

**Optical Properties determined using Cavity Ring-down
Aerosol Extinction Spectroscopy and Particle Soot Absorption
Photometer**

**Campaign: Texas Air Quality and Gulf of Mexico Atmospheric
Composition and Climate Study 2006**

Platform: NOAA WP-3D

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Payload Layout

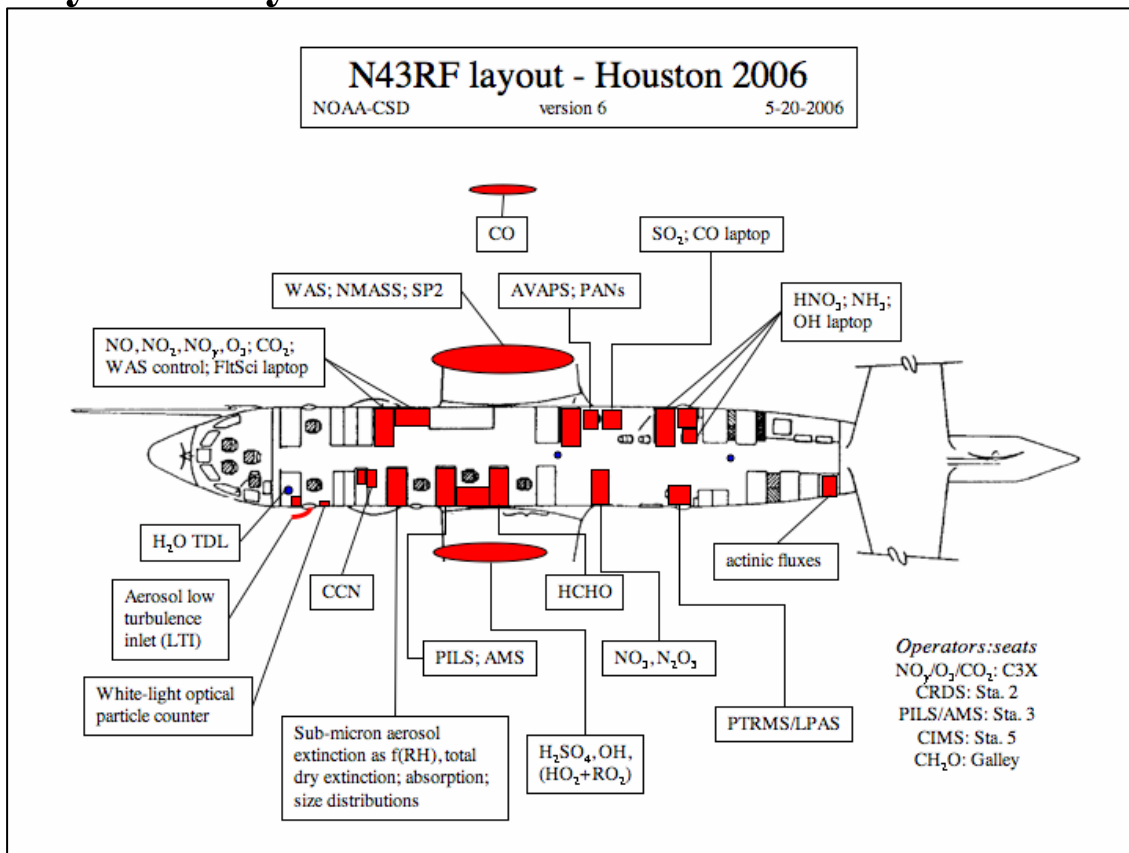
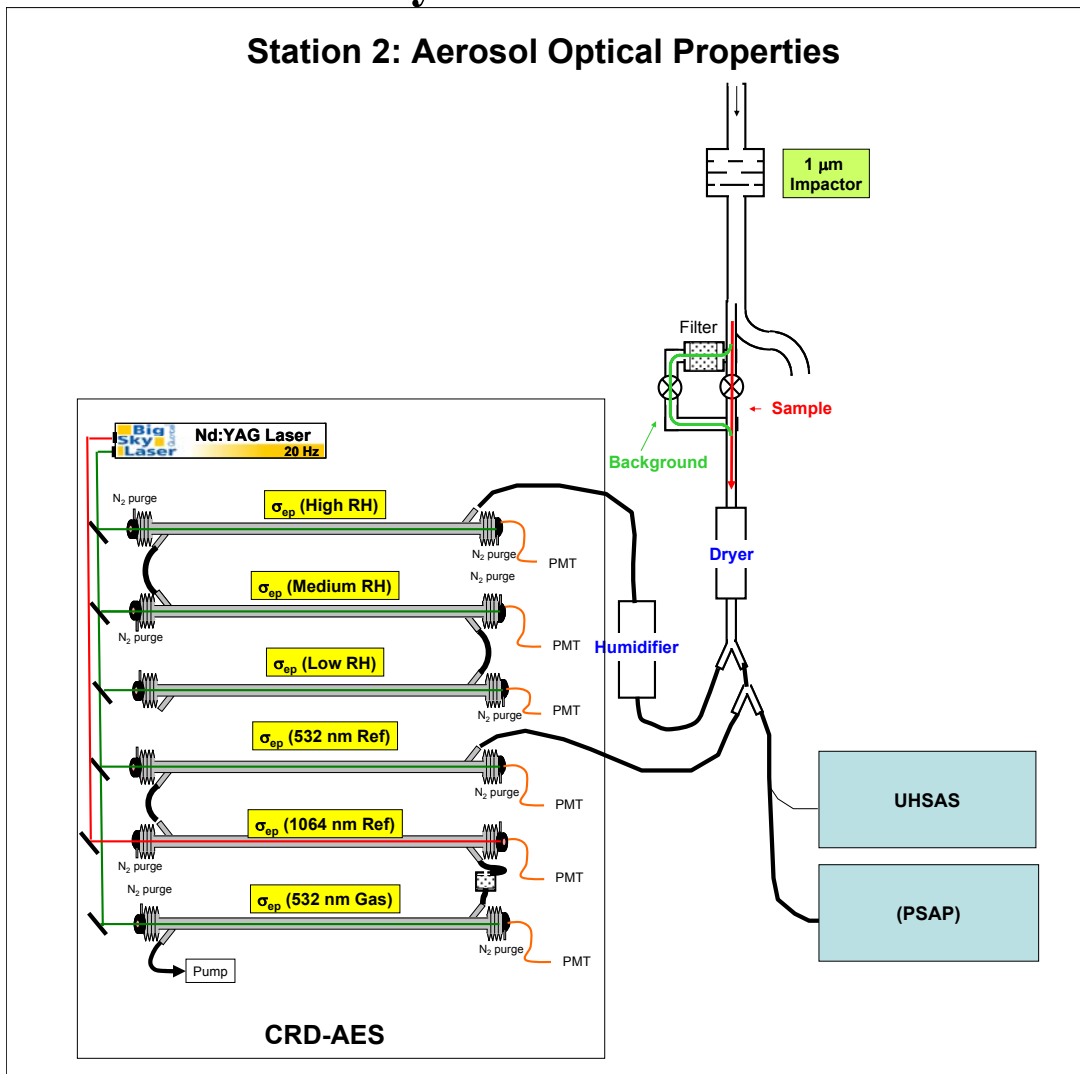


Figure X: Payload layout for TexAQS 2006.

Station 2 Flow Layout



During TexAQS 2006 the filter and dryer were in the opposite order from shown on this diagram. The detailed notes that follow show the flow order of the cells.

Recommended Changes

1. AOD: In future climate research campaigns there should be a ground AOD measurement that can be coordinated with the flight plan. The measurements should include background and plumes. This can be a simple hand held system (e.g. MicroTops Sunphotometer, <http://solarlight.com/products/sunphoto.html>). The main vertical profiles should coincide with the ground measurement location. Ideally there can be coordination with the aircraft and ground personnel to have measurements at the beginning and end of the flight at different locations (e.g. in plume and out of plume).
2. Time Resolution: The time resolution of the CRD-AES is adequate, but could be improved significantly. The current system uses a single data acquisition card and allocates resources to provide 4 separate measurement stages. These stages could be run in parallel. This would provide 1 sec data or faster with the same signal to noise as the current data at 2.4 sec. The time resolution is limited by the residence time of the sample flow.
3. RH Dependence: The RH of the humidified measurements should be shifted. The high RH measurement should be about 90%. The lower humidified channel should be about 55% RH. This will increase the RH range over which gamma is determined without including the reference extinction measurement.
4. Ambient Aerosol Phase (Crystalline/Aqueous): The CRD-AES system used a single sample flows from the LTI. Based on the location of the filter/valve a second valve system would be required. If the position of the filter and dryer are switched (as shown in Station 2 Layout) the ambient phase could be investigated. The RH control of one of these inlets should be controlled in same way as done in 2006 (i.e. Permapure dryer and Accurel humidifier). The other channel should not be dried to low RH during the sampling process, but could be humidified (careful). This would provide a more accurate representation of $f(RH)$ for the ambient aerosol.
5. Sample Temperature Control: The sample temperature could to be improved to avoid evaporation of semi-volatile organics and nitrate. The configuration used in 2006 with the minimal circulation of the front left corner in front of Station 2 and the heat load of the pump for formaldehyde needs to be addressed. This issue might be small for warm climates such as Texas during July and August. Analysis of NEAQS-ITCT RHB extinction measurements indicate a 1% mass loss/C° (ambient temp 14-16 °C).
6. The RH probe for the P3 system should be upgraded. The high quality Vaisala HMP 247 failed in Florida before the campaign. The backup HMP 50 was used for that analysis. The quality was satisfactory with routine salt calibration checks. I would recommend a Rotronics Humicap Probe similar to what I selected for the RHB system for 2006. Two of these probes should be used – one for the dry channels and one for the humidified channels.
7. Automate τ_0 measurement to pressure changes and elapsed time.

8. Video or automated pictures: We should arrange for image capture and recording capabilities. This upgrade was discussed for 2006. This capability will be valuable for indirect effect studies.
9. The zeroing procedure/timing for all instruments could be synchronized to improve the quality of the data set and simplify flights.
10. The total aerosol (coarse plus fine modes) should be measured using CRD-AES. The climate applications should not be limited to the fine mode and comparison with AOD could be simplified with a direct extinction measurement.
11. The RH dependence of extinction for the coarse mode should be measured.

Analysis Comments

Extinction Coefficient

The extinction coefficient and RH dependence was measured using a custom cavity ring-down aerosol extinction spectrometer. This was a new version of the CRD-AES which has not been highlighted in a manuscript. The previous instrument, used in NEAQS-ITCT 2004, was described in Baynard et al. (Aerosol Sci. Tech. 2006). The extinction coefficient was determined using the equation below.

$$\sigma_{ep} = \frac{R_L}{c} \left(\frac{1}{\tau_1} - \frac{1}{\tau_0} \right),$$

where R_L is the ratio of the optical length to sample length, c is the speed of light, and τ is the ring-down time constant. In this analysis R_L was determined from the physical dimensions. The optical length was equal to the distance from mirror surface to mirror surface. The sample length was equal to the distance between the two intersections of the 45° sample flow outer edge and optical path length. The laminar flow and minimal diffusion of particles makes this assumption relatively robust. Appropriate purge flow is necessary to maintain R_L (see Baynard et al.)

τ_0 was determined from filtered ambient air. The bias in the measured aerosol extinction coefficient due to absorption by gases (e.g. O₃ and NO₂) is minimized with a continuous direct measurement of the gas phase absorption.

The extinction coefficient is corrected for dilution due to purge flow. The size of the correction is small but significant for the necessary accuracy of aerosol optical property measurements. Corrections are outlined in the analysis overview for each flight.

Absorption Coefficient

The absorption coefficient was determined using a Radiance Research Three Wavelength Particle Soot Absorption Photometer (PSAP) which was purchased by NOAA CSD in 2005. This PSAP was used in the Laboratory Aerosol Optical Properties Comparison Study performed in the Atmospheric Chemical Processes Group by Baynard, Lack, and Massoli. The study included our Cavity Ring-Down Aerosol Extinction Spectrometers, Photoacoustic spectrometer, TSI Three Wavelength Nephelometer, and Radiance Research Three Wavelength Particle Soot Absorption Photometer.

The absorption coefficient was not corrected as suggested by Bond et al. 1999. Rather we used our findings from the laboratory study to define the calibration, scattering correction, and uncertainty. These details should be available in manuscript form in late 2007. Detailed notes and a poster presentation (Massoli et al. 2006) are currently available.

The corrections are defined in the analysis overview for each flight.

Fine mode

During TexAQS 2006 the sample was size selected without RH control. The combined flow of the PILS (28 lpm), CRD-AES/UHSAS (5.35 to 6 lpm), CCN (1.5 lpm), and AMS (1 lpm) dictated the size cut. The size cut is expected to vary significantly during the campaign because the variation in total flow. On several flights all instruments were not running and no effort was made to make up this flow. The flow for the CRD-AES varied from 5.35 to 6.0 for RH control. The automation software should be changed to maintain a constant 6 lpm. This can be accomplished through a feedback to the dry/reference flow.

STP = Standard Temperature and Pressure

Pressure = 760 torr

Temperature = 0° C

$$\sigma(STP) = \sigma(measured) \left(\frac{T_{measured} + 273.16}{273.16} \right) \left(\frac{760}{P_{measured}} \right)$$

Ambient RH = AOC (RH)

Pre-campaign discussion

The guy on the job is Richard McNamara at AOC. He can provide you with that info. Email is richard.j.mcnamara@noaa.gov and telephone is 813-828-3310 x3038.

The T instrument is a standard Rosemount temperature probe - for what that's worth.

The RH data are generated from dewpoint/frostpoint hygrometer data and the T measurement. A water vapor TDL instrument was recently added to the P-3 payload, also overseen by Richard, and that might be the more precise (but potentially no more accurate) data stream from which to derive RH.

Post-campaign discussion

The DewPtTemp is measured with a chilled-mirror hygrometer. This is then used by AOC to calculate H2Omr (mass mixing ratio in g/kg) and RelHumidity (%). This measurement has a slow response and large overshoot from transition of dry to wet. However, when there aren't obvious problems, this one should be most accurate.

The DewPtTempTDL is a TDL open-path instrument and is quite sensitive.

The H2OmrWVSS is reported in ppmv. It is measured from a TDL with an inlet. The trouble with this measurement is that it has a long settling time at startup and has occasional high-frequency noise.

The parameters in the Extras folder are all from the open-path TDL. The DewPtTemp_f was calculated by calibrating DewPtTempTDL to the DewPtTemp

measurement using a linear fit. Then RelHumidity_f (%), H2Omr_f (g/kg), H2Ovp_f (mb) parameters were all derived from DewPtTemp_f. It isn't perfect, but should be an improvement over the original water vapor data.

Time Resolution

All products associated with the RH dependence of extinction have been smoothed (12 points, i.e. 30 seconds)

Data File

1. AOCTimewave
2. Ext532_stp
3. Ext1064_stp
4. Abs530_stp
5. AngAbs
6. Gamma
7. Ext532_0RH_stp
8. fRH80_30
9. fRH30_0
10. AngExt
11. RH
12. fRHScatAmbRef
13. fRHExtAmb_0
14. Albedo532Amb
15. ExtAmb
16. Scat532_stp
17. Albedo532_refRH

Parameters

A. Ext532_stp = $\sigma_{ep}(\text{fine mode, 10\% RH, 532 nm, STP})$

CRD-AES based extinction coefficient at the reference RH (approx. 10%), standard temperature and pressure (0C, 760 torr), and size selected (approx < 800 nm) at 532 nm.

B. Ext1064_stp = $\sigma_{ep}(\text{fine mode, 10\% RH, 1064 nm, STP})$

See A (1064 nm).

C. $\sigma_{ap}(\text{fine mode, 10\% RH, 467 nm, STP})$

Radiance Research PSAP based absorption coefficient at the reference RH (approx. 10%), standard temperature and pressure (0C, 760 torr), and size selected (approx < 800 nm).

D. Abs530_stp = $\sigma_{ap}(\text{fine mode, 10\% RH, 530 nm, STP})$

See C.

E. $\sigma_{ap}(\text{fine mode, 10\% RH, 660 nm, STP})$

See C.

F. Scat532_stp = $\sigma_{sp}(\text{fine mode, 10\% RH, 532 nm, STP})$

The scattering coefficient calculated from the difference in the extinction coefficient and absorption coefficient at the reference RH (approx. 10%). This parameter is appropriate for comparison to scattering calculated from the UHSAS size distribution. The UHSAS determines the size distribution based on scattering at approximately 1050 nm. The imaginary index of refraction is expected to be different at this wavelength compared to visible wavelengths. Investigation of the deviation between measured extinction and calculated scattering should consider changes to both the real and imaginary index of refraction with composition.

G. Albedo532_refRH = $\omega(\text{fine mode, 10\% RH})$

a.
$$\omega(10\%) = \frac{\sigma_{ep}(10\%) - \sigma_{ap}(10\%)}{\sigma_{ep}(10\%)}$$

This is the single scattering albedo at the reference RH. The RH of the reference measurements was controlled using a PermaPure diffusive dryer. The RH was maintained at 10%.

H. $\gamma = \gamma_{\text{ext}}(\text{fine mode, 532 nm})$

- a. $\gamma(\text{linear})$
- b. $\gamma(\text{part})$
- c. $\gamma(\text{power})$

This investigates the single parameter parameterization of the RH dependence of extinction. The parameter is the slope from the least squares analysis of the four extinction coefficient measurements or humidified measurements. In addition the RH dependence of γ is investigated using a power fit to the measurement points. Extrapolation of γ to high RH (90^+) has not been validated.

I. $\text{Ext532_0RH_stp} = \sigma_{\text{ep}}(\text{fine mode, 0\% RH, 532 nm})$

- d. $\sigma_{\text{ep}(\text{linear})}(\text{fine mode, 0\% RH, 532 nm})$

Extinction coefficient from the intercept of RH dependence analysis

The intercept of the RH dependence analysis has been reported. This provides the starting point for the conversion from chemical composition and size distribution to radiative models. The RH dependence from 0% RH to 30% RH is necessary if the particles are aqueous at the reference RH used to determine $\text{fRH}(80\%,30\%)$. Acidic particles (e.g. H_2SO_4) and particles containing nitrates and/or organics can have a large impact on the RH dependence between 0% and 30% RH. This can be a large bias. Greater details regarding the analysis are presented in a special RH dependence section.

- a. $\sigma_{\text{ep}(\text{power})}(\text{fine mode, 0\% RH, 532 nm})$

Similar to a but using a power fit for γ

- b. $\text{Rep_0} = \text{Ratio } \sigma_{\text{ep}(\text{linear})}(\text{fine mode, 0\% RH}) / \sigma_{\text{ep}(\text{power})}(\text{fine mode, 0\% RH})$

J. $\text{fRH80_30} = \text{fRH}_{\text{ext}}(80\%\text{RH}, 30\%\text{RH})$

- a. $\text{fRH}_{\text{linear}}(80\%,30\%) = \left(\frac{100-30}{100-80} \right)^{\gamma(\text{linear})}$
- b. $\text{fRH}_{\text{power}}(80\%,30\%) = \left(\frac{100-30}{100-80} \right)^{\gamma(\text{power}, \text{RH})}$
- c. $\text{RfRH_80_30} = \text{Ratio } \text{fRH}_{\text{linear}} / \text{fRH}_{\text{power}}$
- d. $\text{fRH30_0} = \text{fRH}_{\text{power}}(30\%,0\%) = \left(\frac{100-0}{100-30} \right)^{\gamma(\text{power}, \text{RH})}$

This parameter for scattering has traditionally been reported (see Charlston *et al.*) because of the convenient reference measurement for scattering measurements and ambient RH levels. Typically the reference measurement is made near 30-40% RH and the elevated RH measurement near 80% RH. Deviations from 80% RH are corrected using the derived gamma. This value is reported for consistency with previous studies. However, the technique used to determine this parameter is different. The largest difference is the

type of RH control used. In this study a permeable membrane was used to avoid evaporation of semi-volatile compounds. The linear analysis is based on least squares fit to the four extinction measurements. The power dependence attempts to capture the extinction coefficient at lower ambient RH. $fRH_{power}(30\%,0\%)$ estimates the ‘missing’ contribution by the water content of ‘typical’ measurements (30% RH).

K. RH for equivalent σ_{ep} from γ analysis and measured $\sigma_{ep}(refRH)$.

This analysis determines the RH based on the measurements at three highest RHs that give an extinction coefficient equivalent to the reference measurement. During 2004 the CRD γ analysis was systematically lower than γ determined by the scanning nephelometer system. The CRD measurements were made at 30% and 65% RH. The systematic deviation could be the result of the RH dependence of gamma.

L. $fRH_{ScatAmbRef} = fRH_{scat}(AmbientRH, ReferenceRH)$

$$e. \quad fRH(AmbientRH, ReferenceRH) = \frac{\sigma_{sp}(AmbientRH)}{\sigma_{sp}(RefRH)}$$

In the analysis we assume no RH dependence for absorption. This is the scale factor of extinction necessary to convert the extinction coefficient measured at the reference RH to the ambient extinction coefficient. The size distribution UHSAS was measured with the same size selection and at similar RH as the reference extinction measurement. The wavelength used for sizing information in the UHSAS decreases the impact of the imaginary index of refraction at the visible wavelengths.

The water content can be approximated using the fRH and size information. A simple approximation uses the angstrom exponent determined from the extinction coefficient at 532 nm and 1064 nm to incorporate the size dependence of fRH and convert to water content at ambient RH. The size distribution can also be scaled until the calculated fRH based on size distribution matches the measured fRH . Both of these approaches assume internally mixed-homogeneous particles. Size resolved chemical composition could be incorporated to improve this analysis.

M. $fRH_{ExtAmb_0} = fRH_{ext}(AmbientRH, 0\%)$

$$f. \quad fRH(AmbientRH, 0\%) = \frac{\sigma_{ep(power)}(AmbientRH)}{\sigma_{ep(power)}(0\%)}, (RH_{amb} < 90\%)$$

$$= \frac{\sigma_{ep(linear)}(AmbientRH)}{\sigma_{ep(power)}(0\%)}, (RH_{amb} > 90\%)$$

N. $ExtAmb = \sigma_{ep}(\text{fine mode, Ambient, 532 nm})$

- g. $\sigma_{ep(power)}(ambient) = \sigma_{ep(power)}(0\%) \left(\frac{100}{100 - AOC(RH)} \right)^{\gamma(power, RH)}$
- h. $\sigma_{ep(linear)}(ambient) = \sigma_{ep(linear)}(0\%) \left(\frac{100}{100 - AOC(RH)} \right)^{\gamma(linear)}$
- i. $\sigma_{ep(part)}(ambient) = \sigma_{ep}(RH_{equivalent} \%) \left(\frac{100}{100 - AOC(RH)} \right)^{\gamma(part)}$
- j. $Rep_amb_linear = Ratio \sigma_{ep(linear)}(ambient) / \sigma_{ep(power)}(ambient)$
- k. $Rep_amb_part = Ratio \sigma_{ep(part)}(ambient) / \sigma_{ep(power)}(ambient)$

This parameter is used for the ambient extinction coefficient (at STP) of the fine mode fraction. The size cut of the fine mode fraction was variable due to RH and flow controls. These three techniques compare the variability in the determined ambient extinction coefficient.

O. σ_{sp} (fine mode, Ambient, 532 nm)

- l. $\sigma_{sp}(ambient) = \sigma_{ep(power)}(AmbientRH\%) - \sigma_{ap}, (RH_{amb} < 90\%)$
- m. $\sigma_{sp}(ambient) = \sigma_{ep(linear)}(AmbientRH\%) - \sigma_{ap}, (RH_{amb} > 90\%)$
- n. $\sigma_{ep(part)}(ambient) = \sigma_{ep}(RH_{equivalent} \%) \left(\frac{100}{100 - AOC(RH)} \right)^{\gamma(part)}$
- o. $\sigma_{ep(power)}(ambient) = \sigma_{ep(power)}(0\%) \left(\frac{100}{100 - AOC(RH)} \right)^{\gamma(power, RH)}$

P. $Albedo_{532Amb} = \omega$ (fine mode, Ambient*)

$$p. \omega(ambient) = \frac{\sigma_{ep(power)}(ambient) - \sigma_{ap}(10\%)}{\sigma_{ep(power)}(ambient)}, (RH < 90\%)$$

$$= \frac{\sigma_{ep(linear)}(ambient) - \sigma_{ap}(10\%)}{\sigma_{ep(linear)}(ambient)}, (RH > 90\%)$$

For radiative forcing the co-albedo (abs/extinction), upscatter fraction, and aerosol optical depth are the sensitive parameters. The single scattering albedo (traditional parameter) and extinction for the fine mode fraction are provided at ambient RH. In this analysis the potential RH dependence of absorption has not been taken into account and we assume $fRH_{abs} = 1$.

Q. $AngExt = \hat{A}_{ext}$ (fine mode, 532nm/1064nm)

$$q. \quad \dot{A} = - \frac{\log\left(\frac{\sigma_{ep}(532nm)}{\sigma_{ep}(1064nm)}\right)}{\log\left(\frac{532}{1064}\right)}$$

The angstrom exponent of extinction is used in remote sensing retrievals and also used to estimate the size distribution. The quality of the extinction coefficient at 532 nm is superior to 1064 nm for the reported time resolution and configuration of the instrument used during TexAQS 2006. The data reported has been filtered for $1064 > 0 \text{ Mm}^{-1}$. The main issue is limited to high altitude measurements where the 1064 nm channel's alignment was not stable.

R. AngAbs = $\dot{A}_{abs}(\text{fine mode, } 467\text{nm}/660\text{nm})$

$$r. \quad \dot{A} = - \frac{\log\left(\frac{\sigma_{ap}(467nm)}{\sigma_{ap}(660nm)}\right)}{\log\left(\frac{467}{660}\right)}$$

Current discussion related to the absorption by brown carbon indicates a different wavelength dependence of absorption than black carbon. The absorption in the UV is expected to be enhanced. The wavelengths of the three-wavelength PSAP are not ideal for this investigation.

Define γ (parameterization of the RH dependence)

γ based on $f(RH) \equiv 1$ at 0% RH

Functional Form

$$f(RH, Ref) = \left(\frac{100 - Ref}{100 - RH} \right)^\gamma$$

Typical

$$f(RH, 30\%RH) = \left(\frac{100 - 30}{100 - RH} \right)^\gamma$$

New Form

$$\begin{aligned} f(RH, 0\%RH) &= \left(\frac{100 - 0}{100 - RH} \right)^\gamma \\ \log(f(RH, 0\%RH)) &= \gamma \log\left(\frac{100 - 0}{100 - RH} \right) \\ \log\left(\frac{\sigma(\%RH)}{\sigma(0\%RH)} \right) &= \gamma \log\left(\frac{100 - 0}{100 - RH} \right) \end{aligned}$$

$$\log(\sigma(\%RH)) - \log(\sigma(0\%RH)) = \gamma(\log(100 - 0) - \log(100 - RH))$$

$$\log(\sigma(\%RH)) = \gamma(\log(100 - 0) - \log(100 - RH)) + \log(\sigma(0\%RH))$$

$$\log(\sigma(\%RH)) = \gamma(2 - \log(100 - RH)) + \log(\sigma(0\%RH))$$

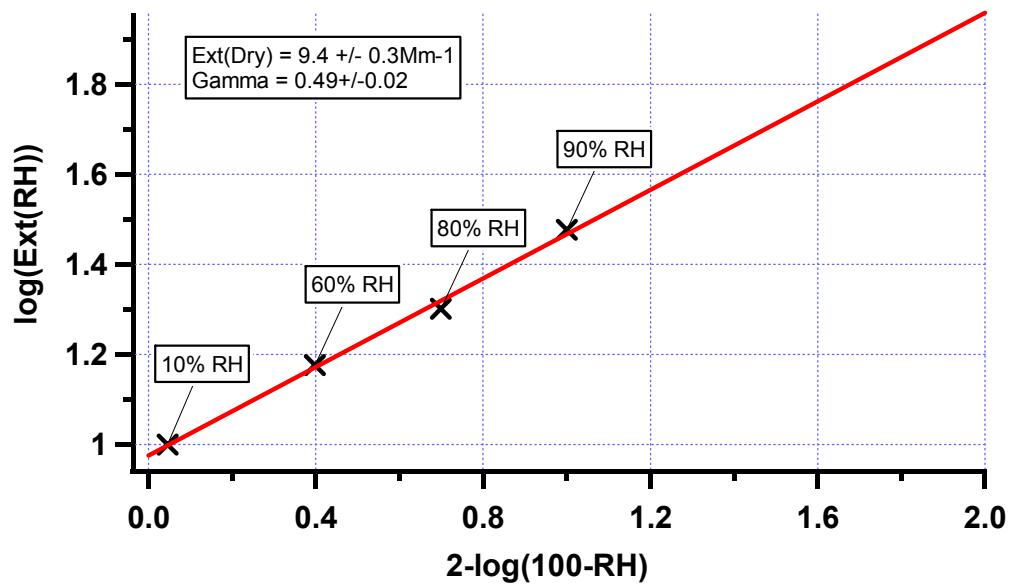


Figure X: Determination of parameterization of the RH dependence (γ) and reference extinction coefficient (0% RH).

The RH dependence can also expressed as

$$f(RH) = a \left(1 - \frac{RH(\%)}{100} \right)^{-b}$$

(Kasten 1969, Hanel 1976, Kotchenruther 1999, Andrews 2004)

Recommended Analysis

1. Determine appropriate use of single parameter RH dependence
 - Issues (low RH, high RH)
 - Mixed components and Single Components
2. Bias of traditional (80% RH, 30% RH) – motivation for this form.
3. Upper and lower hysteresis branch
4. Assumptions regarding upper and lower branch