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

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(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) and Desert Research Institute (DRI, Reno, NV), 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) 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

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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 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) 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 vs. 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 (TOT) and IMPROVE (TOT and TOR) results from the same laboratory-generated samples were compared statistically before and after calibration to see how OC and 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). 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 impact on the samples with different EC/OC ratios.

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## 2.2 Carbon analyzer and temperature protocols

A dual optics carbon analyzer (Sunset Laboratory; Tigard, OR) 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-O<sub>2</sub> 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.

It must be noted that the original NIOSH 5040 method (NIOSH, 1996) does not specify temperatures for either OC (He phase) or EC (He-O<sub>2</sub> phase) step, or the temperatures required to measure different OC and EC sub-fractions. Birch and Cary (1996) used 820 $^{\circ}\text{C}$  as the maximum temperature for OC and 860 $^{\circ}\text{C}$  as the maximum temperature for EC, while two years later Birch (1998) employed a temperature program with maximum temperature for OC at 850 $^{\circ}\text{C}$  and 940 $^{\circ}\text{C}$  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).

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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 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 requirements, increase the reliability of carbon results, and improve inter-instrument comparisons. The calibration kit consisted of a serial temperature data acquisition unit (precision  $\pm 0.3$  °C for temperature range  $-80$ – $500$  °C and  $\pm 0.55$  °C for the  $500$ – $1350$  °C range (Model MDSi8, Omega Engineering, Stamford, CT), 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 # OM-110802626) with 1/16” 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 – Supplement) replaced the quartz boat and quartz filter (Fig. S1a – Supplement) used during normal TOA operation.



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All temperatures reported here as  $T_{\text{FILTER}}$  (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 the each temperature step. Assumption for this study was that at steady state temperature of the quartz boat with 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 – Supplement). This also happens to be where the laser beam ( $\lambda = 632.8 \text{ nm}$ ) used to monitor pyrolysis passes through the filter. Oven calibrations were performed using both the NIOSH 5040 and IMPROVE temperature operating conditions. Details about residence time and temperature ramp rate ( $^{\circ}\text{C s}^{-1}$ ) 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 120 s.

Two temperatures were recorded during the oven calibration routine:  $T_{\text{OVEN}}$  as measured by the built-in oven temperature sensor and  $T_{\text{FILTER}}$  as measured by the calibration kit. Both temperatures were recorded when the readings for the sample oven ( $T_{\text{OVEN}}$ ) were stable at each setpoint temperature ( $T_{\text{SETPOINT}}$ ) 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  $T_{\text{SETPOINT}}$ ,  $T_{\text{OVEN}}$ , and  $T_{\text{FILTER}}$  were determined, and temperature coefficients (approximately equal to temperature biases measured) in the instrument control software parameter files were adjusted so that





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and after TCAL. Paired  $t$  tests were performed to determine whether the calibration produced statistically different concentrations for TC, OC, and 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<sub>2.5</sub> 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  $1 \pm 0.05$ , the regression intercept  $0 \pm 1 \mu\text{gcm}^{-2}$ , and  $r \geq 0.97$ . Comparability criteria were adopted as described in detail by Watson and Chow (2002). Comparability is achieved when the slope equals unity within three standard deviations or average of ratios ( $y/x$ ) equal unity within one standard deviation, the intercept does not differ from zero within three standard deviations, and  $r > 0.90$ .

### 3 Results and discussion

#### 3.1 Temperature calibration results

Table 2 summarizes temperatures required ( $T_{\text{SETPPOINT}}$ ) at each programmed step and the average  $T_{\text{FILTER}}$  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,  $T_{\text{FILTER}}$  values are





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than before TCAL on average. The average OC values were 12 % higher and statistically different ( $P = 0.00$ ) after the calibration. No statistical difference was found for the TC ( $P > 0.05$ ) after the TCAL with the results being comparable and the calibration resulting in  $\sim 2\%$  lower TC values. 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  $\Delta T$ . 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 is neither equivalent nor comparable, while the 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  $0.97 \pm 0.09$  (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  $1.00 \pm 0.06$  (IMPROVE/NIOSH). However, using OC and EC concentrations, the paired  $t$  test shows statistically significant differences between two protocols ( $P < 0.001$ ), and the regression analysis shows



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Pyrolysis (PyC) significantly changed after calibration ( $P < 0.05$ ) and is 10–12% lower than before TCAL for both TOR and TOT analysis. Lower PyC values after TCAL are consistent with lower total OC values discussed in Sect. 3.2.1. ( $\sim 11\%$  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 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 semivolatile OC that contributes the most to the charring) is exposed to higher temperatures, and 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 the same 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-O<sub>2</sub> 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.

### 3.3.2 NIOSH TOT before and after TCAL

Percent differences in TC, OC, EC, four TOT OC and five EC carbon sub-fractions, and PyC measured by the NIOSH method before and after TCAL can be found in Fig. 2c with statistical comparisons in Table 5. 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







## References

- Birch, M. E.: Analysis of carbonaceous aerosols: interlaboratory comparison, *Analyst*, 123, 851–857, 1998.
- Birch, M. E. and Cary, R. A.: Elemental carbon-based method for monitoring occupational exposures to particulate diesel exhaust, *Aerosol Sci. Tech.*, 25, 221–241, 1996.
- 5 Chow, J. C., Watson, J. G., Pritchett, L. C., Pierson, W. R., Frazier, C. A., and Purcell, R. G.: The DRI thermal/optical reflectance carbon analysis system: description, evaluation, and applications in us air quality studies, *Atmos. Environ.*, 27, 1185–1201, 1993.
- 10 Chow, J. C., Watson, J. G., Crow, D., Lowenthal, D. H., and Merrifield, T.: Comparison of IMPROVE and NIOSH carbon measurements, *Aerosol Sci. Tech.*, 34, 23–34, 2001.
- 15 Chow, J. C., Watson, J. G., Kuhns, H. D., Etyemezian, V., Lowenthal, D. H., Crow, D. J., Kohl, S. D., Engelbrecht, J. P., and Green, M. C.: Source profiles for industrial, mobile, and area sources in the big Bend Regional Aerosol Visibility and Observational (BRAVO) study, *Chemosphere*, 54, 185–208, 2004a.
- 20 Chow, J. C., Watson, J. G., Chen, L. W. A., Arnott, W. P., and Moosmuller, H.: Equivalence of elemental carbon by thermal/optical reflectance and transmittance with different temperature protocols, *Environ. Sci. Technol.*, 38, 4414–4422, 2004b.
- 25 Chow, J. C., Watson, J. G., Chen, L.-W. A., Paredes-Miranda, G., Chang, M.-C. O., Trimble, D., Fung, K. K., Zhang, H., and Zhen Yu, J.: Refining temperature measures in thermal/optical carbon analysis, *Atmos. Chem. Phys.*, 5, 2961–2972, doi:10.5194/acp-5-2961-2005, 2005.
- 30 Chow, J. C., Watson, J. G., Chen, L.-W. A., Chang, M. C. O., Robinson, N. F., Trimble, D., and Kohl, S.: The IMPROVE\_A temperature protocol for thermal/optical carbon analysis: maintaining consistency with a long-term database, *J. Air Waste Manage.*, 57, 1014–1023, 2007.
- 35 Chow, J. C., Watson, J. G., Lowenthal, D. H., Chen, L. W. A., and Motallebi, N.: PM<sub>2.5</sub> source profiles for black and organic carbon emission inventories, *Atmos. Environ.*, 24, 5407–5414, 2011.
- Jing, L.: Standard combustion aerosol generator (SCAG) for calibration purposes, 3rd ETH Workshop “Nanoparticle measurement”, ETH Höggerberg Zürich, 9–10 August 1999, 1999.

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- Khan, B., Hays, M. D., Geron, C., and Jetter, J.: Differences in the OC/EC ratios that characterize ambient and source aerosols due to thermal-optical analysis, *Aerosol Sci. Tech.*, 46, 127–137, 2012.
- Kim, E. and Hopke, P. K.: Source apportionment of fine particles at Washington, DC, utilizing temperature-resolved carbon fractions, *J. Air Waste Manage.*, 54, 773–785, 2004.
- Kim, E. and Hopke, P. K.: Improving source apportionment of fine particles in the Eastern United States utilizing temperature-resolved carbon fractions, *J. Air Waste Manage.*, 55, 1456–1463, 2005.
- Lee, P. K. H., Brook, J. R., Dabek-Zlotorzynska, E., and Mabury, S. A.: Identification of the major sources contributing to PM<sub>2.5</sub> observed in Toronto, *Environ. Sci. Technol.*, 37, 4831–4840, 2003.
- Maykut, N. N., Lewtas, J., Kim, E., and Larson, T. V.: Source apportionment of PM<sub>2.5</sub> at an urban IMPROVE site in Seattle, Washington, *Environ. Sci. Technol.*, 37, 5135–5142, 2003.
- NIOSH: Elemental carbon (diesel exhaust), in: NIOSH Manual for Analytical Methods, National Institute for Occupational Safety and Health, Cincinnati, OH, 1996.
- NIOSH: Method 5040 Issue 3 (Interim): elemental carbon (diesel exhaust), in: NIOSH Manual for Analytical Methods, National Institute for Occupational Safety and Health, Cincinnati, OH, 1999.
- Peterson, M. R. and Richards, M. H.: Thermal-optical transmittance analysis for organic, elemental, carbonate, total carbon, and OCX2 in PM<sub>2.5</sub> by the EPA/NIOSH method, in: Proceedings, Symposium on Air Quality Measurement Methods and Technology – 2002, edited by: Winegar, E. D. and Tropp, R. J., Air & Waste Management Association, Pittsburgh, PA, 83-1-83-19, 2002.
- Phuah, C. H., Peterson, M. R., Richards, M. H., Turner, J. H., and Dillner, A. M.: A temperature calibration procedure for the sunset laboratory carbon aerosol analysis lab instrument, *Aerosol Sci. Tech.*, 43, 1013–1021, 2009.
- Schauer, J. J., Mader, B. T., DeMinter, J. T., Heidemann, G., Bae, M. S., Seinfeld, J. H., Flagan, R. C., Cary, R. A., Smith, D., Huebert, B. J., Bertram, T., Howell, S., Kline, J. T., Quinn, P., Bates, T., Turpin, B., Lim, B. J., Yu, J. Z., Yang, H., and Keywood, M. D.: ACE-Asia inter-comparison of a thermal-optical method for the determination of particle-phase organic and elemental carbon, *Environ. Sci. Technol.*, 37, 993–1001, 2003.

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US Environmental Protection Agency (EPA): National Ambient Air Quality Standards for Particulate Matter: Final Rule, Federal Register, 62, 38, 651–38, 701, available at: <http://www.gpo.gov/fdsys/pkg/FR-1997-07-18/pdf/97-18577.pdf> (last access: 2 August 2013), 1997.

5 Watson, J. G. and Chow, J. C.: Source characterization of major emission sources in the imperial and Mexican valleys along the US/Mexico Border, *Sci. Total. Environ.*, 276, 33–47, 2001.

Watson, J. G. and Chow, J. C.: Comparison and evaluation of in situ and filter carbon measurements at the fresno supersite, *J. Geophys. Res.*, 107, ICC 3-1–ICC 3-15 2002.

10 Watson, J. G., Chow, J. C., Lowenthal, D. H., Pritchett, L. C., Frazier, C. A., Neuroth, G. R., and Robbins, R.: Differences in the carbon composition of source profiles for diesel- and gasoline-powered vehicles, *Atmos. Environ.*, 28, 2493–2505, 1994.

Yu, J. Z., Xu, J., and Yang, H.: Charring characteristics of atmospheric organic particulate matter in thermal analysis, *Environ. Sci. Technol.*, 36, 754–761, 2002.

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**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

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

Carbon fraction	NIOSH 5040					IMPROVE				
	$T_{\text{SETPOINT}}$ (°C)	$T_{\text{FILTER}}$ (°C)	Ramp Rate (°C s <sup>-1</sup> )	Residence time (s)	$\Delta T$ °C (% difference)	$T_{\text{SETPOINT}}$ (°C)	$T_{\text{FILTER}}$ (°C)	Ramp Rate (% difference)	Residence time (s)	$\Delta T$ °C
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)					

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

Carbon Fraction	NIOSH 5040			IMPROVE		
	$T_{\text{SETPOINT}}$ (°C); $r^*$	$T_{\text{FILTER}}$ (°C)	$\Delta T$ °C (% difference)	$T_{\text{SETPOINT}}$ (°C); $r^*$	$T_{\text{FILTER}}$ (°C)	$\Delta T$ °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.

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

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

\* TC = Total Carbon = EC + OC; EC = Elemental Carbon; OC = Organic Carbon.

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

Comparisons	Analysis		Average of ratios $y/x \pm$ STD	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 TOT 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
	EC5	EC5	0.31 ± 0.51	0.00

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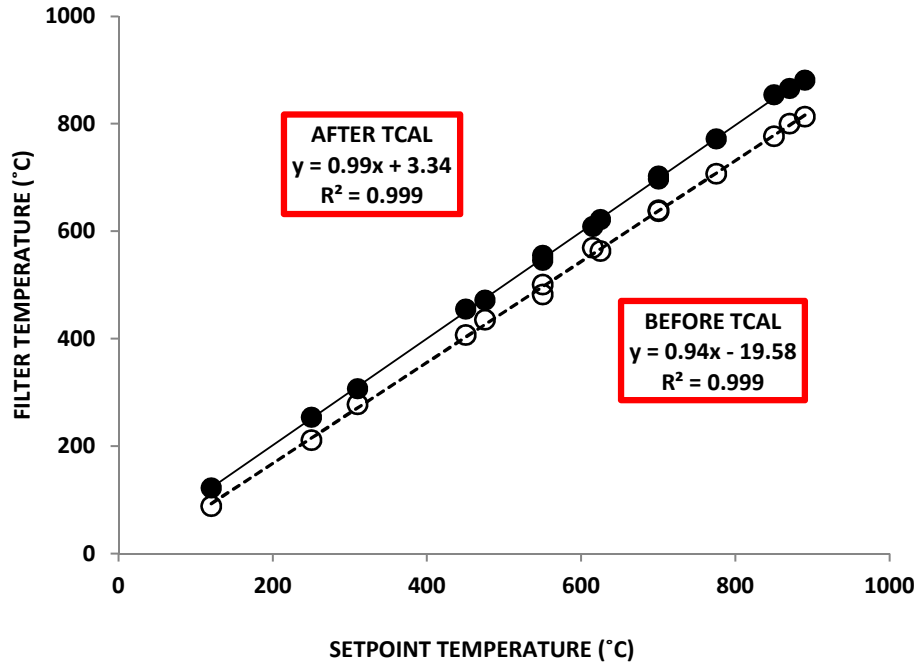
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**Fig. 1.** Linear regression results before and after temperature calibration.

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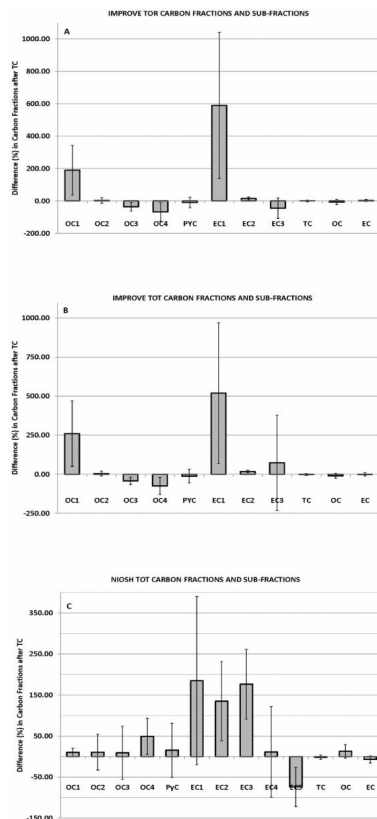
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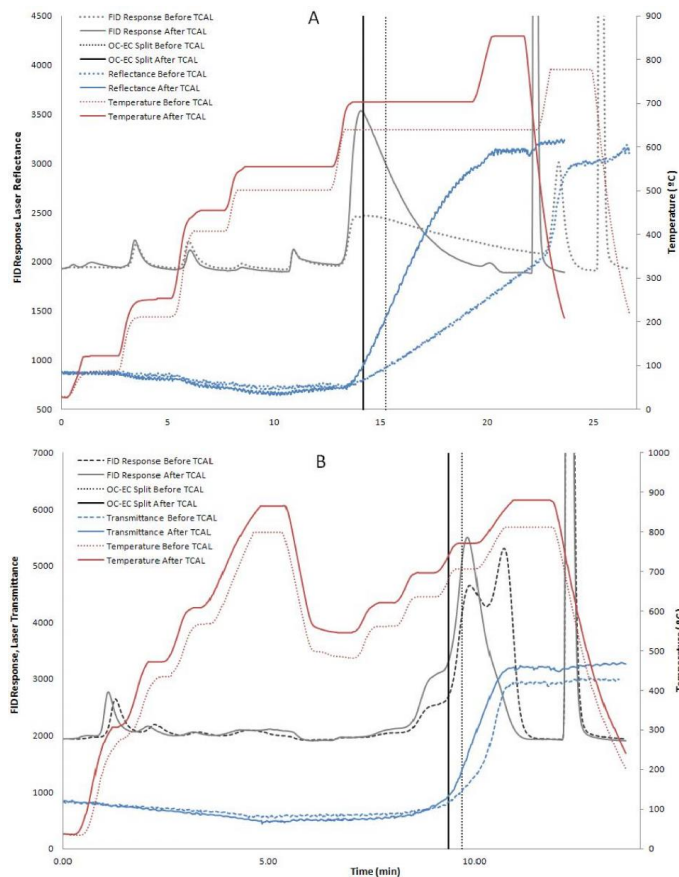
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**Fig. 2.** Percent difference in carbon sub-fractions and standard deviation of the results after temperature calibration for the **(A)** IMPROVE TOR **(B)** IMPROVE TOT and **(C)** NIOSH TOT temperature protocols.

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**Fig. 3.** Typical **(A)** IMPROVE TOR thermogram and **(B)** NIOSH TOT thermogram for the same sample analyzed before and after TCAL.