

## ***Interactive comment on “Refining temperature measures in thermal/optical carbon analysis” by J. C. Chow et al.***

**J. C. Chow et al.**

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We appreciate the reviewers' recognition that users of atmospheric carbon data, especially OC and EC fractions, should have a better understanding of how the data were obtained. For this reason, and because Atmospheric Chemistry and Physics is the journal of record for findings from the 2004 Vienna Carbon Conference, we feel it is important to publish our results here with some perspective on their implications for source apportionment modeling, climate, and health studies. Our responses to the reviewers' comments are as follows:

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## General Comments:

**The paper undermines confidence in carbon “bulk speciation” studies** (*Reviewer 1*). A plethora of published interlaboratory and intermethod comparison studies for OC and EC already undermines this confidence. Our cited paper (Watson et al., 2005) summarizes results from more than 40 comparison studies. Some studies show good agreement, while others show poor agreement between what are said to be the same measurement methods. Watson et al. (2005) conclude that investigators can (and do) select comparison studies that support or refute the equivalence of their methods with those of other investigators rather than examining the accumulated body of knowledge that suggests no consistent comparability. A positive finding is that nearly all of the comparisons show good agreement for total carbon measurements when calibration standards are consistent and sampling artifacts are controlled. Rather than adding complexity, our method allows investigators to evaluate temperature as one of the many variables that might cause disagreements among methods for different samples.

**Temperature calibration is only valid for a given type of instrument** (*Reviewer 1*). This is correct. All instruments need to be calibrated, even those of the same make and model, and all instruments need to be re-calibrated when major changes are made in the temperature sensor, heater, flow system, etc. Temperature differences need to be periodically verified at a few levels with quality control temperature standards. We see this as just another part of a comprehensive quality assurance program similar to regular FID performance tests, replicates, blanks, sucrose and KHP solution standards, etc. We are also developing methods to quantitatively audit levels of oxygen in the carrier gases and the transmittance and reflectance measures that may also result in differences for carbon fractions. Our goal is to demonstrate that OC, EC, and other carbon fraction concentrations are not instrument specific when the conditions to which the sample is exposed are the same.

**Temperature calibration is only valid for a fixed temperature program** (*Reviewer 1*). We don't believe this is the case. Our results show good linearity between the actual and measured temperature. We are applying a linear temperature calibration curve to adjust measured to actual temperature in our future analyses. Once the calibration is made, it is possible to implement any temperature program.

**Other uncontrolled, poorly understood, and variable charring would affect each OC fraction as well as temperature** (*Reviewer 2, Reviewer 3*). We cannot agree more with this statement. Temperature is one, but not the only, parameter that influences the consistency of carbon fraction measurements between different instruments, even with the same presumed protocol. Before other parameters can be evaluated, the exact (to the best extent one can achieve) temperature measurement is needed. We appreciate that *Reviewer 3* makes this point very clear.

**Give more examples of carbon fraction comparisons between real and assumed temperatures** (*Reviewer 1, Reviewer 2*). Figure 5 was meant to be illustrative, not comprehensive. We have performed many tests (Chow et al., 2004, 2005) that evaluate the sensitivity of OC, EC, and other carbon fractions to small and large differences in temperature programs for a variety of sample types. Results are similar to those in Figure 5 of our paper.

Figure I (available via anonymous FTP at: <ftp://ftp.dri.edu/pub/Chow/FigureI.doc>) compares the carbon fractions measured by the DRI/OGC and DRI Model 2001 carbon analyzers, both before and after the temperature calibration. These data are part of a report (Chow et al., 2005) we submitted to the steering committee of the Interagency Monitoring of Protected Visual Environments (IMPROVE). More than 100 representative samples from the IMPROVE network were analyzed. Although the temperature

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bias is not the only difference between the DRI/OCG and DRI Model 2001 analyzers, it appears to be the dominant factor for carbon fraction measurements. Higher OC3 and lower EC2 were generally reported by the DRI/OGC carbon analyzer before the temperature calibration, consistent with a higher sample temperature. Agreement improved after temperature calibration was performed on both instruments.

Though these data could have been included in the paper, we felt it would be more appropriate for a separate publication. We are performing additional tests and will publish the results soon. The objective of the current paper is to let other investigators apply this method or other methods to assess effects of temperature differences for their instruments and procedures.

### Specific Comments:

#### 1. Page 4487, line 1: the reproducibility is not always within $\pm 3^\circ\text{C}$ (Reviewer 2)

Response: We will revise to “ $\pm 1\%$ ”, which is the precision of the Tempilaq° G.

#### 2. Page 4488, line 27: Thermocouple temperature does not always underestimate sample temperature (Reviewer 2)

Response: This statement will be revised to “thermocouple often underestimates the sample temperature”.

#### 3. Page 4489, line 7: Does the Sunset analyzer show a higher nonlinearity than the DRI Model 2001 in terms of temperature measurement? (Reviewer 2)

Response: First, this is based on the data we obtained. We do not claim that the results will be the same for other Sunset instruments. There is variability among the five DRI Model 2001 analyzers. For the five DRI Model 2001 analyzers, however,

the thermocouple always underestimated the sample temperature (with only one exception). One Sunset instrument we tested overestimated the temperature for the two middle temperatures and underestimated the temperature for all other temperatures, and in that sense it is not as linear. We would like to emphasize that every instrument has different calibration factors, and each needs to be separately calibrated.

**4. Page 4480, line 19: OC volatilization temperature could be higher than 550 °C?**  
(Reviewer 3)

Response: This is actually one of the core issues in carbon analysis that remains to be understood. OC could volatilize, char, or resist any change during the heating process. Most PAHs and alkenes volatilize below 550 °C, while polar compounds, including dicarboxylic acids, more likely decompose (or char) at such a high temperature. The fraction of OC that resists any change up to 550 °C is believed to be small. Since we explained the charring in the next sentence, the statement under question will be revised to “OC tends to evolve at a lower temperature (e.g., < 550 °C), and therefore it is separated from EC.”

*Copies of cited articles are available upon request made to judy.chow@dri.edu:*

Chow, J.C.; Watson, J.G.; Chen, L.-W.A.; Arnott, W.P.; Moosmüller, H.; Fung, K.K. Equivalence of elemental carbon by Thermal/Optical Reflectance and Transmittance with different temperature protocols; Environ. Sci. Technol. 2004, 38(16), 4414-4422.

Chow, J.C.; Watson, J.G.; Chen, L.-W.A.; Chang, M.C.; Paredes-Miranda, G. Comparison of the DRI/OGC and Model 2001 Thermal/Optical carbon analyzers; prepared for IMPROVE Steering Committee, Fort Collins, CO, by Desert Research Institute: Reno, NV, 2005.

[http://vista.cira.colostate.edu/improve/Publications/GrayLit/013\\_CarbonAnalyzer/IMPROVEcarbonanalyzerassessmentPres.pdf](http://vista.cira.colostate.edu/improve/Publications/GrayLit/013_CarbonAnalyzer/IMPROVEcarbonanalyzerassessmentPres.pdf)

Watson, J.G.; Chow, J.C.; Chen, L.-W.A. Summary of organic and elemental carbon/black carbon analysis methods and intercomparisons; Aerosol and Air Quality Research 2005, 5(1), 69-102. <http://caart.org.tw>.

**ACPD**

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