P1.5 INFRARED SPECTRA OF AEROSOL SAMPLES FROM MEXICO CITY DURING MILAGRO

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1. INTRODUCTION

Atmospheric aerosols, can impact the earth's radiative balance and climate both directly and indirectly. These effects represent some of the largest uncertainties in the assessment of radiative forcing (IPCC, 2007). The direct aerosol effect refers to the scattering and absorption of solar and infrared radiation in the atmosphere, while the indirect effect refers to the influence of aerosols on cloud formation and on cloud radiative properties. Since aerosols can both scatter and absorb solar radiation, they can contribute to both cooling and heating of the atmosphere and their overall impact on climate will be dependent upon their chemical composition, physical size and shape, and location in the atmosphere (Gaffney, Marley, 1998).

The dominant light-absorbing aerosol species is thought to be black carbon (BC) produced from incomplete combustion of fossil and biomass fuels. Black carbon is a broadband absorber with a wavelength dependence of λ^{-1} over the entire spectral range. Combustion also produces primary organic carbonaceous aerosols, which are composed primarily of smaller molecular weight polycyclic aromatic hydrocarbons (PAHs). This primary organic carbonaceous aerosol is released into the atmosphere along with BC during the burning of hydrocarbon fuels (Finlayson-Pitts and Pitts, 2000; Marr, 1999). As conjugated aromatic species, the PAHs have narrow absorption bands UV-visible range below 400 nm arising from the π → π* electronic transition (Mangu 2007; Mangu et al., 2007). The presence of PAHs in carbonaceous aerosols in spectrally significant quantities can give rise to an enhanced UV absorption over that expected from BC alone.

Secondary organic aerosols, formed from the photochemical oxidation of the primary organic emissions, as well as biogenic emissions of isoprene, monoterpenes, and sesquiterpenes, give rise to conjugated acids, aldehydes and ketones, nitrophenols and nitrated arenes (Finlayson-Pitts and Pitts, 2000) These 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 → π* electronic transition (Mangu, 2007).

Humic-like substances (HULIS) have also been found to be produced in biomass burning and can contribute, along with the PAHs, to give an enhanced absorption over that anticipated by BC alone. (Hoffer et al, 2006, Kirchstetter Novakov, 2004). Normally produced from the decomposition of organic matter in terrestrial ecosystems, both humic acids and smaller molecular weight fulvic acids contain polycarboxylic acid groups and conjugated unsaturated sites that absorb radiation below 400 nm (Gaffney et al., 1996). The atmospheric HULIS are expected to have similar absorption bands to the humic and fulvic acids found in natural waters, (Andreae and Gelencser, 2006; Hoffer et al., 2006).

Megacities, large urban and suburban centers whose populations exceed ten million inhabitants, are steadily increasing worldwide with the most rapid growth in the tropical areas of South America and Asia. In general, megacities suffer from poor air quality due to the cumulative effects of population growth, industrialization, increased vehicle usage and total energy consumption. The Mexico City metropolitan area (MCMA) is the largest urban center in North America and the second largest megacity worldwide. The presence 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 mega-tons per year (Gaffney et al., 1999). Since freshly formed BC aerosols are hydrophobic, they are expected to be more resistant to washout and have longer lifetimes than more hygroscopic aerosols such as sulfate and nitrate (Gaffney and Marley 2005; Dua et al., 1999). In addition, since these aerosols are introduced into the atmosphere at altitudes that would be considered to be in the free troposphere 300 km away they are assumed to have longer lifetimes than aerosols released at lower altitudes (Raga et al., 2001). 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 the radiative balance and climate on a regional scale.

Measurements of aerosol optical properties were made in Mexico City in March 2006 as part of the Megacity Aerosol Experiment, Mexico City 2006 (MAX-Mex), which was sponsored by the U.S. Department of Energy (DOE). This study was part of the multiagency field campaign called the Megacities Initiative: Local and Global Research Observations (MILAGRO). 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.

Twelve-hour integrated samples of fine atmospheric aerosols (<0.1micron) were collected during MAX-Mex for spectral and radionuclide

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characterization from 5 am to 5 pm (day) and from 5 pm to 5 am (night). Samples were collected on quartz fiber filters with high volume impactor samplers located at an urban site at the Instituto Mexicano del Petroleo (IMP), in the northwestern part of the Mexico City center. This site, known as T0, was chosen to represent the fresh emissions in the MCMA. Samples were also obtained at the Technological University of Tecamac, located 18 miles northwest of T0. This site, known as T1, was expected to represent a mixture of fresh and aged pollutants as they exit the basin.

Measurements of aerosol absorption were obtained at site T0 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 aerosol Ǻngstrom absorption exponents ($\lambda^{-\alpha}$) by linear regression. Since, unlike other absorbing aerosol species (e.g. humic like substances, nitrated PAHs), BC absorption is relatively constant from the ultraviolet to the infrared with an Angstrom absorption exponent of -1 (Marley et al., 2001), 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. The Ǻngstrom exponents determined from the aerosol absorption measurements obtained at site T0 varied from – 0.7 to – 1.3 during the study and 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).

Continuous absorption spectra have also been obtained in the laboratory on the 12-hour aerosol samples collected at sites T0 and T1. These spectra were obtained on the samples directly from 280 to 900 nm by using integration sphere reflectance spectroscopy (Marley et al., 2001). 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 typical of conjugated PAH and nitrated aromatic species (Mangu, 2007; Mangu et al., 2007).

In this study, infrared spectra have been obtained on the 12-hour aerosol samples collected during the MAX-Mex study to identify species responsible for enhanced UV absorption observed in both field and laboratory investigations.

2. METHODOLOGY

Samples of fine (<1 micron) atmospheric aerosols were collected from March 1 to March 28, 2006 at the IMP laboratories in Mexico City. This site, known as T0, is 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. Aerosol samples were also collected from March 4 to March 27, 2006 at the Technological University of Tecamac, 30 km (18 mi) north of Mexico City. 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 aerosol samples were collected on quartz fiber filters by using high volume samplers (Hi-Q Environmental Products, Model HVP-3800AFC) equipped with cascade impactors (Thermo Anderson). 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.

Infrared spectra were obtained on the 12-hour aerosol samples from 500 cm^{-1} to 4000 cm^{-1} by diffuse reflectance. The Aerosol samples were removed from the surfaces of the glass fiber filters by using a Si-Carb sample prep kit (Thermo Scientific). This sampler uses adhesive backed silicon carbide paper disks to abrade the surface of the sample, transferring a small amount of sample to the disk, which is then placed into a Smart Collector diffuse reflectance accessory (Thermo-Fischer Scientific – Nicolet). The Smart Collector incorporates unique collection optics that inherently maximize diffuse reflected radiation while minimizing the specular reflected component. This design also eliminates the need for any sample height adjustments since it is always at the optimum position and optical focus. The sample holder is equipped with an integral gold mirror that is used as a background reference.

All Spectra were collected on a Nicolet 6700 FTIR Spectrometer equipped with a DLaTGS/KBr detector at a scan speed of 50 scans per minute, a resolution of 4 cm^{-1} and using a Happ-Genzel apodization function. 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.

3. RESULTS

Infrared spectra of some nitro-substituted PAHs are shown in Figure 1. These species show narrow intense absorption bands between 500 and 1600 cm^{-1}. This region is known as the “fingerprint region” because it usually contains complicated absorption patterns arising from molecular bending vibrations in complex molecules, which can be used to identify pure compounds. The unsubstituted PAHs also display narrow absorption bands in this region.

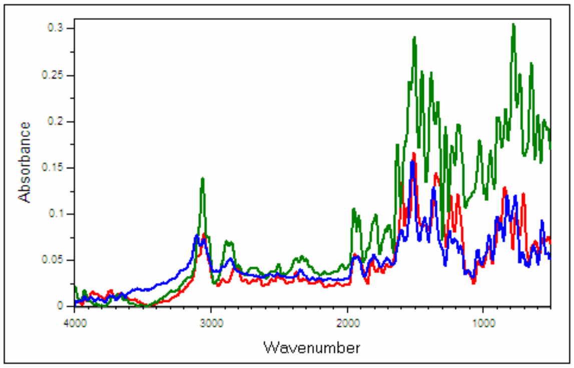

Figure 1. Infrared absorption spectra of 1-nitropyrene (red), 9-nitroanthracene (green), 6-nitrochrysene (blue) and diesel particulate matter (black).

The infrared absorption spectrum of NIST diesel particulate matter is shown in Figure 2. The diesel soot absorption spectrum generally exhibits the expected inverse relationship with wavelength typical of a broadband absorber with an Ångstrom exponent in the mid-infrared of –1. However, it also shows fine structure in the “finger print” region typical of the PAHs.

Figure 2. Infrared absorption spectrum of NIST diesel particulate matter.

The infrared spectra of humic acid and humic acid sodium salt were obtained as mode compounds for atmospheric HULIS. The spectra are shown in Figure 3 and the band assignments for these macromolecular compounds are given in Table 1 (Gaffney et al., 1996). The spectra are dominated by the broad O-H stretch of carboxylic acids from 3300-3450 cm-1 and the narrower stretching bands of the carboxylate group from 1100-1650 cm^{-1}. In addition, superimposed on the broad O-H stretch is the narrower bands arising from the aromatic and aliphatic C-H stretch.

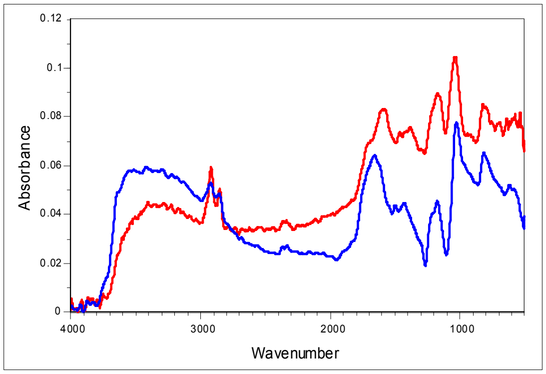

Figure 3. Infrared absorption spectra of humic acid (red) and humic acid sodium salt (blue).

Table 1. Infrared band assignments for humic acids.

cm-1	Assignment
3300-3450	H bonded O-H stretch
3100-3230	Aromatic C-H stretch
2970-2985	Aliphatic C-H stretch
1550-1680	Asymmetric carboxylate COO stretch
1380-1410	Symmetric COO stretch
1180-1045	C-C or C-OH stretch
900-1100	C-CO-O-CO-C stretch

Representative infrared spectra of 12-hour aerosol samples collected at the T0 and T1 sites are shown in Figures 4 and 5. These spectra are also dominated by features attributed to carboxylic acid groups similar to that seen in the spectra of the humic acids. The broad O-H stretch appears from 3345-3450 cm^{-1} and is seen in most all of the spectra. As well, the asymmetric COO stretch is seen between 1620-1640 cm-1 and the symmetric COO stretch appears from 1420-1435 cm^{-1}. In addition, a very intense combination of overlapped bands appears between from 850-1200 cm^{-1}. The C-O-C stretching vibrations of multifunctional esters generally appears in this region along with the stretching vibrations of substituted ethenes. The fine structure in the “fingerprint region” typical of the PAHs and substituted PAHs can be seen below 1000 cm^{-1} in some samples but is not very intense in any of them. Bands in the regions of 1510-1545 cm^{-1} and 1345-1365 cm^{-1} appear as shoulders on the more intense carboxylate bands and can be assigned to the asymmetric and symmetric N=O stretch of nitrated aromatics.

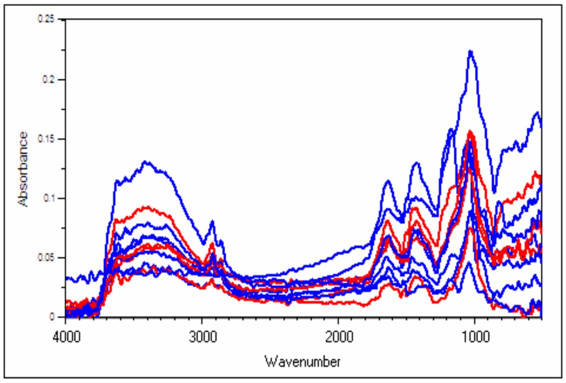

Figure 4. Infrared absorption spectra of 12-hour aerosol samples collected at site T0 during the MAX-Mex field study. Red spectra are day; Blue spectra are night.

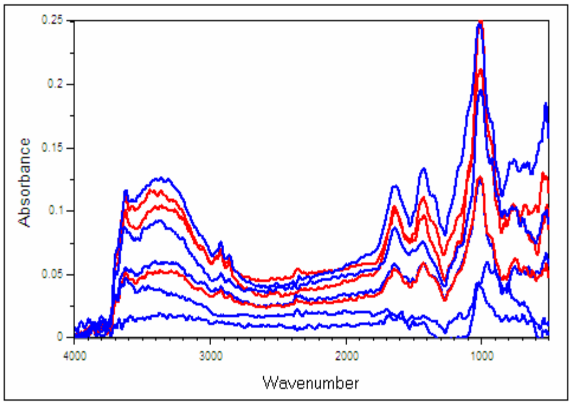

Figure 5. Infrared absorption spectra of 12-hour aerosol samples collected at site T1 during the MAX-Mex field study. Red spectra are day; Blue spectra are night.

The diffuse reflectance infrared technique is most sensitive to compounds at the surface of the particles. Therefore, the very intense carboxylic acid and ester signatures of the aerosols collected in Mexico City is an indication of coating of the original primary aerosols with oxidized secondary organic species. During the first part of the study, the entire region was impacted by biomass burning (Gaffney et al., 2007). This could have produced HULIS materials which coated the primary aerosols. The spectra in Figures 4 and 5 that show a very low intensity of carboxylate bands were obtained from samples collected later in the study period. However, total carbon (determined from isotope ratio mass spectrometry) did not show a decrease during this period. The latter part of the study was dominated by heavy rains which may have contributed to less photochemical production of secondary aerosols, less contribution from biomass burning, and/or washout of the more hygroscopic aerosol species.

4. CONCLUSIONS

Infrared spectra of aerosol samples all show a broad band at 3300-3450 cm^{-1} due to the OH stretch of carboxylic acid groups. In addition samples exhibit bands in the region of 1620-1640 cm^{-1} due to the asymmetric COO stretch and at 1420-1435 due to the symmetric COO stretch. The appearance of these dominant bands in the IR spectra of the aerosol samples is an indication of high concentrations of HULIS on the surface of the aerosols.

The samples collected during the last week of the study period have spectra with less intense bands than those collected during the beginning of the period. The latter part of the study was dominated by heavy rains which may have contributed to less photochemical production of secondary aerosols, less contribution from biomass burning, and/or washout of the more hygroscopic aerosol species.

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