A non-destructive optical color space sensing system to quantify elemental and organic carbon in atmospheric particulate matter on Teflon and quartz filters

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H I G H L I G H T S

- Demonstrate the measurement of EC and OC on Teflon filters using optical color space sensing system.
- Demonstrate the equivalency of Teflon and Quartz for EC and OC measurement by the optical color space method.
- Demonstrate that inorganic components of PM_{2.5} do not lead to bias in the optical color analysis of OC and EC.
- Evidence that different sources of OC have small optical differences using the optical color method that may be exploited.

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Optical color space sensing proved to be a valuable method in particle characterization since it provides a non-destructive, fast, and cost-efficient way to estimate organic and elemental carbon (OC, EC) in atmospheric particulate matter. Here we expand and validate the previous work with the measurement of the CIE-Lab optical color space system and development of a multi-parameter reference calibration model to estimate EC/OC collected on Teflon and quartz filters. Analysis of approximately 500 Teflon and quartz filter samples demonstrated that the described method could be a robust way to estimate EC and OC loadings on the filters. The results showed that the correlation coefficients between predicted and measured loadings for the model-estimated EC and OC were 0.951 (CV (RMSE) = 15.1%) and 0.908 (CV (RMSE) = 20.7%) on Teflon filters and 0.948 (CV (RMSE) = 17.4%) and 0.895 (CV (RMSE) = 21.1%) on quartz filters respectively. The model cross-validation also provided good agreement between the predicted EC and OC loadings on Teflon and quartz filters and the NIOSH thermal-optical method. It was also found that the mixing state of the chemical composition and sources of OC could interfere the absorption and scattering of light, which results in a model estimation uncertainty that should be evaluated within the model estimations. The non-destructive and low analytical cost of the method, when applied to Teflon filters that are used for mass measurement are a cost effective means for estimating EC and OC exposures and concentrations in health studies and large-scale monitoring campaigns.

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1. Introduction

Fine aerosols particles play a significant role in atmospheric processes. Therefore understanding of the physical and chemical characteristics of the particles is of prime importance (Molnár et al., 1999). Airborne carbonaceous aerosols are considered a major

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component of fine particles with an aerodynamic diameter smaller than $2.5\ \mu\text{m}$ ($\text{PM}_{2.5}$) (Pachauri et al., 2013). Based on the findings of Rogge et al. (1993), carbonaceous species make up about 20–40% of the total fine particle mass in highly polluted areas. In addition, Nunes and Pio (1993) found that carbonaceous particles comprised about 80% of the total fine particle mass in suburban and industrialized areas (Molnár et al., 1999; Nunes and Pio, 1993; Rogge et al., 1993). The carbon component in fine particulate matter may contribute to human health problems, including serious respiratory and cardiovascular diseases. This may be due to the high oxidative/reductive potential of specific organic species (Jones and Harrison, 2005; Pachauri et al., 2013).

A variety of different analytical techniques have been used to determine the concentration of organic carbon (OC) and elemental carbon (EC) in fine aerosol particles collected on filters. The most widely used procedures for carbon aerosol analysis are the thermal-optical methods (destructive thermal evolution techniques), which utilize thermal and chemical refractory properties for measurement of both organic and elemental carbon collected on quartz filters over a period of several hours (Birch and Cary, 1996; Chow et al., 1993; Ramanathan et al., 2011). Organic carbonaceous compounds can also be measured using solvent extraction methods (Grosjean, 1975). Both thermal-optical and solvent extraction methods destroy the filter sample during the analysis (Pollard et al., 1990; Ramanathan et al., 2011). In addition, although these EC/OC analysis techniques provide a valuable understanding of particulate matter (PM) composition and its impacts on human health and the environment, they are expensive and require a high level of technical expertise. The thermal-optical method requires preservation and shipment of filters to laboratory; analysis of one filter costs approximately \$50, and the total annual cost using this approach based on typical daily measurements would be about \$18,250 (Ramanathan et al., 2011).

Recently, a number of researchers have investigated the use of optical techniques to estimate PM and its components using various devices, such as scanners and digital cameras. Optical color space sensing has also proven to be a valuable method in particle characterization, for it provides a non-destructive, fast, and cost-efficient way to estimate organic and elemental carbon on quartz filters. Ramanathan et al. (2011) suggested a low-cost optical method that utilizes a dynamic range of conventional cellphone cameras and the standard scanners that measure the red wavelength (ρ -red) of particles collected on filters. They showed that the ρ -red could be a reliable indicator of absorption by black carbon (BC) on a filter within 20% accuracy of a BC reference instrument. In addition, Olson et al. (2016) developed an HSV color space method to determine OC/EC loadings on quartz filter fibers. HSV model is based on a cylindrical-coordinate representations of the optical measurement of hue, saturation, and value components. Although these particle characterization techniques expand understanding of the optical properties of fine particles, there are concerns that the noise produced by the digital cameras and scanners potentially interfere with capturing the accurate color of the filter loadings. Furthermore, summarizing the complete color by parameter models does not include all of the embedded information about the true color. Since the parameters cannot be uniquely mapped to one another, some incremental information can only be obtained by combining different parameterizations. Here we expand and validate the method developed by Olson et al. (2016) to estimate the EC/OC loadings collected on Teflon filters with the measurement of the independent CIE-Lab optical color space sensing of the Teflon filter loadings. The CIE-Lab color system is a color-opponent space with dimension L^* for lightness and a^* for redness/greenness, b^* for blueness-yellowness, C^* for relative saturation and h^* for hue angle

in the color-opponent dimensions. The detailed information about CIE-Lab color system is provided in supplementary material (Text S1).

Estimation of OC/EC on Teflon filters using non-destructive and cost-efficient way will provide significant opportunities, in developing regions and large scale monitoring programs in occupational exposure testing and health studies. We also explore the effects of the mixing state of PM composition in EC/OC model uncertainty. In addition, our analysis begins to illustrate that the sources of OC may also contribute and impact the absorption and scattering of light, which results in a model estimation uncertainty that should be evaluated within the model estimations (Olson et al., 2016; Ramanathan et al., 2011). Both OC and EC reflect and absorb light to varying degrees which cause different ranges of visible color illustrations based on their chemical composition and source (Bergin et al., 2014; Olson et al., 2015). Thus, these color representations can be captured using color space measurement techniques, e.g., colorimeters to estimate the amounts of EC/OC loadings on both Teflon and quartz filters. Color space measurement technique is a specific organization of colors which allows for reproducible representations of color, in both analog and digital representations. This study aims to provide a low-cost and energy-efficient way to measure EC/OC on Teflon filters, which reduces the costs and therefore facilitates air pollution mitigation strategies in remote areas, including rural or resource-constrained locations where financial and instrumental needs are matters of concern.

2. Experimental methods

2.1. Sample collection and instrumentation

Approximately 500 quartz and Teflon filters collected from diverse regions of China were analyzed for particulate matter with an aerodynamic diameter of $2.5\ \mu\text{m}$ or less ($\text{PM}_{2.5}$). The main dataset included $\text{PM}_{2.5}$ samples from 5 representative sampling sites in Ordos city within the Inner Mongolia Autonomous Region. Outdoor 24-hr $\text{PM}_{2.5}$ samples were collected from 1st August 2014 to 30th November 2014 at each sampling site using 4-channel low volume $\text{PM}_{2.5}$ samplers with a Teflon-coated aluminum cyclone inlet that selected aerosols with an aerodynamic diameter less than $2.5\ \mu\text{m}$. The flow rate was set to $18.6\ \text{L min}^{-1}$, as recommended by the standard method for $\text{PM}_{2.5}$ collections (Zhang et al., 2008). Two quartz and two Teflon filters were loaded simultaneously into the sampler. In total, 200 quartz and 120 Teflon filters were collected for this dataset.

Additional samples were collected from independent field campaigns in Beijing and Shenzhen, China. One dataset was comprised of 80 12-hr $\text{PM}_{2.5}$ quartz filter samples collected from 12th August to 19th September 2015 during the Beijing military campaign that used a high volume $\text{PM}_{2.5}$ sampler. Another dataset from Yuquan Road in Beijing included 30 24-hr $\text{PM}_{2.5}$ samples collected on quartz and Teflon filters using a 2-chamber low volume sampler (collected from 1st to 30th Feb 2013). About 50 Teflon and quartz filter samples were obtained from a 2012 Shenzhen Universidad collection that used low volume dual channel $\text{PM}_{2.5}$ samplers (collected from 12th August 2012 to 4th September 2012). Detailed information about the sampling sites, instrumentations, and sample quantities are provided in Table 1. A schematic map of the geographical locations of the sampling sites is provided in supplementary material (Fig. S1).

All quartz fiber filters were baked at $550\ ^\circ\text{C}$ for a minimum of 8 h to remove organic impurities prior to sample collection. Total OC and EC were quantified from the quartz fiber filters using the Sunset thermal-optical carbon analyzer (Sunset Laboratory, Forest

Table 1

The detailed information about the sampling sites, instrumentations, and the analysis method used in the training and test case verification datasets.

Sample dataset	Site characteristics	Sampling period	Location	EC-OC analysis method	Filter type	EC range ($\mu\text{g}/\text{cm}^2$)	OC range ($\mu\text{g}/\text{cm}^2$)	Training samples ^a	Test case samples ^a
Ordos, YA,	Urban Arid and semi-arid	1st Aug to 30th Nov 2014	39°34'36"N; 109°44'6"E	NIOSH/Sunset	Q/T	0.81–14.89	15.34–66.43	23, 19	13, 11
Ordos, KK	Urban Arid and semi-arid	1st Aug to 30th Nov 2014	39°35'55.43"N; 109°46'23.87"E	NIOSH/Sunset	Q/T	0.60–14.35	9.11–48.52	17, 17	11, 10
Ordos, DA,	Urban Arid and semi-arid	1st Aug to 30th Nov 2014	39°47'18.45"N; 109°58'23.47"E	NIOSH/Sunset	Q/T	0.91–18.22	16.40–57.32	14, 11	16, 13
Ordos, DZ	Urban Arid and semi-arid	1st Aug to 30th Nov 2014	39°48'45.81"N; 110°0'8.27"E	NIOSH/Sunset	Q/T	1.01–16.38	18.65–61.32	10, 13	8, 12
Ordos, DB	Sub-urban Arid and semi-arid	1st Aug to 30th Nov 2014	39°49'34.02"N; 109°56'54.76"E	NIOSH/Sunset	Q/T	0.9–18.44	8.88–55.1	11, 17	12, 12
Blank	—	—	—	NIOSH/Sunset	Q/T	0.00084 –0.0012	3.54–5.02	3, 1	2, 2
Beijing, Military campaign	Urban Severe pollution control	12th Aug to 19th Sep 2015	116°23'11"E; 40°0'21"N	NIOSH/Sunset	Q	1.45–12.59	10.12–64.2	39, NA	40, NA
Beijing, Yuquan Rd.	Urban With pollution episode	1st to 28th Feb 2013	116°15'3"E; 39°54'28"N	NIOSH/Sunset	T	1.99–35.94	14.43–76.44	NA, 15	NA, 15
Shenzhen Universidad	Urban Mixed sources	12th Aug to 4th Sep 2012	22.60° N; 113.97° E	NIOSH/Sunset	Q/T	1.11–20.94	9.34–73.23	25, 25	25, 25

YA: Inner Mongolia sampling site, Ordos, Ajina Park, KK: Inner Mongolia sampling site, Ordos, Kangzeyuan, Kangbashan New District, DA: Inner Mongolia sampling site, Ordos, Olympus Garden, Dongsheng District, DZ: Inner Mongolia sampling site, Ordos, Zonghelou, DB: Inner Mongolia sampling site, Ordos, Bayinmengke Forest Office.

Q: Quartz filters.

T: Teflon filters.

^a Numbers separated by a “,”. First represents the total number of Quartz filters and the second represents the number of Teflon filters used in training case and the test case datasets.

Grove OR) by the NIOSH method (Schauer, 2003; Schauer et al., 2003). Reported ambient concentrations of EC and OC have been field blank subtracted. The uncertainties for EC and OC measurements were calculated as the sum of the instrument uncertainty, the standard deviation of the field blanks, and 5% of the measurement. Thus, the reported uncertainty is obtained by multiplying the carbon yield of the sample in $\mu\text{g}/\text{cm}^2$ by 0.05 for the typical sample and instrument variability and adding $0.2 \mu\text{g}/\text{cm}^2$ from the typical instrument background as recommended by the EC/OC instrument manufacturer.

The EC tracer method (Turpin et al., 1991) was used to estimate secondary organic aerosols (SOA) and their effects on OC model underestimation was studied. The EC tracer method is based on the hypothesis that the ratio of primary organic carbon (POC) to EC is relatively constant, making EC a good tracer for SOA estimation (Turpin et al., 1991).

In this research, the Teflon filter samples of the selected dataset were analyzed for their trace metal and ion concentrations. Aerosol PM on the Teflon filters of the selected datasets was solubilized in Teflon bombs using a mixed acid (nitric, hydrochloric, hydrofluoric) microwave-aided digestion procedure. This protocol involves a total digestion of all aerosol components, including the aluminum silicates. Total trace elements were quantified by high resolution inductively coupled plasma mass spectrometry (ICP-MS) (Zhang et al., 2008). Concentrations of water-soluble cations (e.g., K^+ , Na^+ , Mg^{2+} , Ca^{2+} and NH_4^+) and anions (e.g., SO_4^{2-} , NO_3^- , Cl^-) were analyzed using an ion chromatographic system, after leaching of the Teflon filter samples of the selected datasets with 50 g of ultrapure water for 30 min at 40°C in an ultrasonic bath (Shen et al., 2007).

2.2. Optical color space sensing system

In this research, the CIE-Lab color space optical sensing system was applied to measure the optical properties of the $\text{PM}_{2.5}$ samples to develop the EC and OC predictive models. The CIE-Lab color system is a color-opponent space with dimension L^* for lightness and a^* and b^* for the color-opponent dimensions. The CIE-Lab color space includes all perceivable colors, which means that its gamut includes all of the color models. One of the most important characteristics of the $L^*a^*b^*$ model used in this research is device independence, which means all the colors are defined independently of their nature of creation or the device they are displayed on (ICI, 1971). More information about the CIE Lab color space system and its formulation are provided in the supplementary material (Text S1).

All the Teflon and quartz filters collected from Inner Mongolia and samples from other independent field campaigns were analyzed by a 3nh digital colorimeter (NR60CP, Shenzhen Technology INC.). The probe of the colorimeter sensor head was placed directly on the quartz and Teflon filters, and the color components were measured under the D65 instrument internal illumination light source. Each filter sample was analyzed 5 times and the average value of each color coordinate was applied as the optical property of the sample (Olson et al., 2016). CIE Standard Illuminant D65 is a commonly used standard illuminant, as defined by the International Commission on Illumination (CIE). It is a part of the D series of illuminants, which illustrate standard illumination conditions in an open-air setting in different parts of the world. D65 roughly simulates average mid-day light, for it is comprised of both direct sunlight and light diffused by a clear sky. More information about the D65 illumination source and its spectral power distribution is provided in the supplementary material (Text S2 and Fig. S2). To avoid cross-contamination of the samples, the sensor

head of the colorimeter was placed at the edge of the filter deposition area and wiped clean between analyses with laboratory clean wipes. In addition, in order to minimize the area affected by the colorimeter, the smallest 4 mm aperture size sensor head was selected for measurement. Although the applied method is non-destructive, caution should be taken if additional analyses include trace compounds.

2.3. Creating a reference calibration

The results of the NIOSH thermal-optical EC/OC loadings of the filter samples were associated with the CIE-Lab color system. Two different model cases were applied in this method:

- 1) NIOSH thermal-optical EC/OC with CIE-Lab system on quartz filters;
- 2) NIOSH thermal-optical EC/OC with CIE-Lab system on Teflon filters.

For each model case, approximately 110 filters were randomly selected to create training case reference calibration datasets. After creating the calibration model, the test case datasets (new samples that were not included in the training case datasets) were analyzed by the reference calibration determined from the model. The Excel random number generator function was used for the selection. The detailed information about the total number of the Quartz and Teflon filters used in training case and the test case datasets is provided in Table 1. Since there are no reference thermal-optical methods available to determine EC/OC loading amounts on Teflon filters, the associated values had to be measured and reported by using their corresponding quartz filters collected at the same time from the same sampler. The following equation was used in order to calculate the EC/OC loadings on the filter samples:

$$\text{EC/OC} \left[\mu\text{g}/\text{cm}^2 \right] = \frac{[\text{EC/OC}]_{\text{thermal-optical}} \left[\mu\text{g}/\text{m}^3 \right] \times F \left[\text{m}^3 \right]}{A \left[\text{cm}^2 \right]} \quad (1)$$

$A \left[\text{cm}^2 \right]$ is the area of the filter occupied by the EC/OC particles deposited on the filter, and is constant across filters; the filter deposit area is 11.76 cm^2 for the 47-mm quartz and Teflon fiber filters used for sampling in a filter cassette with an inside-diameter of 38.7-mm. $F \left[\text{m}^3 \right]$ is the volume of air that passes through the filter in the sampler and can differ for each sample.

The following assumptions were made to create the model cases: 1) Elemental carbon usually absorbs more light than any other species. In this case, we assume that the color coordinate L^* is mostly dominated by the EC loadings (Andreae and Gelencsér, 2006; Bond and Bergstrom, 2006; Derimian et al., 2008; Olson et al., 2016). The L^* color coordinate defines the amount of lightness/darkness in the samples (supplementary material). 2) The OC loadings on the filter can absorb and reflect the visible light in different intensities, which produces different ranges of visible color illustrations due to their complex chemical nature. We assume that the OC loading is characterized by the C^* and h^* color coordinates. 3) The OC loading determined by the C^* and h^* is also associated with a^* and b^* of the color system.

The perception of aerosols by the human eye is impacted by the presence of EC as well as the hue and Chroma of OC. Therefore, the prediction of OC from the human eye perception is difficult but the ability of the CIE-Lab color space system to isolate these variables allows OC to be quantified. Although direct emissions from sources have very different perceived color by the human eye, Olson et al. (2015, 2016) have shown that the isolated organic carbon does

not have very wide ranges of optical properties when removed from EC and that the hue of a wide range of aerosols from sources and in the atmosphere are typically within a small range, which is exploited in the current work.

Initially, according to the model case assumptions, a multiple linear regression model ($y = \alpha + L^*X_1 + a^*X_2 + b^*X_3 + C^*X_4 + h^*X_5$) that develops a least squares best-fit model between the filter EC/OC loading and the CIE-Lab color coordinates was applied to determine the training case datasets. However, evaluation of the initially developed reference model showed there was sensitivity to OC loadings on both quartz and Teflon filters that was not addressed (supplementary material, Fig. S3). The residuals of OC were not evenly dispersed around higher OC loading values for Teflon or quartz filters. A decrease in OC residuals was observed, along with an increase in sample OC loadings (Fig. S3). This shows that the initial model underestimated OC for both quartz and Teflon filters. The model's underestimation of OC could be the result of the mixing state of the sample's chemical composition and its source, which would interfere with the model analysis; this will be discussed more in proceeding section. In addition, the known issues with optical measurement on filters—including a shadow effect within the filters and uncertainties with thermal-optical EC/OC at low and high loadings—result in loading sensitivities (Olson et al., 2016). Therefore, an additional $(L^*)^2$, $(a^*)^2$, $(b^*)^2$, and $(C^*)^2$ was added in the reference OC calibration model in a stepwise regression platform. Further, model equations with more term values were investigated and found to not significantly improve the estimated OC loading values (Olson et al., 2016). Also, the independent variable $(C^*)^2$, which was added in the reference OC calibration model on Teflon filters, was found to cause co-linearity in our regression model; therefore, it was excluded from the analysis. It should be noted that although the utilized CIE-Lab color space system in our reference model is device-independent, there are correlations for L^* , a^* , and b^* color coordinates and, therefore, the uniform variations of the color coordinates L^* , a^* , and b^* will correspond to uniform changes in perceived color which would impact the OC and EC estimations (Olson et al., 2016). Therefore, using all color coordinates as independent variables in the reference model would result in a potentially more robust model. Equations (2)–(5) show the final results of the model fit determined for EC/OC estimations for the model case assumptions of Teflon and quartz filters. Table 2 reports the specific coefficients for each of the model terms for the investigated model cases. Table 3 shows the results of the regression analysis for the model cases in training and test case datasets.

$$\text{OC}_{\text{Teflon}} \left(\mu\text{g}/\text{cm}^2 \right) = \alpha + \beta(L^*) + \gamma(a^*) - \delta(b^*) + \epsilon(c^*) + \zeta(h^*) - \eta(a^*/b^*) + \theta(L^*)^2 + \lambda(a^*)^2 + \phi(b^*)^2 \quad (2)$$

$$\text{EC}_{\text{Teflon}} \left(\mu\text{g}/\text{cm}^2 \right) = \alpha + \beta(L^*) + \gamma(a^*) - \delta(b^*) + \epsilon(c^*) + \zeta(h^*) - \eta(a^*/b^*) \quad (3)$$

$$\text{OC}_{\text{Quartz}} \left(\mu\text{g}/\text{cm}^2 \right) = \alpha + \beta(L^*) + \gamma(a^*) - \delta(b^*) + \epsilon(c^*) + \zeta(h^*) - \eta(a^*/b^*) + \theta(L^*)^2 + \lambda(a^*)^2 + \phi(b^*)^2 + \omega(c^*)^2 \quad (4)$$

$$\text{EC}_{\text{Quartz}} \left(\mu\text{g}/\text{cm}^2 \right) = \alpha + \beta(L^*) + \gamma(a^*) - \delta(b^*) + \epsilon(c^*) + \zeta(h^*) - \eta(a^*/b^*) \quad (5)$$

3. Results and discussion

3.1. Model case 1: EC/OC with CIE-Lab system on quartz filters

A large randomly selected dataset containing the quartz filter samples obtained from our field campaigns were used as the

Table 2

The specific coefficients for each model used to create the reference calibration for the investigated model cases.

	EC Quartz			OC Quartz			EC Teflon			OC Teflon		
	Coefficient	S.E	P	Coefficient	S.E	P	Coefficient	S.E	P	Coefficient	S.E	P
α (Constant)	31.675	4.862	<0.001	175.218	45.807	<0.001	42.345	5.016	<0.001	300.223	79.459	<0.001
β (L^*)	−0.305	0.018	<0.001	−3.365	1.172	0.005	−0.416	0.037	<0.001	−5.427	2	0.008
γ (a^*)	0.293	0.920	0.75	−1.662	17.913	0.92	0.829	3.196	0.74	28.718	55.659	0.007
δ (b^*)	0.272	0.255	0.28	1.639	8.684	0.35	−6.990	1.346	<0.001	−9.431	19.203	0.12
ϵ (C^*)	0.232	1.507	0.40	−0.031	8.293	0.123	5.966	0.944	<0.001	4.214	4.384	0.33
ζ (h^*)	−0.00711	0.055	0.55	0.03	0.314	0.92	−0.0204	0.0147	0.16	−0.183	0.0998	0.04
η (a^*/b^*)	−8.418	4.789	0.04	7.816	31.536	0.80	−8.236	11.101	0.42	−113.401	100.602	0.26
θ (L^*) ²	—	—	—	0.016	0.008	0.03	—	—	—	0.030	0.0147	0.03
λ (a^*) ²	—	—	—	0.797	3.654	0.82	—	—	—	−0.456	12.417	0.97
φ (b^*) ²	—	—	—	−0.051	0.594	0.93	—	—	—	−0.334	1.422	0.81
ω (C^*) ²	—	—	—	−0.018	0.567	0.25	—	—	—	—	—	—

Table 3

The results of the regression analysis for the model cases in training and test case data sets.

Filter type		R ^a	F ^b	SE ($\mu\text{g}/\text{cm}^2$) ^c	CV(RMSE)	N
Quartz	EC (Training)	0.948	936.714	0.974	17.4%	118
	OC (Training)	0.895	427.577	5.014	21.1%	118
	EC (Training)	0.951	934.606	1.071	15.1%	110
	OC (Training)	0.908	461.373	5.284	20.7%	110
Teflon ^d	EC (Test)	0.952	1023.583	0.988	17.4%	108
	OC (Test)	0.907	464.240	5.398	22.0%	108
	EC (Test)	0.940	958.446	1.180	17.8%	95
	OC (Test)	0.897	351.791	5.347	22.7%	95

^a Correlation coefficient of model estimation.^b Ratio of the Model Mean Square to the Error Mean Square.^c Standard error of the model estimation.^d Independent variable (C^*)² was excluded from Teflon filters analysis due to the variables co-linearity.

training case calibration model. These samples were analyzed by the reference NIOSH thermal-optical EC/OC analyzer and offer particular characteristics associated with geographical and seasonal variability; however, they were less likely to consist of high concentrations of EC/OC and extreme values. Therefore, this dataset provides a good starting point to create the training case reference calibration. The correlation coefficients for the model were calculated as 0.948 and 0.895 for EC and OC, respectively. These results show good agreement for both EC and OC for the training case dataset (Table 3). The respective standard errors of the model estimation for EC and OC were 0.974 (CV [RMSE] = 17.4%) and 5.014 $\mu\text{g}/\text{cm}^2$ (CV [RMSE] = 21.1%) (Table 3). The relatively higher uncertainty for OC is not surprising, since it has complex chemical compositions and sources. This causes OC quantification with the colorimeter and thermal-optical techniques to be more sensitive (Olson et al., 2016). In addition, according to Table 3, both modeled EC and OC show good agreement for the test case datasets. The correlation coefficients were calculated as 0.952 and 0.907 for EC and OC, respectively (Table 3), which is close to the initial reference calibration developed by the training cases; standard errors of the estimates were 0.988 (CV [RMSE] = 17.4%) and 5.398 $\mu\text{g}/\text{cm}^2$ (CV [RMSE] = 22%), respectively. This shows that the model-estimated EC/OC on quartz filters was robust in calculating new test case samples. Fig. 1A and B illustrate histograms of the predicted values divided by the measured values of the test case model-developed calibration for NIOSH thermal-optical EC/OC with CIE-Lab color system on quartz filters. According to Fig. 1A, the ratio of the predicted/measured values for the test case model-developed EC shows a normal distribution (skewness = 0.237); however, the ratio of the predicted versus measured values for OC (Fig. 1B) is slightly

biased/skewed (skewness = 2.443). These results show that the model is slightly biased toward underestimation for OC. The histogram of the model-estimated EC did not show significant bias and, therefore, no sensitivity was found for this model analysis. In addition, according to Fig. 1A and B, about 0.917% and 4.854% of the entire test case dataset was predicted out of range ($\pm 40\%$, which is about the 95% confidence interval) of the accurate model estimation for EC and OC, respectively. In addition, approximately 92.5% of the dataset was calculated within the 95% prediction band of the reference EC thermal-optical uncertainty (average EC uncertainty = $0.694 \pm 0.185 \mu\text{g}/\text{cm}^2$). For model estimated OC approximately 87.7% of the dataset fell within the confidence range of the reference thermal-optical OC uncertainties (average OC uncertainty = $1.315 \pm 0.185 \mu\text{g}/\text{cm}^2$) (supplementary material, Fig. S4).

The samples collected from the Beijing military campaign were more stable and homogenous, because they were collected when severe pollution controls were in effect in Beijing. Therefore, it is expected that this dataset provides more robust model validation and less uncertainty than the other training case datasets for OC ($r = 0.908$) and EC ($r = 0.977$). The slope of the regression line of the Beijing military campaign dataset was calculated as 0.971 and 1.01 for OC and EC respectively (slope is close to 1, slope < 1 indicates model underestimation), which was significantly higher than the other training case datasets (supplementary materials, Fig. S5). This indicates that the bias towards underestimation of the OC model may be mitigated by using a more constant and homogenous sample set when establishing a CIE-Lab color space model (Olson et al., 2016). Additionally, the slight OC model bias between the test case and the training case dataset of quartz filters could be the result of a disparity in loadings between the testing sample dataset and the dataset used for the training case calibration. Some highly loaded samples with more concentrated EC/OC values existed in datasets that were not used for the training case calibration. When some highly loaded samples were excluded from the test case subset, an improved skewness value in the histograms of the test case model estimation for OC was observed. The samples from Inner Mongolia were collected under more varied geographical and temporal conditions as compared to the samples taken during the Beijing military campaign—a time period subject to intensive pollution control. Consequently, the Inner Mongolia samples were more dispersed. The correlation coefficient of the samples collected from the Beijing military campaign for model-estimated EC and OC were higher, which shows there is greater model validation and agreement for this sample dataset compared to the others.

Fig. 2A and B shows the residuals of EC and OC as a function of the NIOSH thermal-optical EC/OC. According to Fig. 2A, the residuals of EC are evenly dispersed for all EC loading values. No significant variations for EC residuals were observed when sample

Fig. 1. Distributions of the ratio of predicted to measured values of EC/OC. A: test-case model developed EC on quartz filters. B: test case model developed OC on quartz filters. C: test-case model developed EC on Teflon filters. D: test case model developed OC on Teflon filters.

EC loadings increased (Fig. 2A). This shows that the model is not sensitive toward underestimation/overestimation with high or low sample EC loadings. According to Fig. 2B, the residuals of OC were also evenly dispersed around different OC loadings. There was a slight sensitivity of OC residuals as the sample OC loadings increased. The more model uncertainty with OC could be the result of the mixing state of the sample chemical composition and source which leads to interfere with our model analysis and OC quantification with the colorimeter and the thermal optical techniques (will be discussed more in proceeding sections).

In order to investigate the effects of chemical composition on the model's tendency to underestimate EC and OC, the trace metals and ions of 3 sampling datasets were measured. The first dataset included more than 90 Teflon filters collected from Inner Mongolia, which correspond to the same quartz filters that were measured for EC/OC and used in the training case and test case subsets. The second selected dataset included over 30 samples collected from the Beijing Yuquan Road campaign, which also correspond to the same quartz samples used for EC/OC measurements and test case samples. This dataset included more highly concentrated samples than the other sampling subsets. Finally, the third dataset contained about 50 Teflon and quartz filters from Shenzhen Universidad. Fig. 3A, B, and C show scatter plots of the residual OC as a function of the selected chemical composition species for a whole dataset. As illustrated in Fig. 3B, the residuals of OC were not evenly dispersed around different SO_4^{2-} and NO_3^- concentration levels. The

OC residuals decreased as SO_4^{2-} and NO_3^- increased. This shows that the described model underestimation to OC increases especially when the concentrations of SO_4^{2-} and NO_3^- exceed 30 and 12 $\mu\text{g}/\text{m}^3$, respectively. In addition, these ions are more active during secondary aerosol formation. Therefore, the secondary organic aerosol (SOA) concentration of the filters were estimated by EC tracer method (Turpin et al., 1991) and their effects on OC underestimation was studied. The results showed that the residuals of OC were not evenly dispersed around different SOA loading levels. The OC residuals decrease with increases in SOA (Fig. 3D). This shows that the described model underestimation to OC increases especially when the loadings of the SOA exceed 25 $\mu\text{g}/\text{cm}^2$. Model underestimation of OC was also observed when concentrations of K^+ and Cl^- exceeded 1 $\mu\text{g}/\text{m}^3$ (Fig. 3A). In addition, we did not observe significant OC model underestimation with K^+/OC and Cl^-/OC ratios showing that the biomass burning did not affect OC model underestimation. The whole dataset did not show any significant correlation between the metallic species and the model underestimation of OC (Fig. 3C). In addition, no significant relationship was found between any of the species and the model underestimation of EC in the whole dataset. This agrees with our results (Fig. 2A and C) that found no significant model sensitivity to EC loadings in the quartz or Teflon filter datasets. The residuals of EC in Teflon and quartz filters were evenly dispersed around different EC loadings.

The model underestimation (for OC) observed in the sampling

Fig. 2. Residuals of predicted EC and OC for test data set (red circles) and the training data set (black circles) for reference NIOSH thermal optical method and the CIE-Lab color space system. A: presents the EC results on quartz filters. B: OC results on quartz filters. C: EC results on Teflon filters. D: OC results on Teflon filters. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

datasets might be a result of the exerted pigmentation powers of the mixing state of the chemical composition (trace metals and ions) and samples' source, which lead to cover the special light absorption and scattering pattern from OC species. The correlation matrix of the selected metals with CIE-Lab color space components is provided in [Supplementary Material Table S1](#). Previous studies have found that the color of PM could be affected by chemical composition, particularly if particles contain alkali and/or alkaline earth metallic compounds. The structural states containing alkali and alkaline earth metals can significantly affect color performance. Iron oxides also have the ability to determine PM's color, since their pigmenting power is strong even in low quantities ([Cornell and Schwertmann, 2003](#); [Schwertmann and Taylor, 1989](#)). The sample's geographic region and source also affect its main chemical composition and, therefore, influence its color variation. The samples collected from Inner Mongolia had mainly soil and dust origin, so their alkali and alkaline components determined their color performance. The samples collected from Beijing Yuquan Road had more concentrated sample and unique values and thus the model underestimation with OC could also be observed with the secondary organic formation.

3.2. Model case 2: EC/OC with CIE-Lab system on Teflon filters

For model case 2, the NIOSH thermal-optical EC/OC with CIE-Lab system was used on Teflon filters. The same procedure as conducted in model case 1 was also employed for the Teflon filter dataset. It should be noted that the EC/OC loadings on Teflon filters were measured using the corresponding quartz filter collected from the same sampler, as there is no reference thermal-optical method

available to determine these measurements directly from Teflon filters. The results showed that the correlation coefficients were 0.951 and 0.908 for the model-estimated EC and OC, respectively, which indicates good agreement for both EC and OC for the Teflon training case dataset ([Table 3](#)). The standard errors of the EC and OC estimates were 1.071 (CV [RMSE] = 15.1%) and 5.284 $\mu\text{g}/\text{cm}^2$ (CV [RMSE] = 20.7%), respectively. The Teflon training case dataset for model-estimated OC also showed better model validation and agreement compared to the quartz training dataset for model-estimated OC (the correlation coefficients were calculated as 0.908 and 0.895 for Teflon and quartz training cases, respectively). The correlation coefficients for EC and OC in the test case dataset were calculated as 0.940 and 0.897, respectively. These values are close to the initial values calculated by the training cases. This shows good validation and agreement between the training case and the test case datasets; the respective standard errors of the estimates were 1.180 (CV [RMSE] = 17.8%) and 5.347 $\mu\text{g}/\text{cm}^2$ (CV [RMSE] = 22.7%).

[Fig. 1C](#) and [D](#) shows histograms of the ratio of predicted/measured values of the test case calibration for NIOSH thermal-optical EC/OC with CIE-Lab color system on Teflon Filters. No distinguishable variation toward model underestimation was found for EC in the test case datasets. The histograms of the predicted/measured EC showed normal distribution (skewness = 0.154). However, the histograms of the model-estimated OC showed a slight model bias/uncertainty. The model-estimated OC showed a skewness value of 2.024, which indicates slight model underestimation. According to [Fig. 1C](#) and [D](#), about 2.150% and 9.911% of the entire test case dataset was predicted out of range of $\pm 40\%$, which is about the 95% confidence interval, respectively. In addition, approximately 90.1% of the Teflon filter dataset was calculated within the range of

Fig. 3. Residual OC as a function of the ions and metals concentration for the CIE-Lab Model A: residual OC with Cl^- and K^+ , B: residual OC with SO_4^{2-} and NO_3^- , C: residual OC with Ca, Al and Fe, D: residual OC with secondary organic aerosol.

the reference EC thermal-optical uncertainty (average EC uncertainty = $0.724 \pm 0.170 \mu\text{g}/\text{cm}^2$). For OC model estimation, 85.5% of the dataset was within the range of the reference thermal-optical OC uncertainty (average OC uncertainty = $2.229 \pm 0.712 \mu\text{g}/\text{cm}^2$) (supplementary material, Fig. S6).

Fig. 2C and D shows the residuals of EC and OC of Teflon filters as a function of the NIOSH thermal-optical EC/OC. The residuals of both EC and OC in Teflon cases are evenly dispersed for all the EC and OC loading values (Fig. 2C and D). There was only a slight decrease for EC residuals as the sample loadings on Teflon filters increased (Fig. 2C). This shows that the model-estimated EC/OC is not sensitive to sample loadings.

The samples collected from Inner Mongolia DA and YA sampling sites showed greater agreement and less model uncertainty for both EC and OC (supplementary material, Fig. S7). The correlation coefficients of the model-estimated OC for Inner Mongolia DA and YA sites were 0.899 and 0.868, respectively, which are significantly higher than the other training case datasets from Inner Mongolia and Shenzhen Universidad samples. The correlation coefficients for the model-estimated EC for Inner Mongolia DA ($r = 0.967$) and YA ($r = 0.919$) sites were also higher than all other training cases from Inner Mongolia and Shenzhen Universidad. The slopes of the OC calibration model for Inner Mongolia DA and YA sites were 0.809 and 0.865, respectively, which are significantly higher (and have lower uncertainty) than the other training case datasets. The slope of the EC calibration model is significantly higher (and has lower uncertainty) for Inner Mongolia DA and YA

sites (0.988 and 0.960).

3.3. Model cross-validation

In order to evaluate the overall agreement of the CIE-Lab model-estimated EC/OC on quartz and Teflon Filters with the reference

Fig. 4. Cross-validation between model developed EC on Teflon filters, Quartz filters and the NIOSH thermal-optical method.

thermal-optical EC/OC, a scatter plot of the NIOSH thermal optical EC/OC as a function of the CIE-Lab model-estimated EC/OC on quartz and Teflon filters—where the samples were matched in terms of day and sampler—was produced (Figs. 4 and 5). As illustrated, the modeled EC/OC on both quartz and Teflon filters showed high agreement with each other, as they agreed with the reference thermal-optical EC/OC. In Fig. 4, the EC model underestimation for quartz filters is slightly higher than that of the Teflon filters (Teflon slope = 0.978, quartz slope = 0.925). However, the correlation coefficient of the EC model estimation on quartz filters (0.953) was slightly higher than the Teflon filters (0.933). The OC model underestimation for Teflon filters (Fig. 5) was slightly higher than the corresponding quartz filter values (Teflon slope = 0.746, quartz slope = 0.769). In addition, as illustrated in Figs. 4 and 5, the model-estimated EC and OC on Teflon filters was more dispersed around the reference calibration line. In addition, the CIE-Lab model-estimated EC/OC on Teflon filters showed good agreement with the corresponding values on quartz filters. The correlation coefficient was 0.950 (slope = 1.01) and 0.959 (slope = 0.930) for model-estimated EC/OC for quartz and Teflon filters, respectively. The greater variation and model underestimation for Teflon filters compared to quartz filters, especially for OC, could be the result of

its material. Teflon filters are more reflective and have greater transmittance than quartz filters. This results in different color illustrations, even if both filters are collected under the same conditions. In order to evaluate the variations of the color illustration from quartz to Teflon filters, the color coordinates from the quartz filter dataset were compared to the corresponding color coordinates from the Teflon filter dataset; both were collected under the same conditions (supplementary material, Fig. S8). As expected, some of the color coordinates did not agree. The correlation coefficients were calculated as 0.977, 0.803, 0.784, 0.744 and 0.404 for L^* , a^* , b^* , C^* and h^* respectively. Due to the disagreement between the color coordinates from quartz and Teflon filters, the EC/OC model will be more dispersed. In addition, according to Olson et al., 2016, The EC loadings are strongly dependent on lightness (L^*) and OC is strongly dependent on Chroma C^* . Given the nature of these parameters, when L^* is darker then C^* has greater uncertainty. However, when C^* increases, there is a slight impact on the L^* parameter within the range of atmospheric PM samples. Therefore, it's believed that the interplay between the EC and OC loadings on these parameters is the reason why EC predictions are better than the OC predictions.

We also conduct multiple random batch sampling of the Teflon and quartz filters dataset in order to evaluate the reference calibration model performance and uncertainties with different combinations of the samples in the database. The correlation coefficients of the random batch samplings were close to the initial reference calibration derived from the training case datasets for both EC ($r = 0.979$ and 0.949 for quartz filters, $r = 0.945$ and 0.947 for Teflon filters) and OC ($r = 0.896$ and 0.892 for quartz filters, $r = 0.902$ and 0.890 for Teflon filters). This showed that the reference calibration model on quartz and Teflon filters was robust in calculating different combinations of samples in dataset (Supplementary material, Table S2).

Estimating EC/OC loading using the optical color space system provides great advantages over reference thermal-optical techniques, for it is less expensive and less labor intensive (Olson et al., 2016). However, it should be noted that the OC estimation is not simply a linear correlation to the particle's EC components. In this case, the ratio of OC_{NIOSH}/EC measured by the reference thermal-optical method was compared to the $OC_{colorimeter}/EC$ as the function of the total EC loadings on both quartz and Teflon filter datasets (Fig. 6). There was not a significant variation between the two data

Fig. 5. Cross-validation between model developed OC on Teflon filters, Quartz filters and the NIOSH thermal-optical method.

Fig. 6. The fraction of OC_{NIOSH}/EC_{NIOSH} measured by reference NIOSH thermal optical EC/OC analyzer and $OC_{colorimeter}/EC_{NIOSH}$ versus the total EC loadings on the filters. A: Quartz filter. B: Teflon filter.

comparisons when EC loadings increased. This indicates the model-estimated OC values for Teflon and quartz sample datasets were not sensitive to increases in EC loadings. In addition, it is not expected that the OC loading estimations are independent of the particle's EC component, since the absorption and scattering of light by carbonaceous aerosols is a function of mixing state, composition, source, particle size, and matrix interferences (as described in previous sections) (Bond and Bergstrom, 2006; Lack et al., 2008; Olson et al., 2016).

4. Conclusion

Low-cost method for optical non-destructive particle analysis has been reported by Olson et al., 2016 for EC/OC analysis of quartz filters. Here, a non-destructive CIE-Lab optical color space system was utilized to develop a multi-parameter reference calibration model to quantify NIOSH thermal-optical EC/OC loading on Teflon and quartz filters. The model was shown to be effective in estimating EC and OC on both Teflon and quartz filters from a large set of samples obtained from diverse regions in China. However, a reduction in the model accuracy was observed for some extreme conditions, including highly loaded samples, extreme dust events, or direct emissions from unique sources. In addition, it was found that the mixing state of the chemical composition (ions and metals) and source of the particulate matter (secondary organic aerosols, in this research) could interfere with OC model estimation, and therefore reduce the model accuracy. In general, the reference calibration models and specific coefficients reported in this manuscript are applicable to typical atmospheric PM conditions that include a mixture of primary and secondary sources. Application of Teflon filters for EC/OC determination resulted in a slightly higher uncertainty for OC model estimations compared to the corresponding quartz filters. Regardless, this method can be valuable to large scale monitoring programs, especially when only Teflon filters are available for analysis. Finally, it should be noted that although the CIE-Lab color space system applied in this manuscript is device-independent (colors are not defined by their nature of creation or by the device), caution must be taken, since the method's main purpose is production quality control, and it has been developed for human color perception. Therefore, the appropriate color coordinates and transformations are required in order to apply to a specific set of model coefficients. The color space method offers the unique ability to estimate EC/OC on both Teflon and quartz membranes with low analytical cost and to approximate EC/OC exposure in developing regions and large scale monitoring campaigns, especially when only Teflon filters are available. We recommend further investigation be carried out using these techniques for other types of filters (e.g., Zeflour, Cellulose, and glass) in order to expand the method validation for other filter types that are common in occupational exposure testing and health studies. In addition, applying a larger set of light spectrums, compared to the visible RGB color spectrum considered in this research, would advance understanding about specific PM composition in a cost-efficient manner.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.atmosenv.2016.11.002>.

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