

Analysis of carbonaceous aerosols using the Thermal Optical Transmittance and Thermal Optical Reflectance Methods

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Gary A. Norris*, M. Eileen Birch, Michael P. Tolocka*, Charles W. Lewis*, Paul A. Solomon*, James B. Homolya*****

* U.S. EPA, ORD/NERL, Research Triangle Park, NC 27711

** National Institute for Occupational Safety And Health, Cincinnati, Ohio 45226-1998

*** U.S. EPA OAQPS, Research Triangle Park, NC 27711

ABSTRACT

Carbonaceous particulate typically represents a large fraction of $PM_{2.5}$ (20 – 40%). Two primary techniques presently used for the analysis of particulate carbon are Thermal Optical Transmission (TOT - NIOSH Method 5040) and Thermal Optical Reflectance (TOR). These two methods both quantify carbon by heating filters and volatilizing the carbon that is oxidized in a granular bed of MnO_2 , reduced to CH_4 in a Ni methanator, and quantified as CH_4 with a flame ionization detector. However, the methods use different techniques to correct for the formation of pyrolysis products and the temperature programs for defining organic and elemental carbon. The TOT and TOR measurement techniques are being compared using samples from the Chemical Speciation Monitor Evaluation Field Study. All of the samples will be measured with TOR and a subset of samples representing a range of mass concentrations will be measured with TOT. This comparison will provide insight into the effect of the measurement technique parameters on organic and elemental carbon concentrations.

INTRODUCTION

Carbonaceous particulate represents a significant fraction of airborne particulate matter less than or equal to 2.5 μm in aerodynamic diameter ($\text{PM}_{2.5}$). Carbonaceous particulate is classified into three main categories: organic carbon (OC), elemental carbon (EC), and carbonate carbon (CC)¹. These categories are operationally defined by the method or analysis technique. OC sources include combustion, industrial, and photochemical process. EC sources are mainly combustion related. CC is found in soil and generally constitutes less than 5 percent of the total carbon². OC and EC typically represent 20 to 40 percent of $\text{PM}_{2.5}$. As a result, quantifying OC and EC is required for reconstruction of the gravimetric mass. In addition, OC and EC can be used in receptor models and as exposure variables for health effects studies.

Two primary thermal-optical methods are used to quantify particulate carbon: thermal optical reflectance (TOR) and thermal optical transmission (TOT). These two methods both quantify carbon by heating a quartz filter punch (0.5 cm^2 for TOR and 1.5 cm^2 for TOT) and volatilizing the carbon which is oxidized in a granular bed of MnNO_2 , reduced to CH_4 in a Ni methanator, and quantified as methane (CH_4) with a flame ionization detector. However, the methods differ in the technique used to correct for the formation of pyrolysis products and they use different temperature programs.

The TOR particulate carbon analysis method has been previously described by Chow².

The temperature profile and the range of times required for the response at each step to

become constant is shown in Table 1. The sample oven is stepped to 500 °C in 4 steps (120 °C (OC1), 250 °C (OC2), 450 °C (OC3), 500 °C (OC4)) to vaporize the organic carbon in a helium atmosphere. In the second part of the analysis a 2 percent O₂/98 percent He mix is introduced, the temperature is then stepped to 800 °C in 3 steps (550 °C (EC1), 700 °C (EC2), and 800 °C (EC3)). The amount of time for each temperature step is operationally defined based on the time required for the FID response to return to baseline. The result of this temperature step routine is the OC and EC are quantified in terms of the temperature steps (OC1, OC2, OC3, OC4, EC1, EC2, EC3). Methane (CH₄) calibration gas is introduced at the end of each sample cycle. Pyrolysis correction is made by monitoring the filter reflectance of a He-Ne laser at 632.8 nm with a photodetector. Pyrolyzed OC is quantified as the carbon evolved from the time the carrier gas is changed from He to 2 percent O₂ in He to the time the laser measured filter reflectance reaches its initial value. Carbonate carbon is determined by acidifying the sample with HCl and measuring evolved carbon at ambient temperature in a 2 percent oxygen/98 percent helium atmosphere.

The TOF method used in this analysis is specified in NIOSH Method 5040^{3,4}. In this method, the sample oven is purged with helium and the temperature is stepped (to 205 °C, 500 °C, 650 °C, and 850 °C) to volatilize the OC, and CC. In the second part of the analysis the temperature is lowered to 650 °C, and a 2 percent O₂/98 percent He mix is introduced, the temperature is then stepped to 940 °C. Table 1 specifies the temperature program and time periods for the steps. At the end of the analysis, a calibration gas standard (CH₄) is introduced. Correction for pyrolysis of the OC is accomplished by

monitoring the transmittance of a He-Ne laser through the filter at 670 nm. The point at which the filter transmittance reaches its initial value is defined as the split between OC and EC. Carbonate carbon is determined using HCl pretreatment or the thermogram will show a quantifiable peak around 820 °C. The National Air Monitoring Station (NAMS) chemical speciation program specifies the NIOSH Method 5040 as the method for OC, EC, and total carbon (TC = EC + OC).

The TOR and TOT methods were evaluated in a methods comparison in 1986⁵. Comparisons were based on ambient PM₁₀, automotive, wood smoke, pyrolyzed ambient PM₁₀, organic aerosol from a smog chamber, and a blank. Results were presented for the laboratories used for this study with Desert Research Institute (DRI) and Sunset Labs (SL) conducting the TOR and TOT analysis, respectively. The coefficient of variation for the TC, OC, and EC for the ambient samples for TOR and TOT were 3.0, 2.5, 3.0 percent; and 2.2, 2.5, and 6.2 percent, respectively. Results for each laboratory were reported as TC normalized to the mean of all of the participants (n = 10) and the ratio of EC to TC (see Table 2). The TC results for both of the methods were similar, however, the EC/TC ratio for TOT was lower than TOR for the ambient, unleaded auto, and wood smoke samples. Wood smoke had the largest difference with TOR and TOT having EC/TC ratios of 0.36 and 0.09, respectively. An interlaboratory comparison between TOR (DRI) and TOT (SL) was conducted as part of the DRI study on Phoenix and Tucson Urban Haze and PM₁₀. This study also found good agreement on three TC measurements of potassium hydrogen phthalate, with an average absolute percent difference less than 3 percent².

The TOR and TOT methods were also evaluated in an interlaboratory comparison⁶. Samples from an urban location, a loading dock with diesel vehicles, and a firehouse bay were evaluated. The comparison also included filters spiked with sucrose, and disodium salt of ethylenediaminetetraacetic acid (EDTA) that have no EC to evaluate the TC and the pyrolysis correction. Table 3 summarizes the results from the methods comparison. TOR results are from one laboratory while the TOT results represent an average of 5 laboratories. Both the TOR and TOT techniques quantified less than 3 percent of the EDTA and sucrose standards as EC. The absolute percent difference between the TOR and TOT methods for the EC measurements were 33, 76, 58, 27, 23 for the wood 1, wood 2, urban, diesel truck, and fire station samples, respectively. The absolute percent difference between the TOR and TOT for the OC measurements were 1, 6, 3 for the diesel truck, and fire station samples, respectively. EC had largest percentage difference for the wood smoke and urban samples. This difference in the EC measurements may be due to either the temperature program, length of analysis at each temperature, (Table 1) or the method used to correct for pyrolysis of the OC.

EXPERIMENTAL DESIGN

This comparison of the TOR and TOT particulate carbon analysis techniques will use ambient PM_{2.5} samples from 3 cities with different sources of carbon; and quality assurance standards of sucrose, wood smoke, diesel, diesel spiked with carbonate, and

blank filters (Table 4). Sunset Laboratory will conduct the TOT analysis using NIOSH Method 5040 and DRI will conduct the TOR analysis following the temperature program in Table 1.

Quality assurance samples were sent to each laboratory. Sunset Laboratory and DRI will each be sent a sample set: sucrose solution and a 47-mm quartz filter, carbonate solution, quartz filter with diesel particulate, and a quartz filter with wood smoke particulate. To determine the potential interference of carbonate when present in a carbonaceous particulate sample (in this case diesel), the sample portion would be analyzed with and without a spike. The labs should obtain the same EC results in both cases if carbonate does not interfere. All of the standards will be provided in triplicate to allow for calculation of the measurement precision of the calibration and source samples.

The ambient samples will be from the Philadelphia and Rubidoux PM_{2.5} Chemical Speciation Sampler Evaluation sites, and the Spokane Particulate Matter and Health Study⁷. Philadelphia particulate carbon is a mix of automobile and industrial source while Rubidoux is a mix of automobile and photochemical organic aerosols. The Philadelphia and Rubidoux samples will be evaluated with and without XAD denuders upstream of the quartz filter to remove organic gases. Spokane filters will be collected in November and December when the particulate carbon is predominately from wood smoke⁷. Two additional wood smoke source samples from EPA will also be evaluated. Samples from the 3 cities and the source samples will represent a range of OC concentrations and EC/OC ratios. Differences between the methods will be highlighted

by using the combination of samples from cities with different sources of carbon, and source samples (see Table 4).

CONCLUSIONS

Particulate carbon typically represents a large fraction of $PM_{2.5}$. OC and EC measurements are routinely used for reconstruction of the gravimetric mass, and receptor modeling. The two primary carbon analysis methods are TOR and TOT. OC and EC are determined operationally by each of the methods. These techniques differ in their temperature programs, step time, and pyrolysis correction. Differences between the methods need to be fully understood to help interpret past and future particulate carbon results.

This comparison of the TOR and TOT particulate carbon analysis methods will add to the analyses conducted by Countess⁵ and Birch⁶. Analysis of $PM_{2.5}$ samples from three cities with different sources of particulate carbon will help provide information on any systematic differences in the OC and EC measurements. In addition, source samples of diesel and wood smoke will be analyzed to evaluate the measurement precision.

Particulate carbon measurements of samples with and without an XAD denuder will provide data on the differences between the TOR and TOT methods for samples which do not have the potential OC artifact caused by gas phase organic compounds. Organic gas denuders have not been used in previous intercomparisons.

DISCLAIMER

This paper has been reviewed in accordance with the U.S. Environmental Protection Agency's peer and administrative review policies and approved for presentation and publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

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Table 1. Optical correction and thermal programs for the TOT and TOR particulate carbon measurement techniques.

Method			
TOT			
Optical correction	Transmission		
Program	OC		EC
Helium	250 °C, 1 min	2 % O ₂ in Helium	650 °C, 30 sec
	500 °C, 1 min		750 °C, 30 sec
	650 °C, 1 min		850 °C, 1 min
	850 °C, 1.5 min		940 °C, 2 min
	Reduce to 650 °C		
TOR			
Optical correction	Reflectance		
Program	OC		EC
Helium	OC1: 120 °C, 3 – 10 min	2 % O ₂ in Helium	EC1: 550 °C, 3 – 10 min
	OC2: 250 °C, 3 – 10 min		EC2: 700 °C, 3 – 10 min
	OC3: 450 °C, 3 – 10 min		EC3: 800 °C, 3 – 10 min
	OC4: 550 °C, 3 – 10 min		
OC = OC1 + OC2 + OC3 + OC4 + pyrolyzed carbon			
EC = EC1 + EC2 + EC3 + pyrolyzed carbon			

Table 2. Comparison of the TOR and TOT analysis methods (Countess)

TC normalized to the mean of the 10 participants in the comparison				
Method	Ambient PM ₁₀	Unleaded Auto	Diesel	Wood smoke sample 1
TOR	1.00	0.98	1.00	1.02
TOT	0.99	0.88	0.95	0.94
Mean loading (µg/cm ²)	30.8	34.0	106.8	96.7
EC/TC ratio				
Method	Ambient PM ₁₀	Unleaded Auto	Diesel	Wood smoke sample 1
TOR	0.30	0.83	0.87	0.36
TOT	0.15	0.70	0.88	0.09
Mean ratio	0.22	0.72	0.81	0.16

Table 3. Comparison of the TOR and TOT analysis methods ($\mu\text{g}/\text{cm}^2$) (Birch)

Sample	TOR		TOT	
	OC	EC	OC	EC
Sucrose	----	0.57	----	0.26
EDTA	----	0.20	----	0.02
Wood 1	----	6.20	----	4.42
Wood 2	----	2.17	----	0.30
Urban	9.70	3.00	10.42	1.65
Diesel Truck	17.33	8.20	18.48	6.25
Fire Station	136	20.27	139.80	16.10

Table 4. Samples to be analyzed using TOT and TOR

Speciation Site	Number of Samples	
W/O XAD Denuder		
Philadelphia	10	Carbon from motor vehicles and industrial processes
Rubidoux	10	Carbon from motor vehicles and secondary aerosols
Spokane	4	Carbon from motor vehicles and wood smoke
Field blanks	4	2 field blanks from Philadelphia, and Rubidoux
Wood smoke source samples	2	2 wood smoke source samples from the EPA, Research Triangle Park, NC
Source sample blank	1	1 source sample blank from the EPA, Research Triangle Park, NC
With XAD Denuder		
Philadelphia	5	
Rubidoux	5	
Quality Assurance		
Sucrose	3	Triplicate evaluation of the calibration
Wood Smoke	3	Triplicate evaluation of a wood smoke sample
Diesel	3	Triplicate evaluation of a diesel sample
Diesel spike with carbonate	3	
Field blanks	2	

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