Instrumentation of a Thermal-Optical Carbon Analyzer and Its Sensitivity in Organic and Elemental Carbon Determination to Analysis Protocols

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Abstract

A thermal-optical transmittance carbon analyzer has been developed to determine particulate organic (OC) and elemental (EC) carbon. Several analysis factors affecting the sensitivity of OC and EC determination were investigated for the carbon analyzer. Although total carbon (TC) is usually consistent in the determination, OC and EC split is sensitive to adopted analysis protocol. In this study the maximum temperature in oxygen-free He in the analysis was examined as a main cause of the uncertainty. Prior to the sensitivity analysis consistency in OC-EC determination of the carbon analyzer and the uniformity of carbonaceous aerosol loading on a sampled filter were checked to be in acceptable range. EC/TC ratios were slightly decreased with increasing the maximum temperature between 550-800°C. For the increase of maximum temperature from 500°C to 800°C, the EC/TC ratio was lowered by 4.65-5.61% for TC loading of 13-44 μg/cm^{2} with more decrease at higher loading. OC and EC determination was not influenced by trace amount of oxygen in pure He (>99.999%), which is typically used in OC and EC analysis. The facing of sample loaded surface to incident laser beam showed negligible influence in the OC-EC split, but it caused elevated PC fraction in OC for forward facing relative to backward facing.

Key Words : Organic carbon, Elemental carbon, Carbon analysis, Thermal-optical method, Aerosol, Particle

1. Introduction

As a major component of atmospheric particulate matter (PM), carbonaceous material plays important roles in visibility (NRC, 1993; U.S. EPA, 1996), radiative forcing (IPCC, 1995; NRC, 1996), and adverse human health effects of PM (U.S. EPA, 1996). Aerosol carbon present in the form of organic material, graphite-like chemical structure, and carbonate compounds is often represented as organic (OC), elemental (EC or black carbon, BC), and carbonate carbon (CC), respectively. Each carbon species have distinct chemical and physical properties associated with environmental issues of carbonaceous aerosols. It is necessary to quantitatively measure the carbon species to investigate its environmental impacts. Analytical methods that fractionate particulate carbon into OC and EC are widely used in aerosol studies. In the analysis it is frequently assumed that carbonate carbon is negligible.

Solvent extraction, thermal (e.g., selective volatilization), and optical (i.e., visible light attenuation) methods have been used to measure OC and EC (Arnott et al., 1999; Horvath, 1993; Lim et al., 2003; Turpin et al., 2000). Two general operational definitions of OC and EC exist: 1) OC combines with oxygen, hydrogen, and other elements, and therefore volatilizes and decomposes upon heating in an

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oxygen-free environment, and EC is an agglomerate of primarily carbon atoms that only combusts in the presence of oxygen; or 2) elemental carbon comprises all visible-light absorbing carbon. Currently, thermal-optical methods are most widely used to measure OC and EC (Birch and Cary, 1996; Chow et al., 2001; Chow et al., 2004). In the methods carbon volatilized by heating up to 550-850°C in oxygen-free atmosphere is defined as OC and carbon evolved by heating up to 900°C in oxygen atmosphere is defined as EC. Pyrolyzed carbon (PC) formed by charring of OC during heating in oxygen-free atmosphere is corrected by optical monitoring of the filter during analysis. The thermal method correcting the pyrolytic conversion by monitoring optical transmittance and reflectance is typically named as thermal-optical transmittance (TOT) and reflectance (TOR), respectively. Pyrolysis reduces the intensity of light after heating the filter and the intensity increases again as EC is removed. PC is estimated as the amount of carbon evolved between the start of adding oxygen and time to regain the optical intensity of pre-pyrolysis level. The quantity is added to OC in the particulate OC and EC determination.

Comparing to clear definition of organic (OC) and elemental carbon (EC), it is very difficult to practically fractionate them. OC and EC data are largely dependent on analysis protocols (Chow et al., 2001, 2004; Cavalli et al., 2010; Zhi et al., 2011). According to Chow et al. (2001) found a large discrepancy in OC and EC data between two most widely used NIOSH and IMPROVE methods, more than 2 times higher EC was occasionally reported for IMPROVE method relative to NIOSH method. In the previous studies, the maximum temperature in oxygen-free mode, catalytic activities of metal oxides, and light properties of transmittance and reflectance were pointed out as possible causes of the sensitivity of OC-EC split. Various OC and EC analysis protocols have been developed to understand

and to minimize the discrepancies (Cavalli et al., 2010; Zhi et al., 2011). Cavalli et al. (2010) used a series of criteria for the optimization of EUSAAR protocol, which is standardized OC-EC analysis protocol of EU. Those are the minimization of charring, completion of evolution/pyrolysis of OC by the end of He mode, minimization of premature evolution of light absorption compound which might be EC containing material, and minimization of uncertainty in OC-EC split by FID response.

Recently, our research group developed a thermal optical carbon analyzer to measure particulate OC and EC. This paper demonstrates instrumental features and analytical performance of a newly developed TOT carbon analyzer. It also characterizes the sensitivity of OC and EC determination to the maximum temperature of He mode. Additional factors of OC-EC determination including the filter facing of particle loaded surface to optical beam and trace oxygen in He were also examined.

2. Materials and Methods

2.1. Instrumentation of Carbon Analyzer

Fig. 1 shows a schematic of the newly developed TOT carbon analyzer (named as KNU carbon analyzer below). KNU carbon analyzer is configured with analytical, pneumatic, and electronic control unit. The analytical unit consists of sample oven, oxidizing catalyst oven, reducing catalyst oven, flame ionization detector (FID), and optical module. Rotameters and solenoid valves are included in the pneumatic unit to control flow rates and directions. The electronic control unit is comprised with several printed circuit boards. The analyzer is designed to put an aliquot of filter vertically inside quartz tubing (OD 25 mm) of sample oven. Sample oven temperature and carrier gas are varied to selectively evolve carbonaceous material. An oxidizing oven of quartz tubing (OD 25 mm x L 150 mm) filled with manganese
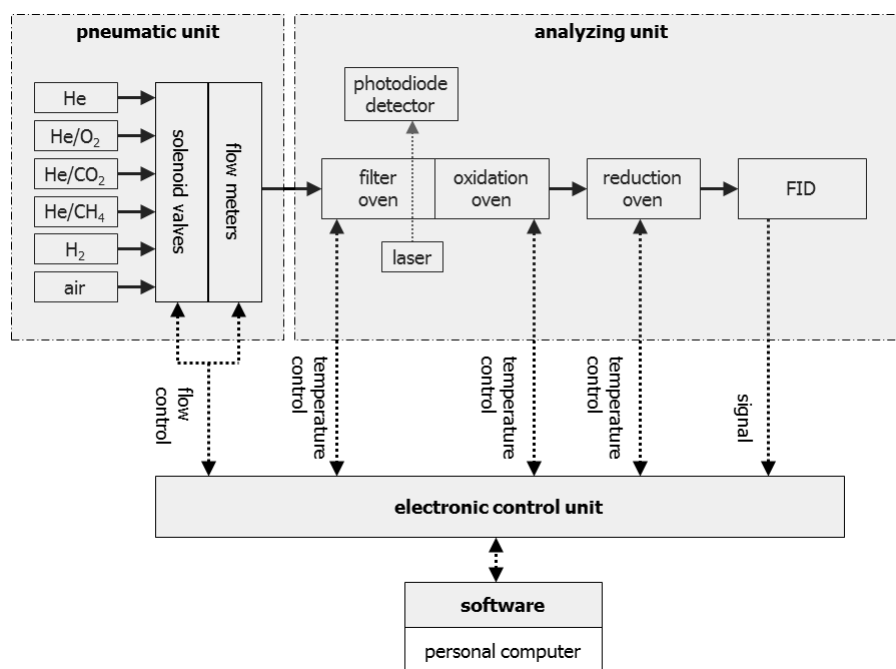
Fig. 1. Schematic of KNU carbon analyzer adopting thermal optical transmittance.

dioxide is connected downstream of sample oven. It is typically kept at a fixed temperature (e.g., 850°C) for the oxidation of evolved carbon to CO_2. CO_2 is converted by hot nickel catalyst (e.g., 650°C) to CH_4 that is quantitatively detected by a flame ionization detector.

Laser beam hits a sample filter after passing an optical-grade quartz rod horizontally connected to the side of quartz tubing in sample oven. Scattered light from the filter is detected by a photodiode detector on the opposite side of laser. A narrow band pass filter is placed in front of photodiode detector to minimize background interferences.

Helium (>99.999%), 2% oxygen in helium, CH_4-helium mixture, hydrogen (>99.999%), and zero grade air in high pressure cylinder are used. CH_4-helium mixture (2-10% CH_4) is used as calibration gas for quantitation. All gases are used as purchased except for helium that is further purified with an oxygen trap to remove trace oxygen.

All electric-actuated devices such as solenoid valves, heaters, and a cooling blower are controlled by a data acquisition system and an operation program for automatic operation of the carbon analyzer. Gas flows in carbon analyzer are controlled by solenoid valves and rotameters. Analysis data are displayed on a computer monitor and saved on the computer. Those are used for the calculation of OC and EC and system maintenance.

2.2. OC−EC Analysis Protocol

IMPROVE and NIOSH OC-EC protocols are 2 most widely used ones. Many variations such as EU protocols are based on those protocols. For this study we developed an OC and EC protocol through literature review as shown in Table 1. It is similar to a protocol of University of Hong Kong Science and Technology that is a combination of IMPROVE and NIOSH (Yang and Yu, 2002). Briefly, filter sample is heated in He, stepwise, to 800°C to volatilize OC.

Table 1. Temperature protocols used to analyze samples used in this study and found in the literature

Step	NIOSH 5040 T, duration (^{o}C, s)	EPA/NIOSH T, duration (^{o}C, s)	IMPROVE T, duration (^{o}C, s)	EUSAAR-1 T, duration (^{o}C, s)	EUSAAR-2 T, duration (^{o}C, s)	This study T, duration (^{o}C, s)
He1	250, 60	310, 60	120, 150-580	200, 120	200, 120	200, 70
He2	500, 60	475, 60	250, 150-580	300, 150	300, 150	550, 120
He3	650, 60	615, 60	450, 150-580	450, 180	450, 180	650, 80
He4	850, 90	900, 90	550, 150-580	650, 180	650, 180	800, 150
He5						550, 60
He/$O_2$1	650, 30	600, 45	550, 150-580	550, 240	500, 120	550, 90
He/$O_2$2	750, 30	675, 45	700, 150-580	850, 150	550, 120	700, 90
He/$O_2$3	850, 30	750, 45	800, 150-580		700, 70	800, 200
He/$O_2$4	940, 120	825, 45			850, 80	
He/$O_2$5		920, 120				

The filter is cooled to 550°C and heated stepwise to 800°C to evolve EC by combustion in 2% O_2 in He. Temperature steps are determined to help understanding sensitivity of OC-EC determination to the maximum temperature of He, which is the most critical issue in the sensitivity (Cavalli et al., 2010; Chow et al, 2007). At the later part of analysis calibration gas injections are made both in He and He-O_2 atmosphere, respectively. This calibration method allows obtaining independent response factors in He and He-O_2. In addition, the status of oxidizing and reducing catalysts can be easily checked out. Peak areas in the calibration should be same if the catalysts work normally. Abnormal difference in the peak areas is associated with malfunction of the catalysts. Fig. 2
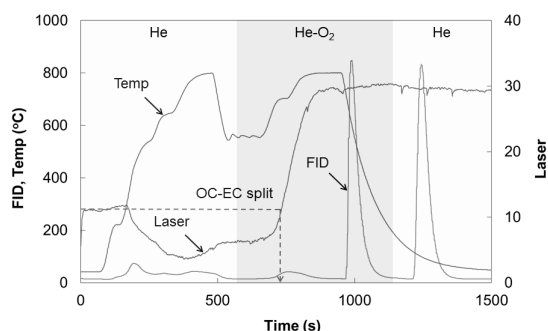
Fig. 2. Typical thermogram for the OC-EC analysis of KNU carbon analyzer showing signals of FID, sample oven temperature, and laser.

shows a typical thermogram for OC-EC analysis. In this work the dependency of OC and EC split on the maximum temperature in He was examined between 550-800°C. The sensitivity of OC-EC determination to facing of filter to laser beam and oxygen level in carrier gas was also characterized.

Carbonate carbon was not separately determined based on previous findings that it is minimal in ambient particles (Nunes and Pio, 1993; Ohta et al., 1998). Contribution of any measurable carbonate carbon is likely to depend on the maximum temperature in He due to the decomposition temperature of carbonate compounds (Birch and Cary, 1996; Cavalli et al, 2010).

For the comparison of OC and EC analysis methods, ambient aerosols were collected on quartz fiber filters using a high volume sampler. Quartz fiber filters were cleaned in a muffle furnace at 550°C for more than 2 hrs before the sampling. Cleaned filters were kept in the freezer after wrapped individually using aluminum foil treated same as them. Filter samples were stored frozen until OC and EC analysis with KNU carbon analyzer. An aliquot (1 cm x 1 cm) of filter sample is used in OC and EC analysis.

3. Results and Discussion

3.1. Uniformity of Carbonaceous Aerosol Loading

One of main focus of this work is the maximum temperature in He that has been pointed out as the principal cause of uncertainty in OC-EC determination. Three filters with differences in carbonaceous particle loadings were used in the examination. It is necessary to use many aliquots per sampled filter with same OC and EC loadings to properly compare analysis protocols. The uniformity of particle loadings was tested before investigating the maximum temperature in He. Pairs of punches from several different positions of a sampled filter were used for the examination. Two or three punches were taken at 3 different positions in a filter. The paired aliquots at a location were punched as close as possible to each other.

Table 2 shows OC and EC data for the examination of particle loading uniformity. For a lower loaded filter (QFF1), OC loadings were 10.08 ± 0.21 (n=3), 10.49 ± 0.45 (n=2), and 10.89 ± 0.55 µg/cm^2 (n=3) at positions A, B and C, respectively. EC loadings were 2.41 ± 0.02 (n=3), 2.53 ± 0.07 (n=2), and 2.55 ± 0.17 µg/cm^2 (n=3) at positions A, B and C, respectively. Mean OC and EC loadings were 10.49 ± 0.52 (n=8) and 2.55 ± 0.17 µg/cm^2 (n=8), respectively. The coefficient of variation (CV) of mean OC and EC is 5.0 and 6.7%, respectively.

For a moderately loaded filter (QFF2), OC loadings were 27.87 ± 0.68 (n=2), 27.52 ± 0.17 (n=2), and 26.85 ± 1.47 µg/cm^2 (n=3) at positions A, B and C, respectively. EC loadings were 4.94 ± 0.23 (n=3), 5.11 ± 0.31 (n=2), and 5.47 ± 0.59 µg/cm^2 (n=3) at positions A, B and C, respectively. Mean OC and EC values are 27.33 ± 1.01 (n=7) and 5.22 ± 0.45 µg/cm^2 (n=7), respectively. The coefficient of variation (CV) of mean OC and EC is 3.7 and 8.6%, respectively. PC and TC were also in good agreements as shown in Table 2.

For OC, the CVs are in the lower end of CV ranging 3.7-11.3% for Kosan samples of ACE-Asia and urban samples of the United States (Schauer et al., 2003). For EC, the CVs are substantially lower than Schauer el al.'s ranging 12.8-21.1%. Note that data of Schauer et al. are results of analyses by 8 laboratories participated in ACE-Asia using Sunset laboratory carbon analyzer and ACE-Asia protocol. Reportedly, their uncertainty for OC is in good agreement with the instrument reported uncertainty, whereas their uncertainty in EC is substantially deviated from the instrument reported uncertainty. Excellent CVs in both OC and EC determinations of this study are indicatives of not only consistency in OC-EC analysis using newly developed KNU carbon analyzer but also good uniformity of carbonaceous particle loadings. It verifies that reliable comparison of OC-EC analysis protocols can be made using the sampled filters.

Table 2. Uniformity of OC and EC loadings for 2 quartz fiber filters (QFF) analyzed by KNU protocols

Filter	n	OC	EC	PC	TC
		µg/cm^2	µg/cm^2	µg/cm^2	µg/cm^2
QFF1A	3	10.08±0.21	2.41±0.02	1.14±0.18	12.49±0.23
QFF1B	2	10.49±0.45	2.53±0.07	1.19±0.17	13.02±0.52
QFF1C	3	10.89±0.55	2.71±0.16	1.17±0.23	13.60±0.70
Mean	8	10.49±0.52	2.55±0.17	1.17±0.17	13.04±0.68
QFF2A	2	27.87±0.68	4.94±0.23	3.15±0.34	32.81±0.91
QFF2B	2	27.52±0.17	5.11±0.31	3.29±0.25	32.64±0.49
QFF2C	3	26.85±1.47	5.47±0.59	3.98±0.91	32.33±2.07
Mean	7	27.33±1.01	5.22±0.45	3.55±0.69	32.55±1.29

3.2. Effects of the maximum temperature in He on OC−EC determination

As described above, the maximum temperature in He atmosphere is $800^{\circ}C$ for standard analysis protocol of KNU carbon analyzer. It was adjusted to 550, 650, 700, and $750^{\circ}C$ to examine the sensitivity of OC and EC split. The lowest temperature of $550^{\circ}C$ is same as that for IMPROVE protocol. The highest temperature was targeted to match $850^{\circ}C$ of NIOSH 5040 method, but somewhat lower temperature of $800^{\circ}C$ is chosen considering stability of laser signal and maintenance of sample oven.

Three quartz fiber filters with different loadings were used in the comparison. Table 3 shows the sensitivity of OC-EC split to the maximum temperature. For lower loaded filter (QFF1) at 550, 650, 700, 750, and $800^{\circ}C$, OC varied from 9.09, 10.46, 10.54, 11.32, and 10.49 $\mu g/cm^2$, respectively, and EC varied from 2.90, 2.95, 2.73, 2.56, and 2.55 $\mu g/cm^2$, respectively. Moderately loaded and highly loaded filters show the same trend as the lower loaded one. For moderately loaded filter (QFF2), OC is 24.10 and 27.33 $\mu g/cm^2$ and EC is 6.57 and 5.22 $\mu g/cm^2$ for 550 and $800^{\circ}C$, respectively. For highly loaded filter (QFF3), OC is 36.19 and 38.44 $\mu g/cm^2$ and EC is 8.88 and 6.31 $\mu g/cm^2$ for 550 and $800^{\circ}C$, respectively.

Fig. 3 shows EC/TC ratios according to the maximum temperature in He. For the maximum temperature increase from 550 to $800^{\circ}C$, EC/TC ratios are lowered by 4.65% from 24.2 to 19.2%, by 5.38% from 21.4 to 16.0%, and by 5.61% from 19.7 to 14.7% for lower and moderately, and highly loaded filter, respectively. It is obvious that EC/TC ratio decrease is increasing for higher loading. Schauer
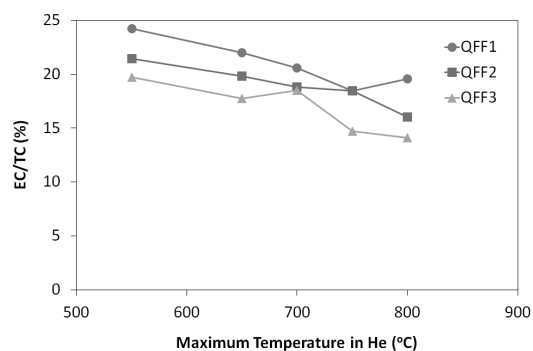

Fig. 3. EC/TC ratios (%) as a function of the maximum temperature in He. QFF1, QFF2, and QFF3 represent lower, moderately, and highly loaded quartz fiber filer, respectively.

Table 3. Sensitivity of OC and EC determination to the maximum temperature of He

Filter	Temp.	n	OC	EC	PC	TC
	^{o}C		$\mu g/cm^2$	$\mu g/cm^2$	$\mu g/cm^2$	$\mu g/cm^2$
QFF1	800	8	10.49±0.52	2.55±0.17	1.17±0.17	13.04±0.68
	750	3	11.32±0.11	2.56±0.10	1.12±0.11	13.88±0.02
	700	3	10.54±0.70	2.73±0.26	1.46±0.21	13.27±0.71
	650	3	10.46±0.12	2.95±0.03	1.79±0.08	13.41±0.13
	550	3	9.08±0.21	2.90±0.12	2.95±0.13	11.98±0.27
QFF2	800	7	27.33±1.01	5.22±0.45	3.55±0.69	32.55±1.29
	750	3	26.27±0.42	5.94±0.10	3.75±0.28	32.21±0.35
	700	3	26.07±0.27	6.05±0.90	4.85±0.21	32.12±0.65
	650	3	26.15±0.70	6.46±0.21	5.49±0.25	32.61±0.52
	550	3	24.10±1.04	6.57±0.46	7.75±0.33	30.67±1.46
QFF3	800	5	38.44±1.06	6.31±0.45	6.24±0.68	44.76±1.48
	750	1	37.14	6.40	6.89	43.54
	700	1	35.88	8.15	6.34	44.03
	650	1	36.79	7.94	9.32	44.73
	550	1	36.19	8.88	11.14	45.07

et al. (2003) presents approximately 6 to 10% decrease in EC/TC ratio of atmospheric samples for the maximum temperature increase from 550 and 870°C. For a later study, it might be worth to investigate the influence of temperature protocol for various source samples. Wood smoke particles are largely influenced by the maximum temperature comparing to coal fly ash, carbon, black, and secondary organic aerosol (Schauer et al., 2003).

Table 3 shows PC fraction in OC is higher at lower maximum temperature in He. On average, PC/OC ratio for 800°C is 13.5% much lower than 31.8% for 550°C. It could be partly caused by incomplete volatilization of OC at relatively lower temperature in He. It is likely also affected by early catalytic removal of EC at higher temperature in He (Chow et al., 2001). Difference in light absorption cross sections of
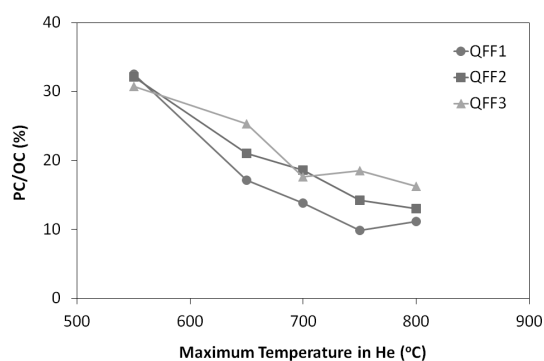

Fig. 4. PC/OC ratios (%) as a function of the maximum temperature in He.

PC and EC (Boparai et al., 2008; Yang and Yu, 2002) might be also involved in the discrepancy. We need more effort to clearly understand and minimize the phenomena in the future.

3.3. Sensitivity of OC–EC determination to trace oxygen in He and filter facing

Oxygen in He will combust EC during analysis in He. OC-EC split is likely to be sensitive to the presence of oxygen in He. We attempted to understand the influence of oxygen in typical operational conditions. In a typical OC-EC analysis, we used pure He which passed an oxygen trap with indicator to eliminate trace oxygen. Highly loaded filer punches were analyzed using base analysis protocol with and without oxygen trap. Table 4 shows OC, EC, PC, and TC. It shows negligible influence of oxygen trap on the OC-EC split. In the presence of O_2 trap, OC and EC were 38.44 ± 1.06 and 6.31 ± 0.45 µg/cm^2, respectively. In the absence of O_2 trap, OC and EC were 37.17 ± 2.18 and 6.32 ± 0.43 µg/cm^2, respectively. The insignificance implies that pure He itself is good enough for proper OC-EC determination. However, it would be better to use an oxygen trap with indicator for quality control of OC-EC data.

In standard analysis particle loaded side of filter punch is put facing forward to laser beam. However, it can be placed oppositely with the face backward to laser beam. The lower loaded filter (QFF1) was used for the examination. For forward facing, OC and EC

Table 4. Sensitivity of OC and EC split to oxygen level in He examined with and without additional oxygen trap

Condition	n	OC	EC	PC	TC
		µg/cm^2	µg/cm^2	µg/cm^2	µg/cm^2
With O$_2$ trap	5	38.44±1.06	6.31±0.45	6.24±0.68	44.76±1.48
Without O$_2$ trap	4	37.17±2.18	6.32±0.43	6.91±0.50	43.49±1.93

Table 5. OC and EC determined with particle loaded side of a quartz filter facing forward and backward to incident laser beam

Condition	n	OC	EC	PC	TC
		µg/cm^2	µg/cm^2	µg/cm^2	µg/cm^2
Forward facing	8	10.49±0.52	2.55±0.17	1.17±0.17	13.04±0.68
Backward facing	4	11.74±0.26	2.12±0.26	0.77±0.06	13.85±0.49

were 10.49 ± 0.52 and 2.55 ± 0.17 µg/cm^2 (n=8), respectively. For backward facing, OC and EC were 11.74 ± 0.26 and 2.12 ± 0.26 µg/cm^2 (n=4), respectively. Filter facing shows negligible influence in the OC-EC split. Interestingly, PC fraction in OC of 11.2 for forward facing is about 2 times higher relative to 6.6 of backward facing. It is unclear about the variation of PC fraction due to filer facing. It is apparent that proper correction of pyrolytic conversion results in consistent OC and EC data, even though the magnitude of PC formation varies by the filter facing.

4. Conclusion

New TOT carbon analyzer has been developed for the analysis of particulate OC and EC in the atmosphere. Consistent OC and EC for pairs of punches of a sampled filter demonstrate both the stability of analysis using the KNU carbon analyzer and uniformity of carbonaceous aerosol loadings on the filter. The influence of the maximum temperature in oxygen-free He on OC and EC determination was investigated as the most critical cause of the uncertainty in OC and EC data. For the temperature increase from 550 to 800°C, EC/TC ratios are lowered by 4.65% to 5.61% for various loadings of OC and EC. The magnitudes are comparable to those observed in previous researches using TOT OC and EC analysis. It implies that a largely discrepancy in EC between NIOSH 5040 and IMPROVE protocols are likely mainly caused by other parameters such as optical methods for the correction of pyrolytic conversion (e.g., transmittance vs. reflectance). OC-EC split was insensitive to the addition of oxygen trap for the further purification of pure He (>99.999%), which is being used in the normal analysis. Although pure He (>99.999%) is quite enough for reliable OC-EC analysis, it might be better to use an oxygen trap with indicator for quality control. The sensitivity of OC-EC

split to the facing of sample loaded surface to incident laser beam was negligible. It was possible by proper correction of PC in the determination of OC and EC split.

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