Optical characterization of atmospheric aerosols on quartz filters using reflectance-based spectroscopy

Michael J. Tackett Jr.
University of Arkansas Little Rock
Department of Chemistry
Department of Earth Science

Why study aerosol absorption?

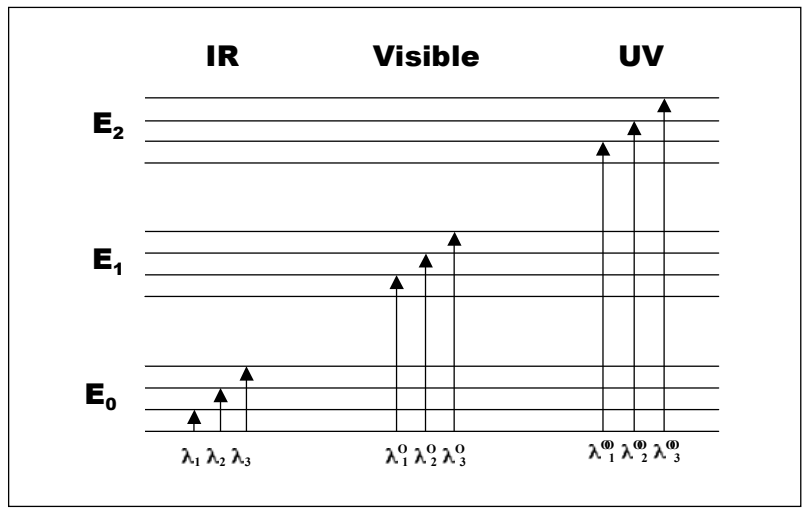
- Atmospheric aerosols can both scatter **AND** absorb
- Aerosol scattering mainly correlated with average particle size; **absorption** correlated with **chemical composition**
- **Black carbon (BC)** aerosols have the ability to scatter light, causing cooling, while simultaneously absorbing solar energy, causing:
  - Significant local warming of boundary layer
  - Similar warming in lower atmosphere as major greenhouse gases
- Important in **UV** for photochemical modeling

Background: Absorption Spectroscopy

- **Spectroscopy**=study of any quantity as a function of wavelength (λ) or frequency (ν); most often, interaction of radiation with matter
- **Overall energy (E)** of molecule described by:

$$E_{molecule} = E_{electronic} + E_{vibrational} + E_{rotational} + E_{translatio}$$

- **UV/Vis=electronic** transitions
  - promotion of e^- from ground state to higher energy orbitals



Background: Absorption Theory

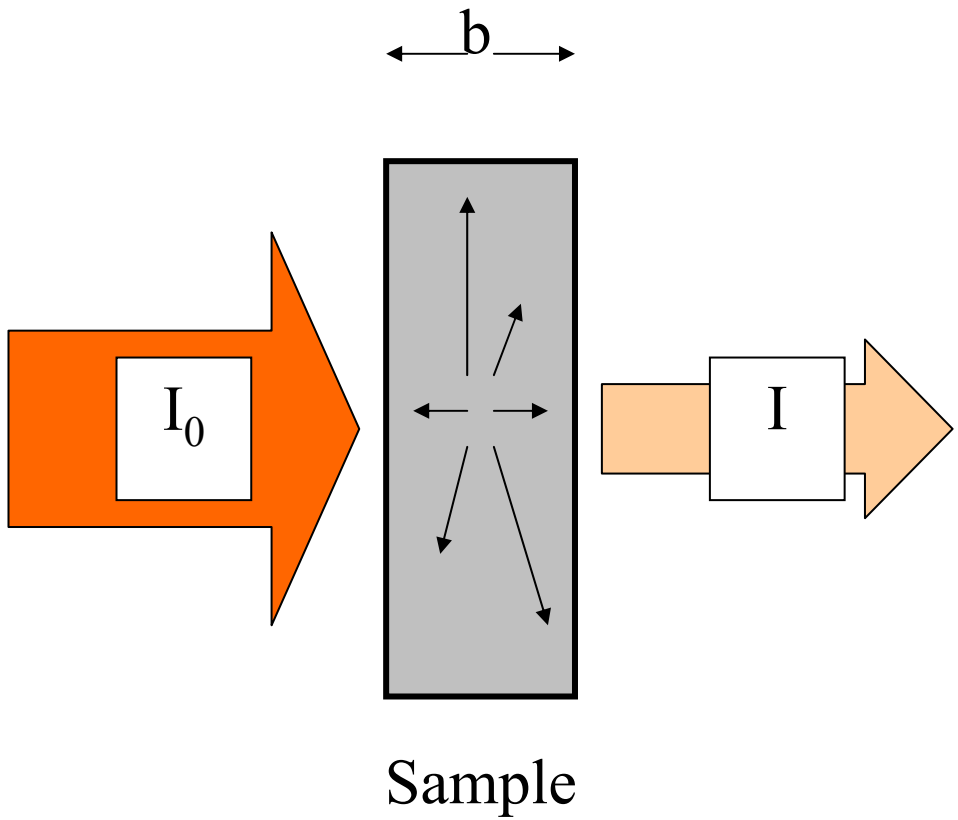
- **Beer-Lambert Law:**

$$A=\varepsilon bc$$

- **Measured property: transmission;**

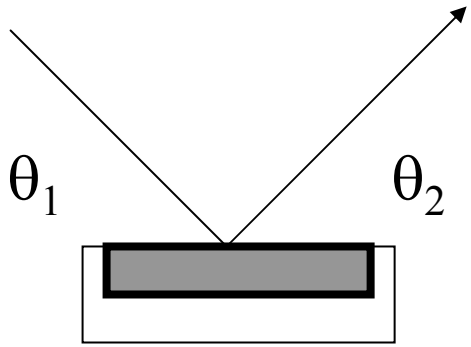
T=(I/I_0);

A=log(1/T) or -log(T)

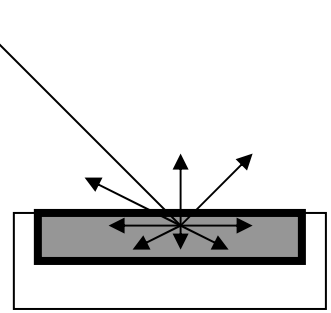


Background: Reflection Theory

- **Used** when transmission through sample not feasable/measurable
- **2 types of reflections:**
  - **Specular**=mirror-type ($\theta_1=\theta_2$)
  - **Diffuse**=scattering in all directions
- **Kubelka-Munk Theory**=developed for paper industry; dyed paper; Kubelka-Munk function ($f(K-M)=\frac{(1-R)^2}{2R}$) linearizes reflectance data by applying scattering factor; corrects for extra path length from scattering within sample



Specular

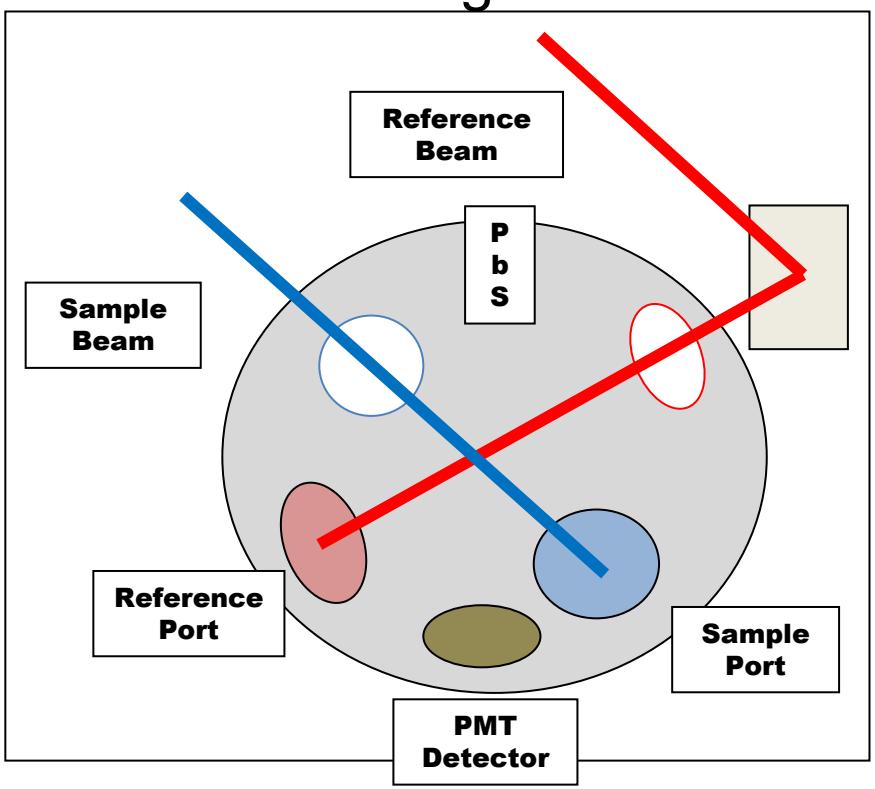


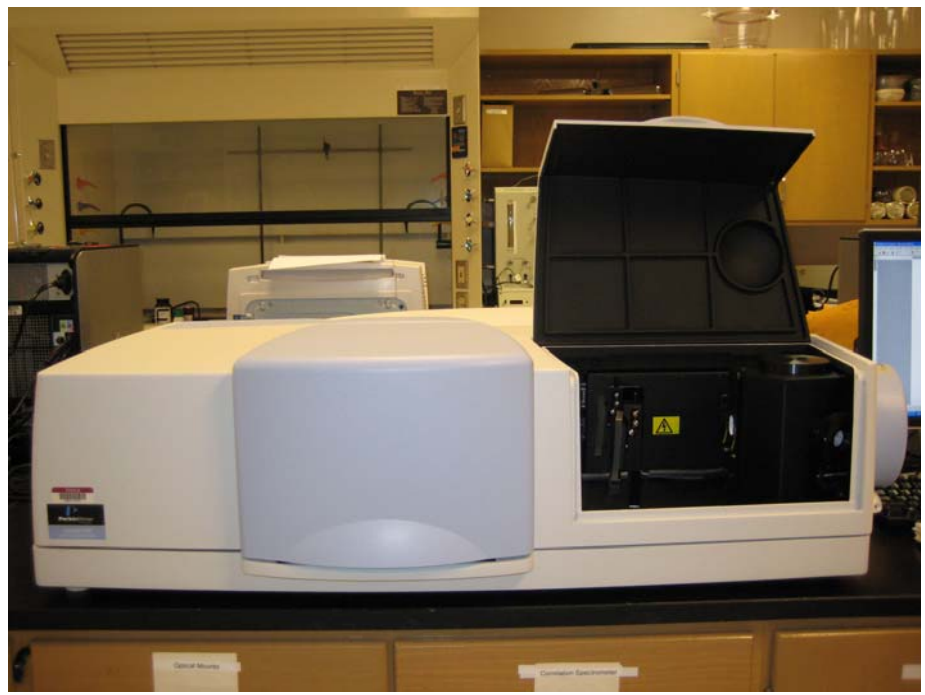
Diffuse

Instrumentation

- **Perkin-Elmer Lambda 850 UV/Vis Spectrometer with 150mm Labsphere Integrating Sphere**
  - **Integrating Sphere**-corrects for scattering off surface of sample

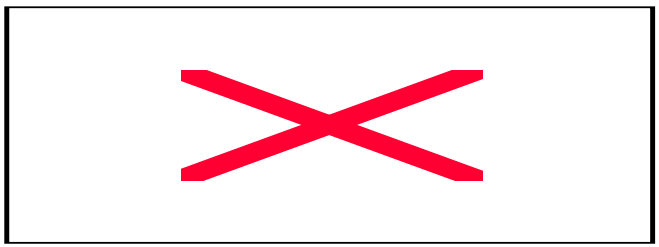
*ability to measure transmittance/reflectance at all wavelengths across the spectrum (250-850 nm)



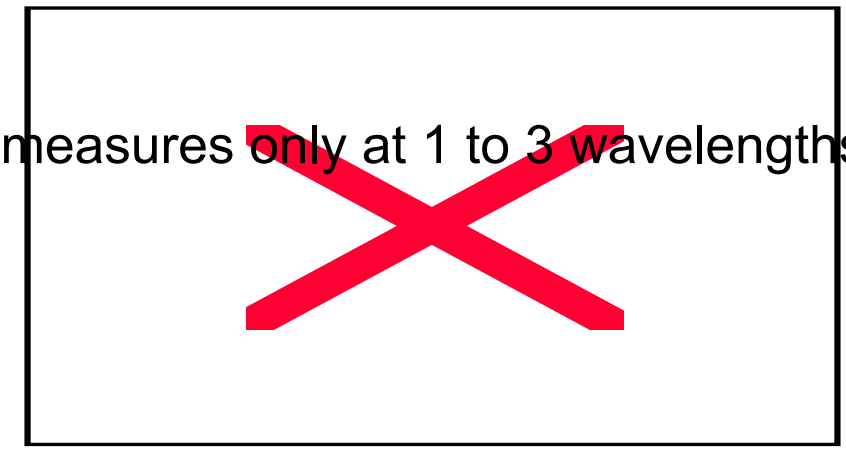


Instrumentation (cont'd)

- Particle Soot/Absorption Photometer (PSAP)

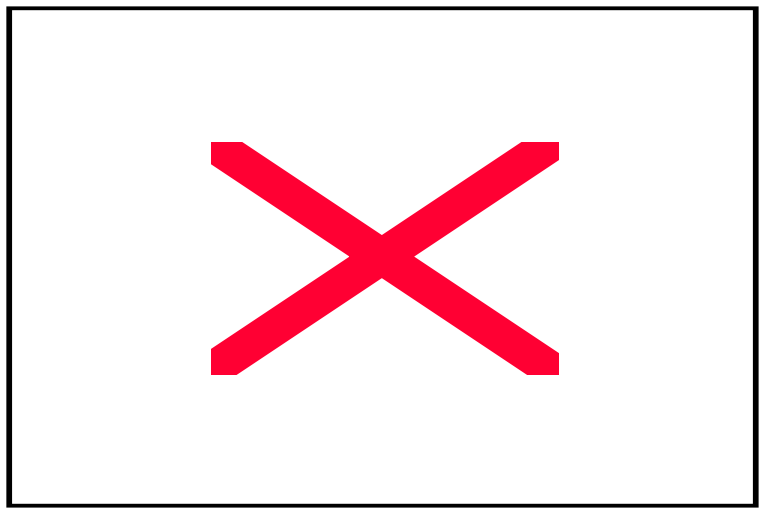


*filters then taken for spectroscopic analysis



*measures only at 1 to 3 wavelengths

- High-volume aerosol impactors



Absorption Angström Exponents (AAEs)

- **Absorption Angström Exponent (AAE; α):** describes wavelength dependence of aerosol absorbance; controlled mainly by chemical composition; results from combination of broadband (BC, HULIS) and narrowband (PAHs, N-PAH) absorption
- **$A=\beta\lambda^{-\alpha}$**

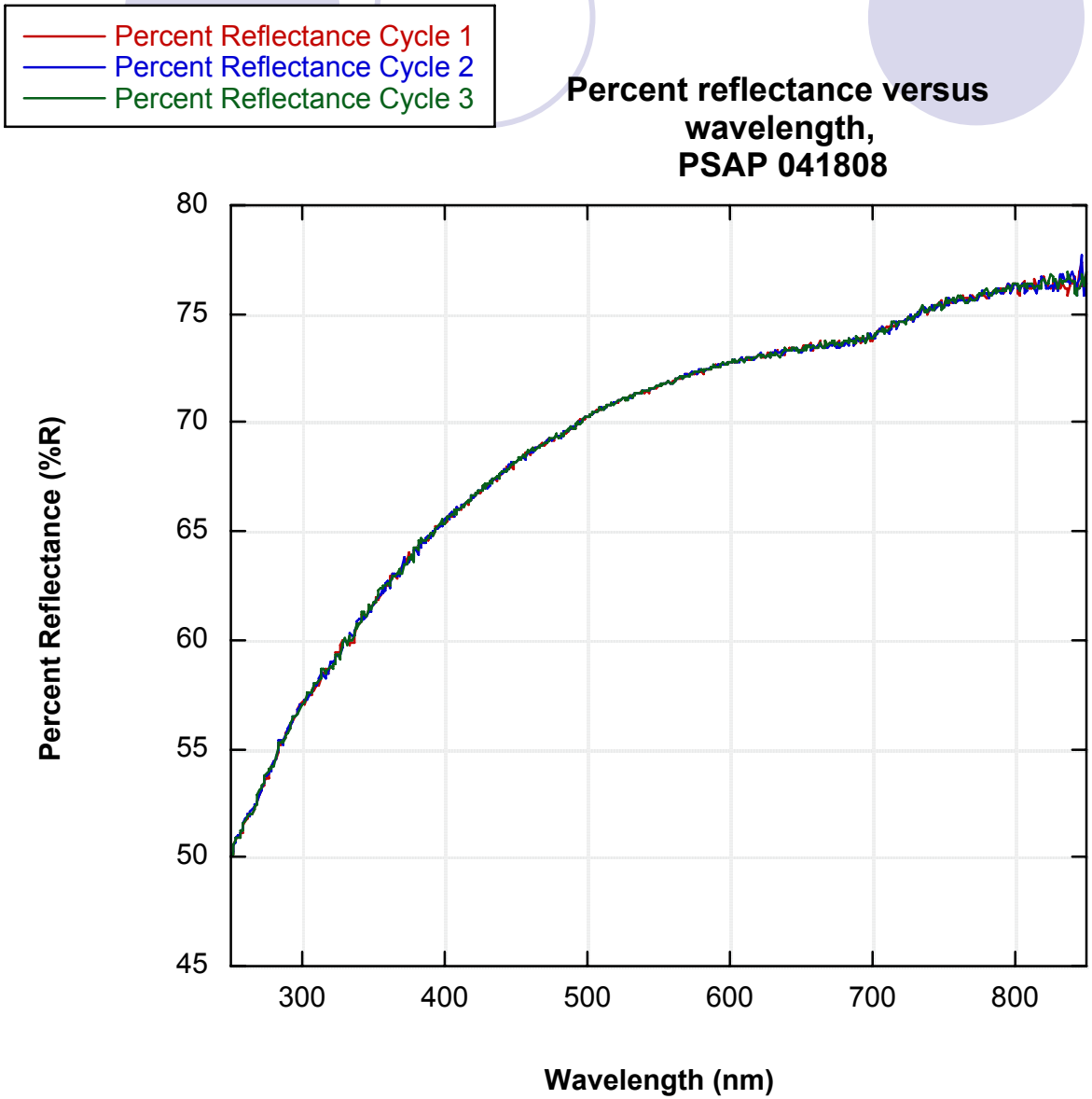
  where A=measured absorbance

  β=Absorption at 1 μm (1000 nm)

  λ=Wavelength (nm)

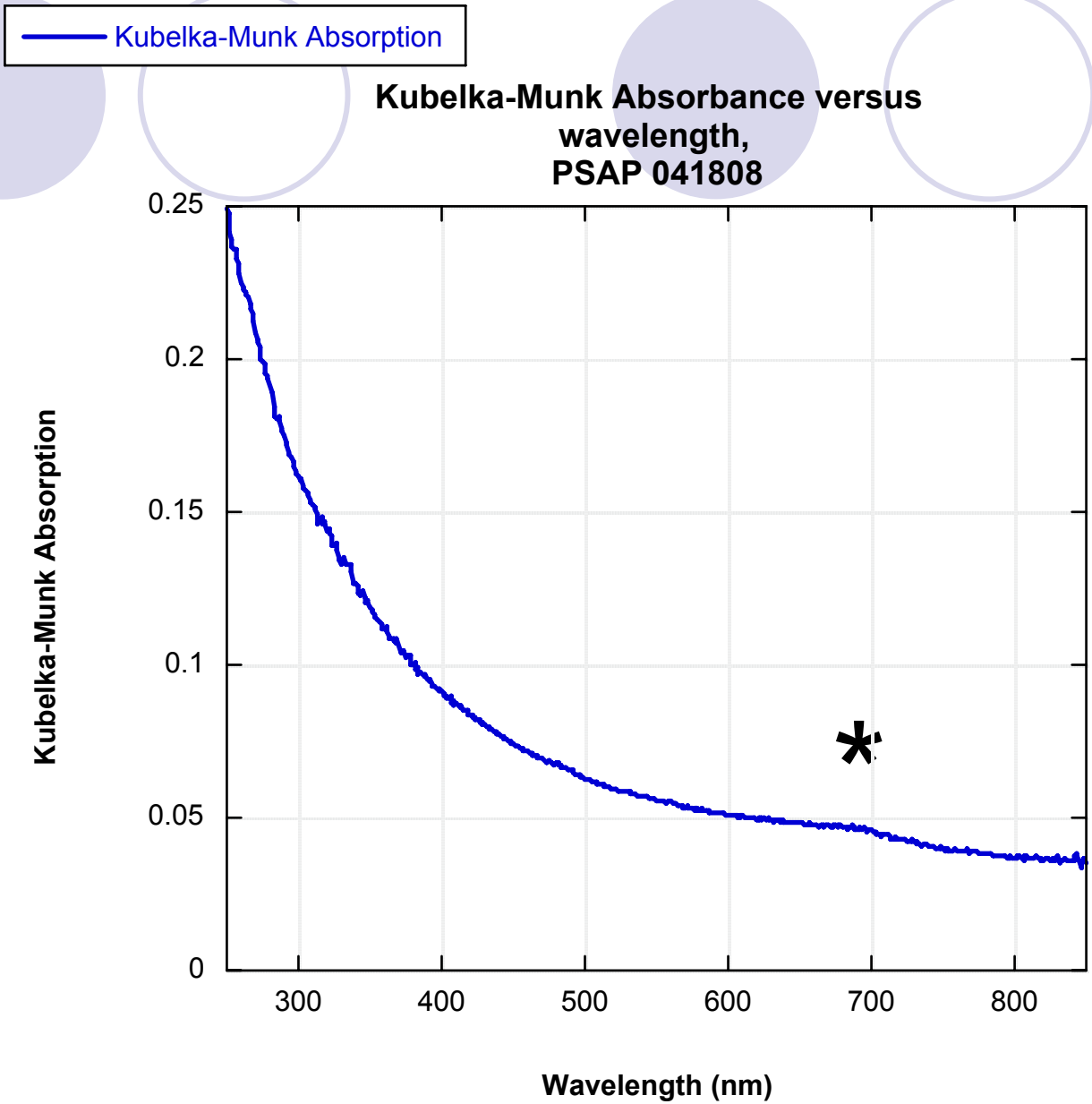
  α=Absorption Angström Exponent (AAE)
- **To solve for the AAE**, take the natural log of both wavelength and absorbance values; plot graph of Ln of absorbance as a function of Ln of wavelength; run linear regression; AAE = slope (m) of the linear equation

UV/Vis Data (Mount Bachelor)

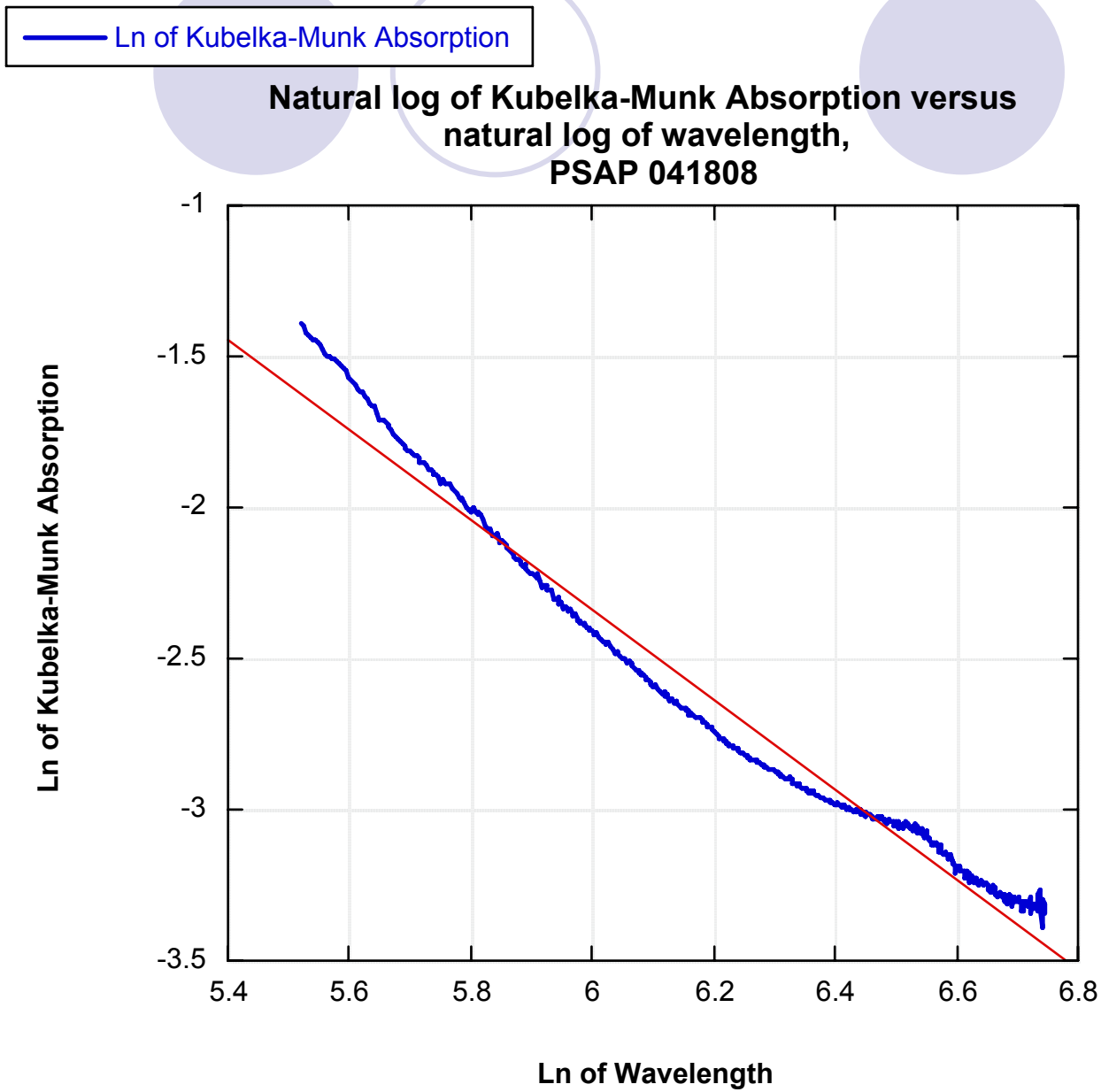


- Complete example of calculating AAE for April 18, 2008

*very small standard deviation



* Example of narrowband absorption within broadband absorption



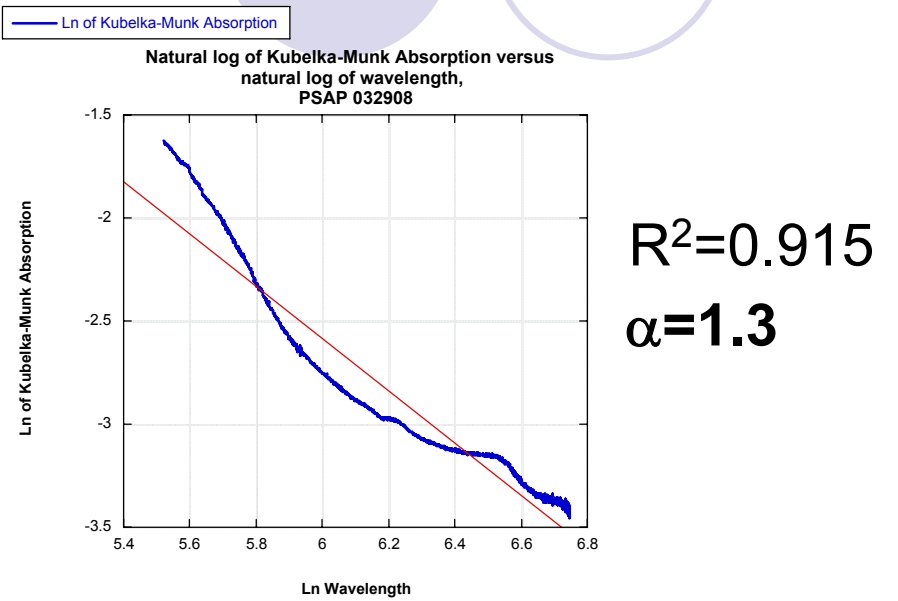
$y = 6.6 - \mathbf{1.5}x$

$R^2 = 0.974$

$\alpha = \mathbf{1.5}$

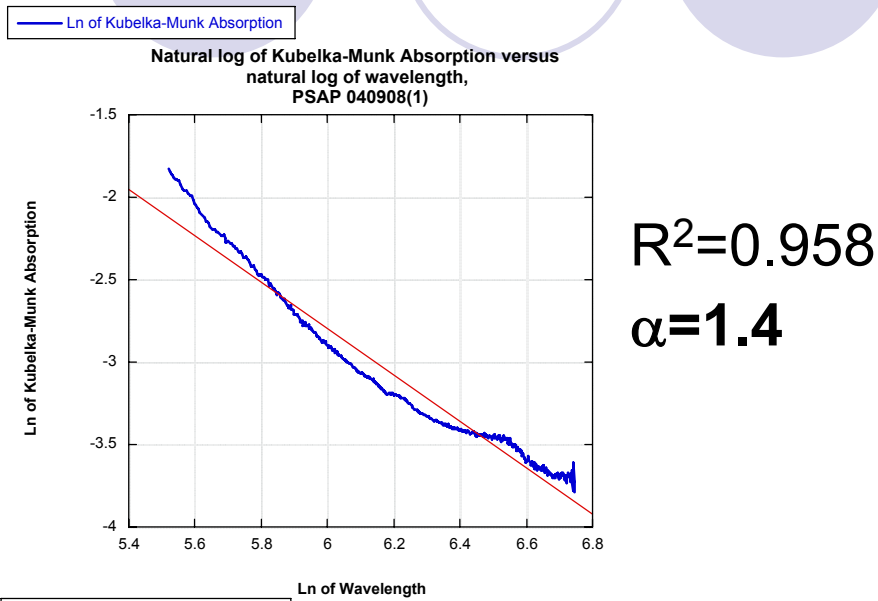
UV/Vis Data (Mount Bachelor) cont'd

- PSAP Spectra (Mt. Bachelor; March-May, 2008)



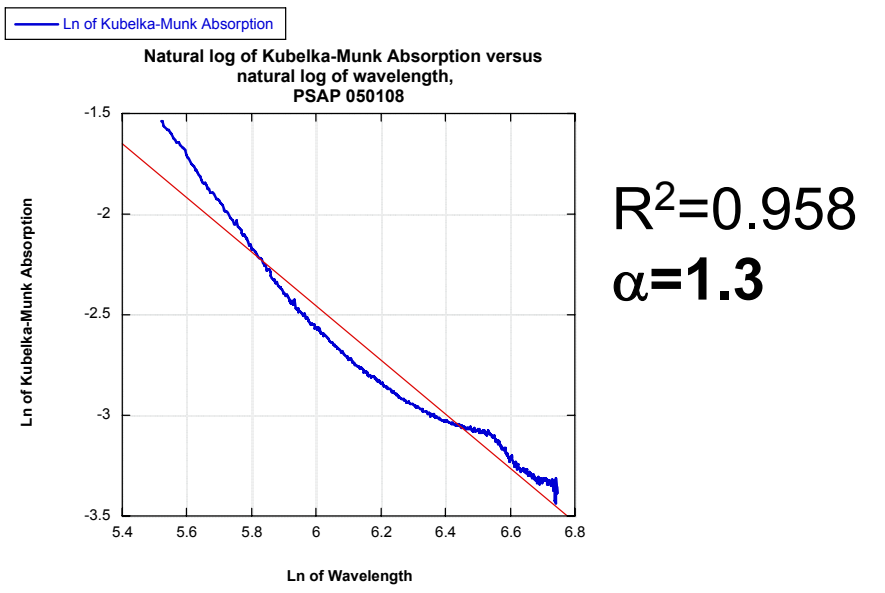
R^2=0.915

α=1.3



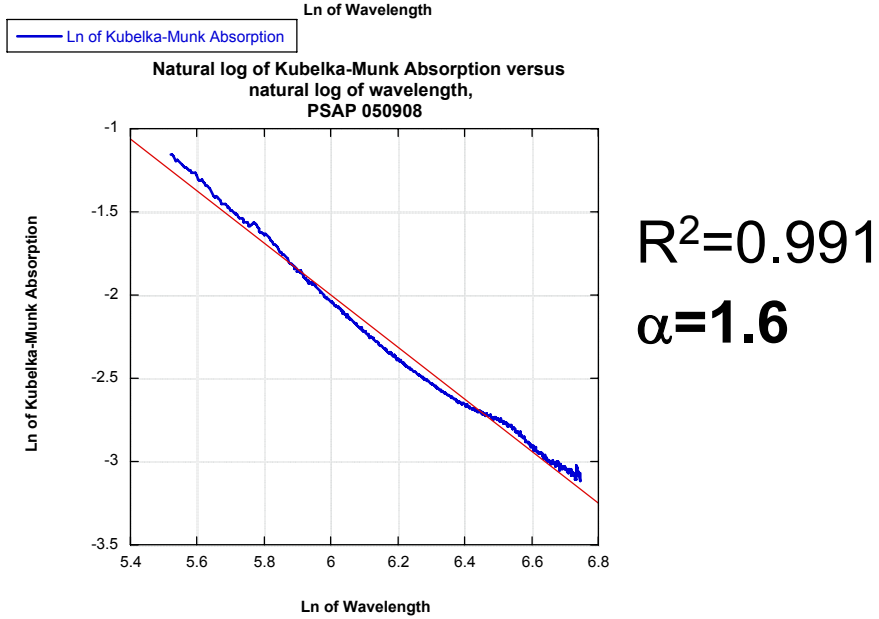
R^2=0.958

α=1.4



R^2=0.958

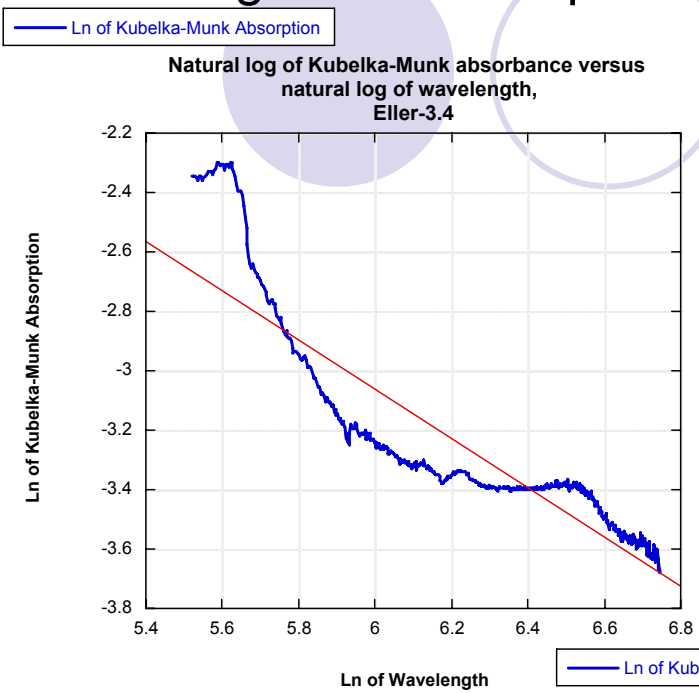
α=1.3



R^2=0.991

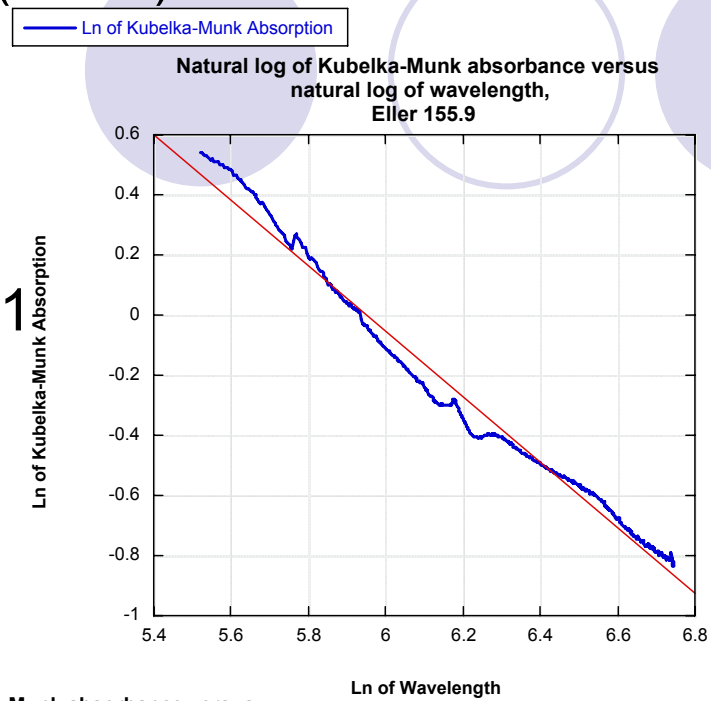
α=1.6

o High-Volume Impactor Spectra (UALR)



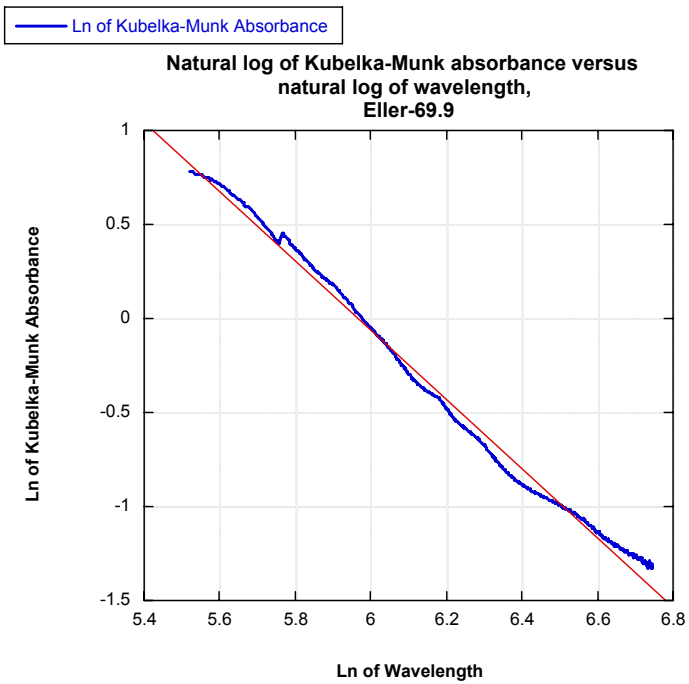
R^2=0.801

α=0.83



R^2=0.982

α=1.1

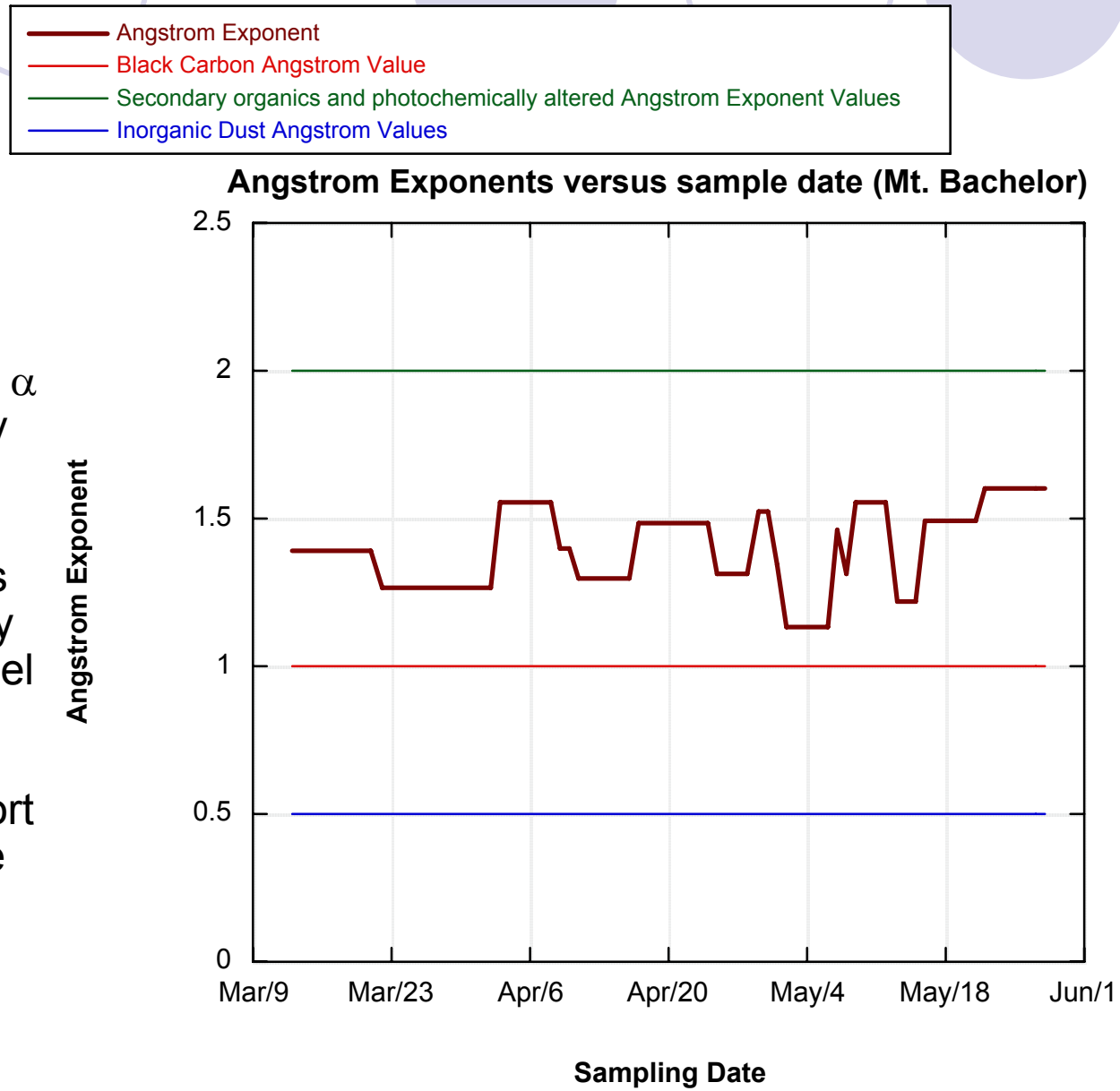


R^2=0.992

α=1.8

UV/Vis: Conclusions (Mt. Bachelor)

- Series of short influxes of maybe slightly photochemically-altered BC aerosols, causing α to become slightly larger
- Long-range transport aerosols from Asia=primary organics (i.e. diesel soots) with little photochemical alteration; transport over ocean where other organic reactants not present



Future Work

- Begin to correlate with aethalometer absorption data
- Run samples using Fourier-Transform Infrared Spectroscopy (FTIR)
- Continue to run UALR impactor samples
- Hopefully soon!: Assemble an in-line combustion-GC system for EC/OC analysis of filters post-spectroscopy

References

Skoog, West, Holler, and Crouch. *Analytical chemistry: An introduction.* 7th Ed. 2000. Brooks/Cole

Labsphere 150mm Integrating Sphere Owner's Manual

Nancy A. Marley, Jeffrey S. Gaffney, Michael Tackett, Neil C. Sturchio, Linnea Heraty, Nancy Martinez, Kavita D. Hardy, Angie Machany-Rivera, Thomas Guilderson, Amanda MacMillan, and Karen Steelman. "The Impact of Biogenic Carbon Emissions on Aerosol Absorption in Mexico City." ACP, Special MILAGRO issue. Submitted.

Acknowledgments

- Dr. Jeff Gaffney (mentor; academic/research advisor)
- Dr. Nancy Marley (mentor; research advisor)
- Emily Fischer (GREF student; PSAP samples)
- Milton Constantin & team
- GCEP/SURE
- DOE and ASP
- Dr. Amy Robinson (academic advisor)

Extras

- Angstrom Exponent as function of sampling duration