Adapting the IMPROVE_A Protocol for Multiwavelength Organic and Elemental Carbon Measurements

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Objectives

- Demonstrate equivalence between single- and multiwavelength (λ) systems for organic carbon (OC) and elemental carbon (EC).
- Introduce a calibration procedure for quantifying OC, EC, and brown carbon (BrC).
- Relate relative reflectance (R) and transmittance (T) values to different sources.

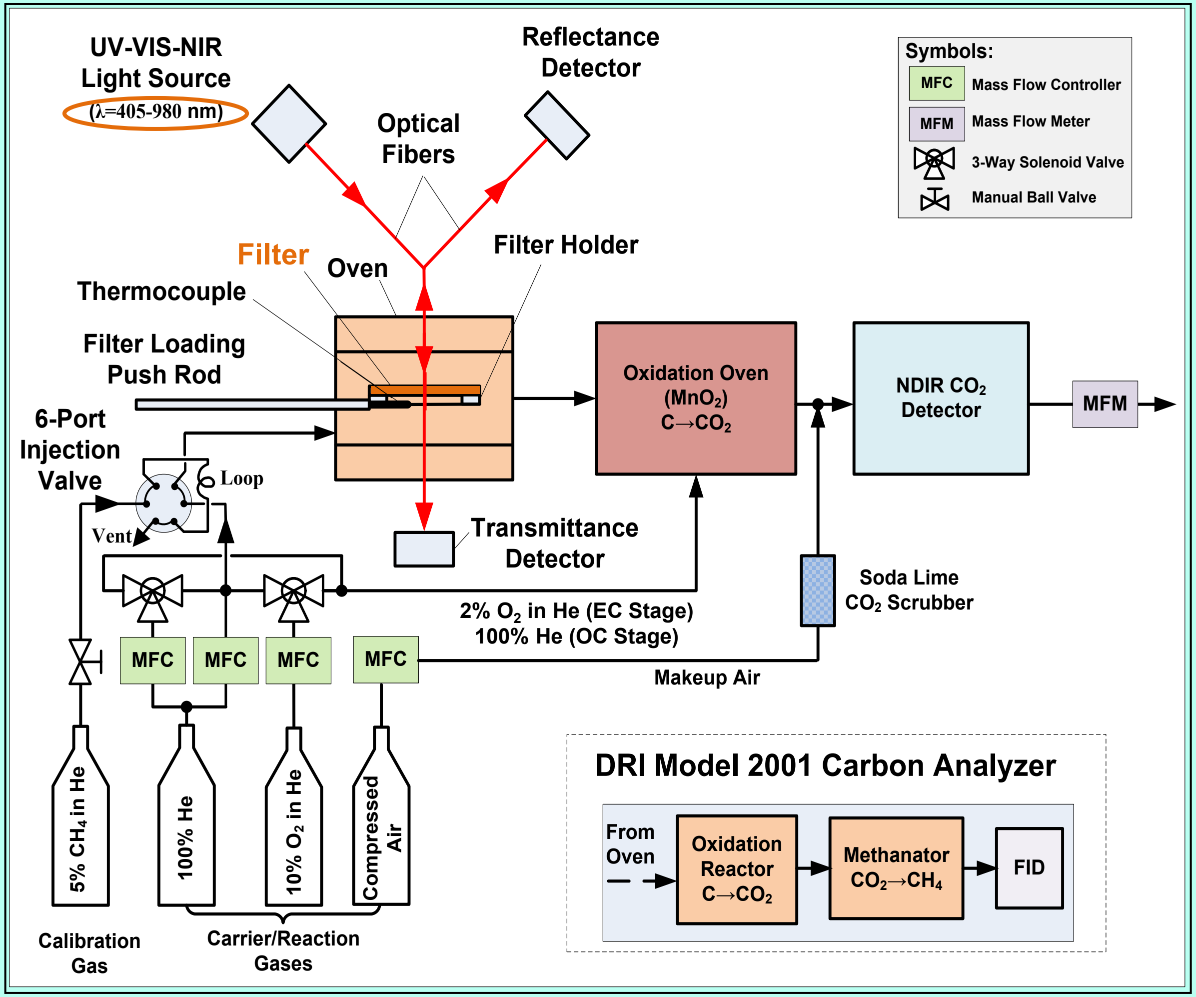
Motivation

- Single λ reflectance (R) and transmittance (T) have only been used for pyrolysis adjustment (i.e., reference to initial R or T). It can also be normalized to final R or T to approximate filter attenuation (ATN).

- The multiwavelength light source/detector combination yields different intensities within and among instruments.

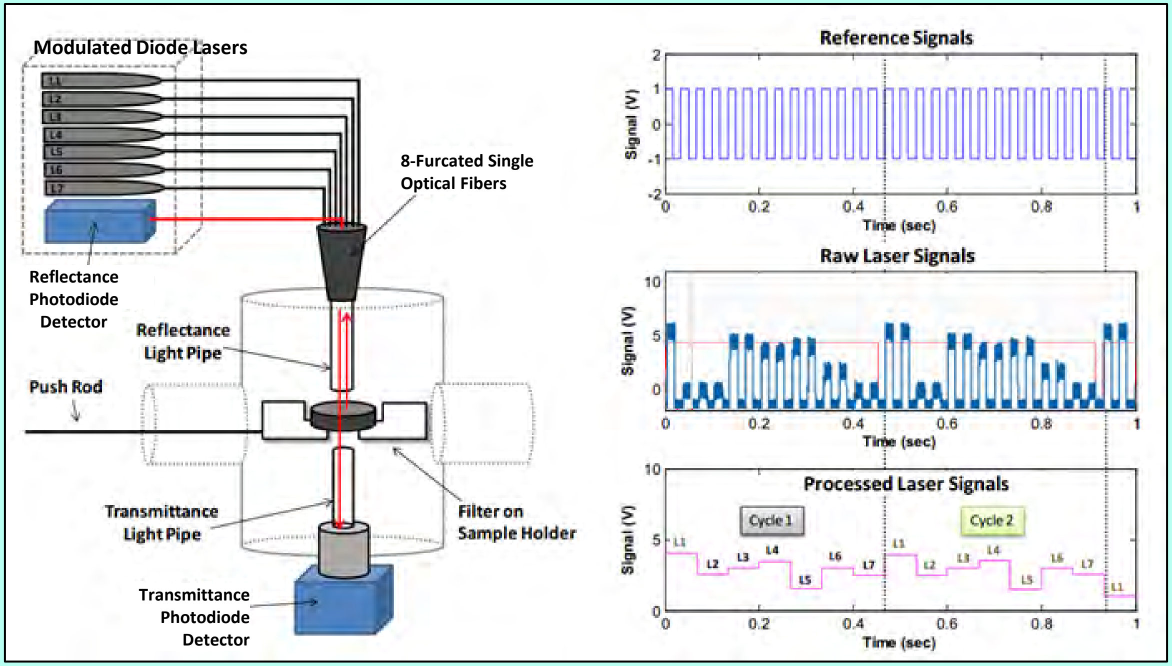
- Absolute R and T (in %) can be used to calculate ATN on filters and/or applied to radiative transfer models (e.g., Beer's Law, Kubelka-Munk Theory, or Monte Carlo Ray Tracing, etc.).

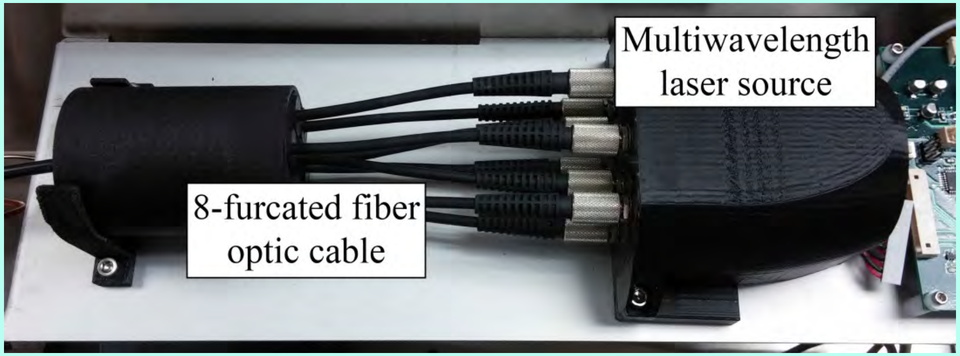
Multiwavelength Thermal/Optical Analyzer reports both reflectance and transmittance at 405, 445, 532, 635, 780, 808, and 980 nm



DRI Model 2015 configuration

The multiwavelength optical configurations allow for absolute calibration and wavelength-dependent OC/EC/BrC splits

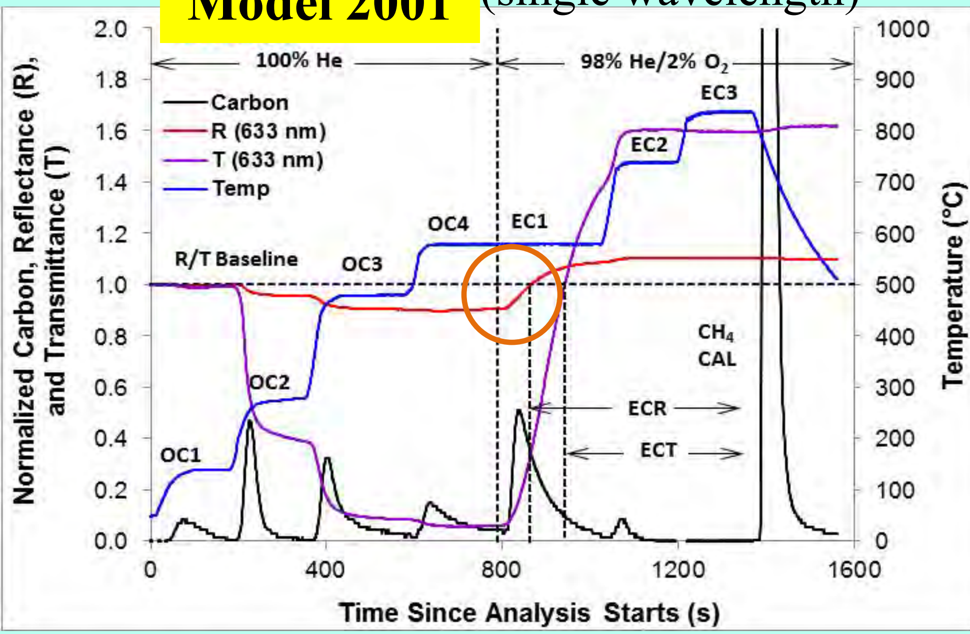




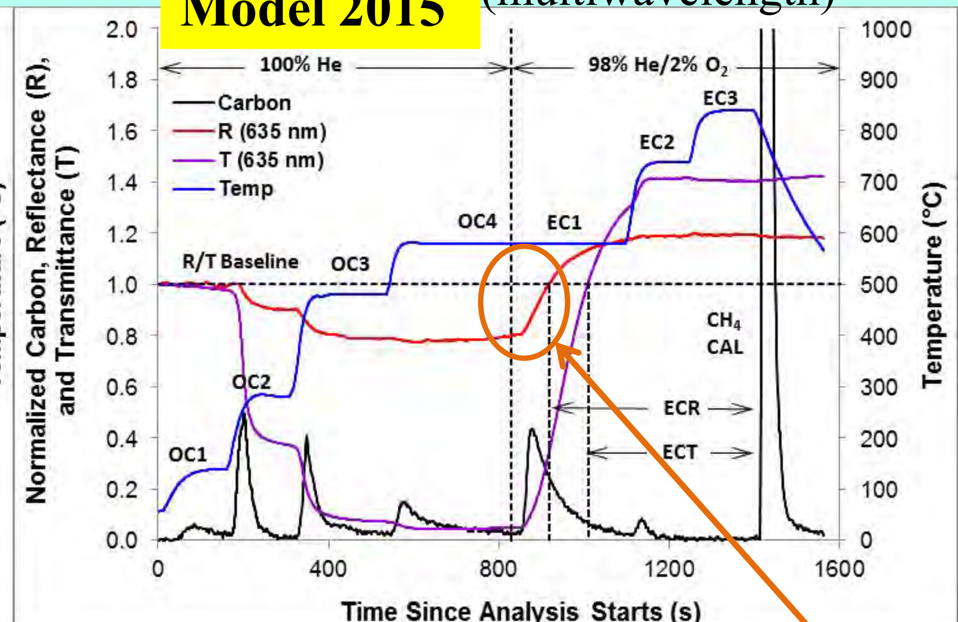
Chen et al., 2015, AMT

Similar thermograms are obtained for Models 2001 and 2015

Model 2001 (single wavelength)



Model 2015 (multiwavelength)



Lower R before adding O_2, implying better sensitivity in detecting OC charring

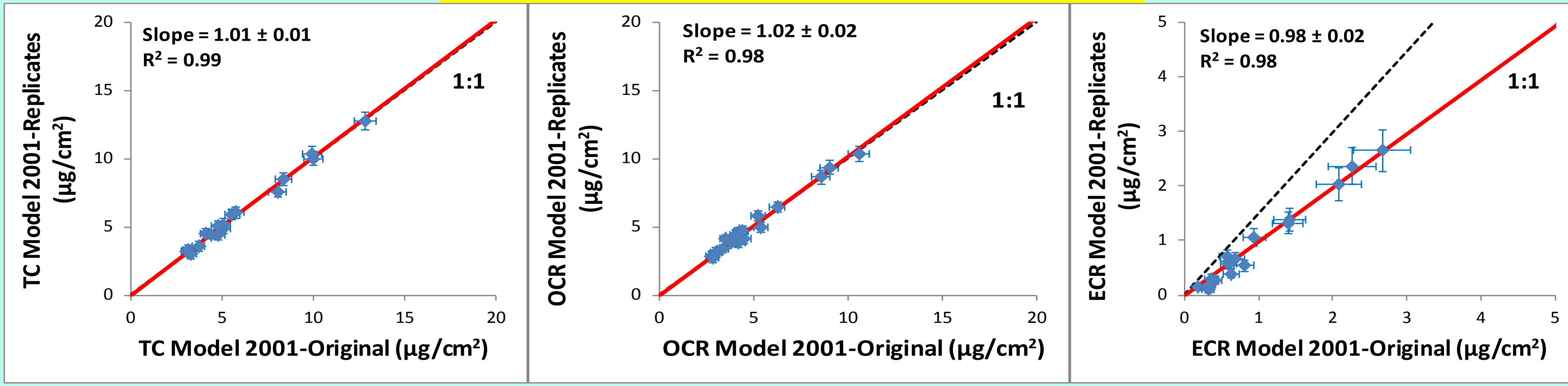
Model 2001

Model 2015

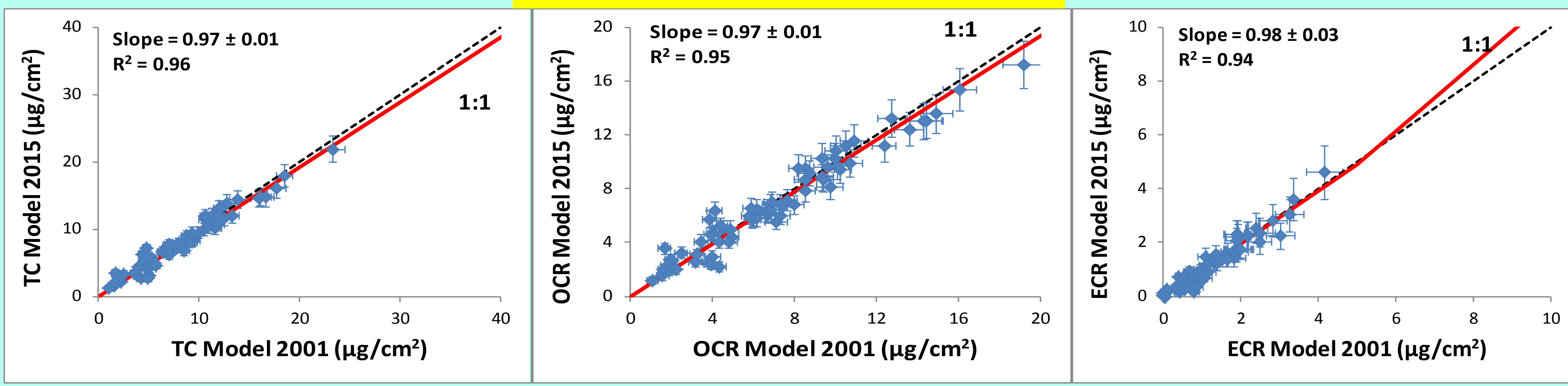
Equivalent OC and EC are obtained for single- and multi-wavelength systems

(633 nm vs 635 nm)

Model 2001 (A) vs Model 2001 (B)



Model 2015 vs Model 2001



OCR and ECR are OC and EC by reflectance.

Filter transfer standards with variable deposits can be standardized against Spectralon* standards (diffusive reflective)

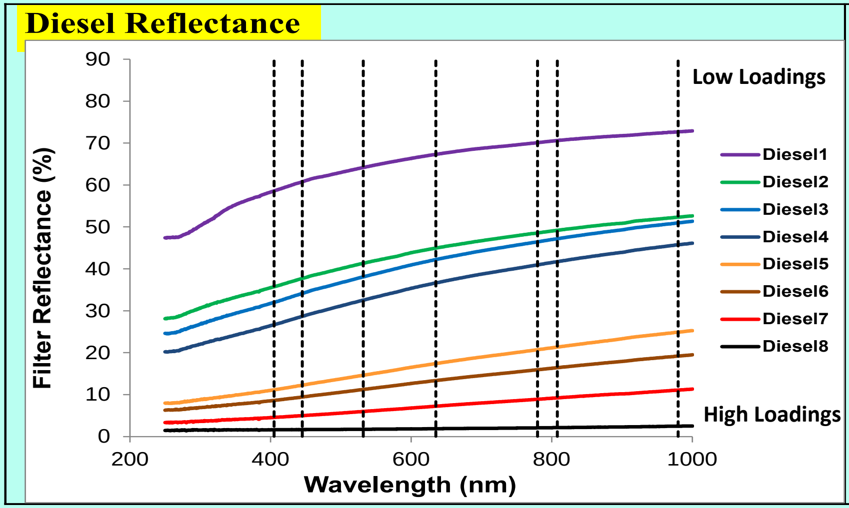
(Lambda 35 UV/VIS Spectrometer, Perkin Elmer, Waltham, MA; an Integrating-Sphere Spectrometer; measures R and T at 0 and 100%, 200-1100 nm)

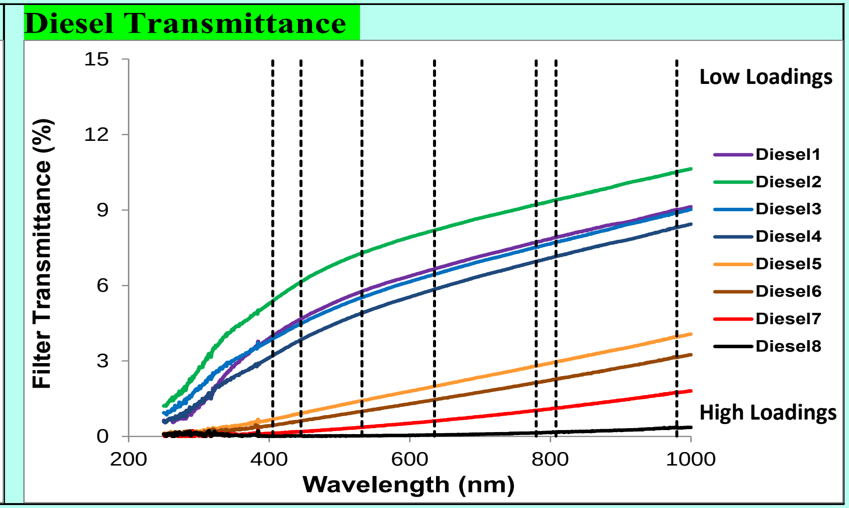
* NIST Certified Labsphere Spectralon® Diffusive Reflectance Standards

R and T are lower for shorter wavelengths

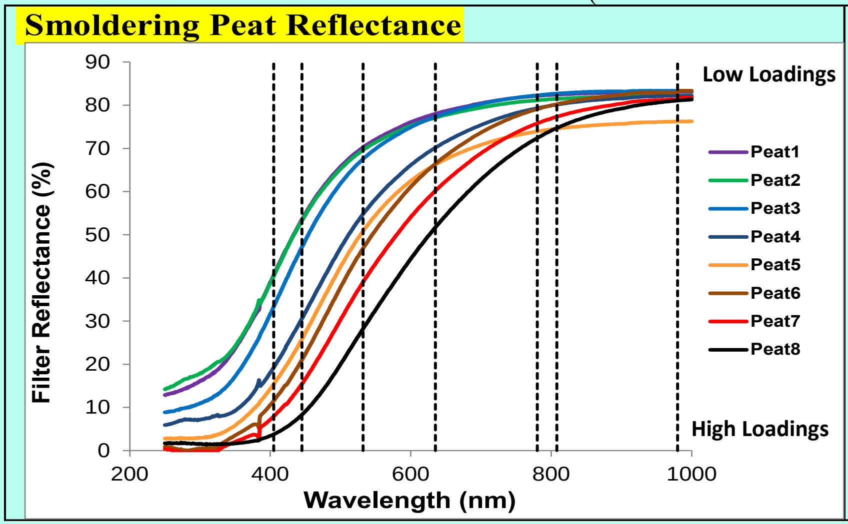
(Vertical lines designate the seven wavelengths in Model 2015)

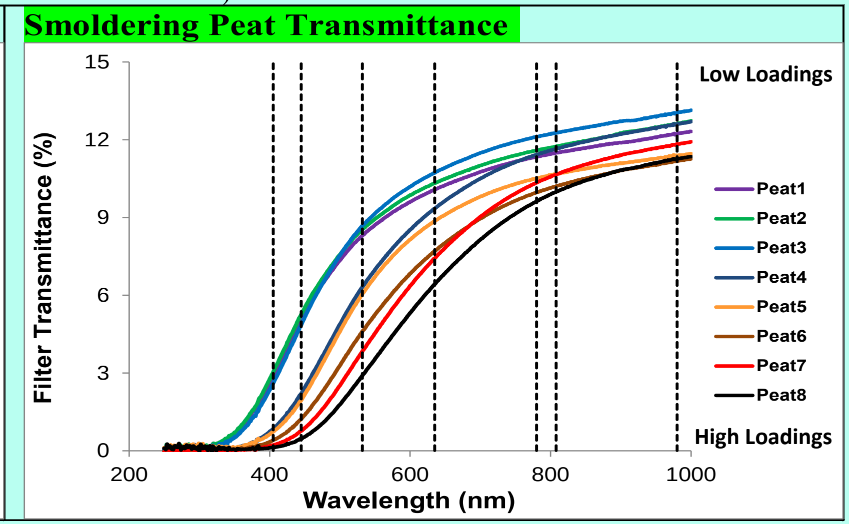
R and T in diesel samples are lower with increasing loadings.



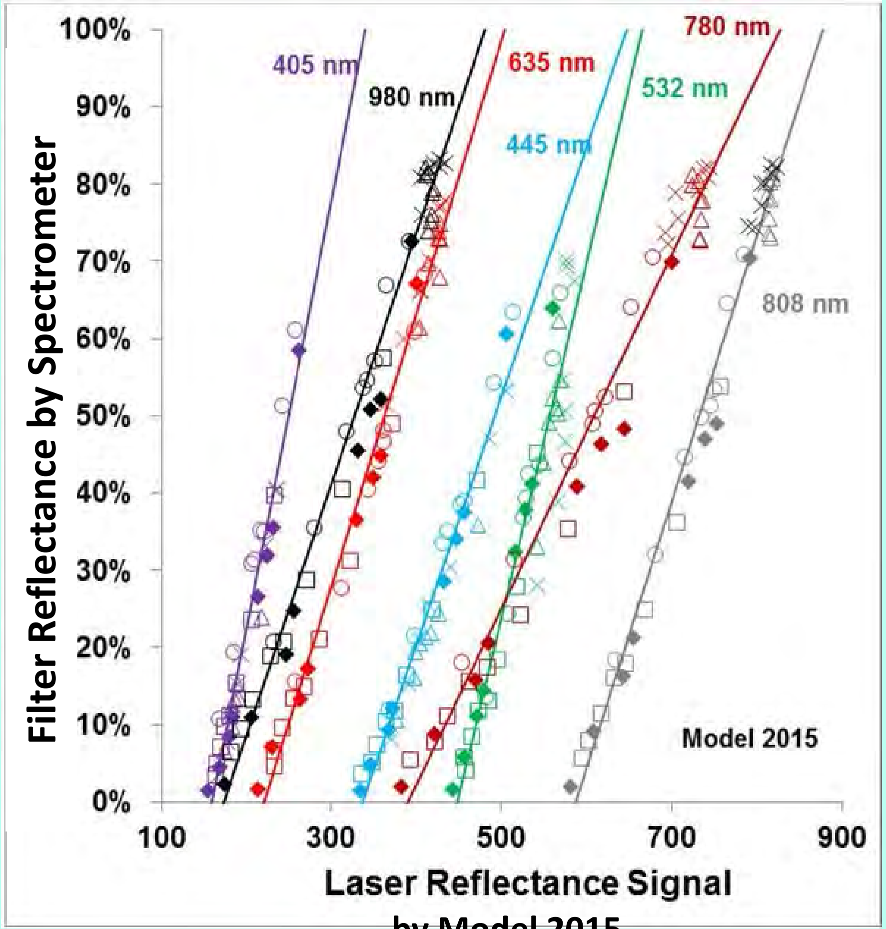


R and T in smoldering samples show minor changes with loading and clustered at high wavelengths (less useful than the blacker standard).

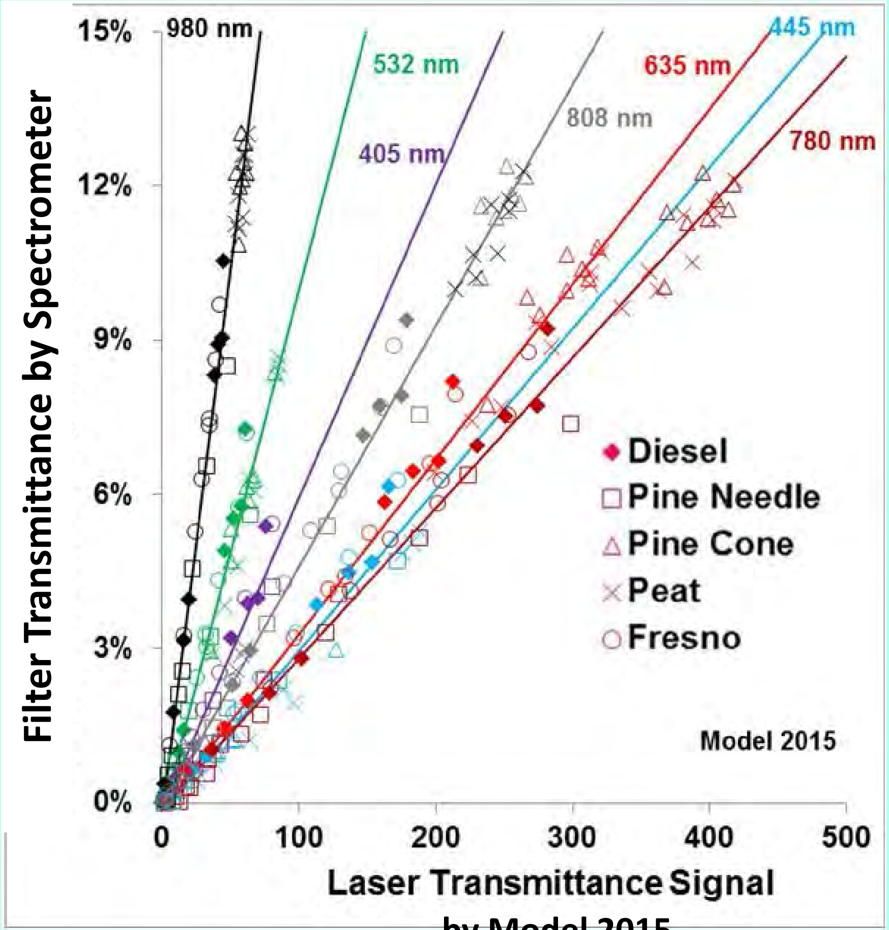




Calibration curves using transfer standards show linear responses independent of sample type or loading



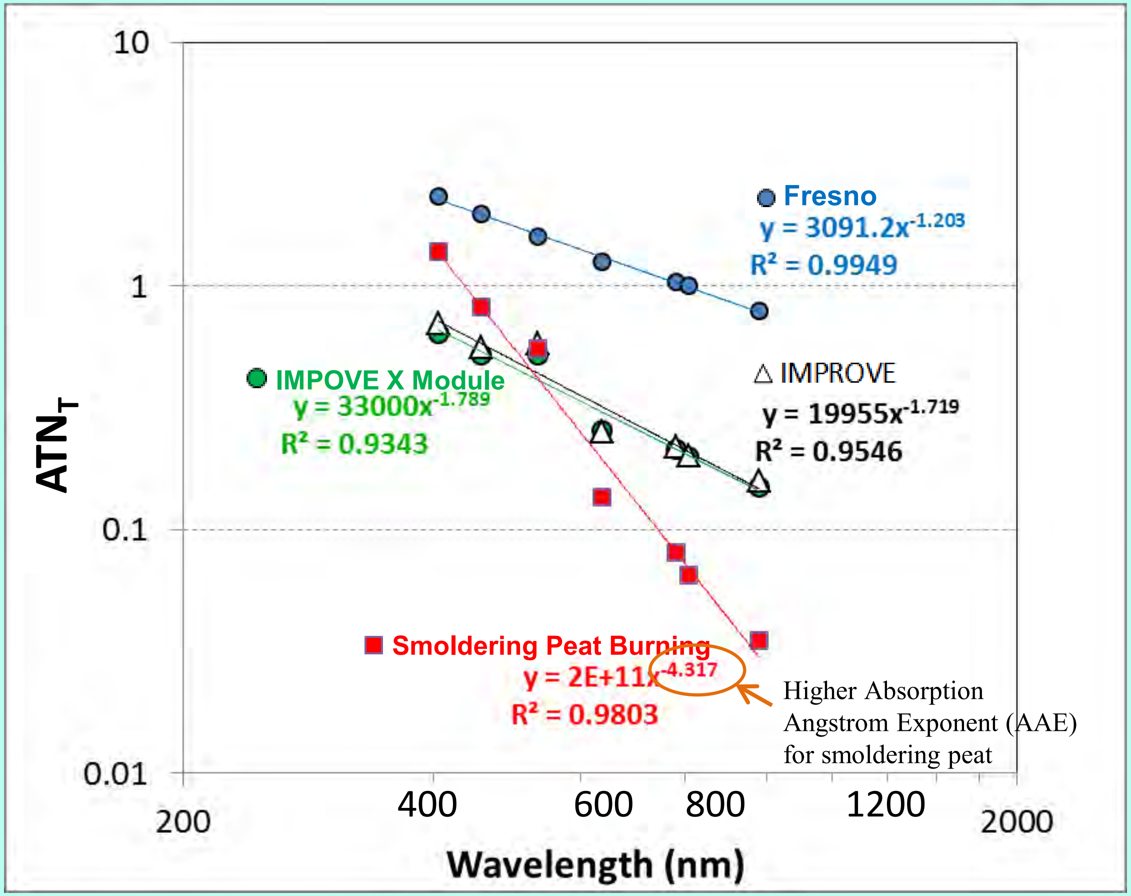
by Model 2015



by Model 2015

Transmittance spectral attenuation varies by sample type

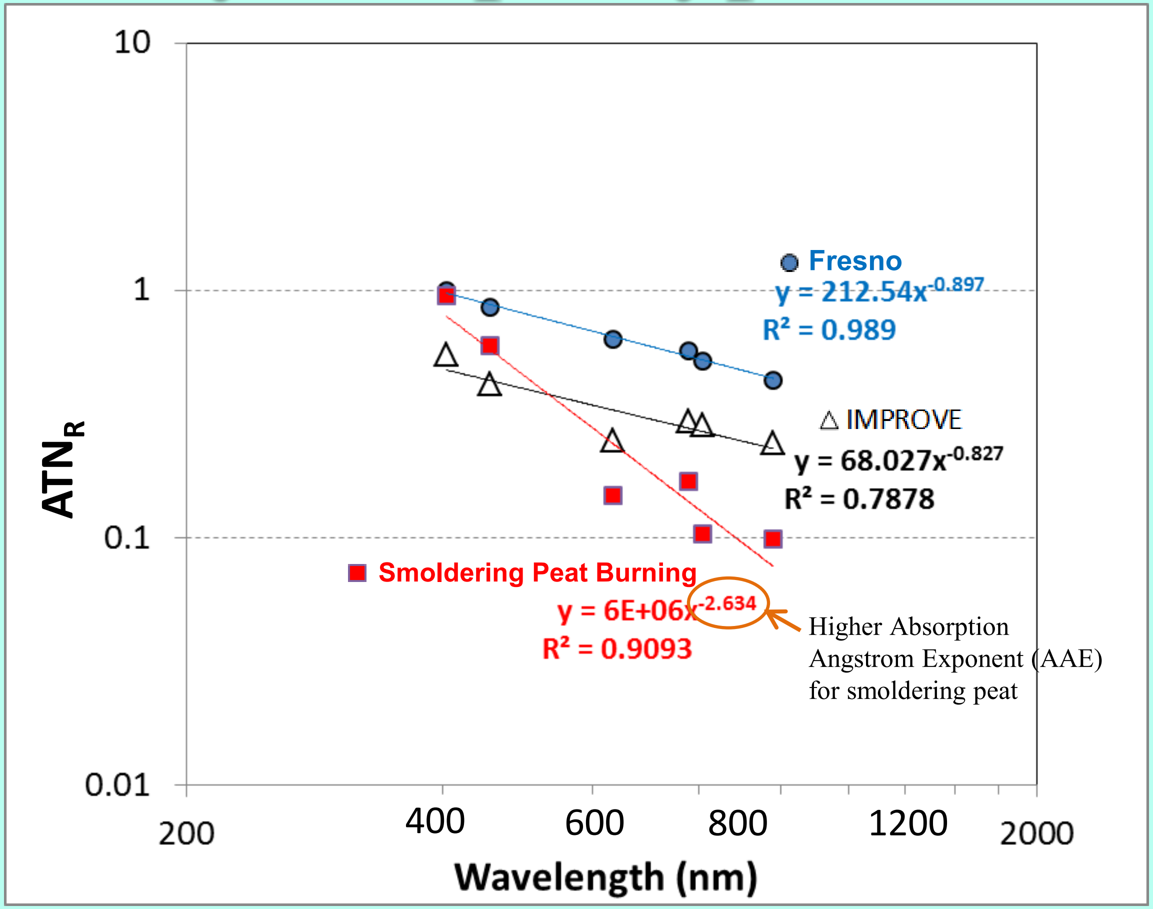
$$ATN_T(\lambda) = -\ln\left(\frac{FT_{\lambda,i}}{FT_{\lambda,f}}\right)$$



- Spectral absorption averaged by sample type.
- Smoldering samples acquired in a wood stove connected to DRI dilution chamber.

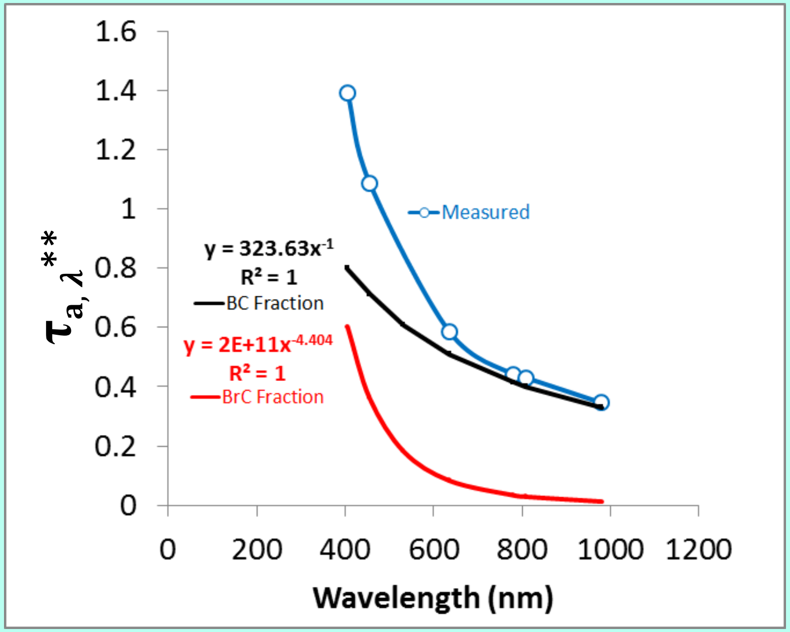
Reflectance spectral attenuation also varies by sample type

$$ATN_R(\lambda) = -\ln\left(\frac{FR_{\lambda,i}}{FR_{\lambda,f}}\right)$$

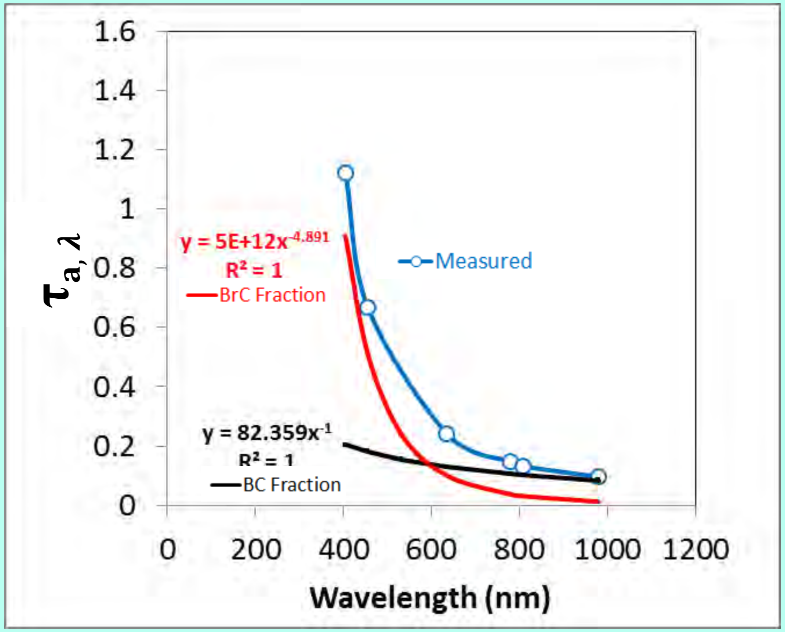


- Reflectance usually has lower signal to noise ratios than transmittance.
- R and T can be combined for better quantification of light absorption as indicated by Petzold and Schonlinner (2004).

AAE* can be used to decouple BC and BrC



Ambient Fresno, CA



Smoldering Biomass Burning

Simplified two-component model:

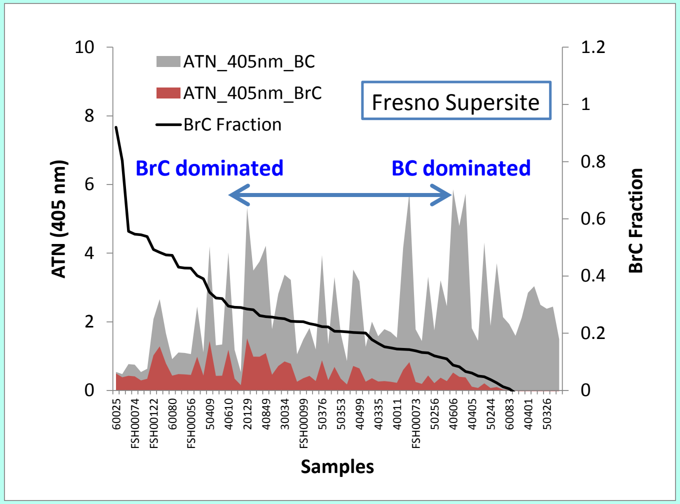
- $\tau_{a,\lambda} = q_{BC} \times \lambda^{-\alpha_{BC}} + q_{BrC} \times \lambda^{-\alpha_{BrC}}$

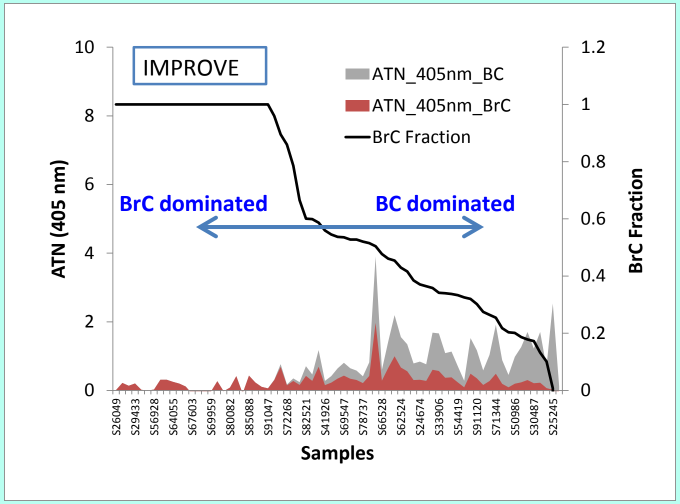
Assuming α_{BC}=1:

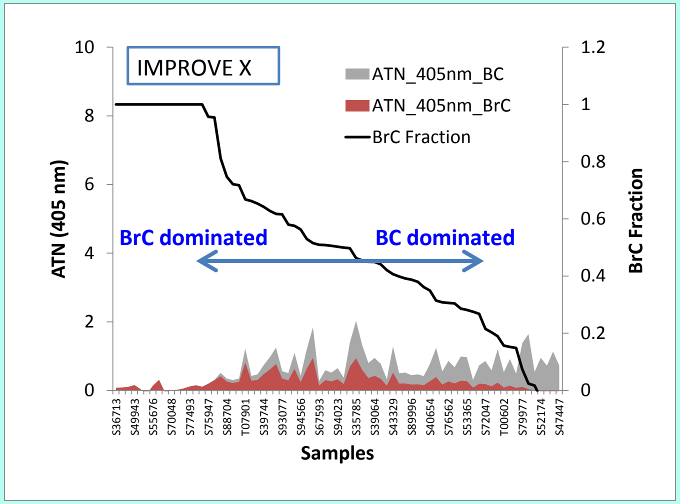
- $\tau_{a,\lambda} \times \lambda = q_{BC} + q_{BrC} \times \lambda^{-(\alpha_{BrC}-1)}$ (q_{BC} and q_{BrC} are fitting coefficients; α_{BC} and α_{BrC} are AAEs)

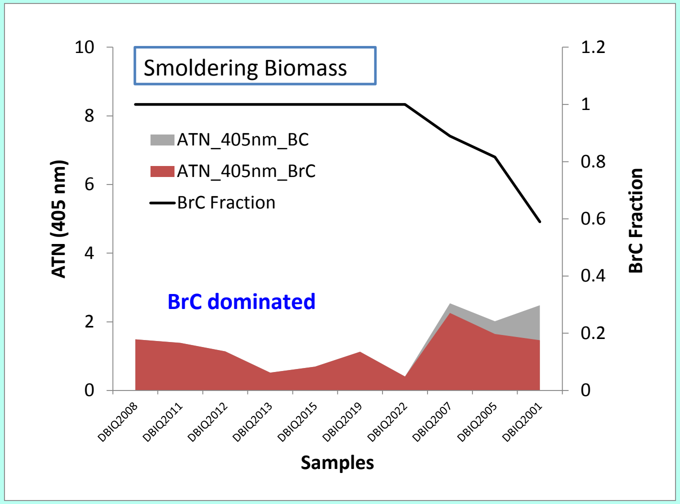
*AAE: Absorption Angstrom Exponent; **$\tau_{a,\lambda}$ is absorption optical depth, $\tau_{a,\lambda}$=ATN_{λ} if there is no filter effect

BC and BrC contributions to light attenuation (ATN_405 nm) vary by sample type









- Assuming only BC absorbs at 980 nm and an AAE_BC of 1 to extrapolate BC absorption to 405 nm.
- Samples sorted by BrC fraction (0 to 100%) in ATN_405 nm.

Potential future uses of calibrated multiwavelength R and T on thousands of samples

- Identifying light absorbing compounds.
- Separating artifact OC from aerosol OC.
- Ground-truthing remotely-sensed BrC.
- Improving radiation transfer estimates.
- Conducting source apportionment for BC and BrC.

More Information

(Chen et al., 2015; Chow et al., 2015)

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Optical Calibration and Equivalence of a Multiwavelength Thermal/Optical Carbon Analyzer

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Atmospheric Measurement Techniques

Multi-wavelength optical measurement to enhance thermal/optical analysis for carbonaceous aerosol

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Chow, J.C.; Wang, X.L.; Sumlin, B.J.; Gronstal, S.B.; Chen, L.-W.A.; Trimble, D.L.; Kohl, S.D.; Mayorga, S.R.; Riggio, G.; Hurbain, P.R.; Johnson, M.; Zimmermann, R.; Watson, J.G. (2015). Optical calibration and equivalence of a multiwavelength thermal/optical carbon analyzer. *AAQR*, online. doi:10.4209/aaqr.2015.02.0106. http://aaqr.org/JustAcceptedManuscripts/AAQR-15-02-OA-0106_accepted.pdf.

Conclusions

- Reflectance (R) and Transmittance (T) can be traceable to primary standards and made consistent among wavelengths and instruments.
- The detailed absorption spectrum can be approximated by the seven wavelengths.
- Brown carbon (BrC) can be separated from black carbon (BC) by a two-component model.

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References

Chen, L.-W.A.; Chow, J.C.; Wang, X.L.; Robles, J.A.; Sumlin, B.J.; Lowenthal, D.H.; Watson, J.G. (2015). Multi-wavelength optical measurement to enhance thermal/optical analysis for carbonaceous aerosol. *Atmos. Meas. Tech.* ., **8**:451-461. http://www.atmos-meas-tech.net/8/451/2015/amt-8-451-2015.html.

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Petzold, A.; Schonlinner, M. 2004. Multi-angle absorption photometry – A new method for the measurement of aerosol light absorption and atmospheric black carbon. *J. Aerosol Sci.*, **35**:421-441.