J17.5 DETERMINING AEROSOL ANGSTROM ABSORPTION COEFFICIENTS: COMPARISON OF FULL SPECTRUM INTEGRATING SPHERE REFLECTION SPECTROSCOPY WITH 3 AND 7 WAVELENGTH FILTER ABSORPTION METHODS.

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1. INTRODUCTION

Atmospheric aerosols have been identified as a major uncertainty in climate forcing due to their direct and indirect radiative effects. Both scattering and absorption of radiation by aerosols is of concern in the direct effect, with absorption of solar radiation a major uncertainty. A key component of light absorbing aerosols is primary carbon soot generated by incomplete combustion, which is non-volatile, non-reactive, and hydrophobic. These particles appear black when collected on filter media due to their broadband absorption properties and have therefore been historically referred to as “black carbon”. Light absorbing aerosols also contain a semi-volatile organic component which may be either primary or secondary in origin and has been referred to generically as “organic carbon”. Light absorbing carbonaceous aerosols are therefore highly heterogeneous in nature and consist of complex mixtures of both semi-volatile and more refractory materials.

The broad band absorption profiles of light absorbing aerosols can be described using a simple exponential fit ($\lambda^{-\alpha}$), known as the Ångstrom absorption exponents (AAE). The absorption spectrum of freshly generated diesel soot has an AAE of 1 with a commonly accepted mass specific absorption coefficient of $10 m^2/g$ at 550 nm (Marley et al., 2001). It was long thought that black carbon was the main light absorbing aerosol species and all aerosol light absorption was described by an AAE of 1. However, other light absorbing species have recently been identified in the semi-volatile aerosol fraction (Andreae and Gelencser, 2006) that show an enhanced absorption in the UV or visible regions over that attributed to black carbon aerosols alone (Kirchstetter et al., 2004). This enhanced absorption leads to variation of the aerosol AAE’s from 1 and the magnitude of this variation can be useful in identifying the species responsible for the enhanced absorption.

Aerosol absorption has been traditionally measured in the field by filter based transmission techniques. The aerosols are collected on filter media and the fraction of light absorbed (A) is recorded as the negative logarithm of the reduction in light intensity transmitted through the particle laden filter according to the Brouguer-Lambert Law;

$$A = 1- \exp(-kd) \tag{1}$$

where k is the linear absorption coefficient of the material making up the particles and d is the thickness of the material.

It is widely accepted that scatter from both the filter medium and the particles deposited on the filter results in light losses not associated with absorption yielding errors in these transmission measurements. There have been several different approaches to correct for these scattering effects including comparison of results from measurements of aerosol composition (Gundel et al., 1984; Allen et al, 1999), the use of laboratory generated “standard” aerosol species (Bond et al., 1999; Virkkula, et al., 2005), the development of empirical corrections from scattering measurements (Weingartner, et al., 2003; Arnott, et al., 2005) and the use of additional detectors to measure the scatter independently of absorption (Petzold, et al., 2005).

The most effective spectroscopic method available for measuring the absorbance of highly scattering samples is the use of state of the art integration spheres, which collect and spatially integrate the total radiant flux reflected from and/or transmitted by the sample (Marley et al., 2001). All radiation not absorbed by the sample is directed towards the detector and any reduction in the intensity of measured light in the presence of the sample is due to absorption only. However, the loss of incident light from scatter is not the only source of error in the measurement of absorbance in non-homogeneous scattering samples.

In the strictest sense, the relationship in Equation 1 is only applicable to transmission measurements on homogeneous samples that have no scatter. For the case of highly scattering samples and diffuse illumination, the distance the light travels through the sample (d in Equation 1) is not equal to the sample thickness. In addition, the sample composition, which affects the magnitude of particle absorption, also affects the distance travelled through the sample. The value of d is therefore not only unknown but is also not constant and the commonly used logarithmic relationship of k with reduction in light intensity is no longer applicable.

There are several mathematical treatments of remission (reflection + scatter + transmission) for highly scattering samples. The most widely used of these is Kebulka-Munk Theory, which treats the propagation of light through a scattering medium as a two flux approximation to the equation of radiative transfer (Dahm and Dahm, 2007; Lindberg et al., 1999). For the case of diffuse reflectance from an infinitely thick

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sample, transmission is 0 and the remission (R) from the sample is given by the Kubelka-Munk function;

$$f(R) = (1 - R)^2/2R = K/S \qquad (2)$$

where K is the absorption coefficient and S is the scattering coefficient of the sample. Although direct measurement of aerosol absorption by diffuse reflection remains problematic due to the fact that S is not easily identified, an absorption profile and therefore the AAE can be obtained. The logarithm of equation 2 yields a curve that corresponds to the real absorption spectrum of the sample that would be obtained by an ideal transmission measurement displaced by an offset in the ordinate direction (Wendlandt and Hecht, 1966).

$$\log f(R) = \log K - \log S \qquad (3)$$

This work overviews the use of integrating sphere reflection spectroscopy to obtain aerosol AAEs from full spectrum (280-900 nm) aerosol absorption profiles. A comparison is presented with AAEs obtained in the field by diffuse transmission measurements made with a 3-wavelength Particle Soot Absorption Photometer (PSAP) and a 7-wavelength aethalometer that indicates the importance and need for full spectrum determinations for improved aerosol absorption evaluations.

2. METHODOLOGY

Aerosol absorption was measured at the University of Arkansas at Little Rock and at the Instituto Mexicano de Petroleo Laboratories (IMP) in the north central part of Mexico City by using a seven-wavelength aethalometer (Thermo-Andersen). The aerosols in the air sample are collected within the instrument by continuous filtration through a paper tape strip. The optical attenuation of light transmitted through the deposited aerosol particles is then measured sequentially at seven wavelengths (370, 450, 520, 590, 660, 880, and 950 nm) by changing the source. As the sample is deposited on the paper tape strip, light attenuation increases steadily. At high sample loadings, the high absorption causes the instrument sensitivity to decrease. Therefore, the instrument automatically advances the tape to a new sample spot when light attenuation becomes severe.

Under normal operating conditions, the instrument calculates the black carbon content of the sample from the optical attenuation measurements, assuming that black carbon is the main absorbing aerosol species in the samples (Hansen et al., 1982). The aethalometer results were converted to aerosol optical absorption at each wavelength by using the manufacturer's values for the black carbon mass absorption efficiency. The aerosol absorption measurements were recorded at five-minute intervals for each of the seven wavelengths and reduced to one-hour averages. Measurements obtained just prior to and immediately after the filter tape advance were discarded as outliers (Arnott et al., 2005). The AAEs were calculated by a least squares fit of the seven aerosol absorption values.

$$\ln(A) = -\alpha \ln\lambda + \ln \beta \qquad (4)$$

Aerosol absorption was measured at the Mount Bachelor Observatory located on the summit of 162 a dormant volcano in central Oregon with a three-wavelength PSAP (Radiance Research, Shoreline, Washington). This instrument records the differential light transmission through a glass fiber filter (E70-2075W, Pallflex 197 Products Corp., Putnam, Connecticut) as particles are loaded onto the filter. The data were corrected for variations in sample flow rate (Bond et al., 1999) and for sample scattering (Virkkula et al., 2005). The raw scattering and absorption data was collected as 20 second averages and then reduced to 1-hour averages. After discarding data below instrument detection limits, aerosol AAEs were calculated from the three absorption measurements at 467, 530 and 660 nm.

The samples collected by the PSAP and aethalometer were removed from the instruments and saved for subsequent spectral analysis. Samples of fine (<1.0 micron) aerosols were also collected at IMP by using high volume samplers (Hi-Q Environmental Products, Model HVP-3800AFC) equipped with cascade impactors (Thermo Anderson). The aerosol samples were collected on 8 in x 10 in quartz fiber filters (Pall Life Sciences).

Absorption spectra were obtained on the samples in the laboratory from 280 to 900 nm by using a high performance Perkin Elmer Lambda 850 spectrometer equipped with a 150 mm integrating sphere accessory. These continuous spectra have also been used to obtain the aerosol AAEs by linear regression over the entire UV-visible spectral range. These results are compared to results obtained from the absorbance measurements obtained in the field by the PSAP and aethalometer.

3. RESULTS

Figure 1 shows a comparison between the aerosol AAEs determined in the field with the three-wavelength PSAP and in the laboratory from continuous UV-Visible spectra using all 260 points. Also shown is a comparison of the AAEs calculated from the UV-visible spectra using only the absorbances at the three wavelengths of the PSAP (467, 530, and 660nm). The relationship has a slope of 0.6 and an intercept of 0.25. This is an indication that limiting the wavelength range to below 460 nm results in a low bias to the AAEs especially for higher values.

A comparison between the AAEs calculated from the seven wavelengths of the aethalometer and those calculated from the full UV-visible spectra (350 points) obtained in the laboratory on the filter samples is shown in Figure 2. Also shown is a comparison of the AAEs calculated from the UV-visible spectra using only the absorbances at the seven wavelengths of the aethalometer (370, 450, 520, 590, 660, 880, and 950 nm). The relationship has a slope of 0.88 and an intercept of 0.06 showing the improvement in the AAE calculation when the UV wavelength at 370 nm is included.

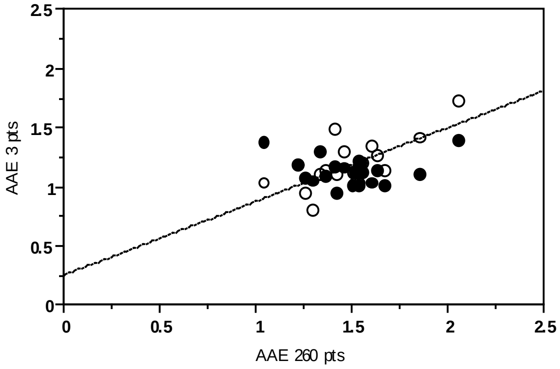

Figure 1. Comparison of aerosol AAEs calculated in the field with a three-wavelength PSAP (•) with those determined on the same samples from continuous UV-visible spectra (260 points). Also shown are the AEAs determined from the UV-visible spectra using only the three wavelengths of the PSAP (o).

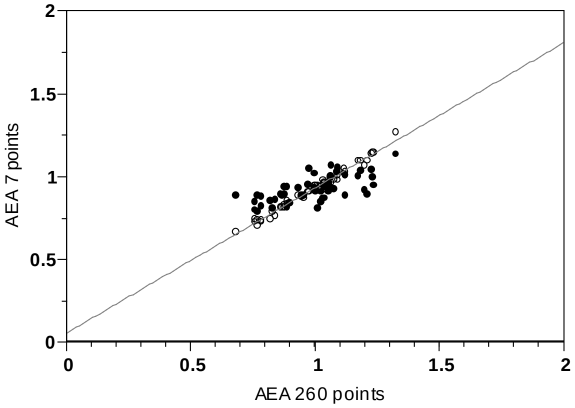

Figure 2. Comparison of aerosol AAEs calculated in the field with a seven-wavelength aethalometer (•) with those determined on the same samples from continuous UV-visible spectra (260 points). Also shown are the AEAs determined from the UV-visible spectra using only the seven wavelengths of the aethalometer (o).

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