Aerosol light absorption measurements during the Reno Aerosol Optics Study: Method comparison for laboratory-generated aerosol.

By W. Patrick Arnott pat@dri.edu, Desert Research Institute, Reno NV

General Collaborators: John Walker, Hans Moosmüller, Fred Rogers, Eric Fujita, Dave Campbell, Barbara Zielinska, John Sagebiel, Rick Purcell, Dan Wermers, Rich Raspet, Willie Slaton **(Univ. Miss.),** James Mehl, Rob Abbott, Mike Ossosfsky, Khadeejeh Hamasha, Ali Rahmah, and Kristin Lewis (**Students**), Adel Sarofim, Kerry Kelly, Dave Wagner, Joanne Lighty **(Univ. Utah CFE),** Otmar Schmid, Meinrat Andreae (**Max Planck Institute for Chemistry**), John Seinfeld, Richard Flagan, and Haflidi Jonnson, **(Cal Tech and CIRPAS)**, John Ogren and Pat Sheridan (**NOAA CMDL**).

Funding over the (10) Years: EPA, NPS, ONR, NSF, DOE, DOD-SERDP, DRI

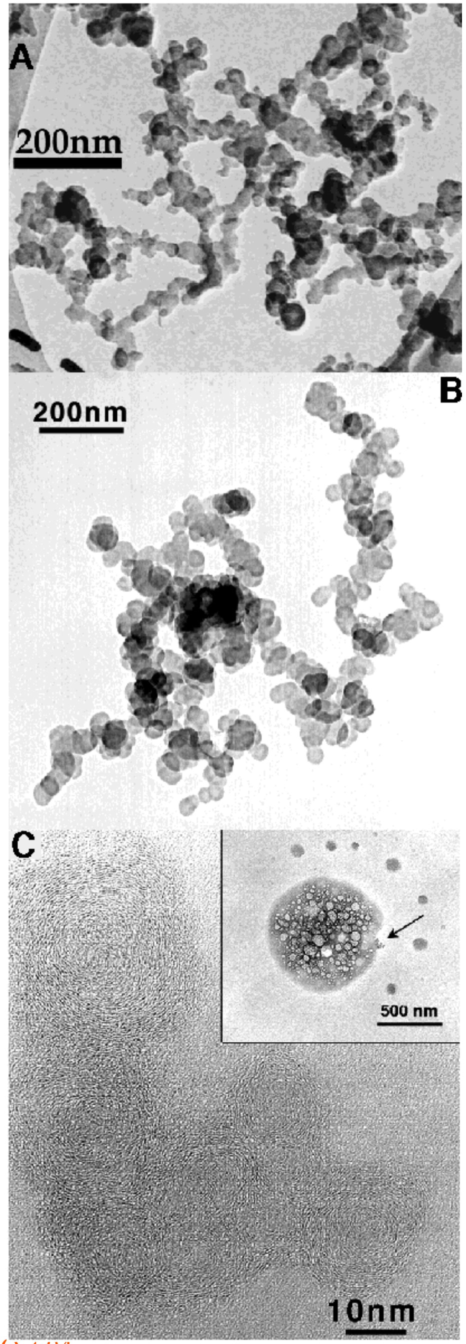
http://photoacoustic.dri.edu

OUTLINE:

1. What is black carbon?
2. The Reno Aerosol Optics Study.
3. Examples of ambient measurements of aerosol light absorption.

Many related references at http://www.dfisica.ubi.pt/~smogo/investigacao/references.html

FIRE!!



Soot: 10 - 50 nm monomers chained together to form larger aggregates. ‘Onion Shell’ structure of the monomers.

IMAGE CREDIT:
http://7starm.asu.edu/Buseck2000%20/figure_10.htm

TEM images of soot.

A, B. Chain-like soot aggregates. (A--Phoenix, after Katrinak et al., 1993; B--Sagres, Portugal, ACE-2).

C. High-resolution TEM image of the arrowed soot aggregate showing the onion-like structure of soot spheres. (Southern Ocean, ACE-1; after Pósfai et al, 1999).

What is Black Carbon (BC)?

BC is an **operationally defined quantity**, as are Elemental and Organic Carbon (**EC and OC**). EC and BC represent the mass concentration of the quasi-graphitic carbon content of a sample.

• **BC** is obtained by an aerosol light absorption measurement.

• **EC** and **OC** are obtained by counting the carbon atoms evolving during various stages of thermal analysis of samples collected on quartz filters, and by an optical measurement to deal with pyrolysis.

By Contrast: Properties with fundamental physical content:

• Light absorption coefficient, $\mathbf{B_{abs}}$, related to optical power converted to heat by particles or gases.

• Light scattering coefficient, $\mathbf{B_{sca}}$, related to optical power redirected from its original direction, by particles or gases.

• Light extinction coefficient, $\mathbf{B_{ext} = B_{abs} + B_{sca}}$.

• A few more radiative parameters are needed to fully quantify the climate impacts of gases and aerosols.

What is Black Carbon (BC)?

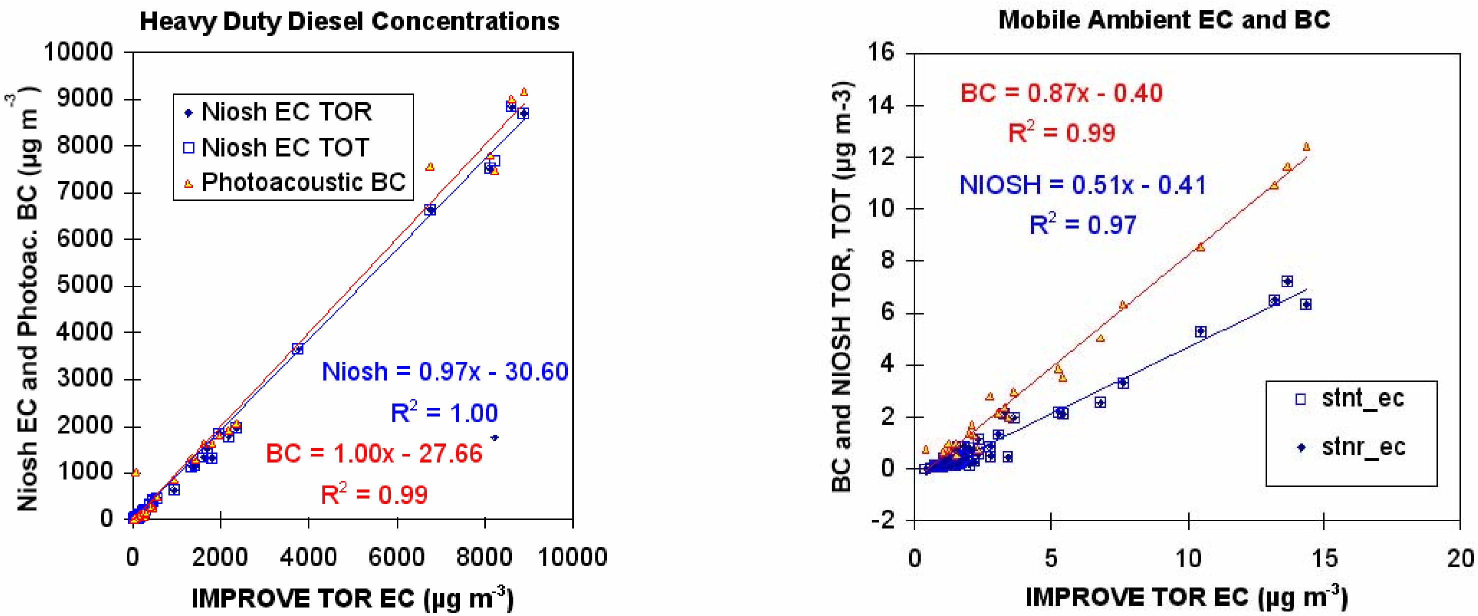
$$BC \left[\frac{\mu g}{m^3}\right] = \frac{B_{abs}\left[Mm^{-1}\right]}{Absorption\ Cross\ Section\ per\ Particle\ Mass\left[m^2/g\right]}$$

I use…

$$BC = \frac{Photoacoustic\ B_{abs}(1047nm)}{5\left[m^2/g\right]}$$

Message: Particle size, composition, mixing state, coating, and the wavelength used for the light absorption measurement can impact the definition of BC. Example: Particle bound PAH’s and dust absorb light in the UV, so the definition of BC would not be satisfactory in these cases.

What is Black Carbon (BC)? Data from the NREL gas/diesel split project.



My definition for BC works very well in source samples from diesel vehicles where most EC is 'quite graphitic' and all methods agree well.

but…

The various methods disagree in amount of EC and BC for ambient samples. Ambient EC has a different thermal profile than source-sampled EC. Pyrolysis correction for EC and OC determination is complex.

Perhaps best to use properties with fundamental physical and chemical content such as light absorption.

The Reno Aerosol Optics Study (June 2002) – Overview and Preliminary Results

P.J. Sheridan[1], J.A. Ogren[1], W.P. Arnott[2], H. Moosmüller[2], D. Covert[3], N. Ahlquist[3], A. Virkkula[4], A.W. Strawa[5], B. Schmid[5], D.B. Atkinson[6], A. Petzold[7]

[1]NOAA Climate Monitoring and Diagnostics Laboratory, Boulder, CO
[2]Desert Research Institute, Reno, NV
[3]University of Washington, Seattle, WA
[4]NOAA Pacific Marine Environmental Laboratory, Seattle, WA
[5]NASA/Ames Research Center, Moffett Field, CA
[6]Portland State University, Portland, OR
[7]Deutsches Zentrum fuer Luft- und Raumfahrt, Oberpfaffenhofen, Wessling, Germany

Objectives

- Characterize new and existing instruments for measuring aerosol light absorption and extinction
- Quantify the uncertainty in the measurements of aerosol light absorption coefficient used by NOAA CMDL for the Department of Energy Atmopsheric Radiation Measurement Program
- Derive methods for determining spectral aerosol absorption from multi-wavelength measurements of absorption and (extinction - scattering)
- Note: **All experiments done at low RH**

Absorption Coefficient Measurements

- **Photoacoustic [dates to Alexander Graham Bell, Motor Vehicle companies made strong contributions. Bill Pierson was our guiding light in pursuing development of these instruments at DRI.]**
    - #1 532 nm
    - #2 1047 nm
- **Filter-based [dates to British Smoke method, Coefficient of Haze.]**
  - Particle/soot absorption photometer (**PSAP**) **[calibrated for B_{abs}]**
    - #1: 565 nm
    - #2 460, 540, 660 nm
  - **Aethalometer [calibrated for BC]**
    - #1 370, 470, 521, 590, 660, 880, 950 nm
    - #2 370, 430, 470, 521, 565, 700, 950 nm
  - **Multiple Angle Absorption Photometer (MAAP)** #1: 670 nm [new method that measures both filter transmission and reflection and uses a multiple scattering model to obtain BC and B_{abs}.]

Extinction Coefficient Measurements

- UW Folded path extinction cell (6.6 m path) [classic method]
    - #1 460, 540, 660 nm
- Cavity-ring down (CRD) [new method, much more sensitive]
    - #1: 532 nm
    - #2: 690, 1550 nm
    - #3: 532, 1064 nm

Scattering Coefficient Measurements

- TSI 3563 integrating nephelometer
  - #1 450, 550, 700 nm
- Radiance M903 integrating nephelometer
  - #1: 530 nm
- DRI integrating sphere nephelometer
  - #1: 532 nm
- NASA/Ames CRD nephelometer
  - #1: 690 nm

The basic ideas for each method are discussed in…
Beutell, R. G. and A. W. Brewer (1949). "Instruments for the measurement of the visual range." Journal of Scientific Instruments **26**: 357-359.

Aerosol characterization

- Size distribution
    - scanning mobility particle spectrometer
- Number concentration
    - TSI condensation particle counters
- Mass concentration
    - TEOM
- Chemical composition
    - elemental carbon
    - organic carbon
- Morphology
    - electron microscopy

Experimental Target Matrix

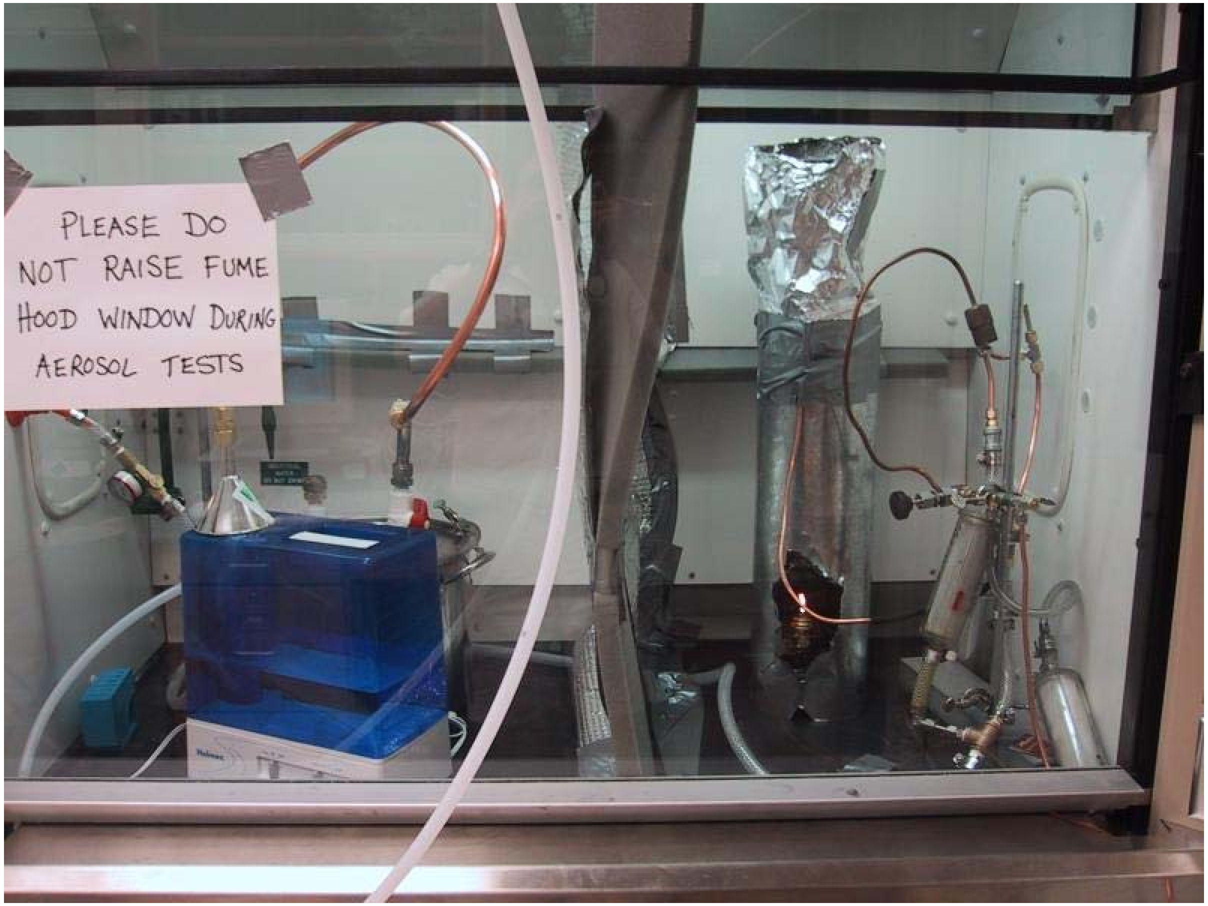
ω_0	Low (5-100)	Med (100-300)	Hi (300-600)
	σ_e (Mm^{-1})		
1.00	AS	AS	AS
0.98	AS+K	AS+K,G	AS+K
0.95	AS+K	AS+K,G	AS+K
0.90	AS+K	AS+K,G	AS+K
0.80	AS+K	AS+K,G	AS+K
0.70	AS+K	AS+K	AS+K
all black	K,D,G	K	K
Other	A,F,PSL		PSL

White aerosols: **ammonium sulfate (AS)**

Black aerosols: **kerosene soot (K), diesel soot (D), graphite (G)**

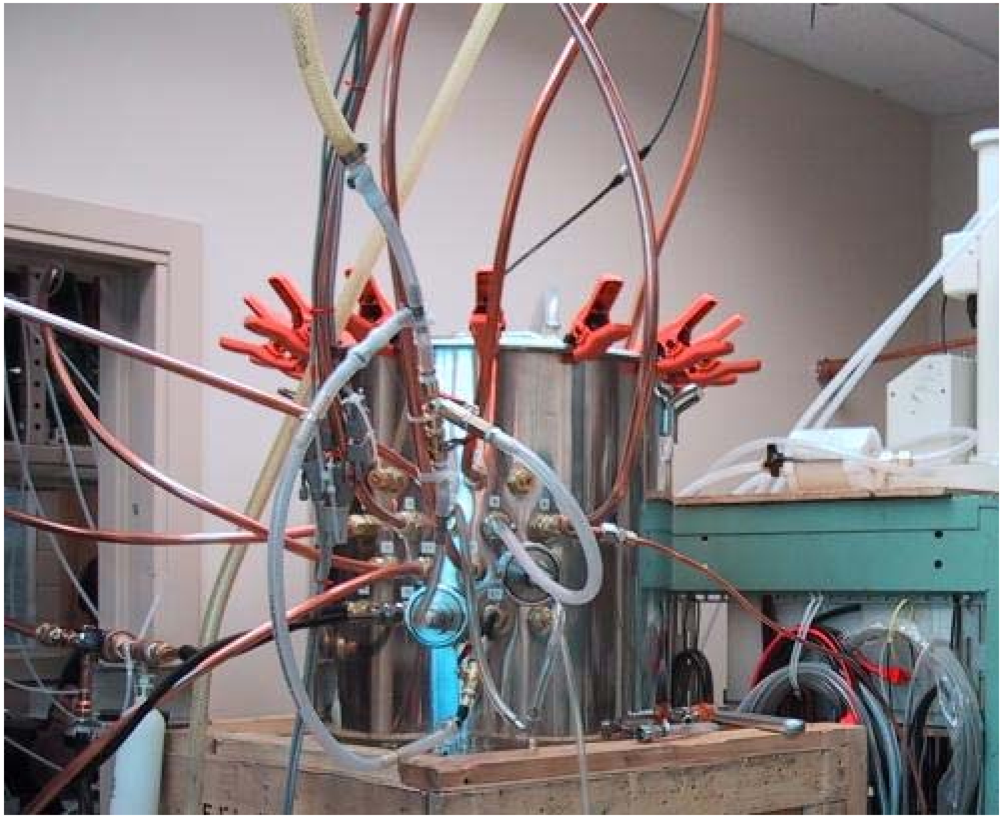
Other: ambient air (A), filtered air (F), polystyrene latex 0.5 μm dia. (PSL)

Aerosol Generation System



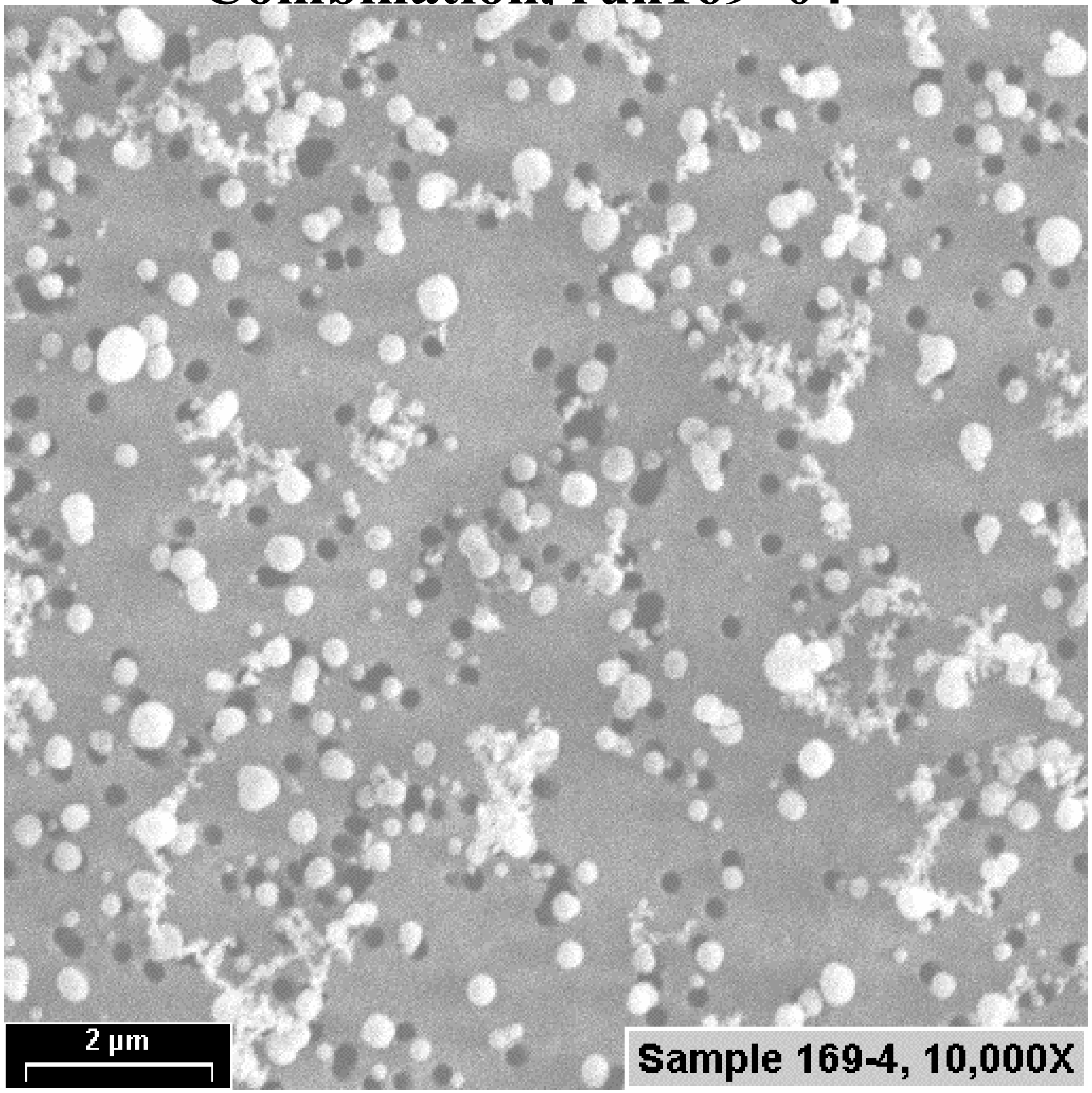
White aerosols produced from ammonium sulfate in ultrasonic humidifier (left)
Black aerosols produced by kerosene lamp (right)

Aerosol Mixing and Distribution



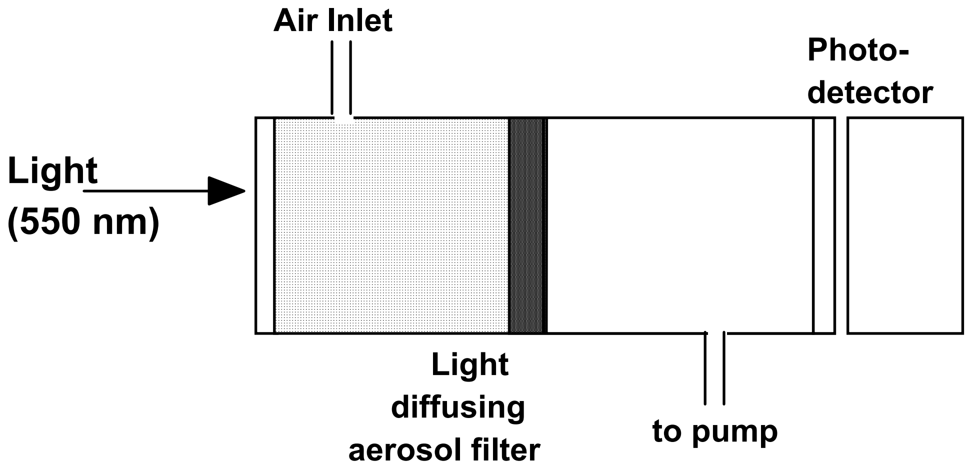
Stirred mixing chamber (76 liters) provides a uniform aerosol to all instruments. Variable mixtures of white particles, black particles, and filtered air can be provided. All kerosene soot and ammonium sulfate measurements were performed with the sampling plenum at positive pressure (above ambient) to reduce issues associated with instrument leaks.

Typical Kerosene Soot and Ammonium Sulfate Aerosol Combination, run169_04



(Ammonium Sulfate 'snowballs' and fractal kerosene soot particles).

Simplified description of filter methods for light absorption. PSAP and AETHALOMETER



- Aerosol are deposited on the light-diffusing filter, multiple scattering substrate.
- Light absorbing aerosol reduce the light power at the photodetector. This is the signal we are after, and want to relate it to *in-situ* aerosol light absorption.
- Light scattering aerosol produce a small, but significant attenuation that must be accounted for, especially at high single scattering albedo,
- As the filter becomes loaded with light absorbing material, the multiple scattering enhancement of attenuation diminishes. This must be accounted for.
- We have noted RH induced artifacts (PSAP) when the RH changes from 40% to 90% in an hour (though likely in other conditions as well.) It is best to dry the aerosol before measurement.

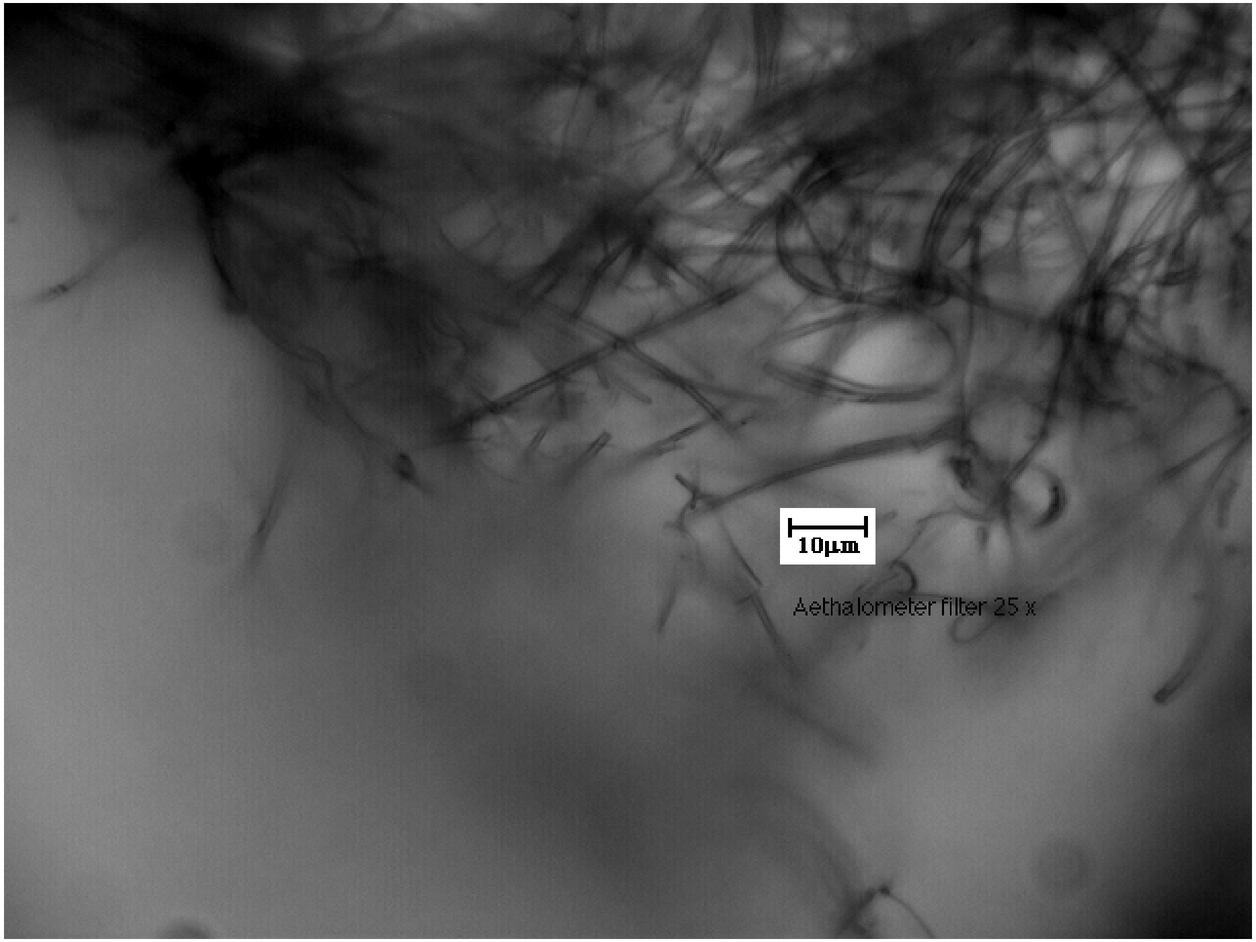
PSAP: Particle Soot Absorption Photometer
A filter-based measure of light absorption.

•Reference filter on the right. Aerosol-loaded filter on the left. Compare light transmission through these filters as a measure of light absorption.

Aethalometer Filter-Based Method for Light Attenuation Measurement

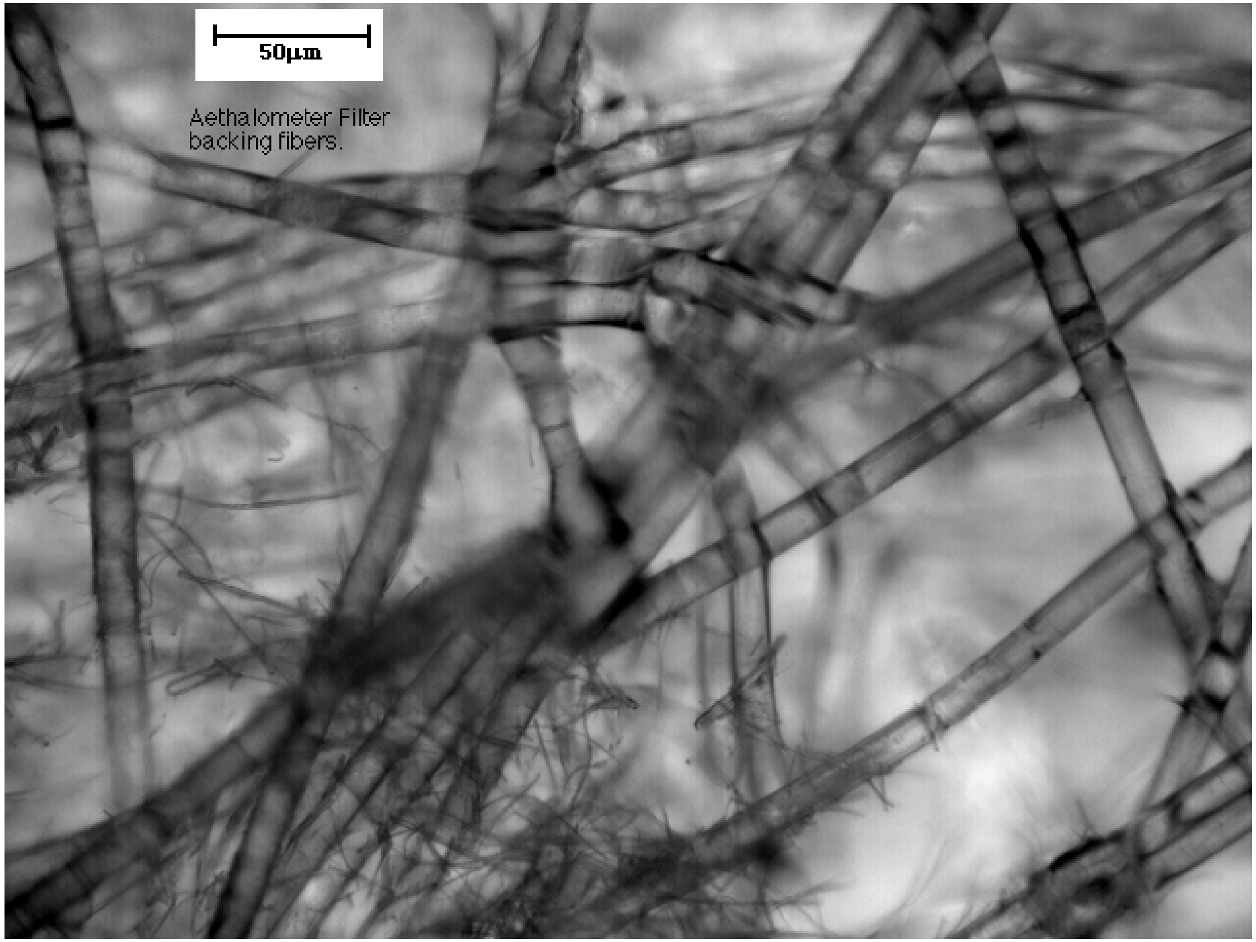
The filter is changed automatically when attenuation=0.75. Be sure the filter does actually change, and that the flow rate is correct.

Quartz fibers on the filter front.



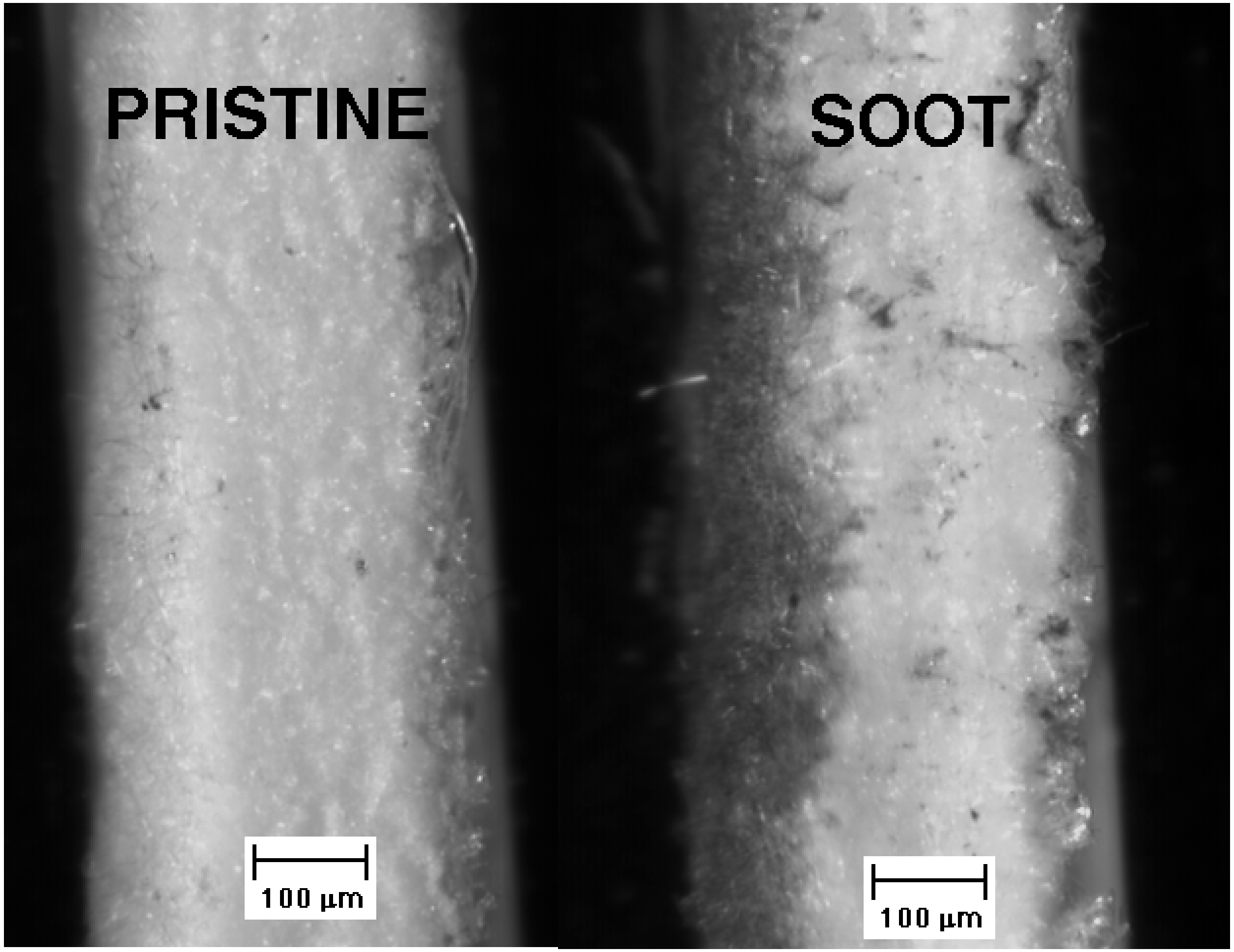
The milky appearance is from multiple scattering of light from fibers out of the field of view of the microscope.

Fiber Filters: Backing fibers.



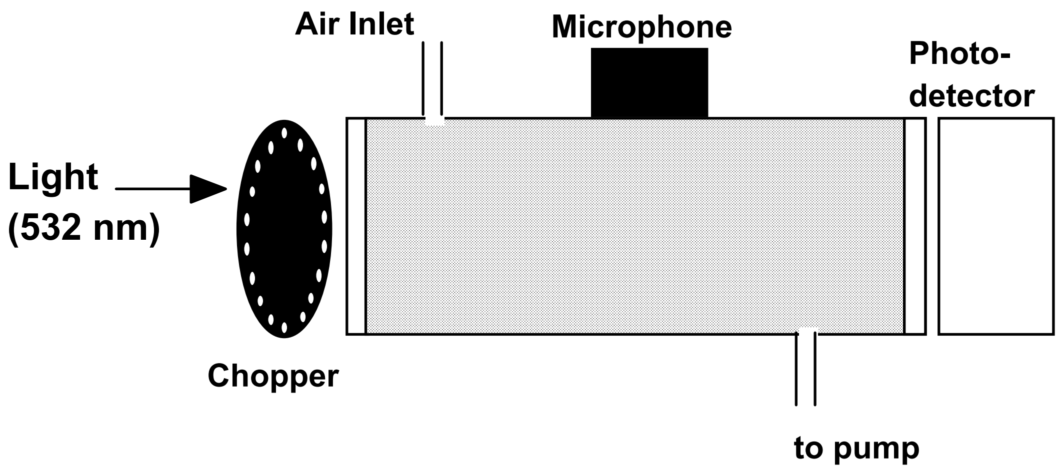
Backing fibers provide support. They are make of cellulose, and are likely hygroscopic, perhaps contributing to the RH artifacts.

Aethalometer Filter Details: Side view.



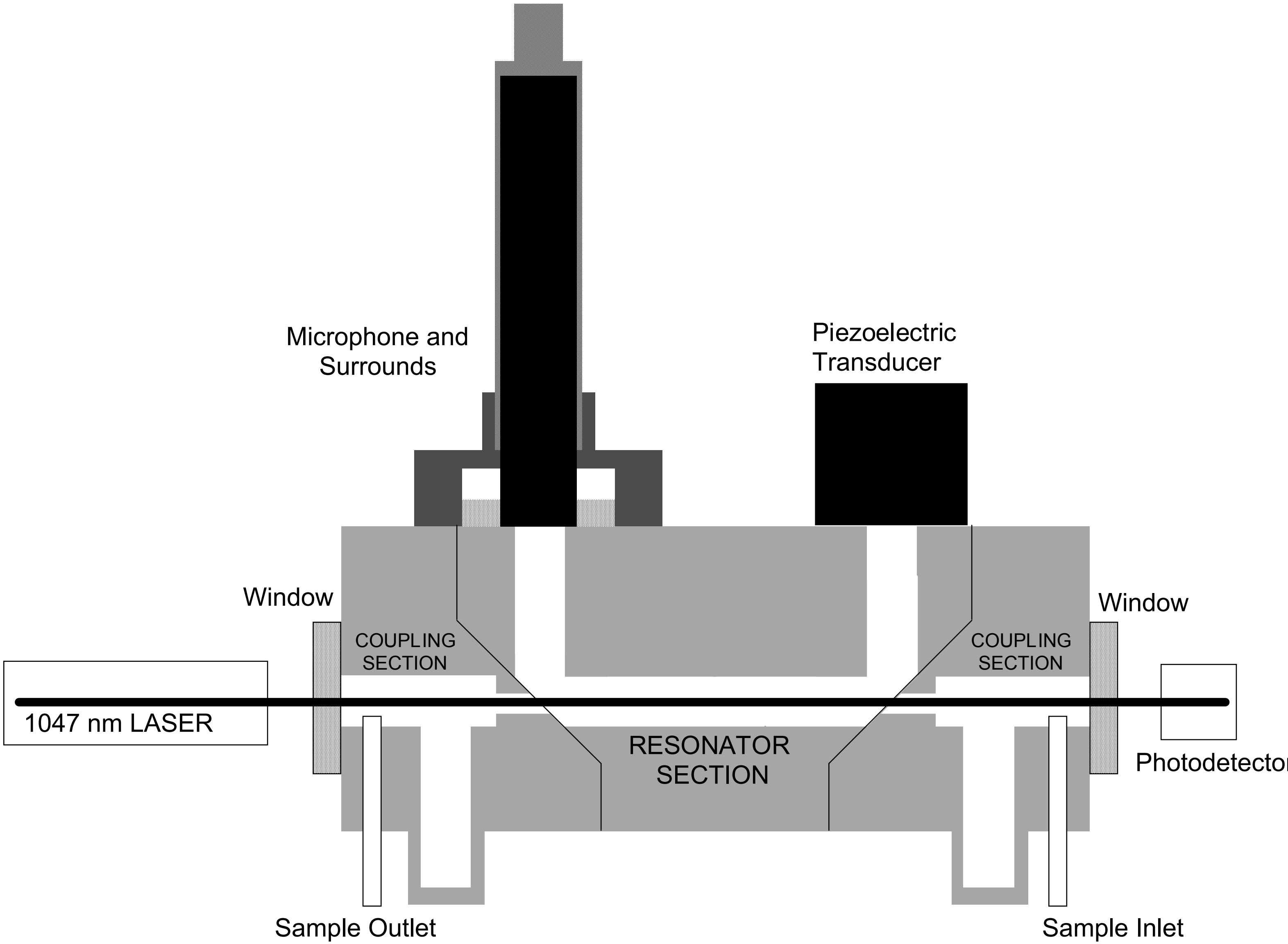
The pristine filter is like a snow bank. The exposed filter has aerosol throughout the first 1/3 of the filter. Model results show that multiple scattering enhancement depends on how deep particles are embedded into the filter. Experimental confirmation has not yet been accomplished.

Photoacoustic Instruments For Light Absorption Measurements

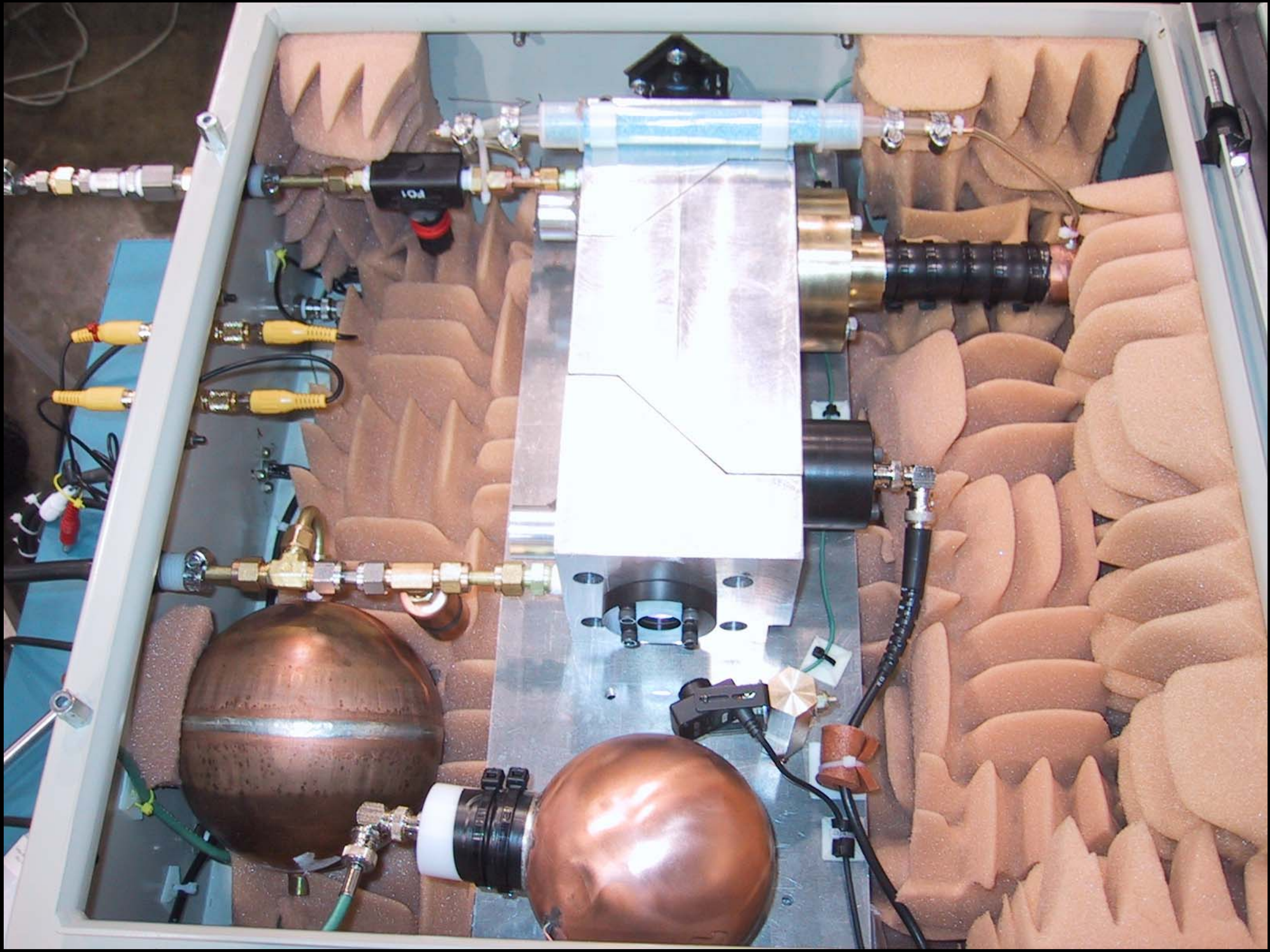


- Basic principles:
- Laser light is power modulated by the chopper.
- Light absorbing aerosols convert light to heat - a sound wave is produced.
- Microphone signal is a measure of the light absorption.
- Light scattering aerosols don't generate heat.

Sketch of the Photoacoustic Instrument



Latest PA, internal workings...



Photoacoustic Instrument Details: Equation to Obtain Light Absorption Coefficient.

Light Absorption in Dimensions of Inverse Distance = B_{abs}

$$B_{abs} = \frac{P_m}{P_L} \frac{A_{res}}{\gamma - 1} \frac{\pi^2 f_0}{Q} ,$$

f_0 = Resonance Frequency.

Q = Resonator Quality Factor.

P_m = Peak Acoustic Pressure at f_0.

γ = Ratio of Isobaric and Isochoric Specific Heats For Air.

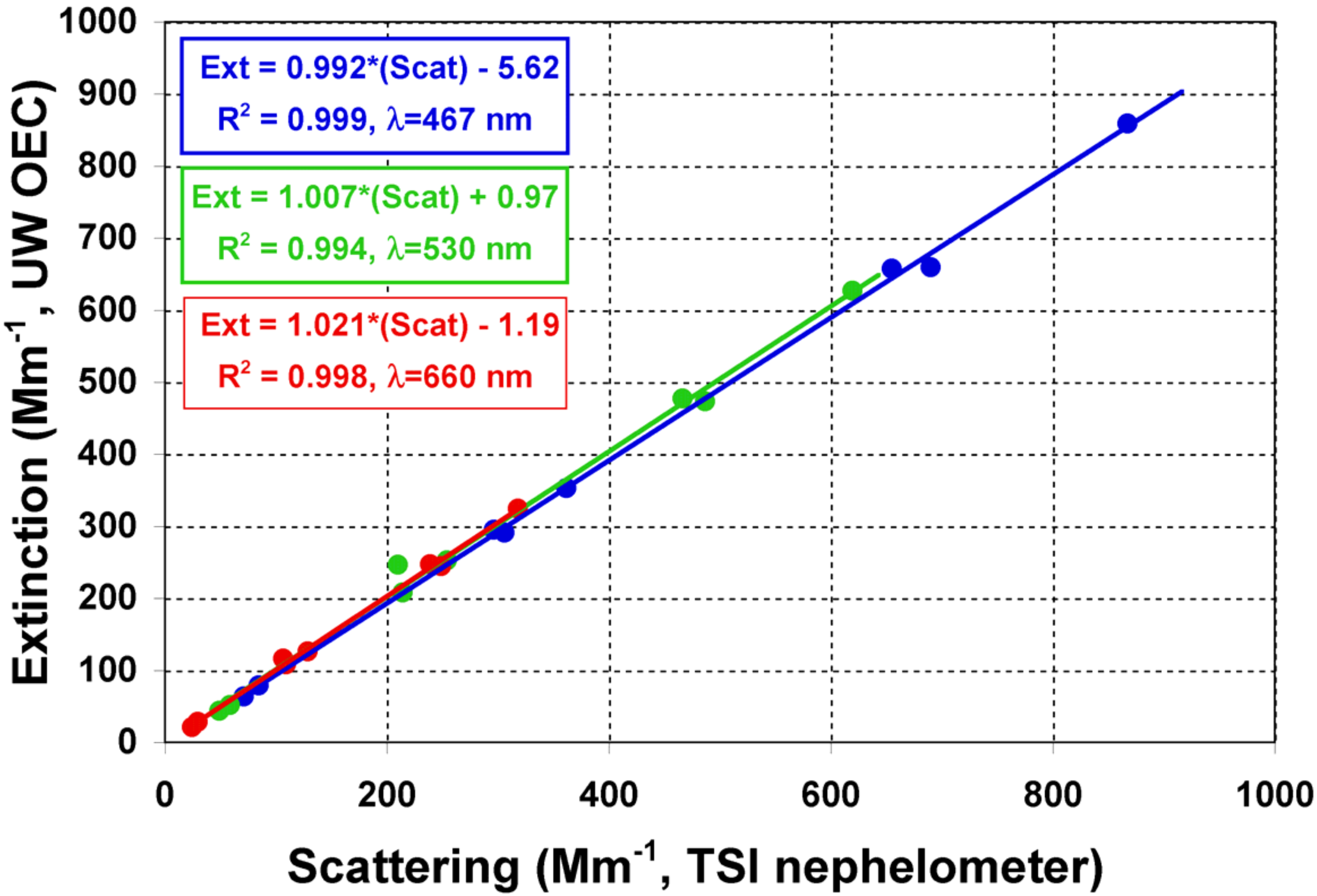
P_L = Peak Laser Beam Power at f_0.

Q = resonator quality factor.

A_{res} = Resonator Cross Sectional Area.

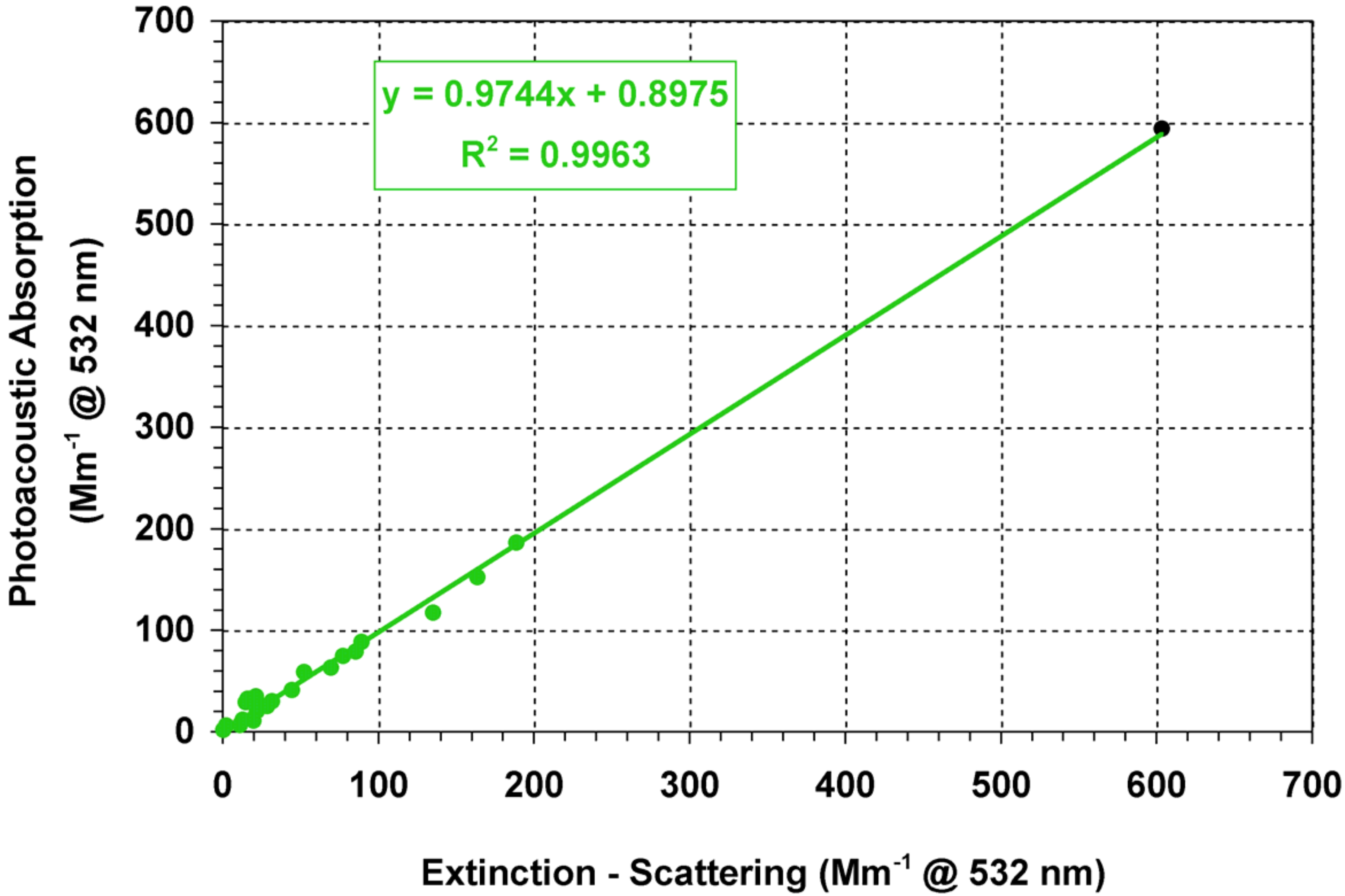
f_0 = 1500 Hz. Acoustic filters are used on the inlet to mitigate ambient noise. A critical orifice is used to mitigate pump noise.

Extinction = Scattering for ‘White’ Aerosols



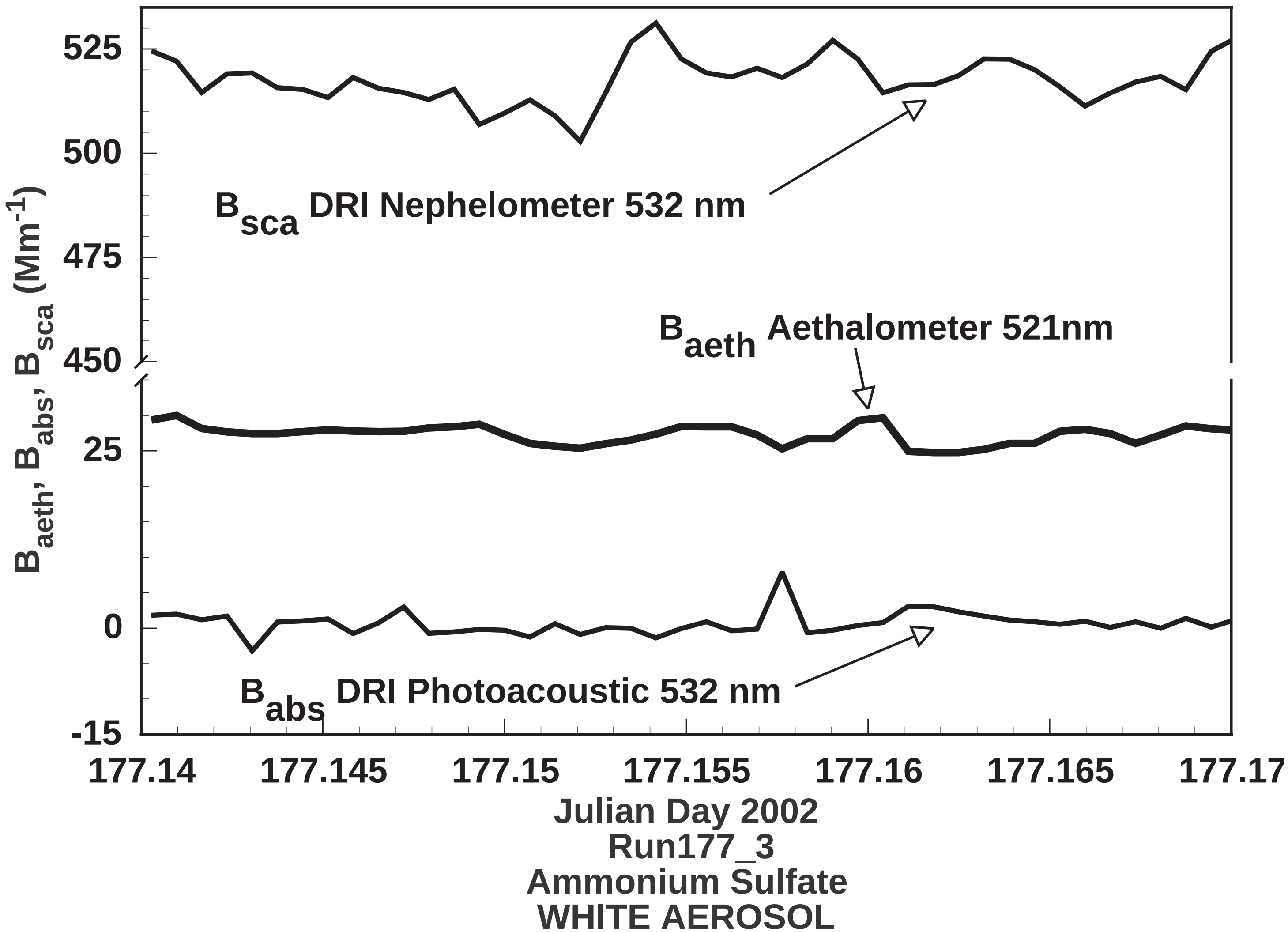
TSI neph scattering was corrected for angular nonidealities using method of Anderson and Ogren (1998).

Agreement of Absorption Standards



Notes: Data points represent kerosene soot runs with varying amounts of ammonium sulfate.

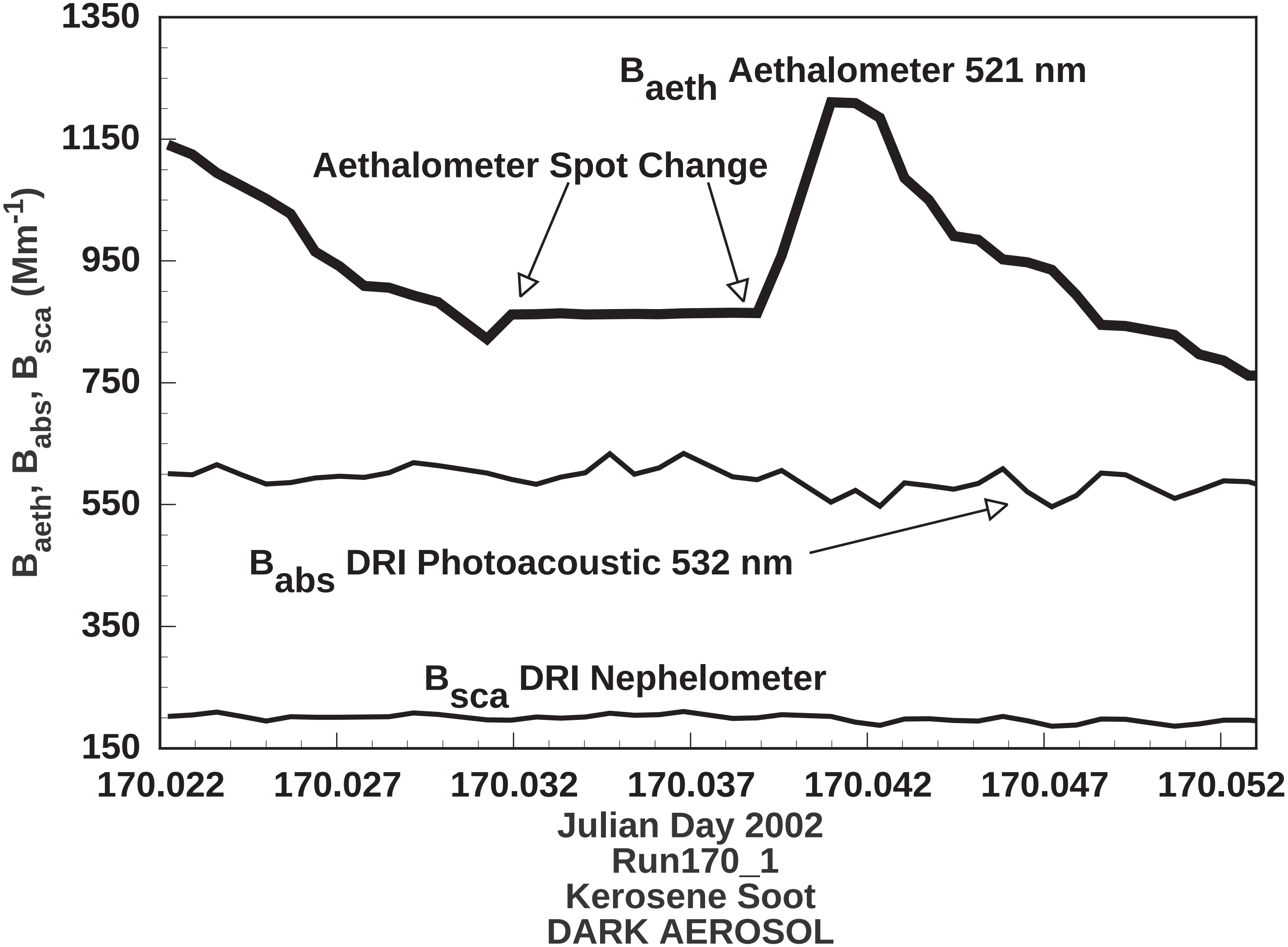
Aethalometer Response to Aerosol with negligible Light Absorption



Message: The Aethalometer (and other filter methods) have a non-negligible response from non-absorbing aerosol that must be accounted for.

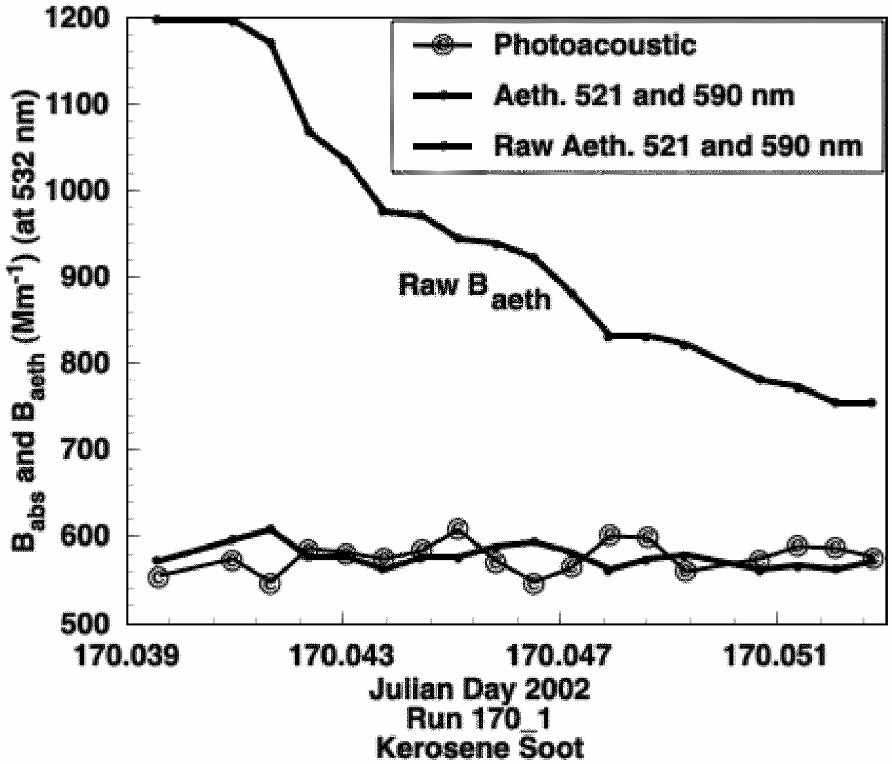
Pat Arnott, DRI, Oct 04

Aethalometer Response to Strongly Absorbing Aerosol



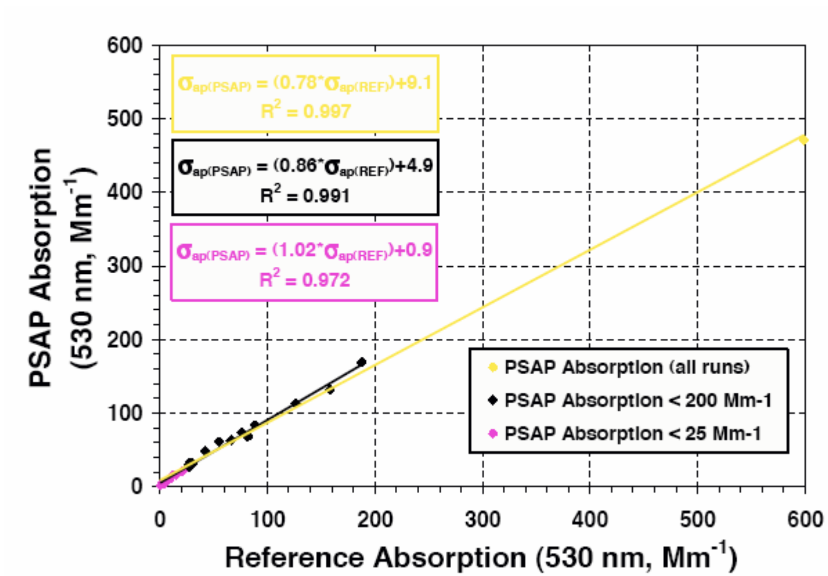
Message: Filter-based methods have a calibration that depends on how much light absorbing aerosol has been loaded on the filter, and this must be accounted for to obtain accurate real-time measurements of aerosol light absorption.

Aethalometer Response to Strongly Absorbing Aerosol



Message: We have developed theory to account for the filter loading on the Aethalometer, see Arnott, W. P., K. Hamasha, H. Moosmueller, P. J. Sheridan and J. A. Ogren (2004). "Towards aerosol light absorption measurements with a 7-wavelength Aethalometer: Evaluation with a photoacoustic instrument and a 3 wavelength nephelometer." Aerosol Science & Technology In Press.

Particle Soot Absorption Photometer Results: Filter loading and Scattering offset accounted for using Bond et.al. 1999 algorithm.



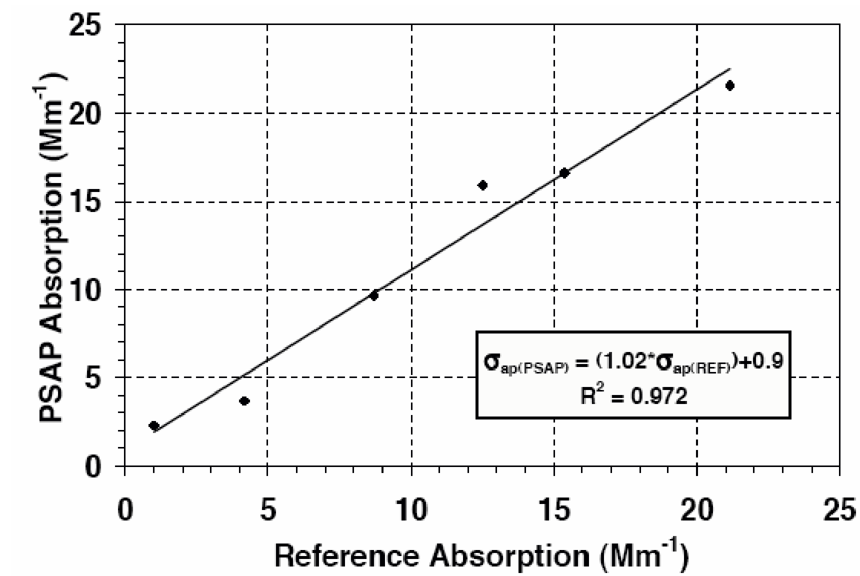


Figure 9. (a) Linear regression fits of the mixed kerosene soot/ammonium sulfate aerosol absorption data (530 nm) over several ranges. (b) Linear fit of the absorption data in the atmospherically-relevant (sap < 25 Mm-1) range.

from

Sheridan, P. J., W. P. Arnott, J. A. Ogren, B. E. Anderson, D. B. Atkinson, D. S. Covert, H. Moosmuller, A. Petzold, B. Schmid, A. W. Strawa, R. Varma and A. Virkkula (2004). "The Reno aerosol optics study: Overview and summary of results." Aerosol Science & Technology **In Press**.

Reference Absorption=Average(Photoacoustic Absorption and (Ext-Sca))

More Particle Soot Absorption Photometer Results from the Overview Paper

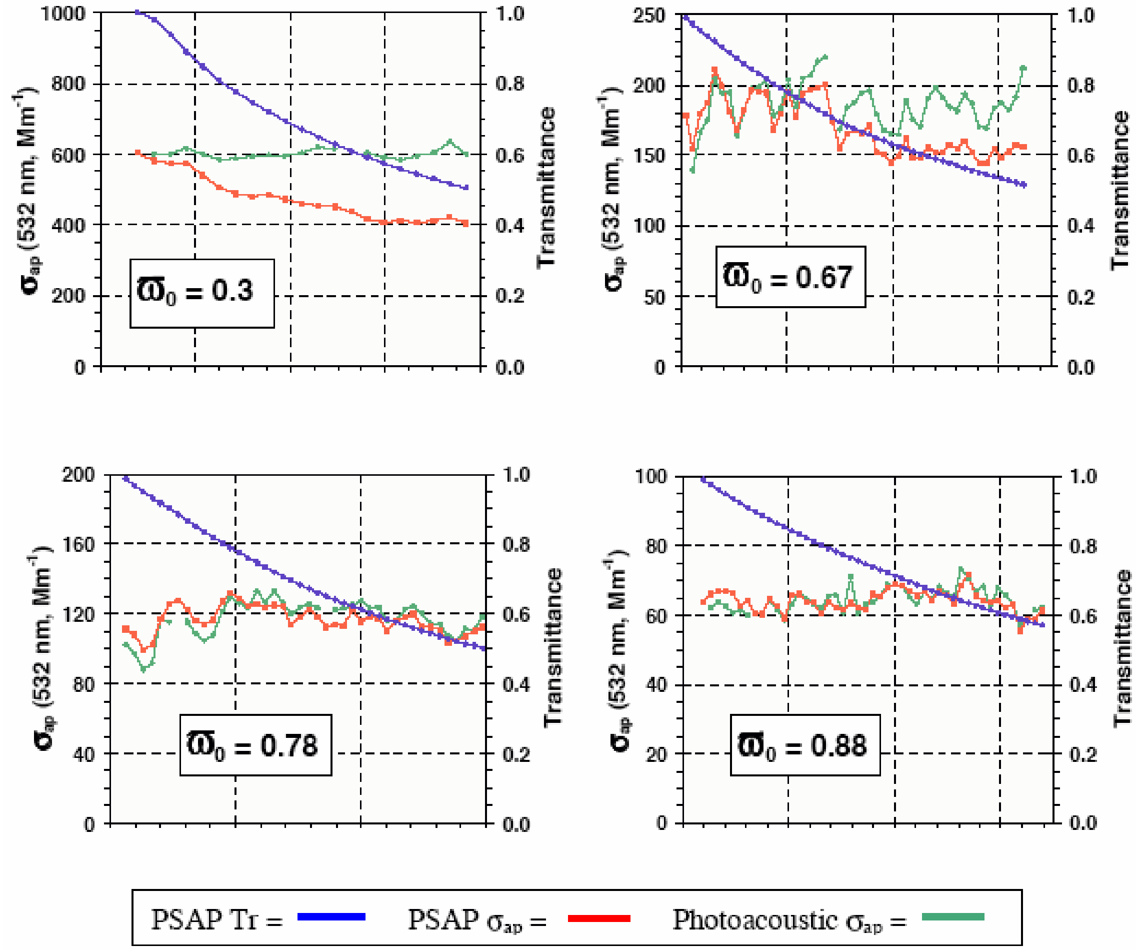
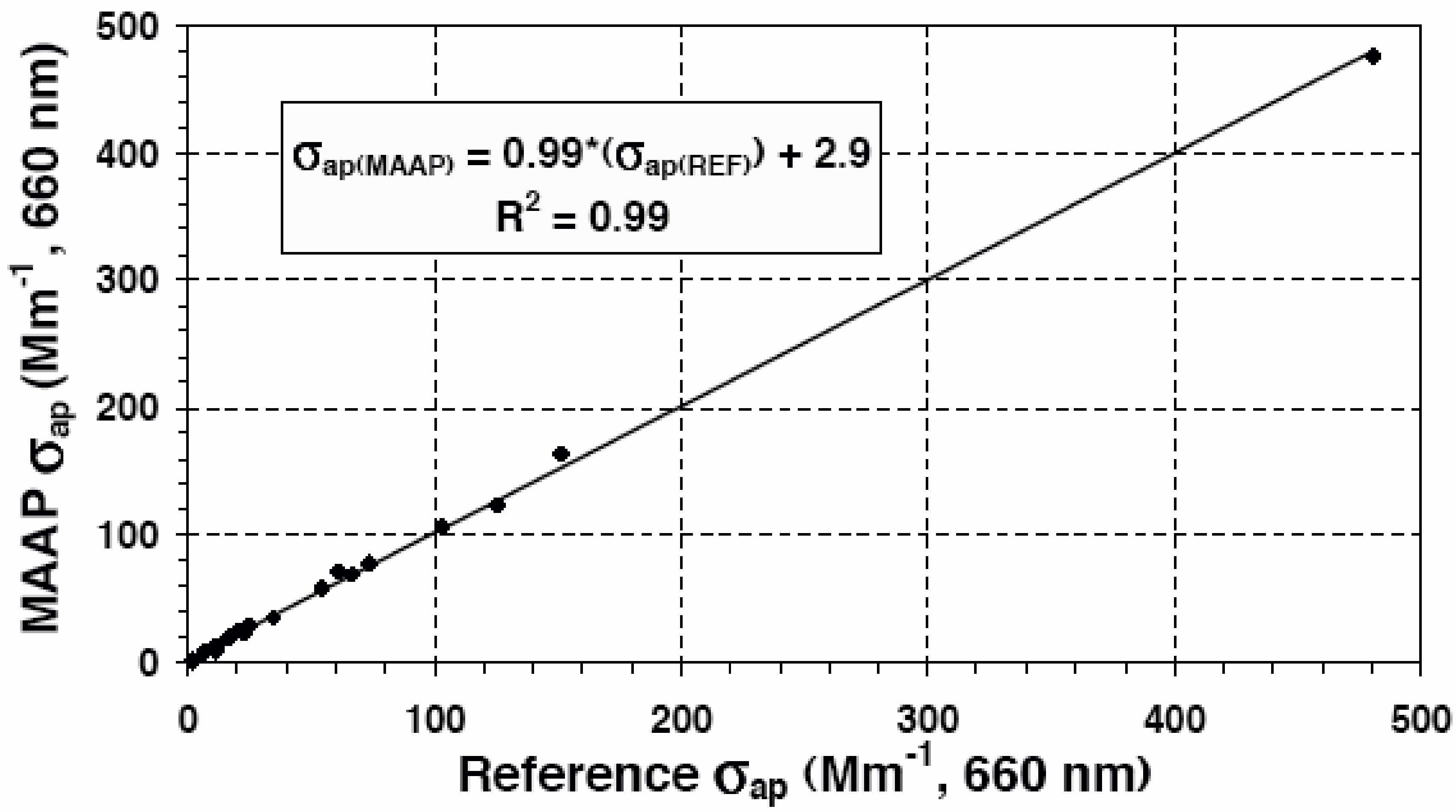


Figure 10(a-d). Time series of 1-min average absorption data from the PSAP and photoacoustic instruments. The divergence between the corrected PSAP absorption and the photoacoustic absorption is greatest at lower single scattering albedo.

The calibration at typical atmospheric single scattering albedos is good, though further work is needed to determine the PSAP calibration at low single scattering albedo for very 'dark' sources such as kerosene or diesel soot.

Comparison of the MAAP filter-based instrument and the reference measurements.



Petzold, A., H. Schloesser, P. J. Sheridan, W. P. Arnott, J. A. Ogren and A. Virkkula (2004). "Evaluation of multi-angle absorption photometry for measuring aerosol light absorption." Aerosol Science & Technology **in Press**.

RAOS Articles for the Special Issue of AS&T

Arnott, W. P., K. Hamasha, H. Moosmüller, P. J. Sheridan and J. A. Ogren (2004). **"Towards aerosol light absorption measurements with a 7-wavelength Aethalometer: Evaluation with a photoacoustic instrument and a 3 wavelength nephelometer."** Aerosol Science & Technology **In Press**.

Petzold, A., H. Schloesser, P. J. Sheridan, W. P. Arnott, J. A. Ogren and A. Virkkula (2004). **"Evaluation of multi-angle absorption photometry for measuring aerosol light absorption."** Aerosol Science & Technology **in Press**.

Sheridan, P. J., W. P. Arnott, J. A. Ogren, B. E. Anderson, D. B. Atkinson, D. S. Covert, H. Moosmüller, A. Petzold, B. Schmid, A. W. Strawa, R. Varma and A. Virkkula (2004). **"The Reno aerosol optics study: Overview and summary of results."** Aerosol Science & Technology **In Press**.

Virkkula, A., N. C. Ahlquist, D. S. Covert, W. P. Arnott, P. J. Sheridan, P. K. Quinn and D. J. Coffman (2004). **"Modification, calibration and a field test of an instrument for measuring light absorption by particles."** Aerosol Science and Technology **in Press**.

Virkkula, A., N. C. Ahlquist, D. S. Covert, P. J. Sheridan, W. P. Arnott and J. A. Ogren (2004). **"A three-wavelength optical extinction cell for measuring aerosol light extinction and its application to determining light absorption coefficient."** Aerosol Science and Technology **in Press**.

Moosmüller, H., R. Varma and W. P. Arnott (2004). "**Cavity Ring-Down and Cavity-Enhanced Detection Techniques for the Measurement of Aerosol Extinction**." Aerosol Science & Technology submitted.

RAOS Findings: Keep in mind, dry, submicron aerosol were studied.

- The photoacoustic instrument emerged as a second primary calibration standard in addition to the usual (Extinction - Scattering) = Absorption.
- The PSAP calibration used by NOAA CMDL is accurate for typical ranges of aerosol loadings and single scattering albedos found in the atmosphere. We also found the range over which this calibration is valid.
- Dramatic effects of kerosene soot on reducing the Aethalometer's filter multiple scattering enhancement factor were observed and mitigated with use of a theoretical model. The Aethalometer does respond to scattering aerosol.
- Cavity ringdown extinction measurements were typically 10% to 15% lower than the primary calibration standards. A new analysis method, cavity enhanced detection, was tested as well. Since then, each instrument has been significantly improved.
- A modified, 3 wavelength PSAP was developed, and its calibration was derived from data provided by the primary calibration standards.
- A new method and instrument (MAAP) for measuring both filter transmission and reflection was tested, and shown to agree well with primary calibration standards.

Some of our Recent Related Work, will show some ambient results for the indicated project.

- 2001 DOE-NREL Gas/Diesel Split. Dynamometer evaluation of spark and compression ignition vehicles, including heavy duty diesel buses, box trucks, and freightliners.

- 2002 Reno Aerosol Optics Study, NOAA and DOE-ARM, paved the way for the IOP …

- 2003 DOE-ARM IOP, CART site in North Central OK, purpose to evaluate closure between radiative measurements, microphysical measurements, and models. CIRPAS Twin Otter Aircraft, Cessna aircraft normally used, and ground-based measurements.

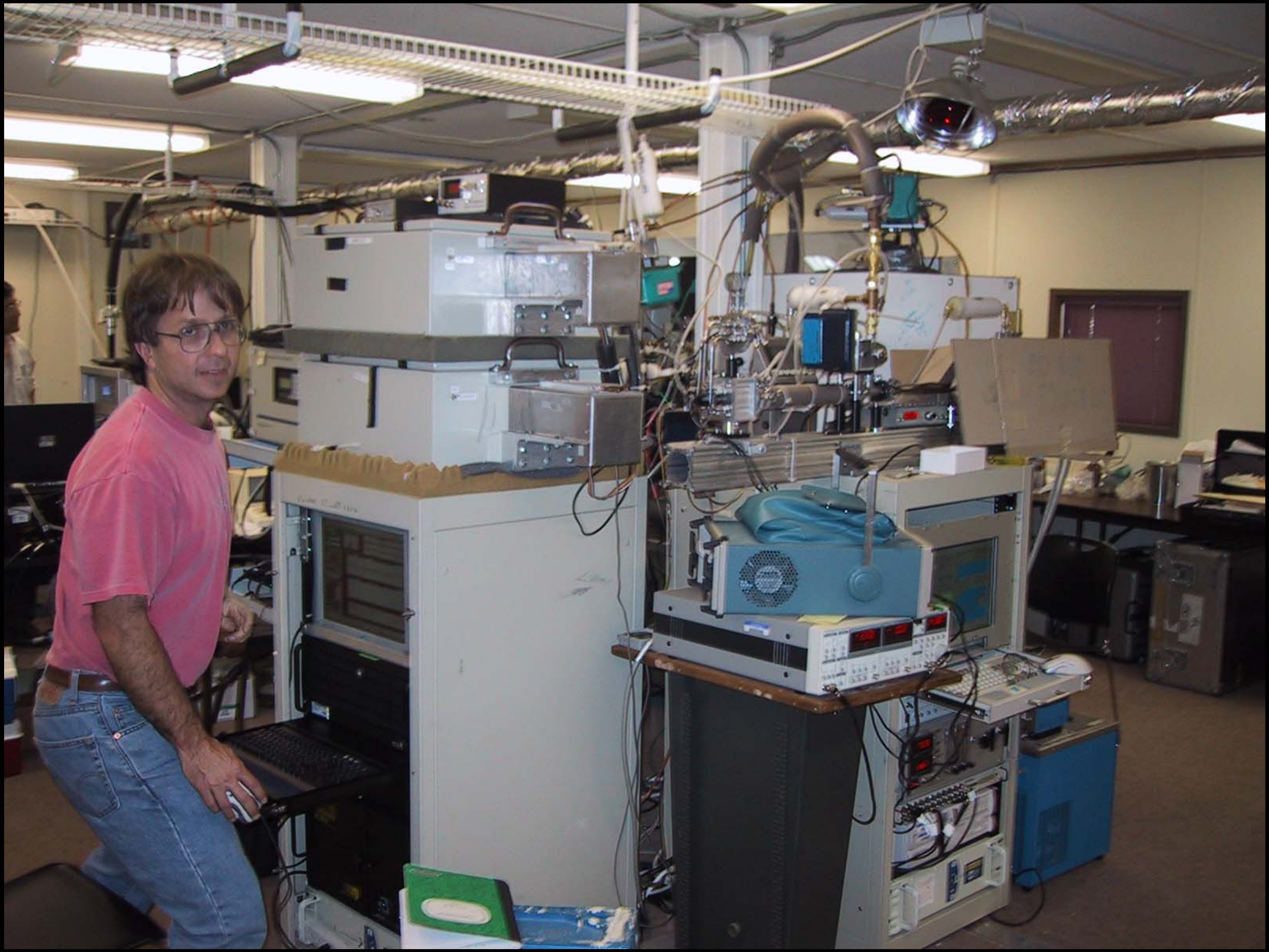
- 2003 C-STRIPE, ONR, NSF, Monterey CA, purpose to study cloud and aerosol interactions and aerosol light absorption. CIRPAS Twin Otter Aircraft.

- 2004 ICARTT, ONR, Twin Otter Aircraft out of Cleveland, purpose to evaluate cloud and aerosol interactions and the evolution of air masses downwind of cities. Large international project.

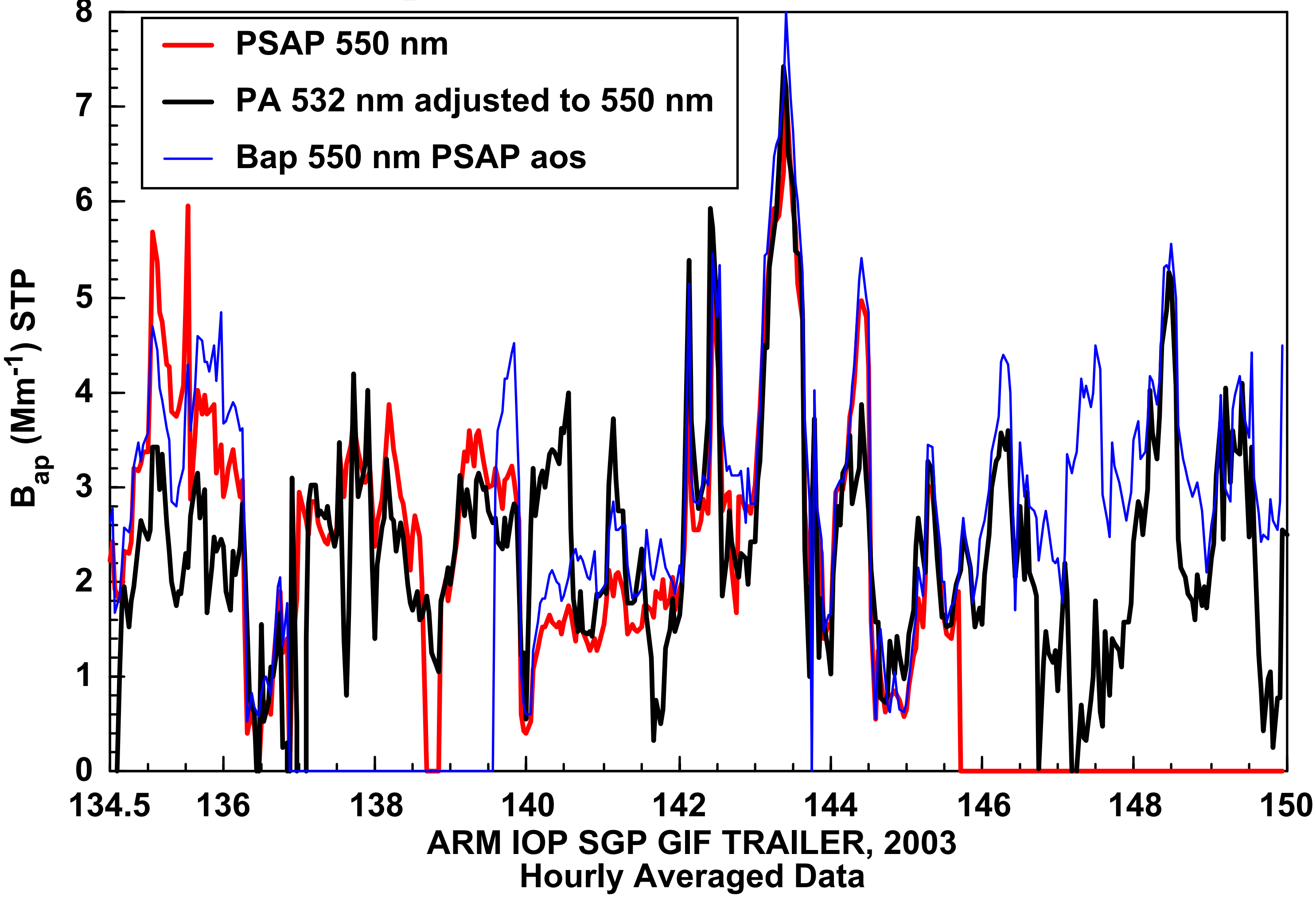
- 2004 Spark ignition vehicle evaluation, EPA, purpose to evaluate continuous methods for emission rate evaluation and well as sensors for on-road, real world measurements.

Otter over GIF Trailer, Photo courtesy Yin-Nan Lee, BNL

Some of the Instruments at the SGP during the IOP

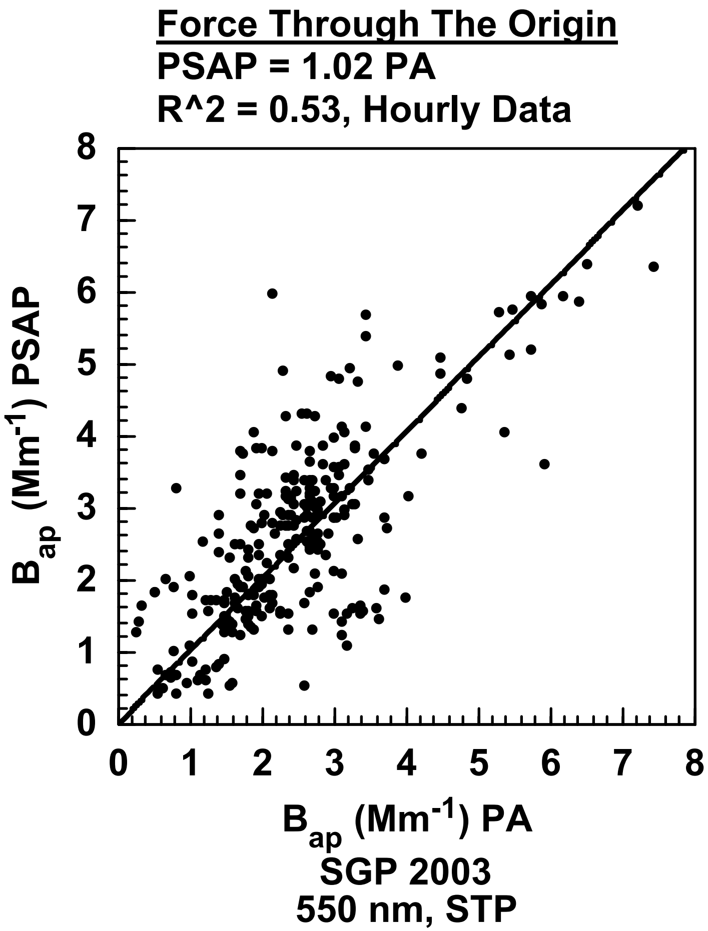


Aerosol Absorption at the CART site: Time Series.



Event around day 143 UTC most well-defined and agreed upon. 23 May 2003.

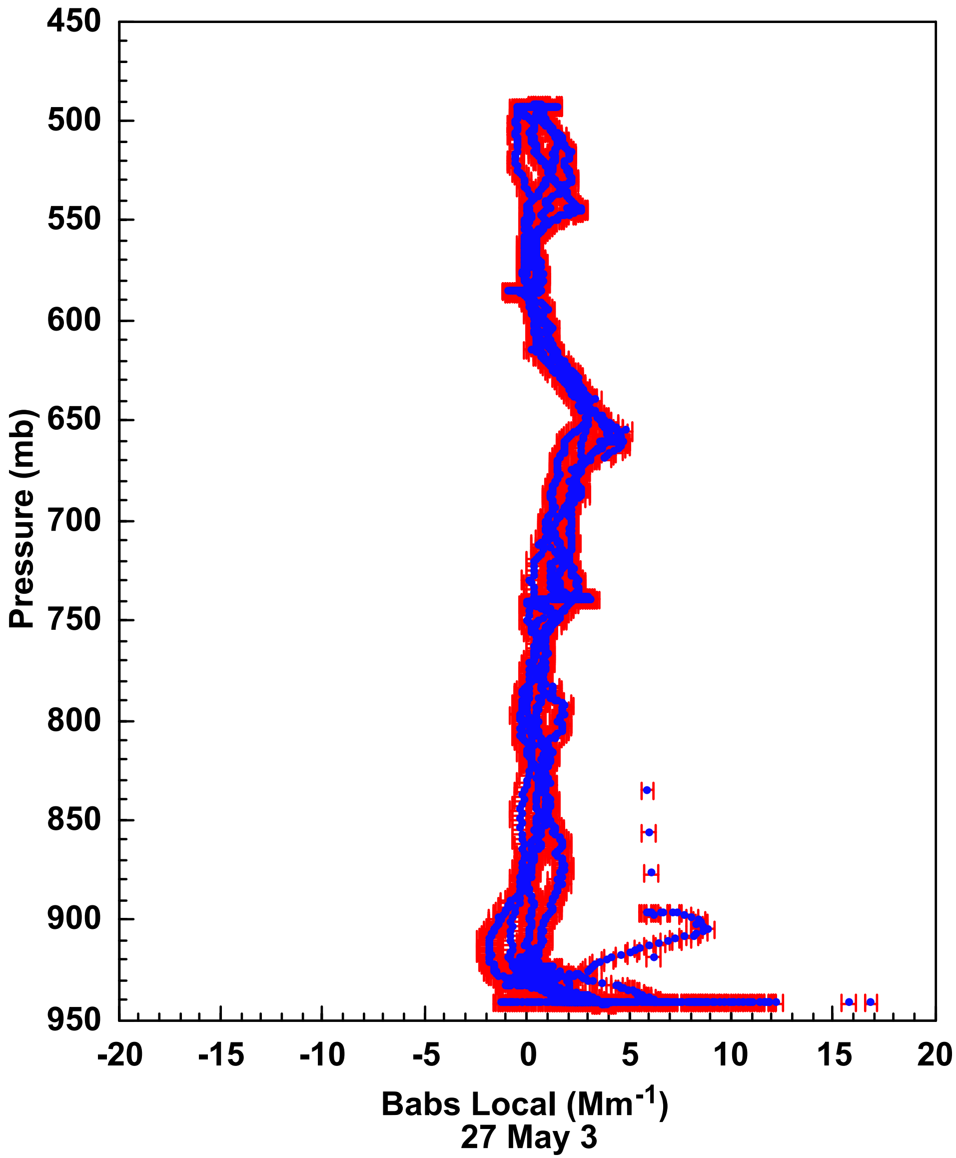
Aerosol Absorption at the CART site: Scatter Plots.



Message: Agreement among PSAP's, and between PA is less good than we have seen in the past.

Photoacoustic measurements from the Twin Otter: Maiden Voyage for the PA

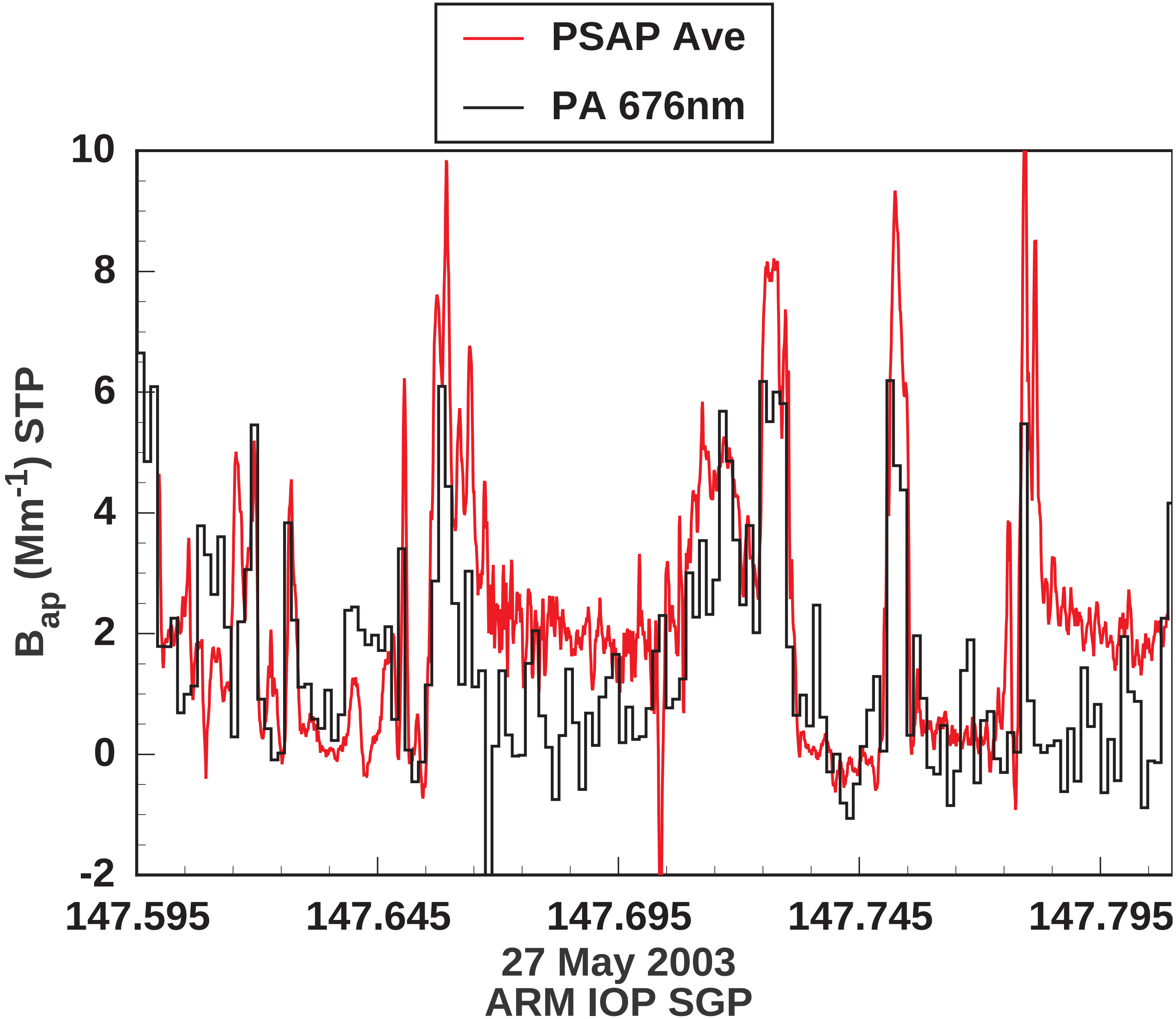
Vertical Profile 27 May 2003: Photoacoustic Light Absorption at 676 nm for Pancaked Layers of Smoke from Fires in Russia



Significant layers of light absorbing aerosol near 650 mb and 550 mb, with a clean layer in between at 600 mb.

Pat Arnott, DRI, Oct 04

May 27th: Layers Aloft Aerosol Light Absorption at 660 nm and 676 nm



Pat Arnott, DRI, Oct 04

Possible Future Topics to Study

- **Aerosol light absorption as a function of relative humidity.** Important because the RH in the atmosphere varies widely, and most measurements are done on dry aerosol. Questions: How do we measure this? Theory for coated spheres indicates an increase of light absorption by 50%, but do light absorbing particles collapse to spheres upon RH processing? Are they hygroscopic enough to take on appreciable coatings?

- **Several measurements aloft seem to point towards a decrease of the single scattering albedo with altitude** (i.e. 'darker' aerosols aloft). Are the measurements correct, why does it happen, and what is the significance of this effect?

- **How can accurately we measure aerosol optics for both sub and super micron aerosol both on the ground and aloft?** Closure studies comparing radiative measurements with in-situ measurements need to consider the super micron aerosol contributions. It is especially important for the UV aerosol optical properties aloft where angular non-idealities in nephelometery are more severe, and where dust can appreciably absorb light.

Thanks for your attention…