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Aerosol Optical Extinction Measurements Using a Pulsed Laser Cavity-Ring Down Transmissometer

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Abstract : A recently developed portable instrument, the pulsed cavity ring-down transmissometer/nephelometer tandem (CRDT/N) allows for the in situ measurement of optical properties of aerosols. An Nd:YAG laser excited CRDT (λ = 532, 1064 nm) is shown to be capable of sensitively measuring the aerosol extinction coefficient (b_{ext}) at the two wavelengths simultaneously. Adding a nephelometer yields a measurement of scattering coefficient (b_{scat}) of the same aerosol. From scattering and extinction measurements, aerosol absorption coefficients (b_{abs}) can be calculated from $b_{ext} = b_{scat} + b_{abs}$. Furthermore, intensive properties single scattering albedo ($\omega_0 = b_{scat}/b_{ext}$) can also be determined. The pulsed cavity-ring down transmissometer/nephelometer (CRDT/N) is validated through a series of laboratory experiments. First agreement between extinction measurements from the cavity ring-down and scattering measurements from the nephelometer is demonstrated for purely scattering particles. Then agreement between measured extinction and Mie theory is demonstrated when using size-selected purely scattering particles. Overall, measurements agree with Mie theory to within 7%, although observed differences could be due to problems with size selection. The limits of detection and quantitation for this instrument are shown to be b_{ext} = 4.0 Mm^{-1} and 13.4 Mm^{-1}, respectively.

Key words: Aerosols, Cavity-Ring Down Transmissometer, Optical Extinction Measurements.

1. Introduction

Airborne particulate matter (PM) has a major impact on environmental issues affecting human health, visibility and climate. Accurate measurements of PM are an important piece of information in monitoring air quality and compliance with EPA emission standards. However obtaining real-time measurements of PM optical properties is an ongoing challenge.

Atmospheric aerosols typically contain (sulfate, nitrate, chloride, ammonium, sodium) trace metals, carbonaceous material, crustal elements and water. The carbonaceous fraction of aerosols consists of both elemental (black carbon, graphitic carbon or soot) and organic carbon. These particles can cause serious health problems by penetrating and delivering coated chemicals into the sensitive regions of the respiratory tract. Fine particles are considered to be more harmful as they remain in the air for a longer period of time. They can be deeply inhaled into the lungs where they can be absorbed into the bloodstream or remain embedded indefinitely [1,2].

A material whose refractive index is different from the surrounding medium can scatter light. The key parameters that govern the scattering of light by spherical particles are the wavelength of the incident radiation and the size of the particle, usually expressed as a dimensionless size parameter, $\alpha = \dfrac{\pi D_p}{\lambda}$ in which D_p and λ are particle diameter and the wavelength respectively. Depending on the particle size, there are two regimes for light scattering. For particle sizes larger than a wavelength ($\alpha \geq 1$), Mie scattering predominates. Rayleigh scattering is isotropic and refers to the scattering of light by molecules, but can be extended to scattering from particles up to about a tenth of the wavelength of the light. The total scattered intensity from spherical particles with diameters much smaller than the wavelength is proportional to λ^{-4} of the incident light, while the wavelength dependence of scattering (Mie) by bigger particles is less pronounced and more complicated. The combined effect of scattering and absorption is referred to as extinction. The extinction cross-section, C_{ext} can be defined by the Beer-Lambert law through the following equation:

$$\ln\left(\frac{I_0}{I}\right) = C_{ext} \times L \times N$$

Where $N = \frac{\text{number of particles}}{\text{volume}}$, L = distance, and $C_{ext} = C_{scat} + C_{abs}$ and C_{ext} has the units of area meaning that the particle casts a shadow of area C_{ext} on the radiative energy passing the particle . When the solar beam is traversing an atmospheric layer containing particles, light extinction occurs due to the attenuation of the incident light by scattering and absorption as it traverses the layer. The extinction coefficient, b_{ext} is defined as

$b_{ext} = C_{ext} \times N$, where N is the total particle number concentration (particles m^{-3}). The extinction coefficient is a measure of the fraction of light that is attenuated per unit distance and has units of inverse length (m^{-1}). The dimensionless scattering efficiency of a particle, Q_{scat}, is $\frac{C_{scat}}{A}$ where A is the cross-sectional area of the particle. Similar definitions hold for Q_{abs} and Q_{ext} such that, $Q_{ext} = Q_{scat} + Q_{abs}$

For a population of monodisperse, spherical particles at a number concentration N, the extinction coefficient is related to the dimensionless extinction efficiency through the following equation:

$$b_{ext} = \frac{\pi D_p^2 N Q_{ext}}{4}$$

The extinction coefficient for the atmosphere can also be apportioned as:

$b_{ext} = b_{sp} + b_{ap} + b_{sg} + b_{ag}$,where

b_{sp} is scattering by particles, b_{ap} is absorption by particles, b_{sg} is scattering by gases, and b_{ag} is absorption by gases [3,4,5].

Visibility is reduced when there is significant scattering because particles in the atmosphere between the observer and the object scatter light from the sun and other parts of the sky through the line of sight of the observer. Local visual range can be determined through the Koschmeider equation, $X = 3.912 / b_{ext}$ where X is the local visual range (m) and b_{ext} is the atmospheric extinction coefficient (m^{-1}).

Tropospheric aerosols exert their influence on climate via both direct and indirect radiative forcing process. The direct effect involves the scattering and absorption of radiation by aerosol particles. The absorption of light by black carbon aerosols warms the atmosphere and reduces the solar radiation at the surface. It is estimated a warming of about 0.2 W/m^2 is attributable to absorption by black particles . In contrast, studies have shown that sulfate aerosols are one of the most important sources of negative radiative forcing in the global atmosphere. Sulfate aerosols yield a cooling of 0.5 W/m^2 globally due to scattering of solar radiation. Indirect effects involve aerosols serving as cloud condensation and ice nuclei, thereby modifying the microphysics, radiative properties, albedo and the lifetime of clouds. Seeding leads to more highly reflective clouds, and thus radiative cooling. Another indirect effect related to black carbon involves the localized heating of clouds by absorbing particles, which can lower precipitation efficiency and ultimately cause formation of less reflective clouds (positive radiative forcing) [6,7,8].

1.1. Cavity Ring-down Spectroscopy (CRDS)

Pulsed cavity ring-down spectroscopy and its use in environmental studies has been extensively reviewed [9,10]. CRDS is based on measuring the rate at which light intensity leaks out of a stable optical cavity. A stable optical cavity is made of two highly reflective mirrors (>99.99%), at least one of which is concave to refocus the light. Nanosecond laser pulses are fired at the cavity and bounces back and forth while becoming less intense due to the various loss processes (mirrors and sample). Since the mirrors are not 100% reflective, a small fraction of the initial photons are transmitted through the mirrors in each pass. The light in the cavity decays exponentially according to the first-order expression, $I_{(t)} = I_0 e^{-t/\tau}$, where τ is the "ring-down time" of the cavity (the time required for the intensity to decay to $I = I_0 / e$) as shown in Fig. 1.

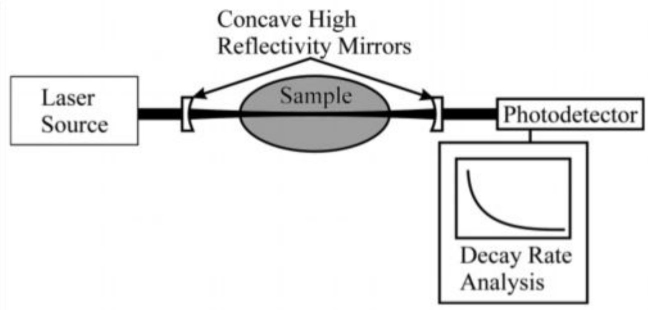

Fig.1 An experimental diagram showing the essential features of any cavity ring down experiment

The ring-down time is determined by the sum of all light loss mechanisms including scattering and absorption by the analyte and transmission by the mirrors. The ring-down time for an empty cavity is related to the mirror reflectivity via $\tau = \frac{L}{c}\left(\frac{\sqrt{R}}{1-\sqrt{R}}\right)$ where L, c and R are the cavity length, speed of light and the mirror reflectivity respectively. The most popular way to extract β is to express the observed signal at any time, S(t), as a function of the signal at the beginning ,S(0).

$$S(t) = S(0) \exp(-\beta t) + C$$

where C is the signal offset level and the derived value for β is the rate constant for the first order loss of light intensity in the cavity. When the decay constant for the blank (all loss processes in the absence of the absorbing species) is subtracted from the losses measured with the absorber, the result is the corresponding rate constant for light intensity loss due to the analyte. Depending on the experiment being performed β can be translated to different parameters. For kinetic studies where absorbance of the analyte as a function of time is used to monitor concentration, β can be converted to absorbance by using following equation:

$$\text{Absorbance} = \log\left(\frac{I_0}{I}\right) = \frac{\ln\left(\frac{I_0}{I}\right)}{\ln(10) \approx 2.3}$$

$$= \frac{L(m) \times \left(\beta_{abs}(s^{-1}) - \beta\,\text{blank}\,(s^{-1})\right)}{c\,(ms^{-1})}$$

Where L is the cavity length and c is the speed of light. For aerosol studies, where the optical properties of particles are the center of interest, optical extinction of the analyte is obtained by dividing β by the speed of light. This can be shown to be dimensionally consistent as,

$$\text{Ext}\,(m^{-1}) = \frac{(\beta_{\text{aerosol}} - \beta_{\text{blank}})(s^{-1})}{c\,(ms^{-1})}$$

A blank sample should be chosen depending on the experiment being performed. For measurements of the extinction of particles in the atmosphere, filtered air (particle free) should be used as the blank. The ring-down decay constant, β, can be converted to an extinction coefficient (b_{ext}) using the following equation:

$$Ext(Mm^{-1}) = \frac{10^6 m}{Mm} \times \frac{(\beta_{aerosol} - \beta_{filtered\ air})(s^{-1})}{Speed\ of\ ligth\,(ms^{-1})} \times \frac{Length\ of\ the\ cavity\,(m)}{Effective\ pathlength\,(m)}$$

By coupling a Radiance Research M903 Nephelometer to the cavity ring-down instrument, the aerosol scattering coefficient (b_{scat}) can also be measured. With the measurement of b_{scat}, aerosol absorption can be derived since $b_{ext} = b_{scat} + b_{abs}$ where b_{abs} is the absorption coefficient. It is also possible to calculate the *intensive* property single scattering albedo defined as $\omega_0 = \frac{b_{scat}}{b_{ext}}$.

For purely scattering aerosols ("white" particles) ω_0 should be identically equal to 1 since scattering will account for all of the measured extinction. For strongly absorbing ("black") aerosols ω_0 should tend toward zero, although scattering never vanishes, even for molecules[11,12].

2. Experimental

The CRD transmissometer which is used in tandem with a Nephelometer (Radiance Research M903 Seattle, WA) is shown in Fig.2.

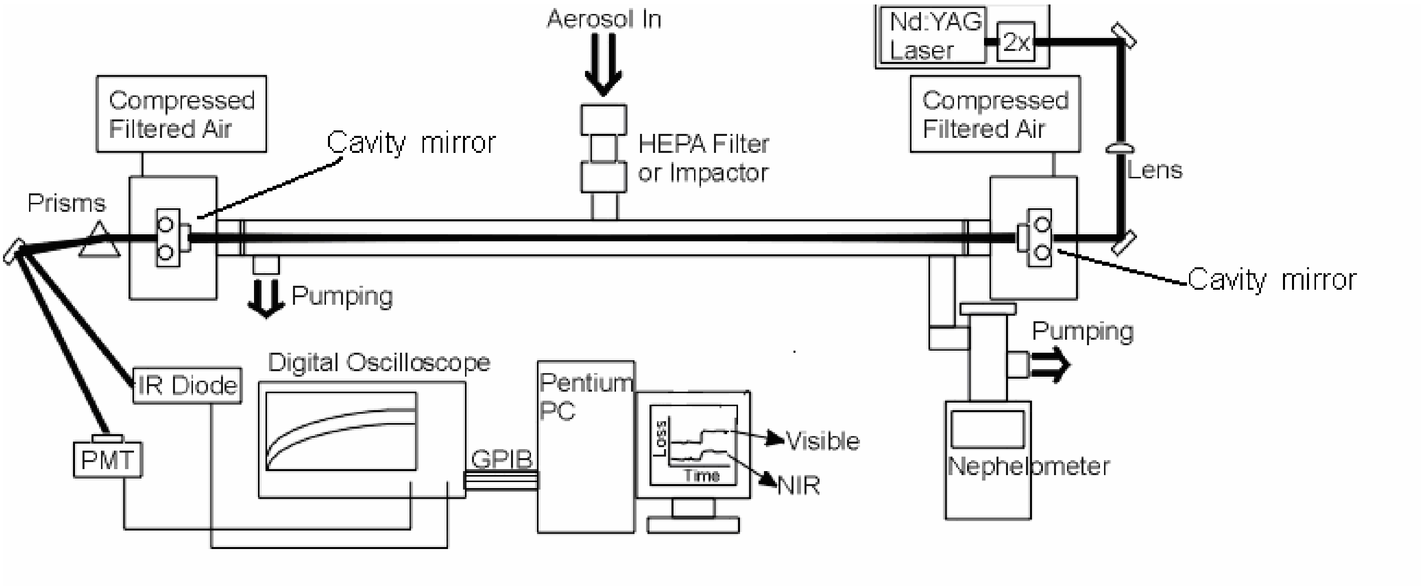

Fig.2 An experimental overview of the cavity ring down aerosol transmitter system

An air tight enclosure with a defined volume (the central tube in Fig 2) was used for air sampling. Airflow for direct ambient air sampling or airflows that have undergone various type of filtering can be drawn through the enclosure. The cavity mirrors are mounted inside rectangular acrylic boxes, while the central section is a copper tube (2.54 cm od, 97 cm length) with a 19 mm inlet in the center and 19 mm outlets for pumping at either end. Both outlets are connected to the inlet port of the nephelometer through a tee (T) connector. The outlet port of the nephelometer was connected to an oil-less vacuum pump (Gast DDA-P104-AA). The pumping speed was throttled to 3000 standard cubic centimeters per minute (sccm) with a needle valve, which provides minimum transmission loss for aerosols during passage through the transmissometer.

The nephelometer measures the scattering coefficient (b_{scat}) by measuring light scattered by the aerosol and subtracting light scattered by the air and the walls of the instrument to the detector. The light source is a flash lamp with a wavelength defining optical filter (530 nm). The nephelometer response is calibrated using clean air and a span gas (HFC-134a). The values of b_{scat} for clean air and the span gas are taken as 5×10^{-5} m^{-1} and 13.2×10^{-5} m^{-1} respectively (at 20° C and 530 nm) . Data taken by the nephelometer was transferred to a 500 MHz Pentium computer via a serial RS 232 connection.

Laser pulses (the fundamental and second harmonic of a New Wave Research MiniLase II Nd:YAG laser operating at 30Hz, λ = 532 and 1064nm) were generated and collinearly delivered to the cavity by right angle turning prisms and a 75 cm biconvex lens. The two wavelengths were separated after the ring-down cavity by a 532 nm 45° reflective dichroic beamsplitter. The visible signal (λ = 532nm) was collected using a Hamamatsu R955 PMT, while the IR signal (λ = 1064nm) was measured with a ThorLabs PDA255 Amplified InGaAs detector. Two 75 mm plano-convex lenses were used to focus each beam through an appropriate band pass filter and a diffuser plate and finally onto the detector's active surfaces. The exponentially decaying signals were digitized using a Tektronix TDS244 100 MHz 4-channel Digital Oscilloscope with 8-bit resolution. The digitized signals were averaged for 128 laser pulses (~ 4 sec) and then transported to a personal computer via a GPIB (IEEE-488) interface. The exponential decay constants were extracted using a non-linear Levenberg-Marquardt fitting routine included in the National Instruments LabView 8.2 and the ring-down and other data are displayed and archived by a set of Virtual Instruments developed in our laboratory. In order to accurately measure aerosol extinction, clean (HEPA filtered) air background measurements were frequently collected. This also allowed for the quantification of instrumental extinction measurement variability and drift over time. Assuming that the effect of absorbing atmospheric trace gases (*i.e.*, NO_2 and O_3) is constant within a given measurement cycle (typically an hour or less) the extinction, scattering and absorption of the matrix, particle-free air, can be effectively removed.

3. Results & Discussion

The agreement of the nephelometer's scattering measurements with the CRD's extinction measurements was evaluated using purely scattering aerosols made from ammonium sulfate and sodium chloride. With these aerosols absorption is negligible and single scattering albedo should be one. Extinction and scattering coefficients for two different concentrations of ammonium sulfate is shown in Fig 3.

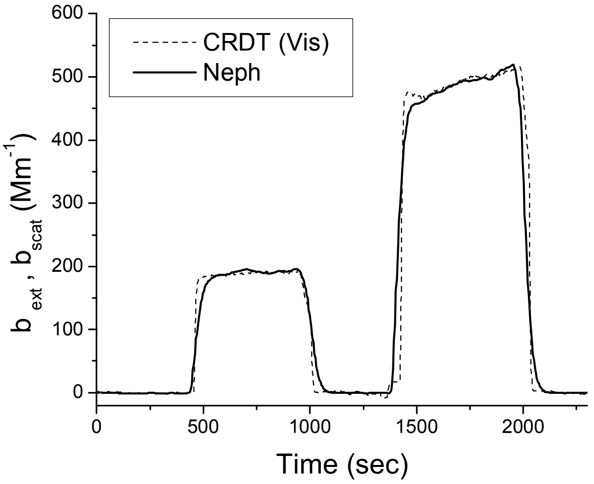

Fig 3 Extinction and scattering (b_{ext} and b_{scat}) of ammonium sulfate at two different concentrations

Table 1 presents the results of these measurements (taken as long time averages of the various properties) and shows that all of the measured single scattering albedo values are within 3 standard deviations of their theoretical value of unity.

Table 1: Measured and theoretical single scattering albedo for white, black and mixed aerosol

Solution	Relative Concentration	Measured ω_0	Standard Deviation	Theoretical ω_0
$(NH_4)_2SO_4$	Low	0.99	0.01	1
	High	1.01	0.007	1
NaCl	Low	0.98	0.04	1
	High	0.97	0.01	1
Nigrosin	Low	0.06	0.004	--
	Medium	0.07	0.004	--
	High	0.08	0.004	--
$(NH_4)_2SO_4$:Nigrosin	Low (12.5:1)	0.9	0.01	0.92
	High (12.5:1)	0.9	0.06	0.92
	Low(1:12.5)	0.14	0.01	0.11
	High (1:12.5)	0.1	0.006	0.11

Strongly absorbing (Nigrosin dye particles) aerosols were used to show that the single scattering albedo may be accurately determined when it is significantly less than one. Since $b_{ext} = b_{scat} + b_{abs}$, the implication is that absorption processes are dominant for Nigrosin. Even though absorption dominates, a small particle size dependent scattering component will still exist [13]. The single scattering albedo of Nigrosin aerosols should increase with Nigrosin concentration because the higher stock Nigrosin concentrations will cause the particle size distribution to shift towards larger particles. This trend is evident from table I.

Mixtures of ammonium sulfate and Nigrosin were analyzed and their single scattering albedo calculated based on a simple external mixing rule. For aerosol mixtures, the values for extinction, scattering and absorption are dependent upon how the aerosol is mixed. If the particles are externally mixed – multiple types of single species particles – then the measured values will be the concentration weighted sum of the species individual optical coefficients. If the particles are internally mixed – all chemical components mixed within the particle – then the measured extinction and scattering will appear as a weighted average of the species properties [14, 15]. The single scattering albedo should be a weighted average of the individual components in the solution atomized, assuming equal particle production efficiency. Table I shows the measured and theoretical values for the mixed aerosol solutions. The trend to higher single scattering albedo with higher proportion of ammonium sulfate is evident in the table. Furthermore, all of the measured values are within 3σ of their theoretical values of an externally mixed aerosol which implies good agreement between the data and the simple theory.

Comparison between the CRD transmissometer and Mie calculation for the ratio of extinction coefficients for (0.1, 0.3, 0.5 µm) polystyrene sphere is shown in table 2. In Mie calculations the refractive index of polystyrene and air are taken as 1.59 and 1.0 respectively. The number of density of polystyrene taken to be 0.1 sphere micron^{-3}. Although the values and trends are qualitatively consistent with the theoretical predictions, the agreement is less than satisfactory. The variation in the ratios at different concentrations of polystyrene could be a result of not having a uniformly generated 0.1 or 0.3 µm-polystyrene particles caused by clustering of the particles or surfactant used in suspensions of polystyrene solution. The deviation from the predicted b_{ext} ratios (from Mie calculations) is more noticeable at different concentrations of the smallest polystyrene spheres (0.1 and 0.3 µm), while the consistency of the ratios of b_{ext} at three different concentrations implies that the aerosol generated from 0.5 µm polystyrene sphere are well separated with minimum coagulation. The average and standard deviations for the ratios of extinction and scattering from the CRDT/N are shown and compared with Mie calculations in table 3.

Table 2: Comparison between the measured (CRDT/N) and Mie calculated Extinction coefficient ratios at 532 and 1064 nm for different size of polystyrene at different concentrations.

Polystyrene diameter (µm)	Extinction coefficient ratios (532nm/1064nm) at different concentrations			Calculated extinction coefficient ratios from Mie calculations
	Low Conc	Med Conc	High Conc	
0.1	9.7	12.4	11.6	16.6
0.3	11.15	8.51	7.33	10.1
0.5	4.08	4.06	3.91	3.77

Table 3: Comparison between the measured (CRDT/N) and Mie calculated extinction coefficient ratios at 475,532 and 1064 nm for polystyrene 0.5 µm spheres.

Ratios	Mie calculations	Mean	Standard deviation
CRD 532 / CRD 1064	3.77	4.01	0.05
Neph 475/CRD 532	1.16	1.12	0.01
Neph 475/ CRD 1064	4.54	4.51	0.05

Agreement between the measured and calculated ratios of extinction and scattering at three wavelengths for 0.5 µm-polystyrene spheres is a final piece of the validation studies. Again, the agreement between the 530 nm nephelometer and the 532 nm CRDT for these purely scattering particles argues for the quantitative accuracy of the CRD method.

4. Conclusion

Validation studies in our lab were pursued by comparing the CRD transmissometer measurements with the standard method of measuring scattering coefficients, the nephelometer. Theoretically calculated optical properties of lab generated aerosols were also compared with the CRDT/N measurements. First, it was shown that the CRDT/N is capable of measuring the extinction, absorption, and scattering coefficients of aerosols separately (scattering and extinction directly and absorption by difference). The accuracy of the CRDT/N measurements was further corroborated by the agreement between the ratios of absorption coefficients of nigrosin in the aerosol phase at two wavelengths (532 and 1064 nm) obtained from the CRDT/N and solution phase nigrosin. Third, the calculated ω_0 values for different concentrations of mixtures of black and white aerosols (0.92 and 0.11) and the measured values by the CRTD/N (0.90 and 0.14) are in close agreement. This is an additional confirmation of the reliability of the single scattering albedo measured by the CRDT/N [73], [63]. Fourth, the agreement between the ratio of the extinction coefficient at two different wavelengths (532 nm / 1064 nm) for purely scattering aerosols (polystyrene 0.5 µm) measured by CRDT/N (3.91) and calculated from Mie theory (3.77) confirms the accuracy of the CRDT/N measurements.

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