Non-selective absorption by atmospheric water vapour
at visible and near infrared wavelengths

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SUMMARY

Measurements of the atmospheric optical thickness at 'window' wavelengths in the visible and near infrared region have been obtained from data of direct solar radiation through clear and hazy atmospheres. At these wavelengths, the weak attenuation of the atmosphere is due to Rayleigh scattering, non-selective absorption by water vapour and extinction by particulate matter.

Since non-linear dependence may exist between the particulate matter optical thickness and the precipitable water vapour, seasonal sets of atmospheric optical thicknesses have been selected, which present linear and direct correlation with the precipitable water vapour, at each wavelength. Thus the slope of the regression line of optical thickness on precipitable water vapour is the sum of (i) the non-selective absorption coefficient of atmospheric water vapour and (ii) the linear variation coefficient of the particulate matter optical thickness as a function of precipitable water vapour. The latter coefficient has been evaluated at the various wavelengths for each set of data, by examining the spectral series of data in terms of Ångström's expression and determining linear relationships between atmospheric turbidity parameters and precipitable water vapour. Each monochromatic estimate of the non-selective absorption coefficient of water vapour has been obtained as the difference between the slope of the regression line and the linear variation coefficient of the particulate matter optical thickness. The resulting estimate has been related to the vertical distribution of absolute humidity, in order to determine the mass absorption coefficient of water vapour at unit air pressure.

1. INTRODUCTION

The visible and near-infrared attenuation spectrum of solar radiation in the atmosphere presents identifiable lines from a large number of water vapour absorption bands related to ground state transitions. Those in the visible are all relatively weak, whereas those in the near infrared are all rather strong, to such an extent as to cause regions of complete absorption. Other less intense bands are due to polyatomic gases such as oxygen, ozone and carbon dioxide.

Within the narrow spectral intervals of high transparency between these bands, atmospheric attenuation is mostly due to scattering by air molecules, to extinction by airborne particles, and to non-selective absorption by water vapour, which is commonly ascribed to accumulated weak effects of the wings of the multitude of absorption lines distributed throughout the spectrum. Thus the non-selective absorption by water vapour is responsible for a contribution to the total optical thickness of the atmosphere, which can be taken, to a good approximation, as being proportional to the water vapour content along the atmospheric path. For clean air, with little extinction by particulate matter, it is expected to play a significant role in the attenuation processes of the atmosphere.

At the beginning of this century, Fowle (1913, 1914, 1915) performed at Mount Wilson (1730 m a.m.s.l.) a large number of extinction measurements of solar radiation at many 'window' wavelengths, from 0.34 to 2.24 μm. The observations were made for very clear conditions of the atmosphere. The logarithms of the monochromatic transmissivity of solar radiation through the atmosphere, vertically above the ground station, were plotted by him as a function of precipitable water vapour, as evaluated from the absorption features of the

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infrared spectrum. At each wavelength, he took the slope of the regression line as a measure of the non-selective absorption coefficient of atmospheric water vapour. Fowle suggested that these estimates should include not only water vapour absorption but also possibly attenuation by small particles formed by the action of ultraviolet light on the moisture present in the air.

Other estimates of the weak absorption coefficient of water vapour at visible and near infrared wavelengths have been obtained by Elder and Strong (1953), Tomasi et al. (1974) and Fraser (1975). In all these, Fowle's regression line method was applied to optical thickness measurements made in very clear atmospheres. In spite of the high transparency conditions, Fraser found that almost all the variance in the atmospheric optical thickness was associated with particulates. Examining the spectral behaviour of the results, he suggested that these water vapour absorption coefficients could have been caused at least partially by particulate matter extinction in some combination with the non-selective absorption of water vapour and concluded that 'the role of water vapour in atmospheric scattering problems is poorly understood'.

A further analysis is, however, possible. The complete set of results obtained by these authors shows that there are appreciable discrepancies between them only at wavelengths shorter than about 1 μm. This can be explained by assuming that the extinction data of the various authors refer to different optical weights of particulate matter in the atmospheres they examined. In the present paper, an attempt is made to separate the slope of the regression line of the atmospheric optical thickness on the precipitable water vapour, as found at various wavelengths, into (i) the variation coefficient of the particulate matter optical thickness with precipitable water vapour, and (ii) the non-selective absorption coefficient of atmospheric water vapour.

2. EXAMINATION OF SOLAR IRRADIANCE DATA

Measurements at the earth's surface of incoming solar radiation at several 'transparent' wavelengths have been made for various sun elevations, during days characterized by anticyclonic conditions, and in different seasons. A large number of solar spectra in the wavelength range 0.65 to 2.27 μm, were taken during autumn 1971, at Buda (10 m a.m.s.l.), near Bologna (Po Valley), by using a KBr prism monochromator (Vittori et al. 1974) giving spectral resolutions of about 30 cm⁻¹ and having an angular field of view of about 40°. Other measurements were made with a sun photometer (Tomasi and Guzzi 1977) provided with pass-band filters centred at 0.50 and 1.03 μm, respectively (half bandwidths of 0.01 μm) and having an angular field of view of 1°40'. These sets of data were obtained at Bologna (35 m a.m.s.l.) during summer and autumn 1973, and at Molinella (10 m a.m.s.l.) during winter and spring 1974. The precipitable water vapour, w, was simultaneously measured with an infrared hygrometer using the solar spectrum (Tomasi and Guzzi 1974) (the calibration curve was carefully made in the free atmosphere to obtain estimates of w with standard deviations varying between 4 and 11%, corresponding to water vapour content in the sun paths from 20 to 0.3 g cm⁻²).

For each measurement of solar radiation, I(λ,θ), taken at wavelength λ and at apparent zenith angle θ of the sun, the atmospheric optical thickness, τ(λ), along the local vertical was computed from the Lambert-Beer law:

\[ I(λ,θ) = R I_0(λ) \exp\{-m(θ) \tau(λ)\}, \]  

(1)

where R is the correction term relative to the earth–sun distance at the observation time, as computed from data of Coulson (1975), I₀(λ) is the equivalent zero-air-mass measurement
of solar radiation at mean earth–sun distance and \( m(\theta) \) is the atmospheric air-mass relative to the vertical direction, as obtained from the tables of Kondratyev (1969) for a standard atmosphere and normalized to air pressure \( p_s = 1\cdot013 \) bar at the surface.

Since each reading \( I(\lambda, \theta) \) includes also a contribution due to the diffusely scattered radiation from the sky, Eq. (1) has been applied only to monochromator readings taken at air-masses, \( m(\theta) \), smaller than 8 (\( \theta < 83^\circ \)), and to sun photometer readings obtained for \( m(\theta) < 5 \) (\( \theta < 79^\circ \)). At these solar elevations, the diffuse light contributions affecting instrumental readings are limited to a few per cent in relatively clear atmospheres (Shaw et al. 1973; Shaw 1976).

The quantity \( I_0(\lambda) \) in Eq. (1) has been determined by correctly applying the ‘Langley plot’ method to daily sets of readings taken during mornings characterized by stable and clean air conditions (visual range at the surface greater than 20 km). For each diurnal set of data and for each wavelength, the logarithms of \( I(\lambda, \theta) \) have been plotted as a function of the relative air-mass \( m(\theta) \), so that the extrapolated value of the least-square line to zero air-mass represents a reliable estimate of \( R I_0(\lambda) \). Divided by the corresponding daily value of \( R \), these results give the average value of \( I_0(\lambda) \) at each ‘transparent’ wavelength. This has been used in Eq. (1) for obtaining ‘instantaneous’ estimates of \( \tau(\lambda) \).

In this regard, it has to be noticed that indiscriminate use of the ‘Langley plot’ method on sets of data taken in atmospheres affected by time variations of turbidity and/or characterized by non-horizontal homogeneous layers, leads to underestimations of \( I_0(\lambda) \) (Guzzi et al. 1972; Vittori et al. 1974; Russel and Shaw 1975; Shaw 1976). Consequently, the resulting total optical thickness, \( \tau(\lambda) \), of the atmosphere is also underestimated. Warm and humid atmospheres are, in general, affected by more marked time turbidity variations. In atmospheres having high water vapour content, \( w \), more marked underestimations of \( \tau(\lambda) \) are expected; in such cases, the slope of the regression line, as obtained by plotting \( \tau(\lambda) \) as a function of \( w \), is also underestimated.

3. FEATURES OF THE ATMOSPHERIC OPTICAL THICKNESS

The monochromatic optical thickness, \( \tau(\lambda) \), of the atmosphere, as given by Eq. (1), is the sum of several terms, each due to an atmospheric constituent. At transparent wavelengths and for limited spectral resolutions (such as to render negligible the contribution given by unresolved absorption lines of water vapour and other minor gases), \( \tau(\lambda) \) can be expressed in the form

\[
\tau(\lambda) = (p_0/p_s)\sigma(\lambda) + d(\lambda) + a(\lambda) + c(\lambda)w, \tag{2}
\]

where \( p_o \) is the surface air pressure, \( \sigma(\lambda) \) the molecular scattering term, \( d(\lambda) \) the optical thickness due to weak absorption bands of ozone, \( a(\lambda) \) the optical thickness of the particulate matter, and \( c(\lambda) \) the non-selective (weak) absorption coefficient of water vapour.

The terms \( \sigma(\lambda) \) and \( d(\lambda) \) have been evaluated for each ‘instantaneous’ value of \( \tau(\lambda) \), as follows:

(i) The molecular scattering term \( \sigma(\lambda) \) has been computed at the selected wavelengths, using the monochromatic optical thicknesses proposed by Penndorf (1957) for an isothermal Rayleigh atmosphere at 0°C, and multiplying by the correction factor for the non-isothermal conditions of the real atmosphere and by the correction term for the surface temperature during observations.

(ii) The term \( d(\lambda) \) is due to the Chappuis band of ozone, which is an array of weak bands from 0·44 to about 0·75 \( \mu \)m. It has been estimated as the product \( \chi(\lambda)q \), where \( \chi(\lambda) \) is the absorption coefficient, as given by Selby et al. (1976) in \( \text{cm–atm}^{-1} \), and \( q \) is the
mean daily value of the atmospheric vertical content of ozone, as measured at Cagliari Elmas (39°15'N) (this is about 600 km from our measurement station (44°30'N), so q should approximate the true value within 20%).

By subtracting \( p_0/p \sigma(\lambda) \) and \( d(\lambda) \) from \( \tau(\lambda) \), the optical thickness for particle extinction and water vapour absorption

\[
b(\lambda) = a(\lambda) + c(\lambda)w
\]

has been obtained for each instantaneous measurement at the selected wavelengths.

Optical thicknesses due to particle extinction and to water vapour absorption depend on the physical structure of the atmosphere, so they can vary appreciably with meteorological conditions. The term \( c(\lambda)w \) is the integral of the mass absorption coefficient of water vapour with respect to the absolute humidity along the vertical path of the atmosphere. Since the mass absorption coefficient is proportional to air pressure and can be assumed, for practical purposes, to be independent of air temperature (Goody 1964), the weak absorption coefficient \( c(\lambda) \) turns out to be basically related to the vertical distribution curve of absolute humidity. Greater fractions of precipitable water vapour are present within the lower atmospheric layers in cold atmospheres (frequently characterized by temperature inversions during autumn and winter in the Po Valley area) than in summer atmospheres, characterized by warm and mixed air conditions (Tomasi 1977). On this basis, seasonal sets can be selected in order to limit the variability of \( c(\lambda) \) inside each set.

Larger variations are expected to affect the particulate matter optical thickness \( a(\lambda) \). Electromagnetic theory predicts that \( a(\lambda) \) depends on a number of parameters, such as the particle concentration, the multimodal shape of the particle size distribution, and the spectral features of both real and complex parts of the refractive index, which are closely related to the origin and chemical composition of the particulate matter (Volz 1972; Fischer 1973; Ilyev and Popova 1973). These optical parameters have rather complex relations with the meteorological conditions of the atmosphere. In particular, changes of relative humidity can lead to considerable variations of particle size and hence of the refractive index (Hänel 1976). Many observations (Filippov and Mirumyants 1972; Andreyev et al. 1972; Zuev et al. 1973; Georgievsky and Rozenberg 1973; Badayev et al. 1975) give evidence of wide variability of particle attenuation, as a function of relative humidity, at visible and near infrared wavelengths. In this regard, Malkevich et al. (1973) suggest that the growth of particles by condensation turns out to be favoured in atmospheres with high moisture content to such an extent as to produce an apparent non-linear dependence of water-enveloped particle attenuation on precipitable water vapour. This suggestion appears well confirmed by measurements of particulate matter extinction carried out by Vittori et al. (1974) in clear and hazy atmospheres.

4. Use of the linear regression method

From the above, a set of optical thicknesses \( b(\lambda) \), obtained according to Eq. (3), should in general present a non-linear dependence on precipitable water vapour, \( w \). The regression line method applied to such a set of data gives a slope of the regression line on \( w \), at each window wavelength \( \lambda \), which is greater than the absorption coefficient \( c(\lambda) \). This is due to a contribution coming from the non-linear variation of the particulate matter optical thickness, \( a(\lambda) \), with \( w \). For the same reason, negative values of the intercept can be found at the selected wavelengths. Only in an unrealistic case, that is when all data have the term \( a(\lambda) \) constant with \( w \) at each wavelength, can the linear regression method be directly used. In this case, the slope of the regression line gives the correct value of \( c(\lambda) \) and the intercept coincides with \( a(\lambda) \). The above considerations suggest that an appropriate use of
the linear regression method can be made only on sets of data showing a linear and direct correlation with \( w \) at all the selected wavelengths. In these cases, the slope of the regression line is the sum of the absorption coefficient \( c(\lambda) \) and of a linear variation coefficient of \( a(\lambda) \) as a function of \( w \).

Accordingly, the experimental data have been divided into seasonal sets selected for limited ranges of both horizontal visibility, \( V_0 \), and ground relative humidity, \( f_0 \). A further selection has been made by examining the scatter diagrams of \( b(\lambda) \) on \( w \) at the various wavelengths and by taking only those data which are well approximated by a straight line. Each set of experimental data resulting from this procedure consists of a certain number of spectral series of \( b(\lambda) \). Each spectral series covers all the selected window wavelengths and refers to a single value of precipitable water vapour. An important aspect of this procedure is that the spectral series of \( b(\lambda) \) contained in each set present similar shapes of the wavelength dependence curve.

Each set of \( b(\lambda) \) has been examined with the linear regression method on \( w \), giving a best-fit solution of the form

\[
b(\lambda) = b_0(\lambda) + b_1(\lambda)w
\]

(4)

at all the selected wavelengths. Since the water vapour absorption term of Eq. (3) is proportional to \( w \), the linear dependence of \( b(\lambda) \) on \( w \) implies that a linear relationship exists also between the particulate matter optical thickness, \( a(\lambda) \), and \( w \). It can be expressed in the form

\[
a(\lambda) = a_0(\lambda) + a_1(\lambda)w.
\]

(5)

By inserting Eq. (5) in Eq. (3), an expression for \( b(\lambda) \) is obtained. From this and from Eq. (4), the intercept \( b_0(\lambda) \) is equal to \( a_0(\lambda) \) and the slope \( b_1(\lambda) \) is related to \( a_1(\lambda) \) through

\[
b_1(\lambda) = a_1(\lambda) + c(\lambda)
\]

(6)

at each wavelength. According to Eq. (6), \( c(\lambda) \) can be obtained from \( b_1(\lambda) \), provided that \( a_q(\lambda) \) is determined in another way. The following section reports how this may be done.

5. Evaluation of \( a_q(\lambda) \)

The spectral dependence curve of the optical thickness \( a(\lambda) \) within the visible and near-infrared range, can be represented with good accuracy for relatively clear atmospheres by Ångström's (1929, 1930, 1961, 1964) expression

\[
a(\lambda) = \beta \lambda^{-\alpha},
\]

(7)

with \( \lambda \) measured in \( \mu \text{m} \). Here \( \beta \) is the atmospheric turbidity coefficient at unit wavelength and \( \alpha \) is the spectral parameter which depends closely on the shape of the particle size distribution.

As mentioned in the previous section, each set of experimental data has been selected in such a way as to present a certain number of spectral series having similar features of the wavelength dependence curve. Thus we expect the parameter \( \alpha \) not to differ much from one spectral series to another within each set. On the other hand, since each set of data has been selected in terms of linear relationships between \( a(\lambda) \) and \( w \) at the various wavelengths, the parameter \( \beta \) is expected to vary linearly with \( w \); therefore, it can reasonably be assumed that both \( \beta \) and \( \alpha \) are related linearly to \( w \). Linear dependence expressions of \( \beta \) and \( \alpha \) on \( w \) could be found having intercepts \( \beta_0 \) and \( \alpha_0 \) (the turbidity parameters of a perfectly dry atmosphere) and slopes \( \beta_s \) and \( \alpha_s \), respectively. From these considerations, the particulate matter optical thickness, \( a(\lambda) \), can be represented explicitly as a function of \( w \), by develop-
ing Eq. (7) in terms of a Maclaurin series to obtain the following expression:
\[ a(\lambda) = \beta_0 \lambda^{-\alpha_0} + \lambda^{-\alpha_0}(\beta_s - \beta_0 \alpha_s \ln \lambda)w - \lambda^{-\alpha_0}(\beta_s \alpha_s \ln \lambda)w^2. \]  

(8)

Considering that the selection of data has been made in such a way as to give similar values of \( \alpha \) within a set of data, a rather small value of \( \alpha_s \) is expected. Thus the last term of Eq. (8) can be neglected, so that Eq. (8) becomes linear with respect to \( w \) and can be compared with Eq. (5), to obtain \( a_s(\lambda) \):
\[ a_s(\lambda) = \lambda^{-\alpha_0}(\beta_s - \beta_0 \alpha_s \ln \lambda). \]  

(9)

The above expression cannot be used directly for evaluating \( a_s(\lambda) \) from the experimental data. These are actually in the form \( b(\lambda) \) of Eq. (3), which is the sum of \( a(\lambda) \) and the water vapour absorption term, \( c(\lambda)w \). Considering that the particulate matter optical thickness, \( a(\lambda) \), is appreciably greater than \( c(\lambda)w \), even in clear atmospheres, it can be correctly assumed that the wavelength dependence curves of all spectral series of \( b(\lambda) \) are actually given by \( a(\lambda) \).

On this basis, estimates of \( \beta_0, \beta_s, \alpha_0 \) and \( \alpha_s \) can be obtained for each set of data. Each spectral series of \( b(\lambda) \) has been examined in terms of the following expression of Ångström's type:
\[ b(\lambda) = B \lambda^{-\omega}. \]  

(10)

with \( \lambda \) measured in \( \mu m \), to obtain a pair of best-fit values of the parameters \( B \) and \( \omega \), corresponding to each single value of \( w \). In this way, for each set of data, as many pairs of \( B \) and \( \omega \) as the number of spectral series of \( b(\lambda) \) are found. Applying the linear regression method on \( w \) to these sets of \( B \) and \( \omega \), best-fit solutions are obtained in terms of the intercepts \( B_0 \) and \( \omega_0 \) and of the slopes \( B_s \) and \( \omega_s \). If the wavelength dependence curve of each spectral series of \( b(\lambda) \) resembles that of \( a(\lambda) \), the values of \( \omega_0 \) and \( \omega_s \) can be taken as reliable estimates of \( \alpha_0 \) and \( \alpha_s \), respectively. Moreover, considering that the turbidity parameter \( B \) in Eq. (10) is given by the sum of the parameter \( \beta \) in Eq. (7) and of the water vapour absorption term \( c(1 \mu m)w \), the intercept \( B_0 \) represents a good estimate of \( \beta_0 \), whereas the slope \( B_s \) is the sum of \( \beta_s \) and of \( c(1 \mu m) \).

From the above, Eq. (9) becomes
\[ a_s(\lambda) = \lambda^{-\alpha_0}(B_s - c(1 \mu m) - B_0 \omega_s \ln \lambda). \]  

(11)

Estimates of \( a_s(\lambda) \) can be obtained from Eq. (11), provided that the correct value of the water vapour absorption coefficient, \( c(\lambda) \), at 1 \( \mu m \) wavelength is known. As mentioned at the outset of this paper, estimates of \( c(\lambda) \) have been made by Fowlé (1913, 1914, 1915), Tomasi et al. (1974) and Fraser (1975), by examining data taken in very clear atmospheres. Although obtained with direct use of the linear regression method on precipitable water vapour (and therefore presumably affected by particle extinction), these values of \( c(\lambda) \) agree well at and beyond 1 \( \mu m \) and are constant in this wavelength range. This indicates that the results proposed by the above-mentioned authors at 1 \( \mu m \) are only slightly altered by particle extinction. In the present work, the coefficient \( c(1 \mu m) \) in Eq. (11) is taken as 0·017 g\(^{-1}\)cm\(^2\), following Fowlé (1915) and Fraser (1975).

Thus estimates of \( c(\lambda) \) can be obtained as differences between \( b_s(\lambda) \) and \( a_s(\lambda) \), the latter being computed from Eq. (11). It is clear that the resulting estimates of \( c(\lambda) \) are normalized to the value of \( c(1 \mu m) \) used in Eq. (11).

6. Results

The procedure proposed in the previous section has been applied to five sets of data. Sets A and B have been obtained from the spectral measurements of solar radiation attenuation made by Vittori et al. (1974) during autumn 1971, at Buda (10 m a.m.s.l.).
Set A consists of data examined by Tomasi et al. (1974) with the direct use of the linear regression method on precipitable water vapour. Nineteen spectral series of $b(\lambda)$ were selected, relating to very clear atmospheres (horizontal visual range, $V_0$, at the ground varying from 25 to 50 km; relative humidity, $f_0$, at the ground between 0.55 and 0.85; $w$ between 0.2 and 1.0 g cm$^{-2}$). At the eleven window wavelengths in the 0.66–1.29 $\mu$m spectral range, the optical thickness, $b(\lambda)$, was plotted as a function of $w$ to determine the slope, $b_s(\lambda)$, of the regression line, as shown on the left side of Fig. 1. The intercept $b_0(\lambda)$, the slope $b_s(\lambda)$, and the correlation coefficient are given in Table 1 for each selected wavelength.

Figure 1. Example of the present procedure applied to data set A. On the left, the monochromatic optical thicknesses $b(\lambda)$ at various wavelengths are plotted as functions of the precipitable water vapour, $w$, to determine the slope $b_s(\lambda)$ of the regression lines. On the right, parameters $B_1$ and $\omega_1$ (obtained for the 0.66–1.05 $\mu$m subrange) and parameters $B_2$ and $\omega_2$ (for the 1.09–1.29 $\mu$m subrange) are plotted as functions of $w$, in order to estimate intercepts and slopes of the regression lines, to be used in Eq. (11).

According to the procedure outlined in the previous section, the spectral series of $b(\lambda)$ are now to be examined in terms of Eq. (10). In order to obtain a better description of the experimental data in terms of Ångström's turbidity parameters, the spectral range has been divided in two subranges, below and above 1.07 $\mu$m, as shown in Fig. 2. Following this procedure, sets of best-fit solutions in terms of $B_1$ and $\omega_1$ have been found for the 0.66–1.05 $\mu$m subrange and sets of $B_2$ and $\omega_2$ for the 1.09–1.29 $\mu$m subrange. These values of $B_1$, $\omega_1$, $B_2$ and $\omega_2$ have been plotted as functions of precipitable water vapour, as shown on the right in Fig. 1, to determine the regression lines on $w$. The intercepts $B_0$ and $\omega_0$ and the slopes $B_s$ and $\omega_s$, separately found for each spectral subrange, have been inserted in Eq. (11) to find estimates of $a(\lambda)$. The results are presented in Table 1, together with estimates of $c(\lambda)$ obtained according to Eq. (6). For such clear atmospheres, particulate matter extinction is responsible for a contribution of about 35% to the slope of the regression line of $b(\lambda)$ on $w$. 
<table>
<thead>
<tr>
<th>Wavelength $\lambda$ ($\mu$m)</th>
<th>Intercept $b_0(\lambda)$</th>
<th>Slope $b_s(\lambda)$ (g$^{-1}$cm$^2$)</th>
<th>Correlation coefficient</th>
<th>$a_s(\lambda)$ (g$^{-1}$cm$^2$) (from Eq. (11))</th>
<th>$c(\lambda)$ (g$^{-1}$cm$^2$) (from Eq. (6))</th>
<th>Parameters used in Eq. (11)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.665</td>
<td>0.101</td>
<td>0.041</td>
<td>+0.94</td>
<td>0.014</td>
<td>0.027</td>
<td>$B_0 = 0.084$</td>
</tr>
<tr>
<td>0.682</td>
<td>0.097</td>
<td>0.037</td>
<td>+0.94</td>
<td>0.013</td>
<td>0.024</td>
<td>$B_s = 0.019$ g$^{-1}$cm$^2$</td>
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<tr>
<td>0.715</td>
<td>0.096</td>
<td>0.037</td>
<td>+0.87</td>
<td>0.012</td>
<td>0.025</td>
<td>$\omega_s = 0.427$</td>
</tr>
<tr>
<td>0.755</td>
<td>0.094</td>
<td>0.031</td>
<td>+0.99</td>
<td>0.010</td>
<td>0.021</td>
<td>$\omega_s = 0.299$ g$^{-1}$cm$^2$</td>
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<tr>
<td>0.784</td>
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<td>0.028</td>
<td>+0.99</td>
<td>0.009</td>
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<td>0.881</td>
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<td>0.018</td>
<td>+0.98</td>
<td>0.005</td>
<td>0.013</td>
<td></td>
</tr>
<tr>
<td>1.01</td>
<td>0.084</td>
<td>0.023</td>
<td>+0.99</td>
<td>0.001</td>
<td>0.022</td>
<td></td>
</tr>
<tr>
<td>1.05</td>
<td>0.083</td>
<td>0.016</td>
<td>+0.98</td>
<td>4.10$^{-4}$</td>
<td>0.016</td>
<td></td>
</tr>
<tr>
<td>1.09</td>
<td>0.077</td>
<td>0.024</td>
<td>+0.99</td>
<td>0.008</td>
<td>0.016</td>
<td>$B_0 = 0.083$</td>
</tr>
<tr>
<td>1.24</td>
<td>0.068</td>
<td>0.026</td>
<td>+0.99</td>
<td>0.010</td>
<td>0.016</td>
<td>$B_s = 0.023$ g$^{-1}$cm$^2$</td>
</tr>
<tr>
<td>1.29</td>
<td>0.065</td>
<td>0.025</td>
<td>+0.99</td>
<td>0.010</td>
<td>0.015</td>
<td>$\omega_s = 0.917$</td>
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<td></td>
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<td></td>
<td></td>
<td></td>
<td>$\omega_s = -0.344$ g$^{-1}$cm$^2$</td>
</tr>
</tbody>
</table>
Figure 2. Two examples of the best-fit procedure based on Eq. (10) and applied to two spectral series of $b(\lambda)$, separately for the two chosen spectral subranges. The best-fit solutions are given in terms of $B_1$ and $\omega_1$ (for the 0.66–1.05 $\mu$m subrange) and of $B_2$ and $\omega_2$ (for the 1.09–1.29 $\mu$m subrange).

Figure 3. Comparison between the present estimates of $c(\lambda)$, obtained from various sets of data, and those found by other authors in very clear atmospheres.
### TABLE 2. RESULTS OBTAINED FROM EXPERIMENTAL DATA SET B

<table>
<thead>
<tr>
<th>Wavelength $\lambda$ (µm)</th>
<th>Intercept $b_0(\lambda)$</th>
<th>Slope $b_s(\lambda)$ (g⁻¹cm²)</th>
<th>Correlation coefficient</th>
<th>$a_s(\lambda)$ (g⁻¹cm²) (from Eq. (11))</th>
<th>$c(\lambda)$ (g⁻¹cm²) (from Eq. (5))</th>
<th>Parameters used in Eq. (11)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.665</td>
<td>-0.058</td>
<td>0.438</td>
<td>+89</td>
<td>0.408</td>
<td>0.030</td>
<td>$B_o = -0.037$</td>
</tr>
<tr>
<td>0.682</td>
<td>-0.057</td>
<td>0.428</td>
<td>+88</td>
<td>0.399</td>
<td>0.029</td>
<td>$B_s = 0.307$ g⁻¹cm²</td>
</tr>
<tr>
<td>0.715</td>
<td>-0.054</td>
<td>0.413</td>
<td>+88</td>
<td>0.384</td>
<td>0.029</td>
<td>$\omega_o = 0.838$</td>
</tr>
<tr>
<td>0.755</td>
<td>-0.050</td>
<td>0.393</td>
<td>+88</td>
<td>0.367</td>
<td>0.026</td>
<td>$\omega_s = 0.012$ g⁻¹cm²</td>
</tr>
<tr>
<td>0.784</td>
<td>-0.051</td>
<td>0.383</td>
<td>+88</td>
<td>0.355</td>
<td>0.028</td>
<td></td>
</tr>
<tr>
<td>0.881</td>
<td>-0.042</td>
<td>0.342</td>
<td>+89</td>
<td>0.322</td>
<td>0.020</td>
<td></td>
</tr>
<tr>
<td>1.01</td>
<td>-0.038</td>
<td>0.306</td>
<td>+88</td>
<td>0.288</td>
<td>0.018</td>
<td></td>
</tr>
<tr>
<td>1.05</td>
<td>-0.034</td>
<td>0.292</td>
<td>+88</td>
<td>0.278</td>
<td>0.014</td>
<td></td>
</tr>
</tbody>
</table>

### TABLE 3. RESULTS OBTAINED FROM EXPERIMENTAL DATA SETS C, D AND E

<table>
<thead>
<tr>
<th>Set</th>
<th>Number of data</th>
<th>Wavelength ($\mu$m)</th>
<th>$b_0(\lambda)$ (g⁻¹cm²)</th>
<th>$b_s(\lambda)$ (g⁻¹cm²)</th>
<th>Correlation coefficient</th>
<th>$a_s(\lambda)$ (g⁻¹cm²) (from Eq. (11))</th>
<th>$c(\lambda)$ (g⁻¹cm²) (from Eq. (5))</th>
<th>Parameters used in Eq. (11)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C</td>
<td>81</td>
<td>0.50</td>
<td>0.354</td>
<td>0.200</td>
<td>+69</td>
<td>0.142</td>
<td>0.058</td>
<td>$B_o = 0.125$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.03</td>
<td>0.119</td>
<td>0.062</td>
<td>+63</td>
<td>0.046</td>
<td>0.016</td>
<td>$B_s = 0.065$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\omega_o = 1.547$</td>
</tr>
<tr>
<td>D</td>
<td>15</td>
<td>0.50</td>
<td>-0.244</td>
<td>0.295</td>
<td>+98</td>
<td>0.233</td>
<td>0.062</td>
<td>$B_o = -0.102$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.03</td>
<td>-0.098</td>
<td>0.159</td>
<td>+91</td>
<td>0.143</td>
<td>0.016</td>
<td>$B_s = 0.163$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\omega_o = 0.688$</td>
</tr>
<tr>
<td>E</td>
<td>38</td>
<td>0.50</td>
<td>0.376</td>
<td>0.355</td>
<td>+80</td>
<td>0.305</td>
<td>0.050</td>
<td>$B_o = 0.114$</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1.03</td>
<td>0.108</td>
<td>0.104</td>
<td>+63</td>
<td>0.087</td>
<td>0.017</td>
<td>$B_s = 0.109$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\omega_o = 1.820$</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>$\omega_s = -0.072$</td>
</tr>
</tbody>
</table>
The set B consists of nineteen spectral series of $b(\lambda)$, taken in relatively clear atmospheres ($V_0$ ranging from 8 to 16 km, $f_0$ from 0.42 to 0.86, and $w$ from 0.6 to about 1·6 g cm$^{-2}$). Applied to eight selected wavelengths within the 0·66-1·05 $\mu$m spectral range, the present procedure gives the results of Table 2. At all selected wavelengths, the larger part (about 93%) of the slope $b_0(\lambda)$ is due to the linear variation of particulate matter optical thickness with precipitable water vapour. The corresponding estimates of $c(\lambda)$ turn out to be in good agreement with previous results obtained for clearer atmospheres.

Three sets of data (herein called C, D and E) taken at 0·50 and 1·03 $\mu$m with a sun photometer (Tomasin and Guzzi 1977) in hazy atmospheres, have also been examined using the present procedure: set C concerns measurements made at Molinella (10 m a.m.s.l.) during winter and spring 1974 ($V_0$ ranging from 5 to 10 km, $f_0$ from 0.50 to 0.86, and $w$ from 0·3 to 2·3 g cm$^{-2}$); set D relates to data taken at Bologna (35 m a.m.s.l.) during summer 1973 ($V_0$ from 9 to 16 km, $f_0$ from 0.45 to 0.65, and $w$ from 3·0 to 4·7 g cm$^{-2}$); set E consists of data taken at Bologna during autumn 1973 ($V_0$ from 5 to 10 km, $f_0$ from 0·45 to 0·87 and $w$ from 0·8 to 1·9 g cm$^{-2}$). For each value of $w$, the parameters $B$ and $\omega$ have been evaluated from the spectral data taken at the two above-mentioned wavelengths, according to Eq. (10). The results obtained by following the present procedure are given in Table 3. The slope $a_0(\lambda)$ due to particle extinction turns out to contribute largely (from 71 to 90%) to the slope $b_0(\lambda)$, at both wavelengths.

In Fig. 3 a comparison is made between the present estimates of $c(\lambda)$ and results given by previous works; there is satisfactory agreement with the results of Fowle (1913, 1914) in clear atmospheres above a mountain station and normalized to the surface pressure of 1·013 bar.

7. MASS ABSORPTION COEFFICIENT AT UNIT AIR PRESSURE

Evaluations of the monochromatic non-selective absorption coefficient of water vapour along sea level paths may be of great value in the interpretation of horizontal transmission data. For this purpose, the present estimates of $c(\lambda)$ can be used. In fact, the absorption coefficient $c(\lambda)$ pertinent to vertical atmospheric paths is related to the mass absorption coefficient $k(\lambda)$ of water vapour at unit air pressure through the simple expression

$$c(\lambda) = \frac{k(\lambda)}{w} \int_{z_0}^{z} p(z) \psi(T(z)) \rho(z) dz,$$

(12)

where $p(z)$ is the air pressure at altitude $z$, $\psi(T(z))$ the temperature dependence form, $\rho(z)$ the absolute humidity, $z_0$ the station altitude and $z_1$ an altitude to be taken near the tropopause level. Assuming that the temperature dependence of water vapour absorption at window wavelengths in the visible and near infrared can be neglected, as suggested by Goody (1964), $\psi(T(z))$ has been taken as unity in Eq. (12). In this regard, computations of the integral of Eq. (12) have been made for the mid-latitude atmospheric models proposed by McClatchey et al. (1972), assuming $\psi(T(z)) = 1$ and $\psi(T(z) = 1) = 273·2/(273·2 + T(z))^{0·5}$. Values have been obtained of 0·675 and 0·684 g cm$^{-2}$bar, respectively, for the mid-latitude winter model ($w = 0·84$ g cm$^{-2}$), and of 2·434 and 2·377 g cm$^{-2}$bar for the mid-latitude summer model ($w = 2·94$ g cm$^{-2}$), indicating that discrepancies of only a few per cent may result from the use of different forms of temperature dependence.

Thus evaluations of $k(\lambda)$ have been obtained from the present estimates of $c(\lambda)$ by using the expression

$$k(\lambda) = (w/P)c(\lambda),$$

(13)
with the parameters

\[
P = \int p(z) \rho(z) \, dz \quad \text{and} \quad w = \int \rho(z) \, dz,
\]

the integrals running from \( z_0 \) to \( z_t \).

According to Eqs. (14) for \( z_t \) taken as 10 km, the quantities \( P \) and \( w \) have been computed for each observation day from local meteorological data and from the 12 GMT radiosonde data taken at Milan Linate Airport (about 200 km from the measurement sites). The average value of the ratio \( w/P \) is given in Table 4 for each set of data, together with the standard deviation; these show that the scatter of \( c(\lambda) \) arising from day to day or seasonal variations of the vertical profile of absolute humidity is limited to a few per cent.

**TABLE 4. AVERAGE VALUES OF METEOROLOGICAL PARAMETERS FROM RADIOSONDE DATA**

<table>
<thead>
<tr>
<th>Set</th>
<th>Season</th>
<th>Temperature at the surface, ( T_0 ) (°C)</th>
<th>Relative humidity at the surface, ( f_0 )</th>
<th>Ratio ( w/P ) and standard deviation (bar⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Autumn</td>
<td>3</td>
<td>0.71</td>
<td>1.185±0.031</td>
</tr>
<tr>
<td>B</td>
<td>Autumn</td>
<td>14</td>
<td>0.67</td>
<td>1.177±0.019</td>
</tr>
<tr>
<td>C</td>
<td>Winter-spring</td>
<td>13</td>
<td>0.77</td>
<td>1.199±0.031</td>
</tr>
<tr>
<td>D</td>
<td>Summer</td>
<td>30</td>
<td>0.55</td>
<td>1.183±0.004</td>
</tr>
<tr>
<td>E</td>
<td>Autumn</td>
<td>15</td>
<td>0.75</td>
<td>1.192±0.044</td>
</tr>
</tbody>
</table>

Making use of Eq. (13), the absorption coefficients \( c(\lambda) \) of Tables 1, 2 and 3 have been converted into evaluations of \( k(\lambda) \), shown in Fig. 4 as a function of wavelength on a bi-logarithmic scale. Estimates of \( k(\lambda) \) at wavelengths longer than 1.5 \( \mu \)m are also shown in Fig. 4, as obtained from Eq. (13) using the values of \( c(\lambda) \) found by Tomasi et al. (1974), together with the value of \( w/P \) found from data set A.

![Graph](image)

**Figure 4.** Estimates of the non-selective absorption coefficient \( k(\lambda) \) of water vapour along homogeneous paths at unit air pressure. The results are plotted as a function of wavelength on a bi-logarithmic scale to show evidence for their spectral dependence in terms of a power law at wavelengths shorter than 1 \( \mu \)m. The regression line is given by Eq. (15) for \( k(1\mu m) = 0.019 \text{g}^{-1}\text{cm}^2\text{bar}^{-1} \) and \( n = 1.62 \).
8. Concluding remarks

Fig. 4 shows that present estimates of the non-selective absorption coefficient $k(\lambda)$ of water vapour for homogeneous paths at unit air pressure tend to decrease gradually from 0.5 to about 1 $\mu$m wavelength, while almost constant values of about 0.02 g$^{-1}$ cm$^2$ bar$^{-1}$ are found at longer wavelengths. Examining the spectral dependence of the complete set of results, within the 0.5–1.05 $\mu$m interval, in terms of a power law of the form

$$k(\lambda) = k(1 \mu m)\lambda^{-n}$$

with $\lambda$ measured in $\mu$m, a best-fit curve is found for $k(1 \mu m) = 0.019$ g$^{-1}$ cm$^2$ bar$^{-1}$ and $n = 1.62$, with a correlation coefficient of −0.92. Considering only results for sets A and B, pertinent to a spectral resolution of 30 cm$^{-1}$, a best-fit solution with $n = 1.24$ is found, within the 0.66–1.05 $\mu$m range. It is interesting to notice that examination of the results found by Fowle (1915) in very clear atmospheres gives the best-fit value $n = 1.39$ in the range 0.62 to 0.99 $\mu$m. These data have been obtained with direct use of the linear regression method on precipitable water vapour. Fowle himself suggests that airborne particle extinction can cause these water vapour absorption coefficients to be overestimated. Since particle extinction in clear atmospheres decreases appreciably with wavelength, the value $n = 1.39$ should be an overestimate. On this view, the value $n = 1.24$ given by the present results appears to be more realistic.

This comparison confirms that reliable estimates of the non-selective absorption coefficient of water vapour can be obtained at window wavelengths with the present procedure. Realistic results can be given by sets of atmospheric optical thicknesses, consisting of spectral series characterized by very similar curves of wavelength dependence and selected in such a way as to present linear relationships with precipitable water vapour at all selected wavelengths.

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References


Ångström, A. 1929 On the atmospheric transmission of sun radiation and on dust in the air, Geogr. Ann., 11, 156–166.

1930 On the atmospheric transmission of sun radiation II, Ibid., 12, 130–159.


Badayev, V. V., Georgievskiy, Yu. S. and Pirogov, S. M. 1964 The parameters of atmospheric turbidity, Ibid., 16, 64–75.

1975 Aerosol extinction in the spectral range 0.25–2.2 $\mu$m, Atmos. Oc. Phys., 11, 321–324.


Hänel, G. 1976 The properties of atmospheric aerosol particles as functions of the relative humidity at thermodynamic equilibrium with the surrounding moist air, *Advances in Geophysics*, 19, 73-138.


