



The influence of temperature calibration on the OC–EC results from a dual-optics thermal carbon analyzer

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Abstract. Thermal–optical analysis (TOA) is a widely used technique that fractionates carbonaceous aerosol particles into organic and elemental carbon (OC and EC), or carbonate. Thermal sub-fractions of evolved OC and EC are also used for source identification and apportionment; thus, oven temperature accuracy during TOA analysis is essential. Evidence now indicates that the “actual” sample (filter) temperature and the temperature measured by the built-in oven thermocouple (or set-point temperature) can differ by as much as 50 °C. This difference can affect the OC–EC split point selection and consequently the OC and EC fraction and sub-fraction concentrations being reported, depending on the sample composition and in-use TOA method and instrument. The present study systematically investigates the influence of an oven temperature calibration procedure for TOA. A dual-optical carbon analyzer that simultaneously measures transmission and reflectance (TOT and TOR) is used, functioning under the conditions of both the National Institute of Occupational Safety and Health Method 5040 (NIOSH) and Interagency Monitoring of Protected Visual Environment (IMPROVE) protocols. The application of the oven calibration procedure to our dual-optics instrument significantly changed NIOSH 5040 carbon fractions (OC and EC) and the IMPROVE OC fraction. In addition, the well-known OC–EC split difference between NIOSH and IMPROVE methods is even further perturbed following the instrument calibration. Further study is needed to determine if the widespread application of this oven temperature calibration procedure will indeed improve accuracy and our ability to compare among carbonaceous aerosol studies that use TOA.

1 Introduction

The Interagency Monitoring of Protected Visual Environment (IMPROVE, outlined by Chow et al., 1993) and National Institute of Occupational Safety and Health Method 5040 (NIOSH, 1996) thermal–optical analysis (TOA) methods have been used widely for decades to quantify total carbon (TC), organic carbon (OC), and elemental carbon (EC) concentrations in ambient and combustion source samples. In addition, differences in the OC and EC sub-fractions were useful in distinguishing between diesel and gasoline emissions (Watson et al., 1994; Kim and Hopke, 2004, 2005), in characterizing different source and combustion profiles (Watson and Chow, 2001; Chow et al., 2011), and in estimating the source contributions to suspended particulate matter (Chow et al., 2004a; Kim and Hopke, 2004, 2005; Lee et al., 2003; Maykut et al., 2003).

NIOSH and IMPROVE carbon fractions have been determined traditionally with instrumentation developed by Sunset Laboratory (Tigard, OR, USA) and Desert Research Institute (DRI, Reno, NV, USA), respectively. Not only are there hardware design and configurational differences between these instruments, but the protocols differ operationally in temperature programming and optical monitoring, as described by Chow et al. (2001) whereby different OC and EC values can be obtained for many sample types. In one example of how protocols differ, the maximum burn-off temperatures used by the NIOSH method are higher (usually 870 °C for the OC and 890 °C for the EC) than those used in the IMPROVE protocol (usually 550 °C for the OC and 850 °C for the EC). Since the concentrations of OC and EC are fully

operationally defined and dependent on temperature, the accuracy in temperature setting is therefore essential for the analysis.

In a previous study, Chow et al. (2005) evaluated temperature bias (target sample oven temperature vs. measured temperature) in three thermal–optical instruments (two DRI models and one Sunset instrument) and the effect of the bias on the concentration of the IMPROVE OC and EC fractions. OC and EC sub-fractions were considered for the DRI 2001 model only. A temperature bias of up to 50 °C was observed, but did not influence the OC and EC concentrations measured with the IMPROVE protocol. Limitations of the temperature calibration method for the DRI analyzer include use of temperature-indicating (Tempilaq° G, Tempil Inc., South Plainfield, NJ, USA) liquids that damage the quartz surfaces of the sample holder and oven, poison the oxidation catalyst, and contaminate downstream components, as noted in Phuah et al. (2009). In addition, Tempilaq° G can only be tested at temperatures for which the calibration liquids are available, not at real operating filter temperatures. More recently, Phuah et al. (2009) confirmed the oven–filter temperature discrepancy on four different Sunset Laboratory instruments and reported statistically insignificant differences for the IMPROVE total carbon (TC), OC, and EC concentrations after temperature calibration. The calibration method developed in that study involved a simple hardware change by way of a temperature probe introduction that did not harm the instrument. However, further information about the effect of oven calibration for the widely applied NIOSH protocol was not offered in Phuah et al. (2009).

The present study measured and corrected the temperature bias but also evaluated the effect of oven temperature calibration on the OC and EC concentrations and the relevant OC–EC sub-fractions considering both the NIOSH and IMPROVE protocols. This aim is accomplished using a single dual-optics TOA instrument capable of measuring reflectance (TOR) and transmittance (TOT) simultaneously and running both NIOSH and IMPROVE protocols. Additional experimental benefits of using the dual-optics analyzer are presented in Khan et al. (2012). The temperature calibration kit that was used in the present study is now available from the manufacturer (Sunset Laboratory, Tigard, OR, USA) together with software. At the time when this study was performed it was not commercially available. Our results suggest the presence of a linear oven versus filter temperature bias that can be corrected through calibration. Possible causes of the bias are the oven thermocouple position in the dual-optics instrument used in the present study and the non-uniform distribution of heating coils around the filter zone and in the sample oven as suggested by Phuah et al. (2009). In addition, NIOSH and IMPROVE (TOT and TOR) results from the same laboratory-generated samples were compared statistically before and after calibration to see how OC, EC, and sub-fractions are influenced.

2 Experimental section

2.1 Test aerosols

Aerosols were produced using a diffusion flame aerosol generator (5201 Mini-CAST burner, Jing, Zollikofen, Switzerland) and collected on 47 mm pre-baked (550 °C for 12 h) quartz fiber filters (Pall Co., Port Washington, NY, USA). The propane-fueled Mini-CAST enables controlled and generally repeatable ($\pm 5\%$) aerosol output in terms of particle size distribution, the number concentration, and the chemical composition. The morphology of soot particles from the Mini-CAST is comparable to the soot particles from diesel exhaust (Jing, 1999). The aerosols were produced under different Mini-CAST operating conditions (different air / fuel ratios) that result in different percentages of the EC and OC in the final aerosol samples. Lean flame (lower propane / air ratio) results in the formation of aerosol with a higher concentration of the EC compared to OC, while the richer flame (higher propane / air ratio) creates aerosol with a larger amount of OC than EC. Note that this study examines *only* the influence of temperature calibration on the carbon results measured under different TOA protocols in the same sample (quartz filter) and not the representativeness of the diffusion flame aerosol to the wide range of source and ambient samples. Response of the system might be different in the presence of highly oxidized species found in ambient samples. However, the use of Mini-CAST and laboratory-generated soot allowed a wide range of OC / TC (9–100 % OC) and EC / TC (0–91 % EC) ratios to be evaluated (Table 1), and this range was comparable to what was observed for other sources and sampling conditions (Chow et al., 2004a, 2011; Khan et al., 2012). Results from this study will show if the temperature changes that resulted from temperature calibration of the instrument have different impacts on the samples with different EC / OC ratios.

2.2 Carbon analyzer and temperature protocols

A dual-optics carbon analyzer (Sunset Laboratory, Tigard, OR, USA) which measured filter transmittance (TOT) and reflection (TOR) simultaneously was used in this study. Samples were analyzed using two temperature protocols: (1) adjustment modified version of the Birch and Cary (1996) NIOSH protocol (referred to in this paper as the NIOSH 5040 protocol) and (2) the IMPROVE protocol as outlined by Chow et al. (1993) and referred to in this paper as the IMPROVE protocol. Details about the residence time and temperature ramp rate ($^{\circ}\text{C s}^{-1}$) set points for the NIOSH 5040 and IMPROVE protocol can be found in Table 2. The residence times at each temperature step within the He and He–O₂ phases are fixed for the NIOSH, but vary for the IMPROVE depending on the sample composition. The IMPROVE protocol does not ramp the temperature until the flame ionization detector (FID) signal returns to its baseline.

Table 1. Summary of laboratory test conditions.

Comparisons	Number of samples	TC range ($\mu\text{g cm}^{-2}$)	OC range ($\mu\text{g cm}^{-2}$)	EC range ($\mu\text{g cm}^{-2}$)	% OC	% EC
IMPROVE before and after TCAL	24	1.80–18.00	0.93–6.15	0.87–15.90	8.90–59.50	40.50–91.10
NIOSH before and after TCAL	24	2.04–17.86	1.23–6.02	0.81–15.18	14.10–62.90	37.10–85.90
IMPROVE and NIOSH before TCAL	32	2.04–29.30	1.04–12.58	0.00–18.60	17.30–100.00	0.00–82.70
IMPROVE and NIOSH after TCAL	68	2.10–19.52	1.29–7.93	0.81–15.60	13.90–65.10	34.90–86.10

It must be noted that the original NIOSH 5040 method (NIOSH, 1996) does not specify temperatures for either OC (He phase) or EC (He–O₂ phase) steps, or the temperatures required to measure different OC and EC sub-fractions. Birch and Cary (1996) used 820 °C as the maximum temperature for OC and 860 °C as the maximum temperature for EC, while 2 years later Birch (1998) employed a temperature program with maximum temperature for OC at 850 and 940 °C for the EC determination. Those later temperatures were adopted in the revised version of the NIOSH 5040 official method (NIOSH, 1999) but again without defining temperature ramps for OC and EC sub-fractions. In summary, the NIOSH 5040 protocol only outlines the necessary principles for operation without detailing individual temperature parameters. As a result, different variations of the NIOSH temperature program and temperature ramps are available in the literature that make data comparison among studies difficult. The present study used a protocol that is comparable to what other studies have recently used when operating the Sunset Laboratory instrument (Schauer et al., 2003; Khan et al., 2012) and very similar to the EPA/NIOSH (called also Speciation Trends Network (STN) method) described in detail elsewhere (Peterson and Richards, 2002).

The “old” IMPROVE temperature protocol used in the present study is described in detail by Chow et al. (1993) except that temperature for the last EC sub-fraction (EC3) is modified from original 800 °C to 850 °C. The new IMPROVE protocol termed “IMPROVE_A protocol” (Chow et al., 2007) differs from the old IMPROVE protocol in 20–40 °C higher temperature steps. The new protocol is the result of a temperature calibration performed on five Desert Research Institute/Oregon Graduate Center (DRI/OGC) analyzers (Chow et al., 2005) that attempts to correct the bias between the oven thermocouple sensors and the actual sample temperatures. The calibration results found that the actual sample temperatures (filter location) were 20–40 °C higher than required by the old IMPROVE target (set-point) temperatures due to the new hardware used in new DRI Model 2001 analyzers. Given that the purpose of the present study was to perform an independent calibration of the dual-optics carbon analyzer that is different in design than a DRI instrument, the old IMPROVE temperature protocol was used in order to independently measure temperature biases for the Sunset dual-optical carbon analyzer under the IMPROVE temperature ramps.

2.3 Temperature calibration

The temperature calibration kit was provided by the manufacturer of the dual-optics TOA instrument and is designed to satisfy QA/QC (quality assurance and quality control) requirements, increase the reliability of carbon results, and improve inter-instrument comparisons. The calibration kit consisted of a serial temperature data acquisition unit with precision ± 0.3 °C for temperature range of -80 to 500 °C and ± 0.55 °C for the 500 to 1350 °C range (Model MDSi8, Omega Engineering, Stamford, CT), National Institute of Standards and Technology (NIST)-traceable thermocouple (type-K), and front oven interface hardware. The thermocouple is an Inconel-shielded K-type thermocouple certified for high temperatures required by the experiment (Omega Engineering Calibration Report no. OM-110802626) with 1/16 in sheath diameter. Thermocouple-produced temperature data were recorded at a frequency of 1 Hz and with 0.1 °C resolution. For calibration, the front oven interface hardware outfitted with the NIST-traceable thermocouple (Fig. S1b in the Supplement) replaced the quartz boat and quartz filter (Fig. S1a in the Supplement) used during normal TOA operation.

All temperatures reported here as T_{FILTER} (measured by the calibration thermocouple) represent the temperatures measured in the center of the filter, while in practice there will be gradients across the filter. In addition, it should be noted here that the quartz boat with filter media used during the normal instrument operation compared with the calibration thermocouple might experience different heating rates inside the front oven of the instrument, given that the heat capacity of the contents inside the oven is different. However, this study focused on the temperatures recorded only when they reach steady state for each temperature step. The assumption for this study was that the steady-state temperature of the quartz boat with the filter inside of the front oven will be the same as the steady-state temperature recorded during the calibration with the thermocouple.

The tip of the oven calibration thermocouple was positioned where the center of the quartz filter typically resides during TOA operation which is about 2 cm upstream of the thermocouple used to monitor oven temperature (Fig. S1 in the Supplement). This also happens to be where the laser beam ($\lambda = 632.8$ nm) used to monitor pyrolysis passes through the filter. Oven calibrations were performed using

Table 2. Filter temperatures measured before calibration for NIOSH 5040 and IMPROVE protocol.

Carbon fraction	NIOSH 5040					IMPROVE				
	T_{SETPOINT} (°C)	T_{FILTER} (°C)	Ramp rate (°C s ⁻¹)	Residence (s)	ΔT °C (% difference)	T_{SETPOINT} (°C)	T_{FILTER} (°C)	Ramp rate (°C s ⁻¹)	Residence (s)	ΔT °C (% difference)
OC1	310	278	4	70	32 (10)	120	88	1.25	150	32 (27)
OC2	475	435	8	60	40 (8)	250	211	2.5	150	39 (16)
OC3	615	569	10	60	46 (7)	450	407	3	150	43 (10)
OC4	870	800	8	105	70 (8)	550	501	4	150	49 (9)
EC1	550	482	9	60	68 (12)	550	501	4	150	49 (9)
EC2	625	563	10	60	62 (10)	700	639	5	150	61 (9)
EC3	700	637	12	60	63 (9)	850	777	6	150	73 (9)
EC4	775	707	13	60	68 (9)					
EC5	890	813	8	110	75 (8)					

both the NIOSH 5040 and IMPROVE temperature operating conditions. Details about residence time and temperature ramp rate (°C s⁻¹) set points for the NIOSH 5040 protocol can be found elsewhere (Khan et al., 2012) and in Table 2. For calibration during the IMPROVE protocol, the residence time at each temperature step was 150 s.

Two temperatures sets were recorded during the oven calibration routine: T_{OVEN} as measured by the built-in oven temperature sensor and T_{FILTER} as measured by the calibration kit. Both temperatures were recorded when the readings for the sample oven (T_{OVEN}) were stable at each set-point temperature (T_{SETPOINT}) required by the NIOSH 5040 and IMPROVE protocol for each temperature step. Before calibration $T_{\text{SETPOINT}} = T_{\text{OVEN}}$. However, the previous studies showed that $T_{\text{FILTER}} \neq T_{\text{SETPOINT}}$ and therefore $T_{\text{FILTER}} \neq T_{\text{OVEN}}$. Differences among T_{SETPOINT} , T_{OVEN} , and T_{FILTER} were determined, and temperature coefficients (approximately equal to temperature biases measured) in the instrument control software parameter files were adjusted so that $T_{\text{FILTER}} = T_{\text{SETPOINT}}$. In other words, coefficient values were adjusted to force the temperature at the sample oven thermocouple (T_{OVEN}) to reflect the value required to achieve T_{SETPOINT} at the filter because $T_{\text{OVEN}} \neq T_{\text{FILTER}}$ either before or after the calibration. For each TOA method (NIOSH 5040 and IMPROVE), the oven calibration procedure was performed in triplicate with the calibration unit removed and then replaced for each trial. This was accomplished before adjustment of the temperature coefficients. After the coefficients were adjusted in the software, the calibration/checking procedure was performed again in triplicate to measure and record T_{FILTER} during each temperature step required by NIOSH 5040 and IMPROVE methods and to be sure that $T_{\text{FILTER}} = T_{\text{SETPOINT}}$.

2.4 Sample analysis

IMPROVE carbon results have been usually TOR-corrected and NIOSH carbon results TOT-corrected. However, in this study, for the IMPROVE and NIOSH protocols, both TOT and TOR results were used to evaluate the effect of the oven

temperature calibration (TCAL) on the OC–EC fractionation and to be sure that results found are consistent and selection of optical correction is not a reason for possible changes found in the carbon results. The following scenarios for sample analysis were compared in the present study: (a) IMPROVE carbon fractions and sub-fractions before and after TCAL; (b) NIOSH carbon fractions and sub-fractions before and after TCAL; and (c) IMPROVE versus NIOSH carbon fractions before and after TCAL. A summary of the tests performed is shown in Table 1. For each filter sample ($n \geq 12$), four punches (1.5 cm²) were taken and analyzed by TOA. For scenarios a and b, two punches each were analyzed before and after the TCAL was performed. For scenario c, two punches each were analyzed using the IMPROVE and NIOSH protocols. These duplicate sample measurements allowed the evaluation of reproducibility and sample homogeneity. Acceptance criteria for duplicate measurements are based on the relative percent difference (RPD) of the duplicate measurements. The acceptance criterion for samples at low filter loadings ($\leq 5 \mu\text{g cm}^{-2}$) is $\leq 20\%$ RPD; at medium filter loadings ($5\text{--}10 \mu\text{g cm}^{-2}$), $\leq 15\%$ RPD; and at high filter loadings ($\geq 10 \mu\text{g cm}^{-2}$), $\leq 10\%$ RPD.

Differences between each TC, OC, and EC fraction, as well as OC and EC sub-fractions for the IMPROVE and NIOSH temperature protocols, were investigated before and after TCAL. Paired t tests were performed to determine whether the calibration produced statistically different concentrations for TC, OC, EC, and sub-fractions for both methods or if significant differences were observed when comparing the NIOSH method with the IMPROVE protocol and their main carbon fractions before and after TCAL. Concentrations were statistically different if the null hypothesis was rejected at $P < 0.05$. Depending on the sign of the average difference ($y - x$) and if the average ratio (y / x) is greater than or less than 1, one can infer if the calibration produced significantly higher or lower results than those obtained without temperature calibration. Linear regression results (slope, y intercept, and correlation coefficient, r) were used to evaluate equivalence and comparability of carbon concentrations before and after TCAL and between

the IMPROVE and NIOSH methods to gain improved understanding of the impact of calibration. Criteria described by the US Environmental Protection Agency (EPA) (1997) for PM_{2.5} Federal Equivalent Methods (FEM) to meet the equivalence requirements when compared with a Federal Reference Method (FRM) were used in this study. Equivalence is achieved when the regression slope is 1 ± 0.05 , the regression intercept $0 \pm 1 \mu\text{g cm}^2$, and $r \geq 0.97$. Comparability criteria were adopted as described in detail by Watson and Chow (2002). Comparability criteria are met when (1) the slope equals unity within three standard deviations or the average of ratios (y/x) equals unity within one standard deviation, (2) the intercept does not differ from zero within three standard deviations, and (3) $r > 0.90$.

3 Results and discussion

3.1 Temperature calibration results

Table 2 summarizes temperatures required (T_{SETPOINT}) at each programmed step and the average T_{FILTER} measured by the calibration kit, along with the average temperature deviations (% difference) for the dual-optics analyzer tested as part of the current study. Over the entire temperature range evaluated for both TOA protocols, T_{FILTER} values are systematically lower than T_{SETPOINT} prior to calibration. This was presumably due to (1) the unique location of each thermocouple as shown in Fig. S1 in the Supplement and (2) as already indicated, due to different allocation of heating coils around the sample boat and in the sample oven. Phuah et al. (2009) attributed the lower T_{FILTER} temperatures to the less tightly packed heating coils around the quartz tube where the transmittance laser passes compared to the tightly packed heating coils in the sample oven. These existing instrument limitations most likely resulted in mean temperature difference or bias (ΔT) between T_{SETPOINT} and T_{FILTER} measured in this study between 32 and 75 °C. The ΔT observed is less at low temperatures (≤ 43 °C for temperatures ≤ 475 °C) than at high temperatures (≤ 75 °C for temperatures between 550 and 890 °C). The ΔT under the NIOSH and IMPROVE protocols varied at the T_{SETPOINT} of 550 °C. Inherent to the NIOSH temperature protocol was a higher ΔT (70 °C) at the He–O₂ introduction step where temperature declines from 870 to 550 °C. The high ΔT at that particular step is presumably due to the wide temperature gap (870 to 550 °C) and short residence time.

Consistent with our findings, Phuah et al. (2009) observed ΔT values of 35–85 °C that varied with each Sunset laboratory instrument, while Chow et al. (2005) found that ΔT depends on the temperature ramp. Chow et al. (2005) did not observe a linear correlation between T_{FILTER} and T_{SETPOINT} , although Phuah et al. (2009) and the present study do indicate such a correlation. Figure 1 shows that the T_{FILTER} and T_{SETPOINT} relationship is linear based on temperature

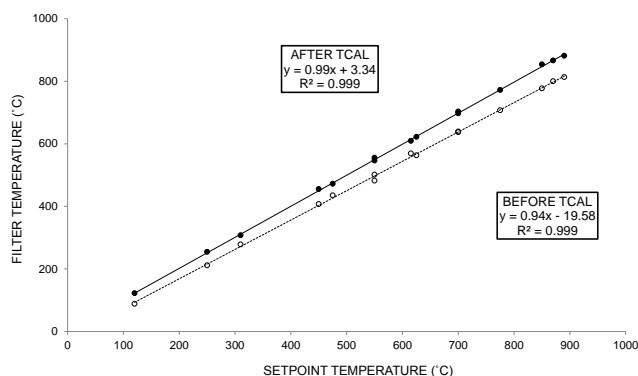


Figure 1. Linear regression results before and after temperature calibration.

data obtained at nine NIOSH and six IMPROVE temperatures that precede calibration. Regression analysis shows the slope approaching unity (0.94 ± 0.01) but lower than the values measured on four other Sunset Laboratories instruments by Phuah et al. (2009). A regression correlation ($r = 1.000$; $R^2 = 0.999$) suggests that the T_{SETPOINT} can be systematically increased until $T_{\text{FILTER}} = T_{\text{SETPOINT}}$ and T_{FILTER} meets the T_{SETPOINT} requirements of NIOSH and IMPROVE protocols.

Following oven calibration, T_{FILTER} was within 1 and 1.7 % of T_{SETPOINT} for the NIOSH and IMPROVE protocols, respectively (Table 3). The ΔT at temperatures below 475 °C was ≤ 5 °C compared with $\Delta T \leq 43$ °C before TCAL. And at temperatures of 550–890 °C, ΔT was ≤ 9 °C compared with $\Delta T \leq 75$ °C before TCAL. The T_{FILTER} and T_{SETPOINT} linear relationship after calibration is also shown in Fig. 1. A higher regression slope (0.99 ± 0.01) and a significantly lower intercept (3.34 ± 3.05) confirm the effectiveness of the temperature calibration.

3.2 Influence of TCAL on measurement of TC, EC, and OC

3.2.1 IMPROVE TOR and TOT before and after TCAL

For IMPROVE, TC, OC, and EC, fractions were compared before and after oven temperature calibration for $n = 12$ filters (24 samples). Results of statistical comparisons are shown in Table 4. Neither the TOR nor TOT pyrolysis monitoring method produced a statistical difference ($P > 0.05$) for TC or EC before and after calibration. The linear regression results show high correlations ($r > 0.97$) and that equivalence was met for TC and EC but not for OC. The insensitivity of IMPROVE TC and EC concentrations to temperature calibration was observed previously using both the Sunset Laboratories (Phuah et al., 2009) and DRI instruments (Chow et al., 2005). However, in this study, the IMPROVE OC fraction at higher filter temperatures significantly changed after the TCAL for the TOT method ($P < 0.05$) but not for TOR

Table 3. Filter temperatures measured after calibration and software adjustments.

Carbon fraction	NIOSH 5040			IMPROVE		
	T_{SETPOINT} (°C); r^*	T_{FILTER} (°C)	ΔT °C (% difference)	T_{SETPOINT} (°C); r^*	T_{FILTER} (°C)	ΔT °C (% difference)
OC1	310; 24	307	3 (1.0)	120; 48	122	2 (1.7)
OC2	475; 28	472	3 (0.6)	250; 39	254	4 (1.6)
OC3	615; 40	609	6 (1.0)	450; 42	455	5 (1.1)
OC4	870; 65	866	4 (0.5)	550; 50	555	5 (0.9)
EC1	550; 61	546	4 (0.7)	550; 50	555	5 (0.9)
EC2	625; 54	622	3 (0.5)	700; 61	703	3 (0.4)
EC3	700; 56	697	3 (0.4)	850; 74	854	4 (0.5)
EC4	775; 61	772	3 (0.4)			
EC5	890; 71	881	9 (1.0)			

* Temperature correlation coefficients implemented in the software parameter files.

($P > 0.05$). The IMPROVE TOT OC values were 12 % lower after TCAL. The reasons for the lower OC when higher temperatures are applied after TCAL are discussed in more detail in Sect. 3.3.1. Use of TOT for pyrolysis monitoring responds to char being produced from organic vapors or liquids adsorbed within the filter whereas TOR monitors only the filter surface (Chow et al., 2004b). The significant reduction of OC by 12 % and no difference in EC and TC results are explained by the fact that average OC concentration in the samples analyzed by the IMPROVE protocol was 2 times lower than the average EC concentration in the same samples (Table 1). Therefore, a different sample matrix with higher OC / TC ratio and, in particular, higher semi-volatile OC concentration (susceptible to pyrolysis, as discussed in Sect. 3.3.1.) might result in a significant increase in the EC concentration in addition to the decrease of the OC, while keeping TC values the same before and after the TCAL.

3.2.2 NIOSH TOR and TOT before and after TCAL

Table 4 shows that NIOSH-produced OC and EC fractions (both TOT and TOR) were significantly different after TCAL ($P < 0.05$). The EC results after calibration were 6 and 7 % lower than before TCAL for TOR and TOT, respectively. The linear regression confirmed non-equivalence of the OC TOT and TOR fractions, and the average OC values were 8 and 12 % higher for TOR and TOT, respectively. No statistical difference was found for the TC ($P > 0.05$) after the TCAL with the results meeting “equivalence” criteria and the calibration resulting in ~ 1 –2 % lower TC values (TOR and TOT, respectively). To our knowledge, no study has previously analyzed NIOSH-generated TC, OC, and EC concentrations after temperature correction. Results from the present study confirm that NIOSH-based carbon fractions can vary due to ΔT . Higher filter temperatures after the calibration also likely affect the OC and EC sub-fractions to be discussed later.

3.2.3 IMPROVE TOR vs. NIOSH TOT before TCAL

Previous work demonstrates that IMPROVE EC is typically higher than NIOSH EC (Chow et al., 2001, 2004b) with the opposite found for OC. For the laboratory-generated aerosol evaluated here, on average, the IMPROVE-measured EC concentrations were higher by 5 % while the IMPROVE OC was 16 % lower compared with NIOSH values (Table 4). The paired t test results confirm a statistical difference between the two methods for the OC and EC results ($P < 0.05$). According to the linear regression results, the EC and OC results satisfied the criteria for comparability but not for the equivalence. These protocols are usually equivalent for TC, and TC differences were insignificant between IMPROVE and NIOSH ($P = 0.919$). In addition, the regression analysis showed equivalence between the TC data, with average of ratios at 0.97 ± 0.09 (IMPROVE/NIOSH).

3.2.4 IMPROVE TOR vs. NIOSH TOT after TCAL

After calibration, the IMPROVE TOR and NIOSH TOT protocols are determined to be equivalent for TC (Table 4) with an average ratio of 1.00 ± 0.06 (IMPROVE/NIOSH). However, using OC and EC concentrations, the paired t test shows statistically significant differences between two protocols ($P = 0.00$), and the regression analysis shows non-equivalence and non-comparability for the OC, while the EC results show comparability but not equivalence. IMPROVE EC is 17 % higher than NIOSH EC and in turn IMPROVE OC is 31 % lower, on average, after TCAL.

3.3 Influence of TCAL on measurement of carbon sub-fractions

Nine carbon sub-fractions (four OC and five EC) for the NIOSH method and seven carbon sub-fractions (four OC and three EC) for the IMPROVE protocol were compared before and after TCAL. Temperature ramp details contributing to

Table 4. Comparability statistics results for NIOSH and IMPROVE TOR and TOT carbon fractions before and after temperature calibration*.

Comparisons	Analysis		Regression			Average of ratios $y/x \pm SD$	Paired t test P	Equivalence Y: yes N: no	Comparability Y: yes N: no	
	y	x	Slope $\pm SE$	Intercept $\pm SE$	r					Average $y - x \pm SD$
IMPROVE before vs. after TCAL TOR	TC after	TC before	0.98 ± 0.03	-0.07 ± 0.45	0.99	-0.25 ± 0.75	0.98 ± 0.06	0.11	Y	n/a
	EC after	EC before	1.01 ± 0.04	0.01 ± 0.37	0.98	0.08 ± 0.66	1.00 ± 0.07	0.56	Y	n/a
	OC after	OC before	0.87 ± 0.07	0.04 ± 0.22	0.94	-0.33 ± 0.52	0.89 ± 0.17	0.33	N	Y
IMPROVE before vs. after TCAL TOT	TC after	TC before	0.99 ± 0.03	-0.08 ± 0.45	0.99	-0.25 ± 0.76	0.98 ± 0.06	0.12	Y	n/a
	EC after	EC before	1.02 ± 0.04	-0.06 ± 0.41	0.98	0.11 ± 0.73	1.00 ± 0.10	0.48	Y	n/a
	OC after	OC before	0.87 ± 0.09	0.01 ± 0.29	0.89	-0.35 ± 0.59	0.88 ± 0.18	0.01	N	N
NIOSH before vs. after TCAL TOT	TC after	TC before	0.98 ± 0.03	0.07 ± 0.43	0.99	-0.21 ± 0.69	0.98 ± 0.05	0.17	Y	n/a
	EC after	EC before	0.91 ± 0.04	0.14 ± 0.41	0.98	-0.60 ± 0.84	0.93 ± 0.08	0.00	N	Y
	OC after	OC before	1.01 ± 0.08	0.33 ± 0.29	0.95	0.39 ± 0.47	1.12 ± 0.14	0.00	N	Y
NIOSH before vs. after TCAL TOR	TC after	TC before	0.99 ± 0.03	-0.02 ± 0.43	0.98	-0.16 ± 0.69	0.99 ± 0.06	0.14	Y	n/a
	EC after	EC before	0.97 ± 0.04	-0.19 ± 0.33	0.97	-0.45 ± 0.64	0.94 ± 0.07	0.00	Y	n/a
	OC after	OC before	1.00 ± 0.06	0.30 ± 0.23	0.93	0.28 ± 0.40	1.08 ± 0.12	0.01	N	Y
IMPROVE TOR vs. NIOSH TOT before TCAL	TC IMPROVE	TC NIOSH	1.02 ± 0.02	-0.29 ± 0.31	1.00	0.01 ± 0.71	0.97 ± 0.09	0.92	Y	n/a
	EC IMPROVE	EC NIOSH	1.09 ± 0.03	-0.23 ± 0.35	0.99	0.61 ± 0.91	1.05 ± 0.08	0.00	N	Y
	OC IMPROVE	OC NIOSH	0.93 ± 0.05	-0.32 ± 0.32	0.96	-0.60 ± 0.83	0.84 ± 0.18	0.00	N	Y
IMPROVE TOR vs. NIOSH TOT after TCAL	TC IMPROVE	TC NIOSH	1.02 ± 0.01	-0.09 ± 0.19	0.99	0.13 ± 0.59	1.00 ± 0.06	0.07	Y	n/a
	EC IMPROVE	EC NIOSH	1.06 ± 0.03	0.69 ± 0.25	0.98	1.23 ± 0.83	1.17 ± 0.13	0.00	N	Y
	OC IMPROVE	OC NIOSH	1.04 ± 0.04	-1.28 ± 0.22	0.95	-1.09 ± 0.74	0.69 ± 0.21	0.00	N	N

* TC stands for total carbon (EC + OC); EC stands for elemental carbon; OC stands for organic carbon.

the carbon sub-fraction features are given in Table 2. Pyrolyzed organic carbon (PyC) or char, which affects the OC–EC split, is also evaluated before and after TCAL. Paired t tests and mean ratios were computed to determine if the two protocols resulted in statistically different values for carbon sub-fractions and PyC.

3.3.1 IMPROVE TOR and TOT before and after TCAL

Percent differences in carbon fractions and sub-fractions after TCAL for the IMPROVE protocol are shown in Fig. 2a for the TOR data and Fig. 2b for the TOT data, with statistical results given in Table 5. Regardless of the optical correction technique in use, higher filter temperatures significantly increase OC1, EC1, and EC2 mass and reduce OC3 and OC4 carbon mass whereas changes measured in the OC2 and EC3 sub-fractions are insignificant ($P > 0.05$). It appears after TCAL that more carbon evolves sooner (OC1, EC1, and EC2) rather than later (OC3, OC4, and EC3) due to the higher filter temperatures associated with each protocol ramp or step after TCAL. Phuah et al. (2009) did not find any difference in the EC1 after the calibration, but did find significant changes in the OC2, OC3, EC2, and PyC fractions. This may be due to differences in sample composition between the studies; the effect of oven temperature calibration on carbon sub-fractions is likely to be sample-specific and not applicable to all aerosol source samples. Moreover, it is likely that calibration results are not transferable across instruments and each carbon analyzer must be calibrated separately.

Pyrolysis (PyC) significantly changed after calibration ($P < 0.05$) and is 10 and 12 % lower than before TCAL for TOR and TOT analysis, respectively. Lower PyC values

after TCAL are consistent with lower total OC values discussed in Sect. 3.2.1. (~ 11 % lower after TCAL) given that $OC = OC1 + OC2 + OC3 + OC4 + PyC$. In addition, lower PyC values after the TCAL and at higher temperature operating conditions are in agreement with findings from previous studies (Chow et al., 2005; Phuah et al., 2009) that also observed higher PyC values (more charring) at lower temperatures before TCAL for the IMPROVE temperature protocol. A likely explanation for such results is that the higher temperatures to which the sample is exposed after the TCAL caused more OC to evolve at earlier steps (OC1 was higher after TCAL by a factor of 2.1 and 3.6 for TOR and TOT, respectively). Therefore, the less OC (in particular the semi-volatile OC that contributes the most to the charring) is exposed to higher temperatures, the less OC will pyrolyze at higher temperature steps. In addition, the same effect (lower PyC after TCAL) was found for both TOT- and TOR-corrected results, indicating that both optical corrections are influenced similarly after the TCAL for the IMPROVE temperature protocol, therefore eliminating the optical correction as a possible cause for this effect. A characteristic IMPROVE TOR thermogram for the samples analyzed in the present study is shown in Fig. 3a. All samples show a similar He–O₂-phase-based OC–EC split point, and for all samples, the OC–EC split following TCAL occurs earlier. This is consistent with lower PyC and total OC values measured after the TCAL. Although the earlier OC–EC split was observed after TCAL, it did not significantly influence the results for total organic (OC) and elemental carbon (EC) as discussed earlier in Sect. 3.2.1.

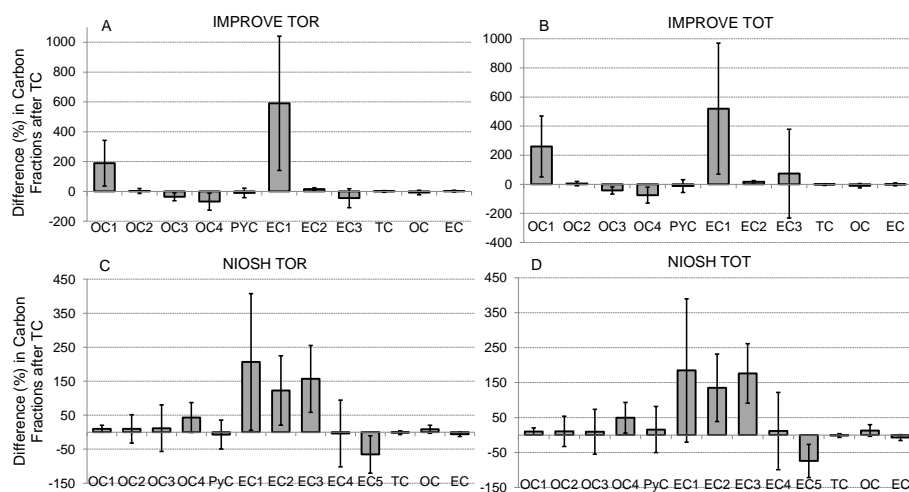


Figure 2. Percent difference $((y - x)100\%/x)$ and standard deviation in carbon fractions and sub-fractions of the results after temperature calibration for the (a) IMPROVE TOR, (b) IMPROVE TOT, (c) NIOSH TOR, and (d) NIOSH TOT temperature protocols.

3.3.2 NIOSH TOT and TOR Before and After TCAL

Percent differences in TOT and TOR TC, OC, EC, four OC and five EC carbon sub-fractions, and PyC measured by the NIOSH method before and after TCAL can be found in Fig. 2c (TOR) and 2d (TOT) with statistical comparisons in Table 5. For both optical corrections, a statistically significant increase in carbon mass was again measured for lower temperature OC (OC1) and EC (EC1, EC2, and EC3) sub-fractions. A significant reduction in carbon mass was found for the highest temperature EC (EC5) sub-fraction. No significant changes are observed for the middle temperature OC (OC2 and OC3) and EC4 sub-fractions as well as for the PyC fraction. A significant increase was measured also for the high temperature OC4 ($\sim 50\%$) indicating that the 70°C difference in temperature after the calibration plays an important role in the measurement of the total organic carbon fraction (12% higher results after the calibration as stated in Sect. 3.2.2).

A typical NIOSH TOT thermogram for the samples analyzed in the present study is shown in Fig. 3b. The OC–EC split point was positioned in the He–O₂ phase (EC4) both before and after TCAL, and for all samples, the OC–EC split occurs earlier after TCAL. However, this “early” OC–EC split did not result in lower OC and PyC values, or in higher EC results after TCAL. On the contrary, NIOSH OC and PyC values were higher by ~ 12 and 16% , respectively and EC values lower by $\sim 7\%$ after the TCAL. The higher filter temperatures after the TCAL caused more OC and PyC to evolve at earlier temperature steps, and therefore the measured laser transmittance reaches its initial value (OC–EC split) earlier than TCAL. The same effect has been seen in the IMPROVE TOR thermogram (Fig. 3a). Contrary to the IMPROVE TOT and TOR results where PyC was lower (by ~ 10 – 12%) after TCAL, the NIOSH TOT PyC results were higher by $\sim 16\%$ after TCAL (not statistically significant change). The higher

NIOSH temperature regime in the He phase with the maximum temperature of 870°C after TCAL compared to 800°C measured before TCAL furthermore favors PyC formation. In addition, the shorter residence times during the NIOSH OC temperature steps cause less complete organic carbon evolution at lower temperatures (OC1 was higher after TCAL only by a factor of 1.1) and, consequently, increase charring formation during the higher temperature steps (Yu et al., 2002).

4 Conclusions

Calibration of the oven temperature sensor in a dual-optics carbon analyzer revealed differences as high as 75°C from expected filter temperatures (EC5 sub-fraction of the NIOSH protocol). A software-based modification of parameters successfully reduced that variation. The advantage of the present study is that it has been performed with a temperature calibration kit provided by the instrument manufacturer, and if the same device is used to calibrate different instruments, it can significantly improve inter-instrument comparison and increase the reliability of carbon results. IMPROVE TOT OC, NIOSH TOT, and TOR carbon fractions (OC and EC) were significantly different after the TCAL whereas the calibration procedure did not significantly influence the IMPROVE TOR EC and OC and IMPROVE TOT EC carbon fractions. In addition, the calibration increased the difference in the OC–EC split known to exist between the NIOSH and IMPROVE methods. Thermal carbon sub-fractions before and after calibration were different for both protocols with many differences being statistically significant. However, differences observed in this study may be instrument- and sample-specific (although the same results were found for samples with different OC / EC ratios) and not perfectly representative of all combustion and atmospheric aerosols.

Table 5. Average ratios and paired *t* test results for NIOSH TOR and TOT and for IMPROVE TOR and TOT carbon sub-fractions before and after temperature calibration.

Comparisons	Analysis		Average of ratios <i>y</i> / <i>x</i> ± SD	Paired <i>t</i> test <i>P</i>
	<i>y</i> – after	<i>x</i> – before		
IMPROVE TOR before vs. after TCAL	OC1	OC1	2.14 ± 1.53	0.00
	OC2	OC2	1.04 ± 0.15	0.48
	OC3	OC3	0.60 ± 0.27	0.00
	OC4	OC4	0.39 ± 0.63	0.05
	PyC	PyC	0.90 ± 0.31	0.00
	EC1	EC1	6.95 ± 5.24	0.00
	EC2	EC2	1.16 ± 1.09	0.02
	EC3	EC3	0.55 ± 0.64	0.29
IMPROVE TOT before vs. after TCAL	OC1	OC1	3.58 ± 2.58	0.00
	OC2	OC2	1.05 ± 0.16	0.29
	OC3	OC3	0.58 ± 0.24	0.00
	OC4	OC4	0.26 ± 0.55	0.03
	PyC	PyC	0.88 ± 0.44	0.02
	EC1	EC1	6.22 ± 5.51	0.00
	EC2	EC2	1.17 ± 1.08	0.04
	EC3	EC3	1.74 ± 4.04	0.32
NIOSH TOR before vs. after TCAL	OC1	OC1	1.10 ± 0.10	0.00
	OC2	OC2	1.11 ± 0.44	0.19
	OC3	OC3	1.09 ± 0.64	0.97
	OC4	OC4	1.49 ± 0.44	0.00
	PyC	PyC	1.16 ± 0.66	0.78
	EC1	EC1	2.82 ± 2.09	0.00
	EC2	EC2	2.36 ± 0.97	0.00
	EC3	EC3	2.76 ± 0.85	0.00
	EC4	EC4	1.11 ± 1.11	0.07
NIOSH TOT before vs. after TCAL	OC1	OC1	1.10 ± 0.11	0.00
	OC2	OC2	1.10 ± 0.42	0.11
	OC3	OC3	1.12 ± 0.68	0.44
	OC4	OC4	1.43 ± 0.44	0.00
	PyC	PyC	0.93 ± 0.43	0.12
	EC1	EC1	2.81 ± 1.98	0.00
	EC2	EC2	2.23 ± 1.02	0.00
	EC3	EC3	2.57 ± 0.98	0.00
	EC4	EC4	0.96 ± 0.98	0.15
EC5	EC5	0.42 ± 0.59	0.00	

In addition, given that there are different variations of the NIOSH 5040 temperature protocol, the temperature biases and carbon results measured in the present study might not be the same for each NIOSH 5040 temperature modification. Thus, to improve comparability over more studies and instrument types, oven temperature calibration is a necessary tool. Results from the present study suggest that careful calibration of each individual instrument is required to avoid misinterpretation of future carbonaceous aerosol and air quality data.

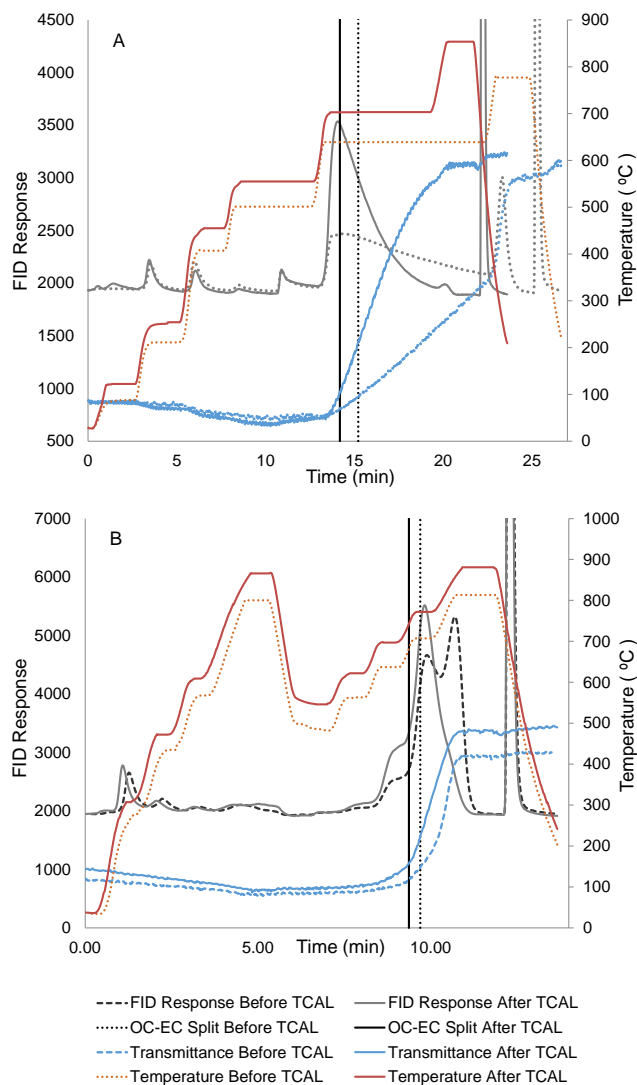


Figure 3. Typical (a) IMPROVE TOR thermogram and (b) NIOSH TOT thermogram for the same sample analyzed before and after TCAL.

The Supplement related to this article is available online at doi:10.5194/amt-7-2829-2014-supplement.

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