

A Method for Inferring Total Ozone Content from the Spectral Variation of Total Optical Depth Obtained with a Solar Radiometer¹

MICHAEL D. KING² AND DALE M. BYRNE³

The University of Arizona, Tucson 85721

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ABSTRACT

A solar radiometer has been used to monitor solar irradiance at eight discrete wavelengths. From these monochromatic measurements at varying zenith angles the total optical depth has been deduced by a computerized curve-fitting method. A unique technique will be described whereby the ozone absorption optical depths, and hence total ozone content of the atmosphere, can be inferred directly from the spectral variation of total optical depth. This procedure permits a systematic determination of total ozone content on a daily basis when other measurements are not available. Using the ozone absorption optical depths determined in this manner, the values of aerosol optical depth may be obtained more accurately by subtracting the molecular scattering and estimated ozone absorption contributions from the total optical depth.

A technique is also described for estimating the absorption optical depths at wavelengths where additional molecular absorption other than ozone occurs. Results are presented as 1) daily values of total ozone content and 2) molecular absorption optical depths due to water vapor and oxygen at two of the radiometer wavelengths. The total ozone content exhibits the characteristic seasonal cycle with peak values in April.

1. Introduction

In recent years much interest has developed in background levels of turbidity, especially possible changes in these levels due to man's direct influence. Results of the first relatively long-period study (1961-66) of turbidity have been presented by Flowers *et al.* (1969) for urban, suburban and rural localities, with all measurements made using a Volz sunphotometer. Porch *et al.* (1970) have measured the volume scattering coefficient k_v , which is proportional to the turbidity, by means of an angular integrating nephelometer at sites far removed from local aerosol sources. Comparing these results with minimum values of k_v at urban locations, the existence of a background level of atmospheric aerosols was postulated. Both of these studies were conducted using a single, narrow-bandpass filter. Other studies of turbidity indicating seasonal and annual trends have been made over wide wavelength bands with either a pyranometer or pyrliometer, but their importance is diminished because of the wavelength averaging involved.

More information concerning the properties of atmospheric aerosols is contained in measurements of the wavelength dependence of optical depth or extinction

coefficient. Spectral atmospheric transmission measurements at 10 wavelengths were taken over the first half of the twentieth century by the Smithsonian Institution and have been analyzed by Roosen *et al.* (1973). More recent spectral measurements of turbidity have been made by Knestrick *et al.* (1962), Quenzel (1970), Herman *et al.* (1971), Rangarajan (1972) and Shaw *et al.* (1973). Combining these measurements with proper corrections for molecular scattering and absorption, one can infer values of aerosol turbidity. Ångström (1961), Yamamoto and Tanaka (1969) and others have demonstrated that parameters of an aerosol size distribution can be inferred from values of aerosol turbidities at several wavelengths.

The contribution to total optical depth due to molecular (Rayleigh) scattering is well known as a function of wavelength and is relatively constant from day to day. However, the contribution from molecular absorption sources, such as ozone, is highly variable both daily and seasonally (Dobson, 1930; Ångström, 1972). More accurate determinations of aerosol optical depths result when measurements of turbidity are accompanied by measurements of total ozone content, preferably at the observing station, since large horizontal gradients in total ozone are often observed (Reiter and Lovill, 1974). From the literature it appears that no one has measured total ozone content and total optical depth simultaneously. A customary procedure is either to assume a constant value for total ozone content (e.g., Rangarajan, 1972) or to assume a seasonal

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² Institute of Atmospheric Physics.

³ Optical Sciences Center.

cycle based on measurements made at a different location. Shaw *et al.* (1973) assume an average seasonal variation based on data collected by Dobson (1930) and summarized by Bates (1954). Both of these procedures could result in large systematic and/or random errors.

In the present study a procedure for inferring the total ozone content of the atmosphere based upon total optical depth measurements at several wavelengths is developed. Additional molecular absorption at two wavelengths in the visible spectrum is estimated from the inferred ozone content and the resultant aerosol optical depth. Daily results of total ozone content and molecular absorption optical depths are presented for an 8-month period.

2. Determination of total optical depth

A multi-wavelength filter-wheel radiometer described by Shaw *et al.* (1973) has been used for a period of about 6 years at Tucson, Ariz., starting on 1 May 1970. A new instrument which incorporated improvements in data acquisition techniques, but did not differ substantially from the original radiometer, was installed in November 1974. Data are presented here which have been collected with filters whose wavelengths are centered at 0.4400, 0.5217, 0.6120, 0.6893, 0.7120, 0.7797, 0.8717 and 1.0303 μm .

The relative irradiance of the directly transmitted sunlight at several wavelengths was measured during the course of each clear day. For all the filters reported here the full bandwidth at half-peak transmittance was less than or equal to 0.014 μm , rather than 0.1 μm as stated by Shaw *et al.* (1973). With the exception of the very small contribution due to multiple scattering within the field of view of the radiometer, in this case 3° , the directly transmitted solar irradiance is given by the well-known Lambert-Beer Law as

$$F(\lambda) = F_0(\lambda)e^{-\tau_t(\lambda)m(\theta_0)}, \quad (1)$$

where $F(\lambda)$ is the solar irradiance reaching the detector at wavelength λ ; $F_0(\lambda)$ the irradiance incident on the top of the atmosphere ($\tau=0$ level); $m(\theta_0)$ the atmospheric air mass, a function of solar zenith angle θ_0 ; and $\tau_t(\lambda)$ the total optical depth. Taking the natural logarithm of (1) yields

$$\ln F(\lambda) = \ln F_0(\lambda) - \tau_t(\lambda)m(\theta_0), \quad (2)$$

and thus a plot of $\ln F(\lambda)$ vs $m(\theta_0)$ will yield a straight line of slope $-\tau_t(\lambda)$, and y -intercept of $\ln F_0(\lambda)$, assuming that the optical depth remains constant during the course of observation. The empirical expression for air mass suggested by Rozenberg (1966), i.e.,

$$m(\theta_0) = (\cos\theta_0 + 0.025e^{-11 \cos\theta_0})^{-1}, \quad (3)$$

was used. The second term in this expression accounts for the curvature of the earth-atmosphere system, but this modification contributes significantly only for $\theta_0 \gtrsim 80^\circ$ (Shaw, 1971). Zenith angles were computed

with the aid of tabulated right ascension and declination values for a particular day using a well-known formula for computing the local sidereal time as obtained from the *American Ephemeris and Nautical Almanac* for 1975 and 1976.

Methods are also available (Shaw, 1971; Shaw *et al.*, 1973) for determining the time-dependent optical depth by having an absolute calibration of $F(\lambda)$ as well as a knowledge of $F_0(\lambda)$. With the above calibrations $\tau_t(\lambda)$ may be computed by application of (2) for each separate data point, and thus time variations of the optical depth can readily be determined. Since absolute calibrations are difficult to obtain accurately and may not be reliable for extensive field observations, repeated calibration checks have not been made. Instead, a best-fit straight line (computed by the method of least-squares) to all the data on a particular day was made.

Fig. 1 illustrates a typical Langley plot [$\ln F(\lambda)$ vs $m(\theta_0)$] which has been obtained for Tucson at three wavelengths (0.4400, 0.6120 and 0.8717 μm) on 29 August 1975. The lines drawn in Fig. 1 represent the best fit to the data in a least-squares sense, with the resulting slopes being the negative of the total optical depths as described earlier. When occasional clouds appear in the field of view of the radiometer, the additional extinction for that time results in a lower value of $F(\lambda)$. In these situations the appropriate optical depth should be determined by making a least-squares fit to the "cloudless" data points, since only atmospheric optical depths are desired. The times at which clouds appear in the field of view of the radiometer are determined by consulting charts taken at the University of Arizona with an Eppley pyrheliumeter since intermittent cloudiness is marked by reductions in the solar irradiance recorded. After elimination of the data for these times the majority of the radiometer measurements yield linear plots similar to those illustrated in Fig. 1. In the few instances in which large temporal fluctuations occur (i.e., nonlinear Langley plots) no analysis has been pursued since a single optical-depth value does not characterize the atmospheric transmission for the entire day.

3. Determination of ozone and aerosol optical depths

From the values of total optical depth τ_t one can determine corresponding values of the aerosol optical depth, designated τ_a , for each day. This is obtained by subtracting from τ_t the contribution due to molecular scattering τ_R , known as the Rayleigh optical depth, and the contribution of the ozone Chappuis absorption band τ_{O_3} , known as the ozone optical depth. Thus,

$$\tau_a = \tau_t - \tau_R - \tau_{O_3}. \quad (4)$$

In addition to being express functions of wavelength the Rayleigh optical depth is a function of surface

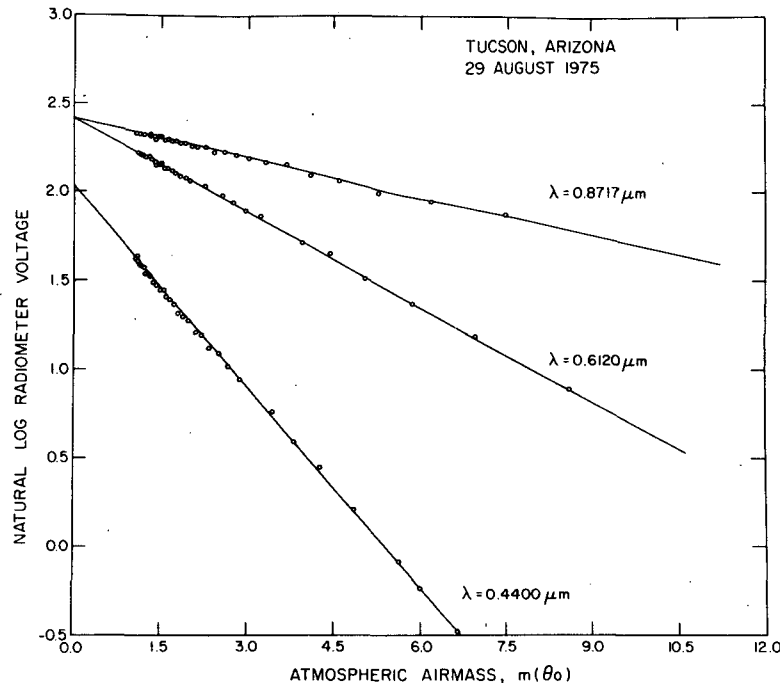


FIG. 1. The linear relationship which exists between the log solar irradiance (or alternatively the radiometer voltage levels) and the atmospheric air mass for stable conditions.

pressure p , while the ozone optical depth is a function of total ozone content η measured in atm-cm.⁴ Expressing these dependencies explicitly,

$$\tau_R(\lambda, p) = \frac{p}{p_0} \tau_R(\lambda, p_0), \quad (5)$$

$$\tau_{O_3}(\lambda, \eta) = \eta a(\lambda), \quad (6)$$

and thus (4) may be rewritten as

$$\tau_a(\lambda, p, \eta) = \tau_i(\lambda) - \tau_R(\lambda, p) - \eta a(\lambda), \quad (7)$$

where $\tau_R(\lambda, p_0)$ are the spectral values of the Rayleigh optical depth at $p_0 = 1013$ mb and $a(\lambda)$ are the ozone absorption coefficients per centimeter of pure gas at STP. It is to be noted that (5) and (6) are separable and, as such, p and η appear as daily scaling factors. The wavelength dependence is predetermined.

Although the surface pressure is relatively constant from day to day and easily measured with a barometer, the total ozone content is highly variable, both daily and seasonally. Since total ozone is not measured at the University of Arizona, large systematic errors can arise in the inferred values of aerosol optical depth due to this highly variable daily uncertainty. Fig. 2 illustrates the effect of ozone content on the spectral dependence of aerosol optical depth for 7 August and 13 November, 1975. The family of curves for each day represents the resulting τ_a values for varying amounts

of ozone concentration, where η_0 represents the total ozone content as determined by the method described below. It is readily seen that the inferred aerosol optical depths at wavelengths in the heart of the ozone Chappuis band (centered near $0.6120 \mu\text{m}$) are characteristically high for little ozone correction ($\eta = 0$), and are noticeably low for large amounts of ozone correction ($\eta = 2\eta_0$). Examination of Fig. 2 suggests that a statistical method exists whereby an optimum value of η can be determined from total optical depth measurements on a given day.

Since the spectral aerosol optical depth values for a particular day are primarily determined by the aerosol size distribution, not all values of η predict τ_a vs λ values which are physically realizable. For example, a Junge size distribution of the form

$$n(r) = cr^{-\nu^*-1},$$

where the radius r extends from 0 to ∞ , will predict that (Junge, 1963)

$$\tau_a = \beta \lambda^{-\nu^*+2}, \quad (8)$$

which is Ångström's empirical formula for the wavelength dependence of aerosol optical depth. Taking the logarithm of (8), this equation becomes

$$\begin{aligned} \log \tau_a &= \log \beta - (\nu^* - 2) \log \lambda \\ &= a_0 + a_1 \log \lambda, \end{aligned} \quad (9)$$

which is linear when $\log \tau_a$ is plotted against $\log \lambda$.

⁴ 1 atm-cm = 2.687×10^{19} molecules-cm⁻² in a vertical column.

In general the aerosol size distribution will neither be Junge nor have radii extending from 0 to ∞ . Both non-Junge size distributions and Junge distributions extending over finite radii limits introduce some curvature on a $\log \tau_a$ vs $\log \lambda$ plot, but do not drastically alter the basic shape (Shaw, 1971). Since (9) implies no curvature, a second-order term was added, and the observations of $\log \tau_a(\lambda, \rho, \eta)$ calculated from (7) were fitted to a quadratic of the form

$$\log \tau_a = a_0 + a_1 \log \lambda + a_2 (\log \lambda)^2 \quad (10)$$

in order to determine the total ozone content η_0 .

If the observed measurement y_i is Gaussian distributed with a standard deviation σ_i about $y(x_i)$, Bevington (1969) shows that maximizing the probability that y_i observations have the functional form $y(x_i)$ is equivalent to minimizing the statistic χ^2 defined as

$$\chi^2 = \sum_i \frac{1}{\sigma_i^2} [y_i - y(x_i)]^2.$$

In order to maximize the probability that the $\log \tau_a(\lambda, \rho, \eta)$ observations have the functional form of (10), χ^2 must be written as

$$\chi^2 = \sum_i \frac{1}{\sigma_i'^2} [\log \tau_a(\lambda_i, \rho, \eta) - a_0 - a_1 \log \lambda_i - a_2 (\log \lambda_i)^2]^2, \quad (11)$$

where the summation extends over all λ_i for which no additional molecular absorption occurs and σ_i' represents the standard deviation of the $\log \tau_a(\lambda_i, \rho, \eta)$ values. The wavelengths at 0.6893 and 0.7120 μm have some unknown amount of molecular absorption and hence are neglected in (11). Absorption at these two wavelengths is discussed in Section 4.

Minimizing χ^2 as defined by (11) is equivalent to making a weighted least-squares fit to the data. The weighting factors σ_i' appropriate to the logarithmic scale can be calculated by the method of propagation of errors. If w is a function of several variables y_1, y_2, \dots, y_n , known with uncertainties $\sigma_1, \sigma_2, \dots, \sigma_n$, the resulting uncertainty in w can be estimated by

$$\sigma_w^2 = \sum_i \sigma_i^2 \left(\frac{\partial w}{\partial y_i} \right)^2. \quad (12)$$

In this instance, $\sigma_i'^2$ can be written as

$$\begin{aligned} \sigma_i'^2 &= \sigma_i^2 \left(\frac{\partial \log \tau_a}{\partial \tau_a} \right)^2 \\ &= \sigma_i^2 \left[\frac{\log e}{\tau_i(\lambda_i) - \tau_R(\lambda_i, \rho) - \eta a(\lambda_i)} \right]^2, \end{aligned} \quad (13)$$

where σ_i represents the uncertainty in $\tau_a(\lambda_i)$. If σ_i were to be used in lieu of σ_i' as defined above, there would

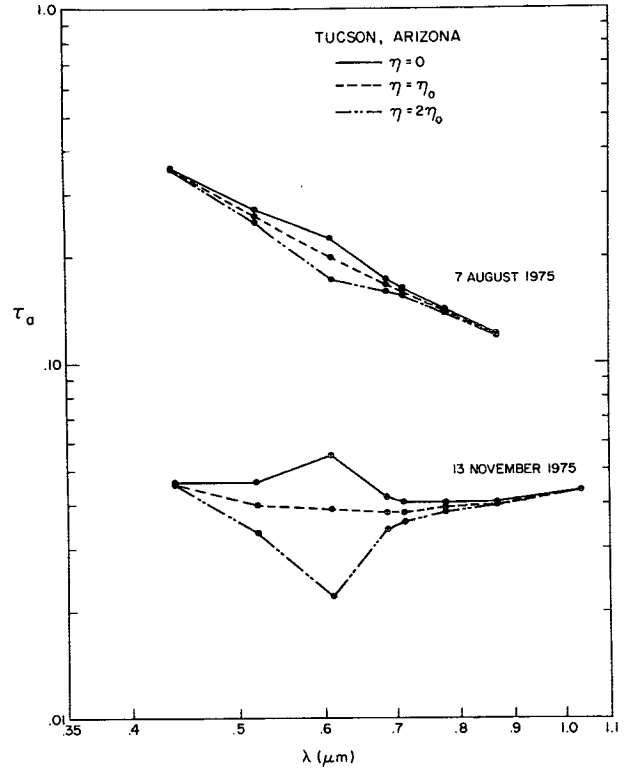


FIG. 2. The effect of atmospheric ozone content on the resulting spectral values of aerosol optical depth for 7 August and 13 November, 1975. The optimum values of total ozone η_0 obtained for these days are 246.5 and 137.6 m atm-cm, respectively.

be an underestimation of the uncertainties for small values of τ_a .

The minimum value of χ^2 can be determined by setting the partial derivative of χ^2 with respect to each of the coefficients (a_0, a_1, a_2, η) equal to zero. This procedure results in a set of four simultaneous equations:

$$\frac{\partial \chi^2}{\partial a_0} = -2 \sum_i \frac{1}{\sigma_i'^2} \epsilon_i = 0, \quad (14)$$

$$\frac{\partial \chi^2}{\partial a_1} = -2 \sum_i \frac{1}{\sigma_i'^2} \epsilon_i \log \lambda_i = 0, \quad (15)$$

$$\frac{\partial \chi^2}{\partial a_2} = -2 \sum_i \frac{1}{\sigma_i'^2} \epsilon_i (\log \lambda_i)^2 = 0, \quad (16)$$

$$\begin{aligned} \frac{\partial \chi^2}{\partial \eta} &= -2 \sum_i \frac{1}{\sigma_i'^2} \left[\frac{a(\lambda_i)}{\tau_i(\lambda_i) - \tau_R(\lambda_i, \rho) - \eta a(\lambda_i)} \right] \\ &\quad \times [\epsilon_i \log e + \epsilon_i^2] = 0, \end{aligned} \quad (17)$$

where

$$\epsilon_i = \log \tau_a(\lambda_i, \rho, \eta) - a_0 - a_1 \log \lambda_i - a_2 (\log \lambda_i)^2.$$

Note that σ_i' is a function of η as given by (13). The set of equations (14)–(17) is nonlinear in the unknowns

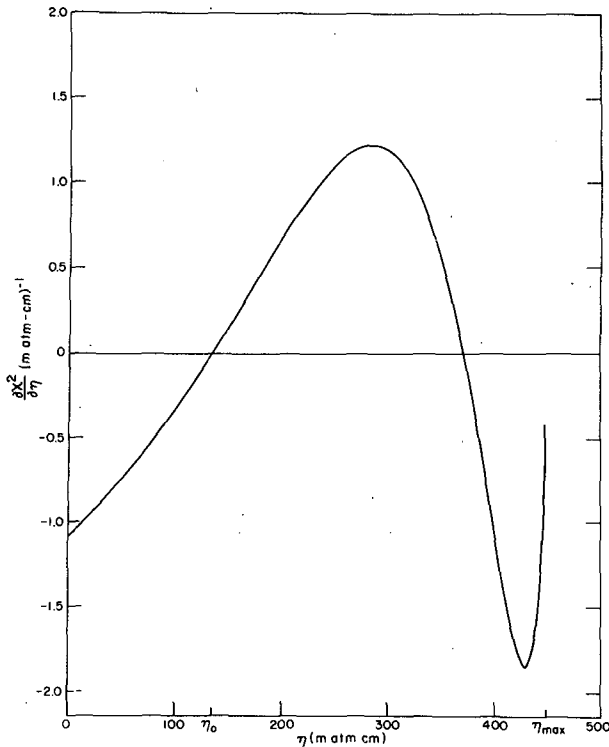


FIG. 3. Variation of χ^2 with η for 13 November 1975 showing the pronounced minimum which occurs for values of η (total ozone) equal to η_0 .

a_0 , a_1 , a_2 and η , and as such no analytic solution for them exists.

However, the three equations [(14)–(16)] can be rewritten to show the interaction of the coefficients as

$$\sum_i \frac{1}{\sigma_i'^2} \log \tau_a(\lambda_i, p, \eta) = a_0 \sum_i \frac{1}{\sigma_i'^2} + a_1 \sum_i \frac{\log \lambda_i}{\sigma_i'^2} + a_2 \sum_i \frac{(\log \lambda_i)^2}{\sigma_i'^2}, \quad (18)$$

$$\sum_i \frac{\log \lambda_i}{\sigma_i'^2} \log \tau_a(\lambda_i, p, \eta) = a_0 \sum_i \frac{\log \lambda_i}{\sigma_i'^2} + a_1 \sum_i \frac{(\log \lambda_i)^2}{\sigma_i'^2} + a_2 \sum_i \frac{(\log \lambda_i)^3}{\sigma_i'^2}, \quad (19)$$

$$\sum_i \frac{(\log \lambda_i)^2}{\sigma_i'^2} \log \tau_a(\lambda_i, p, \eta) = a_0 \sum_i \frac{(\log \lambda_i)^2}{\sigma_i'^2} + a_1 \sum_i \frac{(\log \lambda_i)^3}{\sigma_i'^2} + a_2 \sum_i \frac{(\log \lambda_i)^4}{\sigma_i'^2}, \quad (20)$$

which are a set of simultaneous equations linear in the unknowns a_0 , a_1 and a_2 for a specific value of η . For any arbitrary value of η , however, χ^2 will not necessarily be a minimum since $\partial \chi^2 / \partial \eta$ will not be identically zero as required by (17). As η is varied, the coefficients

a_0 , a_1 and a_2 are calculated using (18)–(20), from which χ^2 and $\partial \chi^2 / \partial \eta$ can be computed using (11) and (17), respectively. The variation of χ^2 and $\partial \chi^2 / \partial \eta$ as a function of η for the spectral optical depth measurements obtained on 13 November 1975 is illustrated in Figs. 3 and 4. In these figures and in the discussion which follows the value of η at which χ^2 attains a minimum is denoted by η_0 . The value of η_0 is found by making use of the condition that $\partial \chi^2 / \partial \eta = 0$, (see Fig. 4) rather than by searching for the minimum value of χ^2 . Fig. 4 shows two such roots, one of which corresponds to a maximum as is readily seen by examination of Fig. 3. In the computations involving σ_i' it is assumed that the uncertainty in $\tau_a(\lambda_i)$ is approximately equal to the measurement uncertainty in $\tau_i(\lambda_i)$. Though this is not strictly true for values of η far from η_0 , where large systematic errors in $\tau_{O_3}(\lambda_i)$ occur, it is a good approximation in the region of the minimum χ^2 .

There is a restricted range of values over which η may vary. The *minimum* value of η is clearly zero, which corresponds to no atmospheric ozone. As previously stated, the aerosol optical depth at $0.6120 \mu\text{m}$ is the most sensitive to the magnitude of the ozone correction. Therefore, the *maximum* amount of ozone correction permitted is that amount which produces an aerosol optical depth of zero at $0.6120 \mu\text{m}$. Making use

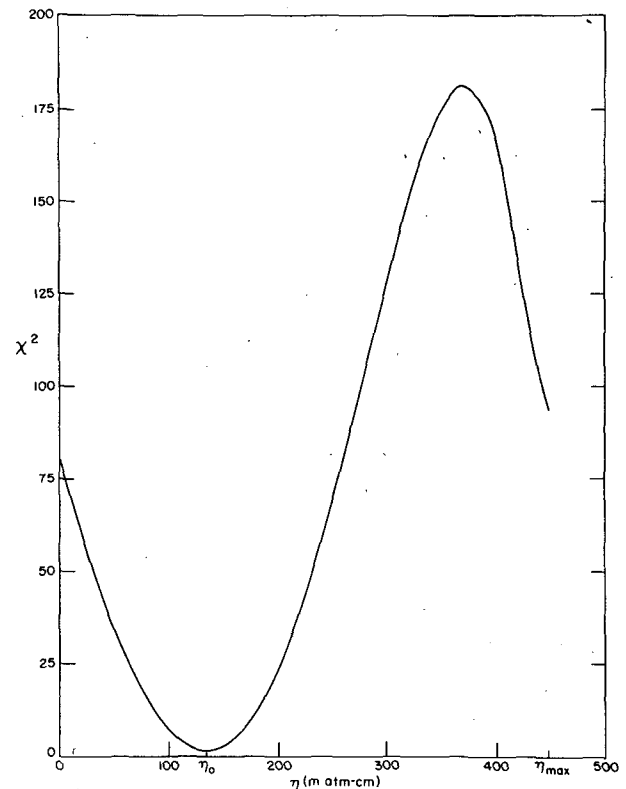


FIG. 4. Variation of $\partial \chi^2 / \partial \eta$ with η for 13 November 1975. The point at which this function equals zero, while increasing, defines η_0 as described in the text.

of (7), the maximum value of η becomes

$$\eta_{\max} = \frac{\tau_t(0.6120) - \tau_R(0.6120, p)}{a(0.6120)} \quad (21)$$

The value of η is therefore confined to a range given by

$$0 \leq \eta < \eta_{\max} \quad (22)$$

as indicated in both Figs. 3 and 4.

In the previous discussion it has been assumed that χ^2 attains a minimum for a value of η within the range defined by (22). Though this is usually the case, χ^2 can attain a minimum value outside these limits if the points to be fitted with a quadratic are highly irregular. Examination of the Langley plots for these days usually indicates a nonlinear curve due to temporal fluctuations in τ_t , and hence the spectral optical depth values used in the fit are not representative of any individual time. In these situations, attempting to minimize χ^2 within the physically realizable range of η values may be unsuccessful.

Having determined the minimum value of χ^2 and the optimum values of the coefficients a_0, a_1, a_2 and η , the variance and covariance in these coefficients can be estimated. Bevington (1969) shows that the uncertainties are related to the symmetric matrix α , whose elements are given by

$$\alpha_{jk} = -\frac{1}{2} \frac{\partial^2 \chi^2}{\partial \xi_j \partial \xi_k} \quad (23)$$

where ξ_j represents the coefficients a_0, a_1, a_2 and η . The matrix α is called the *curvature matrix* because of its relationship to the curvature of the χ^2 hypersurface in coefficient space. The covariances $\sigma_{\xi_i \xi_k}^2$ are then obtained from the elements of the error matrix (α^{-1}),

$$\sigma_{\xi_i \xi_k}^2 = [\alpha^{-1}]_{jk} \quad (24)$$

and thus the diagonal elements represent the variances $\sigma_{a_0}^2, \sigma_{a_1}^2, \sigma_{a_2}^2$ and $\sigma_{\eta_0}^2$.

In order to examine the factors which influence $\sigma_{\eta_0}^2$, consider as a first approximation that the variation of χ^2 with respect to each parameter is independent of the values of the other parameters. It then follows from (23) that the curvature matrix α is diagonal, and hence the variance in η_0 may be approximated by

$$\sigma_{\eta_0}^2 \approx \frac{1}{\alpha_{44}}$$

By using (23), (17) and (13), α_{44} can be shown to yield

$$\begin{aligned} \alpha_{44} &= \sum_i \frac{1}{\sigma_i^2} \left[\frac{a(\lambda_i)}{\tau_a(\lambda_i, p, \eta_0)} \right]^2 [\log^2 e + 3\epsilon_i \log e + \epsilon_i^2] \\ &= \sum_i \frac{a^2(\lambda_i)}{\sigma_i^2} \left[1 + \frac{3\epsilon_i}{\log e} + \frac{\epsilon_i^2}{\log^2 e} \right] \\ &\approx \sum_i \frac{a^2(\lambda_i)}{\sigma_i^2} \end{aligned} \quad (25)$$

where the final approximation is valid in cases in which (10) accurately describes the spectral variation of aerosol optical depth and hence the ϵ_i terms are negligible in comparison with 1. In this approximation, (25) is simply a weighted mean of the ozone absorption coefficients, weighted by *absolute* (rather than relative) errors in the measurements. Examination of (25) indicates that (i) the wavelengths with the largest ozone absorption have the largest influence on α_{44} and hence on $\sigma_{\eta_0}^2$ (if the absolute errors are about the same at all wavelengths), and (ii) that the magnitude of the absolute error σ_i at that wavelength has nearly a linear effect on the magnitude of σ_{η_0} .

The procedure described above for finding η_0 is very similar to the conventional differential absorption technique (Dobson and Harrison, 1926; Dobson, 1931) often applied to two wavelengths in the ultraviolet (Huggins) absorption band. The differences lie in the fact that the Chappuis band is not as strongly absorbing as the Huggins band, and that the wavelengths are not close to one another. Dobson (1931) assumes that τ_a is *not* a function of wavelength (i.e., a_1 and a_2 are zero), and hence the difference of total optical depth measurements at two wavelengths is a function only of Rayleigh and ozone optical depths. In this paper a wavelength dependence of τ_a is required, since the wavelengths are more widely spaced. Using (10) as a fitting equation, four coefficients must be determined, and hence at least five wavelengths are required in order to obtain even one degree of freedom (number of measurements minus number of coefficients to be determined). Fitting equations other than (10) could be used for a different type of wavelength dependence of τ_a , but the technique would be the same. A summary of results is presented and discussed in Section 5.

4. Determination of molecular absorption optical depths at 0.6893 and 0.7120 μm

For wavelengths at which absorption due to molecular species other than O_3 cannot be neglected, τ_a is obtained by subtracting from τ_t the contribution due to molecular absorption, designated τ_{ma} , in addition to the contributions due to molecular scattering and ozone absorption described above. Thus (4) must be rewritten as

$$\tau_a = \tau_t - \tau_R - \tau_{\text{O}_3} - \tau_{ma} \quad (26)$$

For the filters centered at 0.6893 and 0.7120 μm , additional molecular absorption occurs due to O_2 and H_2O , and hence τ_{ma} as well as τ_a is unknown. However, having determined η_0 and the coefficients a_0, a_1 and a_2 as described in Section 3, the value of τ_a at the wavelengths where molecular absorption occurs can be estimated by applying the fitting equation (10). At these wavelengths, therefore,

$$\tau_a = 10[a_0 + a_1 \log \lambda + a_2 (\log \lambda)^2] \quad (27)$$

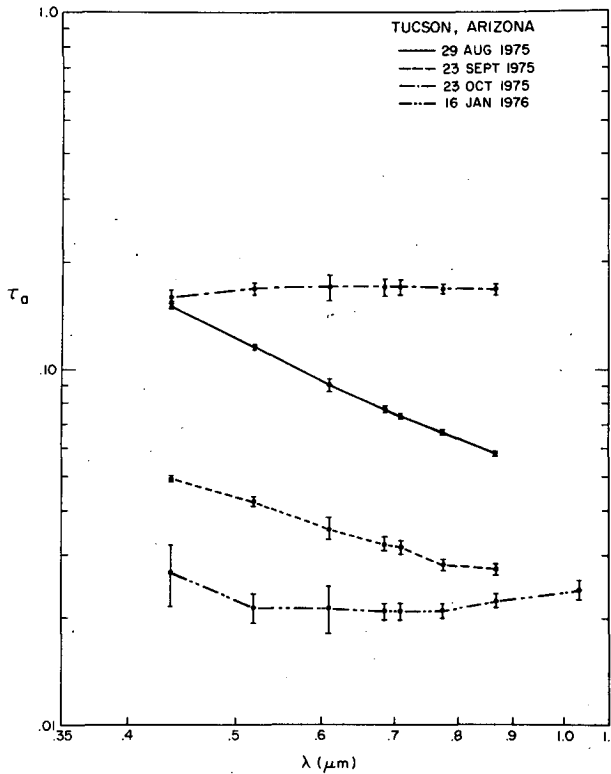


FIG. 5. Resulting values of aerosol optical depth, including error bars, as a function of wavelength for four representative days. Note the overall linear character with modest amounts of curvature.

It therefore follows from (26) and (27) that

$$\tau_{ma} = \tau_t - \tau_R - \tau_{O_3} - \tau_a. \tag{28}$$

Since τ_a for the additional absorbing wavelengths is computed by (27), any uncertainty in the a_j coefficients propagates into an uncertainty in τ_a . The covariances in the a_j coefficients have been calculated with the aid of (24). With the additional aid of (27), (6) and (28), the uncertainties in τ_a , τ_{O_3} and τ_{ma} can be expressed as

$$\sigma_{\tau_a} = \frac{\tau_a}{\log e} \left[\sum_{j=1}^3 \sum_{k=1}^3 \sigma_{\xi_j \xi_k}^2 (\log \lambda)^{j+k-2} \right]^{\frac{1}{2}},$$

$$\sigma_{\tau_{O_3}} = a(\lambda) \sigma_{\eta_0},$$

$$\sigma_{\tau_{ma}} = (\sigma_{\tau_t}^2 + \sigma_{\tau_R}^2 + \sigma_{\tau_{O_3}}^2 + \sigma_{\tau_a}^2)^{\frac{1}{2}}.$$

Compared with the measurement uncertainty σ_{τ_t} and the computed uncertainties σ_{τ_a} and $\sigma_{\tau_{O_3}}$, the uncertainty in τ_R is negligible. This follows since systematic errors in τ_R have been reduced through the use of the measured surface pressure p . Thus, $\sigma_{\tau_{ma}}$ can be approximated by

$$\sigma_{\tau_{ma}} \approx (\sigma_{\tau_t}^2 + \sigma_{\tau_a}^2 + \sigma_{\tau_{O_3}}^2)^{\frac{1}{2}}. \tag{29}$$

The values of τ_a for the other non-absorbing wavelengths are computed using (7) rather than (27). A

summary of results for the molecular absorption optical depths at 0.6893 and 0.7120 μm is presented and discussed in Section 5.

5. Results

The method for inferring total ozone content described in the preceding sections has been carried out at The University of Arizona (latitude $32^\circ 14'$) since August 1975 in order to more accurately determine aerosol optical depths. In Fig. 5 the resulting aerosol optical depths and error bars for four representative days are illustrated. For these days the aerosol optical depths very nearly follow the Ångström power law, exhibiting only a modest amount of curvature. It will be noted that the error bars on τ_a are generally larger at the 0.6120 μm wavelength due to ozone absorption. This is a consequence of the propagation of errors and the effect which the large value of the ozone absorption coefficient at that wavelength has on $\sigma_{\tau_{O_3}}$ and hence on σ_{τ_a} . Estimates of the daily errors in total ozone content computed from (24) indicate that σ_{η_0} is typically on the order of 20 m atm-cm and is approximately linearly correlated with σ_{τ_t} at 0.6120 μm , which typically has a value of 0.001.

Fig. 6 illustrates the inferred ozone content for forty days between August 1975 and March 1976. The large daily variability which characterizes the measurements of total ozone is readily seen. Inspection of the data indicates an overall seasonal variation in which total ozone content is highest in early spring and lowest in early autumn. Worldwide measurements of total ozone content, summarized in the CIAP (1975) report, indicate that atmospheric ozone varies seasonally in an approximately sinusoidal manner with the amplitude and mean being related to the latitude.

A sinusoidal function given by

$$\eta(x) = \bar{\eta} + A \sin(2\pi x - \phi) \tag{30}$$

(where x is the fractional time of year) was fitted to the data points using a least-squares procedure similar to that described in Section 3 in order to determine the amplitude, mean and phase of the annual variation. The resulting curve is plotted in Fig. 6 and indicates that the maximum ozone content occurs about 23 April and that the minimum occurs about 23 October, with a mean annual value of 255.3 ± 4.0 m atm-cm and a seasonal amplitude of 42.6 ± 5.0 m atm-cm. Monthly averages of total ozone obtained at Table Mountain, California (latitude $34^\circ 22'$), between 1928 and 1929 using a Dobson ozone spectrophotometer are also presented in Fig. 6. It is readily seen that these results agree very well with monthly average values obtained for Tucson at nearly the same latitude. In addition to the monthly averages indicated here, Dobson (1930) tabulates values for individual days which exhibit a very large daily fluctuation similar to that presented here.

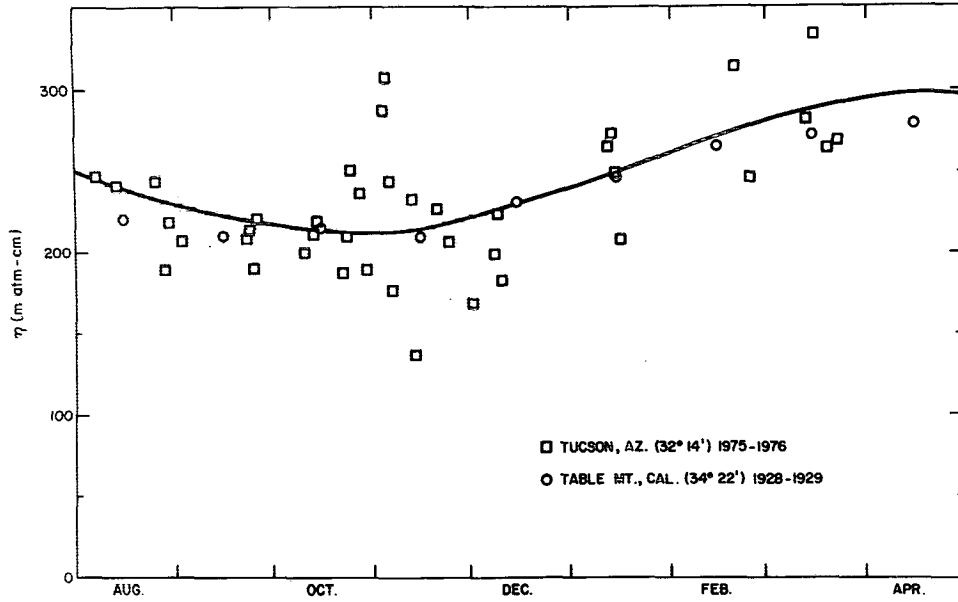


FIG. 6. Daily values of total ozone content inferred from the spectral variation of total optical depth for Tucson. The solid curve represents a sinusoidal fit to the data of the form $\eta(x) = 255.3 + 42.6 \sin(2\pi x - 0.402)$. This curve agrees well with monthly averages for Table Mountain, California, at a similar latitude (Dobson, 1930).

The molecular absorption optical depths at 0.6893 and 0.7120 μm have been determined by the method described in Section 4. Results of this analysis for τ_{ma} are illustrated in Fig. 7 for these two wavelengths. The molecular absorption which occurs in the filter centered near 0.7120 μm is due to water vapor absorption and exhibits the largest values in August. In Tucson, July

and August are characterized by regular, late-afternoon cloudiness and accompanying thunderstorms with the requisite large precipitable water content. As a result, it is quite natural to expect the largest values of τ_{ma} to occur in August. The absorption which occurs in the bandpass of the 0.6893 μm filter is due both to water vapor and to O_2 (B band). As a consequence of this

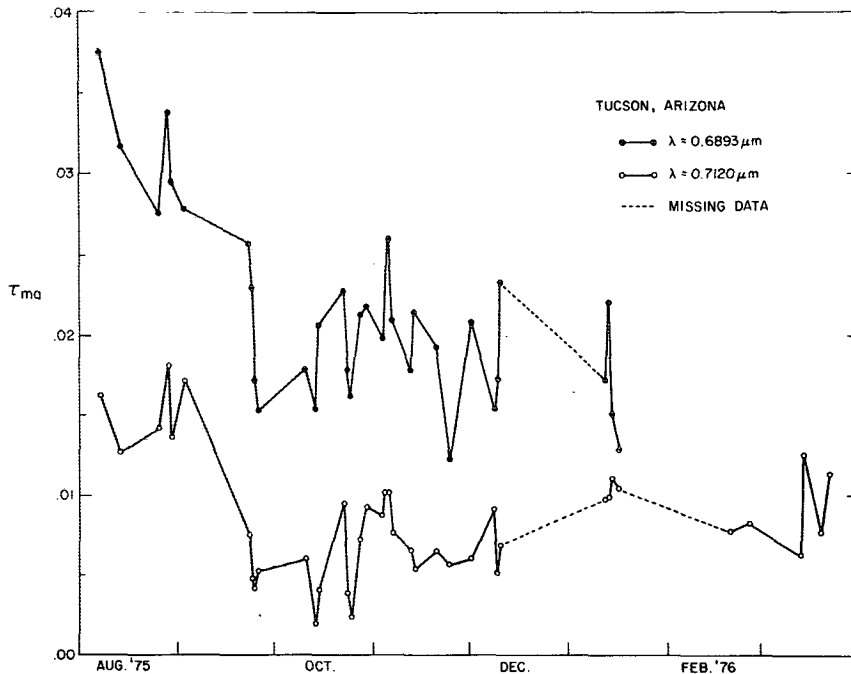


FIG. 7. Daily values of molecular absorption optical depths at 0.6893 and 0.7120 μm .

double absorption, there is some seasonal correlation of τ_{ma} for both filters due to water vapor in addition to an overall larger background at $0.6893 \mu\text{m}$ resulting from O_2 . The absence of data for the $0.6893 \mu\text{m}$ filter after 16 January 1976 is due to its removal from the radiometer. Due to the positive correlations of the a_0 , a_1 and a_2 coefficients, the uncertainty in τ_a (and hence τ_{ma}) for these wavelengths is relatively small as can be seen by examination of Fig. 5. Computations using (24) indicate that only in a few instances do values of $\sigma_{\tau_{ma}}$ exceed 0.002. The τ_{ma} values are, of course, very dependent on the bandpass characteristics of the filter used to measure the total optical depth.

6. Summary and conclusions

As illustrated by the family of curves in Fig. 2, the determination of aerosol optical depth values from measurements of total optical depth is very sensitive to one's assumption of the daily value of total atmospheric ozone. Due to the high daily variability of total ozone which has been reported in the literature (e.g., Dobson, 1930; Reiter and Lovill, 1974; Dütsch, 1969; and others), large errors in the inferred spectral values of aerosol optical depths can arise even if the appropriate average seasonal cycle is employed. In locations where other direct measurements of ozone are not available, the statistical technique described in this paper can be used to infer the total ozone content.

The principal assumptions upon which the technique is based are that $\log \tau_a$ can be adequately described by a quadratic in $\log \lambda$, and that the coefficients which describe the quadratic (and hence total ozone) can be determined by minimizing the statistic χ^2 . Both experimental observations and theoretical calculations confirm that $\log \tau_a$ is essentially a linear function of $\log \lambda$, exhibiting only slight amounts of curvature for a variety of aerosol size distributions. Minimization of the statistic χ^2 is a result of the principle of maximum likelihood and forms the basis of least-squares curve fitting.

The values of total ozone content presented here (see Fig. 6) indicate the presence of an overall seasonal cycle with peak values obtained in April. These ozone results are in agreement with other measurements obtained with a Dobson ozone spectrophotometer for similar latitudes, both in average seasonal characteristics and in the magnitudes of the daily fluctuations. Since the effect of ozone becomes more pronounced in arctic regions, the errors inherent in the determination of aerosol optical depths are necessarily greater at these latitudes. The application of the analysis described in this paper will greatly increase the accuracy with which spectral values of aerosol optical depths can be determined in polar regions, where few other measurements of total ozone are available.

With the application of methods described in Section 4 for determining molecular absorption optical depths

it is possible to monitor properties of the absorbing constituent. Fig. 7 illustrates the pronounced August maximum in τ_{ma} which results from water vapor absorption at both wavelengths. These results are consistent with the high precipitable water content which normally occurs during the summer "monsoon" period in Tucson. Using this technique, therefore, water vapor content can also be monitored with a solar radiometer.

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REFERENCES

- Ångström, A., 1961: Techniques of determining the turbidity of the atmosphere. *Tellus*, **13**, 214–223.
- , 1972: Turbidity of the atmosphere over India. *Tellus*, **24**, 597–598.
- Bates, D. R., 1954: The physics of the upper atmosphere. *The Solar System*, Vol. 2, G. P. Kuiper and B. M. Middlehurst, Eds., The University of Chicago Press, 576–643.
- Bevington, P. R., 1969: *Data Reduction and Error Analysis for the Physical Sciences*. McGraw-Hill, 336 pp.
- Climatic Impact Assessment Program, 1975: The natural stratosphere of 1974. CIAP Rep. DOT-TST-75-51, Monogr. No. 1, Washington, D. C., Dept. of Transportation, 3–10 to 3–29.
- Dobson, G. M. B., 1930: Observations of the amount of ozone in the earth's atmosphere and its relation to other geophysical conditions, Part IV. *Proc. Roy. Soc. London*, **A129**, 411–433.
- , 1931: A photoelectric spectrophotometer for measuring the amount of atmospheric ozone. *Proc. Phys. Soc. London*, **43**, 324–339.
- , and D. N. Harrison, 1926: Measurements of the amount of ozone in the earth's atmosphere and its relation to other geophysical conditions. *Proc. Roy. Soc. London*, **A110**, 660–693.
- Dütsch, H. U., 1969: Atmospheric ozone and ultraviolet radiation. *World Survey of Climatology*, Vol. 4, D. F. Rex, Ed., Elsevier, 383–432.
- Flowers, E. C., R. A. McCormick and K. R. Kurfs, 1969: Atmospheric turbidity over the United States, 1961–1966. *J. Appl. Meteor.*, **8**, 955–962.
- Herman, B. M., S. R. Browning and R. J. Curran, 1971: The effect of atmospheric aerosols on scattered sunlight. *J. Atmos. Sci.*, **28**, 419–428.
- Junge, C. E., 1963: *Air Chemistry and Radioactivity*. Academic Press, 382 pp.
- Knestrück, G. L., T. H. Cosden and J. A. Curcio, 1962: Atmospheric scattering coefficients in the visible and infrared regions. *J. Opt. Soc. Amer.*, **52**, 1010–1016.
- Nautical Almanac Office, U. S. Naval Observatory, 1973: *The American Ephemeris and Nautical Almanac for the Year 1975*. Washington, D. C., U. S. Govt. Printing Office, 568 pp.
- , 1974: *The American Ephemeris and Nautical Almanac for the Year 1976*. Washington, D. C., U. S. Govt. Printing Office, 574 pp.
- Porch, W. M., R. J. Charlson and J. F. Radke, 1970: Atmospheric aerosol: Does a background level exist? *Science*, **170**, 315–317.
- Quenzel, H., 1970: Determination of size distribution of atmospheric aerosol particles from spectral solar radiation measurements. *J. Geophys. Res.*, **75**, 2915–2921.
- Rangarajan, S., 1972: Wavelength exponent for haze scattering in the tropics as determined by photoelectric photometers. *Tellus*, **24**, 56–64.

- Reiter, E. R., and J. E. Lovill, 1974: Longitudinal movement of stratospheric ozone waves as determined by satellite. *Arch. Meteor. Geophys. Bioklim.*, **A23**, 13-27.
- Roosen, R. G., R. J. Angione and C. H. Klemcke, 1973: World-wide variations in atmospheric transmission: I. Baseline results from Smithsonian observations. *Bull. Amer. Meteor. Soc.*, **54**, 307-316.
- Rozenberg, G. V., 1966: *Twilight: A Study in Atmospheric Optics*. Plenum Press [translated from the Russian], 358 pp.
- Shaw, G. E., 1971: An experimental study of atmospheric turbidity using radiometric techniques. Ph.D. dissertation, University of Arizona, 182 pp.
- , J. A. Reagan and B. M. Herman, 1973: Investigations of atmospheric extinction using direct solar radiation measurements made with a multiple wavelength radiometer. *J. Appl. Meteor.*, **12**, 374-380.
- Yamamoto, G., and M. Tanaka, 1969: Determination of aerosol size distribution from spectral attenuation measurements. *Appl. Opt.*, **8**, 447-453.