Genetic Algorithm Determined Real Refractive Indicies of Various Secondary Organic Aerosols

By Hwajin Kim, Brian Barkey and Suzanne Paulson University of California, Los Angeles

Introduction

In determining single scattering and hence the bulk radiative properties of aerosols, the refractive index of the particulate matter is key. There are very few measurements of the real refractive index (m_r) of secondary organic aerosols (SOA). Dick et al. [1] measured the refractive index of 1.494 for dry aerosol and 1.415 for wet aerosols at the Smokey Mountains National Park. Hand et al. [2] retrieved a refractive index of 1.556 for the atmospheric aerosol Big Bend National Park. Hock et al. [3] measured atmospheric aerosol in a rural area and found values of m_r between 1.4-1.45. Laboratory measurements include Schnaiter et al [4] who studied SOA generated from oxidizing α-pinene with O_3 and found m_r = 1.5, and our group determined the refractive index of similar SOA to be 1.42 ± 0.02 [5].

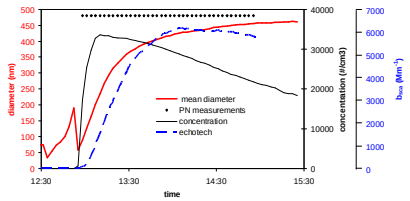
In this study the polar nephelometer data is used to determine the m_r of (SOA) particles generated by oxidizing α-pinene, β-pinene and toluene in the UCLA solar reaction chamber.

Experimental setup

Experiments occur in a large (24 m^3) Teflon chamber on the roof of the Math Sciences building at UCLA as shown to the left. Concentrations of O_3, NO, NOx and hydrocarbons in the chamber are continuously monitored.

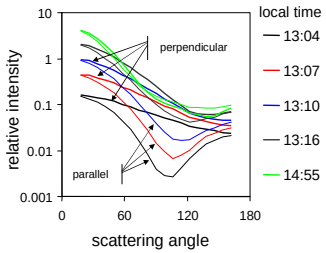
Instrumentation:

- Scanning mobility particle sizer (TSI model 3080) measures the particle size distribution every 3 minutes.
- An 700 nm integrating nephelometer (Ecotech M9008) records particle scattering coefficient (β_{sp}) every 1 minute.
- An updated version of the polar nephelometer developed at UCLA[5] provides angular intensity measurements. This instrument is operating near its detection limit when β_{sp} below ~1000 Mm^{-1}.



Time evolution of the SOA particles generated from 500 ppb α-pinene and 250 ppb NOx in the Teflon bag that was exposed to solar radiation at about 12:00 local time on October 21, 2009.

The particle concentration is very low until about 13:00 local time when the particle concentration rapidly rises due to homogeneous nucleation of the aerosols. The polar nephelometer signal is viable at about 13:07 when the particle concentration is about 32000 cm^3 and the particles have grown to a mean diameter of about 200 nm. The particles continue to grow to a maximum radius of about 450 nm at about 15:30 while the particle concentration drops as a result of sedimentation and wall losses. The polar nephelometer records the scattering intensities every 14 seconds. Also shown is the time evolution of the particle scattering coefficient measured by the integrating nephelometer.

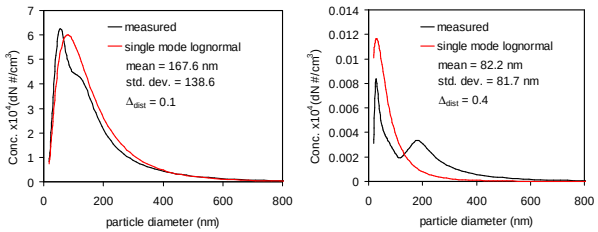


The PN measures the light scattered at 21 angles, the incident light (wavelength = 670 nm) is polarized either parallel or perpendicular to the measurement plane. The intensity of the measured signal increases as the particle size and concentration increase during the initial rapid growth phase, then as the particle growth slows, the change in the scattered intensity slows. Also as the particles grow, the shape of the angular intensities change, i.e., the dip at about 90º shifts towards 120º.

Accuracy of GA refractive index

Real refractive indicies and size distribution parameters are derived using the Genetic Algorithm (GA) method [5] in which the desired variables are selected from within a predetermined search space. Mie-Lorenz scattering is assumed. Electronic noise is significant only at the lower limits of the instrument response, (i.e., minimum signal level of 0.003 vdc corresponding to β_{sp} ~ 500 to 1000 Mm^{-1}). Calibration errors introduce an average error of about 3%. Assessing the amount that spurious reflection affect the retrieval is done via measurements of various sizes of polystyrene latex particles and water-ammonium sulfate droplets in which the m_r is a known function of humidity. Because the GA method of determining m_r from scattering data is highly insensitive to noise [6],[7], all of these error sources produce an absolute error in the GA retrieved m_r of ± 0.013. [5]

The GA retrieval assumes a mono-modal lognormal distribution, however actual distributions do not often follow the lognormal assumption. Shown here, are the actual SMPS measured size distribution of ammonium sulfate/water aerosols compared to the single mode lognormal distribution based on the SMPS mean and standard deviation.



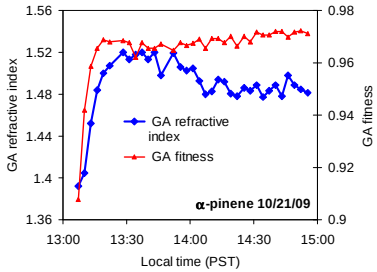
Δ_{dist} is a measure of the difference between the measurement ($PDF_{meas}(x)$) and the lognormal assumption ($PDF_{calc}(x,\mu,\sigma)$) is given by;

$$\Delta_{dist} = \int \left| PDF_{meas}(x) - PDF_{calc}(x,\mu,\sigma) \right| dx$$

and the distributions are normalized via;

$$\int PDF_{meas}(x)dx = \int PDF_{calc}(x,\mu,\sigma)dx = 1.0$$

The GA m_r determined from PN measurements of these aerosols are within ±0.014 of the expected values despite Δ_{dist} values up to 0.4. However, the GA required the size distribution search space to be increased to ±30%, which is much higher than the SMPS error of 10%. [9] This is because the scattering is dependent on the actual particle size distribution which is not sufficiently described by the lognormal assumption.



Refractive indicies

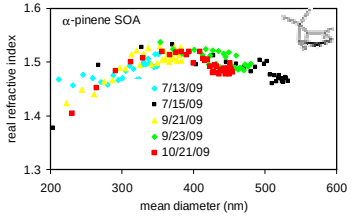
The GA determined m_r for aerosols produced from the α-pinene experiment of October 21, is shown here as a function of local time. The m_r increases rapidly from about 1.4 to a maximum value of 1.52 and then settles at about 1.48.

The fitness value is a measure of how well the GA was able to fit the measured results to the Mie-Lorenz expectation. Noisy data produce fitness values less than 0.95 and have errors greater than the ±0.013 described above. The fitness levels are low at the start of the experiment due to the lower signal level, and is a phenomena common to all the pinene based experiments.

SOA Growth Summary

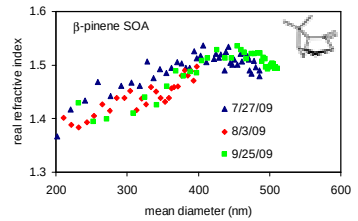
Several SOA growth experiments with α-pinene, β-pinene and toulene based precursors were performed with initial conditions and yields.

	Initial Conditions						Results				
Date	Hydrocarbon	HC (ppb)	NOx (ppb)	HC/NO_x	Temp(ºC)	RH(%)	ΔHC (ppb)	# density (#/cm^3)	Size mode (nm)	Mass (μg/m^3)	Yield (%)
15-Jul-09	α-pinene	840	760	11.1	30.5-39.0	13	838	18100	572.5	2050	43.9
23-Sep-09	α-pinene	540	480	11.3	29.9-48.1	14	540	9250	514	824.7	27.4
21-Oct-09	α-pinene	500	250	20	25-38.4	15	485	21800	478.3	1630	60.3
13-Jul-09	α-pinene	460	270	17	31.6-42	14	456	27800	358.7	973.2	38.3
21-Sep-09	α-pinene	550	240	22.9	27-39.8	16	547	31100	429.4	1530	50.2
27-Jul-09	β-pinene	570	230	24.8	28.4-38	16	428	6640	495.8	554.4	23.2
25-Sep-09	β-pinene	640	230	27.8	30.1-45.8	17	529	9140	532.8	902.3	30.6
3-Aug-09	β-pinene	400	350	11.4	29-40.8	25	323	9210	399.5	428	23.8
10-Aug-09	toluene	1700	800	16.1	28-38.6	16	607	19000	289	311	13.6
12-Aug-09	toluene	3670	920	29	24-38.5	15	914	18500	371.8	561.7	16.3
7-Oct-09	toluene	3240	820	29	21-31.5	16	773	19000	385.4	679.1	23.3
14-Aug-09	toluene	3700	3100	8.7	26.8-38.3	21	1170	10400	414.2	488	11.1
23-Oct-09	toluene	3200	3000	7.8	26.1-41.6	19	1030	9300	414.2	414	10.7
9-Oct-09	toluene	3200	2800	8.4	19-34.2	19	476	12400	322	242	13.5



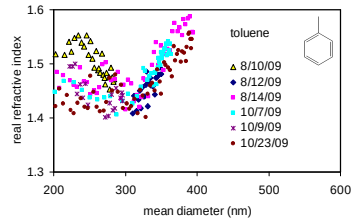
α–pinene/NO_x GA m_r

In all cases, m_r starts low at about 1.4, increases rapidly to about 1.52 and then decreases to about 1.47. Results from experiments with and with out an OH scavenger shown, and the particles appear to be optically indistinguishable



β-pinene/NO_x GA m_r

The GA determined m_r for SOA developed via ozonolysis of β-pinene exhibits some of the same properties of the α-pinene SOA, but has an overall slower growth rate. The initial $m_r \approx 1.4$ and the final $m_r \approx 1.5$ are similar to the α-pinene value.



Toluene/NO_x SOA GA m_r

This precursor is very different from the pinenes and thus shows a different m_r vs. size and a larger final m_r (~1.6) but in this case m_r is increasing as the particle size increases, while the pinene indicies both display a decreasing trend.

Discussion

- The real refractive index of SOA particles changes as the particles grow, and also as it ages. The final m_r for the pinene derived SOA is about 1.47 to 1.49, which are quite different for the final value of about 1.55 to 1.6 retrieved for the toluene based SOA. The toluene based m_r also drops during its initial growth and then increases, while the pinene SOA m_r increases initially and then drops.
- Further study is underway to examine SOA particles of different precursors and developed under different conditions. We also plan to investigate the SOA m_r with another PN with a laser wavelength of 980 nm and also a higher powered laser allowing instrument sensitivity in ambient conditions.

References

[1] Dick, et al., "Multiangle Light-Scattering Measurements of Refractive Index of Submicron Atmospheric Particles," *Aerosol Sci.Technol.*, vol. 41, 2007, p. 549.
[2] Hand and Kreidenweis, "A New Method for Retrieving Particle Refractive Index and Effective Density from Aerosol Size Distribution Data," *Aerosol Sci. Technol.*, vol. 36, 2002, p. 1012.
[3] Hock, et al., "Rural continental aerosol properties and processes observed during the Hohenpeissenberg Aerosol Characterization Experiment (HAZE2002)," *Atmos. Chem. Phys. Discuss.*, vol. 7, Jun. 2007, pp. 8617-8662.
[4] Schnaiter, et al., "Absorption amplification of black carbon internally mixed with secondary organic aerosol," *J. Geophys. Res.*, vol. 110, 2005.
[5] Barkey, et al.,"Genetic Algorithm Inversion of Dual Polarization Polar Nephelometer Data to Determine Aerosol Refractive Index," *Aerosol Sci. Technol.*, vol. 41, 2007, pp. 751-760.
[6] Goldberg, *Genetic Algorithms in Search, Optimization, and Machine Learning*, Reading, Mass.: Addison-Wesley Professional, 1989.
[7] Hodgson, "Genetic Algorithm Approach to Particle Identification by Light Scattering," *J. Colloid and Interface Sci.*, vol. 229, Sep. 2000, pp. 399-406.
[8] Ye, et al., "Inversion of Particle-Size Distribution from Angular Light-Scattering Data with Genetic Algorithms," *Appl. Opt.*, vol. 38, Apr. 1999, pp. 2677-2685.
[9] Barkey, et al. "Genetic Algorithm Retrieval of Real Refractive Index from Aerosol Distributions that are not Lognormal", *Aerosol Sci. Technol*, Submitted.

contact: bbarkey@ucla.edu