Optical Extinction Spectroscopy at Moderate Resolution: Insights into Problems of Weak Absorption Bands

J. J. MICHALSKY

Atmospheric Sciences Research Center, State University of New York, Albany, New York

B. A. LEBARON

Pacific Northwest Laboratory, Richland, Washington

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ABSTRACT

Sunphotometry is a common technique for characterizing aerosol properties. Photometers used for these measurements have a series of narrow-band filters that are chosen to avoid molecular absorption features, except for the very broad Chappuis ozone band centered near 600 nm. This note reports on a set of moderate resolution spectra that were used to derive optical depth every 10 nm throughout the visible and near infrared. The usefulness of this type of continuous optical depth spectrum for selecting sunphotometer filters and the importance of often-ignored, weak molecular bands near 600 nm are discussed.

1. Introduction

In nature, aerosol particles are not monodispersed, but may have many sizes. Mie calculations show that even a modest size distribution leads to a smooth, rather than abrupt, change in aerosol optical depth with wavelength. This justifies sampling aerosol optical depth at only a limited set of widely separated wavelengths. In sunphotometer measurements of aerosols, these wavelengths are defined by narrowband interference filters.

In order to select the central wavelength and the acceptable width of these filters, one must know the atmospheric absorption features within the sampling region. Presumably, one selects filters by consulting the literature for atmospheric spectra. As an example, we used the spectra of Beckers et al. (1976) to select regions relatively free of absorption lines. It has a resolution better than 0.1 nm, and it identifies most of the spectral lines as solar or atmospheric. Even with a knowledge of the contaminator, however, it is difficult to assess the effect on a given filter, particularly if the contaminator is a highly variable species such as water vapor.

We have developed an instrument that measures global and diffuse solar photometric radiation (Michalsky et al. 1986) and calculates direct illuminance as part of its operational algorithm. Its photometric response is directly proportional to that of the average human eye. It is possible to calculate a total column optical depth for the visible using the direct illuminance obtained from this instrument. A question arose when comparisons with standard narrowband sunphotometer measurements near the photometric peak wavelength of 555 nm indicated that the photopic filter optical depth data were, on the average, 0.005 higher (LeBaron et al. 1989). It appeared that the photopic filter was contaminated by an attenuator other than aerosol even after ozone and Rayleigh scattering contributions were removed. Molecular oxygen absorbs strongly at about 690 nm, but in the wings of the photopic band and, consequently, has little impact. McClatchey et al. (1972) acknowledged the existence of very weak water vapor and oxygen bands below this wavelength, which were omitted in the popular LOWTRAN atmospheric transmittance code (Kneizys et al. 1983) because of the unreliability of data in this region.

This note describes an optical depth spectrum having a resolution of 10 nm from 380 to 1100 nm that we used to investigate our photometry questions. A spectrum of optical depth appears in Leiterer and Schulz (1987), but it has lower spectral resolution than that presented here, and the points we wish to make concerning these weak bands are not clearly made using their spectrum.

2. Description of measurements

To examine this contamination question more closely, optical depths were calculated every 10 nm from 380 to 1100 nm for a clear October morning.

Corresponding author address: Dr. Joseph J. Michalsky, Atmospheric Sciences Research Center, SUNY at Albany, 100 Fuller Road, Albany, NY 12205.

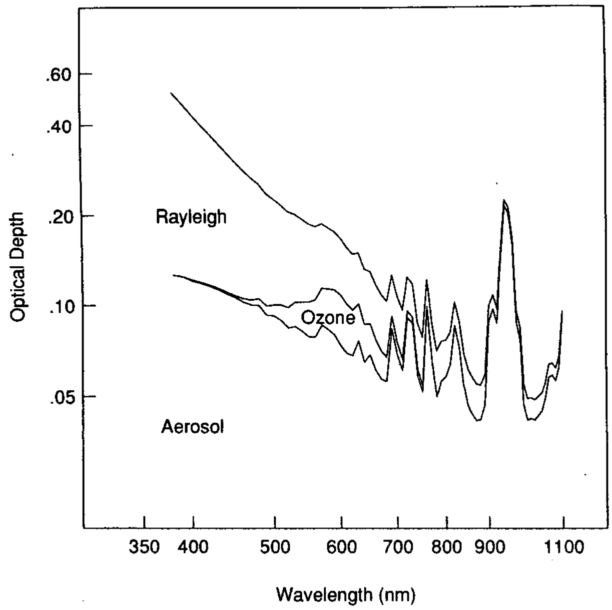

FIG. 1. Total optical depth versus wavelength (top line), optical depth with Rayleigh scattering removed (middle line), and optical depth with seasonal ozone also removed (bottom line).

The data to calculate these were obtained using a portable spectroradiometer (LiCor Model LI-1800) that acquired 22 spectra as the solar path changed from 6 to 2 air masses. Plots of the natural logarithm of the intensity versus the air masses at which the 22 spectra were acquired were made for all wavelengths. These plots indicated that the slopes could be used as optical depths, i.e., the plots were nearly linear and, therefore, the atmosphere was relatively stable during the measurements.

Figure 1 is a plot of the log total optical depth versus log wavelength derived from these spectra (top line). The next lower line is the result of subtracting the Rayleigh scattering contributions from the total optical depth. The lowest line results from the subtraction of a seasonal ozone contribution. In Fig. 2, this last spectrum is replotted along with the lowest air mass irradiance spectrum in the dataset that was used to derive the optical depth spectrum. Obviously, several of the features in the solar spectrum match features in the optical depth spectrum. This is especially true at the near-infrared wavelengths and implies that these absorbers are within the earth's atmosphere. At shorter wavelengths, spectral features do not have matches in the optical depth spectrum, implying that this spectral structure is formed in the solar atmosphere. The strong molecular absorption features in the near infrared at 690 nm and longer wavelengths are produced by either water vapor or molecular oxygen. The smooth spectrum at the shortest wavelengths results from aerosol extinction. To the best of our knowledge, the structure centered at about 600 nm has not been considered before in aerosol measurements. The fact that these features can, in some circumstances, have a significant impact on aerosol measurements is examined in the next section.

3. Discussion

Four distinct peaks in the structure appear to be centered around 600 nm. Using the tables of Rothman et al. (1987), these are identified with weak water vapor bands and a weak oxygen band. The calculated enhancement to the photopic optical depth resulting from this contamination is 0.004. This value was calculated by measuring the excess optical depth for those wavelengths affected (excess over an interpolated aerosol optical depth), weighting by the photopic response curve, and normalizing by the photopic response curve. It agrees closely with the offset found in our measured comparisons in LeBaron et al. (1989).

An optical depth spectrum, as in Fig. 2, can also be useful in making the selection of sunphotometer filters. For example, the World Meteorological Organization recommendations for primary and secondary wavelengths for aerosol optical depth measurements (Frohlich 1977) are 368, 384, 500, 778, and 862 nm. The first three and the last are well chosen based on the optical depth spectrum in Fig. 2, but it appears that a filter near 670 nm may have been a better selection for an intermediate wavelength than 778 nm.

The filter selection for our own narrowband photometers was similarly flawed. In Fig. 3 the log optical depth versus the log wavelength are plotted for the narrowband filters we use routinely. It was presumed that these filters sampled aerosol only. The filter at 630 nm

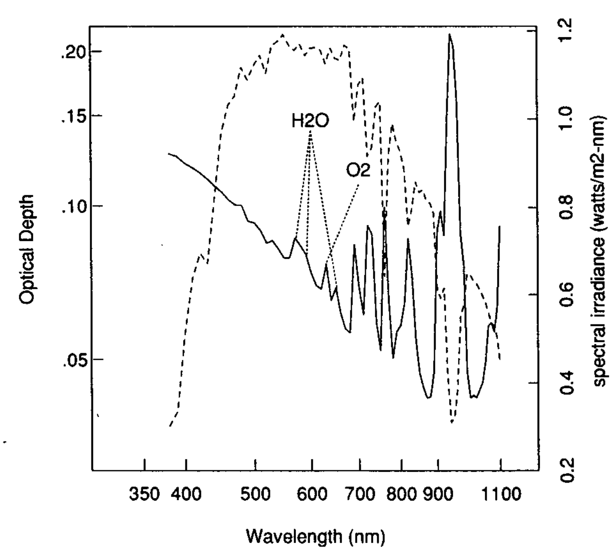

FIG. 2. Optical depth with Rayleigh scattering and ozone absorption removed versus wavelength. A spectrum of direct solar radiation at the same spectral resolution as the optical depth plot. Weak water vapor and molecular oxygen absorption features are clearly marked.

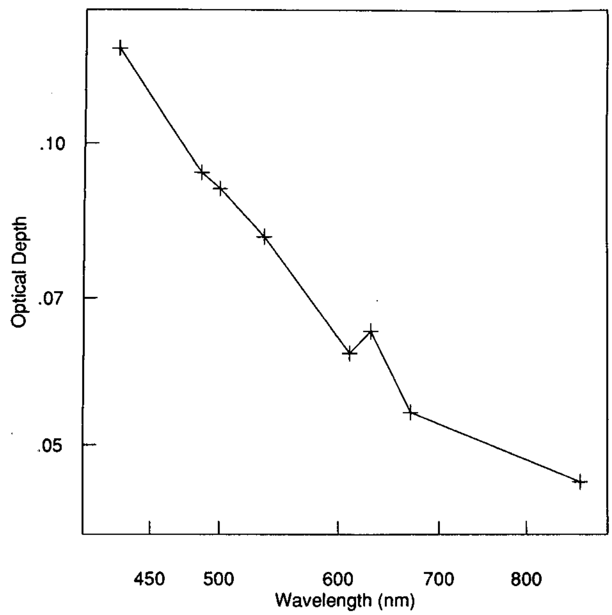

FIG. 3. Typical plot of log aerosol optical depth versus log wavelength for several narrowband filters. The 630-nm filter clearly deviates from the trend indicating its contamination by weakly absorbing molecular oxygen.

is clearly higher than the expected smooth trend. The use of an optical depth spectrum to establish the significance of weak molecular absorption bands in this region explains the anomalous optical depth values calculated for this filter. From Fig. 2 it is obvious that the filter is influenced by the oxygen band near that wavelength.

Failure to account for these weak features can affect other measurements as well. For some time we have attempted to use the technique of King and Byrne (1976) to derive ozone from the Chappuis band in the visible spectrum. The technique involves adjusting the ozone abundance until a reasonable aerosol wavelength dependence is obtained. Because the technique is very sensitive to the aerosol wavelength dependence, using filters that contain these weak bands greatly affects the results.

Besides improving one's ability to measure aerosol optical depths, moderate-resolution spectra should permit reasonable measurements of ozone and water vapor. Several approaches for calculating total column ozone from these data are under consideration. The mere fact that we increase sampling in the Chappuis band by a factor of 10 should decrease the noise in the ozone signal considerably. Water vapor appears in several bands and a simultaneous extraction of information from these bands should increase the accuracy of this determination over the typical measurement that uses the 940-nm band only.

In summary, it would seem that identification of filter contaminants would be a simple matter of referring to a spectral line atlas. Relatively weak lines, however, which are often ignored as insignificant, can introduce large errors into sunphotometer results. For these reasons, an optical depth spectrum with the moderate resolution described here should be useful for assessing the actual impacts on sunphotometry studies. It has answered some puzzling questions in our own studies related to ozone measurement, the photopic filter aerosol optical depth measurement, and an anomaly in our 630-nm sunphotometry filter data. It should lead to better molecular abundance measurements of ozone and water vapor in the optical region of the spectrum.

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