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TOTAL OZONE DETERMINATION BY CHAPPUIS BAND ABSORPTION AT AN URBAN LOCATION

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RESUMEN

Se calculó el ozono total columnar en College Park, Maryland, a partir de mediciones espectrales de la radiación solar directa en la longitud de onda visible abarcando el continuo de Chappuis ($550 < \lambda < 700$ mn). Una comparación del ozono total derivado mediante mediciones de la banda de Chappuis con mediciones de ozono total hechas con el espectrómetro de Dobson demostró que el método de la banda de Chappuis difería del de Dobson aproximadamente en ±20% en los días más estables. Estas diferencias pueden atribuirse a la combinación de: grandes profundidades ópticas de aerosol, variación diurna de la profundidad óptica del aerosol; la desviación de la supuesta relación de ley de energía utilizada para estimar el cambio de la profundidad óptica del aerosol con la longitud de onda, y la incertidumbre en los valores de los coeficientes de absorción del ozono.

ABSTRACT

Total columnar ozone was estimated at College Park, Maryland, from spectral measurements of the direct beam solar radiation in the visible wavelength spanning the Chappuis continuum ($550 < \lambda < 700$ nm). A comparison of total ozone derived by the Chappuis band measurements with Dobson spectrometer measurements of total ozone showed that the Chappuis band method differed from the Dobson method by approximately ±20% on the most stable days. These differences can be attributed to a combination of: large aerosol optical depths; diurnal variation of aerosol optical depth; the deviation from the assumed power law relationship used to estimate the change in aerosol optical depth with wavelength; and uncertainty in the values of ozone absorption coefficients.

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INTRODUCTION

Total ozone amounts have been determined for the last fifty years by ground based Dobson spectrometer measurements (Dobson, 1968) and more recently, from satellite observations by the SBUV (Solar Backscatter Ultraviolet) (Heath *et al.*, 1975) and TOMS (Total Ozone Mapping Spectrometer) instruments (Fleig *et al.*, 1982). All of these methods are based on the measurement of the absorption of solar radiation by ozone in the ultraviolet region of the spectrum. The Dobson ozone spectrophotometer operates at wavelengths between 305.5 and 339.8 nm. The accuracy of the measurements is a function of the magnitude of the differences between the ozone absorption coefficients of the pairs of wavelengths used. In the SBUV and the TOMS based techniques total ozone is determined by using almost identical wavelength bands. The retrieval algorithms are also similar except that the TOMS algorithm accounts for the variation of the scattered and absorbed ultraviolet radiation as a function of view angle (Fleig *et al.*, 1982). The SBUV instrument is a nadir-viewing double monochromator that measures the radiance backscatter from the atmosphere at twelve discrete wavelengths between 255 to 340 nm, using a 1 nm bandpass. Radiances between 312 and 340 nm are used to calculate total ozone while radiances at the lower part of the spectrum are used for obtaining ozone profiles. TOMS retrievals of total ozone are considered to be more appropriate for comparison with ground station data due to the better spatial resolution of the TOMS and daily global coverage. A possible error in ozone determination from UV spectral measurements could result from changing solar Fraunhofer absorption-line strengths that would cause fluctuations in the solar spectral irradiance at closely spaced UV wavelength bands (Shaw, 1979). Therefore total ozone derived from spectral UV measurements could fluctuate due to changes in the solar irradiance. This lead Shaw (1979) to determine the total ozone from measurements in the visible Chappuis band where the solar irradiance is believed to be constant. Shaw's observations were made at Mauna Loa, Hawaii where there is a very low background level of atmospheric aerosols. King and Byrne (1976) determined total ozone from spectral solar radiation measurements in the Chappuis bands at the low turbidity desert region of Tucson, Arizona. The present study reports on the determination of total ozone from Chappuis band measurements at an urban location in the mid-Atlantic U. S., which has considerably higher levels of background aerosol concentration.

INSTRUMENTATION AND MEASUREMENTS

A solar transmissometer was used to measure the direct beam solar radiation in narrow wavelength bands. Description of the radiometer can be found in Shaw *et al.* (1973) or Spinhirne (1983). Briefly, eight narrowband interference filters arranged in a filter wheel isolate the energy within selected wavelength intervals in the visible and near IR regions between 400 and 900 nm. The filters have passbands about 10 nm which are sufficiently narrow so that little variation in flux occurs across the passband for continuous sources such as solar radiation. The transmissometer was uncalibrated prior to this experiment. Subsequently, calibration was derived from observations taken during the experiment, using the Langley plot method.

The justification for the selection of the wavebands is given by King *et al.* (1980), who used the prototype of this radiometer in their study in Tucson. The major concern in the selection process is the avoidance of bands of strong selective absorption by the atmosphere. The gases in the atmosphere which produce strong rotation-vibration absorption bands in the visible and near infrared regions are water vapor and oxygen. In addition to the Chappuis continuum, a continuum absorption band for nitrogen dioxide extends from 340 to 500 nm. However, it is very small and relatively unimportant for surface based optical thickness measurements. Since all of the wavelength bands were chosen to avoid the H_2O and O_2 absorption bands, there is no need to make additional corrections for water vapor absorption. For the eight wavelength regions of the solar transmissometer, the molecular absorption ranges from 0 to approximately 0.03%, when the NO_2 and O_3 continuums are not included.

Days which are completely cloudless and stable are fairly rare in the College Park, Maryland, area. The most cloud free days occur in winter, spring or fall with a strong influx of continental polar air. During the summer months, cloudless days are very infrequent due to the high humidities and resultant haze and cumulus cloud development. Most of the cloudless sky data were obtained during the morning hours since small diffuse cumulus clouds would often rapidly form in the afternoon. Transmissometer measurements were taken for solar elevation angles ranging from 10° to 42°.

DETERMINATION OF OPTICAL DEPTHS

The total optical depth of the atmosphere was estimated by the Langley plot method, which is accomplished by measuring the direct beam solar radiation at the earth's surface through a range of solar elevation angles. The measured radiometer voltages are then fitted by the least squares method to Beer's law. Application of this method is best demonstrated by using the logarithmic form of Beer's law which is given by

$$\ell nF(\lambda) = \ell n(1/S) + \ell nFo(\lambda) - m\tau(\lambda) \qquad (1)$$

Fo(λ) is the spectral flux at the top of the atmosphere, m is the relative optical air mass, S is the earth-sun distance factor, F(λ) is the spectral flux at the earth's surface, and $\tau(\lambda)$ is the total optical depth. Since there is a linear relationship between the radiometer voltage and the measured flux, a plot of data having m on the x-axis and $\ell nV(\lambda)$ (V = voltage) on the y-axis, will yield a straight line with a slope of $-\tau(\lambda)$ if the total optical depth is constant during the observing period. Figure 1 shows the Langley plot for all 8 transmissometer wavebands for September 16, 1979.

As was discussed earlier, at high altitude, low turbidity locations, narrow waveband solar radiation measurements such as those made with the solar transmissometer have been used to determine total columnar ozone by measuring attenuation in the visible Chappuis continuum. King and Byrne (1976) describe a method for determining ozone which depends on measurements of spectral total optical depth some of which are influenced by the Chappuis bands and others which are outside these bands. The absorption in the Chappuis band occurs in a continuum which means that there are no strong peaks in the absorption spectrum. One approach to compute the ozone amount from the Chappuis bands is by making the assumption that the aerosol optical depth is approximated by a power law of the form

$$\tau = c \cdot \lambda^{-n} \qquad (2)$$

where c and n are constants. For the Chappuis band region, Diermendjian (1968) has found that the aerosol optical thickness always varies slowly and gradually with wavelength. Ozone can be determined from the power law relationship graphically on $\log\tau$ versus $\log\lambda$ paper, as a function of the deviation of the optical depth from the aerosol power law in the range of $\lambda = 500 - 700$ nm due to ozone absorption. Knowing the spectral ozone absorption coefficients one can calculate the amount of total columnar ozone that would result in the observed values of the ozone optical depth. Shaw (1979) notes, however, that the uncertainties of the Langley method calibration are directly proportional to the optical depth itself and that for a low elevation rural station having aerosol optical depths of 0.1 to 0.2, the inferred ozone by the Chappuis band method could result in accuracies of only 10 - 20%. For high altitude, low turbidity stations, the total ozone derived by the Chappuis band method can have comparable accuracy to that of Dobson spectrometry.

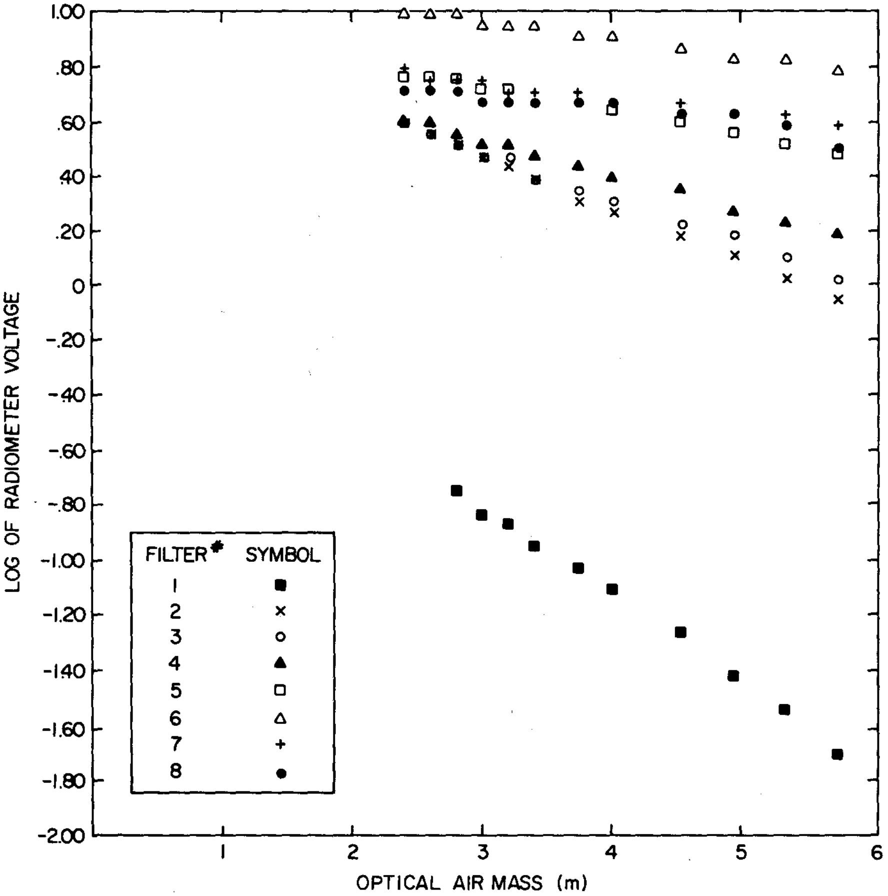

Fig. 1. Langley plots for transmissometer measurements at 440.0 nm, 521.7 nm, 557.5 nm, 612.0 nm, 670.8 nm, 750.0 nm, 779.7 nm, and 871.7 nm for September 16, 1979.

RESULTS

In Figures 2 and 3, the variation of total optical depth as a function of wavelength for 10 nm wide bands is plotted for two consecutive days, September 16 and 17, 1979. Both of these days had cloudless, clear "deep blue" skies at sunrise and the presence of cirrus cloud later in the morning which terminated the measurements. The correlation coefficients from the regression lines in the Langley plots for λ = 521.7 were −0.9997 for September 16, 1979 and −0.9976 for September 17, 1979. There was a 6.1% difference in the extrapolated value of the zero air mass intercept on these two days at this wavelength. The sum of the aerosol plus ozone optical depths as a function of wavelength are also plotted. These values are obtained by using the slopes of the Langley plots as total optical depths and then subtracting the Rayleigh optical depth from the total for each wavelength to obtain the ozone plus aerosol optical depth. For both days there is a pronounced "hump" or increase in the ozone plus aerosol optical depths in the region of the Chappuis continuum, with a maximum at 612.0 nm, the peak absorption region of the continuum. In both figures the straight dashed lines are the assumed aerosol optical depths as a function of wavelength, following a power law type relationship, similar to Eq. (2). Thus, the slope of the aerosol power law distribution is determined empirically from the measurements by connecting the values of total minus aerosol optical depths for the wavelengths immediately outside of the Chappuis continuum. Estimates of the total ozone were made from the two plots by obtaining the ozone optical depths from the differences of aerosol and aerosol plus ozone optical depths and then dividing the ozone optical depths by the values of the ozone absorption coefficients at each wavelength. The ozone absorption coefficients were computed from the ozone cross sections interpolated from Ackerman (1971). On September 16, 1979, this method resulted in a total ozone estimate of 223 matm-cm at 612.0 nm and 238 matm-cm at 521.7 nm. The average of these two estimates is 19.4% lower than the value measured by a Dobson spectrometer at Wallops Island, Virginia, which was 286 matm-cm on this day. Wallops Island is located approximately 190 km to the southeast of College Park. The total ozone amount determined from the TOMS instrument of the Nimbus 7 satellite, which has a field of view of 50 km x 50 km at nadir, was 273 matm-cm for the Wallops Island area and 283 matm-cm for the College Park region. On September 17, 1979 the Chappuis method estimates of total ozone yielded a value of 336 matm-cm at 612.0 nm and 416 matm-cm at 521.7 nm. The total ozone measured at Wallops Island on this day was 308 matm-cm which differed from the average Chappuis estimate by 18.1%. Since the Chappuis method ozone estimates varied so much for the two different wavelengths on Sep-

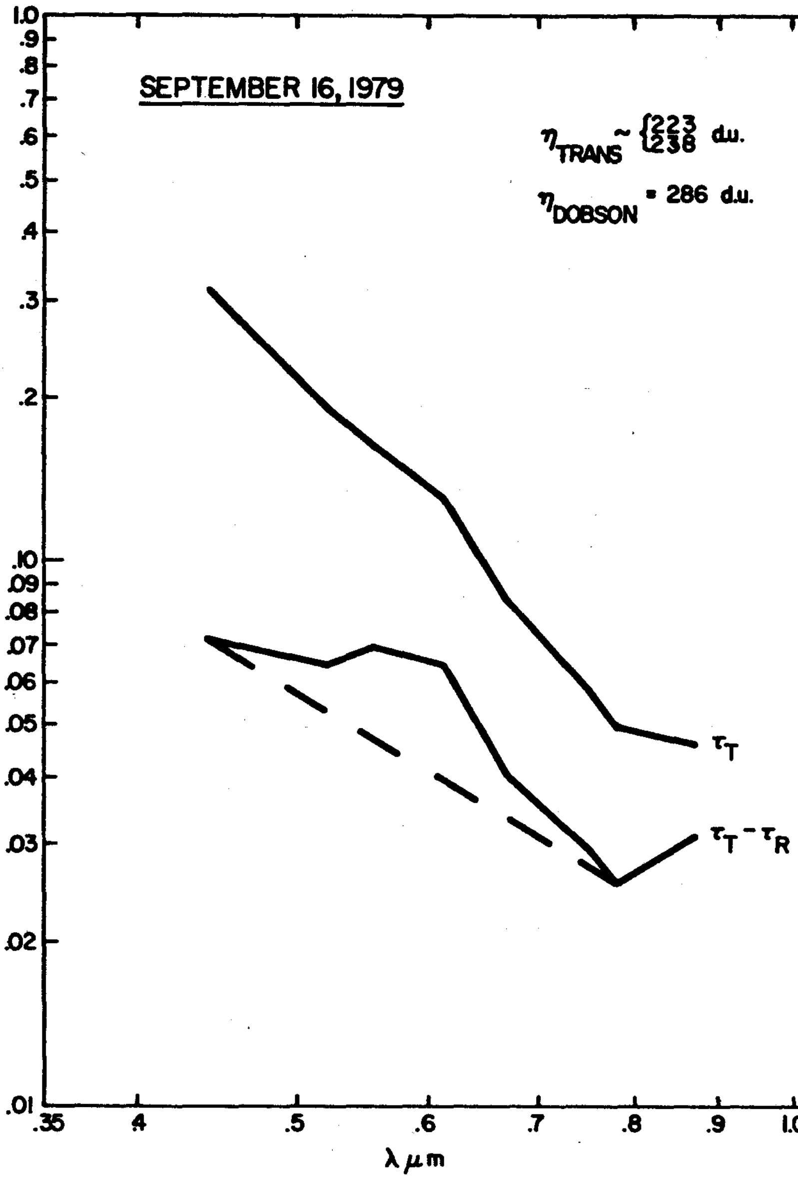

Fig. 2. The variation of total optical depth with wavelength and the variation of aerosol plus ozone optical depth with wavelength for September 16, 1979. The dashed line is the assumed power law variation of aerosol optical depth with wavelength. Also given are the transmissometer estimates of total ozone from the ozone optical depths and the total ozone measured at Wallops Island, VA. by Dobson spectrometer.

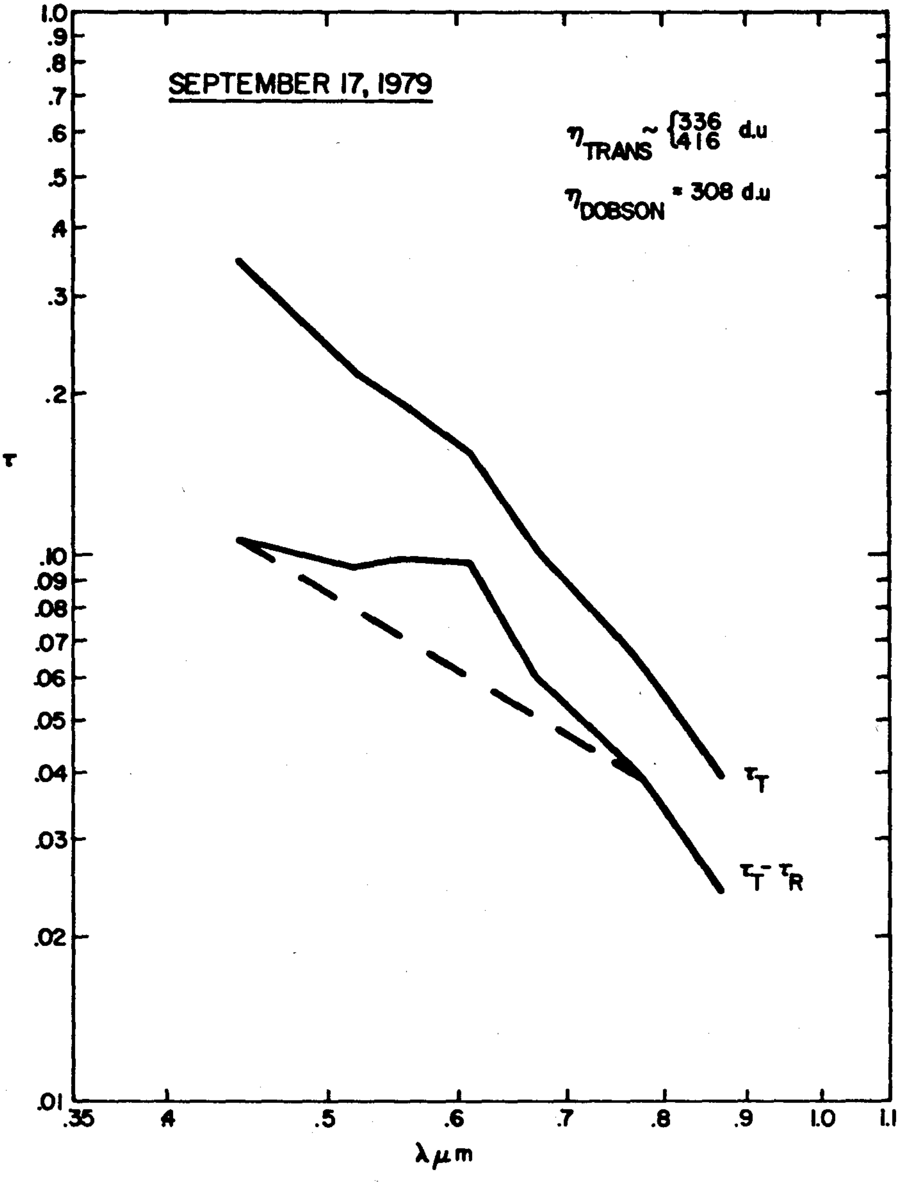

Fig. 3. Same as Figure 2 except for September 17, 1979.

tember 17, it is likely that the true aerosol optical depth variation with wavelength was quite different than the assumed variation. The TOMS estimate of total ozone was 293 matm-cm at Wallops and 285 matm-cm at College Park. It is also noted that the aerosol optical depth at 871.7 nm is greater than that at 779.8 nm on September 16, 1979. This increase in aerosol optical depth in the near infrared is also a deviation from the assumed power law variation of aerosol optical depth. This anomalous value of aerosol optical depth in the near infrared (871.7 nm) possibly resulted from the change in aerosol size distribution due to the growth of particle size from condensation of water vapor. Guzzie *et al.* (1972) found anomalous slopes in Langley plots of near infrared wavelengths which they attributed to the condensation of water vapor on aerosols.

CONCLUSIONS

A comparison of total ozone derived by the Chappuis method to Dobson spectrometer measurements of total ozone at an urban mid-Atlantic station of the U.S. showed that the Chappuis band method differed by ±20% from the Dobson method on the most stable days. These differences can be attributed to a combination of large aerosol optical depths, diurnal variation of aerosol optical depths, and deviation from the assumed power law relationship used to estimate the change in aerosol optical depth with wavelength. Also, the differences between the two estimates may be due to uncertainties in the Chappuis band absorption coefficients.

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