that point. This decision is based on the analyst's experience and information about the sample.

VIII Results

a) The analysis software automatically stores the data in a spreadsheet format for compilation. The spreadsheet format is illustrated in Attachment B. The data for each sample may also be printed in graphic form with the temperature, laser absorbance, and

NDIR profiles. The net results are tabulated and a line is provided for the analyst's signature. An example of this results output is provided in Attachment C.

Table 4. Acceptance Criteria

Parameter	Number	Limit
Single point external standards	1 per week	Calculated ± 5.0 %
Instrument blanks	1 per week	Value ± 0.3 µg C
Multipoint external standard set	1 per 100 samples	Calculated ± 5.0 %

IX Remedial Action

a) External standard out of range - carefully prepare and re-run two standards. If standards are still uniformly out range then;
- i) Check gas flows
- ii) Check for leaks
- iii) Check system temperatures
- iv) Re-make stock solution. Re-run samples
- v) Perform multipoint calibration and update calibration parameter file

b) System blanks too high
- i) Check for leaks
- ii) Check system pressure
- iii) Check oxygen trap
- iv) Check gas lines to be sure no Teflon is used

c) External methane standard out of range
- i) Check carrier gas flow rates. Recalibrate if necessary
- ii) Check system pressure
- iii) Check for leaks

X Instrument/Equipment Inspection, Testing, and Maintenance

a) Routine instrument inspection
- i) Check cylinder pressures - replace as necessary
- ii) Observe oven pressure - check for leaks if out of typical range (1.0 - 1.7 psi).
- iii) Observe standby temperatures of back oven and methanator oven prior to startup. If out of range, determine cause and initiate repair.
- iv) Check gas flows on computer output and verify that they are within required set points. If out of range, look for system leaks. Repair or adjust as necessary.

b) Testing
- i) Daily
  - (1) Check instrument for error flags showing hardware problems.
- ii) Weekly
  - (1) Run calibration check
  - (2) Replace sample filters
  - (3) Check Gases

iii) Monthly
   (1) Replace denuder filters
   (2) Clean Cyclone
iv) Semi-annual
   (1) Re-calibrate flow sensors using NIST traceable calibration source.

c) Maintenance

i) The instrument requires virtually no routine maintenance over extended periods of time. Breakage or failure can occasionally occur with the components described below. If breakage or failure occurs, components should be replaced as necessary with replacements from Sunset Laboratory. Sunset Laboratory has Power Point presentations available for many of the typical maintenance repair procedures.

ii) Replacement of quartz oven - the quartz oven/MnO_2 converter almost never fails except in the case of operator breakage or development of cracks. If this occurs, the oven will have to be replaced. Begin by cooling the oven to ambient and shutting off all gas flows. Unplug all electrical power. Begin disassembly by removing the thermocouple, photodetector and top cover. Next, carefully remove all insulation from the oven area. Disconnect the heating coils and carefully unwrap them from the oven assembly. Remove the top oven supports and lift out the oven. Remove the thermocouple from the back of the instrument. Remove the desorption oven thermocouple by disconnecting the Swagelok fitting. Replace in reverse order using care in installing the oven thermocouple, heating coils and insulation. Once installed, re-start gas flows to purge with helium and initiate startup sequence in the software.

iii) Replacement of heating coils - heating coils will occasionally burn out. When this happens, they will have to be replaced. Follow the replacement steps for the appropriate component above (Maintenance, Steps 1 and 2) until the coil can be removed. Replace with Sunset Laboratory replacement part. Assemble in reverse order.

XI References

a)NIOSH Method 5040 (1998), In *NIOSH Manual of Analytical Methods (NMAM)*, 4th ed., 2nd Supplement, ed. Cassinelli M.E., O'Connor P.F. [Supplement to DHHS (NIOSH) Publication No. 94-113]

b)M. E. Birch, *Analyst* (1998), **123**:851-857

c)M. E. Birch, R. A. Cary (1996) *Aerosol Science and Technology*, **25**:221-241

d)Cass, et. Al.

XII Revision History

XIII Attachments

A. Sample Temperature Parameter File

```
' NIOSH 5040.par   quartz filter analysis profile
' Parameter file for Sunset Lab
' analyzes for organic and elemental carbon
' mode <comma> time <comma> temperature
' purge for 10 sec with blower off.
'
Helium, 10, 1
' start ramping the temperature
Helium, 60, 310
Helium, 60,480
Helium,60,615
Helium,90,870
' let the oven cool before starting elemental
Helium, 30,0
'Start Oxygen for elemental carbon
Oxygen, 45, 550
Oxygen, 45, 625
Oxygen,45,700
Oxygen, 45, 775
Oxygen, 45, 850
Oxygen, 120, 900
' Internal methane calibration standard
CalibrationOx, 120, 0
'  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.
```

Pre-start checklist - New Installation

(1) Install Sample inlet using 3/8 inch tubing. The sequence should be:

(a) Air Intake at 2.5 um cut Cyclone
(b) 3/8 inch tubing to area of instrument
(c) Denuder (note directional flow of air)
(d) 3/8 inch tubing into Ball Valve inlet

Note: Either Copper or S.S tubing can be used. It must be extremely clean from the standpoint of organics such as manufacturing oils. S.S tubing is preferred. If there is any doubt as to cleanliness, the tubing can be cleaned with reagent grade methylene chloride and then dried. Alternately, a propane torch can used to heat the length of tubing to remove any volatile organics.

(2) Install tubing from gas cylinders.

Use clean 1/8 inch copper or S. S. tubing. NoOx tubing may be used, but the length should be kept to a minimum. DO NOT use Teflon because of the diffusion of CO2 through its walls.

(3) Install tubing to pump.

Use ¼ inch copper or plastic tubing. This does not have to be clean because it is downstream of the sampling filter. Make sure **NOT** to use thin wall tubing that might collapse under vacuum. The sequence should be:

(a) ¼ inch tube to one end of ballast tank
(b) ¼ inch tube containing bleed orifice and vacuum gauge at other end of ballast tank
(c) ¼ inch tube to 120 VAC Sampling Solenoid – if used
(d) ¼ inch tube to vacuum pump

(4) Connect Control cable of Pump (or Solenoid) to 120 VAC control box. The 120 VAC Solenoid may be left out and the outlet of the ballast tank connected straight to the vacuum pump. In this case, the pump itself should be connected to the 120 VAC control box
(5) Connect the 120 VAC Power Cord to the plug on the back of the instrument
(6) Connect the CPU serial cable from the computer to the CPU Serial Port
(7) Connect the NDIR serial cable from the computer to the NDIR Serial Port

B. Sample spreadsheet data tabulated by Analysis Program.

Sample ID	Thermal OC (ugC/M3)	Thermal EC (ugC/M3)	OptOC (ugC/M3)	OptEC (ugC/M3)	TC (ugC/M3)	Start Date/Time	Mid-time of Collection	Sample Volume
2 hour samples	3.175	0.354	3.151	0.379	3.529	1/7/2005 16:35	1/7/2005 17:35	974.7
2 hour samples	2.243	0.378	2.232	0.390	2.621	1/7/2005 18:47	1/7/2005 19:47	974.6
2 hour samples	2.333	0.305	2.331	0.307	2.638	1/7/2005 20:58	1/7/2005 21:58	974.3
2 hour samples	2.111	0.288	2.081	0.318	2.399	1/7/2005 23:09	1/8/2005 0:09	973.7
2 hour samples	2.216	0.332	2.176	0.372	2.548	1/8/2005 1:20	1/8/2005 2:20	973.6
2 hour samples	2.309	0.428	2.398	0.339	2.737	1/8/2005 3:31	1/8/2005 4:31	972.9
2 hour samples	2.474	0.373	2.511	0.335	2.846	1/8/2005 5:42	1/8/2005 6:42	971.9
2 hour samples	2.808	0.325	2.831	0.301	3.133	1/8/2005 7:53	1/8/2005 8:53	972.0
2 hour samples	2.422	0.340	2.490	0.271	2.761	1/8/2005 10:04	1/8/2005 11:04	970.7
2 hour samples	2.904	0.469	2.934	0.439	3.373	1/8/2005 12:15	1/8/2005 13:15	970.1

* Calculated errors are based on long-term historical data for replicates and instrument blanks (see Reference #4). Over the course of hundreds of replicate runs, the relative standard deviation is typically 5%. True instrument blanks measured by running previously run filters without re-opening the oven report an average of 0.2 $\mu gC/cm^2$ background. Thus, the reported error is obtained by multiplying the carbon yield of the sample in $\mu gC/cm^2$ by 0.05 for the typical sample and instrument variability and adding 0.2 $\mu gC/cm^2$ from the typical instrument background.

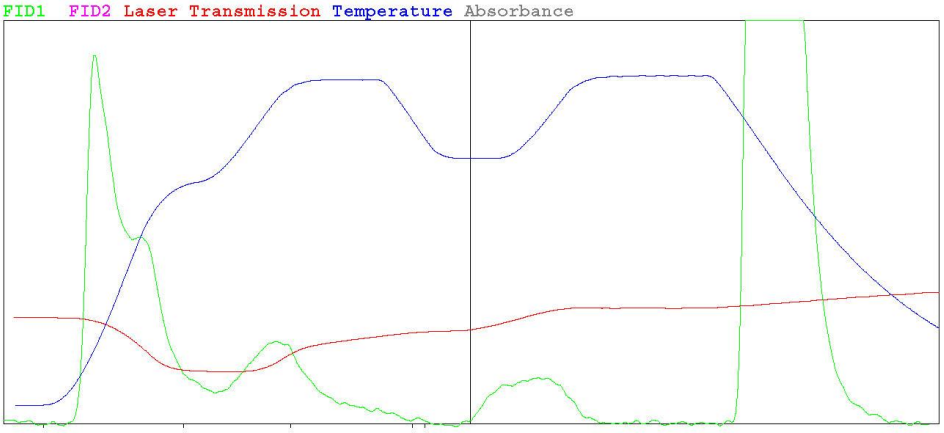
Sample ID: 60 min samples
Analysis Date/Time 01/12/2005 17:26:01

Organic C =	**5.46 +-0.47**	**ugC**	**5.63 ugC / M3**
Carbonate C =	**0.00 +-**	**ugC**	
Elemental C =	**0.73 +-0.24**	**ugC**	**0.76 ugC / M3**
Total C =	**6.19 +-0.61**	**ugC**	**6.38 ugC / M3**
EC/TC ratio =	**0.118**		

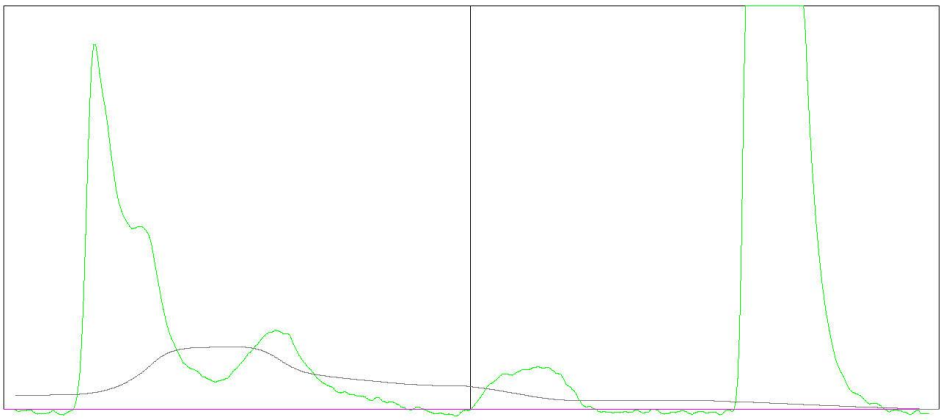
Sample Volume (M3) = 0.97 Punch Area, sq cm = 1
Calibration area Used = 32754.0 Calibration Constant = 18.1
Laser correction factor = 0.88
Split time Used = 234 seconds Split time Calculated = 234 seconds
Pk1= 3.76 Pk2= 1.12 Pk3= 0.57 Pk4= 0.01

FID GRAPHIC SCALE= 152

FID1 FID2 Laser Transmission Temperature Absorbance



Inital absorbance = 0.210 Absorbance at StartPyrolize = 0.350
Absorbtion Coefficient of original elemental C = 28.7
Absorbance plotted from 0 to 6



OC/EC Analysis Program (c) Sunset Laboratory, Inc. Analyst -