

# **Thermal-Optical-Transmittance Analysis for Organic, Elemental, Carbonate, Total Carbon, and OCX2 in PM2.5 by the EPA/NIOSH Method - #83**

**Max R. Peterson and Melville H. Richards**

Research Triangle Institute  
3040 Cornwallis Road  
P.O. Box 12194  
Research Triangle Park, NC 27709

## **ABSTRACT**

Research Triangle Institute (RTI) performs thermal-optical-transmittance (TOT) analyses for carbon species in PM<sub>2.5</sub> collected on quartz fiber filters in support of several Federal and State ambient air monitoring programs and human exposure studies. U.S. National Institute for Occupational Safety and Health (NIOSH) Method 5040, an evolved gas TOT method, was chosen for measurement of organic carbon (OC), elemental carbon (EC), carbonate carbon (CC), total carbon (TC), and OCX<sub>2</sub> (the most refractory component of OC) in PM<sub>2.5</sub> samples collected in the U.S. Environmental Protection Agency's (EPA's) nationwide chemical speciation program. Primary instrumentation in RTI's OC/EC Laboratory includes three Sunset Laboratory Thermal/Optical Carbon Analyzers and a muffle furnace used to pre-clean quartz filters.

This paper presents: an overview of the EPA/NIOSH TOT analysis method, sometimes called the Speciation Trends Network (STN) method; observations on the challenges posed by using multiple instruments for an analysis in which the analytes are defined by the conditions of the analysis; a comparison of the conditions used for the EPA/NIOSH method with the conditions used for other thermal-optical analysis methods and how these differences affect measurement results; and the dependence of the OC-EC analysis split time, which is used to determine the proportions of OC and EC in a sample, on sampling location.

## **INTRODUCTION**

In July 1999, Research Triangle Institute (RTI) was awarded the laboratory support contract for the U.S. Environmental Protection Agency's (EPA's) Chemical Speciation of PM<sub>2.5</sub> monitoring program. In February 2000, the first PM<sub>2.5</sub> samples in the national monitoring program were collected on 30 PM<sub>2.5</sub> samplers at 10 sites. Organic carbon/elemental carbon (OC/EC) analysis by National Institutes of Safety and Health (NIOSH) Method 5040 using an EPA- approved heating profile (sometimes called the Speciation Trends Network, or STN, method) is one of six routine analyses performed by RTI. During the period from February 2000 through September 2002, RTI's OC/EC Laboratory analyzed and reported results for 27,240 quartz filter samples under the laboratory support contract. Current throughput on the national contract is approximately 1,800 PM<sub>2.5</sub> samples per month.

## **OVERVIEW OF THE EPA/NIOSH (OR STN) METHOD**

NIOSH Method 5040<sup>1</sup> is an evolved gas analysis performed on a thermal-optical analyzer with timed heating ramps and cool down cycles. While the stated analyte for Method 5040 is

elemental carbon, which is used as a surrogate for diesel particulate, the method measures all carbon species that evolve during the analysis to give a measure of total carbon (TC) loading on the filter. All carbon evolving from the filter is oxidized to carbon dioxide, the carbon dioxide is reduced to methane, and the methane is measured using a flame ionization detector (FID). A red-light laser and photocell are used to monitor transmittance of the filter, which typically darkens as refractory OC chars during a non-oxidizing heat ramp and then lightens as the char burns off during an oxidizing heat ramp. The calculation software divides TC into OC and EC by setting the split time between the two as the time in the analysis when the transmittance of the filter returns (after darkening then lightening) to its original value at the beginning of the analysis.

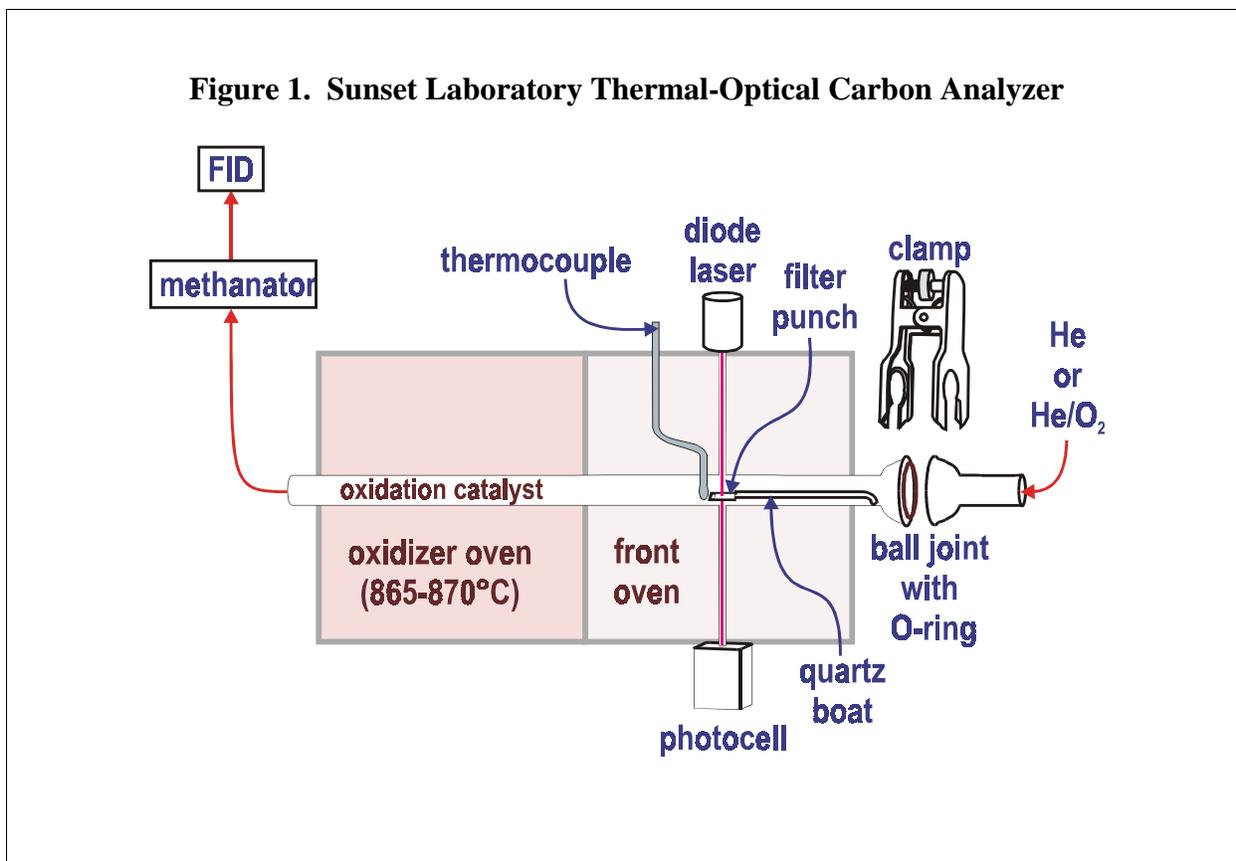
A punch with a nominal area of 1.5 cm<sup>2</sup> is used to remove a portion of a quartz filter sample for analysis. At the end of each analysis, an injection loop in the analyzer is used to inject a fixed volume of a nominal 5% methane in helium standard, which is treated as an internal standard. The mass of carbon in the loop is determined by running a three-point calibration using standard aqueous solutions of sucrose, calculating an average FID response factor for the calibration runs, and applying that average calibration response factor to the average FID response to the internal standard for the calibration runs to calculate the average measured mass of carbon (as methane) in the loop. For analysis of a filter sample, the FID response to the known mass of carbon (as methane) in the loop is used by the software to determine the FID response factor (counts/μgC) for the methane standard for a given analysis, and this FID response factor is then used to calculate OC, EC, and TC loading for the filter portion used in the analysis. Use of an internal standard allows automatic adjustment for minor changes in FID response factor from one analysis to the next.

According to the published method, the range for NIOSH Method 5040 is 1 to 105 μgC per filter portion. The limit of detection is about 0.3 μgC per filter portion. The precision is 0.19 at 1 μgC and 0.01 at 10 to 72 μgC.

## **Sunset Laboratory Thermal-Optical Carbon Aerosol Analyzer**

A schematic diagram of the Sunset Laboratory Thermal-Optical Carbon Aerosol Analyzer, which is used for all carbon analyses in the STN program, is shown in Figure 1. A punch from a quartz filter sample is placed in a quartz boat and positioned in the path of a red light diode laser, which is used to monitor transmittance of the filter (used to determine the OC-EC split time) during analysis. A thermocouple at the end of the boat is used to monitor sample temperature during analysis. All carbon species evolved from the filter are converted to carbon dioxide in an oxidation oven immediately downstream from the primary oven, and the carbon dioxide is reduced to methane before passing into a flame ionization detector (FID).

**Figure 1. Sunset Laboratory Thermal-Optical Carbon Analyzer**



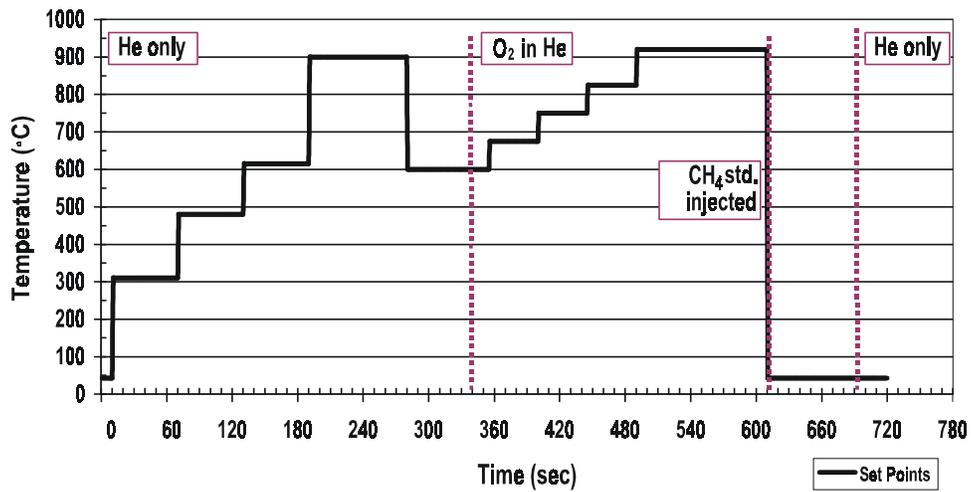
### Parameters for the EPA/NIOSH (or STN) Method

The parameter file for the EPA-approved heating profile is shown in Table 1. Figure 2 shows a plot of the temperature set points and the times when the gas valves are switched to change the gas mixtures going into the oven. The analysis starts in a non-oxidizing atmosphere (helium) with a 10-second purge followed by four temperature ramps to a maximum of 900°C. A cooling blower then comes on and the temperature drops to 600°C. Approximately 10 seconds before the temperature reaches 600°C, an electronic gas valve switches to 2% oxygen in helium, which arrives at the sample about the time the temperature drops to 600°C. A series of four heating ramps, this time with the sample in an oxidizing atmosphere, then brings the sample to a temperature of 920°C. Any carbon remaining on the filter is burned off during these final heat ramps. Two minutes after the 920°C set point is initiated, a gas valve switches to flush the methane standard from the loop and into the analyzer and the heater is switched off. Thirty seconds later the cooling blower is switched on again to cool the oven. The entire analysis sequence is 12 minutes (or 720 seconds) long.

**Table 1.** EPA/NIOSH (or STN) Method Parameter File.

```
Mode, Time, Temperature
Helium, 10, 1
Helium, 60, 310
Helium, 60, 480
Helium, 60, 615
Helium, 90, 900
Helium, 30, 0
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
Offline, 1, 0
End
```

**Figure 2. Temperature Set Points and Gas Valve Changes in the EPA/NIOSH (or STN) Method**





$$OC_{\text{IMPROVE}} \simeq OC_{\text{STN}} - OCX2_{\text{STN}}$$

$$EC_{\text{IMPROVE}} \simeq EC_{\text{STN}} + OCX2_{\text{STN}}$$

Values calculated for IMPROVE comparisons using OCX2 do not always agree well with IMPROVE- measured values.

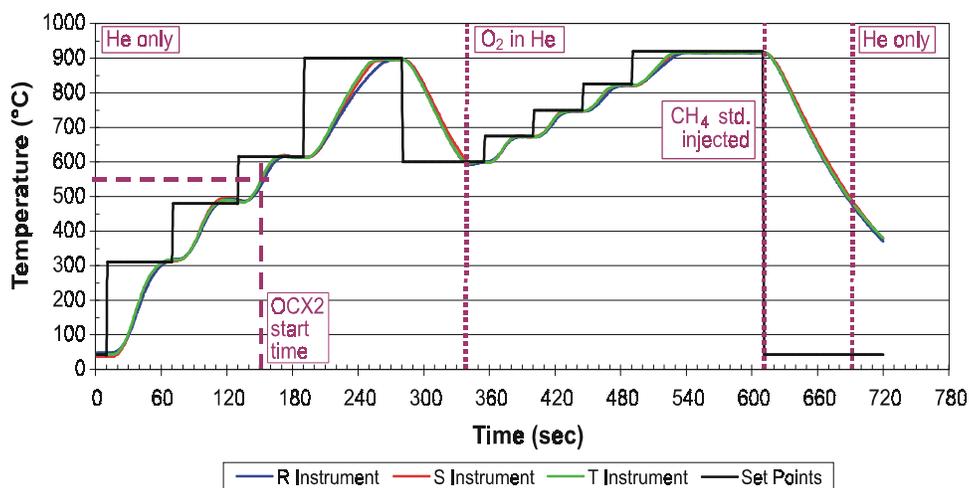
## COMPARISONS

This section includes a comparison of the actual heating profiles for RTI's three carbon analyzers, a comparison of thermograms with OC-EC splits that occur before the addition of oxygen (pre-oxygen splits) and after the addition of oxygen (post-oxygen splits), a comparison of results when the same filters are analyzed on all three instruments, a comparison of results when replicate punches from the same filter are run on the same instrument, and a comparison of results when replicate filter samples are collected on the same PM<sub>2.5</sub> speciation sampler. Comparisons of OC, EC, and TC measurements are complicated by the fact that separate punches from the same filter may differ slightly because of some degree of nonuniformity in the loading on the filter. For this reason, if the duplicate analyses run on about every tenth filter fall outside the duplicate acceptance criteria (given in a later section), only the filter from which the duplicate punches were taken is flagged as having a nonuniform deposit.

### Comparison of Heating Profiles

Figure 4 shows plots of front oven (Figure 1) temperature versus time for RTI's three carbon aerosol analyzers (designated R, S, and T). Insulation around the front oven determines to a significant extent the rate at which the oven heats and cools. The R instrument heats to 900°C (analysis time of 210-270 sec on graph) at a slightly slower rate than the S and T instruments, but cools from 900°C to 600°C (analysis time of 280-340 sec on graph) slightly faster. Adjusting the insulation to increase the heating rate on the R instrument also increased its cooling rate so that the temperature reached 900°C more quickly during the heating ramp but dropped significantly below the target of 600°C during the cool down. Figure 4 shows the temperature profile after an insulation compromise on the R instrument, which now gives an acceptable heating rate and an acceptable cooling rate.

**Figure 4. Heating Profiles for RTI's Three Carbon Aerosol Analyzers.**

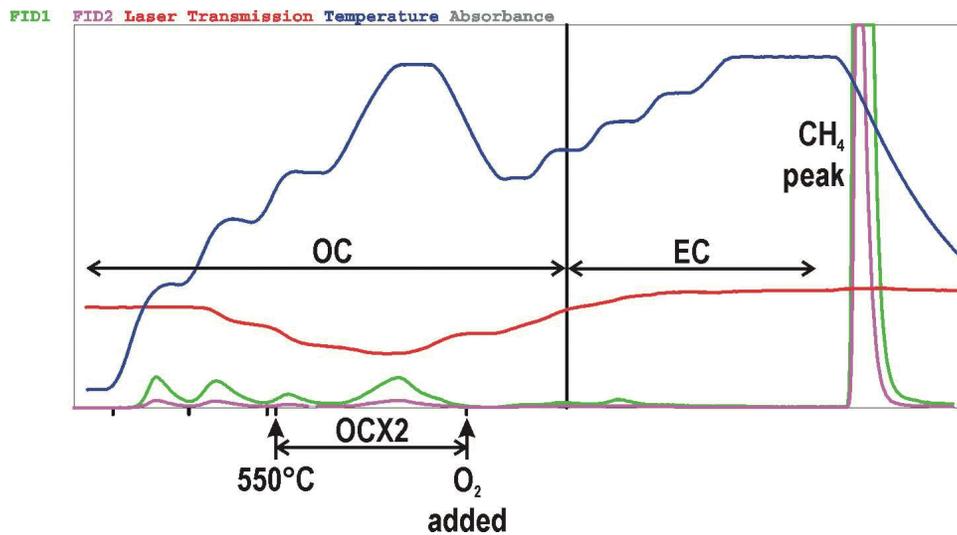


### Pre-Oxygen and Post-Oxygen OC-EC Splits

The Sunset Lab calculation software allows OC-EC splits to occur before as well as after the addition of oxygen during the analysis. The split is determined by the time at which the transmittance of the filter punch returns to the original value it had at the beginning of the analysis. Filter samples from sites with  $PM_{2.5}$  aerosol containing significant amounts of carbon tend to have post-oxygen splits. Blank filters (instrument, acceptance testing, field, and trip blanks) virtually always have pre-oxygen splits. Lightly loaded filters also often have pre-oxygen splits. The laser intensity reading, which is used to monitor transmittance of the filter punch during analysis, drifts slightly during the heating ramps and cool down stages of the analysis. As a result, the OC-EC split for blanks, which presumably do not form char, is determined by the slight temperature-induced changes in laser intensity readings. A link between  $PM_{2.5}$  composition (as determined by the sampling location) and split time is discussed near the end of this paper.

Figure 5 shows a typical thermogram with post-oxygen split, and Figure 6 shows a typical thermogram with pre-oxygen split. Response of the FID is shown at two attenuations (FID1 in green and FID2 in purple), laser transmission is shown in red, front-oven temperature is shown in blue, and absorbance (which is plotted in a separate graph) is shown in gray. Labels for OC, EC, the  $CH_4$  peak,  $550^\circ C$ ,  $O_2$  added, and OCX2 and several arrows were added to the thermograms in the figures for clarity.

**Figure 5. Typical Thermogram with Post-Oxygen Split.**



**Figure 6. Typical Thermogram with Pre-Oxygen Split.**

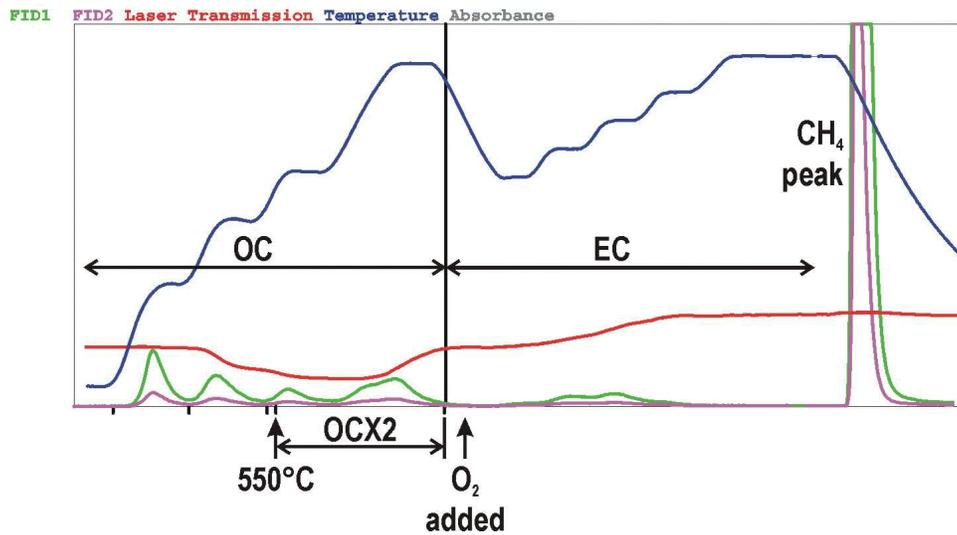


Table 2 gives operational information about the EPA/NIOSH (or STN) method. The Pk1 C, Pk2 C, Pk3 C, and Pk4 C referred to in Table 2 are calculated by integrating between specific times in the analysis. The small black lines extending below the bottom boundary of the thermograms in Figures 5 and 6 indicate the integration start times that define the FID areas used to calculate Pk1 C, Pk2 C, Pk3 C, and Pk4 C. For the STN method, Pk4 C is defined as and reported as OCX2.

**Table 2.** EPA/NIOSH (or STN) Method Considerations.

- Analysis time is 720 sec (not counting final cool down).
- Data are recorded once per second during analysis.
- Calculations are based on a parameter file containing:
  - size of punch (cm<sup>2</sup>)
  - mass of carbon (µgC) in methane loop
  - transit time (sec)
  - start integration times (sec) for Pk1 C, Pk2 C, Pk3 C, and Pk4 C
- OC/EC split time is determined using transmittance of the filter to a red light laser.

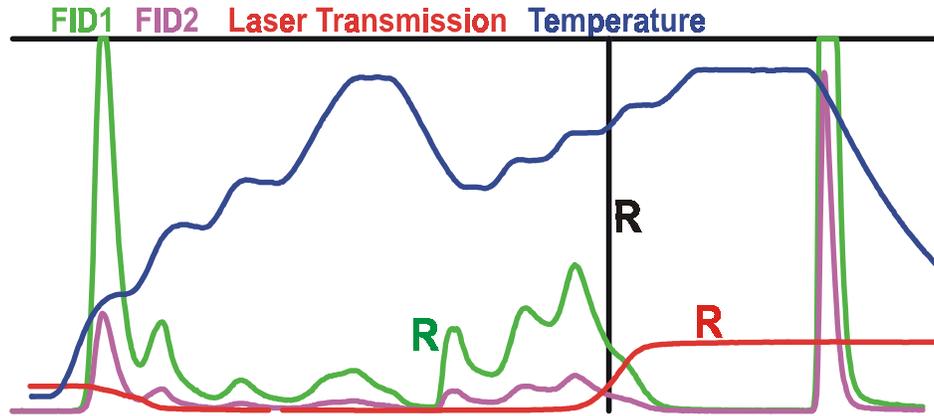
## Between Instrument Comparison

In the fall of 2002, replicate pairs of three sets of filters (six filters total) were analyzed on all three aerosol carbon analyzers. The results of comparisons between instruments indicated that the analyzers were reporting the same measured loadings for OC, EC, and TC within the limits expected for duplicate punches from the same filter run on the same analyzer on the same day.

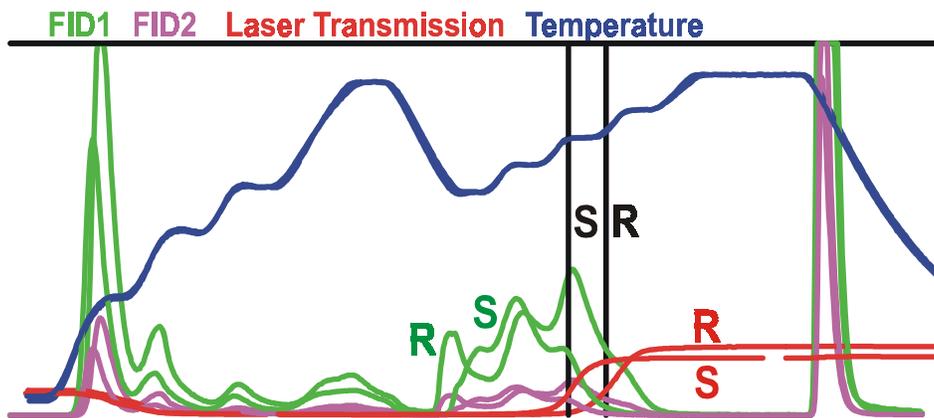
Figure 7 shows a progressive overlay of thermogram plots from the R, S, and T instruments for a moderately loaded filter. The top of Figure 7 shows the thermogram from the R instrument alone, the middle of the figure shows an overlay of the thermograms from the R and S instruments, and the bottom of the figure shows an overlay of the thermograms from all three instruments. The flame ionization detector (FID) traces (in green), the laser transmittance traces (in red), and the split times (vertical black lines) have been labeled with R, S, and T to facilitate between-instrument comparisons. The thermograms appear exactly as they were generated by the calculation software. No adjustments were made for the sensitivities of the FID's or for the ages of the ovens (which affects the absolute value of the laser reading used to monitor transmittance changes) in the respective instruments. FID traces for the S and T instruments overlay almost perfectly, but the laser readings are quite different. The FID trace for the R instrument is somewhat different from the other two instruments, especially following the addition of oxygen near the end of the cool down step in the middle of the thermograms. The differences in the FID traces and laser readings do not affect the calculated results because the FID's are calibrated separately and the laser readings are only used to establish the split time, which also differ and thus compensate for any differences in pattern of carbon evolution from the filter during analysis. Table 3 gives the OC, EC, and TC loadings measured by each instrument and includes values for a duplicate punch run on the T instrument.

Figure 7. Progressive Between Instrument Comparison Using Filter Q02-10430.

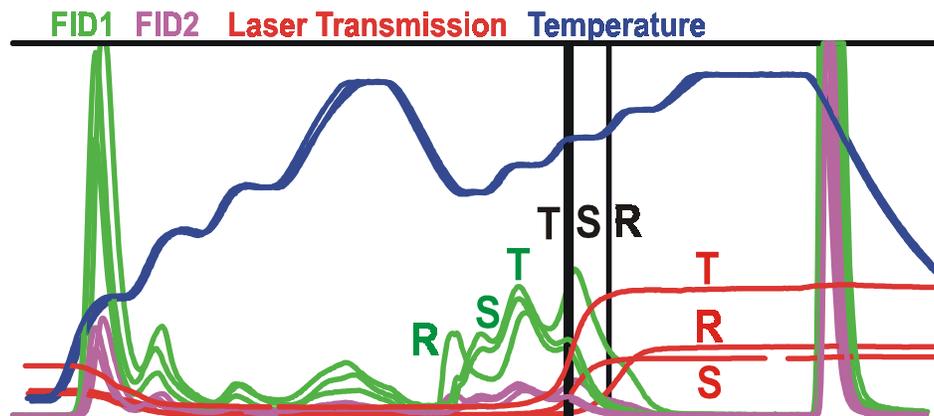
### R Instrument



### R Instrument      S Instrument



### R Instrument      S Instrument      T Instrument



**Table 3.** Measured Filter Loadings for Between Instrument Comparison Using Filter Q02-10430.

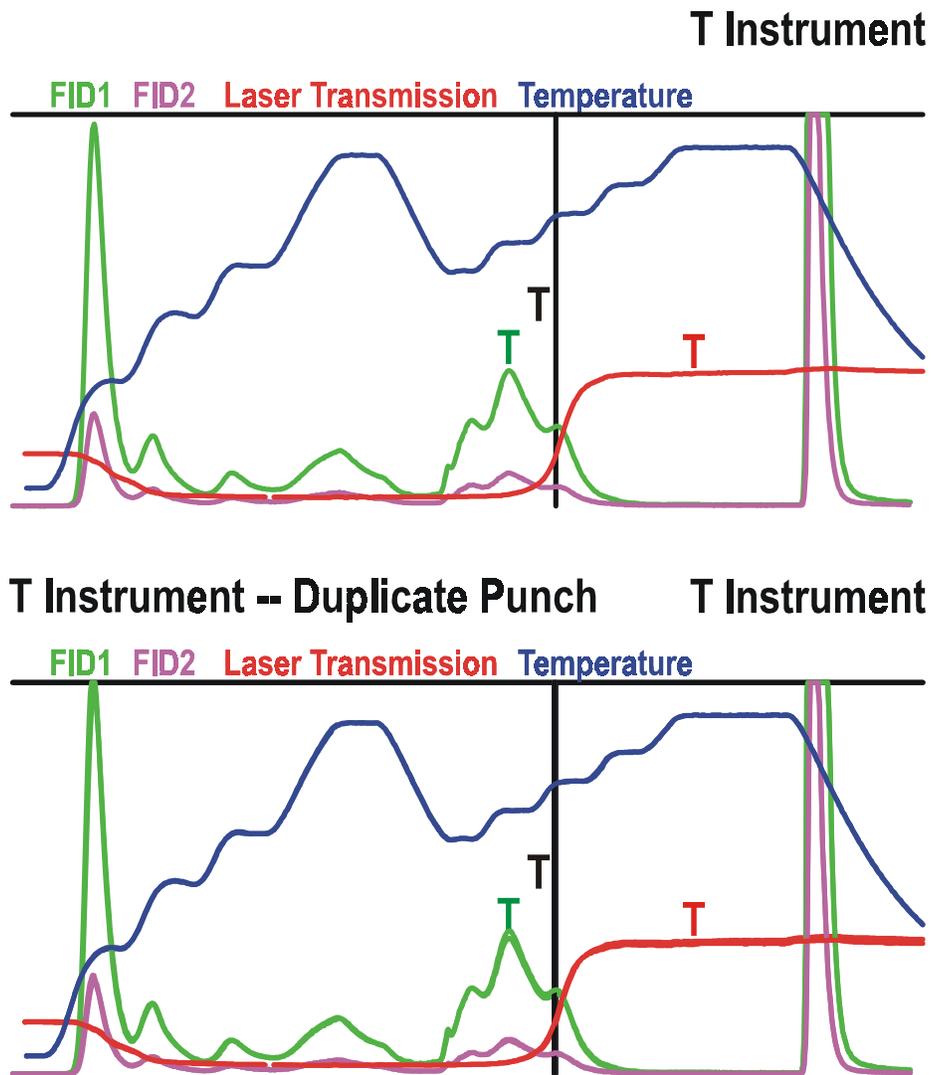
Analyzer	OC (ug/cm <sup>2</sup> )	EC (ug/cm <sup>2</sup> )	TC (ug/cm <sup>2</sup> )
R	22.89	1.41	24.30
S	21.52	1.44	22.96
T	22.46	1.78	24.24
T (dup)	23.14	1.82	24.96

### **Between Replicate Punches Comparison**

The last two rows of data in Table 3 show results for replicate punches from the same filter (Q02-10430) run on the T instrument. The agreement between measurements is typical of that observed of replicate (or duplicate) punches from the same filter analyzed as quality control samples.

The top portion of Figure 8 shows the thermogram from the analysis of filter Q02-10430 on the T instrument, and the bottom portion of Figure 8 shows the same thermogram overlaid with the thermogram from the analysis on the T instrument of a replicate punch from the same filter. The FID and laser traces coincide almost perfectly in the two thermograms, and the split time is the same on both.

**Figure 8. Replicate Punch Comparison on the T Instrument Using Filter Q02-10430.**



### **Between Replicate Filters Comparison**

Punches from each of two replicate filters (Q02-10429 and Q02-10430; collected on the same PM<sub>2.5</sub> speciation sampler at the same time at the same nominal sampling flow rate) were analyzed on all three carbon analyzers (R, S, and T). Results of the six analyses arranged by analyzer are shown in Table 4. TC, expressed as a percent of the average for the two filters on each instrument, was slightly above 100% of the average for filter Q02-10429 and slightly below 100% of the average for filter Q02-10430. The most plausible explanation for the small

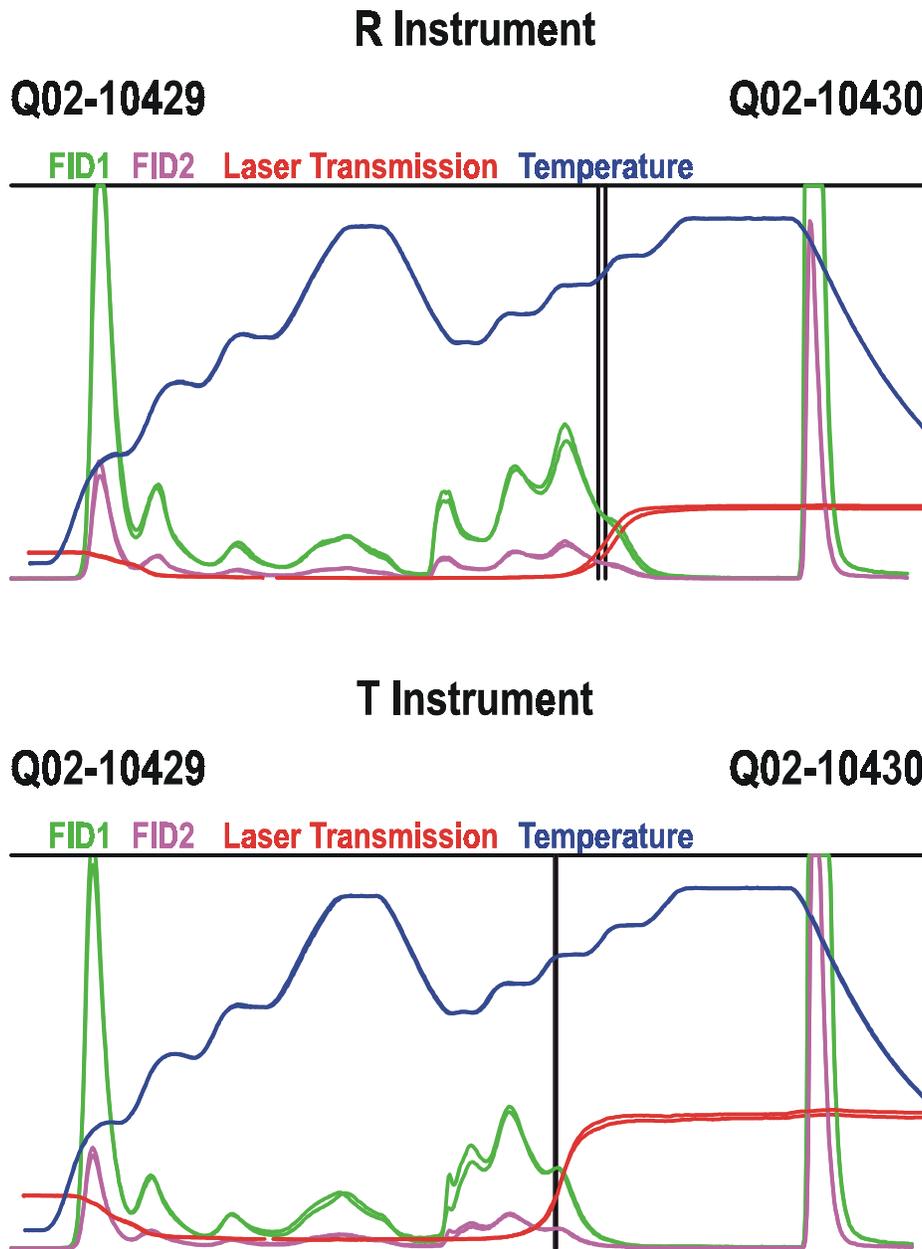
consistent difference would be a slight difference in actual sampling flow rate (which was not provided with the filters).

**Table 4.** Measured Filter Loadings for Between Replicate Filter Comparison.

Analyzer	Replicate Filter	OC (ug/cm <sup>2</sup> )	EC (ug/cm <sup>2</sup> )	TC (ug/cm <sup>2</sup> )	TC (% of Avg)
R	Q02-10429	23.14	1.32	24.45	100.32%
	Q02-10430	22.89	1.41	24.30	99.68%
S	Q02-10429	22.96	1.19	24.15	102.52%
	Q02-10430	21.52	1.44	22.96	97.48%
T	Q02-10429	23.22	1.76	24.97	101.50%
	Q02-10430	22.46	1.78	24.24	98.50%

Figure 9 shows overlays of thermograms from the analysis of filters Q02-10429 and Q02-10430 on the R and T instruments. FID traces (green) and split times (vertical black lines) show very good agreement between the punches from the two replicate filters on both analyzers.

Figure 9. Replicate Filter Comparisons Using Filters Q02-10429 and Q02-10430: Overlays from the R and T Instruments .



### Quality Control

Table 5 gives a list of quality control samples, the frequencies at which they are run, and the acceptance criteria for each. Filter acceptance blanks are used to test batches of quartz filters that have been fired in a muffle furnace for 3 hours at 900°C to verify that the filters are clean before

they are sent to the sample handling facility for shipment to the field. Instrument blanks are used to verify that the inside of the carbon analyzer oven and sample transfer lines are clean. As explained earlier, three-point calibrations with standard sucrose solutions are used to determine the mass of carbon (as methane or CH<sub>4</sub>) in the internal standard loop, which is flushed into the gas stream of the analyzer at the end of each analysis. Daily calibration checks are used to confirm that the FID response has not shifted substantially since the last 3-point calibration. Duplicate punches from the same filter are analyzed to determine the uniformity of the deposit on that particular filter, which is the only filter analysis flagged if duplicate punches do not meet the appropriate acceptance criterion.

**Table 5.** Quality Control Samples.

QC Sample Type	Frequency	Acceptance Criteria	
Filter-Acceptance Blank	2 or 2%, whichever is more, of filters in each pre-fired batch	all analyzed filters must have TC < 1 µg/cm <sup>2</sup>	
Instrument Blank	beginning of each day and after about 30 samples	TC ≤ 0.3 µg/cm <sup>2</sup> and area counts for CH <sub>4</sub> internal standard 90-110% of the average area counts for the last 3-point calibration	
3-Point Calibration (3 concentrations of sucrose solution)	at least weekly	R <sup>2</sup> >0.99, recovery of 90-110% at each concentration, and area counts for CH <sub>4</sub> internal standard within 90-110% of the average area counts for this 3-point calibration	
Daily Cal Check (mid-level standard)	daily	recovery of 90-110% and area counts for CH <sub>4</sub> internal standard 90-110% of the average area counts for the last 3-point calibration	
Duplicate Punch	about every 10 <sup>th</sup> filter	<u>Conc. Range</u>	<u>Criterion</u>
		>10 µg/cm <sup>2</sup>	<10% RPD
		5-10 µg/cm <sup>2</sup>	<15% RPD
		<5 µg/cm <sup>2</sup>	± 0.75 µg/cm <sup>2</sup>

FID area counts for the methane internal standard, which is injected at the end of each OC-EC analysis, are used to monitor FID response on an analysis-by-analysis basis and to check for leaks. Any instrument blank or calibration analysis giving an area count for the internal standard that falls outside 90-110% of the average area counts for the current (or last) 3-point calibration is repeated. Any analysis of a sampled filter giving an area count for the internal standard that falls outside 95-105% of the average area counts for all analyses run on the same instrument on the same day is repeated.

## DEPENDENCE OF OC-EC SPLIT TIME ON SAMPLING LOCATION

In an effort to determine factors affecting split time (which is used to partition TC into OC and EC), a data set containing analysis results for 8,000+ samples collected from January-June of 2002 was extracted from RTI's database. Split times (available in laboratory data files) were linked to OC-EC analysis data in the data set. Plots of analyte concentration versus OC-EC split

time showed no obvious correlations for any of the carbon species or other dominant  $PM_{2.5}$  species present.

The data set was then sorted by sampler location, and a count of number of analyses was determined for each sampler. The data set included 60-65 analyses from each of 33  $PM_{2.5}$  speciation samplers operating on an every-third-day sampling schedule during the entire period. The minimum, maximum, and mean split times for these 33 samplers, sorted by mean split time, are shown in Figure 10.

In Figure 10, the minimum and maximum values for the split time are remarkably similar, but the mean value differs by almost 100 sec from highest to lowest. At least some samples from all samplers gave pre-oxygen splits, and at least some samples from all samplers gave post-oxygen splits.

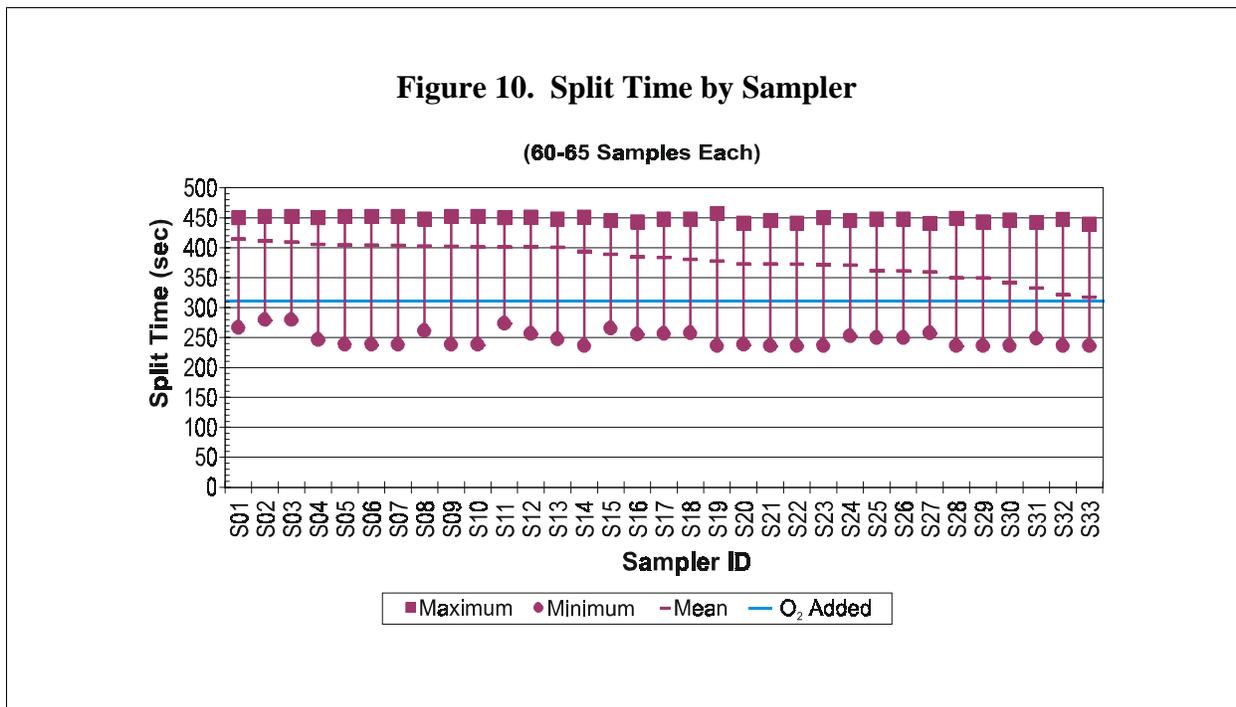


Figure 11 shows a comparison of laser transmittance changes during OC-EC analysis of a subset of filters collected on the sampler with the latest mean split time (S01) and a subset of filters collected on the sampler with the earliest mean split time (S33). Laser transmittance readings vary from analyzer to analyzer and change for a given analyzer as the quartz optical flats used as windows in the oven and as the filter punch holder on the sample boat age. To minimize instrument-to-instrument variability, all of the plots shown in Figure 11 come from analyses run on the R carbon analyzer over a 2- to 3-month period.

In Figure 11, OC and EC filter loadings are given in the legend for each graph. Filter loadings for sampler S01, which had the highest mean split time (415 sec), are significantly higher than filter loadings for sampler S33, which had the lowest mean split time (317 sec). Sampler S01 is located at an urban site; and Sampler S33 is located at a very clean site in a national park.

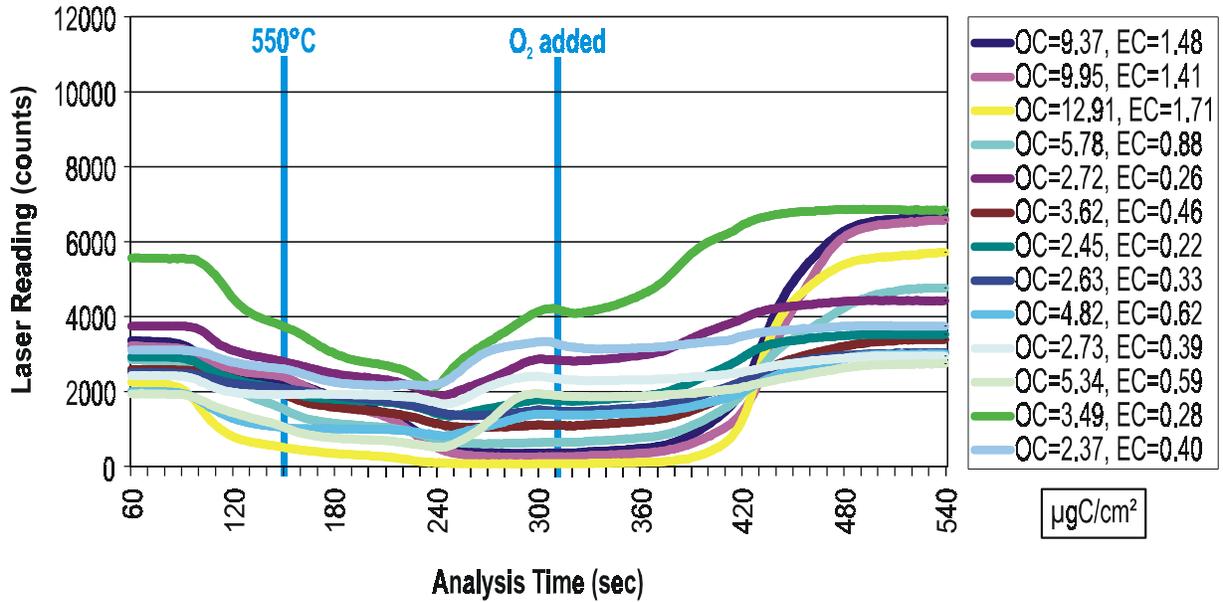
The laser transmittance of the filter continued to decrease (due to the formation of additional char) as the temperature during the non-oxidizing heat ramps continued to rise above 550°C to 900°C for every analysis in Figure 11. This continued darkening of the filter above 550°C (the temperature at which the IMPROVE carbon method assumes all OC has been volatilized off the filter) clearly indicates the presence of OC still remaining on the filter. About half of the filters from the urban site (S01) showed increases in laser transmittance as the temperature approached 900°C beginning at about 240 sec; and all of the filters from the very clean site (S33) showed increases in laser transmittance at about the same time in the analysis. This lightening of the filter is due to removal of light absorbing material, which could be light-absorbing OC or oxidation of OC due to the presence of inorganic materials that can act as oxidizing agents at high temperatures. Increases in laser transmittance as the oven temperature approaches 900°C does not seem to be related to sulfate or nitrate loading on the filter. The four filters (all from S01) that gave the lowest and the flattest laser transmittance readings (four bottom lines of the top graph in Figure 11) were the most heavily loaded of all the filters whose data were plotted in Figure 11, but filters with only slightly lower loadings showed significant increases in laser transmittance as the oven temperature approached 900°C.

In summary, the range of OC-EC split times observed for quartz filter samples is fairly constant across all sampler locations, but the mean split times calculated for individual samplers can differ significantly (317 sec to 415 sec for the examples in Figure 10). Heavily-loaded filters are less likely to give significant increases in laser transmittance as the oven temperature approaches 900°C, and these filters are therefore less likely to have the OC-EC split time occur before the addition of oxygen.

**Figure 11. Laser Reading Versus Analysis Time Plots for Filters Collected on S01 and S33 and Analyzed on the R Carbon Analyzer.**

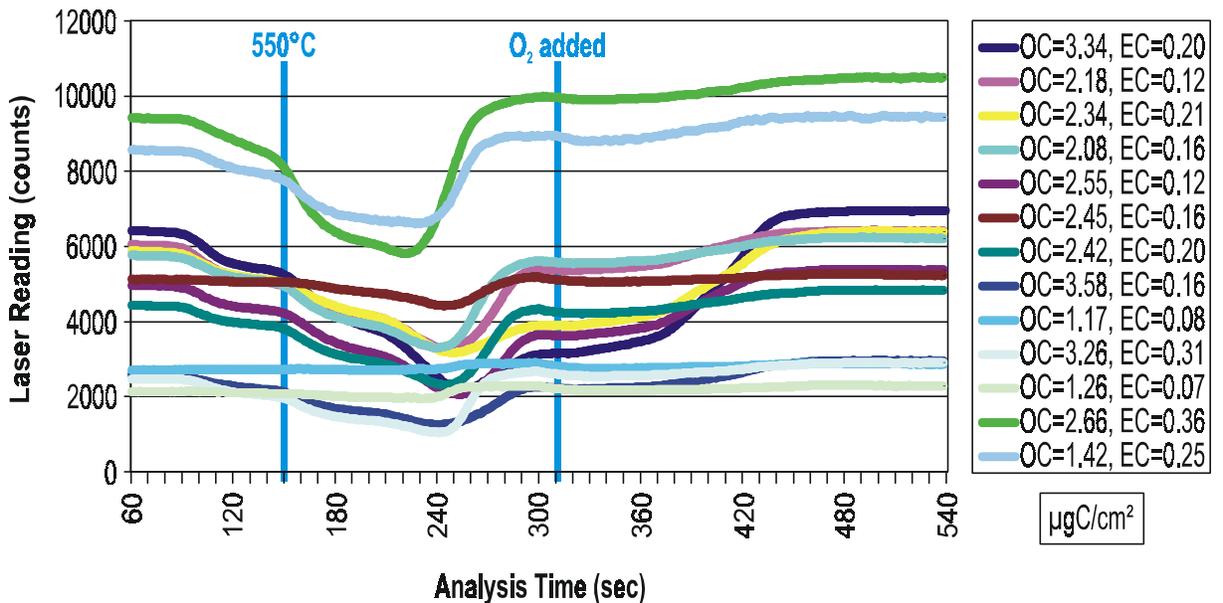
**S01: LASER READING VS. ANALYSIS TIME**

Average Split Time = 415 sec  
R Instrument Plots Only



**S33: LASER READING VS. ANALYSIS TIME**

Average Split Time = 317 sec  
R Instrument Plots Only



## **CONCLUSIONS**

The EPA/NIOSH (or STN) method is an effective way to measure and to monitor method-defined OC and EC in PM<sub>2.5</sub>. The method has been demonstrated to give reproducible results for OC and EC when punches from the same filter are analyzed on three different Sunset Lab carbon aerosol analyzers.

OC-EC split time is dependent upon both the composition of the sample (which depends upon the location of the sampler) and the carbon-loading on the filter. The STN method appropriately (as evidenced by the continued formation of char) includes in the measured loading of OC the carbon that evolves at temperatures above 550°C in a non-oxidizing atmosphere.

Data from analyses by the STN method could perhaps be used to provide site-specific information about the composition of carbonaceous material in PM<sub>2.5</sub>. The OC peaks data could provide information about spatial and seasonal changes in the composition of the organic component of PM<sub>2.5</sub> at individual sampling sites and could facilitate comparisons between sites.

## **REFERENCES**

1. NIOSH Method 5040, *Elemental Carbon (Diesel Particulate)*, NIOSH Manual of Analytical Methods

