

SMITHSONIAN MISCELLANEOUS COLLECTIONS
VOLUME 123, NUMBER 3

Hodgkins Fund

A METHOD FOR THE MEASUREMENT
OF ATMOSPHERIC OZONE USING THE
ABSORPTION OF OZONE IN THE
VISIBLE SPECTRUM

By

OLIVER R. WULF

U. S. Weather Bureau
California Institute of Technology
Pasadena, Calif.

AND

JAMES E. ZIMMERMAN

Astrophysical Observatory
Smithsonian Institution
Table Mountain, Calif.



(PUBLICATION 4177)

CITY OF WASHINGTON
PUBLISHED BY THE SMITHSONIAN INSTITUTION
OCTOBER 27, 1954

SMITHSONIAN MISCELLANEOUS COLLECTIONS
VOLUME 123, NUMBER 3

Hodgkins Fund

A METHOD FOR THE MEASUREMENT
OF ATMOSPHERIC OZONE USING THE
ABSORPTION OF OZONE IN THE
VISIBLE SPECTRUM

By

OLIVER R. WULF

U. S. Weather Bureau
California Institute of Technology
Pasadena, Calif.

AND

JAMES E. ZIMMERMAN

Astrophysical Observatory
Smithsonian Institution
Table Mountain, Calif.



(PUBLICATION 4177)

CITY OF WASHINGTON
PUBLISHED BY THE SMITHSONIAN INSTITUTION
OCTOBER 27, 1954

The Lord Baltimore Press
BALTIMORE, MD., U. S. A.

Hodgkins Fund

A METHOD FOR THE MEASUREMENT OF
ATMOSPHERIC OZONE USING THE
ABSORPTION OF OZONE IN
THE VISIBLE SPECTRUM

By OLIVER R. WULF

*U. S. Weather Bureau, California Institute of Technology
Pasadena, Calif.*

AND

JAMES E. ZIMMERMAN

*Astrophysical Observatory, Smithsonian Institution
Table Mountain, Calif.*

1. INTRODUCTION

By measuring the transmission of the atmosphere for sunlight over a region of the spectrum in which ozone possesses absorption of intensity known from laboratory measurements, the amount of ozone in the vertical path through the atmosphere can be determined. A large variation of the intensity of the absorption with wavelength is in general advantageous.

The measurement of atmospheric ozone ordinarily utilizes a spectral region in the near ultraviolet. Ozone in the amount existing in the vertical atmospheric path possesses absorption of convenient strength in that region, and the variation of the absorption coefficient with wavelength is relatively large there.

Ozone also exhibits absorption across the visible spectrum, with a maximum in the yellow-orange that leads to the blue color of this gas in sufficiently large paths. In the atmospheric path the amount of ozone is relatively small and this absorption is weak, making the visible region of the spectrum less suited, so far as this factor is concerned, for atmospheric ozone measurement than the ultraviolet region. Also the variation of the absorption coefficient with wavelength is less rapid in the visible. Nevertheless, some effort has been given to the measurement using this absorption, and if the atmospheric scattering and character of the sky in general is also a matter of interest, this region of the spectrum should be a fruitful one for investigation.

Craig has reviewed the subject of atmospheric ozone in a recent monograph.¹ Concerning the visible region of the spectrum in particular, we wish to mention here the work of Cabannes and Dufay² and of Fowle³ having to do with data obtained in the work of the Smithsonian Astrophysical Observatory, as does the present paper; of Gauzit⁴ who used a method of visual spectrophotometry; and of Duninowski⁵ who employed an apparatus that recorded the spectral distribution of the intensity of solar radiation in a manner similar to that in the regular work of the Smithsonian Astrophysical Observatory. More recently Tien Kiu⁶ made a detailed study of atmospheric optical density using Smithsonian data from the station at Montezuma, Chile. This work includes a graphical evaluation of ozone.

A convenient means of adequately measuring atmospheric ozone using the visible region of the spectrum would make possible a helpful comparison with daily measurements employing the ultraviolet region. Moreover, such work in the visible region is, in certain respects, somewhat less demanding instrumentally than that in the ultraviolet, and it seems possible that a procedure, reliable though somewhat less precise than that commonly employed in the ultraviolet, might be developed for the visible.

2. PURPOSE OF THE PRESENT WORK

The atmospheric transmission coefficients, obtained in the work of the Smithsonian Astrophysical Observatory on days of especially clear skies when the "long method" of observing is employed in the determination of the solar constant, offer an unusual opportunity to determine the vertical-path ozone using the visible region of the spectrum. It is on these transmission coefficients at appropriately chosen places in the spectrum that most of the relatively small amount of earlier work in this spectral region has been based (see, however, footnotes 4 and 5). The present investigation attempts to put the use of these transmission coefficients for the determination of ozone on any one day on as accurate a basis as practicable and to provide a rapid computational method for making the determination.

¹ Craig, R. A., *Amer. Meteorol. Soc., Meteorological Monographs*, vol. 1, No. 2, 1950.

² Cabannes, J., and Dufay, J., *Journ. Phys. et Rad.*, ser. 6, vol. 7, p. 257, 1926; *ibid.*, ser. 6, vol. 8, p. 353, 1927.

³ Fowle, F. E., *Smithsonian Misc. Coll.*, vol. 81, No. 11, 1929.

⁴ Gauzit, J., Thesis, Paris, 1935.

⁵ Duninowski, A. L., Thesis, Montpellier, 1932.

⁶ Tien Kiu, *Journ. Phys. et Rad.*, ser. 7, vol. 9, p. 297, 1938.

It is the purpose of the present work to provide an adequate method using the visible absorption in order that this may be employed generally wherever the transmission of the atmosphere for radiation in this spectral region can be measured. At the same time the method yields information concerning the character of the atmospheric scattering at the time of the observations. Also it is believed that the results of the application of this method will serve as a calibration for a relative method of ozone determination from a single measurement of the relative intensities of the radiation across the visible region. A preliminary description of this has been given elsewhere.⁷

3. METHOD

The optical density of the atmosphere at any particular wavelength, that is, the negative logarithm of the transmission coefficient at this wavelength, may be expressed very roughly as the sum of two terms, one in the -4 th power of the wavelength representing pure molecular scattering, and the other a term independent of wavelength but differing from day to day, representing a "white" scattering or ground-glass effect arising from relatively large particles of dust and haze. Where selective absorption by an individual atmospheric constituent is also present, an additional term describing this must be included. An example of this last is the absorption of ozone in which we are interested.

In general, however, owing to the presence of haze of small and intermediate particle size, some additional scattering will be present, requiring, as a closer approximation to the actual scattering, an additional term in the wavelength. Depending upon the size of the haze particles, this term might contain the wavelength to the -4 th or to some lower power.⁸ For most of the observational data used in the present work the wavelength-dependent scattering in excess of the pure Rayleigh scattering is not large. However, if relatively heavy haze were present it might become large, and an additional term or terms might be required to adequately describe the scattering.

From a study of the data used in the present work we believe that a term in the wavelength to the power -2 describes the additional scattering in this observational data sufficiently closely for the purpose of the ozone determination. On relatively hazy days the scattering

⁷ Wulf, O. R., *Ann. Astrophys. Obs.*, Smithsonian Inst., vol. 7, p. 177, 1954.

⁸ It should be noted that Tien Kiu (see footnote 6) studied the behavior of data from the Montezuma station using an expression containing a constant term and a term in the -4 power of the wavelength with a variable coefficient. See also Dermendjian and Sekera, *Journ. Opt. Soc. Amer.*, vol. 43, p. 1158, 1953.

represented by the sum of the wavelength-independent term and the term in the reciprocal of the square of the wavelength should be relatively large, while on clear days it should be correspondingly small. However, the distribution between the two terms appears to depend rather sensitively on the measured values of the transmission coefficients, and the computed value of one or the other term may be negative. Such negative values are probably without physical significance since they may arise from the normal experimental error in the observations.

It seems important to emphasize that so far as the determination of ozone itself is concerned, the object of the method is to approximate as closely as possible the background optical densities as they would be in the absence of ozone absorption, without particular regard as to how these came about, that is, from molecular scattering, haze, etc. The additional information contained in δ and ζ (see equation (1) below) is from this point of view a byproduct, but from the point of view of the state of the sky it may be as interesting as the ozone determination.

In the interests of simplicity and rapidity of calculation it would be helpful to limit the number of unknowns to as small a number as sufficed for the ozone determination. From what has been said above, the optical density of the atmosphere at any particular wavelength can, for our purposes, probably be expressed, in the absence of other selective absorption, as the sum of a term representing the ozone absorption, a term representing the pure Rayleigh scattering by the molecules of the atmospheric gases themselves, a term, just discussed, representing the scattering by particles of haze of intermediate size, and finally a wavelength-independent term representing the scattering by large particles of haze.

We should like to emphasize here that, with the method of calculation to be described below, an additional term in another power of the wavelength with unknown coefficient could be introduced without excessive increase of the computational work. Observations at additional spectrum places might be required to justify the use of such a term, but this, too, would not mean an excessive increase in the computations. If work such as the present were attempted at lower altitudes, a term of this kind should permit a closer approximation to the scattering, which would in general be more intense there.

The value for the Rayleigh-scattering term for dry air can be calculated⁹ (see section 6). The other terms in the total optical

⁹ See footnotes 2 and 6. In equation (3) of Tien Kiu (footnote 6) we believe that the coefficient of ρ in the denominator was intended to be 7.

where the subscripts 19, 20, 22, 24, 26, 28, and 30 refer to the seven spectrum places. On the left-hand side of each equation is the total optical density minus the scattering due to the air molecules, the first being measured and the second known from theory. This difference is equated to the ozone absorption plus the remaining scattering which is described by the term in λ^{-2} and the term ζ . These three terms on the right-hand side of the equation contain the three unknowns, x , δ , and ζ , each with a known coefficient that does not change from day to day.

4. THE ABSORPTION OF WATER VAPOR AT 0.57μ

Concerning Place 24, at wavelength 0.570μ near the maximum of the ozone absorption, in addition to the absorption by ozone, there is absorption by water vapor. This is very weak at this wavelength, and correction for it does not appear to be warranted, in spite of the fact that the ozone absorption is itself weak, unless the precipitable water amounts to about 0.5 cm. Above this we believe correction for water absorption is warranted, and it illustrates helpfully that one need not forego the use of a particular wavelength for ozone determination merely because detectable water absorption exists there. In addition to the subtraction of the Rayleigh scattering from the total optical density ($-\log T_n$), a small contribution by water absorption should also be subtracted (if warranted), comprising an additional term on the left-hand side of this one equation (for Place 24). This term is taken here as of the form $\eta \cdot \text{ppt H}_2\text{O}$, where ppt H_2O (expressed in cm of liquid water) is the water vapor in the vertical atmospheric path, a quantity regularly evaluated from the observations.

The water absorption coefficient, η , at Place 24 must of course be determined. This is an apparent absorption coefficient in the present work, depending on the slit width and resolution of the apparatus, since the absorption arises from the many fine lines of a vibration-rotation band of water,¹⁰ and the fine structure is not resolved. However, the absorption is very weak and the correction for it is usually small. We believe that as an approximation for the present purpose a term of the form $\eta \cdot \text{ppt H}_2\text{O}$ suffices. It assumes that this absorption, also, is of the simple exponential form.

From a careful comparison of bolograms at Place 24 on days of low and of high water we estimate that η has a value for our data of $0.0009 \text{ cm}^{-1} \pm 50\%$. With this value, the water absorption amounts to 0.1% at about 0.5 cm ppt H_2O .

¹⁰ The combination band $2\nu_1 + 3\nu_3$. See, for example, Herzberg, G., *Infrared and Raman spectra*, p. 281, 1945. New York.

It should be possible to improve the value of η in the course of a program of ozone measurements, taking advantage especially of days of high precipitable water. Each day, with the current value of η , should yield a new value of this quantity from the equation for Place 24 separately with the values of x , δ , and ζ for the day, and a running average of η may be kept. However, in attempting to do approximately this in the course of the present work a further point arose which is of some interest in the matter of method.

With the adopted value of the ozone absorption coefficient for Place 24 (section 6), essentially the excess of the left-hand side of the equation over the right-hand side did not appear to approach zero with decreasing water, but rather a finite positive value. The points, indeed, fluctuated greatly and were not sufficient to approximate a linear relation, but it seems clear that for the lowest water values the apparent excess absorption is more than can be accounted for by water alone. This means either that the adopted value for the ozone-absorption coefficient at Place 24 is a little low compared with the values at the other places, or that there is another, not so far considered, weak atmospheric absorption here. This matter is discussed further in section 6.

At the precipitable water values experienced in the present work, the spectrum Places 22, 26, 28, and 30 do not appear to be influenced by water absorption of intensity sufficient to be important in the measurement of ozone. The transmission coefficients of Places 19 and 20 are determined from the envelope of the hologram trace in this region (see p. 179 of footnote 7 reference).

5. REDUCTION AND SOLUTION OF THE EQUATIONS

The set of seven equations under (2) above is of the form

$$c_n = k_n \cdot x + l_n \cdot \delta + m_n \cdot \zeta \quad (3)$$

where the c_n 's contain the observational data and certain known quantities that do not change from day to day, and the coefficients k_n , l_n , and m_n (all the m_n 's are unity) of the three unknowns x , δ , and ζ , are known quantities that also do not change from day to day. Given the values of the transmission coefficients at the n places (in the present work seven) in the visible spectrum, the n values of c , the left-hand side of (2), can be readily computed since the other quantities contained in c are at hand. (In computing c_{24} the value for the precipitable water at the time of the observations is also needed if this is high enough to warrant correction for water absorption, as described in section 4.)

For the reduction and solution of these equations it will be helpful to express them in matrix notation.¹¹ Thus the set of seven equations represented by (3) above may be written

$$L = A \begin{bmatrix} x \\ \delta \\ \zeta \end{bmatrix} \quad (4)$$

where L is a seven-row by one-column matrix comprising the c values, and A , the matrix coefficient of $\begin{bmatrix} x \\ \delta \\ \zeta \end{bmatrix}$, is a seven-row by three-column matrix comprising the k_n , l_n , and m_n values, in (3) above.

We should like now to condense with proper weighting the information contained in the several equations represented by (4). The seven ordinary equations contained in (4) can be reduced to three equations by the method of least squares by multiplying both sides of equation (4) by A' , the transpose of A . This gives

$$A'L = A'A \begin{bmatrix} x \\ \delta \\ \zeta \end{bmatrix} \quad (5)$$

Solving for the unknowns

$$\begin{bmatrix} x \\ \delta \\ \zeta \end{bmatrix} = (A'A)^{-1}A'L \quad (6)$$

The reciprocal of the matrix $A'A$ is given by the adjoint matrix of $A'A$ divided by the determinant of $A'A$. Substituting this in (6) yields

$$\begin{bmatrix} x \\ \delta \\ \zeta \end{bmatrix} = \frac{\text{adj}(A'A)A'L}{|A'A|} \quad (7)$$

The matrix L alone contains the observed data for the day. The remainder of the right-hand side of (7) reduces to a three-row by seven-column matrix that is calculable once and for all, and is at hand for the indicated multiplication. The values for the three unknowns for any set of observations are obtained by multiplying L by this three-row by seven-column matrix, $\frac{\text{adj}(A'A)A'}{|A'A|}$. Since the seven-row by one-column matrix L consists simply of the seven values of the optical density reduced by the molecular scattering at the particular wavelength (and, at Place 24, by the water absorption if necessary),

¹¹ See, for example, Perlis, S., Theory of matrices, 1952. Cambridge, Mass.

the calculation of x , δ , and ζ from the observations for any one day is a relatively simple matter.

6. THE MOLECULAR SCATTERING AND THE OZONE-ABSORPTION COEFFICIENTS

For the Rayleigh scattering by the molecules of the air we have used the expression of Cabannes (footnote 9), as did Tien Kiu (footnote 6), which takes into account the anisotropy of the air molecules, namely

$$k_o = 0.4343 \frac{8\pi^3}{3} \frac{(\mu^2 - 1)^2}{n_o \cdot \lambda^4} \frac{6 + 3\rho}{6 - 7\rho} \quad (8)$$

where k_o is the apparent absorption coefficient due to scattering at standard conditions, the quantity k being defined by $k = \frac{1}{d} \log_{10} \frac{I_o}{I}$, where I_o and I are the incident and emergent intensities of a monochromatic beam in passing over a path d (cms) of the gas. Common logarithms have been used throughout the present work accounting for the factor 0.4343 in (8). The number of molecules per cc at standard conditions, n_o (Loschmidt's number), has been taken as 2.687×10^{19} , and the depolarization factor ρ for air (see footnote 9) as 0.042. The index of refraction of dry air at standard conditions, μ , for the several wavelengths was taken from table I of Tien Kiu (footnote 6).

The contribution of the molecular scattering to the total optical density at an altitude at which the pressure is p is then $k_o h_o p / p_o$, where h_o is the height of the homogeneous atmosphere, here taken as 7,993 meters. The ozone result is not very sensitive to small changes in p , and the use of an average value for the station for these observations is probably satisfactory. In this work we have used an average pressure for long-method days at Table Mountain of 585 mm. This value is probably subject to some improvement. Since the index of refraction μ is a number very little greater than unity, $(\mu^2 - 1)^2$ may be approximated as $4 (\Delta\mu)^2$, where $\Delta\mu = \mu - 1$. These data yield for the optical density due to molecular scattering over Table Mountain, that is, the second term on the left-hand side of each equation under (2), the expression

$$\beta (\mu_n^2 - 1)^2 \lambda_n^{-4} = 0.0353 (\Delta\mu_n)^2 \lambda_n^{-4} \quad (9)$$

where a factor of 10^{-6} from $(\Delta\mu)^2$ and a factor of 10^{16} from λ^{-4} have been taken into the constant 0.0353. This permits us in the numerical work to express $\Delta\mu$ as $\Delta\mu \times 10^3$ and λ in microns instead of centimeters, a convenient procedure.

The intensity of the absorption of ozone in the visible region of the spectrum has been the subject of a number of researches. Recently this has been measured by Inn and Tanaka and by Vigroux. References are here given to these and related earlier papers.¹² From a study of these results we have adopted the following values of α (to the base 10) for the present work.

TABLE I

Place	19	20	22	24	26	28	30
$\lambda(\mu)$	0.722	0.686	0.614	0.570	0.532	0.499	0.470
α	0.007	0.014	0.049	0.052	0.031	0.013	0.004

We believe that at present allowance must be made for the possibility of a few percent error in the scale of the values in table I. Also there may be small relative inconsistencies in them. There is, as mentioned in section 4, the indication in our results that the value at Place 24 of 0.052 is a little low relative to the other values, if we assume that there is no other selective atmospheric absorption at this wavelength. It is known that there is absorption of water vapor (see section 4), of O_2 , and of O_4 (or $(O_2)_2$) at or close to this wavelength¹³ though these appear to be very small. Thus, while we believe that the values in table I are adequate for useful ozone measurement, they are probably still open to some improvement. We should like to repeat here that the main purpose of the present work is to establish a practical method for ozone measurement using the visible region. The constants that enter may be improved in subsequent work.

7. COMPUTATIONAL PROCEDURE

As shown in equation (7), the values of the three unknowns for any one set of observations are obtained by multiplying the matrix L , which alone contains the observed data, by the matrix representing the other portion of the right-hand side of the equation. This other portion can be evaluated once and for all, for it contains only the coefficients of the three unknowns, and these, comprising the ozone

¹² Inn, E. C. Y., and Tanaka, Y., *Journ. Opt. Soc. Amer.*, vol. 43, p. 870, 1953; Vigroux, E., *C. R. Acad. Sci. Paris*, vol. 235, p. 149, 1952; *ibid.*, vol. 227, p. 272, 1948; Vassy, A., and Vassy, E., *Journ. Chem. Phys.*, vol. 16, p. 1163, 1948; Humphrey, G. L., and Badger, R. M., *Journ. Chem. Phys.*, vol. 15, p. 794, 1947; Lefebvre, L., *C. R. Acad. Sci. Paris*, vol. 200, p. 653, 1935; Wulf, O. R., *Smithsonian Misc. Coll.*, vol. 85, No. 9, 1931; Colange, G., *Journ. Phys. et Rad.*, ser. 6, vol. 8, p. 254, 1927.

¹³ Dufay, J., *Ann. d'Astrophys.*, vol. 5, p. 93, 1942.

absorption coefficients and the wavelengths of the spectrum places, do not change from day to day. The evaluation of this portion of equation (7), namely $\frac{\text{adj}(A'A)A'}{|A'A|}$, is as follows:

The matrix A is

$$A = \begin{bmatrix} 0.007 & 1.918 & 1 \\ 0.014 & 2.125 & 1 \\ 0.049 & 2.653 & 1 \\ 0.052 & 3.078 & 1 \\ 0.031 & 3.533 & 1 \\ 0.013 & 4.016 & 1 \\ 0.004 & 4.527 & 1 \end{bmatrix} \quad (10)$$

where the first column comprises the values of the ozone-absorption coefficient at the seven spectrum places, the second column comprises the values of λ^{-2} (λ in microns) at these places, and the third column comprises the values of the coefficient of ζ which are all unity.

Multiplying A by its transpose A' , which is a three-row by seven-column matrix, one obtains the 3×3 matrix

$$A'A = \begin{bmatrix} 0.006496 & 0.51307 & 0.170 \\ 0.51307 & 73.811 & 21.850 \\ 0.170 & 21.850 & 7 \end{bmatrix} \quad (11)$$

The adjoint of $A'A$ is

$$\text{adj } A'A = \begin{bmatrix} 39.254 & 0.12302 & -1.3373 \\ 0.12302 & 0.016572 & -0.054717 \\ -1.3373 & -0.054717 & 0.21624 \end{bmatrix} \quad (12)$$

The determinant of $A'A$ is

$$|A'A| = 0.090769 \quad (13)$$

These are the quantities needed for the evaluation of the right-hand side of equation (7) exclusive of the matrix L . They yield the 3×7 matrix

$$\frac{\text{adj}(A'A)A'}{|A'A|} = \begin{bmatrix} -9.11 & -5.80 & 10.05 & 11.93 & 3.46 & -3.67 & -6.87 \\ -0.2431 & -0.1959 & -0.0520 & 0.0296 & 0.0842 & 0.1480 & 0.2291 \\ 1.123 & 0.895 & 0.061 & -0.239 & -0.204 & -0.230 & -0.406 \end{bmatrix} \quad (14)$$

When the 7×1 matrix, L , is multiplied by this matrix there results

the 3×1 matrix $\begin{bmatrix} x \\ \delta \\ \zeta \end{bmatrix}$ which comprises the three unknowns that we seek.

8. CALCULATIONS FOR A PARTICULAR DAY

The seven elements of the matrix L are obtained from the transmission coefficients found for the day at the seven spectrum places. Each one is the negative logarithm of the transmission coefficient (an optical density) minus (see expression (2)) the optical density due to the Rayleigh scattering by the molecules of the air, which latter is given in equation (9). This quantity, which is written for an average value of the atmospheric pressure, has a given value for each spectrum place. These values are contained in table 2.

TABLE 2

	19	20	22	24	26	28	30
$0.0353(\Delta\mu)^2\lambda^{-4} \dots$	0.01099	0.01351	0.02116	0.02857	0.03783	0.04908	0.06266

In the following illustrative calculation of the values of the three unknowns the data of September 29, 1953, have been used. Both δ and ξ were of moderate size on this day. The measured values of the transmission coefficients are given in table 3 together with the optical densities (the negative logarithms of these numbers) corresponding to them.

TABLE 3

Place	19	20	22	24	26	28	30
Trans. coefs.....	0.961	0.952	0.915	0.894	0.888	0.872	0.847
Optical densities...	0.01728	0.02136	0.03858	0.04866	0.05159	0.05948	0.07212

Subtracting from the optical densities of table 3 the corresponding Rayleigh-scattering values of table 2 one has the elements of the 7×1 matrix L of equation (7)

$$L = \begin{bmatrix} 0.00629 \\ 0.00785 \\ 0.01742 \\ 0.02009 \\ 0.01376 \\ 0.01040 \\ 0.00946 \end{bmatrix} \quad (15)$$

Multiplying now this matrix L for these observations by the 3×7 matrix $\frac{\text{adj}(A'A)A'}{|A'A|}$ of (14) yields

$$\begin{bmatrix} x \\ \delta \\ \xi \end{bmatrix} = \begin{bmatrix} 0.256 \text{ cm ozone} \\ 0.00149 \text{ (microns)}^2 \\ 0.00131 \end{bmatrix} \quad (16)$$

where each one of these three quantities is the result of the summation of seven terms arising in the multiplication.

The final results are thus given in (16). It is instructive to substitute these values of x , δ , and ζ into equation (1) and compute the optical densities for each of the seven spectrum places. These may be compared with the measured optical densities. This gives an idea of how satisfactorily the measured transmission coefficients at the seven spectrum places have been represented by (1). The calculated optical densities for this day have the values given in table 4. Com-

TABLE 4

Place	19	20	22	24	26	28	30
Computed optical densities	0.01695	0.02157	0.03897	0.04779	0.05234	0.05970	0.07174

parison of these values with the values of table 3 shows that the average difference between the measured and calculated values is roughly 0.0005. In the transmission coefficients this means a difference of about one unit in the third figure, which indicates that for this day the measured values have been well represented by equation (1). In this respect this particular day is somewhat better than average.

In the above illustrative calculations no correction was made for water absorption. The precipitable water for this day was, however, 0.628 cm, for which (see section 4) we believe a correction at Place 24 is warranted. For this water value the term $\eta \cdot \text{ppt H}_2\text{O}$ is 0.00057. Subtracting this from the value 0.02009 for Place 24 in the matrix L of (15) yields 0.01952 as the value corrected for water absorption. Inserting this in place of the value 0.02009 in L and solving otherwise as before gives

$$\begin{aligned} x &= 0.250 \\ \delta &= 0.0147 \\ \zeta &= 0.0145 \end{aligned} \quad (17)$$

as compared with the values given in (16) which were obtained before the water correction. Recomputing the optical densities, using (17) instead of (16), we get the values given in table 5.

TABLE 5

Place	19	20	22	24	26	28	30
Computed optical densities	0.01701	0.02158	0.03876	0.04811	0.05222	0.05968	0.07176

As to the accuracy of the ozone determination, this can be better estimated after an intensive study of a series of measurements have

been made, and in particular it should be helpful to carry out a series of observations at some one station using both the ultraviolet and the visible absorptions.

SUMMARY

An analytical method has been developed for computing the vertical-path atmospheric ozone from the measurements of atmospheric transmission coefficients at several wavelengths across the visible spectrum using the absorption of ozone in this region. In the computational procedure a large part of the calculations is carried out once and for all, the evaluation of the ozone corresponding to any one set of observations being a relatively small matter.

The method also yields information concerning atmospheric haze. The optical densities corresponding to the measured transmission coefficients are represented in the present work by four terms. Two of these are the scattering by the molecules of the air and the absorption by ozone. The other two represent the scattering by haze, one a wavelength-independent portion, and the other a term in the square of the reciprocal of the wavelength with unknown coefficient. The values of this coefficient and of the wavelength-independent scattering, in addition to the ozone path, are given by the calculations, and constitute information on the character of the optical density of the haze.

ACKNOWLEDGMENTS

The efforts of a number of people have contributed to the present research. The authors gratefully acknowledge assistance received from Alfred F. Moore, Fred A. Greeley, Alfred G. Froiland, Merwyn G. Utter, and Albert M. Pezzuto, and the encouragement and support received from L. B. Aldrich, director of the Astrophysical Observatory, Smithsonian Institution, and from the late W. H. Hoover, chief of the Division of Astrophysical Research. Grateful acknowledgment is also made to Verner Schomaker, of the California Institute of Technology, for valuable discussions and suggestions.