# P 1.8 DETERMINATION OF AEROSOL ABSORPTION CONSTANTS BY USING INTEGRATING SPHERE SPECTROMETRY FROM MILAGRO AND MCMA 2003 FIELD SAMPLES

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## 1. INTRODUCTION

Atmospheric aerosols are known to have direct and indirect effects on radiative balance and climate. The direct effects of aerosols on radiative balance are due to their ability to both absorb and scatter solar radiation, which contributes to heating and cooling of the atmosphere, respectively. The absorption properties of atmospheric aerosols are determined by their chemical composition and mixing state, while their light scattering strengths are determined from both composition and the size and shape of the particles. Understanding the direct aerosol effect and its "sign" (heating or cooling) is essential to accurately estimate the overall impact of anthropogenic aerosols on climate change and to develop working parameterizations for global climate modeling. Additionally, in order to predict the future aerosol effects on the climate system, the species responsible for the aerosol absorption and scattering must be identified and their optical properties quantified.

The dominant light-absorbing aerosol is thought to be black carbon (BC) produced from combustion. The absorption of solar light by BC particles is broad band and exhibits a wavelength dependence of $\lambda^{-1}$ with a commonly accepted mass specific absorption coefficient of 10 $m^2/g$ at 550 nm (Marley et al., 2001). However, BC does not usually occur alone in the atmosphere. It is associated with varying amounts of small molecular weight primary organic carbonaceous aerosols (OC), primarily polycyclic aromatic hydrocarbons (PAHs) also produced from combustion (Finlayson-Pitts and Pitts, 2000). It can also be associated with secondary OC, formed from the photochemical oxidation of the primary organic emissions, as well as biogenic emissions of isoprene, monoterpenes, and sesquiterpenes. These photochemical reactions give rise to conjugated acids, aldehydes and ketones, nitrophenos and nitrated arenes (Finlayson-Pitts and Pitts, 2000). In many cases the OC constitutes the major fraction of the total carbon with typically 70% OC and 30% BC (Marr, 1999; Gaffney and Marley, 2006).

As conjugated aromatic species, the PAHs have narrow absorbtion bands in the UV-visible range below 400 nm arising from the $\pi \rightarrow \pi^*$ electronic transition (Mangu 2007; Mangu et al., 2007). The presence of these PAHs in carbonaceous aerosols can give rise to an enhanced UV absorption over that expected from BC aerosols alone. The oxidized products also have strong narrow band absorption bands in the UV-visible range. The nitrated species especially have prominent absorption bands below 500 nm due to the addition of the lower energy $n \rightarrow \pi^*$ electronic transition (Mangu, 2007). Humic-like substances (HULIS) have been found to be produced in biomass burning and can also contribute to an enhanced shortwave absorption (Hoffer et al., 2006). Therefore, it is important to determine the actual aerosol absorption profiles for the mixed carbonaceous aerosols in order to quantify the aerosol effects on climate change and to evaluate the performance of climate models.

The primary effect of the atmospheric aerosols on atmospheric radiation can be expressed in terms of the extinction coefficient $\sigma_e$ defined as in equation (1).

$$\sigma_e = \sigma_a + \sigma_s \qquad (1)$$

The absorption ($\sigma_{a)}$ and scattering ($\sigma_s$) coefficients are derived from the real and imaginary parts of the complex refractive index defined as $m(\nu) = n(\nu) - ik(\nu)$, where $\nu$ is the frequency of light, n is the refractive index of the aerosol particle, and k is the aerosol absorption index. For the purpose of radiative transfer calculations, these optical constants are usually combined in a single-scattering albedo defined as in equation (2) (Twomey, 1977).

$$\omega = \sigma_s/\sigma_e = 1 - \sigma_a/\sigma_e \qquad (2)$$

The absorption profiles can be obtained for aerosol samples collected on filter media by using integration sphere reflectance spectroscopy (Marley et al., 2001). The integration sphere acts as an integrating detector to collect and spatially integrate the total radiant flux reflected from or transmitted by the sample. If the layer of aerosol particles on the substrate is optically thick, the effective real and imaginary components of the complex refractive index of the bulk aerosol sample can then be approximated, as a function of wavelength, from the reflectance spectra of the samples.

Urban areas are the primary sources of absorbing aerosols. Mega-cities, large urban and suburban centers whose populations exceed ten million inhabitants, are found to have some of the highest concentrations of polycyclic aromatic hydrocarbons and carbonaceous aerosols in the world (Marr, et al., 2004; Valasco, et al., 2004). The Mexico City metropolitan area (MCMA) is the largest urban center in North

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America and the second largest megacity worldwide. The presence of large amounts of highly absorbing carbonaceous aerosols in the MCMA basin leads to a reduction in solar flux of 17.6 % locally (Raga et al., 2001). The mass of these absorbing aerosols exported from this megacity into the surrounding region is estimated to be 6,000 metric tons per day or 2 megatons per year (Gaffney et al., 1999). The MCMA is therefore a major source of carbonaceous aerosols to the surrounding regions and the release of these highly absorbing aerosols will have an impact on radiative balance and climate on a regional scale.

Twelve-hour integrated samples of fine atmospheric aerosols (<0.1micron) were collected in Mexico City during April 2003 as part of the Mexico Megacity 2003 field study in collaboration with the MCMA 2003 air quality study. Samples were again collected in March 2006 as part of the Megacity Aerosol Experiment, Mexico City 2006 (MAX-Mex), which was part of the multiagency field campaign called the Megacities Initiative: Local and Global Research Observations (MILAGRO).

Measurements of aerosol absorption were obtained during these studies by using a 7-channel aethalometer (Thermo-Anderson). The absorption measurements obtained in the field at 370, 470, 520, 590, 660, 880, and 950 nm were used to determine the wavelength dependence of the aerosol absorption at the sites. This wavelength dependence is commonly referred to as the aerosol Ǻngstrom absorption exponent ($\lambda^{-\alpha}$). Since, unlike other absorbing aerosol species (e.g. humic like substances, nitrated PAHs), BC absorption is broadband with an Angstrom absorption exponent of -1, a comparison of the Ǻngstrom exponents serves as an indication of the presence of aerosol components with an absorption different from that expected from BC content alone (Marley et al., 2001). The Ǻngstrom exponents determined from the aerosol absorption measurements obtained in 2003 varied from -0.8 to -1.5 and those determined in 2006 varied from – 0.7 to – 1.3. Values were generally lower in the afternoon than the morning hours, indicating an increase in secondary aerosol formation and photochemically generated UV absorbing species in the afternoon (Marley et al., 2007).

Absorption profiles have been obtained in the laboratory on the 12-hour aerosol samples collected in Mexico City. Spectra were obtained on the samples directly from 280 to 900 nm by using integration sphere reflectance spectroscopy (Marley et al., 2001; Marley at al., 2007). The results confirm an enhanced absorption in the UV over that expected from BC absorption alone. In addition, some samples show spectral features that can be attributed to the presence of narrow band absorbers below 400 nm (Mangu, 2007; Mangu et al., 2007). These spectra are presented here along with spectra of the individual aerosol species to attempt to identify the aerosol components responsible for the enhanced UV absorption observed in both field and laboratory investigations. In addition, the effective real and imaginary components of the refractive index of the bulk samples have been approximated from the reflectance spectra

## 2. METHODOLOGY

Samples of fine (< 1 micron) atmospheric aerosols were collected in Mexico City from April 3 to May 1, 2003 as part of the Mexico Megacity 2003 effort of the Department of Energy's Atmospheric Science Program (DOE/ASP) in collaboration with the MCMA 2003 air quality study organized by Mario J. Molina and Luisa T. Molina, then at the Massachusetts Institute of Technology. Samples were collected on the rooftop of the CENICA (Centro Nacional de Investigación y Capacitación Ambiental) laboratory building ($19^0$ 21' 44.541" N, $99^0$ 04' 16.425 W) on the UAM Iztapalapa campus (Calle "Sur 10" No. 230, Colonia La Vicentina, Delegación Iztapalapa, México, D.F.)

Aerosol samples were again collected in Mexico City from March 1 – 28, 2006 as part of the DOE/ ASP's MAX-Mex (Megacity Aerosol Experiment – Mexico City) component of the MILAGRO (Megacity Initiative: Local and Global Research Observations) field campaign. The samples were collected at the Instituto Mexicano del Petróleo (T0 site) located in the north central part of Mexico City at latitude $19^o$ 29' N, longitude $99^o$ 09' W, and at an altitude of 2240 m above sea level. The aerosol samplers were located on the rooftop of Building No. 32 (Héctor Lara Sosa Building) 15 m above ground level. This site is approximately 16.1 km (10.0 mi) north-northeast of the site at CENICA that was used in 2003. Samples were also collected from March 4 to March 27, 2006 at the Technological University of Tecamac (T1 site), 30 km (18 mi) north of Mexico City and 18 miles northwest of site T0. This site, known as T1, is at latitude $19^o$ 43' N and longitude $98^o$ 58' W at an altitude of 2340 m above sea level.

The Mexico Megacity 2003 effort was undertaken to study the optical properties of the aerosols emitted in the MCMA. The MAX-Mex study was initiated to better understand the evolution and transport of pollutant aerosols from the Mexico City basin and to investigate their direct radiative effects in the Mexico City plume as a function of time, location and processing conditions. While site T0 was chosen to represent the fresh emissions in the MCMA, site T1 was expected to represent a mixture of fresh and aged pollutants as they exit the basin.

The aerosol samples were collected on quartz fiber filters by using high volume samplers (Hi-Q Environmental Products, Model HVP-3800AFC) that were equipped Sierra-type cascade impactors (Thermo Anderson), flow monitors and automated timers. The air samplers are equipped with brushless, three stage centrifugal fan blowers controlled by an electronic mass flow sensor that detects changes in the operators pre-set flow rate caused by changes in temperature, barometric pressure, and pressure drop due to dust loading on filter media. It compensates for these changes by adjusting the motor speed to maintain the pre-set flow rate at 40 standard cubic feet per minute (SCFM). Three separate LCD's, display elapsed time, total volume of air sampled, and instantaneous flow rate. The quartz filter samples were taken at 12-hour intervals from 5 am to 5 pm (day) and from 5 pm to 5 am (night). The volume of air sampled during the 12-hour time period averaged 740 $m^3$ with an average aerosol loading of 13 mg total carbon content.

The samplers were set up with the entrance and stage 4 impactor plates such that the top stage collected the particles with a size range of 1-10 micron on slotted filter media and the final stage collected the aerosol particles in a size range of 0.1-1 micron on an 8 inch x 10 inch quartz fiber filter. The size of the particles collected at each stage of the impactor is given by equation (3) where $d_{50}$ is particle diameter that is collected with 50% efficiency (a measure of the performance of the impactor) $C_c$ is a slip correction factor, $\eta$ is the viscosity of air, $D_j$ is the slot width and U is the gas velocity.

$$d_{50}\, C_c^{1/2} = [9\, \eta\, D_j\, (Stk_{50})/\, \rho_p\, U]^{1/2} \qquad (3)$$

The Stokes number ($Stk_{50}$) for a rectangular slot is equal to 0.53. For particles with a density ($\square_p$) of 1000 $kg/m^3$ the $d_{50}$ for the aerosols collected on the slotted filter media is 1-10 □m using the 4th stage of the impactor, and that collected on the final filter paper is less than 1 micron.

UV-visible spectra of the samples were obtained from 250 to 900 nm at 240 nm/min and 0.2 nm resolution on a Beckman DU-640 UV/visible spectrometer in percent transmission mode for reflectance measurements. The spectrophotometer employs a focused source beam and a photodiode array detector and is equipped with a Labsphere reflectance accessory (RSA-BE-65). The optical diagram of the reflectance accessory is shown in Figure 1.

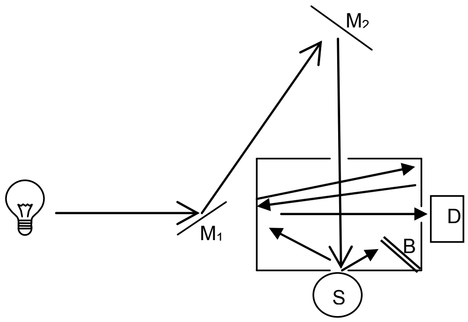

**Figure 1. Optical diagram of the reflectance accessory and integration sphere, mirrors (M1 and M2), sample (S), light baffle (B), sample placement (S) and detector (D).**

This reflectance accessory redirects the sample beam of the Beckman DU by means of two mirrors (Figure 1, M1 and M2) into the sample port of a 50 mm diameter integrating sphere coated with Spectralon diffuse-reflectance material. The integrating sphere collects and spatially integrates the total radiant flux reflected by the sample and therefore allows for the measurement of absorption on highly reflective or diffusely scattering samples. To prevent the detector from viewing the light that was directly irradiated by the incident flux and allow only light that has undergone at least two reflections from the sphere surface, the integrating sphere makes use of an internal Spectralon baffle (Figure 1, B).

Samples of aerosols collected from Mexico City were found to be very highly absorbing so that a small portion of the sample from the 8 in x 10 in filter papers were taken using a 10 mm punch. A mask, cut from a clean quartz filter was used to reduce the aerosol sample surface viewed by the reflectance accessory to approximately 6 mm. Samples were placed at the reflectance port by using either a 0° or an 8° sample mount (Labsphere). The 0° mount causes the specular component of the reflection to direct out of the sphere through the entrance port and therefore excludes it from the measurements yielding only a diffuse reflectance measurement, while the 8° mount collects both specular and diffuse components of the reflected light giving a measurement of total reflectance. A light trap was fitted behind the sample holder to prevent unreflected stray light from entering the sample compartment. The wavelength dependence of the mass specific aerosol absorption is obtained from these spectra and total carbon measurements.

The spectra obtained on the 12-hour aerosol samples were compared with those obtained on standard diesel particulate matter (NIST, SRM1650b), reference air particulate matter collected on filter media (NIST, RM 8785), reference humic acid, (Fluka) humic acid sodium salt (Aldrich), two standard PAH mixtures (Fischer Scientific; Cat # US-EPA-2138N; Cat # US-EPA-2139N), as well as pure substituted aromatic species known to be major aerosol components. The standard PAH mixtures included acenaphthene, anthracene, benzo[k]fluoranthene, chrysene, fluorine, indeno[1,2,3-cd]pyrene, naphthalene, and pyrene in mixture 1 and acenaphthylene, benzo[a]anthracene, benzo[b]floranthene, fluoranthene, benzo[ghi]perylene, benzo[a]pyrene, dibena[a,h]anthracene, and phenanthrene in mixture 2. The single species included 2-nitrophenol, 3-nitrophenol, 4-nitrophenol, 1-nitropyrene, 1-nitronaphthalene, 9-nitroanthracene, and 6-nitrochrysene.

The optical constants of the aerosol samples were determined by using a combination of the Kramers-Kronig ransformation (KK) and the Kubelka-Munk function (Marley et al., 2001). The KK is a numerical method for obtaining the absorbance and refractive index data from reflectance spectra (Lichvar et al., 2002). The real (n) and imaginary (k) parts of the complex index of refraction can be calculated from the reflectance spectrum using equations (4) and (5) where R is the reflectance spectrum, $\upsilon$ is the wavenumber, $\theta$ is the phase shift angle of the sample.

$$n(\upsilon) = \frac{1-R(\upsilon)}{1 + R(\upsilon) - 2\sqrt{R(\upsilon)}\cos(\theta(\upsilon))} \qquad (4)$$

$$k(\upsilon) = \frac{-2[R(\upsilon)\cos(\theta(\upsilon))]}{1 + R(\upsilon) - 2\sqrt{R(\upsilon)}\cos(\theta(\upsilon))} \qquad (5)$$

For a given wavenumber the phase shift is calculated using the equation (6).

$$\theta(\upsilon_m) = \frac{2\upsilon_m}{\pi} \int_0^\infty \frac{\ln\sqrt{R(\upsilon)}\,d\upsilon}{\upsilon^2 - \upsilon^2_m} \qquad (6)$$

The KK transform often gives good results for the real refractive index (n). However, the results for absorption index (k) are often negative due to irregularities in aerosol surfaces. Therefore, the values for absorption index were estimated from the Kubelka-Muck function shown in equation (7) (Marley et al., 2001).

$$F(R) = K/S = (1-R^2)/2R = (8/3)(k/s) \qquad (7)$$

## 3. RESULTS

The UV-visible spectra of the PAH mixtures and some nitrated PAHs are shown in Figures 2 and 3. The PAHs have narrow band maxima at 320, 340, 360, and 405 nm. The nitro substituted PAHs have narrow band maxima shifted to lower energies. The band maxima for the nitro PAHs are as follows; 1-nitropyrene at 345, 470, and 495 nm, 1-nitronaphthaleneat 356 nm, 9-nitroanthracene at 380 nm, and 6-nitrochrysene at 355 and 420 nm.

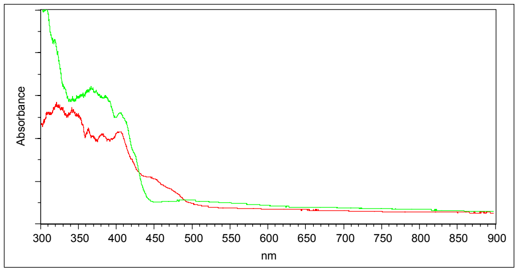

**Figure 2: UV-visible spectra of the PAH mixtures.**

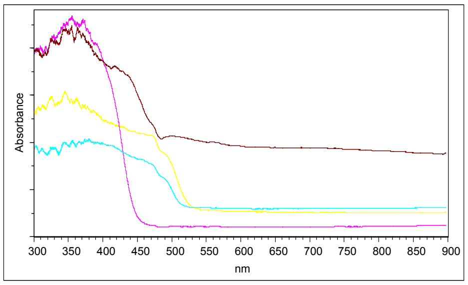

**Figure 3: UV-visible spectra of 1-nitropyrene (yellow), 1-nitronaphthalene (pink), 9-nitroanthracene (blue), and 6-nitrochrysene (brown).**

Some representative UV-visible spectra obtained on 12-hour aerosol samples collected during the Mexico Megacity 2003 field study are shown in Figure 4. The absorption profiles did not vary significantly during the study. Narrow band absorbances were observed in some spectra between 320-360nm similar to that observed in the PAH mixtures. The absorption profiles in Figure 4 would be expected from an external mixture of small amount of mixed PAHs and the broadband absorbing BC as shown in Figure 5.

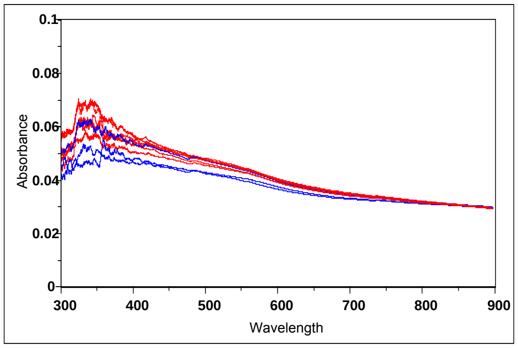

**Figure 4. UV-visible spectra of 12-hour aerosol samples collected at CENICA during the Mexico Megacity 2003 field study. Red spectra are day; Blue spectra are night.**

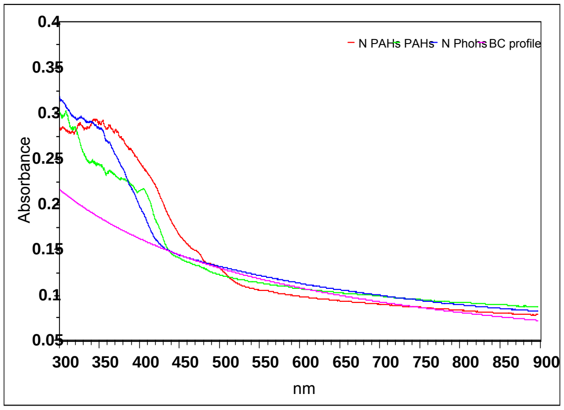

**Figure 5. Calculated absorption profiles for diesel soot (pink) and some mixed aerosols; BC and mixed PAHs (blue), BC and nitrated PAHs (red), BC and nitrophenols (green).**

Some representative UV-visible spectra obtained from 12-hour aerosol samples collected during the MAX-Mex study are shown in Figure 6. The absorption profiles of samples collected at site T0 during 2006 were much more variable than those obtained in 2003. In many cases, very intense narrow band absorbances were observed at 325, 330 and 360 nm typical of the PAHs. The absorption profiles from samples collected at site T1 were less variable and more representative of the broadband absorptions typical of BC aerosols or HULIS. However, in general higher absorptions were more evident on the nighttime samples at site T1 whereas there was no clear trend of differences observed between daytime and nighttime samples collected in Mexico City either in 2003 or 2006.

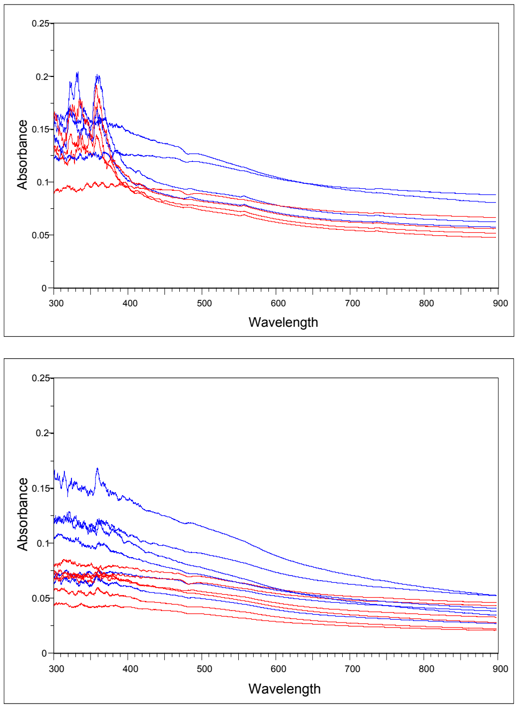

**Figure 3. UV-visible spectra of 12-hour aerosol samples collected at site T0 (top) and site T1 (bottom) during the MAX-Mex field study. Red spectra are day; Blue spectra are night.**

## 5. ACKNOWLEDGEMENT

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