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REVIEW OF THE DOBSON SPECTROPHOTOMETER AND ITS ACCURACY

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FOREWORD

During the first four years of the implementation of the WMO Global Ozone Research and Monitoring Project, efforts were, to a large extent, concentrated on improving the quality and quantity of ozone observations. This was mainly achieved by upgrading almost half of the Dobson spectrophotometers in the global network.

By mid-1979 it was becoming increasingly obvious that an assessment of the performance characteristics of various ozone observing systems was necessary, and the WMO Executive Committee approved a meeting on this subject in 1980, the report of which is available as Ozone Report No. 9. It was evident at that meeting that there was a pressing need for a comprehensive review that would attempt to quantify all the errors associated with the taking of ozone observations with Dobson spectrophotometers. This fact was further reinforced at the WMO Meeting of Experts on Source of Errors in Detection of Ozone Trends (Toronto, 1982, Ozone Report No. 12). Until that time, no such study had ever been undertaken. WMO consequently arranged for Dr. Reid E. Basher of the New Zealand Meteorological Service to prepare the review. Dr. Basher was uniquely qualified for the task, because he had spent some years at Oxford University in the United Kingdom, and had had access to the original papers of G.M.B. Dobson, the inventor of the spectrophotometer.

This detailed report entitled "Review of Dobson Spectrophotometer Total Ozone Measurement Accuracy" is the result of his labours. As you will note, it contains chapters on every known and potential source of errors affecting Dobson instruments from a physics point of view, and where possible, quantifies the errors likely in the total ozone measurements, which the author prefers to refer to as "measurements of column ozone amount". This report should be considered as representing his own scientific findings and judgement.

I wish to take this opportunity to thank Dr. Basher on behalf of the WMO Global Ozone Research and Monitoring Project for what has undoubtedly been a difficult and painstaking task.

Geneva,

Rumen D. Bojkov

December, 1982

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Forward to Abstract

"Review of the Dobson spectrophotometer and its accuracy"

ABSTRACT

A detailed analysis of the Dobson spectrophotometer and its accuracy has been made. The spectrophotometer is the principal instrument used for measuring the atmosphere's ozone overburden. Emphasis has been put on the physics of the measurement method. Among topics considered are: the theoretical basis of the measurement and its limitations, such as those due to aerosol scattering and interfering gaseous absorption; the optical design and its limitations, such as due to stray light) and the techniques of operation and calibration and their limitations. With some topics the available literature is very limited and a number of original contributions have been made by the author. Summarising the effects of the various error sources is difficult owing to the great variety of error sources, their large variation from instrument to instrument in some cases, and their dependence on external parameters which are often unknown. Three broad generalisations can be made; firstly, that instrument-related errors form the greatest aggregate source of error; secondly, that the largest instrument-related errors arise from faulty extraterrestrial constants, stray light and defective optical adjustment; and thirdly, that atmosphere-related errors are small except at sites affected by severe air pollution. It seems that perhaps two thirds of recent years' standard AD direct sun method ozone estimations are accurate to 3% or better, relative to the current absolute scale, and that this absolute scale is itself accurate to about 3%. Some error sources which change with time can cause erroneous ozone trends of 10% per decade, and erroneous trends equivalent to a few percent per decade may be common in individual instruments. The review makes recommendations for further research into error sources and for improvements in the operation of the world's Dobson instrument network.

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Forward to Introduction

1. INTRODUCTION

1.1 Purpose and scope

Ozone plays a key role in the photochemical processes of the atmosphere and is intimately involved in the chemistries of the high altitude air pollutants such as fluorocarbons. Its strong absorption of radiation of wavelengths less than about 300 nm provides a shield to the sun's biologically damaging ultraviolet radiation, and it is under the protection of this shield that most living creatures have evolved. Any long-term changes of ozone concentrations due to natural causes or increasing pollution would be of considerable importance to the biosphere and to the physics and chemistry of the atmosphere. A great deal of research has been undertaken, especially in recent years, to better understand the processes involved and the risks of changes, and it is toward this end that this series of WMO reports is directed.

The measurement of ozone is of course an essential element of the attack on the problem. The most basic of ozone measurements is the measurement of the ozone overburden, or ozone column amount (total ozone) made by the sixty or more Dobson instruments around the world. The Dobson network has been the prime source of our knowledge about the global, seasonal and synoptic variations of ozone in the Past, and it will continue in the future to provide a means for calibrating the developing satellite-based measurement systems and virtually the only records of sufficient length suitable for the analysis of long term trends.

This report aims to provide a thorough review of the error sources in the Dobson instrument's measurement of column ozone amount. It approaches the problem from the point of view of the physics of the measurement method rather than from the point of view of the statistics of collected data. Error sources associated with various physical factors, for example instrument stray light, or atmospheric scattering, are examined one by one, and quantitative estimates of error for operational conditions are made for each. The relevant literature is reviewed, though for many of the topics considered there is very little published material, presumably owing to the specialised technical character of the problems, and partly for this reason the author has in places drawn heavily upon his own unpublished and largely theoretical work. Actual measurements have been used whenever possible to verify theoretical models.

It is hoped that the review's emphasis on the underlying physical basis of each error source will provide a basis for further understanding, further experimentation, and eventually increased accuracies. The approach used does have some inherent limitations. In particular, some error sources may be badly overestimated or underestimated, and the net effect of the described errors for any particular instrument is difficult to assess owing to the wide variation in standards of instrument maintenance and calibration, the variety of operational conditions, and the lack of firm information on many of the error sources. The complement to the approach is the careful analysis of laboratory and field data by those experienced with the Dobson instrument and its measurements. No doubt some studies of this sort already exist in unpublished form. Perhaps this review will encourage their revision and dissemination.

Ideally, the accuracy of Dobson measurements of column amounts of ozone should be 1%. Some error sources can contribute errors of 20% or more on occasion, while errors of less than 1% may be important if their effects are additive. By comparison, extreme natural variations in ozone are roughly ±50% of the mean. There are practical limits to accuracy and error estimations of course, and it seems that any effort to push accuracy figures to ever-lower levels is usually confounded by the greater numbers of the smaller error sources, by greater uncertainty in the estimation of the smaller errors, and by complicated second order effects and interactions among the error sources. Of course the accuracy figure sought, or estimated, will depend on whether one is concerned with absolute accuracy, instrument intercomparability, or instrument repeatability.

Note that the review does not concern itself with the Umkehr method of measuring height profiles of ozone concentration used with the Dobson instrument. However, most of the error sources discussed do have a direct bearing on the accuracy of the Umkehr method, and it would be most desirable that their impact on it be studied more closely.

No study of the Dobson instrument such as this could fail to emphasize its indebtedness to the instrument's designer and exploiter, G.M.B. Dobson, FRS. His International Geophysical Year (IGY) instrument manuals (Dobson, 1957a, 1957b, and Dobson and Normand, 1962) have guided operational practice for over twenty years, and the original theoretical basis and physical design of the instrument (Dobson and Harrison, 19261 and Dobson, 1931) have stood the test of time for more than twice this period. These papers, together with his working papers in Walshaw (1975), show qualities of experimental ingenuity, scientific dedication, and attention to detail which all can admire. It is well worthwhile and very interesting to read through his papers, including tile history of his work at Oxford (Dobson, 1968) and his biography (Houghton and Walshaw, 1977), to see the extent to which an era of discovery about atmospheric ozone, and hence our own present knowledge, are so dependent on his work.

1.2 Theory of Measurement

Ozone is readily measured by means of its absorption of solar radiation in the 300 to 350 nm ultraviolet spectral region. The absorption changes rapidly across this limited region: it is so great at 290 nm that virtually no radiation of this wavelength penetrates to the surface of the earth, but at 310 nm it is only comparable in effect to Rayleigh scattering, and by 350 nm it is less than one hundredth the effect of Rayleigh scattering and so is of negligible effect (Figure 1.1). The choice of wavelength range in which to make measurements is dictated by the balance between ozone information content (decreasing wavelength) and transmitted energy flux (increasing wavelength), and in practice the principal ozone measuring bands are in the 305 to 315 nm range. The theoretical basis of the Dobson instrument's measurement method is given in Dobson and Harrison (1926) and Dobson (1931) and additional information may be found in Dobson (1957a) and Dobson and Normand (1962). Craig (1965, pp. 177 to 179) gives a particularly clear and succinct derivation of the measurement equations, and Khrgian (1975) discusses the theory as part of a detailed review of atmospheric ozone and of the history and practice of its measurement.

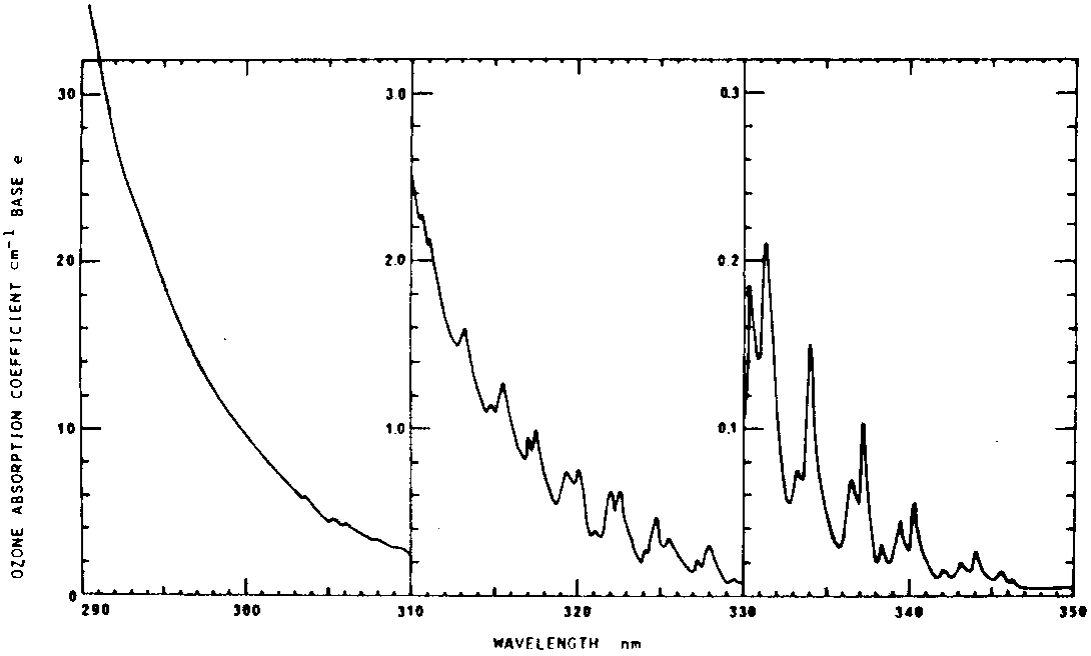

Figure 1.1: Ozone's absorption coefficient spectrum in the near UV at -44°C (see Section 5.2 for source of data).

The measurement equation is found by calculus, with the effect of an infinitessimally thin layer of the atmosphere on a monochromatic band of direct sunlight being integrated with height front the earth's surface to the outside of the atmosphere. After some approximation of the integrals, the equation becomes, in simplest form,

$$\log I(\lambda) = \log I_0(\lambda) - \mu_h X\alpha(\lambda) - m\beta(\lambda) - \sec Z\delta(\lambda) \qquad (1.1)$$

where:

λ = the wavelength of a monochromatic band.

$I(\lambda)$ = the intensity at the earth's surface.

$I_0(\lambda)$ = the intensity outside the atmosphere.

X = the vertically integrated amount of ozone, called the column amount of ozone or total ozone.

$\alpha(\lambda)$ = the ozone absorption coefficient (to base 10) per unit of column amount.

$\beta(\lambda)$ = the Rayleigh (molecular) scattering coefficient for a vertical path.

$\delta(\lambda)$ = the atmospheric aerosol scattering coefficient for a vertical path.

μ_h = the secant of the solar zenith angle at the mean ozone height (usually assumed to be 22 km).

m = the slant pathlength for air relative to a vertical pathlength and which accounts for atmospheric sphericity and refraction.

sec Z = secant of the solar zenith angle at ground level. Note that, except when the sun is very low in the sky, the terms μ_h, m and sec are nearly equal. They are often collectively termed the "airmass" in this review.

A particular feature of equation (1.1) is its simple linear form. This greatly facilitates the manipulation and exploitation of the measurement method, as we shall see. For example, the Dobson instrument's measurement of two bands at wavelengths λ and λ', where $\lambda < \lambda'$ can be described simply by the difference of two such equations, i.e. as:

$$\log \frac{I(\lambda)}{I(\lambda')} = \log \frac{I_0(\lambda)}{I_0(\lambda')} - \mu_h X(\alpha(\lambda)-\alpha(\lambda')) - m(\beta(\lambda)-\beta(\lambda')) - \sec Z(\delta(\lambda)-\delta(\lambda')) \quad (1.2)$$

which is usually abbreviated to:

$$L_k = L_{0k} - \mu_h X\Delta\alpha_k - m\Delta\beta_k - \sec Z\Delta\delta_k \quad (1.3)$$

where k = A, B, C and D identifies the standard Dobson bandpair used. Equations (1.2) and (1.3) describe the measurement of relative intensity and they have three important advantages over the measurement of absolute intensity described by equation (1.1). Firstly, the stability and calibration of an intensity ratio poses many fewer problems than the stability and calibration of an individual intensity since it requires no absolutely calibrated reference source or detector and since many of the factors affecting stability, e.g. photomultiplier gain, will affect the two bands in equal proportion. Secondly, the variation in the intensity ratio is less than that of the individual intensities and therefore the dynamic range required of the instrument is less. Thirdly, because the average spectral gradient of Rayleigh scattering and aerosol scattering is much less than that of ozone absorption, the difference equations, (1.2) and (1.3), significantly reduce the contribution of the scattering components relative to that of the ozone absorption and therefore significantly increase the ozone information content.

The expression for column amount of ozone derived from equation (1.3) is:

$$X = \frac{L_{0k} - L_k - m\,\Delta\beta_k - \sec Z\Delta\delta_k}{\mu_h\,\Delta\delta_k} \quad (1.4)$$

Most of the parameters required to solve the equation are readily determined: L_k is measured, μ_h, m and sec Z are calculated from a knowledge of the solar position at the time of the measurement, $\Delta\beta_k$ is found from scattering theory and is essentially a constant, and $\Delta\alpha_k$ is found from laboratory measurements and is also essentially a constant. The standard coefficients used with the Dobson instrument are given below in Table 1.1. Note that the traditional unit of atm cm is used here and throughout the review.

However, there is a good case for preferring the SI unit of mole per square metre as the unit for column amount of any atmospheric gas, and hence the mmol m^{-2} as the unit for column amounts of ozone (Basher, 1982a). In principle, the L_{0k} term may be determined experimentally by exploiting the linearity of equation (1.3). A series of measurements of L_k for a clear half day is plotted against μ_h and extrapolated to find the intercept L_{0k} at $\mu_h = 0$. Equally well, equation (1.4) may be used, in which case the gradient of X against $1/\&mu_h\Delta\alpha_k$, where X is calculated with an existing or assumed L_{0k}, gives the error in the L_{0k} used. In both cases the atmospheric attenuation terms $X\Delta\alpha_k$, $X\Delta\beta_k$ and $X\Delta\delta_k$ must remain constant, but in practice this condition is often not met and such determinations of L_{0k} are often unreliable. Increasingly, L_{0k} are being found by the direct intercomparison of instruments against one of a few very well-calibrated reference instruments.

TABLE 1.1

Standard coefficients used with the Dobson instrument

k	A	B	C	D	
$\Delta\alpha_k$	1.748	1.140	0.800	0.360	atm-cm^{-1}
$\Delta\beta_k$	0.116	0.113	0.110	0.104	

It is worth digressing at this point to clarify the meaning of the term "extraterrestrial constant", since although this constant is indeed the quantity that is determined by the experimental methods described above, it is in fact not the same as L_{0k}. Ozone measuring instruments like the Dobson instrument are not calibrated to measure intensities directly or even intensity ratios directly. Their output is an electrical or mechanical analogue:

$$P(\lambda) = C(\lambda)\, I(\lambda) \qquad (1.5)$$

where $C(\lambda)$ represents the instrument's spectral responsitivity to $I(\lambda)$ and is dependent on such things as slit widths and detector spectral sensitivity. The quantity measured by the Dobson instrument is therefore:

$$\log P(\lambda)/P(\lambda') = \log I(\lambda)/I(\lambda') + \log C(\lambda)/(\lambda') \qquad (1.6)$$
$$= L_k + K_k$$

where K_k is a relative spectral response constant, dependent only on the instrument's design and adjustment. The extraterrestrial value, which is the extraterrestrial constant, is then:

$$\text{Log } P_0(\lambda)/P_0(\lambda') = L_{0k} + K_k \qquad (1.7)$$

The extraterrestrial constant thus comprises an extraterrestrial intensity ratio, which is presumed to be a constant, and an instrument-dependent constant, which will vary among instruments and which will change with time as changes occur to, or are made to, the instrument and hence to its relative spectral response. The constants K_k are fairly small for Dobson instruments, but they may be large for other instrument types, depending on the instrument design. The stability of the K_k, but not the L_{0k}, can be checked by reference to very stable incandescent lamps. This should be done both on a regular basis, and also before and after any adjustment or replacement of parts.

The final term in equation (1.4) to be discussed, and the most problematic, is the aerosol attenuation term $\Delta\delta_k$. This term is very variable, owing to varying atmospheric conditions, and it is impossible to routinely estimate its size to sufficient accuracy by independent means. An ozone measurement made with only one bandpair is therefore an estimate X_k based on the equation:

$$X_k = \frac{L_{0k} - L_k - m\Delta\beta_k}{\mu_h\Delta\alpha_k} \qquad (1.8)$$

which is related to the true ozone amount by the equation:

$$X_k = X + \frac{\sec Z \Delta\delta_k}{\mu_h \Delta\alpha_k} \qquad (1.9)$$

Equation (1.9) shows that the aerosol error component of X_k is airmass independent, since sec Z ≈ μ_h, and will tend to increase with decreasing $\Delta\alpha_k$, i.e., in going through the sequence k = A, B, C and D, owing to the $l/\Delta\alpha_k$ weighting. The error for the C bandpair may reach ±15% on occasion (see Section 10).

The solution to the problem of aerosol error lies in the linear combination of the measurements of two bandpairs. If the two bandpairs are labelled k and j, then the difference of the equation (1.3) for each bandpair is formed and solved to give:

$$X = \frac{L_{0k} - L_{0j} - (L_k - L_j) - m(\Delta\beta_k - \Delta\beta_j) - \sec Z(\Delta\delta_k - \Delta\delta_j)}{\mu_h(\Delta\alpha_k - \Delta\alpha_j)} \qquad (1.10)$$

As before, the aerosol component of the equation is unknown and the ozone estimate for the pair of bandpairs is:

$$X_{kj} = \frac{L_{0k} - L_{0j} - (L_k - L_j) - m(\Delta\beta_k - \Delta\beta_j)}{\mu_h (\Delta\alpha_k - \Delta\alpha_j)} \qquad (1.11)$$

which is related to the true amount by the equation:

$$X_{kj} = X + \frac{\sec Z(\Delta\delta_k - \Delta\&delta_j)}{\mu_h(\Delta\alpha_k - \Delta\alpha_j)} \qquad (1.12)$$

The aerosol error component of equation (1.12) is much less than that of equation (1.9) for the single bandpair. This is due to the approximate equality of $\Delta\delta_k$ and $\Delta\delta_j$, which is a result of the combination of the approximately linear spectral variation of aerosol attenuation δ(λ) in the limited spectral range of 305 to 340 nm and the similar wavelength separation of the bands within each Dobson bandpair.

The double bandpair method is the preferred method of ozone estimation, and the standard recommended bandpairs which are used are the A and D bandpairs. It can be noted that equation (1.10) increases the ozone information content by decreasing the relative size of the scattering terms, and will tend to reduce the effect of systematic errors in the L_0 and L. Equation (1.11) can also be written as a weighted linear combination of the individual bandpair ozone estimates X_k and X_j, i.e., as:

$$X_{kj} = \frac{X_k \Delta\alpha_k - X_j \Delta\alpha_j}{\Delta\alpha_k - \Delta\alpha_j} \qquad (1.13)$$

This approach to aerosol scattering may be extended by explicitly expressing the scattering spectrum by an arbitrary polynomial and using the measurements of say n bandpairs to estimate the true ozone amount X and the n-1 coefficients of the polynomial. The set of simultaneous linear equations which result are of the same form as equation (1.9) and can be solved by standard matrix means, using the least squares method if only n-2 or fewer polynomial coefficients are sought. However, error anlyses have shown that, for various reasons, the linear polynomial is actually the most practical assumption, and hence that mathematical representations more sophisticated than equations (1.11) and (1.13) are not needed.

The theory of the preceding paragraphs describes the measurement of direct solar radiation when the sky is clear. When the direct radiation is insufficiently intense, or the sky is cloudy, it is possible to derive ozone estimations from measurements of the intensity of the blue, or cloudy, zenith sky, and such

estimations form an important part of the available data archives. There is no simple theory to base them on, however, and instead they are found by means of their empirical relationship to the direct solar measurement type. The relationship is established over a period of time, sometimes years, by many sets of quasi-simultaneous measurements of the two types. The methods work reasonably well because, firstly, the light received from the zenith sky is scattered mostly at low altitudes, below the bulk of the ozone layer, and so experiences an optical path through the ozone which is similar to that of the direct beam, and secondly, the scattering by cloud water droplets has only a small spectral dependence.

Various assumptions have been made in the development of the above measurement theory and each may contribute some error to the ozone estimation. The important ones are listed at this point along with the section in which the relevant error sources are considered. It is assumed that the effect of other UV absorbers in the atmosphere, e.g., SO_2, is negligible (see Section 11), and that atmospheric sources of radiation within the instrument's field of view, e.g., due to emission (see Section 11), or to atmospheric scattering (see Section 4), are also negligible. It is assumed that the means described above for dealing with aerosol attenuation are sufficiently accurate (see Section 10). It is assumed that the Rayleigh scattering coefficients are known to good accuracy (see Section 10), and that the ozone absorption coefficients are independent of atmospheric conditions and are also known to good accuracy (see Section 9). It is assumed that the extraterrestrial intensity ratio L_{0k} is constant (see Section 13) and that the atmosphere is, on occasion, sufficiently stable to allow the determination of the extraterrestrial constants (see Section 7). It is assumed that the mean values of the slightly height dependent secant terms in the height integrals of absorption and scattering, in particular μ_h can be calculated to sufficient accuracy (see Section 12). Lastly it is assumed that the empirical clear and cloudy zenith sky measurements are valid (see Section 10).

1.3 Instrument design

A considerable amount of material describing many aspects of the Dobson instrument already exists (in particular, Dobson, 1931; Normand and Kay, 1952; Dobson, 1957a and 1957b; Dobson and Normand, 1962; Dobson, 1968; and Komhyr, 1980b), but for the sake of completeness and to emphasize those things relevant to this study of the sources of error, a brief description is given here.

The first instrument, number 1, was built by G.M.B. Dobson in his own workshop and is described by him originally in Dobson (1931), and also later in the historical review (Dobson, 1968). The historical review discusses the evolution of the design, and it shows how the 1931 design grew out of the previously available ozone measuring instruments and overcame their disadvantages. For example, it incorporated the good stray-light rejection and similar dispersive capability of the Fabry-Buisson double monochromator (see Figure 2 in Dobson, 1968), but by means of its mirrors M_1 and M_2 (see Figure 1.2) it halved the number of dispersive prisms required and folded the optical path to occupy a much more compact space. It also eliminated the need for the rather tedious photographic methods used with the Fabry-Buisson instrument and with Dobson's earlier Féry prism spectrograph, yet it exploited the optical wedge and photocell techniques developed by Dobson and his colleagues to analyse the photographic plates produced by the Féry spectrograph. It incorporated many other features, in particular, the AC amplification and null measurement method. The greatest significance of the instrument however, lay in it being the first instrument to give essentially instantaneous values of ozone amount and to be sufficiently straightforward to operate on a routine basis.

In subsequent years the instrument was commercially manufactured by R. and J. Beck Limited, and a number of improvements were gradually introduced, though it is a quite remarkable fact that the basic design, established in that short period before 1931, has continued virtually unaltered to this day. Perhaps the most important change was the use of photomultipliers from 1947 onwards, since these greatly increased the instrument's sensitivity and allowed the measurement of bandpairs at wavelengths shorter than the one bandpair at about 311.4 and 332.4 nm previously used. This in turn led to the discovery of the method of using two wavelength bandpairs to reduce aerosol effects. Of course, the electronics systems of most instruments have been continually upgraded, in line with technological developments.

Normand and Kay (1952) described the state of development of the instrument at that time, and

succinctly summarised the principles of the design, adjustment and calibration of the instrument. Dobson expanded upon these, in preparation for the IGY, in his detailed instruction manuals for the instrument's operation (1957a) and adjustment and calibration (1957b). Later, Dobson and Normand (1962) gave a detailed discussion of the determination of instrument constants and of the accuracy of the ozone measurements under various conditions. Further studies by Dobson of the instrument's accuracy may be found in Walshaw (1975). The resurgence of interest in ozone in recent years and the consequent need to improve and standardize operational practice led to the publication in this WMO-Global Ozone Research and Monitoring Project series of an updated Operations Handbook prepared by Komhyr (1980b).

The essential features of the instrument are summarised in Figure 1.2 and are illustrated as follows by the passage of direct sunlight through the instrument. The light enters the prismatic sun director and is reflected downward through the lens to enter the main body of the instrument at the ground quartz plate (GQP). The prism and lens concentrate a rectangular swath of light on the GQP. The lens may also be adjusted to focus, with the GQP removed, a weak solar or lunar image directly onto the entrance slit S_1. The GQP ensures a relatively diffuse, uniform and depolarised illumination of S_1. The light from the GQP is reflected onto S_1 by a small prism. The slit S_1 is curved to correct for the instrument's greater dispersion of off-axis rays, and its width, along with those of slits S_2 and S_3, controls the spectral shape and energy throughput of the chosen wavelength bands.

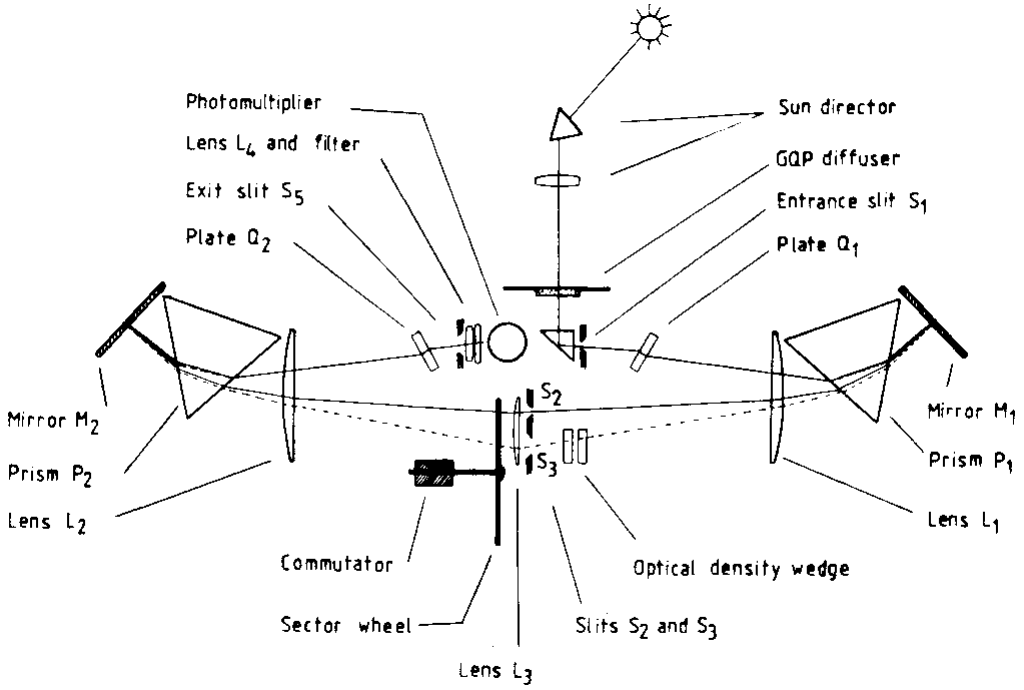

Figure 1.2 Schematic diagram of the main optical and mechanical parts of the Dobson spectrophotometer.

The light from S_1 passes through the thick quartz plate Q_1 and is corrected by lens L_1, dispersed by prism P_1, and in due course, focussed by L_1 as a spectrum on the S_2S_3 slit plane. Plate Q_1, when rotated, shifts the apparent position of S_1, as seen at L_1, and hence shifts the spectrum up and down at the S_2S_3 slit plane, thus allowing the selection of different wavelength bandpairs by S_2 and S_3, and also the correction of small temperature dependences. P_1 is the instrument's principal dispersive element, and its top leading edge acts as a stop. Mirror M_1 folds the beam back through P_1 to double the instrument's dispersion, and its adjustment sets the initial wavelength position of the spectrum in the S_2S_3 slit plane. Slits S_2 and S_3 select the desired pair of wavelengths. The band transmitted by S_2 has a wavelength in the 305 to 320 nm region, depending on the orientation of Q_1, and a bandwidth of about 1 nm, and the band transmitted by S_3 has a wavelength about 20 nm greater than that of S_2 and a bandwidth of about 3

nm. The focal plane is actually not parallel to the slit plane but is oriented at about 55° to it. The focal plane is adjusted by means of L_1 to coincide with S_2 and hence to lie well behind S_3. (Note that below S_3 there is actually another slit, S_4, which is not shown in Figure 1.2. A discussion of S_4 and its associated components is omitted for brevity's sake.)

The optical density wedge device in front of S_3 is used during a measurement cycle to attenuate the greater intensity of the longer wavelength band until it is registered by the null detection system (see below) as equal to the intensity of the shorter wavelength band. There are actually two wedges, which are simultaneously moved in mutually opposite directions (in and out of the plane of the diagram) by means of an externally mounted, manually operated mechanical dial. The dial must be calibrated in terms of the log intensity attenuation it produces.

The principal purpose of the right-hand half of the instrument is the selection of the desired bands, while the principal purpose of the symmetrical left-hand half is the rejection of the stray light in those bands. Light from S_2 and S_3 is directed by lens L_3 towards lens L_2 which collects it and focusses it via prism P_2, mirror M_2, and plate Q_2 onto the exit slit S_5. It is longer wavelength stray light in the short wavelength band that is the main problem, but the dispersion by P_2 ensures that most of this stray light will be projected below slit S_5 and will not be seen by the photomultiplier detector mounted behind the slit. There is also a filter at S_5 which strongly absorbs stray radiation of wavelengths greater than about 400 nm. The lens L_4 at S_5 projects an image of P_2 onto the detector so that both of the selected bands fall on the same area of the detector. The lens L_3 projects an image of the top leading edge of P_2 backwards via L_1, P_1, and M_1, to lie between L_1 and P_1 and so form a lower stop acting on undispersed light, this stop being complementary to the stop formed by the top of P_1.

The motor-driven sector wheel beside L_3 is part of the null detection system. It is this system which tells an operator when his adjustment of the optical wedge has equalised the intensities of the two bands being measured. The wheel continuously rotates and alternately transmits the beams from S_2 and S_3, allowing them to alternately impinge upon the photomultiplier. The alternating component of the photomultiplier's output is amplified, and this in turn is rectified by the commutator which is mounted on the sector wheel shaft (or by means of an optical switch at the wheel edge) to give a DC current which is proportional to the difference of the intensities of the bands. The current is displayed to the operator by a meter. When the intensities have been equalised the meter reading is zero.

The main sources of error associated with the instrument itself are now listed, along with references to the Sections in which they are considered in more detail. Experience has shown that the accuracy of the instrument is less affected by fundamental design limitations than by inaccurate optical adjustment, (Section 2), wedge calibrations (Section 3), and extraterrestrial constants (Sections 5 and 7). Poor operational practice may also be a problem (Section 7). Among the more fundamental limitations are the sensitivity of the ozone measurements to the uncertainty in band centre wavelengths arising from normal calibration and operational practice (Section 5), the effect of finite spectral bands (Sections 6), mechanical and temperature stability (Section 2), the limitations of focussing, optical stopping and other optical peculiarities (Section 2), and the effect of stray light (Section 4). Various electronics problems may also arise (Section 8).

Note added in press

The wavelengths selected by slit S_2 and S_3 are usually assumed to be those listed for the standard A, B, C and D bandpairs in Dobson (1957a, p. 47), namely, A (305.5, 325.4), B (308.8, 329.1), C (311.45, 332.4) and D (317.66 and 339.8), all in nm. However, C.L. Mateer (personal communication) has pointed out that the A band 325.4 nm value is inconsistent with the other values and probably should be about 324.14 nm, the value listed in a less obvious table in Dobson (1957b, p. 110). If so, the resulting wavelength change would affect many of the calculations in this review, though only to a small extent.

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Forward to Optics

2. OPTICS

2.1 Introduction

The Dobson instrument has the character of a laboratory instrument even though it is used in routine outdoor use, and its adjustment and maintenance requires a relatively high level of skill and technical knowledge. For example, the widths of slits S_1 and S_2 must be set to an accuracy of 0.4 ±0.01 mm, which gives a bandwidth accuracy of 1.0 ±0.025 nm, and the tilt angle of mirror M_1 must be stable to a precision of about 9×10^{-6} radians or 1.9 seconds of arc to provide a wavelength accuracy at S_2 of 0.025 nm. Other problems to be overcome are: the physical confinement of some of the components which have to be adjusted, the temperature dependence of some adjustments, and the fact that alignments and focussing must be done for ultraviolet light which, of course, is not visible to the human eye.

Detailed methods for the instrument's adjustment are given in Dobson (1957b). It is now generally accepted and recommended that these adjustments should be attempted only by skilled technicians (Komhyr, 1980b), and preferably only with the guidance and assistance of WMO or of those experienced and expert in these adjustments. It is important to note that although the instrument in principle can be made to operate satisfactorily wider a variety of adjustment regimes, the necessary intercomparability of instruments demands that all instruments in fact use a common set of wavelengths and transmission band shapes and therefore be adjusted and calibrated in a uniform fashion to common standards.

2.2 Optical adjustment

The main objectives of the adjustments specified in Dobson (1957b) are to ensure that the alignment, stopping, focussing and wavelength band selection of the instrument are properly set. The general effect of inadequate adjustments are as follows. Poor alignment of the optical components can cause many problems, including defects in optical stopping, increased effects of optical aberrations, increased stray light and decreased sensitivity. Defects in stopping, which can also arise from an incorrect focal length of lens L_3, cause the instrument to have a varying spectral sensitivity for light near the edge of the field of view (Basher, 1980). Improper focussing of lens L_1 results in a broadening of the wavelength bands, particularly those transmitted by slit S_2, and excessive effects of lens aberrations. Errors in the focussing of lens L_2, in the adjustment of plate Q_2 and in the width of slit S_5, can reduce the sensitivity of the instrument, can alter the relative spectral sensitivity, and can increase the effect of stray light. Errors in the adjustment of mirror M_1 and plate Q_1, and in the positions of slits S_2 and S_3, will cause errors in the centre wavelengths of the desired bands, while errors in the width and parallelness of the slits S_1, S_2 and S_3 will cause errors in the shape of the bands.

The effect on ozone measurements of the residual uncertainty in the effective centre wavelength, width and shape of the transmitted bands arising from normal correct adjustments is considered in more detail in Section 5. The effects of stray light are discussed and estimated in Section 4. Error estimates are generally not available for the other uncertainties of adjustment, and it would be very difficult to estimate the size and behaviour of errors arising from abnormal and poor adjustments.

Gross faults in the optical system have been found on occasion (Komhyr, 1980b). These are such things as lenses of the wrong focal length, optical components made of material which are poor transmitters of ultraviolet light (e.g., crown glass), poor quality quartz glass, mechanical overtightening and stressing, looseness and slippage of parts, objects obstructing the optical path, oily or dirty optical surfaces, and mechanical delamination of the optical wedges found in early instruments.

The results of the intercomparisons of Dobson instruments listed in WMO (1982) give some idea of the possible limits of error due to poor adjustment. The early intercomparisons show differences of up to 10% for instruments which have been independently adjusted and calibrated, whereas instruments which have been more recently adjusted and calibrated by direct intercomparisons, and then intercompared a year or two later, generally agree to better than 2%. These error figures also include errors due to wedge calibrations and extraterrestrial constants. Ozone errors due to poor adjustment will tend to be dependent on operating conditions, particularly airmass, and therefore will tend to be very variable and may severely limit the operating range of an instrument.

The steady improvement in the results of the intercomparisons is in large part due to the systematic and rigorous test and adjustment procedures and instrument modernisations which are often carried out just prior to

the field intercomparisons. WMO has sponsored much of this work, and with a view to its further encouragement and coordination, has recently designated the United States National Oceanic and Atmospheric Administration's Air Resources Laboratory in Boulder, Colorado as the World Dobson Spectrophotometer Central Laboratory. The data in WMO (1982) indicate that at least fifty instruments have been upgraded and calibrated, which is well over half of the network. It seems likely that most of these have intercomparabilities near the 2% level for ordinary direct sun observations with the AD bandpairs, and therefore errors due to deficient optical adjustment of less than 2% for such measurements.

2.3 Fundamental optical limitations

Dobson (1931) and Normand and Kay (1952) discussed the fundamentals of the instrument's optical design, but since then there has been no comprehensive study of its optical characteristics, for example, as might be done by computer ray tracing techniques. Bearing in mind the current demands for better accuracy and the known existence of certain optical problems, as detailed below, it would seem now timely for such a study to be undertaken. Two particular matters which require further investigation are, firstly, the aberrations of simple lenses (e.g. chromatic aberration, spherical aberration, astigmatism, etc.) and their effect on focussing and wavelength band definition, and secondly, the reflection of light from optical surfaces and its contribution to stray light in the instrument.

It was pointed out by Dobson (1931) that the instrument's focal plane is inclined to the slit plane. This problem was circumvented in the 1931 design by first ensuring a focus at slit S_2 and then using auxiliary lenses on either side of S_3 (and S_4) to bring the longer wavelength bands to focus. However, in the later multi-wavelength design described by Normand and Kay (1951) and Dobson (1957a) the lenses adjacent to the S_3 slit were omitted and only those near S_4, the "achromatising" lenses, were retained. Basher (1980) found that the inclination angle is 55° and that if a sharp focus is present at S_2, then the focus at S_3 lies about 14 mm behind the slit.

About 4 mm of the focal error is due to the extension of the focus by the optical wedge, since flat plates extend focal lengths. The plate Q_1, also extends the focus of both wavelengths, and since the extension is proportional to plate thickness, the focus for both will vary as the plate is rotated away from the normal to the beam. When the rotation is such as to choose shorter wavelength bands, the focus extension will partly compensate for the reduced focal length of the shorter wavelengths, but when the longer wavelength bands are chosen the extension of focus exacerbates the existing lack of focus.

Two effects of the lack of focus at the S_2S_3 slit plane were discussed by Basher (1980). One is the greater spread of wavelengths transmitted by the slit and hence a smearing of the slit transmittance function and an alteration of the band's ozone absorption coefficient (see Figure 2.1). Fortunately it is the longer wavelenqth bands which are most affected and their absorption coefficients' accuracy has only a small effect on the ozone estimation accuracy. Preliminary measurements of the transmittance spectra of the World Reference Dobson Spectrophotometer No. 83 have been made recently by W.D. Komhyr (personal communication). The calculated spectrum in Figure 2.1 is in good general agreement with these measured spectra.

The other, and more important effect is the dependence of the transmitted wavelength on the incidence direction within the internal field of view as illustrated in Figure 2.2 (where this field of view is defined by the stops and not the GQP diffuser). The calculated shift in the S_3 band's centre wavelength in traversing the field of view is about 2 nm. This means that the instrument's spectral sensitivity will vary across the field of view, with a log I/I' measurement varying by about 0.030 for an incandescent standard lamp, and by possibly up to 0.075 for solar irradiance. This appears to be the explanation for the "directional effect" described by Dobson in Walshaw (1975). It will cause significant problems when the light distribution within the field of view is variable, in particular, when an image of the sun or moon is focussed on the entrance slit.

It can be noted here that a further change in the L_o value appropriate to the focussed solar (but not lunar) image will arise owing to the solar limb darkening and its spectral dependence. As an example, at three quarters of the solar radius the intensity at 322 nm has dropped to 70% of that at the disc centre (see also Moe and Milone, 1978). Computations by Svensson (1958) of L_{oA}, L_{oC} and L_{oD} for the case of a solar eclipse suggest changes in L_o of the order of 0.010. Focussed lunar images may have L_O values different to those for sunlight, to the extent that the moon's reflectivity is not spectrally constant.

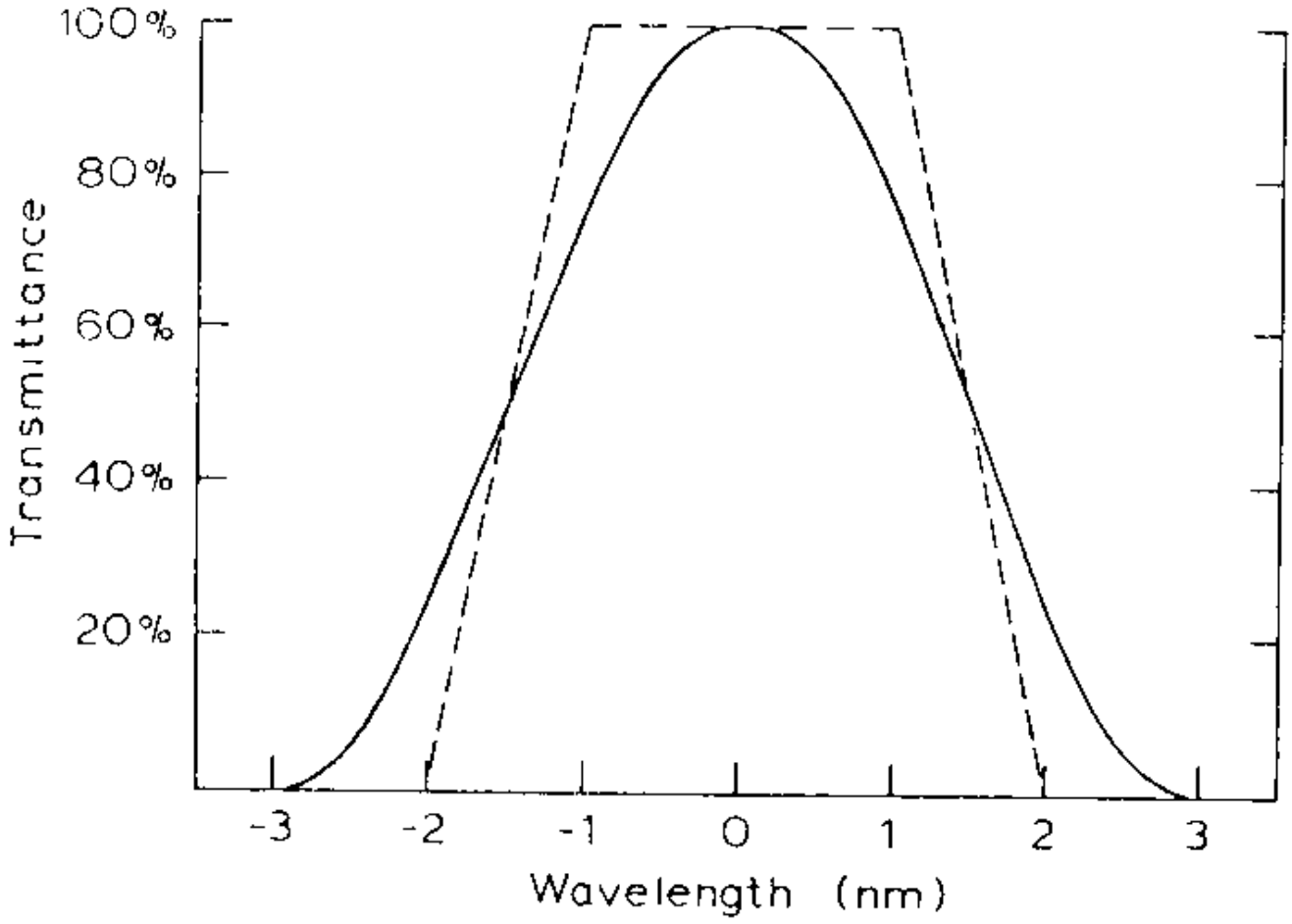

Figure 2.1 Transmittance function of a longer wavelength Dobson band, for a 14.3 mm focus error at slit S_3 (_____), and for a perfect focus at S_3 (-------).

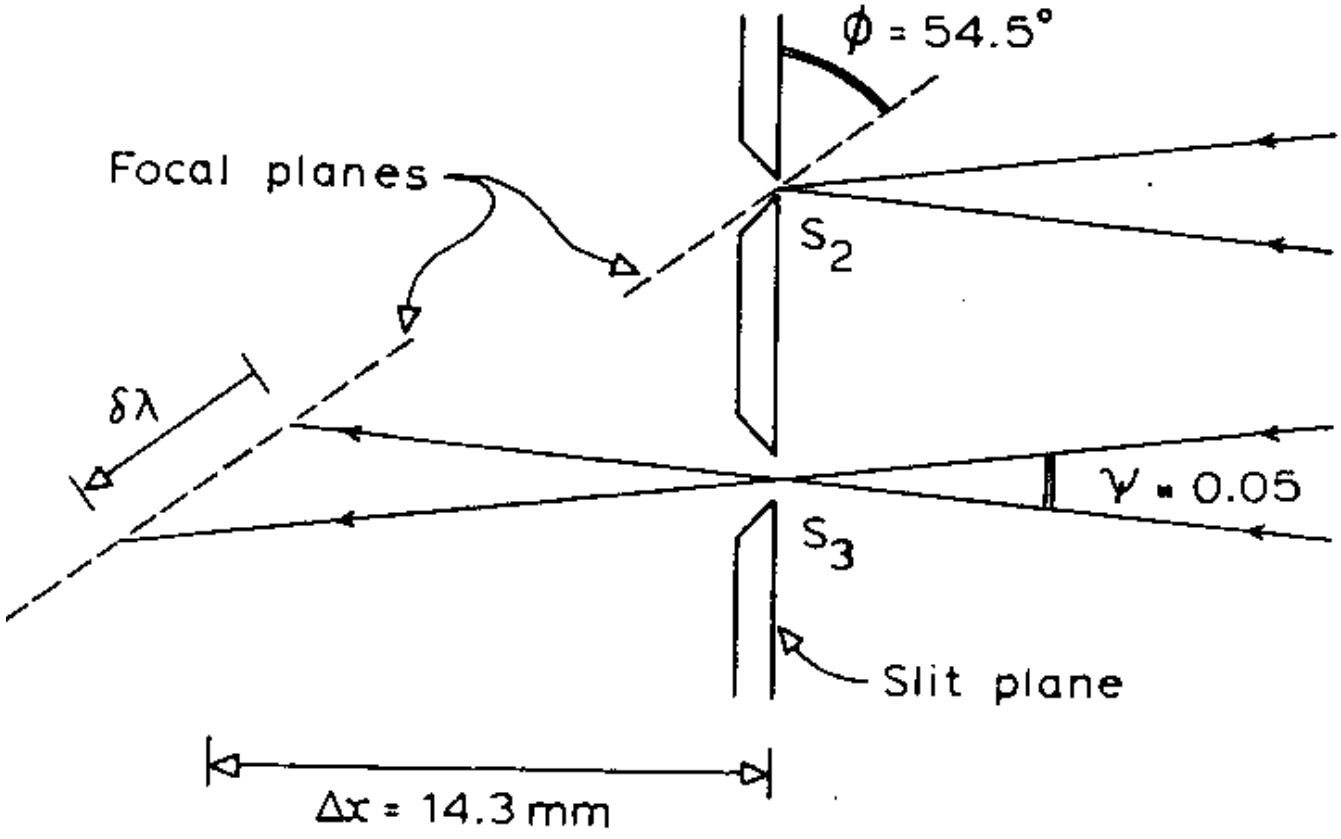

Figure 2.2 Illustration of how the focus error at S_3 generates a wavelength spread in the transmitted band. The rays mark the boundaries of the internal field of view.

The effects of reflections within the Dobson instrument are not well known. A beam of light entering the instrument must pass through about thirty optical surfaces before reaching the detector, and since the reflectivity of the air to quartz interface at normal incidence at 310 nm is about 3.8%, there is a considerable amount of energy in the reflected light. The relative amounts of reflected and refracted energy at an interface depend on the incidence angle and polarisation of the beam. The GQP diffuser provides a well scattered and well depolarised light, and Dobson (Walshaw, 1975) found no noticeable effects from the variation of polarisation of natural skylight. However, when the GQP is not present there will exist the possibility of large error if the source of light projected onto the entrance slit has large or varying polarization. It is possible that the large variation in relative spectral response found by Dziewulska-Losiowa (1978) when using a polaroid film at varying orientation arose as a result of the GQP being absent. (The film has potential for reducing ozone errors in cloudy conditions - see Section 10).

Reflected energy contributes to the instrument's stray light problem, which in turn limits the effective dynamic range of the instrument. Two particular optical problems noted by the author and discussed below are the internal reflection of light in plate Q_1, and the direct reflection of light from slit S_1 onto the S_2S_3 slit plane by lens L_1. Of course there may be other similar problems awaiting discovery.

It can be shown that when a tilted, thick flat plate like Q_1 is used to displace a beam to one side of an optical axis there will be produced by internal reflection a second beam of reduced intensity which is displaced to the opposite side. In the Dobson instrument this produces a displaced "ghost" image of the entrance slit S_1 and hence a displaced "ghost" spectrum at the S_2S_3 slit plane. The intensity of the ghost spectrum is about 0.14% of the intensity of the main spectrum. It results in a significant stray light level at the S_2 slit when the Q_1 plate is tilted to select short wavelength bands since the ghost band is then shifted in the opposite direction, to longer and therefore more intense wavelengths bands. The author calculates that when the A bandpair is selected, the ghost band at S_2 is centred at about 323.8 nm and its energy contribution at an airmass of 3 is about 20% of that of the desired 305.5 nm band. The stronger atmospheric attenuation of the 305.5 nm band thus serves to magnify the effect of the ghost band as the airmass increases.

The faces of lens L_1 reflect white light from S_1 directly onto the S_2S_3 slit plane. It is possible to calculate approximately the energy contribution of this light relative to that of the desired short wavelength band from a consideration of the reflectivity of quartz, the relative solid angles subtended by the sources, and the relative atmospheric attenuation. The "white light" detectible by the instrument can be assumed to lie in the range 380 ±40 nm. The author calculates that at an airmass of 3, the energy of the reflection transmitted by S_2 is perhaps twice that of the band being measured.

It is therefore clear that the role of the second monochromator in rejecting stray light is a very important one, and that the adjustment of this monochromator deserves special attention. The rejection is to a large extent effective, but it is limited: by intrinsic focussing deficiencies, by the relatively broad 3 mm slit width of S_5, which is equivalent to a 8 nm acceptance band, and by the rapid relative increase of the stray light with airmass. Komhyr (personal communication) reports that a characteristic of those well adjusted, well calibrated instruments which exhibit severe internal light scattering, is light attenuation at the short wavelengths by poor quality quartz optics, particularly prisms. Further discussion of the effects of stray light is given in Section 4.

Temperature affects the Dobson instrument's optics directly through the temperature dependence of the refractive indices of the prisms, lenses and flat plates, and indirectly by the distortion of the optical path imposed by differential thermal expansion. The temperature dependences of the optical components can be calculated from textbook formulae and data, such as is given in Basher (1980), and knowing the temperature dependence of the refractive index of quartz to be about 10^{-5} °C^{-1}. It turns out that only the prism's dispersion dependence is of importance.

The instrument's temperature dependence is corrected for by small changes in the orientation of the Q_1 plate, the required changes being determined by earlier experiments using line sources over a range of temperatures. Dobson (1957b) gives some results in the range of about 0.1 to 0.2 °Q/°C (where °Q refers to the angle change of the Q plate in degrees). Since the centre wavelength dependence on the Q_1 angle, $d\lambda/dQ$, is about 0.2 nm °Q^{-1}, the centre wavelength dependence on temperature is about 0.02 to 0.04 nm °C^{-1}.

To provide a centre wavelength accuracy of 0.025 nm, which is very desirable (see Section 5), it is necessary, therefore, to ensure:

- that the temperature corrections are made for every 1°C change in temperature;
- that the temperature in the vicinity of the prism and the thermometer is uniform to better than 1°C;
- and that this temperature changes by less than 1°C during any single sequence of measurements (i.e., over one or two minutes).

These requirements may present rather stringent demands when the indoor to outdoor temperature difference is high or under conditions of bright sunshine. The instrument is provided with a reflective insulating jacket to improve its temperature stability. However, Dobson (in Walshaw, 1975, p.82) reports that Grasnick (in Ozone Symposium, Albuquerque, 1964) has shown large differences in air temperatures within the instrument under certain conditions. In addition, Dobson notes that the importance of temperature control and the use of the jacket is sometimes not appreciated by station observing staff.

To ensure a rigid instrument, free from the effects of mechanical deformation, the body is constructed of two boxlike halves bolted together, each half made of a single casting in aluminium alloy. It sits on three legs, to avoid the distortion which can occur with four legs. Mechanical stress due to people leaning on the instrument or resting objects on it may possibly have significant effects and should be avoided. Asbridge (personal communication) reports that distortions can arise if the gasket between the instrument's halves is very compressible and the tightening of the bolts is consequently uneven. The distortion in the instrument concerned was detected by means of wavelength checks with a mercury line source before and after assembly of the instrument. Incompressible spacer washers were used on some bolts to overcome this problem.

An approximate estimate of the effect of thermal expansion may be made as follows. Let us assume a temperature gradient from the top to the bottom of the instrument such that the top is 1°C hotter than the bottom, and a coefficient of expansion for the alluminium alloy of 1×10^{-5} °C^{-1}. The resulting angular displacement in the vicinity of the prism P_1 then would be approximately $500 \times 10^{-5}/200 = 2.5 \times 10^{-5}$ radians, where 500 mm is the length of the right-hand half of the body and 200 mm is the height. This figure of $2.5 \times l0^{-5}$ is larger than the figure of 9×10^{-6} needed to maintain the centre wavelengths to an accuracy of 0.025 nm, which would suggest that temperature differences across the instrument should be kept to less than about a quarter of a degree celsius, and that, quite possibly, thermal expansion stresses may contribute significant error on occasion. However, this is a very approximate calculation and the topic requires further study and experimental investigation.

The effective refractive index of quartz is slightly pressure dependent. Normand and Kay (1952) give the required correction of Q plate angle as one-half degree per 100 mb, which is equivalent to a centre wavelength change of about 0.1 nm per 100 mb. Atmospheric pressure changes at any site usually are within the range of ±30 mb, but on occasion can be ±50 mb, and so corrections for these changes are generally not attempted. However corrections are required if an instrument is shifted in altitude after a calibration has been done (see Komhyr, 1980b, p. 73).

Dobson, in Walshaw (1975), points out that moisture condensing on optical surfaces can be a problem. The dish of silica gel in the instrument will generally avoid any problems, provided it is kept replenished with fresh (blue) silica gel. Dobson reports that in one case when calibrating a wedge, it was necessary to change the silica gel every second day in order to get consistent calibration data.

The ultraviolet light within the instrument could induce fluorescence, and therefore stray light, if fluorescent materials such as paper, certain cloth, or lint or dust derived from them, are present. There is no information on this in the literature on the Dobson instrument, and it is probable that it is not a significant problem.

2.4 Summary

(i) The Dobson instrument is a precision optical instrument and its optical adjustment should be attempted only by skilled technicians trained for the task.

(ii) Inadequate adjustment causes, principally, increased wavelength band uncertainty, increased stray light, and varying spectral sensitivity. It is virtually impossible to reliably assess the quality of a particular instrument's past adjustments and the errors associated with them. Uncertainties remaining after a correct adjustment are discussed in Section 5.

(iii) Experience indicates that poor adjustment has been an important source of error in the past. On occasion, gross optical faults have been found.

(iv) Intercomparisons have shown that, in the past, independently adjusted and calibrated instruments could differ by 10% in their measurements, but that recently adjusted instrument calibrated against a reference instrument generally differ by less than 3%. The improvement is largely due to the intercomparisons and the accompanying efforts to upgrade instrument optics, electronics and calibration.

(v) A number of fundamental optical problems have been identified, as noted in items (vi) and (vii) below. These point to the need for a comprehensive study of the instrument optics, for example by computer ray tracing methods.

(vi) The inclination of the focal plane smears the transmittance band functions and gives rise to the "directional effect", the varying spectral sensitivity across the internal field of view.

(vii) The multiple reflection of light in the Q_1 plate, and the direct reflection of light from lens L_1, contribute significant amounts of stray light to the shorter wavelength band. It is very important that the second monochromator be properly adjusted to effectively reject as much of this stray light as possible (see also Section 4).

(viii) Focussed image method ozone measurements are affected by the "directional effect" (possibly by up to some tens of percent, depending on the bandpair used), and by the solar limb darkening effect (possibly by up to 2%), or the lunar spectral reflectivity variations (possibly by up to 2%).

(ix) The temperature dependence of the wavelength bands is significant. This requires an internal temperature uniformity of 1°C or better, and the correction of wavelength settings at at least 1°C intervals.

(x) Mechanical deformation of the instrument can cause wavelength band errors. Temperature gradients across the instrument can cause deformations and may possibly be a problem.

(xii) Wavelength setting corrections are required when instruments are shifted in altitude, owing to a pressure dependence. A dessicant is required inside all instruments to prevent condensation on optical parts. Fluorescence inside the instrument does not seem to be a problem.

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3. WEDGE CALIBRATION

3.1 Introduction

The optical density wedge has a pivotal role to play in the Dobson instrument, and the accuracy of its density calibration is crucial to the accuracy of the ozone estimations. Originally, Dobson (1931) confidently assumed the wedge density to be essentially linear with wedge length and determined the density gradient by reference to a metal gauze of known transmittance. Subsequent experience, however, showed that linearity could not be assumed and that more sophisticated calibration methods were necessary (Normand and Kay, 1952, Dobson, 1957b, Walshaw, 1975).

The first density wedges were constructed from gelatin containing carbon black sandwiched between two quartz plates, but these were found to be subject to delamination and mould growth on the gelatin. Evaporated metal films were later developed which had sufficient linearity (Dobson, 1968). Note that the wedge device consists of two individual density wedges. Komhyr and Grass (1972) reported that the Canada balsam cement which joined the two quartz plates of each wedge was not stable in transmittance. They described a better joining method which had given very good constancy in spectral transmittance over a period of more than ten years in the wedge of instrument number 83. (This instrument is now designated the World Primary Standard.)

In principle, the wedge could be calibrated independently of the Dobson instrument, but in practice it is more accurate to calibrate it in situ, i.e., in the same configuration as is used operationally (Normand and Kay, 1952). Because the instrument's electrical response to intensity is not linear, the wedge density cannot be measured directly. Instead, the null detection system is used to obtain the change in wedge position, ΔR, as measured by the angle R of the external dial, that is needed to balance an applied and known change in intensity at the S_3 slit, relative to a temporarily fixed intensity at either S_2 or S_4. The log of the intensity ratio for the change is then equal to the wedge density interval ΔD required to balance the change. A measurement sequence usually consists of a set of ΔR measurements as a function of R, such as is shown in Figure 3.1.

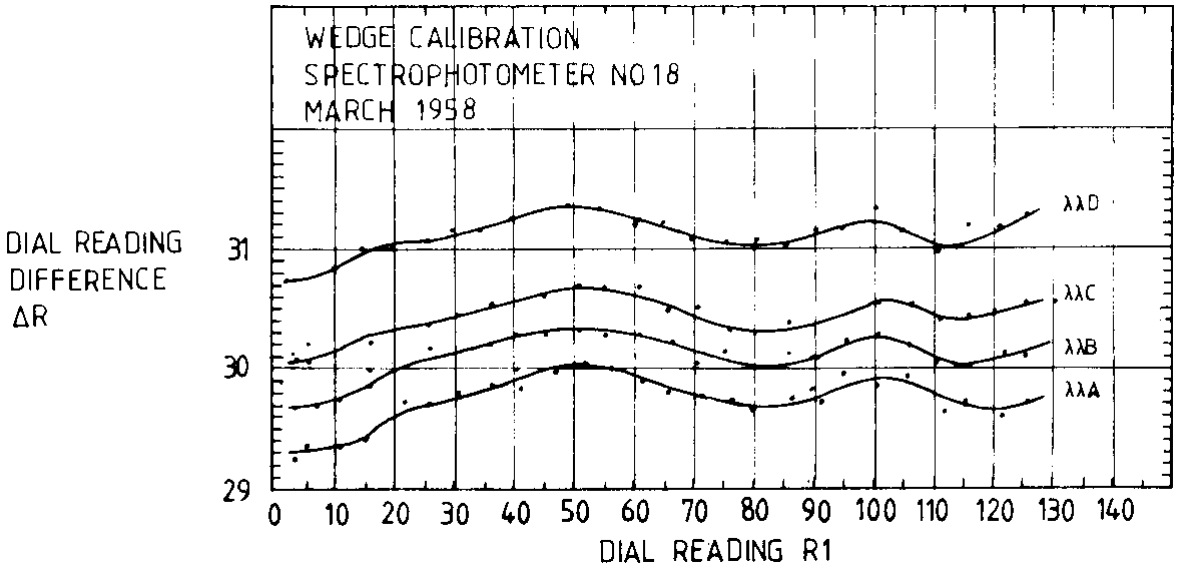

Figure 3.1 Dobson optical wedge calibration data using the two lamp method (data from Komhyr, 1980b).

In essence, the calibration of the wedge consists of, first, the measurement of the coarse density gradient $\Delta D/\Delta R$ as a function of dial angle R, and second, the integration of this gradient with respect to R to obtain the density function D(R). The unknown constant of the integration forms part of the instrument's extraterrestrial constant which is determined by independent means (see Section 7). However, in practice, a more elaborate analysis procedure involving the "minor interval" method is used to calibrate the wedges.

3.2 Apparatus

The most common means for providing known changes of intensity are the two-source intensity doubling or halving devices, in which two sources of closely equal intensity are alternately exposed singly and in combination to give an intensity step of 2 and therefore a log intensity step of 0.301. These are mounted just above the instrument's optical entrance, and may consist of:

- two independently shuttered, closely spaced lamps (Dobson, 1957b, Komhyr, 1980b);
- a single lamp with a beam splitter whose two separate beams can be independently shuttered (Walshaw, 1975);
- two independently shuttered lamps whose beams are made to appear of coincident origin (Komhyr, 1980b, Olafson et al., 1981);
- or, lastly, a single lamp above a finely perforated plate which is shuttered by another perforated plate to expose half or all of the holes (Funk, 1959).

The lamps available before about 1960 were large and of low wattage and low colour temperature, and their intensities were insufficient to allow accurate calibrations at the higher density end of the wedge. Present day designs use small quartz halogen lamps of higher wattage and higher colour temperature and can be used to calibrate the whole wedge. Komhyr (1980b) reports that essentially identical results were obtained in 1977 from the Canadian device, which uses two 350 W lamps with a prism to ensure coincident beams and is water cooled, and a United States device, which uses two 600 W lamps side by side and is air cooled. The intensity incident on the instrument needs to be stable to about 1% over a measurement cycle and this requires a very stable lamp power supply, good electrical contacts at the lamp, and good mechanical stability of the lamp and its mount. The direct heating of the instrument, largely by conduction, can also be a problem for lamps of large power consumption (Walshaw, 1975, p.66).

To obtain an initial null balance for the halved intensity at the various points along the wedge, a small lamp and diffuser is mounted in front of slit S_4, whose intensity, as measured by the instrument detector, is adjusted until it equals the halved intensity transmitted by the chosen part of the wedge and by S_3. Slit S_1 is shuttered. The intensity of the S_4 lamp should be as stable as those in the two-source device.

The alternative method of producing intensity step changes is by means of neutral density filters of known transmittance placed inside the instrument in the path of one of the spectral beams, usually that through S_3. For example, before the two lamp device was developed, neutral density filters of transmittance 0.25 and 0.75 were used to calibrate the whole wedge (Normand and Kay, 1952). Dobson (1957b) described the use of a rhodium plated neutral density filter to calibrate only the optically dense part of the wedge. The filter's transmittance was calibrated against the optically thin part which had been calibrated with the two lamp method.

Neutral density filters are relatively easy to make and to use. They may be made of evaporated metals on quartz plates, of perforated plates, or of metal gauzes. Their density may be chosen to be small enough to map small scale variations in wedge density, though it should be noted that because of the density averaging of the S_3 slit's length of about 1 cm, such variations will be limited to the order of 0.15 in density. The disadvantage of filters is that their transmittance must be independently calibrated to high accuracy and must be specifically checked for spectral transmittance variations, temperature dependences and temporal changes. As with the two lamp devices, they must provide a uniform intensity across the instrument's field of view, to avoid errors associated with the instrument's spectral sensitivity variation across the field of view (see Section 2.3), and for this reason the use of a single variable iris aperture (Sinha and Sanyal, 1965), which is, in effect, a very spatially non-uniform filter, cannot be recommended.

3.3 Data analysis methods

The measured (ΔR, R) data set is best checked graphically to eliminate bad data and to ensure sufficient coverage, especially where the density gradient varies rapidly or the data are noisy. The data

are smoothed and it is upon this smoothed curve that subsequent processing is done. The simplest method of processing is to assume that the local density gradient dD/dR at any value of R is equal to the coarse density gradient ΔD/ΔR centred on R, and then to integrate ΔD/ΔR, which is the inverse function of the (ΔR, R) function, as a function of R. Some extrapolation at the ends of the density range would be required. This method is briefly discussed by Dobson (1957b, p. 107).

The recommended analysis procedure in Dobson (1957b) and Komhyr (1980b) makes use of the "minor interval" method, an ingenious procedure which is designed to better describe small scale wedge density variations. There appears to be no wholely mathematical description of the method in the literature, and the descriptions of it in the above two references, and in what follows, are in terms of the steps needed to carry it out. The notation used below is the same as that used in the above references.

The method is illustrated in Figure 3.2. Using the (ΔR, R) data, sequences of major density intervals F (where F equals 0.301 for a two lamp calibration) are formed along the wedge such that the differences between successive starting points in R (and therefore also between successive end points in R) of each sequence define a set of unknown smaller density intervals f_i. The sequence starting points in R are chosen to divide the first major interval into five minor intervals of approximately equal size in R. The sum of the f_i, i.e., $f_1 + f_2 + f_3 + f_4 + f_5$ equals F. With some thought, it may be seen that the sequences formed repeat the minor density intervals along the wedge. The values of f_i are estimated from the R values noted as the sequences are formed, by assuming that the local density gradient is equal to the coarse density gradient over the major R interval in which it is centred. If there are n major density intervals along the wedge, it is possible to make n-l individual estimates of each f_i, and these are averaged to give the final value of each f_i. The f_i are then added up and interpolated, in proper sequence, to give the density at any point along the wedge.

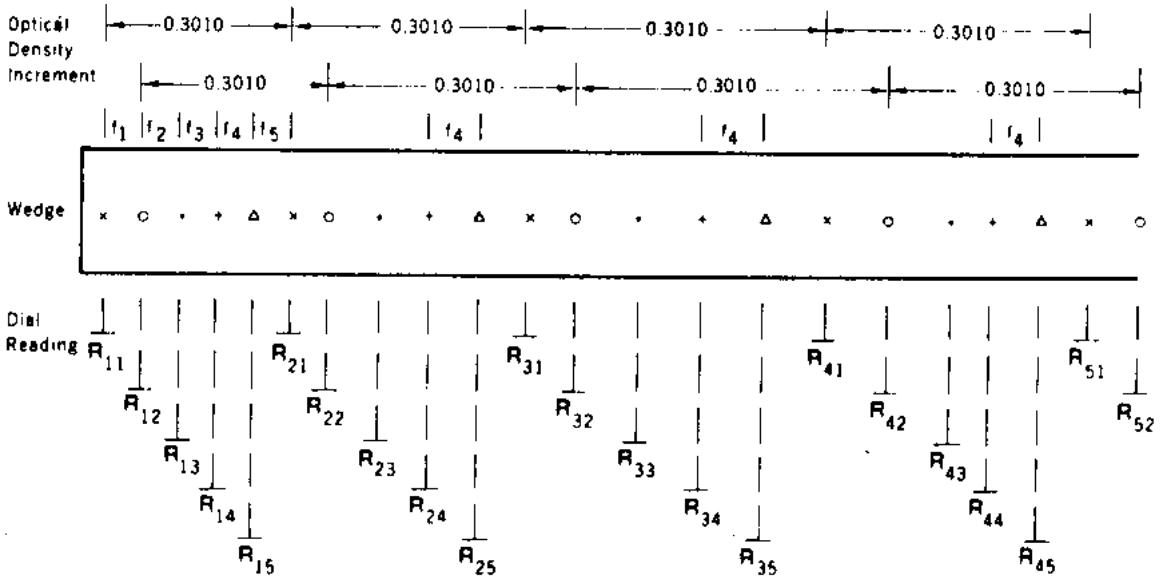

Figure 3.2 Illustration of minor interval method of analysing the Dobson optical wedge calibration data (from Komhyr, 1980b).

The minor interval method is not easy to understand from such a brief description, and for further details the reader should consult Dobson (1957b) and Komhyr (1980b). It can be noted that the only significant advantage of the minor interval method, compared to the simple integration, is its averaging of up to ten estimates of the f_i, and the tendency for this to reduce any systematic error in the estimation of the local gradient from the surrounding coarse gradient. The question as to whether the application of the minor interval method is really necessary can only be answered by an inspection of the density function of the wedge under consideration.

3.4 Error analysis of standard methods

Let it be assumed, firstly, that there are random uncertainties of 0.1° in the dial readings, secondly, that any systematic measurement uncertainties in dial readings, such as due to operator bias,

tend to cancel for differences in dial readings, and thirdly, that a suitable criterion of performance is for the uncertainty in X_A total ozone at an airmass of 1 to be less than 0.0015 atm cm (about 0.5%). This criterion implies a wedge density uncertainty of less than 0.0026 at a density of about 0.65, or equivalently 0.4% in density. The corresponding density uncertainties for the C and D bandpairs are 0.35% and 0.25% respectively.

The random uncertainty for a dial reading difference, ΔR, is thus assumed to be 0.14°. (This may be a conservative value, since the scatter in ΔR in Figure 3.1 appears to be about 0.07°.) This results in an uncertainty of about 2.4% in individual f_i estimates for minor intervals of approximately 6° in R, which is in reasonable agreement with the uncertainty apparent in the experimental data of Table 14.3 in Dobson (1957b). If a large number of data contribute to the (R, R) function, then the size of the random error will reduce, for example, to 1.2% if there are four data per 6° in R, and if nine minor intervals contribute to the average estimate of f_i, then the random error in this average will reduce to 0.4% in density, which, by coincidence, equals the error criterion. The constraint that:

$$\sum_{i=1}^{n} f_i = F \qquad (3.1)$$

within each major interval prevents this uncertainty from accumulating along the wedge.

To minimise the random uncertainty, it is clear, firstly, that many (ΔR, R) data are needed, say, at least four per 6° in R, and secondly that the minor intervals should be no smaller than necessary. Since the S_3 slit's length is equivalent to about 20° in R, it would seem sensible to divide the major interval of approximately 30° into only three minor intervals and not the five usually used.

In both the simple integration method and the minor interval method, it is assumed that the density gradient at a point is closely equal to the coarse density gradient of the ΔR interval in which it is centred. It is not difficult to derive expressions for the systematic error arising from this assumption as applied to polynomial forms. If the density function over the ΔR interval is linear or quadratic, the error is identically zero, but if it is cubic, the error is $c(\Delta R)^2/4$, where c is the coefficient of the polynomial's cubic term. This means that there will be essentially no systematic error in the density estimates made from those parts of the (ΔR, R) function which are constant or linear, and hence that particular weight should be given to the minor interval f_i estimates made in these parts.

The variation among a group of f_i estimates will give an indication of the size of any cubic or higher order error components present. Another indication may be found, as follows, by comparison to the error that would arise if the quadratic components of the (ΔR, R) function in Figure 3.1 were neglected, i.e., if the function was represented by a linear function. If the proportional error in $\Delta D/\Delta R$ is taken as equal to the corresponding proportional error in ΔR, i.e.:

$$\delta(\Delta D/\Delta R)/(\Delta D/\Delta R) = \delta(\Delta R)/\Delta R \qquad (3.2)$$

then the largest deviation in Figure 3.1 from a mean linear function (a triangular shape of height $\delta(\Delta R) = 0.25°$ and base length R = 40°), would result in a density error of 0.0017, which is only about two thirds of our error criterion. If quadratic errors are so small, then cubic and higher order errors are likely to be insignificant. Indeed, it would seem that for the wedge shown, the simple integration method would give results little different to those given by the minor interval method. However, it is possible that this wedge is a particularly linear one and that other wedges will show greater nonlinearity.

It is necessary with the simple integration method to extrapolate the (ΔR, R) function by $\Delta R/2$ at either end of the wedge. Exercises similar to that of the preceeding paragraph show that the errors associated with these extrapolations are very small. In any case, the very low density end does not play an important part in operational measurements, and the errors present when the very high density end is in use will be swamped by other instrument error sources, such as stray light.

Intercomparisons have shown that the variations with airmass (and therefore with wedge density) of the difference between the X_{AD} ozone measurements made by well calibrated instruments can

amount to 0.5% or less. This shows that the wedge calibrations were accurate to at least this level, which is the same as the criterion assumed here.

3.5 Error analysis of filter methods

The effect on wedge calibrations of the transmittance uncertainty in fixed transmittance neutral density filters is analysed here in terms of the error criterion used above, namely, 0.0026 in wedge density at a density of 0.65. A filter's density D and transmittance T are related by:

$$T = 10^{-D} \qquad (3.3)$$

and the proportional uncertainties, d and t in D and T respectively are related by:

$$t = T^{d} - 1 \qquad (3.4)$$

The transmittance accuracies required to ensure that the criterion of d = 0.004 is met are given below in Table 3.1. The listed product Tt is the actual uncertainty in transmittance.

TABLE 3.1

Transmittance uncertainties for various filter densities.

D	T	t	Tt
0.10	0.794	0.0009	0.0007
0.15	0.708	0.0014	0.0010
0.20	0.631	0.0019	0.0012
0.30	0.501	0.0028	0.0014
0.50	0.316	0.0047	0.0015
1.00	0.100	0.0094	0.0009
2.00	0.010	0.0187	0.0002

Table 3.1 could be used as an aid to choosing filter transmittances. Thus to map small scale density variations directly a filter transmittance of about (80±0.07)% might be chosen, while to provide an approximate halving of intensity a transmittance of about (50±0.14)% would be needed. The accuracy requirements for the filters are similar, so the high transmittance filter may be used without serious disadvantage. The corollary is that if a high transmittance filter is insufficiently accurate on its own, then a similarly calibrated halving filter would not be adequate as its calibration reference.

The most important lesson from the table is that very high accuracies, of about 0.1%, are required of the filter transmittances. Filters may be independently calibrated with quality laboratory spectrophotometers, but even with very careful work these accuracies will be difficult to obtain. Spectral and temperature dependencies and temporal variations must also be accounted for. Transmittance accuracies are likely to be, in general, no better than 0.5%. For these reasons, independently calibrated filters cannot be recommended for calibrating wedges.

The standard Dobson rhodium plated filters are satisfactory, however, because they are calibrated against the wedge's optically thin end which has been calibrated by the two lamp method, thus making use of the appropriate wavelength bands and the instrument's intrinsic high accuracy for measurements of relative density. The uncertainty of rhodium filter wedge calibrations is probably no greater than twice that of a full two-source calibration, provided the filters' transmittances and any temperature dependences of them are regularly checked.

3.6 Summary

(i) Modern evaporated metal wedges are very stable and are relatively linear. The original wedges made of carbon black in gelatin were much less stable and linear.

(ii) The wedges are best calibrated in situ, and by means of the two-source device, which nowadays usually comprises two cooled quartz halogen lamps. The apparatus measures a coarse density gradient and its design and use are well established.

(iii) Neutral density filters which are independently calibrated cannot be recommended for

calibrating wedges as the transmittance accuracy of about 0.001 (i.e., 0.1%) required of the filters is very difficult to obtain and to maintain. The standard rhodium plated neutral density filters are satisfactory if they are calibrated in the standard way against the optically thin end of the wedge.

(iv) The "minor interval" method is generally the preferred method for processing the coarse density gradient data, but for a wedge of relatively linear gradient, a simple integration will be sufficient. Minor intervals need be no smaller than 10° in dial angle R.

(v) To minimise systematic error, the averages of the estimates of the minor densities f_i should be weighted in favour of those estimates determined from parts of the density gradient function (or R, R function) which are closely linear.

(vi) Error analysis shows that, with reasonable care, a two-source calibration can give accuracy of 0.4% in wedge density, which is equivalent to an accuracy of about 0.5% in X_A. This is supported by field intercomparisons of Dobson instruments, the results of which strongly suggest that the uncertainty in X_{AD} due to wedge calibration can be less than 0.5%.

(vii) The accuracy of wedge calibrations for gelatin carbon wedges, and for calibrations not made with the two source device, will be less, perhaps equivalent to about 2% in X_{AD}.

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Forward to Stray Light

4. STRAY LIGHT

4.1 Introduction

The term "stray light" is considered here in the wide sense as being any radiation which contaminates the radiation measurements defined by the equations of Section 1. It thus includes unwanted radiation scattered within the instrument and unwanted radiation scattered in the atmosphere and entering the instrument's field of view. A useful distinction can be made between homochromatic and heterochromatic stray light, the former being unwanted radiation of the same wavelengths as those of the bands being measured, and the latter being unwanted radiation of wavelengths outside the desired bands.

Strong evidence for the importance of stray light in the Dobson instrument can be found in Dobson and Normand (1962), Walshaw (1975), Basher (1978), and Olafson and Asbridge (1981a). Each of the particular instruments concerned shows the characteristic effect of ozone amounts apparently declining with airmass above an airmass of about 2.5 (e.g. as in Figure 4.3). For direct sunlight A or AD measurements, errors of 1%, 3% and 10% may be present at airmasses as low as 2.5, 3.2 and 3.8 respectively. For the C bandpair these errors occur at higher airmasses, perhaps at 4.5, 5.1 and 6.4 respectively. It is principally the addition of stray light to the shorter wavelength, and therefore the lower intensity band of a bandpair that is the problem. There appears to be a wide variation in the effect among instruments.

It is obvious that stray light will cause the greatest problems at high latitude sites. The general instruction in the WMO Operations Handbook (Komhyr, 1980b) is to limit the ordinary direct sun AD measurement to airmasses less than 3 and to use one of the less reliable or less accurate methods such as direct sun CD or focussed image AD types.

4.2 Stray light from atmospheric scattering

Radiation scattered by the atmosphere into the instrument's field of view contributes a stray light intensity which is approximately proportional to field of view and to airmass. This light contributes homochromatic and heterochromatic components and will include single and multiple scattered components. Its effect on the ozone measurement is usually negative but may be positive and will depend on the relative intensity of the bandpair's intensities, the amount of the scattering material, the material's spectral and angular (phase function) scattering properties and the optical depth along the beam's path.

Rayleigh scattering's inverse fourth power dependence on wavelength and broad $\cos^2\varphi$ phase function results in a rather spatially uniform and bright (i.e. very hazy) sky radiance at 300-320 nm. Its main effect is the contribution of homochromatic stray light to the shorter wavelength bands and hence a reduction in the measured ozone amount.

The attenuation by aerosol scattering (due to particles typically from 0.05 to 5 μm in diameter) has a weak spectral dependence as discussed in Section 10, and a multi-lobed forward-peaked phase function. Both vary with the ratio of aerosol diameter to wavelength. Because of the strong forward peak, most of the scattered energy lies in the sun's aureole, i.e. within a cone of a few degrees around the sun and therefore within the Dobson instrument's field of view. The homochromatic component and the internally scattered heterochromatic component both serve to reduce the measured ozone amount.

The attenuation by individual cloud droplets (typically 10 to 1000 μm in diameter) is essentially spectrally uniform but colouring effects as shown by coloured rings about the sun and moon can arise owing to the dependence of the very strongly peaked and multi-lobed phase functions on the diameter/wavelength ratio and to internal reflection and refraction in the droplets. For all but the thinnest of clouds multiple scattering becomes dominant. The effect of these factors on stray light is unclear.

In Walshaw (1975) G.M.B. Dobson describes a detailed investigation of total ozone measurement errors when the sun is low in the sky. He shows that by using the Dobson instrument's sun-director lens to focus an image of the sun directly onto the entrance slit, instead of using the usual ground quartz plate diffuser, it is possible to extend the usable range of the C bandpair from an airmass of 4 to an airmass of 6. The limits are dependent on the actual amount of attenuation by ozone, and the advantage is gained presumably as a result of restricting the instrument's field of view. The WMO Operations Handbook (Komhyr, 1980b) recommends this focussed image method for the AD band combination for airmasses 2.5 to 4.0, and for the CD band combination for airmasses 2.5 to 6.0.

The focussed image method is not an easy one to carry out however, and there are two particular questions concerning its accuracy. Firstly, because the sun's image does not fully fill the length of the slit, errors will arise owing to the varying spectral sensitivity within the instrument's field of view (Basher, 1980; see also Section 2). Secondly, because the sun's image overlaps the width of the slit, errors will arise owing to the sun's limb darkening, i.e. to the relative richness of UV in the centre of the solar disc. In each case there will be a change in the extraterrestrial constants. Dobson (1957a) notes that there is a "small difference" in the constants, but Kulkarni (1968) found that for his instrument the difference was relatively large, at about 0.15, equivalent to a 40% increase in the ratio of the short wavelength intensity to the long wavelength intensity. It is quite clear that wherever the focussed image method is used, the size of the change in the extraterrestrial constants must be determined and if necessary applied as a correction. Brief mention of this need is made in the WMO Operations Handbook.

Dobson also describes (in Walshaw, 1975) a test to determine the "skylight" error, in which the sun's image is positioned firstly on the slit, and secondly just off the slit, and the error is estimated from the difference in the measurements. Presuming that other effects such as those described above can be neglected, the data shows the skylight error is equal to 1% in total ozone at an airmass of about 6.0 to 6.5 for all wavelength pairs. Correction procedures for both skylight and scattered light when the focussed image method is used are described by Hamilton (1964).

A computer modeling experiment to determine ozone errors due to atmospheric scattering was carried out by Thomas and Holland (1977). They used a Monte Carlo simulation of radiative transfer through an atmosphere of fifty 2 km layers which included a Haze-C aerosol size distribution of 0.11 decimal optical depth. Receiver instrument fields of view of 2°, 4°, 8° and 10° diameter were considered. They refer to a paper by Olafson (Ozone Symposium, Monaco, 1968) which indicates that an 8° diameter is appropriate to the Dobson instrument, presumably with the diffuser plate in place. The actual field of view at any time will depend on the fore-optics, such as the sun director, which are being used. For the 8° field of view, and at an airmass of 2, the proportion of single and multiple scattered radiation to attenuated direct radiation amounted to less than 1% for Rayleigh scattering and to about 2.5% for the aerosol scattering. The proportions increased with decreasing wavelength and increasing field of view. The ozone errors arising solely from this extra radiation received were less than 0.5% for single bandpairs and less than 0.2% for the double bandpair combinations. The calculations were limited to an airmass of 3, but extrapolation beyond this to an airmass of 4 suggests that there the errors for single bandpairs may be about 2%. This is a larger estimate than that given by Dobson's work and noted above, which may be due in part to the greater density of the aerosol model used by Thomas and Holland. The authors showed that the errors are approximately linearly dependent on aerosol amount. The aerosol optical depth of 0.11 used by them may be compared with visible (500 nm) optical depths of 0.02 for very clear conditions to 0.5 for extremely hazy conditions (Flowers et al., 1969). A value of 0.3 usually gives a milky sky in which clouds are difficult to discern. Note that Thomas and Holland's computations consider only homochromatic stray light.

4.3 Stray light from internal scattering

Radiation entering the Dobson instrument must pass through either twenty eight or thirty two optical surfaces and undergo three reflections before reaching the photomultiplier The possibility of undesired stray reflections is high, and since for quartz surfaces the reflection coefficient at 310 nm is about 3.8% for normal incidence, the energy involved in the stray reflections will be also high. In addition there will be present the usual optical aberrations of lenses and prisms, and finite slit widths, which will reduce the spectral purity of the instrument's images. Attenuation of short wavelength bands

by poor quality quartz optics has been found to be associated with stray light problems (W.D. Komhyr, personal communication). Any such depletion will serve to magnify the effects of longer wavelength stray light.

Some of the stray radiation will be homochromatic but by far the more troublesome is the heterochromatic component, particularly from about 350 to 400 nm whose incoming energy in the direct beam is orders of magnitude greater than that of the narrow and highly-attenuated bands being measured. For example, for the 305.5 nm band at an airmass of 3 the incoming energy ratio is about 10^{+4} and hence the rejection of the stray radiation must be better than 10^{-6} in order to obtain an accuracy of 1% in the 305.5 nm band energy measurement. The second monochromator in the instrument is the essential means for reducing the effect of the heterochromatic stray radiation transmitted by slits S_2 and S_3. It casts a spectrum onto slit S_5 such that, in principle, only radiation in the immediate vicinity of the desired bands is passed. An absorption glass filter at S_5 removes radiation of wavelength greater than about 400nm. The effectiveness of the second monochromator depends on the nature of the spectra of light presented to it, as well as on its basic optical design.

Dobson (in Walshaw, 1975) examined the stray light spectrum transmitted by slit S_2 by rotating mirror M_2 and therefore sweeping the spectrum across the exit slit S_5, and found a broad peak with half-intensity points at about 350 and 400 nm. He explained how a solution of nickel sulphate could act as a filter to this band, though this method is not now described as a recommended method in the WMO Operations Handbook, possibly because of the temperature dependence of the transmittance of the solution.

The writer had the opportunity to observe stray light directly within the prototype Dobson instrument, number 1, at Oxford, and was surprised to see reflected in lens L_1 two bright white-light images of slit S_1 and two less bright spectral images. A simple calculation shows that the ratio of this reflected energy transmitted by slit S_2 to the energy in the 305.5 nm band is about 3×10^{-3} at zero airmass and about 2×10^{0} at an airmass of 3. The 3 mm width of the S_5 slit will accept a wavelength interval of approximately 8 nm in the vicinity of the 305.5 nm band and therefore might accept a not insignificant proportion of this stray radiation. The lens L_2 will also directly reflect onto S_5 a portion of the stray light transmitted by S_2, but calculations show that the energy contribution is insignificant relative to that of the 305.5 nm band, even at an airmass of 3.

A second surprise was the realisation that the thick Q_1 quartz plate, used mainly for the selection of wavelength pairs, creates a ghost image by internal reflection whenever it is aligned away from normal to the beam. This ghost reflection has an intensity of about 1.4×10^{-3} times the intensity of the main beam and is displaced from, but is nearly parallel to the main beam. Hence at the S_2S_3 slit plane there is a ghost spectrum, displaced in wavelength in the opposite direction to that of the wavelength pair selected. For example, the selection of the A bandpair will present at slit S_2 the desired 305.5 nm band and a ghost band at about 323.8 nm. The energy contribution of the ghost image at S_2 will be approximately 1%, 5% and 21% at airmasses of 1, 2 and 3 respectively. The second monochromator can be expected to reject most of this unwanted radiation, though its effectiveness will be limited by the quality of its optical adjustment and by the relatively broad 8 nm acceptance bandwidth of the exit slit S_5. Note also that the second quartz plate Q_2 will create ghost images at S_5 of the S_2 and S_3 slits, and that for the A bandpair the ghost image of the 323.8 nm stray light will be aligned almost directly on S_5.

4.4 Non-linearity of log intensity ratios versus airmass

The stray light contribution to the short wavelength band of a pair results in a non-linearity of the log intensity ratio versus airmass function. This gives rise to two errors, as is shown in Figure 4.1. The first is the obvious one of the reducing log intensity ratio and therefore reducing ozone measurement with airmass. A less obvious second error is the overestimation of extraterrestrial constant (ETC) that would be derived from the log intensity versus airmass data. This second error is a rather insidious one since the wrong ETC will make the ozone measurements appear more constant with airmass and the

residual curvature in the data seem small, but at the same time it may be concealing a relatively large systematic negative error in the ozone measurements.

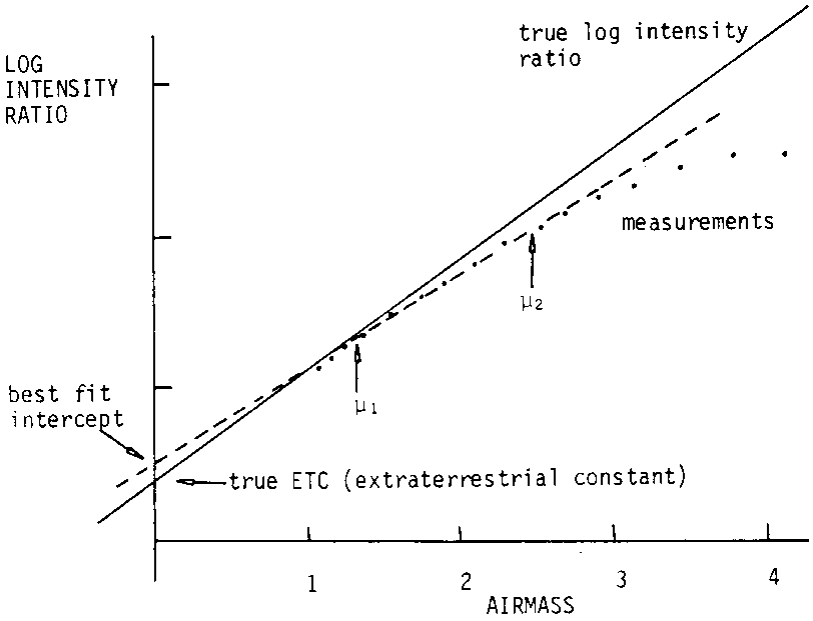

Figure 4.1 Illustration of the effect of stray light on log intensity ratios and on the determination of extraterrestrial constants.

Non-linearity errors have been investigated by the writer for a simple monochromatic, heterochromatic stray light model. The stray light is defined, firstly by R_0, the ratio of the energy of the monochromatic stray light source to that of the desired band as would be measured under the imaginary conditions of zero airmass, and secondly by a, the atmosphere's relative attenuation coefficient of the stray light band to the desired band. If the stray light band was centred at 370 nm, corresponding to the centre of the band measured by Dobson (Walshaw, 1975), and the desired band is at 305.5 nm, then R_0 would range from perhaps 10^{-5} to 10^{-3}, depending on the quality of the instrument, and the parameter a would range from about 0.7 to 1.2, depending on ozone amount. The contribution of the stray light to the longer wavelength band of a pair, in this example the 325.4 nm band, is negligible, and the errors are not very dependent on the assumption of monochromaticity or centre-wavelength of the stray light band. The resulting equations for ΔETC, the error in extraterrestrial constant, and for ΔX the total error in the ozone measurement are:

$$\Delta ETC = \frac{1}{\mu_2 - \mu_1} \log \frac{(1 + R_0 10^{\mu_2 a})^{\mu_1}}{(1 + R_0 10^{\mu_1 a})^{\mu_2}} \qquad (4.1)$$

$$\Delta X = \frac{-1}{\mu \Delta \alpha} (\Delta ETC + \log (1 + R_0 10^{\mu a})) \qquad (4.2)$$

where μ_1 and μ_2 are the airmass values at which the straight line used to determine the ETC intersect the log intensity versus airmass curve and Δa is the bandpair's ozone absorption coefficient.

A selection of results is given in Table 4.1 and Figure 4.2. In the calculation of the X_{AD} ozone errors it has been assumed, for convenience only, that the relative attenuation, a, and therefore the ozone amount, is the same at the time of measurement as at the time of calibration of the ETC, and that the error source affects only the A bandpair. Attention is drawn to:

(i) The dependence of the ETC error, and therefore any ETC determination, on the airmass range used, and on the value of the parameter a, and therefore on the ozone amount. This may be a main cause for the difficulty of obtaining consistent ETCs for an instrument and for the lack of agreement between independently calibrated instruments.

(ii) The relative uniformity of the ozone error in the operating range of 1 to 3 in airmass, and the way this tends to conceal what may be a significant underestimation of ozone amount.

(iii) The increased error at low airmasses, which is principally due to ETC error. In middle latitudes this will result in noon values that in summer are lower than morning and afternoon values, and that in winter are higher. This sort of behaviour has been observed in the Wallops Island Dobson instrument data (Geraci and Luers, 1978).

(iv) The strong dependence of the error on the parameters R_0, a, μ_1, and μ_2. An instrument whose R_0 is 10^{-4}, might agree very well with another instrument whose R_0 is 10^{-5} during a summer intercomparison when the ozone level is low, i.e. when a is about 0.8, but it would disagree by 5% or more under winter-spring high ozone conditions.

The measurements of any instrument can be compared to the calculated values to estimate the stray light levels present. The fact that for most Dobson instruments the X_{AD} measurement is not satisfactory beyond an airmass of 3 suggests that R_o is typically about 10^{-4}. The writer made measurements of X_{AD} beyond this airmass using the Wallops Island Dobson instrument in 1977, and the average of the results for a range of ozone values is compared with two models in Figure 4.3. It suggests that the instrument's R_0 value at that time, was about $10^{-3.8}$ to $10^{-3.6}$. The data of Figure 4.2 show that a value of 10^{-5} is the maximum desirable value. The airmass dependences shown by Olafson and Asbridge (1981) indicate that the Canadian No. 77 instrument is of this higher quality, which in turn indicates that the goal of $R=10^{-5}$ is not unattainable.

TABLE 4.1

Errors in the determination of extraterrestrial constants for various stray light error models.

Airmasses		R_0 =	10^{-5}	10^{-4}	10^{-4}	10^{-4}	10^{-3}
m_1	m_2	a =	1.0	0.8	1.0	1.2	1.0
1.25	2.0	ΔETC =	.0003	.0012	.0035	.0094	.0327
1.25	2.5	=	.0008	.0024	.0083	.0264	.0724
1.25	3.0	=	.0021	.0050	.0200	.0717	.1440
1.25	3.5	=	.0053	.0102	.0471	.1640	.2417
1.25	4.0	=	.0137	.0209	.0998	.2870	.3414

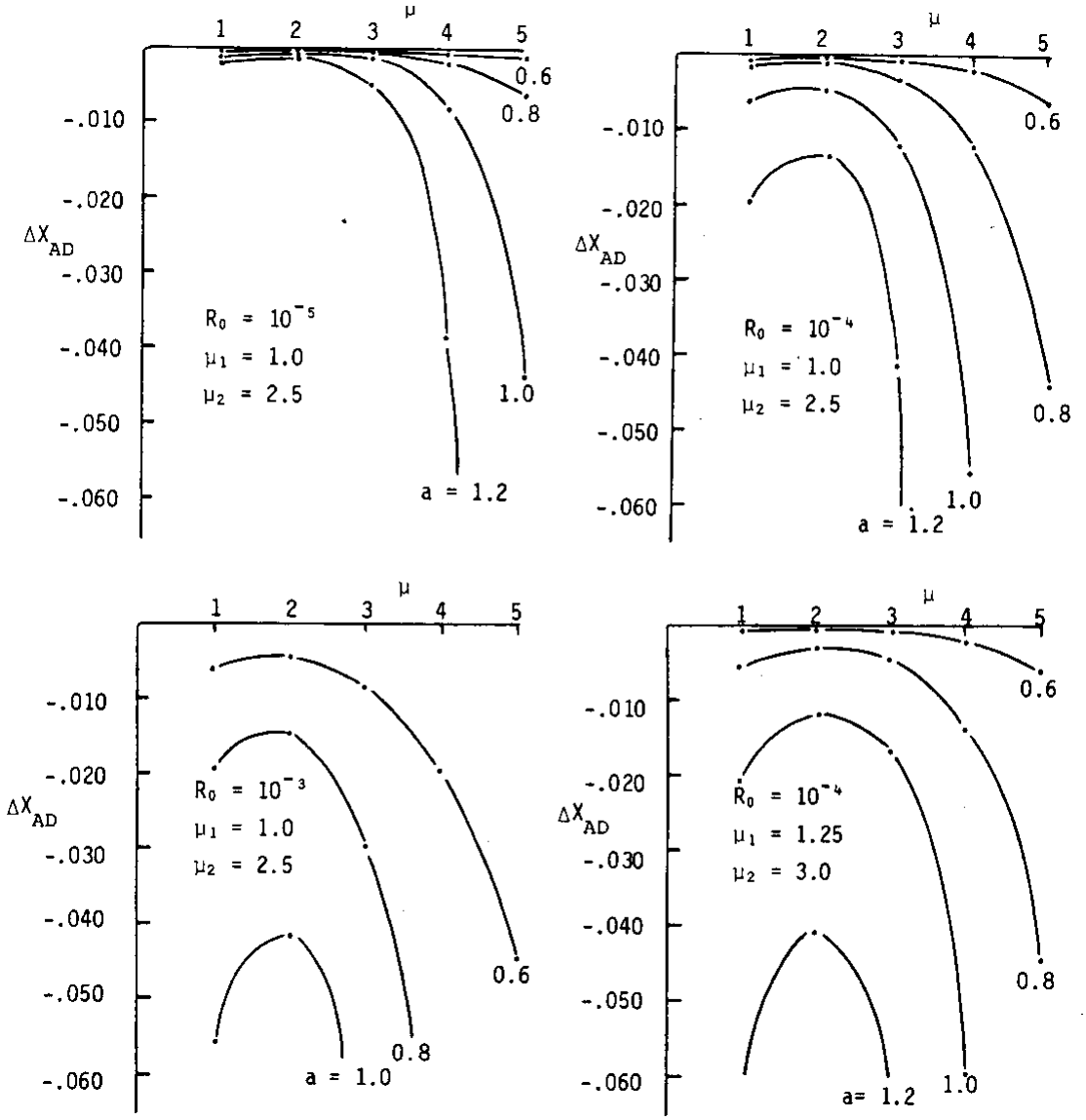

Figure 4.2 Variation of zone error X_{AD} as a function of airmass μ, for various values of model parameters, as calculated by the stray light model.

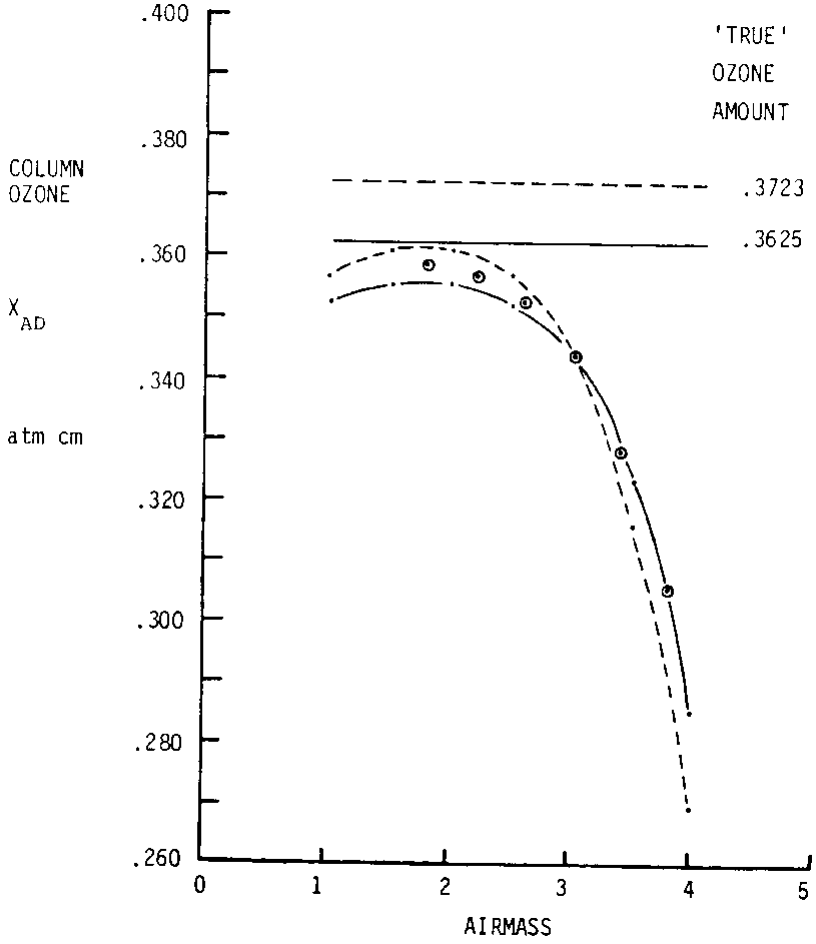

Figure 4.3 Comparison of experimental data with stray light models:

(_____) R_0 = 10-3.8 a = 1.0 μ_1 = 1.0 μ_2 = 2.5

(-----) R_0 = 10-3.6 a = 1.0 μ_1 = 1.0 μ_2 = 2.5

See text for details.

4.5 Possible solution to stray light problems

Up until now very little attention has been given to the question of stray light in the Dobson instruments. However, there is every indication from the above studies that it is one of the most important sources of ozone measurement error, and it is highly desirable that suitably equipped laboratories with Dobson instruments begin to study directly the origins and transfer of stray light in the instrument, both theoretically and experimentally. Of particular interest are the direct reflections from lens L_1, and the ghost image spectrum from plate Q_1 . Simple optical stops may be a solution. Olafson and Asbridge (1981a) describe an alteration to the orientation of Lens L_1, which serves to increase the usable airmass range for the A bandpair from 2.5 to 3.5, presumably as a result of stray light reduction. Some of the stray light problem simply may be due to a poor quality of quartz in the optics, or to poor adjustment of the instruments of course.

As was pointed out above, it is possible to test for stray light by taking measurements out to high airmass and comparing the results with a stray light model. Another method, which has been used very successfully by the author to detect a long wavelength leakage band in a faulty UV interference filter, is to use soda glass plates to selectively block out the desired UV band in favour of the undesired stray light band. Measurements are made by successively adding from one to six or more plates of about 7 mm thickness to the optical path. If the A bandpair is being measured, the main 305.5 nm band is virtually eliminated by the time two or three plates are added and successive plates then give rise to a log intensity ratio versus plate number function that depends only on the 325.4 nm band and the stray light band, and is nearly linear. The intercept at zero plate number gives the "extra-terrestrial" energy ratio of the stray light band relative to the 325.4 nm band, and the slope will indicate the mean wavelength of the stray light if the glass spectral transmission is known. The experiment can also be

done as a function of airmass. Preliminary experiments with Dobson instrument number 1 were carried out by the author at Oxford in 1978, but owing to a lack of dynamic range and sensitivity in the instrument's detection system, they met with little success. Additional neutral density filters would be needed to reduce the relative intensity of the 315.4 nm or other shorter wavelength band, and one of the modern, sensitive detection systems now being used in Dobson instruments probably would be needed also.

4.6 Summary

(i) There is strong evidence of the effects of stray light on the Dobson instrument. It is a major error source and it sets a major limitation to the instrument's operating range, typically at an airmass of about 3.

(ii) The errors due to homochromatic stray light scattered by the atmosphere into the instrument's field of view appear to be on average no more than 1% at an airmass of 3. The error is approximately proportional to aerosol amount and field of view and it increases with airmass.

(iii) The focussed image method can extend the instrument's operating range of airmass, presumably owing to its restriction of the field of view. It will result in changes to the extraterrestrial constants however, and these changes must be determined and corrected for.

(iv) Heterochromatic stray light, in the 350 to 400 nm wavelength region, undoubtedly the most troublesome form of stray light. A white light reflection from lens L_1 and a ghost image from quartz plate Q_1 are important candidate sources. Other sources may be present, including some dependent on the instrument's optical quality and quality of adjustment.

(v) A model of heterochromatic stray light shows that the resulting ozone measurement errors can be large yet may remain undetected. The errors are very dependent on the model conditions, and will vary widely among different instruments and under different operating conditions.

(vi) Insufficient is known about the details of stray light propagation in the instrument and how to avoid its effects. Further study is most desirable.

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Forward to Wavelength Band Uncertainty

5. WAVELENGTH BAND UNCERTAINTY

5.1 Introduction

The bandwidth, band shape and centre wavelength of the Dobson instrument's bands depend on the mechanical adjustment of the instrument's slits and other optical components. Absolute centre wavelengths can be determined by interpolation between measured lines of spectral line sources. For each of these adjustments and calibrations, and also for each operational wavelength pair selection, there be some uncertainty and the resulting uncertainty in the wavelength bands will propagate through to the instrument's ozone measurement as it is defined by equation (1.1). It is only through the spectrally very variable solar extraterrestrial irradiance and ozone absorption coefficient terms in equation (1.1) that any significant error arises.

Dobson (1957b) was well aware of the problem. He made spectral intensity measurements with the instrument to help guide his choice of band centre wavelengths and bandwidths and his recommendations for calibration precisions. However, as far as is known, the only specific study of band uncertainty propagation is that summarised by Basher (1981), and it is this study to which the remainder of this Section 5 is devoted.

The study is based on a Taylor expansion of the measurement equation in terms of varying band centre wavelength and band shape. Only the first linear term in the expansion is used and only the variations of extraterrestrial irradiance and ozone absorption coefficient are considered. The ozone uncertainties depend non-linearly on airmass and ozone and so the calculations are repeated for a range of likely conditions of airmass and ozone.

There were three components to the study. Firstly, high resolution spectra of solar irradiance and ozone absorption were used to find band-integrated linear dependences, called here sensitivities, to changes in band position and band shape about mean model bands. Secondly, uncertainties in band position and shape were deduced from the recommended adjustment and operating procedures. Thirdly, the above sensitivities and uncertainties were combined to calculate the propagated uncertainties in band ozone absorption coefficients, in extraterrestrial constants, in standard lamp calibrations, and in column ozone estimations.

The accuracy of the calculations is necessarily poor, owing to the uncertainty in the input sensitivities and the deduced band uncertainties, but the calculations do clearly indicate the general magnitude and behaviour of the various uncertainties and the general quality requirements for the relevant adjustments and calibrations. They also give some insight into the difficulties of using standard lamps and the relative merits of the various methods for obtaining extraterrestrial constants.

5.2 Basis of calculations

The very high resolution extraterrestrial flux spectrum of Furukawa et al. (1967), which is a composite of the experimental spectra available at the time, was integrated to provide a spectrum at 0.05 nm resolution, and from this the irradiance sensitivities were calculated. The Furukawa et al. spectrum has only modest accuracy in absolute flux, but is notable for its considerable wavelength detail and high wavelength accuracy, which makes it well suited to this sensitivity study. A section of the original spectrum is shown in Figure 5.1 and helps illustrate this point.

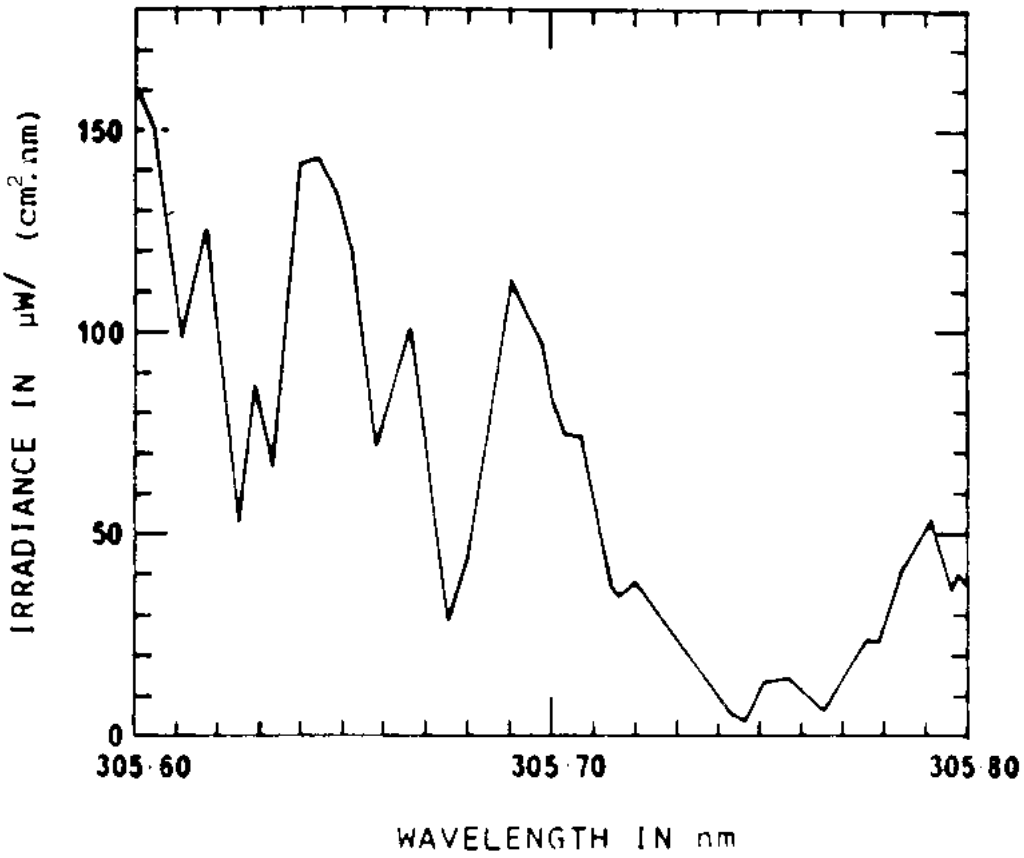

Figure 5.1 Section of the Furukawa et al. (1967) solar spectrum illustrating its wavelength detail and variability.

The ozone absorption data of Vigroux (1953 and 1967) for -44°C were plotted and a continuous spectrum was hand drawn to give realistic band shapes, especially in the data-sparse regions (see Figure 1.1). This was then integrated to provide a 0.05 nm resolution spectrum from which the ozone absorption coefficient sensitivities were calculated. The spectrum used has its greatest concentrations of original data in the vicinity of the Dobson bands.

The transmittance bands of the instrument were modelled as simple symmetrical triangular or trapezoidal shapes, unaffected by lens aberrations or other optical effects. Each band was thus assumed to be defined by, firstly, a centre wavelength, as given by the standard wavelengths in Table 1 of Dobson (1957a), secondly, a bandwidth of 1.0 nm for the short wavelength of a bandpair and 3.0 nm for the long wavelength, and thirdly, a "slopewidth", the spectral width of the bands' sloping sides, of 0.9 nm for all bands. Actually, the bands are smoothed to some extent by optical aberrations (see Figure 2.1) and the spectral widths of the bands increase slightly as wavelength increases owing to the decreasing prism dispersion with wavelength, but these factors will not substantially alter the conclusion of the study.

The sensitivities to change of centre wavelength, calculated as the mean in just the 0.1 nm interval surrounding the band centre wavelength, are listed in Table 5.1 below. The calculated sensitivities to change in bandwidth and slopewidth are relatively small and are not listed, but their effects are generally included in subsequent calculations. For bandwidth changes, the sensitivity of flux per unit bandwidth was calculated, in order to avoid the linear flux increase with bandwidth. The effect of this increase is eliminated in normal calibration techniques.

TABLE 5.1

Sensitivities of band-integrated extraterrestrial irradiance and ozone absorption coefficient to change in band centre wavelength.

λ	305.5	308.8	311.45	317.6	325.4	329.1	332.4	339.8 nm
$dI/Id\lambda$	-11.4	-11.4	-4.0	-22.2	8.4	0.9	-3.0	1.3 % nm^{-1}
$d\alpha/\alpha d\lambda$	-8.0	-13.2	-16.8	-17.1	-10.7	-20.3	-20.1	-12.9 % nm^{-1}

The predominance of negative values in Table 5.1 for both irradiance and absorption implies that, to some extent, the effect of one will compensate the effect of the other, since a decrease in absorption will result in an increase in transmitted irradiance. This compensation is by no means perfect and will vary with airmass and ozone. Figure 5.2 shows the calculated sensitivities of irradiance and absorption as a function of wavelength between 303 and 308 nm for the 1.0 nm triangular passband. Some very large sensitivities are evident. The spectra suggest that the original choice of the 305.5 nm short wavelength band of the A bandpair was partly dictated by the need to minimise the nett effect of the sensitivities.

In the calculation of ozone uncertainties, the ozone absorption coefficient sensitivities are weighted by the coefficients themselves, and therefore it is the shorter wavelength sensitivites which are most significant. The irradiance sensitivities combine with equal weight. It is worth noting that the sensitivities to centre wavelength change are approximately inversely proportional to bandwidth, and that this sets fundamental limits to the narrowness of the bands of any UV ozone measuring instrument. Practical bandwidths are 0.5 to 1.0 nm.

The uncertainties of adjustment, calibration and operation, and their mutual dependences, were deduced largely from the recommended procedures in Dobson (1957b). There is a wide variety of possibilities, especially for the bandwidths and slopewidths and their interdependences, but for the purposes of this study, these have been condensed to the following. Firstly, calibration uncertainties are assumed to comprise: independent centre wavelength uncertainties of 0.025 nm, mutually dependent bandwidth uncertainties of 0.025 nm for the four shorter wavelength bands, mutually dependent bandwidth uncertainties of 0.05 nm for the four longer wavelength bands, and mutually dependent slopewidth uncertainties of 0.025 nm for all bands. (It is thus somewhat arbitrarily assumed that the bandwidths are defined by the slit S_2 and S_3, and that all the slopewidths are defined by the slit S_1.) Secondly, routine operational uncertainties are assumed to comprise uncertainties of 0.025 nm in centre wavelength only, which are mutually dependent within each bandpair, but independent between bandpairs.

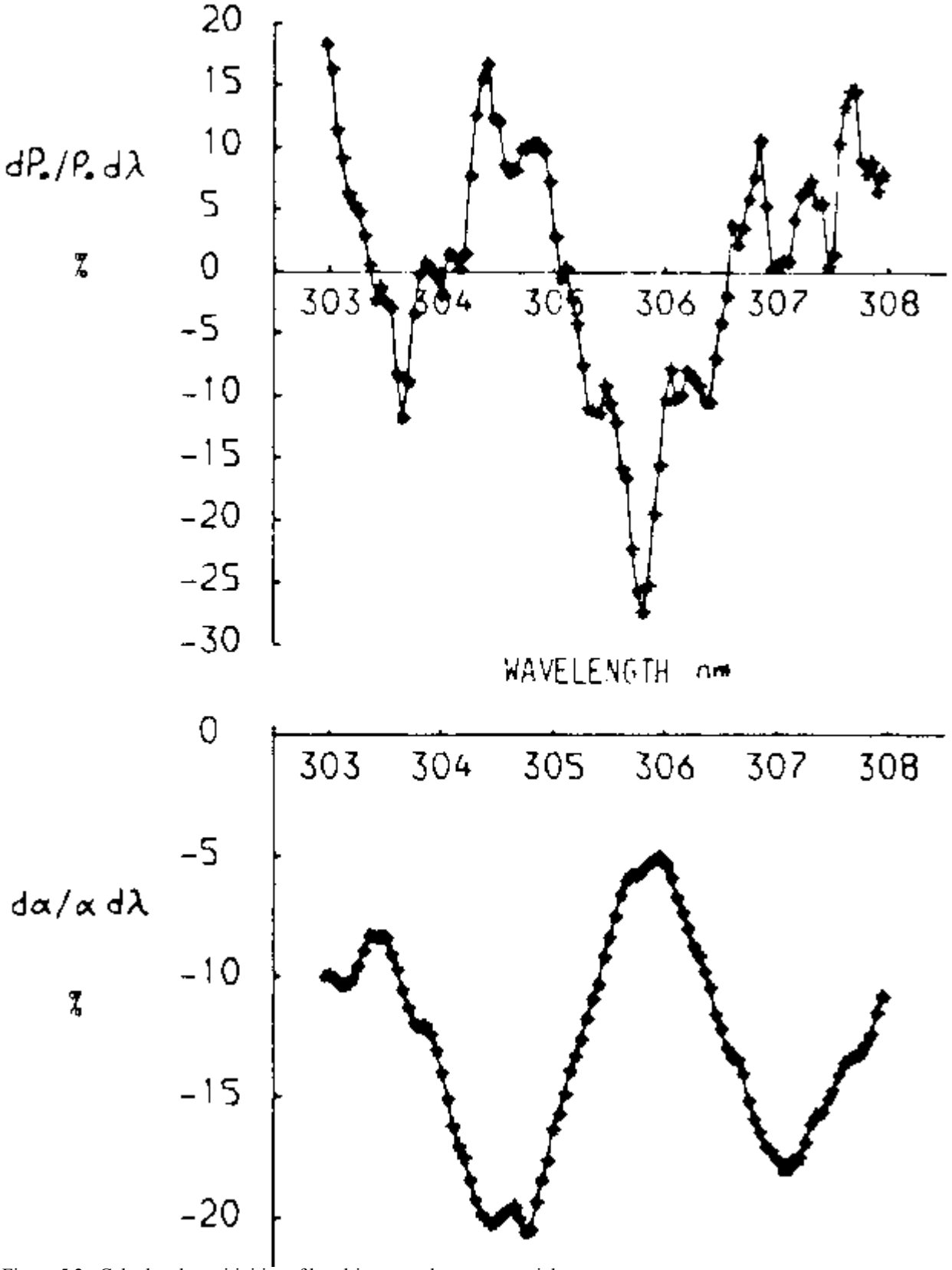

Figure 5.2 Calculated sensitivities of band-integrated extraterrestrial irradiance $P_{\odot}$ and absorption coefficient α as a function of wavelength, for a short wavelength Dobson band.

Instruments for which the above calibration uncertainties hold true are termed here "well calibrated", while instruments for which the above operational uncertainties hold true are termed here "well operated". These standards of calibration and operation should he attainable by a conscientious, skillful technician, knowledgeable about the instrument's principles of design.

In the following calculations, the above model uncertainties are taken to represent the standard errors of a normal distribution of uncertainties which is assumed to be present in the population of

Dobson instruments. Dependent uncertainties are combined by simple addition, and independent uncertainties are combined by summing their variances.

The calculations have been made separately for routine operation and for each of the three methods for establishing an instrument's extraterrestrial constants. These methods are:

firstly, the traditional Langley method, which is the ultimate means of calibrating reference instruments, but which in general can be very inaccurate if atmospheric conditions are poor or the instrument has a stray light problem;

secondly, the transfer of a reference instrument's constants by means of transportable incandescent lamps, which is a very attractive option, but which in the past has been plagued by large errors of uncertain origin;

and thirdly, by direct intercomparison with a reference instrument, which, although a rather expensive and tedious option, is reliable and has become the recommended standard practice.

The total error in any case is the combination of the calculated standard errors arising from the calibration and from routine operation.

A general point, applicable in all three cases, is that uncertainties in ozone absorption coefficients contribute ozone errors which are essentially constant with airmass, whereas uncertainties in extraterrestrial irradiance, and therefore extraterrestrial constants, contribute ozone errors which are inversely proportional to airmass and therefore are most important at low airmass, i.e., high solar elevation.

5.3 Routine operation

During routine operation, the Dobson instrument's wavelength bandpairs are manually selected and the settings are periodically adjusted to account for temperature changes. The resulting band uncertainty gives rise to uncertainty in the appropriateness of the standard ozone absorption coefficients and in the appropriateness of the extraterrestrial constants. The calculated standard errors in ozone for "well operated" instruments due solely to operational uncertainties are given in Table 5.2. This shows, among other things, standard errors for the AD and CD combinations which are generally less than 0.5% and 1% respectively, but which rise to 1% and 2.5% respectively at an airmass of 1 and an ozone amount of 0.200 atm cm. The standard error for the C bandpair is less than 0.5% for all conditions. (Note that this nominal minimum value of 0.200 atm cm is an extreme minimum. Typical minima, found in the tropics, are near 0.230 atm cm).

The random component of the errors can be reduced by averaging a set of observations, though of course operator and temperature errors will remain. The standard error of the differences between two instruments will be √2 times the values shown.

TABLE 5.2

Standard errors in column ozone measurements
due solely to wavelength-pair selection uncertainty in routine
operation for "well operated" instruments.

	A	B	C	D	AB	AC	AD	BC	BD	CD	
X=.200 atm cm											
μ = 1	.41	.23	.35	3.10	1.45	.83	.95	.98	1.34	2.54	%
μ = 2	.11	.05	.38	1.34	.37	.39	.37	.78	.56	1.26	%
μ = 3	.01	.14	.39	.75	.31	.34	.19	.89	.37	.92	%
μ = 4	.04	.18	.40	.45	.44	.35	.13	.97	.32	.80	%
X=.300 atm cm											
μ = 1	.21	.04	.37	1.92	.70	.51	.56	.76	.81	1.67	%
μ = 2	.01	.14	.39	.75	.31	.34	.19	.89	.37	.92	%
μ = 3	.06	.20	.40	.35	.49	.36	.12	1.00	.32	.77	%
μ = 4	.09	.23	.40	.16	.60	.39	.12	1.06	.33	.73	%
X=.400 atm cm											
μ = 1	.11	.05	.38	1.34	.37	.39	.37	.78	.56	1.26	%

μ = 2	.04	.18	.40	.45	.44	.35	.13	.97	.32	.80	%
μ = 3	.09	.23	.40	.16	.60	.39	.12	1.06	.33	.73	%
μ = 4	.12	.25	.40	.01	.69	.41	.15	1.11	.36	.73	%

X=.500 atm cm

μ = 1	.05	.10	.39	.98	.28	.35	.26	.84	.44	1.05	%
μ = 2	.07	.21	.40	.28	.53	.37	.12	1.02	.32	.75	%
μ = 3	.11	.25	.40	.04	.67	.41	.14	1.10	.35	.73	%
μ = 4	.13	.26	.41	.08	.74	.43	.17	1.13	.38	.73	%

A comparison of the calculated standard errors with experimental data may be made. If from the intercomparison of ten instruments at Belsk (Dziewulska-Losiowa and Walshaw, 1975) we take $1/\sqrt{2}$ times the standard deviation of the log P_i/P_j differences between each instrument and a reference instrument (no. 83), with the bias and the airmass dependence removed, and at an approximate airmass of 1.7 and approximate ozone amount of 0.375 atm cm, we find that for the A, C and D bandpairs, the ozone standard errors are 0.4, 0.7 and 1.7% respectively, as compared to calculated values of 0.1, 0.4 and 0.8%, respectively, from Table 5.2. The experimental standard errors are about twice the calculated values, and although other error sources will be involved, there remains the suggestion that at the time of the intercomparison the operational uncertainties were greater than the "well operated" criteria assumed here.

5.4 Case where extraterrestrial constants are determined independently

Uncertainty in the calibration of the wavelength bands in this case implies uncertainty only in the appropriateness of the standard ozone absorption coefficients used. The calculated standard errors for "well calibrated" instruments are given in Table 5.3.

TABLE 5.3

Standard errors in the appropriateness of the standard ozone absorption coefficients for "well calibrated" instruments.

A	B	C	D	AB	AC	AD	BC	BD	CD	
0.22	0.35	0.45	0.48	1.09	0.58	0.31	1.38	0.53	0.87	%

Of note is that the AD standard error is the smallest of those for double bandpairs and that the CD standard error is about three times the AD standard error. The total standard error for instruments calibrated independently is the RMS addition of these standard errors and the operational standard errors of Table 5.2. Again, when two instruments are compared, the standard errors of the differences are $\sqrt{2}$ times these values.

The independently determined extraterrestrial constants are appropriate to the bands irrespective of any band uncertainty, (although in practice the constants often have large errors). However, the small wavelength differences between any two instruments will result in different standard lamp readings for the instruments. This arises because the measured intensity ratios for sunlight, and hence the extraterrestrial constants, depend on the sensitivities shown in Table 5.1, which are generally negative, whereas the intensity ratios for the lamp light depend on the lamp sensitivites, which are positive, with values of about +3.0% nm^{-1} being found for the 3000 K blackbody assumed here. Table 5.4 shows, for a comparison of two instruments, the calculated standard error in the difference of their lamp log intensity ratios when their solar log intensity ratios are equal, or vice versa. The listed values incorporate an arbitrary increase by a factor $\sqrt{2}$ to provide some account of the operational measurement uncertainties. These data go some way toward explaining the otherwise puzzling discrepancies in standard lamp readings between instruments.

TABLE 5.4

Standard errors in the difference of lamp log intensity ratios for two instruments whose measurements of solar log intensity ratios agree or vice versa.

A	B	C	D	AB	AC	AD	BC	BD	CD
.0025	.0014	.0020	.0042	.0028	.0030	.0052	.0024	.0044	.0047

A comparison with experimental data from the Belsk intercomparison (Dziewulska-Losiowa and Walshaw 1977, Table IIA) is possible here too. The standard deviations of the differences in lamp log intensity ratios between nine instruments and a reference instrument were 0.0100, 0.0074 and 0.0106 respectively for the A, C and D bandpairs. These are approximately three times the calculated values, which suggests that the calibration standard of the instruments concerned were not up to the "well calibrated" criteria assumed here. By contrast, the corresponding standard deviations for the 1977 Boulder intercomparison (Komhyr et al., 1981a) were 0.0052, 0.0039 and 0.0060 respectively for the A, C and D bandpairs. These represent a considerable improvement on the Belsk results, though they are still about twice the calculated values.

5.5 Case where extraterrestrial constants are established by standard lamp transfer

In this case there will be uncertainty in the secondary instrument's extraterrestrial constant owing to band uncertainty in both the reference instrument and the secondary instrument and the different sensitivities of sunlight and lamplight, as described in the previous section. Also, there will be uncertainty in the appropriateness of the fixed ozone absorption coefficients for the secondary instrument, and there will be operational uncertainties.

The combined effect of these uncertainties was calculated but the results are not listed since the lamp transfer method is not often used now. The ozone standard errors are very approximately 1.6 times those of Table 5.2, and range from about 0.5% to 0.6% for the C pair, from 0.4% to 1.5% for the AD combination, and from about 1.1% to 4.1% for the CD combination. The largest values occur for low airmass, low ozone situations, and are appreciable then, especially for the CD combination. It must be noted that these calculated values do not include any account of the uncertainty in the reference instrument's extraterrestrial constants or the large uncertainty found in practical lamp transfer calibrations.

5.6 Case where extraterrestrial constants are established by direct intercomparison

In Dobson instrument intercomparisons, it is assumed that the standard ozone absorption coefficients apply to both instruments. The extraterrestrial constants of the secondary instrument are then adjusted to ensure the best agreement in total ozone over the normally used range of airmass. However, because of band uncertainties, the absorption coefficients appropriate to the two instruments are in fact different. The resulting small difference in the instruments' absolute ozone scale is automatically accomodated by the adjustment of the secondary instrument's extraterrestrial constants. However, the compensation is only perfect at one condition of airmass and ozone, and as the airmass or ozone departs from this condition there develops an increasing residual ozone error.

The calculated calibration standard errors in ozone for this situation are not given here on their own, but instead are combined with $1/\sqrt{2}$ of the operational errors listed in Table 5.2, in order to give an idea of the minimum ozone error, or best performance, among a group of instruments calibrated by direct intercomparison. The $1/\sqrt{2}$ factor is intended to represent a possible reduction in random error by the taking of means. An airmass of 1.5 and an ozone amount of 0.300 atm cm has been assumed as the point of perfect agreement. The results are shown in Table 5.5. Briefly, the standard errors are generally less than 0.5%, 0.4%, and 1.3% for C, AD and CD band combinations respectively, but at an airmass of 1.0 and the extreme minimum ozone amount of 0.200 atm cm they rise to 0.9%, 1.1% and 3.0% respectively.

TABLE 5.5

Standard errors in ozone estimates due to band uncertainty arising from both calibration and operation, for a "well calibrated", "well operated" instrument whose extraterrestrial constants are gained by direct intercomparison.

	A	B	C	D	AB	AC	AD	BC	BD	CD
X=.200 atm cm										
μ = 1	.57	.66	.87	3.21	2.41	1.32	1.10	2.62	1.64	2.97 %
μ = 2	.12	.08	.39	1.34	.42	.40	.37	.82	.57	1.27 %
μ = 3	.08	.18	.42	.77	.50	.39	.22	1.02	.42	.97 %
μ = 4	.15	.28	.49	.54	.80	.50	.23	1.29	.46	.97 %

X=.300 atm cm											
μ = 1	.26	.25	.49	1.95	1.04	.65	.60	1.23	.89	1.78	%
μ = 2	.08	.18	.42	.77	.50	.39	.22	1.02	.42	.97	%
μ = 3	.17	.32	.51	.49	.91	.55	.25	1.39	.49	.99	%
μ = 4	.21	.39	.57	.45	1.13	.64	.30	1.61	.57	1.06	%
X=.400 atm cm											
μ = 1	.12	.08	.39	1.34	.42	.40	.37	.82	.57	1.27	%
μ = 2	.15	.28	.49	.54	.80	.50	.23	1.29	.46	.97	%
μ = 3	.21	.39	.57	.45	1.13	.64	.30	1.61	.57	1.06	%
μ = 4	.25	.43	.60	.48	1.30	.71	.35	1.77	.65	1.14	%
X=.500 atm cm											
μ = 1	.06	.11	.39	.98	.32	.36	.26	.86	.45	1.06	%
μ = 2	.18	.34	.53	.46	1.00	.58	.27	1.48	.52	1.01	%
μ = 3	.25	.43	.59	.47	1.26	.70	.34	1.74	.63	1.13	%
μ = 4	.27	.46	.64	.53	1.39	.76	.38	1.87	.69	1.20	%

5.7 General remarks

Estimates of uncertainty in the above calculations were made by recalculating the tables using as input, not the sensitivities, but the uncertainties in the sensitivities as defined by the change in the sensitivity for a 0.05 nm change in the centre wavelength. The uncertainty in the lamp sensitivity was taken as the difference in sensitivity between 3000 K and 3200 K blackbodies. The resulting uncertainties vary greatly among the calculations, but generally they are best represented as one part in five, except for the C bandpair whose uncertainties sometimes rise to one part in two. The additional uncertainty arising from inaccuracy in the spectral modelling of solar irradiance, ozone absorption and band transmittance is difficult to assess, but may perhaps raise the uncertainty to one part in three.

Bearing in mind the assumptions made and the uncertainties involved, the calculated standard errors should be used as a guide to instrument performance rather than as a specification of accuracy. Also, it should be remembered that the calculations describe the standard errors of a large group of instruments, and hence that the performance of any individual instrument can be considerably different to these statistics.

All of the standard errors calculated here will vary in inverse proportion to the degree that instruments are "well calibrated" and "well operated". The standards of calibration and operation assumed are not exceptionally high and would appear to be readily attainable by reasonably dedicated scientifically trained staff, such as those who take part in international comparisons. The 1974 Belsk intercomparison data suggests that the standards were not met at that time, but the better results of more recent intercomparisons (Komhyr et al., 1981a) indicate a much improved standard, of calibration in particular.

Overall, the calculations show that for instruments which are properly adjusted and operated and which are calibrated by the direct intercomparison method, the standard error in AD ozone estimates due to wavelength band uncertainty can be less than 0.5% usually, and less than 1% for low ozone, low airmass situations. The corresponding standard errors for the CD ozone estimates are about 1.5% and 3%. However, there is some suggestion from past intercomparisons that these calculated values may underestimate the true standard errors, by up to a factor of two. An important point is that, although often small, the standard errors are not negligible, especially for the CD band combination, and that every effort should be made to meet, and preferably exceed the recommended precisions for wavelength band calibration and for operational bandpair selection.

5.8 Summary

(i) Uncertainty in the spectral transmittance of the Dobson instrument's bands, particularly in centre wavelengths, contributes uncertainty to the ozone measurements via the spectrally very variable extraterrestrial irradiance and ozone absorption coefficient, whose band-integrated sensitivities to centre wavelength change are typically 10 to 20% nm^{-1}.

(ii) Calculated ozone standard errors due to band uncertainty among instruments calibrated and operated to the recommended standards depend on the band combination, on airmass and ozone amount, and on the method by which the instrument's extraterrestrial constants are determined.

(iii) Band uncertainty explains at least part of the differences in measured standard lamp log intensity ratios between instruments, and, similarly, the errors in extraterrestrial constants transferred by standard lamps. Calculated standard errors in these quantities lie between 0.002 and 0.005. The experimental values for the A, C and D bandpairs found at intercomparisons are about twice the calculated values.

(iv) Calculated ozone standard errors due solely to operational bandpair selection are generally less than 0.5%, 0.5% and 1% respectively for the C, AD and CD ozone estimates, though the latter two rise to nearly twice these values when the airmass is 1 and the ozone amount is at the nominal extreme minimum of 0.200 atm cm. Values for the A, C and D bandpairs found at the Belsk intercomparison are about twice the calculated values.

(v) Calculated ozone standard errors due to both calibration and operational uncertainty for the C, AD and CD band combinations are generally less than 1%, 1% and 2% respectively among instruments whose extraterrestrial constants are obtained independently or by lamp transfer, and less than 0.5%, 0.5% and 1.5% respectively where the constants are obtained by direct intercomparison. Maximum values, of about twice these values, generally occur when the airmass is very low and the ozone amount is very low.

(vi) The calculations indicate deficiencies in the adjustment or operation of instruments at the Belsk intercomparison. Subsequent intercomparisons have shown rather better performances, probably as a result of the greater attention given to prior laboratory adjustment and calibration.

(vii) Overall, the standard error due to band uncertainty among properly calibrated and operated, directly intercompared instruments can be less than 0.5% for the standard AD ozone estimate in most circumstances. Greater standard errors will occur for other situations and other band combinations. To obtain such levels of uncertainty, assiduous efforts are required to meet, or if possible exceed, the recommended standards of calibration and operation.

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Forward to The Bandwidth Effect

6. THE BANDWIDTH EFFECT

6.1 Introduction

In Section 1.2 the theory of the Dobson instrument measurement was developed for monochromatic spectral bands and no account was made of the spectral variation of parameters, particularly of ozone absorption, across the instrument's finite bandwidths. The principal deficiency of this assumption of monochromaticity is its failure to account for the small monotonic decrease in the effective absorption coefficient of a finite band with increasing airmass and absorber amount. This effect is known as the bandwidth effect, or the Forbes effect. It arises from the relative attenuation, with increasing airmass and absorber amount, of those wavelength intervals within the band which are more strongly absorbed, and hence the relative increase in the energy weighting of the wavelength intervals within the band which are less absorbed, i.e., which have smaller absorption coefficients.

The calculation of the bandwidth effect relies on a knowledge of the slit transmittance functions but these are not in fact well known. The exact widths and shapes of the transmittance functions will, of course, vary among a group of instruments according to the particular adjustment of the slits and of the other optical components. Furthermore, the functions usually assumed (triangular for S_2 and trapezoidal for S_3) will be convoluted (i.e., smeared) by the effects of lens aberrations and other optical imperfections (see Section 2), and will have low-transmittance "wings" owing to these effects and to stray light. Indeed, the bandwidth effect and stray light effects have the same origin, namely, lack of perfect monochromaticity in the band, and are described by the same mathematical expressions. Generally, the smearing or broadening of the slit transmittance functions will result in greater bandwidth effect errors.

The choice of bandwidths for the Dobson instrument is largely a compromise between the bandwidth effect on the one hand, and the need for high energy transmission and low wavelength sensitivity (see Section 5) on the other. If the slits S_1 and S_2 remain equal, then the energy transmitted by the pair is proportional to the square of their slitwidth, which means that any increase in resolution is costly in energy transmission. As we shall see, the bandwidth effect for the present bandwidths of about 1.0 nm for S_2 and 3.0 nm for S_3 is usually less than 1%, and so these bandwidths are quite satisfactory.

6.2 Theory and calculations

The bandwidth effect for various ozone measuring instruments has been discussed by Vanier and Wardle (1969), Khrgian (1975) and Basher (1977). The effective ozone absorption coefficient of a band at any time is the integral over wavelength of the ozone absorption spectrum weighted by not only the slit transmittance function, but also the spectral irradiance incident on the instrument at that time, and, less importantly, the detector spectral sensitivity and the spectral transmittance of any filters present. It can be shown that this effective ozone absorption coefficient, α may be written as:

$$\alpha = \frac{-1}{\mu_h X} \log \frac{\int P_0(\lambda) 10^{-\mu_h X \alpha(\lambda) - mB(\lambda) - \sec Z \delta(\lambda)} d\lambda}{\int P_0(\lambda) 10^{-mB(\lambda) - \sec Z \delta(\lambda)} d\lambda} \qquad (6.1)$$

where $P_0(\lambda)$ is the electrical response of the instrument per unit wavelength outside the atmosphere (this is indicated by the subscript zero) and is the product of solar spectral irradiance, slit spectral transmittance, filter spectral transmittance and detector spectral sensitivity. The other terms are defined in Section 1.2. (Note that here in equation (6.1) wavelength λ is a continuous variable, whereas in equations (1.1) to (1.7), the convention of λ being used to label the centre wavelength of a band is followed. This results in some inconsistency, for example, P(λ) here is a spectral quantity whereas in equation (1.5) it is the band integral of this spectral quantity.) Expressions similar to equation (6.1) can be written for an effective Rayleigh scattering coefficient, B, and an effective aerosol scattering

coefficient, δ, but in practice this is not necessary as the variation in these coefficients is negligible. The aerosol scattering term in equation (6.1) can be safely neglected (Basher, 1977).

Vanier and Wardle (1969) calculated α for the Dobson instrument's A, B, C and D bandpairs and gave the range of variation for the A bandpair coefficient as 0.003, which is equal to about 0.2% in α. They state that the ranges of variation for the other bandpairs are also small and conclude that the bandwidth effect is negligible. Basher's (1977) results showed some small differences to these results but this was probably due to differences between the absorption spectra, solar spectra and slit spectra used by the authors.

Some new and more extensive calculations of the bandwidth effect are presented below in Table 6.1. The method and basic data used are essentially the same as those described by Basher (1977), but the resolution of the calculations was increased from 0.2 nm to 0.05 nm and an improved and more detailed ozone absorption spectrum was constructed and used (see Section 5.2 for more details). Of course it must be remembered that no amount of improving can overcome the relatively high uncertainty in the available absorption data (see Section 9). The calculations assume triangular and trapezoidal slit transmittance functions of 1.0 and 3.0 nm bandwidth for the S_2 and S_3 bands respectively, and of 0.9 nm slopewidth (the spectral width of the sloping sides). The results are given in Table 6.1 as the corrections in percent that need to be applied to the absorption coefficients calculated for zero airmass.

The tabulated corrections are positive (except for some double bandpair combinations) and increase approximately linearly with ozone amount and airmass. This reflects the expected decline in α with increasing absorber amount. The linearity of the dependences allows their representation by simple equations for data correction by computer, though as far as is known, Dobson data are never corrected for the bandwidth effect. Note that the second decimal place is given in the table's data to show trends, but is otherwise not significant. The corrections appear to be quite dependent on band centre wavelength, which implies that the values calculated will be rather dependent on the accuracy of the absorption data and slit data used. The accuracy of the corrections listed is probably no better than 0.2% of the relevant coefficient.

The bandwidth effect errors tend to be smallest for the shorter wavelength bands, and this is due to the smaller spectral variability of α(λ) at the shorter wavelengths (see Figure 1.1). This is a fortunate thing since it is the shorter wavelength bands which dominate the bandpair absorption coefficients. The magnitudes of the errors for the recommended AD bandpair combination are smaller than their uncertainty for all conditions and are therefore negligible. In contrast, the errors for the often-used C and CD methods are the largest of the usual band combinations, and, while mostly they are less than 1%, under the conditions of high ozone and airmass when these methods are most important, they will rise to 2%.

TABLE 6.1

Bandwidth effect corrections for the ozone absorption coefficients of Dobson instrument bands and band combinations, in percent, and as a function of ozone amount in atm cm and airmass.

OZONE	μ_h	305.	309.	311.	318.	325.	329.	332.	340.	A	B	C	D	AB	AC	AD	BC	BD	CD
0.200	1.0	0.06	0.12	0.15	0.14	0.48	0.66	0.43	0.06	0.04	0.09	0.13	0.14	-0.09	-0.05	0.01	0.02	0.07	0.12
	2.0	0.12	0.25	0.29	0.28	0.95	1.31	0.86	0.12	0.07	0.19	0.26	0.28	-0.20	-0.10	0.01	0.04	0.15	0.25
	3.0	0.18	0.37	0.44	0.42	1.43	1.95	1.28	0.18	0.10	0.29	0.40	0.43	-0.33	-0.16	0.02	0.07	0.23	0.38
	4.0	0.24	0.51	0.60	0.57	1.90	2.57	1.69	0.25	0.13	0.40	0.54	0.58	-0.47	-0.22	0.02	0.11	0.32	0.51
	5.0	0.29	0.64	0.75	0.71	2.38	3.19	2.11	0.32	0.16	0.51	0.68	0.73	-0.63	-0.29	0.01	0.16	0.42	0.65
0.250	1.0	0.07	0.14	0.17	0.16	0.54	0.75	0.48	0.07	0.04	0.11	0.16	0.17	-0.11	-0.05	0.01	0.02	0.09	0.15
	2.0	0.14	0.29	0.35	0.33	1.09	1.49	0.95	0.15	0.08	0.23	0.32	0.34	-0.25	-0.12	0.02	0.06	0.19	0.30
	3.0	0.21	0.45	0.53	0.50	1.63	2.21	1.42	0.22	0.12	0.36	0.48	0.51	-0.41	-0.19	0.02	0.10	0.29	0.46
	4.0	0.28	0.61	0.72	0.67	2.17	2.91	1.88	0.30	0.16	0.49	0.65	0.69	-0.60	-0.27	0.02	0.16	0.41	0.63
	5.0	0.34	0.77	0.91	0.85	2.72	3.60	2.33	0.38	0.19	0.63	0.83	0.87	-0.81	-0.37	0.01	0.22	0.53	0.80
0.300	1.0	0.08	0.17	0.20	0.18	0.61	0.84	0.53	0.08	0.05	0.13	0.18	0.19	-0.13	-0.06	0.01	0.03	0.11	0.18
	2.0	0.17	0.34	0.41	0.38	1.22	1.66	1.05	0.17	0.10	0.27	0.37	0.39	-0.30	-0.14	0.02	0.08	0.23	0.36
	3.0	0.24	0.53	0.62	0.58	1.83	2.46	1.56	0.26	0.14	0.42	0.57	0.59	-0.50	-0.23	0.02	0.13	0.35	0.55
	4.0	0.31	0.72	0.84	0.75	2.44	3.25	2.06	0.35	0.18	0.58	0.77	0.80	-0.73	-0.33	0.02	0.20	0.49	0.75

	5.0	0.38	0.91	1.06	0.99	3.05	4.01	2.56	0.45	0.21	0.75	0.98	1.01	-0.99	-0.44	0.01	0.29	0.64	0.95
0.350	1.0	0.10	0.19	0.23	0.22	0.68	0.93	0.57	0.10	0.06	0.15	0.21	0.22	-0.16	-0.07	0.02	0.04	0.13	0.20
	2.0	0.19	0.39	0.47	0.44	1.36	1.83	1.14	0.20	0.11	0.32	0.43	0.44	-0.36	-0.16	0.03	0.09	0.26	0.42
	3.0	0.27	0.60	0.71	0.66	2.04	2.72	1.70	0.30	0.16	0.49	0.66	0.68	-0.60	-0.27	0.03	0.17	0.42	0.64
	4.0	0.35	0.82	0.96	0.90	2.71	3.58	2.25	0.40	0.20	0.68	0.89	0.91	-0.88	-0.39	0.02	0.26	0.58	0.87
	5.0	0.43	1.05	1.22	1.13	3.38	4.41	2.79	0.51	0.24	0.88	1.13	1.15	-1.20	-0.53	0.01	0.37	0.76	1.11
0.400	1.0	0.11	0.22	0.26	0.24	0.75	1.02	0.62	0.11	0.07	0.17	0.24	0.25	-0.18	-0.08	0.02	0.05	0.14	0.23
	2.0	0.21	0.44	0.52	0.40	1.50	2.01	1.23	0.22	0.12	0.36	0.49	0.50	-0.41	-0.19	0.03	0.11	0.30	0.47
	3.0	0.30	0.68	0.80	0.78	2.24	2.97	1.84	0.34	0.18	0.56	0.74	0.76	-0.70	-0.31	0.03	0.20	0.48	0.73
	4.0	0.39	0.94	1.08	1.01	2.98	3.90	2.43	0.46	0.22	0.78	1.01	1.03	-1.03	-0.46	0.02	0.31	0.68	1.00
	5.0	0.47	1.20	1.38	1.28	3.71	4.81	3.01	0.58	0.27	1.01	1.29	1.30	-1.42	-0.62	-0.00	0.45	0.89	1.28
0.450	1.0	0.12	0.24	0.29	0.27	0.82	1.11	0.67	0.12	0.07	0.19	0.26	0.27	-0.20	-0.09	0.02	0.05	0.16	0.26
	2.0	0.23	0.49	0.58	0.54	1.63	2.18	1.33	0.25	0.14	0.41	0.54	0.55	-0.47	-0.21	0.03	0.13	0.34	0.53
	3.0	0.33	0.76	0.89	0.83	2.44	3.22	1.97	0.38	0.19	0.64	0.83	0.84	-0.80	-0.36	0.03	0.24	0.55	0.82
	4.0	0.42	1.05	1.21	1.12	3.24	4.22	2.61	0.51	0.24	0.88	1.13	1.14	-1.20	-0.52	0.01	0.38	0.77	1.13
	5.0	0.51	1.35	1.54	1.42	4.04	5.20	3.23	0.64	0.29	1.14	1.45	1.45	-1.65	-0.71	-0.01	0.54	1.02	1.45
0.500	1.0	0.13	0.26	0.31	0.20	0.89	1.19	0.72	0.14	0.08	0.22	0.29	0.30	-0.23	-0.10	0.02	0.06	0.18	0.29
	2.0	0.25	0.55	0.64	0.60	1.77	2.35	1.42	0.27	0.15	0.45	0.60	0.61	-0.53	-0.24	0.03	0.15	0.39	0.59
	3.0	0.36	0.85	0.98	0.91	2.64	3.47	2.11	0.42	0.21	0.71	0.92	0.93	-0.91	-0.40	0.03	0.28	0.62	0.92
	4.0	0.46	1.16	1.34	1.23	3.50	4.54	2.79	0.56	0.26	0.99	1.26	1.26	-1.37	-0.59	0.01	0.44	0.87	1.26
	5.0	0.55	1.50	1.70	1.57	4.36	5.58	3.46	0.70	0.31	1.28	1.61	1.60	-1.90	-0.81	-0.02	0.64	4.15	1.62

6.3 Summary

(i) The effective ozone absorption coefficient for a band of finite bandwidth decreases with increasing absorber amount, owing to the spectral variation of absorption across the band. The customary use of fixed ozone absorption coefficients therefore gives rise to an error which depends on airmass and ozone amount.

(ii) Bandwidth effect errors calculated for the Dobson instrument are neglibily small for the AD band combination. The errors for the C and CD band combinations are among the largest found, and while these are mostly less than 1%, they do rise to 1.5% when the airmass and ozone amount are very high.

(iii) Bandwidth effect errors are approximately linear with airmass and ozone amount and are easily corrected for. The uncertainty in the calculated errors is possibly 0.2% for the relevant coefficient.

(iv) The Dobson slit transmittance functions are not well known. Optical effects, such as lens aberrations will smear and broaden the functions and generally will increase the bandwidth effect errors.

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7. FIELD OPERATIONS AND CALIBRATIONS

7.1 Introduction

The purpose of this section is to discuss those aspects of field operations which affect the accuracy of the Dobson network's observations. Particular attention is given to organisational factors, which are of importance owing to the international nature of the network and the manual character of the instrument, and to the determination of extraterrestrial constants, which is well known to be an important source of error.

7.2 Organisational factors

The present global Dobson ozone monitoring network has evolved slowly over many decades, and it continues to be dependent on the cooperation and goodwill of many scientists and many countries. The approximately sixty instruments in use throughout the world are owned and operated by a variety of institutions, often national meteorological services or associated research institutes, and so do not constitute an homogeneous, centrally organised network. Some are operated without much support or encouragement from the institution concerned, which may see little benefit in such long term specialist monitoring to its own current research work or other goals. Clearly there is the potential for wide variation of operational practices.

The instrument is manually operated. This means that there is a decidedly human element to its operation, and that considerable attention must be given to personnel matters to ensure a successful operation. Staff must be trained in routine operations, and for some, in calibration work. The instrument and the procedures used must be inspected periodically. The procedures themselves must be well thought out and clearly described. There should be rapid feedback to the operator when quality control measures show that the performance of either the instrument or the operator is not up to standard.

It is important that senior officers and scientists take an active interest in the observers' work and convey to them something of the international significance of their observations. The Dobson observations are likely to comprise only a small part of the observers' duties, and may be accorded a lower priority if other immediately pressing duties or demands arise. Also, the level of experimental care and judgement required may be inconsistent with the other duties. To compound the difficulties, in some organisations the staff may change frequently according to shift schedules and as promotions and other movements occur.

Before 1957, instructions for calibrating and operating the instrument were provided by the manufacturer using material prepared by G.M.B. Dobson. In that year, more detailed sets of instructions (Dobson, 1957a and 1957b) were published, as part of an International Geophysical Year instruction manual. These were aimed at fairly expert readers, and it is probable that, in due course, many Dobson instrument scientists prepared simpler, more fully explained instructions for the use of their operators. For example, a comprehensive instruction manual (Komhyr, 1962) was prepared for use in the United States network. More recently, the WMO Operations Manual (Komhyr, 1980b) was prepared in order to encourage more modern and uniform standards of operation throughout the whole network. It is not clear to what extent the WMO manual's procedures are being followed at present.

The international intercomparisons of instruments, and the designation of the Central Dobson Spectrophotometer Laboratory at Boulder, Colorado, have done a great deal to improve the consistency of instrument calibrations. What is now required is a similar international effort to improve the consistency and quality of routine operations. The production of the WMO Operations Handbook was an important step in this direction. Other activities which could be considered are:

- a survey of current operational practices;

- the preparation and regular distribution to all stations of standard forms for such things as defining times of observations, for reporting results, etc.;

- the training of operators or their supervisors at the Central Laboratory or at regional centers;

- the further development and dissemination of improved operating practice;

- and possibly the circulation of an operations newsletter.

Ideally, any such improvements would be best set in the context of a comprehensive quality assurance programme designed specifically for the network using the principles of quality assurance already established in the manufacturing industries.

7.3 Field calibrations and tests

An important source of error, especially in past data, is that arising from the uncertainty in extraterrestrial constants determined independently at each site by the Langley method. The method is briefly described in Section 1, and further details are to be found in Sections 4 and 5. Before the mid-1970s, when direct intercomparison calibrations became established, all instruments were calibrated by the Langley method, and even now perhaps a third of the network relies on such calibrations.

Extraterrestrial constants were supplied with each instrument upon delivery. These were obtained by G.M.B. Dobson at Oxford by Langley method measurements and by direct intercomparison with his own instrument, No. 1 (Dobson, 1968). However Dobson and Normand (1962) showed that although the Langley method worked well for the instruments at Mauna Loa and at certain sites in Canada, it gave inconsistent results at Oxford, i.e. it failed to give the linearity of data expected from equation 1.3 or the constancy expected of the extraterrestrial constants. They attributed this to the atmospheric conditions at Oxford, though stray light also could have played a large part (see Section 4).

The standard errors in the daily extraterrestrial constants reported by Dobson and Normand (1962) for the Mauna Loa and Canadian instruments imply average ozone errors of less than 1%. The ozone errors are not constant of course, but vary with relative absorption coefficient and inversely with airmass (see equation 1.4), and hence vary with wavelength pair, latitude, season and time of day.

For determinations made under changeable atmospheric conditions, or with poorly adjusted instruments, or with instruments having a stray light problem, the average error in AD ozone measurements should be similar to those shown by Dobson and Normand (1962) for Oxford, namely about 5% or less. Worst case average errors of 10% or more cannot be ruled out. In some cases the manufacturer's constants obtained at Oxford were used for many years before any independent Langley determinations were made. The size of these errors are consistent with the differences of up to 10% found in the early intercomparisons, and with the range of about 10% found in a recent set of mean differences of co-located Dobson and BUV-TOMS satellite observations (WMO, 1982).

It is instructive to look in detail at the results of the international Dobson spectrophotometer intercomparisons at Belsk, Poland in 1974, and at Boulder, Colorado, U.S.A. in 1977. Table 7.1 lists the published ΔN_k corrections for the Belsk intercomparison (Dziewulska-Losiowa and Walshaw, 1977, Table I) along with the resulting percentage AD ozone corrections calculated for an ozone amount of 0.300 atm cm. This 1977 publication corrected some of the original data in Dziewulska-Losiowa and Walshaw (1975) and gave the dates of the wedge calibration tables to which the corrections apply.

TABLE 7.1

Published results of the international intercomparison of Dobson spectrophotometers at Belsk, Poland in 1974. Correction are to be added to old values. X_{AD} corrections are calculated for an ozone amount of 0.300 atm cm.

Instrument	Country	Required N-Value corrections					Resulting X_{AD} Corrections in %			
		ΔN_A	ΔN_C	ΔN_D	ΔN_{AD}	ΔN_{CD}	μ=1	μ=2	μ=3	Mean
41	U.K.	.002	.006	-.014	.016	.020	3.9	1.9	1.3	2.3
64	G.D.R.	-.216	-.212	-.244	.028	.032	6.7	3.4	2.2	4.1

77	Canada	-.017	-.003	-.006	-.023	-.009	-5.5	-2.8	-1.8	-3.4
83	U.S.A	..... Reference instrument					...	...	...	...
84	Poland	.048	.014	-.011	.059	.025	14.2	7.1	4.7	8.7
96	Egypt	-.036	-.026	-.049	.013	.023	3.1	1.6	1.0	1.9
101	Switzerland	.001	-.007	-.017	.018	.010	4.3	2.2	1.4	2.6
108	U.S.S.R.	-.015	-.012	-.040	.025	.028	6.0	3.0	2.0	3.7
110	Hungary	.077	.139	.148	-.071	-.019	-17.1	-8.5	-5.7	-10.4
112	India	-.030	-.025	-.006	-.024	-.019	-5.8	-2.9	-1.9	-3.5

Note: The X_{AD} correction are accurate to no better than ±0.5%

The listed mean AD ozone errors, which are the mean of the errors for airmasses 1, 2 and 3, lie in the 2% to 10% range of magnitudes and reflect the level of accuracy to be expected of independently calibrated, independently maintained instruments. Some very large differences for individual bandpairs are shown. These and various other unsatisfactory features not evident in the final AD ozone corrections listed in Table 7.1 are discussed by Dziewulska-Losiowa and Walshaw (1975), and in paragraphs below.

The published results of the 1977 Boulder intercomparison (Komhyr et al., 1981a) are reproduced in Table 7.2. Considerable attention was given at this intercomparison to properly adjusting and calibrating, and in some cases modernising, the instruments' optics and electronics. The final correction factors include the effect of these changes as well as the errors in the extraterrestrial constants. As noted by Komhyr et al. (1981a), the comparability of the instruments' AD ozone estimation, i.e., of their standard ozone measurement type, was better than at the Belsk intercomparison, with five of the eight instruments needing corrections of only about 1% or less.

TABLE 7.2

Published results of the international intercomparison of Dobson spectrophotometers at Boulder, Colorado, U.S.A. in 1977.
Correction are to be added to old values.
X_{AD} corrections are calculated for an ozone amount of 0.300 atm cm.

Instrument	Country	Required N-Value corrections					Resulting XAD corrections in %			
		ΔN_A	ΔN_C	ΔN_D	ΔN_{AD}	ΔN_{CD}	μ=1	μ=2	μ=3	mean
41*	U.K.	.0378	.0335	.0308	.0070	.0027	1.7	0.8	0.6	1.0*
71	G.D.R.	-.0488	-.0721	-.0920	.0432	.0199	10.4	5.2	3.5	6.3
77*	Canada	.0373	.0275	.0450	-.0077	-.0175	-1.8	-0.9	-0.6	-1.1*
83	U.S.A.	..... Reference instrument					...	...	...	...
96*	Egypt	-.0871	-.0536	-.0691	-.0180	.0155	-4.3	-2.2	-1.4	-2.6*
105	Australia	.0069	-.0130	-.0119	.0188	-.0011	4.5	2.3	1.5	2.8
108*	U.S.S.R.	.0662	.0423	.0713	.0051	-.0290	-1.2	-0.6	-0.4	-0.7*
112*	India	.0286	.0315	.0270	.0016	-.0045	0.4	0.2	0.1	0.2*
116	Japan	.0025	.0029	.0069	-.0044	-.0040	-1.1	-0.5	-0.4	-0.6

Notes: (i) * denotes those instruments previously calibrated against the no.83 reference instrument at Belsk.

(ii) The accuracy of the N corrections is less than the number of decimal places implies. The X_{AD} corrections are accurate to no better than ±0.5%

TABLE 7.3

Corrections arising from the error in sign (see text), to be added to the N-values of the World Reference Spectrophotometer No. 83 between its calibration dates in 1972 and 1976, and to any instruments calibrated against No. 83 during this period. Approximate equivalent ozone corrections, also to be added, calculated for an ozone amount of 0.300 atm. cm.

Band Combination	N-value correction	Approximate ozone correction, % μ=1	μ=2	μ=3	mean
A	0.028	5.3	2.7	1.8	3.3
C	0.023	9.6	4.8	3.2	5.9
D	0.031	------ Not relevant ------			
AD	-0.003	-0.7	-0.4	-0.2	-0.4
CD	-0.008	-6.1	-3.0	-2.0	-3.7

Table 7.2 does show some rather disquieting features, however. In particular, the ΔN_k corrections for the individual bandpairs of the instruments, No.s 41, 77, 96, 108, and 112, which had been previously calibrated against the No. 83 reference at the 1974 Belsk intercomparison, are surprisingly large. A typical value, 0.0400, represents an error in an intensity ratio of about 10%, and is much larger than the precisions available from either the independent Langley method, or the routine standard lamp checks.

Fortunately, there is a simple explanation for at least some of these large values. After the completion of the Langley calibration of the World Reference Spectrophotometer No. 83 at Mauna Loa Observatory in 1972, the required corrections to the instrument's extraterrestrial constants were inadvertently made using the wrong sign (Peterson, 1978). The effect on the standard AD ozone estimation was very small, and the error remained undiscovered until the results from the next calibration at Mauna Loa in 1976 were processed. The N-value corrections needed to account for these errors of sign (Peterson, 1978) are given in Table 7.3.

It is important that the nature of these corrections and their application be clearly stated. The significant points are as follows

- The errors in the standard AD ozone estimations, due to the reference error, average to about 0.4%. Therefore the great bulk of ozone data is affected only to about 0.4%, which is relatively small.

- The errors in the A, C and CD ozone estimations, due to the reference error, are about 3%, 6% and 4%, respectively, and hence are significant.

- The calibration of the reference Dobson spectrophotometer No. 83 was in error at the 1974 Belsk intercomparison, by the amounts listed in Table 7.3. The results of the intercomparison, published by Dziewulska-Losiowa and Walshaw (1975 and 1977) and also listed in Table 7.1, have not been corrected for these errors.

- The No. 83 reference Dobson spectrophotometer was correctly calibrated at the time of the 1977 Boulder intercomparison, and the final calibrations of the participating instruments are correct.

- The final corrections which resulted from the Boulder intercomparison, and which appear in Peterson (1978), Komhyr et al. (1981a), and in Table 7.2 above, include, for those instruments which also participated in the Belsk intercomparison, a component which compensates for the reference error inadvertently imposed at the Belsk intercomparison.

- The reference error was reported to the 1977 Boulder intercomparison participants, at the time of the intercomparison, and to the World Meteorological Organisation (W.D. Komhyr, personal communication).

- The changes in the calibration of the No. 83 reference instrument arising from the 1972 Mauna Loa calibration are exactly half the corrections given in Table 7.2, and hence amount to about 0.2% for the AD ozone estimate and to a few percent for the other main band combinations.

Approximate mean ozone corrections for the Boulder intercomparison are shown in Table 7.4; (a) for the data as published, and (b) with the reference error component removed from those instruments which had also been intercompared at Belsk. As before, the corrections are calculated as the mean of the corrections for airmasses 1, 2 and 3, and for an ozone amount of 0.300 atm cm. The values remaining after the removal of the reference error component represent the intrinsic changes to the instruments' calibrations between 1974 and 1977, and are generally much smaller than the "as published" values. Overall, the results for the United Kingdom, Canadian, Australian, Indian and Japanese instruments are very satisfactory. It is worth noting that the No. 83 reference instrument, and the No. 77 Canadian instrument were calibrated independently of each other at Mauna Loa Observatory in 1980, and that the resulting calibrations were found to be "virtually identical" (W.D. Komhyr, personal communication).

TABLE 7.4

Boulder 1977 intercomparison: Approximate average ozone corrections in percent, calculated (a) for the results as published, and (b) with inadvertently imposed reference error component removed from those instruments (*) present at the Belsk 1974 intercomparison (see text for further explanation).

		Approximate mean ozone correction, %							
		(a) As published				(b) Component removed			
Instrument	Country	A	C	AD	CD	A	C	AD	CD
41*	U.K.	4.4	8.5	1.0	1.2	1.1	2.6	1.4	-2.5
71	G.D.R.	-5.7	-18.4	6.3	9.2	-	-	-	-
77*	Canada	4.3	7.0	-1.1	-8.1	1.0	1.1	-0.7	-11.8
83	U.S.A.	----- Reference --------				------ Reference -------			
96*	Egypt	-10.1	-13.6	-2.6	7.2	-13.4	-19.5	-2.2	3.5
105	Australia	0.8	-3.3	2.8	-0.5	-	-	-	-
108*	U.S.S.R.	7.7	10.8	-0.7	-13.4	4.4	4.9	-0.3	-17.1
112*	India	3.3	8.0	0.2	2.1	0.0	2.1	0.6	-1.6
116	Japan	0.3	0.7	-0.6	-1.9	-	-	-	-

Table 7.4 also illustrates the variation in calibration quality that exists among the individual bandpairs and their combinations. The CD band combination has large corrections owing principally to the small CD ozone absorption coefficient, which confers upon this combination an inherently lower accuracy. In practice, the CD combination is usually only used at higher average airmasses and this results in a reduction of the effective mean corrections, perhaps to about half of those shown in Table 7.4. It should be borne in mind that the mean AD corrections tell only part of the story and do not necessarily represent the generally larger corrections for other band combinations or the relative overall quality of the instruments' calibrations. Also, they give no direct indication of the airmass dependence of the corrections or the intrinsic air mass dependences of the instruments due to such things as stray light. It is reported in Peterson (1978) that light scattering effects within instruments 71 and 96 are most pronounced. Possibly this is the main source for the relatively large corrections shown for these instruments in Table 7.4.

The AD results for a large number of other intercomparisons, mainly against instrument No. 83, at Boulder, are reported in WMO (1982), and show generally similar characteristics to those of Table 7.2. Of particular interest are the calibration histories of instruments which have been calibrated more than once, over periods which in some cases extend to twenty years. If the calibration stability of these instruments is summarised by the magnitude of the maximum calibration correction following the initial calibration, then of the nine instruments intercompared more than once with instrument No. 83, two instruments had maxima of less than 1%, a further three had maxima of less than 2%, a further two had maxima of about 3%, and the remaining two had maxima of about 4%. There appears to be no systematic reduction in the magnitudes with time, which suggests that the quality of these particular calibrations has remained stable over the period. The calibration histories each tend to show corrections of the same sign, indicating systematic drifts in instrument calibration with time. Seven of the nine instruments show predominantly negative corrections. This is significant in that the systematic calibration drifts, and the resulting fictitious trends in uncorrected ozone data, will affect large regions, and hence may give the appearance of real ozone trends.

Some difficult questions arise with the retrospective application of calibration corrections. Should the mean corrections be applied as constants to all data, or should the airmass dependences of the corrections be accounted for? Should an attempt be made to separate the correction component due to extraterrestrial-constant error from other components with different functional dependences, such as that due to wedge calibration error? Should the corrections be considered as fixed in time, or be weighted in some retrospectively declining fashion? Should any attempt be made to correct the archives of the World Ozone Data Center? Should the responsibility for making corrections lie with the Center or with the national or station authorities? Some general rules may be formulated in due course, but ultimately the answers to the questions will depend on the characteristics of the particular instrument being considered. Further discussions of these problems are to be found in WMO (1982).

An important issue is the weakness in the current practice of relying on the one instrument (No. 83) as the measurement standard. This is underlined by the presence of the sign error in the calibration

of the reference instrument No. 83 between the Belsk and Boulder intercomparisons. Where measurement standards are embodied in reference instruments, it is common, and very desirable, to maintain a group of three or more reference instruments and to represent the measurement standard by the mean result of the largest subset of the group which is operating satisfactorily. This approach allows the prompt detection of any error drift or malfunction in any of the reference instruments and it preserves the measurement standard in the event of any accidental loss of or damage to a reference instrument.

On these grounds it is argued that two additional reference Dobson instruments should be established, by upgrading and independently calibrating two existing instruments to the same high quality as No. 83. Some national reference instruments may already be very close to the quality required. Regular intercomparisons between the three designated reference instruments would be required, and at least two of them would be needed to represent the standard at each international intercomparison of working instruments.

The determination of extraterrestrial constants forms only part of the on-site calibration work. In addition, there are a number of more routine tests which need to be carried out on a regular basis. These comprise:

- the mercury lamp test, which checks the instrument's wavelength calibration and its temperature dependence;

- the standard lamp test, which checks the stability of the instrument components of the extraterrestrial constants;

- the wedge calibration test, which checks the density gradient of the optical wedge;

- and the sensitivity test, which checks the overall sensitivity of the instrument.

Descriptions of the tests, with full instructions, are given in the WMO Operations Handbook (Komhyr, 1980b).

Errors can arise if there are instrument drifts and the tests are neglected, or if the tests are improperly done, improperly interpreted, or improperly documented. As was noted earlier, it is not clear to what extent the detailed instructions in the WMO Operations Handbook are rigorously followed throughout the network. The comparisons given in Section 5.4 between calculated and measured standard errors in standard lamp readings indicate that there is still room for improvement in the use of the standard lamp test. Standard lamps can also age with use and a set of lamps must be maintained to guard against this. The errors due to the set of tests and their execution are difficult to estimate, but might amount to a few percent, if gross error is excluded. Olafson and Asbridge (1981b) report the curious discovery that some of their mercury lamps appear to give inaccurate wavelength calibrations. This certainly needs further study.

Recently, the Central Dobson Spectrophotometer laboratory has begun circulating reference standard lamps around the network. The application of a similar lamp, UQ1, to 15 instruments which had just been calibrated by direct intercomparison yielded a standard deviation of 0.006 in N_{AD} (Komhyr et al., 1981a). This suggests that N_{AD} errors of greater than, say 0.015, equivalent to X_{AD} mean errors of about 2%, could be corrected on the basis of these lamp measurement

The WMO Operations Manual also gives instructions for a variety of electronics and optics maintenance tasks which may be carried out on site, for such things as cleaning the commutator and replacing the photomultiplier. The instructions and advice reflect a considerable accumulation of practical experience and should be followed carefully. Generally, any effects of poor maintenance will show up in the routine tests. The design of the instrument does not call for any precise electrical calibrations.

7.4 Routine operation

Errors in day to day operation can be attributed to either deficiency of judgement or error of execution. In the first category come questions such as: deciding what measurement type to use, e.g., direct sun AD versus zenith sky AD, choosing the null balance when the light is weak and the ammeter is consequently unsteady, deciding when to take a measurement, judging when a measurement is affected by extraneous factors and needs repeating, and deciding what notes, if any, should be recorded. The quality of the judgements affects not only the current day's ozone estimate, but also any subsequent use of the data in constructing empirical charts for zenith sky clear and cloudy estimations. Generally, the quality of judgements are most crucial when the observing conditions are difficult, such as when the solar elevation is low or is changing rapidly, or the weather is poor. Local practises in making these judgements are likely to be varied.

Errors of execution include: errors in aligning the instrument and the sun director; errors in the choice of appropriate accessories; errors in setting the Q plate levers; failure to properly adjust for changing instrument temperature; error in reading the wedge dial; and error in recording the readings. Gross errors, such as confusing the A and C bandpairs, are readily detectable by elementary quality control measures, and in any case are likely to be rare and to have little effect on climatological mean data. Small systematic errors may be a problem though. Particular systematic error sources are:

- the failure to keep the ground quartz plate diffuser clean and free of UV absorbing oils;

- the failure to minimise, and frequently adjust for, the temperature changes of the instrument (see Section 2);

- and the failure to refresh the silica gel dessicant sufficiently often.

Individual operators may exhibit systematic biases in setting the Q levers and in reading the wedge dial, but the resulting errors should be fairly small, i.e. less than 0.5%.

The precision of the Dobson instrument under normal circumstances is very good, with standard errors being small compared to potential systematic errors. The standard error in single routine observations is of the order of 0.5% in the mean AD ozone estimate, according to the work of Dobson and Normand (1962) and to the analysis of wavelength band uncertainty in Section 5. Occasionally it may rise to 1%. Dziewulska-Losiowa and Walshaw (1975) found a standard error of about 0.6% from a study of the Belsk intercomparison data.

The AD ozone measurement random standard errors given in NASA (1979, Table 6.2), and thence copied to WMO (1981, Table 2.1) and WMO (1982, Table 3.1), are estimates which include the effects of such things as: short term calibration fluctuations; observer error; varying haze conditions; and the temperature dependence of ozone absorption, and are therefore not the same as the precisions discussed above. The NASA (1979) standard error estimates were 1.5% for optimally maintained and operated instruments and 3% for an average network instrument for direct sun AD measurements, and similarly, 2.5% and 5% for zenith sky observations. These estimates are approximate of course, and there are obvious questions as to how well such "random" standard errors actually represent the variable systematic errors. Overall summaries of error for the present study are given in Section 14.

Special mention must be made of high latitude stations, for most operational difficulties are exacerbated by increasing latitude. The greater airmasses and greater ozone amounts result in low light levels and high differential absorption, both of which tax the capabilities of the instrument and necessitate the use of the less accurate C and CD longer wavelength hand combinations and possibly the focussed image method. During winter, focussed image moon measurements may be the only possibility. The greater variation in the ozone layer's mean temperature (see Section 9) and mean height (see Section 12) at higher latitudes introduces greater uncertainty. Meteorological conditions may bring extensive cloudiness which requires the use of the less accurate cloudy sky estimation methods (whose empirical charts may be difficult to construct at such latitudes). The instrument will be subjected to the stresses of very low temperatures and of rapidly varying temperatures. The stations can be very isolated and the observing work can be very difficult. To some extent, however, these intrinsic difficulties will be offset by the higher standards of operation expected of the well motivated, well trained staff who usually man the high latitude stations.

Sampling errors may be of importance to statistical averages. Day to day variation in column ozone amounts can be large, of up to about 5% in the tropics and about 30% at high latitudes, and so losses of data due to weather or operational conditions may cause biases of several percent in some monthly means, especially since ozone amounts are strongly correlated with synoptic weather conditions (WMO, 1982). Mean diurnal variations are thought to be negligible. Spatial sampling errors also exist, of course, owing to the very uneven spatial distribution of the network. It would seem that further quantitative work on both temporal and spatial sampling errors is needed. Satellite data will be very useful in this respect.

A certain amount can be done to improve the instrument's ease of operation, especially in the more severe climates. For example, in the United States network, the instruments are operated from an out-building which is equipped with a heater, an air conditioner, a rotating instrument table, and a motor driven astronomical dome roof. In Toronto, the instrument is mounted indoors with a periscope system projecting through the ceiling. Westbury, Thomas and Simmons (1981) report an ergonomic design for a null balance display consisting of a ring of sixteen light-emitting diodes. The Q levers can be equipped with permanent, though adjustable, stops at the A and D positions.

The degree of possible automation of the instrument is restricted by the need to make accessory changes to suit the airmass and sky conditions. Raeber (1973) described the partial automation of instrument No. 51, at Arosa, in which the instrument's temperature, Q lever settings, photomultiplier voltage, null balancing and data acquisition were controlled. Komhyr (1982, personal communication) reports a similar development using readily available electronic sub-assemblies which are programmable and can process data, and which can be added to existing instruments with the minimum of interference. Such semi-automated systems relieve the operator of much of the tedium of the operation of the instrument, and they ensure a more efficient and accurate data collection. They are especially valuable for the collection of Umkehr data. It is to be hoped that their use becomes more widespread.

7.5 Summary

(i) The success of the Dobson network is dependent on the continued goodwill and cooperation of the many independent institutions throughout the world who own and operate the instruments.

(ii) The instrument is manually operated. Careful attention is needed to the human aspects of its operation. Instructional material, and therefore actual practice, has varied in the past, but the new WMO Operations Manual (Komhyr, 1980b) should gradually unify practices throughout the network. It would be desirable to institute a comprehensive quality assurance programme.

(iii) The accuracy of extraterrestrial constants independently determined under particularly clear and stable atmospheric conditions can be equivalent to an accuracy of better than 1% in the mean AD ozone estimates. However, under more usual conditions, a figure of 5% or more is common. The resulting ozone errors vary inversely with airmass.

(iv) Extraterrestrial constants for network instruments are best obtained from direct intercomparisons against well-calibrated reference instruments. Successive intercomparisons over many years have shown that AD calibrations can be maintained to within 3% (in mean ozone) for most instruments, and to within 1% for perhaps a third of the instruments.

(v) Errors were present in the calibration of the World Reference Dobson Spectrophotometer No. 83 between 1972 and 1976, but the effect on the standard AD ozone estimation was only about 0.4%. The errors for other band combinations amount to several percent however. The errors were transferred to the instruments calibrated against No. 83 at the 1974 Belsk intercomparison. The 1977 Boulder intercomparison results implicitly include corrections for these errors in the Belsk-calibrated instruments present.

(vi) The present reliance on only one primary reference instrument is unsatisfactory. A further two instruments should be upgraded to the primary reference quality and the mean result of the three instruments taken to represent the World Standard.

(vii) There are a number of important problems yet to be resolved in how to best apply to archived data the corrections deduced from intercomparisons.

(viii) Routine (usually monthly) tests allow the detection of calibration changes equivalent to errors of a few percent in mean AD ozone estimations. Travelling standard lamps can ensure a network consistency in extraterrestrial constants equivalent to 2% in mean AD ozone.

(ix) The precision or standard error, of individual AD ozone measurements is in the 0.5% to 1% range for normal circumstances. Systematic errors associated with routine operation, such as due to instrument temperature drifts or poor choice of measurement type, might add a further 1% to 3% error, depending on the circumstances.

(x) Most systematic error sources become much greater at higher latitude sites, owing principally to the lower light levels, higher differential absorption, and more difficult observing conditions encountered there. Less accurate estimation methods, e.g. CD direct sun, often must be used.

(xi) Uneven temporal and spatial sampling may result in errors in some average data statistics of up to a few percent on occasion. More study of this problem is needed.

(xii) The development and use of systems which semi-automate the Dobson instrument should be encouraged. Such systems improve the quality and quantity of data collected, and are especially valuable for Umkehr measurements.

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Forward to Electronics

8. ELECTRONICS

8.1 Accuracy considerations

The original Dobson instrument electronic system (Dobson, 1931) was quite advanced for its day, though by today's standards it was relatively simple. It comprised a photocell, an AC amplifier, a motor driven chopper and commutator, and a microammeter display. Subsequent developments (Normand and Kay, 1952; Else et al., 1968) Olafson, 1968; Raeber, 1973; Komhyr and Grass, 1972; Chopra et al., 1977; Michiej and Sztanga, 1981; and Westbury et al., 1981) have altered various of the components of the system, and have thereby greatly improved its performance, but the basic design has remained unchanged. The replacement of the photocell by a photomultiplier was an especially important improvement. Komhyr and Grass (1972) describe a number of problems with the original componetry, in particular, bulky power supplies, tube amplifiers which were electrically noisy and for which parts were difficult to obtain, and dirty and electrically noisy copper split-disc electromechanical commutators. Most instruments nowadays are fitted with solid state amplifiers and power supplies and with optical switch "commutators", such as are described by Komhyr and Grass (1972).

The electronics system has a number of features which prevent it from being an important error source. Firstly, the use of the null detection method means that there is no need for linearity of response or long term constancy of response. Secondly, the AC detection system is insensitive to constant DC sources, such as photomultiplier dark current. Thirdly, the 27.5 Hz (or 33 Hz) frequency of the chopper wheel/commutator device effectively rejects AC leakages, in particular that coming from 50 Hz (or 60 Hz) mains supplies.

Component failures may make the instrument unuseable on occasion, but generally problems in the electronics system manifest themselves not as any systematic error, but as increased electrical noise which is seen as an increase in the unsteadiness of the microammeter needle. This results in an increase in the random error of the measurement and a loss of sensitivty, and hence in a reduction of the operating range of a given measurement type (e.g. AD direct sun). Komhyr and Grass (1972) and Komhyr (1980b) give practical details on the components, the adjustments and the maintenance required to obtain optimum performance.

Photomultipliers can be a source of systematic error. Photomultipliers are valued for their great sensitivity, linearity and dynamic range, and the types used in the Dobson instrument are usually the RCA 1P28 or EMI 9781 side window types. (See manufacturers' handbooks, such as RCA, 1970; and EMI, 1970.) The instrument's relative spectral sensitivity constants K_k (see equations 1.6 and 1.7) depend directly on the photomultiplier's effective spectral sensitivity, and this can vary in several ways.

Cathode spectral sensitivities are temperature dependent, but the dependences are poorly known. In the spectral region 300 to 350 nm the temperature dependence of caesium antimony cathodes is about 1.5×10^{-3}% (°C nm)$^{-1}$, (RCA, 1970). If this value is also typical of the RCA 1P28 caesium bismuth cathode and the EMI 9781 cathode, then the temperature dependence of relative sensitivity for a Dobson bandpair of 20 nm separation would be 0.03% °C^{-1}, which would give, for a maximum temperature range of 30°C, a maximum range in the bandpair's extraterrestrial constant of about 0.004, or equivalently, a 1.5% range in the C bandpair's ozone estimate. The data for caesium antimony show the dependence to be similar for all bandpairs and hence its effect would be largely eliminated in double bandpair ozone estimate. Of course these are just estimates, and the actual temperature dependences remain to be determined.

Cathode sensitivity and cathode spectral sensitivity can vary significantly spatially across a photomultiplier's cathode. Variations in effective spectral sensitivity therefore can occur if the spatial distribution of the illumination of the cathode is varied, and for this reason a small lens, L_5 (see Figure 1.2), is placed at S_5 to focus a fixed image of prism P^2 onto a fixed area of the cathode. The photomultiplier's position must of course remain fixed. Also, the prism P^2 must be fully and uniformly

illuminated. Variations in effective relative spectral sensitivity can be detected, and hence corrected, by means of the standard lamp test, and such tests should always be done both before and after any adjustment or replacement of the photomultiplier or lens L_5.

Variation in effective spectral sensitivity can also occur as a result of variations in the cathode to first dynode voltage, owing to the combination of the spatial variation in cathode spectral sensitivity and the spatial dependence of cathode emission and dynode collection on applied voltage. A common method used to avoid this problem is to fix the voltage between the cathode and first dynode (and sometimes also between the first and second dynodes) by means of zener diodes, but this approach does not appear to have been taken with, or considered for, the Dobson instrument. The very great range in the ultraviolet light intensity being measured requires a very large variation in photomultiplier sensitivity and hence a large variation in overall applied voltage. Thus there certainly exists the potential for such spectral sensitivity variations.

Photomultiplier sensitivity is very dependent on applied high voltage, by typically 10% for each 1% change in voltage, and photometric instruments generally need highly stable high voltage supplies. However, the Dobson instrument's AC null detection system is relatively insensitive to mains ripple, drift and other minor fluctuations, and so requires only modest stability from its photomultiplier power supply.

It would be desirable for further investigations to be made of the temperature and voltage dependences of photomultiplier relative spectral sensitivity in Dobson instruments. The tests could be readily made with the aid of standard lamps of sufficient brightness.

8.2 Summary

(i) The basic design of the electronic system is simple and robust, and the system is not an important source of systematic error under usual operating conditions.

(ii) Deficiencies in the electronic system generally result in decreased sensitivity and increased signal noise and therefore in limited operational range and greater random error. The introduction of photomultipliers, solid state amplifiers and solid state commutating switches has significantly improved the system's performance and reliability.

(iii) The photomultiplier's relative spectral sensitivity may have small temperature and voltage dependences involving ozone estimate errors of possibly more than 1%. These should be investigated further.

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Forward to Ozone Absorption Coefficients

9. OZONE ABSORPTION COEFFICIENTS

9.1 Introduction

The accuracy required of the ozone absorption coefficients depends on the application. Within the Dobson network there is a need for consistency between the various measurement types and hence between the coefficients of the various bandpairs. Within a larger integrated observing system comprising many different sorts of instruments, both ground based and satellite based, there is a more general need for consistency of coefficients throughout the whole spectrum. Absolute accuracy is usually of little significance, but it can be important for some purposes, such as atmospheric chemistry and radiative transfer studies. The temperature dependences of the coefficients must also be considered.

Several papers in 1980 focussed on the question of the coefficients' accuracy. These papers, by Klenk (1980), Komhyr (1980a) and DeLuisi (1980), and a brief review of them by Mateer (1981), showed significant inconsistencies between the independent laboratory absorption data, and between the coefficients used by different instrument types and by different bands within individual instrument types. Also, in Komhyr (1980a) it is argued that the standard Dobson AD ozone estimation is too large by about 5% and that this is probably due to error in the standard AD coefficient. Before considering these papers further, it is necessary to review the considerable amount of work done on the topic before 1980.

9.2 Laboratory spectral absorption measurements

The ultimate source of ozone absorption coefficients is the laboratory measurement of the spectral transmission of a chemically determined quantity of ozone. An absorption coefficient spectrum is shown in Figure 1.1. The measurements are by no means simple. The concentration, temperature and purity of a range of ozone samples must be accurately determined, the linearity and stability of the detection method must be ensured, the monochromator's wavelength calibration and stability must be verified, and stray light in the equipment must be rigorously rejected if it is not to swamp the very small amount of energy in the very narrow bands (less than 0.1 nm) being measured. The situation is in some ways similar to that of the field measurement of atmospheric ozone by UV optical means. However it would appear that the strenuous efforts made over many years to investigate and improve the field instruments, Dobson and other, have not been sufficiently well supported by similar efforts in the laboratory.

The most widely used ozone absorption coefficient data are those of Vigroux (1953). We should not be too surprised to find that his data have been found wanting when applied to the very specific purpose of atmospheric ozone measurement with the Dobson instrument, since the scope of his experiments was very broad. The main aims were to investigate the wide differences in absorption coefficients measured by earlier workers, notably Buisson and Fabry (1913) and Ny and Choong (1933), to create an homogeneous set of coefficients over a wide and well-detailed spectral range from 230 nm to 10,000 nm, and to investigate the temperature and pressure dependences of the coefficients. Indeed Vigroux (1967) later clearly stated that the measurements were made without the least knowledge of their possible application to the Dobson instrument. Ozone absorption coefficients derived from the Vigroux (1953) data at -44°C, corresponding to stratospheric temperatures, were used for the Dobson instrument from 1 July 1957 to 31 December 1967. They were found to be about 36% smaller than the coefficients previously in use which were derived from Ny and Choong (1933) (Dobson, 1957).

Also in 1953, measurements were made in the UV and visible regions by Inn and Tanaka (1953), but only at 18°C. Their results at this temperature differ from Vigroux's by up to 7% in some wavelength ranges, and no use has been made of them in the Dobson instrument. Further laboratory measurements have since been made by Hearn (1961), DeMore and Raper (1964), Vigroux (1967), Griggs (1968) and Simons et al. (1973), and another effort currently underway has been reported by Bass and Paur (1981). Vigroux's 1967 paper was specifically aimed at the Dobson instrument and shall be discussed in following paragraphs. Limited comparisons and discussions of these data sets may be found in Hudson (1971 and 1974) and Klenk (1980). Klenk's tabulations of band-integrated coefficients, some of which are reproduced here in Table 9.1, show differences of up to 15% for Dobson bands in the 300 nm to 340 nm region. It should be noted that all of the available data have limitations of one sort or another, particularly those of limited spectral range, limited spectral density of measurements, and limited temperature range, which restrict their accuracy or their direct application to the Dobson instrument bands. E. Vigroux (personal communication) has pointed

out that the spectral density of his 1953 data generally did not justify the precision implied by the standard 1957 to 1967 coefficients. He states that for the short wavelength C band, values of 0.8 or 0.9 atm-cm^{-1}, depending on the interpolation used, would have been as equally valid as the standard 0.865 atm-cm^{-1} value.

TABLE 9.1

Comparison of Dobson instrument ozone absorption coefficients and their combinations. All data are corrected to either -44°C or -50°C.

Type	Laboratory Spectra					Dobson experiments					Ad hoc		Units
Original Source Original Temp Obtained from	VIG53 -44 DOB57	VIG67 18 VIG67	VIG67 18 BSH	ITN53 18 KLK80	SIM73 18 KLK80	DOB63 18 lab	VIG67 18 lab	W&P71 -50 lab	DOB63 atmos Oxf'd	DOB63 atmos Edm'n	IOC68 W&P71	KMH80 KMH80	°C
Wavelength, nm													
305.5	1.882	1.863	1.871	1.999	2.139	-	-	-	-	-	-	1.976	atm-cm^{-1}
308.8	1.287	1.276	1.284	1.330	1.400	-	-	-	-	-	-	1.287	" "
311.45	0.912	0.850	0.858	0.922	1.014	-	-	-	-	-	-	0.903	" "
317.6	0.391	0.377	0.373	0.400	0.422	-	-	-	-	-	-	0.395	" "
325.4	0.120	0.117	0.112	0.123	0.123	-	-	-	-	-	-	0.120	" "
329.1	0.064	0.070	0.064	0.075	0.087	-	-	-	-	-	-	0.064	" "
332.4	0.047	0.043	0.044	0.050	0.050	-	-	-	-	-	-	0.047	" "
339.8	0.017	0.012	0.012	0.017	0.021	-	-	-	-	-	-	0.017	" "
A	1.762	1.746	1.759	1.876	2.016	1.742	1.756	1.748	1.741	1.742	1.748	1.856	atm-cm^{-1}
B	1.223	1.206	1.219	1.255	1.313	1.142	1.133	1.159	1.144	1.155	1.140	1.223	" "
C	0.865	0.807	0.814	0.872	0.964	0.808	0.799	0.810	0.791	0.804	0.800	0.856	" "
D	0.374	0.365	0.360	0.383	0.401	0.354	0.360	0.360	0.353	0.354	0.360	0.378	" "
AD	1.388	1.381	1.398	1.493	1.615	1.388	1.396	1.388	1.388	1.388	1.388	1.478	" "
CD	0.491	0.442	0.454	0.489	0.563	0.454	0.439	0.449	0.438	0.450	0.440	0.478	" "
A/D	4.711	4.784	4.886	4.898	5.027	4.921	4.878	4.856	4.932	4.921	4.856	4.910	
B/D	3.270	3.304	3.386	3.277	3.274	3.226	3.147	3.219	3.241	3.263	3.167	3.235	
C/D	2.213	2.211	2.261	2.277	2.404	2.282	2.219	2.250	2.241	2.270	2.222	2.265	

Note: The author abreviations are: VIG-Vigroux, ITN-Inn and Tanaka, SIM-Simons et al., DOB-Dobson, W&P-Walshaw et al., and Powell,
KMH-Komhyr, KLK-Klenk, and BSH-Basher. All the sources are discussed in the text. The purpose of including the author's (BSH)
calculations is to show the degree to which interpretations of the Vigroux 1967 data may differ. Those sets scaled to
give the AD coefficient equal to 1.388 are shown by underlining thus 1.388.

9.3 Investigations using the Dobson instrument

Indirect information on the accuracy of the absorption coefficients used with the Dobson instrument may be found from the consistency of the ozone measurements made with different pairs of bands. A preliminary discussion of this approach is made in Dobson and Normand (1962). A basic limitation is the lack of information on the exact effect of aerosol spectral attenuation on the derived coefficients (Basher, 1976). Dobson (1963) reported 10% differences between different band pairs and used data from days with clear skies at Oxford, England to estimate a consistent set of coefficients, scaled such that the AD band combination's coefficient remained as before at 1.388 atm-cm^{-1}. These coefficients differed from the standard coefficients by -1.2%, -6.5%, -8.6% and -5.6% for the A, B, C and D bandpairs respectively. This approach was followed by a number of others whose results, summarised by Shah (1968), show differences, one with another, of several percent, this probably being due to aerosol scattering effects and to differences in instrument adjustment and calibration.

An alternative method of determining the absorption coefficients appropriate to the Dobson instrument bandpairs is to use the instrument itself to measure the coefficients directly in the laboratory. Measurements of this sort by Dobson (1963) at 5°C and 50°C, when corrected to -44°C and scaled such that the AD band combination's coefficient was 1.388 atm-cm^{-1}, agreed to within 2% of his field measurements referred to above. No measurement of laboratory ozone amount was made. Vigroux (1967) carried out a similar experiment at Mont-Louis in the French Pyrenees at about 18°C and using direct sunlight as a source. The absolute amount of ozone was determined from near-simultaneous photographically recorded transmission spectra together with the spectral absorption coefficients for 18°C found by Vigroux (1953). The correction of the coefficients to the -50°C temperature chosen was made using the temperature dependences also reported by Vigroux (1953). The resulting ozone absorption coefficients were found to differ from the standard coefficients by 0.6% for the AD band combination and by -0.3%, -7.4%, -7.6% and -3.7% for the A, B, C, and D bandpairs respectively. Notice that these differences are very similar to those

found by Dobson (1963). Vigroux also redetermined the actual absorption coefficient spectra in much finer detail in the vicinity of the Dobson bands using the photographic spectrograph and again using the earlier 1953 work for temperature correction and absolute calibrations. The differences between the coefficients calculated from these "fine structure" measurements and the standard coefficients were -0.5% for the AD band combination coefficient and -0.9%, -1.4%, -6.7%, -2.4% for the A, B, C and D bandpairs respectively. The result for the B bandpair is not consistent with the direct measurements of Vigroux or Dobson, but the A, C and D results agree satisfactorily.

The evidence available in 1967 was sufficiently compelling that the International Ozone Commission recommended a new set of coefficients, 1.748, 1.140, 0.800 and 0.360 atm-cm^{-1} for the A, B, C and D bandpairs respectively to be used from 1 January 1968 onward. They are still currently used. The 1.388 atm-cm^{-1} value for the AD bandpair combination was retained partly to ensure the continuity of the data records, and partly because the new Vigroux (1967) values of 1.396 atm-cm^{-1} and 1.381 atm-cm^{-1} were very close to the existing value. The evidence does not support Komhyr's (1980a) view that the retention of 1.388 was "highly arbitrary." At the same time, it can be noted that this standard of absolute calibration was totally reliant on the Vigroux (1953) measurements which show some differences with other experimenters' data sets, and that there remained an uncertainty of about 5% in the Vigroux (1967) coefficients for the B wavelength pair, which, even today, remains unexplained (Vigroux, personal communication).

Further efforts to determine mutually consistent ozone absorption coefficients using the Dobson instrument in the laboratory at low temperatures were made by Walshaw et al. (1971) and Powell (1971). The results show excellent agreement one with another, and their mean values estimated by the author for -50°C differ from the standard 1968 values by 1.5% or less. Walshaw et al. also raise the question as to the importance of the light source used for determining effective ozone absorption coefficients with the Dobson instrument. They state that Vigroux considered it important to use direct sunlight since the weighting of the coefficient spectrum by the spectrally very variable solar spectrum would give different results to those found when an incandescent lamp is used. Measurements by Dobson (1963), Walshaw et al. (1971) and Powell (1971) on lamps and sunlight showed no differences, however. The author has investigated this question by calculating the band-integrated coefficients that would be measured for various sources, using the 0.05 nm spectra described in Section 5.2. Table 9.2 lists the coefficients for a 3000°K blackbody lamp and the deviations from these values for direct sunlight at various conditions of airmass and ozone. The results give support to both sides of the arguments on the one hand relatively large deviations, of up to 6%, do exist for some wavelength bands, but on the other hand, the deviations for the standard bandpairs and particularly the AD band combination are relatively small.

TABLE 9.2

Calculated effect of the light source used in the determination of Dobson ozone absorption coefficients.

Wavelength or bandpair	Lamp, 3000 K blackbody. Coefficient and its percent difference from the unweighted value.		Direct sunlight, for airmass mh and total ozone X. Percent difference relative to lamp coefficients					
			μ_h = 0 X = 0	μ_h = 1 X = .2	μ_h = 1 X = .3	μ_h = 1 X = .4	μ_h = 2 X = .3	μ_h = 3 X = .3
nm	atm-cm^{-1}	%	%	%	%	%	%	%
305.5	1.8644	-0.04	0.20	0.11	0.08	0.04	-0.04	-0.15
308.8	1.2823	-0.06	0.21	0.02	-0.06	-0.15	-0.36	-0.67
311.45	0.8549	-0.08	0.56	0.33	0.22	0.12	-0.13	-0.49
317.6	0.3692	-0.09	1.44	1.22	1.12	1.02	0.78	0.44
325.4	0.1141	-0.50	-1.14	-1.87	-2.14	-2.41	-3.14	-4.14
329.1	0.0648	-0.81	-2.35	-3.35	-3.70	-4.04	-5.00	-6.25
332.4	0.0425	-0.66	1.69	1.06	0.87	0.68	0.06	-0.73
339.8	0.0124	0.00	0.11	-0.21	-0.26	-0.31	-0.42	-0.57
A	1.7503	-0.01	0.29	0.24	0.22	0.20	0.16	0.11
B	1.2175	-0.02	0.35	0.20	0.13	0.06	-0.11	-0.38
C	0.8124	-0.05	0.50	0.29	0.19	0.09	-0.14	-0.48
D	0.3568	-0.10	1.50	1.27	1.17	1.06	0.82	0.47
AD	1.3936	0.02	-0.02	-0.02	-0.02	-0.02	-0.01	-0.02

9.4 Temperature dependence of absorption coefficients for the Dobson instrument

Ozone's absorption in the 300 nm to 340 nm wavelength region increases with temperature (Vigroux,

1953; Simons et al., 1973). Vigroux's measurements, made at nine temperatures, show that the principal minima increase steadily with temperature, by as much as 0.7%°C^{-1} for deep minima beyond 315 nm, whereas the principal maxima show a turning pattern, at first decreasing, by about 0.1%°C^{-1} from -92°C to -75°C, remaining relatively constant from there until -44°C, then increasing, slowly at first, then more rapidly. Fortunately, the dependences are relatively low for the important region of 305 nm to 318 nm and for stratospheric temperatures. Band integrated dependences have been estimated for the A, B, C and D bandpairs respectively at 0.11, 0.10, 0.18 and 0.12%°C^{-1} by Walshaw et al. (1971) and at 0.14, 0.17, 0.18 and 0.27%°C^{-1} by Thomas and Holland (1977). The differences are indicative of the uncertainty of the estimations. Walshaw et al. gave histograms of temperature at the region of the main ozone maximum for 1965 at four sounding stations, while Thomas and Holland integrated mean ozone temperature from a number of standard ozone and temperature profiles, and both arrived at a maximum range of about -40°C to -65°C. For this range the errors in mean absorption coefficient would be about ±1% to ±3%, depending on the bandpair, and about ±l.5% for the AD band combination. Any changes in the mean profiles of both temperature and ozone induced by changing amounts of chlorofluorocarbons and carbon dioxide might conceivably result in a systematic change of 5°C in the mean ozone temperature and therefore of 0.5% in the mean AD absorption coefficient. It can be noted that at present there is no firmly established reference temperature for which coefficients are defined and there are few, if any, experimenters who correct for changing mean stratospheric temperature.

9.5 Absolute accuracy of Dobson absorption coefficients

The strict definition of band-integrated absorption coefficients (equation 6.1) involves weightings of the laboratory absorption data by the spectra of solar irradiance, atmospheric transmittance and instrument transmittance. However the Dobson instrument's fixed coefficients are usually calculated from just simple weightings by nominal triangular or trapezoidal slit transmittance functions. This leads to small errors, since solar irradiance and atmospheric transmittance are spectrally very variable, and the true shape of the Dobson transmittance functions are poorly known (see Sections 2, 5, and 6). Further errors arise from the interpolation of the currently available absorption spectra in data-sparse regions, and from the bandwidth effect (see Section 6). Overall, these various factors may contribute errors of up to 1 to 3%, depending on the circumstances, which are in addition to the errors associated with the laboratory data and their temperature dependences. The differences between the coefficients calculated by Vigroux (1967) and by the author, and shown in Table 9.1, under VIG67 and BSH respectively, give some indication of the size of the errors.

Klenk's (1980) principal aim was to determine the most suitable ozone absorption coefficients for use with the satellite back-scattered ultraviolet (BUV) experiments. He took each of the laboratory data sets of Vigroux (1953 and 1967), Inn and Tanaka (1953) and Simons et al. (1973), and computed band averaged coefficients for both BUV and Dobson instruments at -44°C, correcting the latter two sets from 18°C and -78°C respectively, with the aid of the temperature dependences determined by Vigroux (1953). The results are reproduced in Table 9.1, along with other comparative data. Differences between the Vigroux data and the Inn and Tanaka data are generally less than 6%, but differences between these data and those of Simons et al. are larger, rising to 25% in one case. The only independent test of the merit of the various coefficients is that of consistency, as evidenced for example by the A/D, B/D, and C/D ratios in the table, and by the data comparisons given by Klenk of Dobson CD versus AD band combinations, BUV-B bandpair versus Dobson AD, and BUV-A versus BUV-B bandpairs. These tests indicate that the Inn and Tanaka coefficients (for -44°C) are at least as consistent as the Vigroux (1967) coefficients. All of the band-integrated data will suffer from errors of interpolation of course.

In his examination of the absolute accuracy of the Dobson instrument, Komhyr (1980a) compared sets of ozone measurements made by the Dobson instrument with those made by other types of ozone measuring instruments, and concluded on the basis of five separate comparisons that the Dobson AD measurements may be too high, by about 5%. However, it has since been shown that each of the comparisons is subject to large uncertainties, and that for some, the data were not in fact independent (Basher, 1982b). There still remains the possibility of a small positive bias, though with an uncertainty of several percent. The preliminary NBS absorption cross sections now also indicate a small positive bias (A.M. Bass, W.D. Komhyr, personal communications).

The differences between the 1957 and 1968 standard A, B, C. and D absorption coefficients, and therefore between their resulting ozone estimates, cover a range of about 7%, while the corresponding

differences for the paired bandpairs, e.g. AD, BC, etc., extend to a range of 23% Komhyr (1980a). No special explanation is required for the large 23% range, since, as is discussed by Basher (1982b), its larger size is due solely to the linear combination of the differences of from +1% to +8% found in the individual A, B, C and D bandpair coefficients. These +1% to +8% differences are comparable with, and are almost certainly mostly due to, the uncertainties in the laboratory absorption data.

DeLuisi (1980) used the measurements of a UV double monochromator to estimate ozone amounts as a function of wavelength. The results, displayed as a spectrum of departures from the mean of the values between 298 to 313 nm, show a definite structure with an RMS departure of about 0.010 atm cm in ozone, or about 3%. This is twice the estimated measurement precision. The structure may be partly due to the bandwidth effect and the sensitivity of the ozone absorption coefficients and extraterrestrial irradiance to uncertainty in the instrument's wavelength calibration, since these are very spectrally dependent and could easily contribute spectrally varying errors of a few percent (Basher, 1982b). However, as suggested by DeLuisi, the error in the Vigroux (1953) absorption coefficient data used to derive the ozone estimates must be considered a primary cause.

Calculations of band-integrated coefficients by the author (see Section 5) for the Brewer grating instrument show agreement to better than 2% with the atmospheric estimations and the laboratory determinations of Kerr et al. (1977) for their band combinations "2,4" and "2,3,4", but for those band combinations involving the important shortest wavelength number 1 band, at 309.95 nm band, the calculated values were all too high within the range of 0.096 ±.004 atm-cm^{-1}, or about 10% in the coefficient at 309.95 nm. This suggests a systematic error at about 309 nm, either in the original Vigroux data, or in their interpolation by the author. Shaw (1979) found that his filter photometer measurements in the Chappuis band (500 to 700 nm) at Mauna Loa gave ozone amounts 17% lower than concurrent Dobson AD ozone measurements, though this may simply reflect the unsuitability of the Chappuis band for ozone measurement, or an even lower accuracy of the absorption coefficients in that band.

It is clear that few improvements in the absolute accuracy of ozone measurements can be expected without further improvement in the available laboratory ozone absorption coefficient data. Fortunately, the ozone absorption measurements by Bass and Paur (1981) at the United States National Bureau of Standards (NBS) are being made for just this purpose, and are now becoming available. The International Ozone Commission has recently established (in 1982) a working group to thoroughly examine the absorption coefficient question, and if possible, to recommend new Dobson coefficients based on the NBS data (C.L. Mateer, personal communication). The working group will, among other things, assess the accuracy of the NBS data and directly measure the spectral transmittances of Dobson instrument bands. McPeters and Bass (1982) report an accuracy of 2% or less for the NBS data. This, together with the various other uncertainties in the calculation of band?integrated coefficients discussed in this Section, and in Basher (1982b), suggests that the total uncertainty in the effective coefficients of UV ozone instruments may become about 2% in the near future.

9.6 Summary

(i) Published ozone absorption coefficient spectra mesured by independent investigators can differ by 10% or more in the 300 nm to 340 nm wavelength region. The implied magnitude of systematic error in the determination of atmospheric ozone is intolerable for present-day measurement needs.

(ii) The self-consistency of the Dobson instrument's standard A, B, C, and D bandpair absorption coefficients appears to be better than 2%.

(iii) There is some evidence that the absolute values of the standard absorption coefficients used for the Dobson instrument may be too low by a few percent, i.e., that Dobson ozone column amount estimates may be too high by a few percent.

(iv) The accuracy of band-integrated ozone absorption coefficients is limited by their dependences on the method of interpolating laboratory absorption data, on stratospheric temperature, and on the detailed UV spectral characteristics of the sun, the atmosphere and the instrument. The dependence on mean ozone layer temperature limits the accuracy of the fixed AD coefficient to about ±l.5%.

(v) The agreement between spectrally independent instruments in the UV region (e.g., BUV instrument versus Dobson instrument) at present cannot be expected to be better than about 3%.

(vi) A greatly improved accuracy, of 2% or less, has been reported for the new laboratory absorption measurements of Bass and Paur (1981). These data are being examined by the International Ozone Commission with a view to recommending a new, more accurate set of coefficients for the Dobson instrument.

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Forward to Atmospheric Scattering

10. ATMOSPHERIC SCATTERING

10.1 Introduction

The atmosphere scatters part of the radiation of the solar direct beam, and in doing so, attenuates the direct beam intensity and creates skylight. It is principally the effect of the attenuation on the direct beam measurements that is considered here, though some comment also will be made on the measurement of the scattered light of tile zenith sky. Errors in the direct beam measurements due to skylight scattered into tile Dobson instrument's field of view are considered in Section 4 on stray light. The scattering processes divide conveniently into scattering by molecules of the air (Rayleigh scattering), by aerosols (particles of approximately 0.05 to 5μ in diameter), and by clouds (water droplets or ice crystals of approximately 5μ to 500μ in diameter). Virtually all the attenuation by particles is due to scattering, i.e., is energy conserving.

The physics of the scattering processes is well known. However, the great temporal and spatial variation in the concentrations and characteristics of the scattering media make it virtually impossible to calculate the scattering effects for any one situation. Aerosols vary greatly in composition, concentration, size distribution and refractive index, and clouds are notoriously variable and transitory. The exception, of course, is Rayleigh scattering, which essentially depends only on surface air pressure, and which can be calculated accurately. The only means available to cope with the effects of aerosols and clouds on ozone measurements are those of optimum experiment design and of empirical correction. In both cases the methods must be tested not only by their effect on actual observation sets, but more importantly, by their consistency with physically well based models of atmospheric scattering.

10.2 Rayleigh scattering

Rayleigh scattering is approximately proportional to the inverse fourth power of wavelength, and a simple approximation for the base 10 scattering coefficients used in the Dobson instrument equation is:

$$\beta = 1.787 \times 10^{10} \lambda^{-4.25} \qquad (10.1)$$

where λ is the wavelength in nm. The approximation is accurate to 0.2% and the coefficients themselves are thought to be accurate to about 1%. Further discussion and tabulations of Rayleigh scattering coefficients may be found in Penndorf (1957). Hoyt (1977) and Frohlich and Shaw (1980) have claimed that these coefficients are in error by two or three percent, but this has been strongly disputed by Young (1980 and 1981) on the grounds of incorrect definitions.

From the equations of Section 1 it can be calculated that the Rayleigh scattering contribution to an estimation of ozone column amount using direct sunlight is equivalent to about 0.066, 0.138, and 0.009 atm cm for the A, C and AD band combinations respectively. The standard AD estimation is clearly insensitive to error in the Rayleigh scattering coefficient, and even for the C bandpair an accuracy of 1% would be acceptable. At the same time, it is desirable that the controversy referred to above be resolved and the coefficient error reduced to below the 1% level. It should be noted that the Rayleigh scattering coefficients for the Dobson instrument given by equation 10.1 and by Table 1.1 apply to a mean sea level pressure of p_o = 1013 mb, and that at other pressures, p, which may be due to natural air pressure variations or to the elevation of the Dobson station, the coefficients must be corrected in proportion to p/p_o. Generally, the corrections are significant only for a single bandpair combinations, and even then, only for pressure deviation of 1% or more.

Measurements of the light of the zenith blue sky can be used to estimate ozone column amounts, and to estimate an approximate profile of the ozone concentration with height using the Umkehr method. The zenith light is the integral with height of the light produced principally by Rayleigh scattering, but also by aerosol scattering. Because most of the molecular atmosphere lies below the bulk of the ozone layer, the absorption path for zenith light is similar to that of direct sunlight, and the zenith log intensity ratio is therefore closely related to the direct solar log intensity ratio. The relationship does

depend on the zenith angle of the sun and the column amount and height distribution of the ozone concentration owing to their effect on the absorption components of the above integral. In practice, large numbers of near-simultaneous measurements of direct sun and zenith blue log intensity ratios are used to construct tables or charts which can then be used for empirically estimating the ozone column amounts (for examples of charts, see Figures 2 and 3 in Appendix A).

The accuracies of the zenith blue and zenith cloudy estimations of ozone amount are affected by natural variations in ozone profiles and surface albedo, and may be poor, i.e., worse than 10%, in conditions of high airmass, high ozone and high albedo (Mateer et al, 1977). Other systematic errors such as stray light may cause errors. Errors due to aerosol extinction along the beam, as distinct from aerosol scattering into the beam, will be similar for zenith sky and direct solar radiation and so should not contribute significant additional aerosol error. Accuracies can be estimated from the comparison data used to create the empirical charts or tabulations. Dobson and Normand (1962) indicate an RMS deviation in the difference of direct sun and zenith blue sky estimations of 0.005 atm cm or about 1.5% for the AD band combination. Komhyr (1960) reports differences equivalent to a 1.5% RMS deviation also, and Farkas (private communication) finds a similar value for her AD measurements at Invercargill. These will be the minimum errors. Under routine operational conditions, larger errors, perhaps two times larger, should be expected owing to variations of the error with airmass, with instrument adjustment and with observational practice. Extracts from Komhyr (1960) concerning his study of the accuracy of both clear and cloudy zenith measurements are presented in Appendix A, in order to make the results of this useful study more accessible.

The consideration of error sources associated with ozone profile estimations using the Umkehr method and the Dobson instrument is beyond the scope of the present work. However, most of the error sources discussed here for ozone column measurements will have a direct effect on the accuracy of the Umkehr estimations, and because the technique provides a limited information content and is sensitive to input parameters and the accuracy of the raw measurements, some of the error effects are likely to be significant. For further information on the Umkehr technique see DeLuisi and Mateer (1971), DeLuisi (1979), Mateer and DeLuisi (1981), and Dave et al. (1981). It can be noted that the modelling of Umkehr zenith intensities also provides the means for analysing the accuracy of the zenith blue sky estimation of ozone column amount.

10.3 Aerosol scattering

Aerosol scattering coefficients (i.e., coefficients to base 10 of attenuation or extinction) experimentally measured in the visible at 500 nm range from 0.02 for very clear conditions to 0.5 for particularly hazy conditions (Flowers et al., 1969). Monthly average values in the United States in summer have maxima that range from 0.1 to 0.3. A value of 0.3 usually gives a milky sky in which clouds are difficult to discern. In the 300 to 340 nm region, the figures are likely to be one to two times these values.

The principal defences of the Dobson instrument against the effects of aerosol scattering lie in, firstly, its optical design, and secondly, the variability of aerosol characteristics, which can be expected to result in a spectrally smooth extinction spectrum. By making only relative and not absolute measurements, and by siting the bands close together and in a spectral region where the ozone absorption changes rapidly with wavelength, Dobson was able to discriminate strongly against a smooth and flat aerosol attenuation. From the work of Rat'kov (1971) it seems that the maximum ozone errors due to aerosols for the A, C and D bandpairs are about ±0.029, ±0.065 and ±0.156 atm cm respectively. Shah's (1968) work indicates maxima of about two-thirds of these values. When the aerosol extinction spectrum is constant, there will be no error. Further, by combining the measurements of two bandpairs, such as in the standard AD method, it is possible to discriminate against aerosol error for the more general case of a linearly varying extinction spectrum.

If, as is reasonable, one assumes that the aerosol error contribution to X_{AD} is a few percent or less, it is possible, with accurately calibrated instruments, to use the differences between the single bandpair ozone estimations and X_{AD} :

- to determine corrections to the single bandpair ozone estimations (Shah, 1968; see also

Ramanathan and Karandikar, 1949);

- to determine trends in this aerosol error correction (Kulkarni, 1973);

- to determine the gradient of the assumed linear aerosol spectral attenuation function (Basher, 1976).

Kulkarni (1973) went further and attempted to determine, using X_A and X_D, the aerosol error contribution to the long term trend in X_{AD}, but the method was shown by Basher (1976) to be invalid owing to a lack of independence in the equations used.

In an attempt to better describe the aerosol extinction spectrum and its effects, Basher (1976) expressed the spectrum explicitly as a quadratic polynomial:

$$\delta(\lambda) = \delta(\lambda_0) + g_1(\lambda - \lambda_0) + g_2(\lambda - \lambda_0)^2 \qquad (10.2)$$

and obtained expressions for the "true" ozone and the coefficients g_1 and g_2. The approximation was found to explain very well the systematic and previously unexplained differences amongst a set of double bandpair measurements given by Dobson and Normand (1962) and gave an ozone estimation about 4% higher than the X_{AD} value. However Gardiner (1978) challenged this approach on mathematical grounds, pointing out that the restriction of the polynomial to a quadratic was arbitrary unless well supported by independent knowledge of the extinction spectrum, and worse, that the inclusion of higher orders of polynomial increases the sensitivity of the ozone determination to experimental uncertainty, to the extent that any possible improvement in accuracy due to a more complete representation of the aerosol extinction spectrum could be swamped by the increase in the effect of experimental uncertainty. It is worth noting that Shah (1979) proposed a power law approximation which may be criticised on exactly the same grounds.

The situation at that time was quite unsatisfactory in that the questions as to which was the best estimation method and what the aerosol error was in each case remained unanswered. A simple answer to the second question was given by Basher and Thomas (1979). They considered the Mie extinction efficiency spectrum for a nominal aerosol particle and calculated the maximum efficiency difference for the bands of a Dobson instrument bandpair, firstly for a monodisperse aerosol, and secondly for aerosols of realistic polydispersion and optical depth. Of note is the way the variability in aerosol size and refractive index results in a relatively smooth extinction spectrum with at most two or three spectral features over the small range of wavelength of interest. The authors concluded that the maximum errors for the particularly hazy conditions of $\delta = 0.5$ are about 0.022, 0.048, 0.0106 and 0.009 atm cm respectively for the A, C, D and AD band combinations (cf. above-noted figures of Rat'kov, 1971; and Shah, 1968.) Most sites do not encounter such hazy conditions, and certainly for averages over periods of one month or more the error in the standard AD estimation will be 1% or less.

Mateer and Asbridge (1981) analysed a sample of 252 A, C and D band pair data in terms of the Basher (1976) and the Shah (1979) approaches as well as by a simple least square method. They note the four-fold increase in the sensitivity of the Basher and Shah methods to measurement uncertainty and conclude that the standard AD method is to be preferred, presumably on the grounds of simplicity and greater stability. Of course, there was no way of knowing which of the estimation methods had the least systematic aerosol error. Basher and Thomas (1980) calculated the propagation of nominal uncertainties in the A, B, C and D bandpair measurements through to the various multi-bandpair ozone estimations for various polynomial orders. They concluded that the uncertainties magnify rapidly as the polynomial order is increased, i.e., the equations rapidly become poorly conditioned, that for a given order there is little advantage in using more than the minimum number of bandpairs needed (in agreement with the above Mateer and Asbridge study), that the most practical combinations are those of the standard AD method and the quadratic ACD method, and most importantly, that the expected aerosol errors as determined by Basher and Thomas (1979) will rarely justify the use of more than the linear polynomial standard AD method.

Further insight into the effect of aerosol extinction can be gained from the calculation reported by

Thomas and Basher (1981) of Mie extinction efficiencies for monodisperse aerosols of constant optical depth, and the presentation of the resulting ozone errors as a function of particle diameter. This work shows clearly how the use of the polynomial models reduces the lower frequency components of the error spectrum (with respect to particle diameter) but at the expense of increasing the magnitude of the higher frequency components, how the polynomial methods magnify not only errors of measurement, but also errors in the appropriateness or accuracy of the polynomial model itself, and how, relative to the single wavelength pairs, the standard AD method serves to reduce markedly the error due to particles in the 0.0 to 1.0 um diameter range. Of particular note is the confirmation that for realistic size distributions and especially hazy conditions ($\delta = 0.5$), the maximum error in the AD estimation is about 0.010 atm cm.

10.4 Cloud attenuation

Very little of substance can be said about the effect of clouds on the measurement of ozone. Two measurement types are possible, the first being of the direct solar beam when the cloud is relatively thin, i.e., sufficiently thin that the measurements are not significantly affected, and the second being the zenith light from a cloudy sky, in which the log intensity measurement is empirically related to the measurement of the zenith blue sky and thence to the measurement of the direct solar beam. The empirical charts which are used are built up from years of simultaneous pair measurements. Further information on the methods may be found in Appendix A. When the cloud is optically thin, there will be uncertainty about the cloud-induced errors and about when to change the observation type from the direct sun type. On occasion, optically thin clouds may not be obvious to an observer, especially when the clouds are near the solar position, though the author's experience suggests that the AD ozone estimation is little affected even by quite noticeable amounts of cirrus and other thin cloud.

It may be useful to note a few theoretical considerations. From Mie theory it can be shown that for the large droplets of clouds the scattering efficiency is essentially spectrally flat, and hence, apart from minor refraction and reflection effects within the droplet, the spectral character of a solar beam passing through a cloud is largely unchanged. However, the intensity of the scattered light received by an instrument's field of view does have a small spectral dependence, owing to the spectral dependence of the angular distribution of the scattered light (cf. visible coloured rings around the moon). The intense scattering that occurs in clouds can quickly extinguish any beam and create in its place a very diffuse radiation flux. The mean optical path of the diffuse flux is greater than that of a direct zenith beam so there will be a small increase in absorption due to the presence of the tropospheric ozone within the cloud. The spectral character of the radiation emanating from the bottom of the cloud also depends on the spectral character of the radiation illuminating the cloud, both at the bottom from the irradiance of the ground, and at the top from the direct attenuated solar radiation and the Rayleigh scattered skylight. Its intensity and spectral character therefore will depend on the surface albedo, the cloud thickness and type and the solar zenith angle. It is possible to model these factors and their effect on column ozone measurements. The study by Mateer et al. (1977) is a worthwhile step in this direction.

The accuracy of measurements of ozone under cloudy conditions may be assessed through the comparison of quasi-simultaneous measurements under cloudy and clear conditions. Dobson and Normand (1962) indicate that RMS differences of about 0.010 atm cm, or approximately 3%, occur both for the comparison of AD measurements under zenith cloud and direct sunlight, and for the comparison of CC^{l} cloud measurements and AD direct sun measurements. For the same measurement types, Komhyr (1960) found similar values, of about 2.5% and 2% respectively. Further details of this work by Komhyr may be found in Appendix A. When the cloud thickness is great the differences can be greater, and on occasion differences as large as 0.200 atm cm have been found (Dobson et al., 1946, Dobson and Normand, 19621 and Kerr, 1973). Such unexplained large differences have been termed the "cumulus effect". The accuracy of any cloud measurement will depend on the quality of the empirical correction charts used, and on the constancy of the zenith light during the sequence of bandpair measurements. Under cloudy conditions this zenith light is frequently not constant, and this, together with the virtual impossibility of obtaining comparisons of cloudy sky and zenith clear sky measurements for some cloud types, means that often the cloudy sky ozone estimations will have relatively large errors.

Brewer and Kerr (1973) proposed the use of a polarizing filter to improve cloudy sky

measurements. The filter is oriented to eliminate the clear sky's singly scattered and strongly polarised component of Rayleigh scattering, and hence to greatly reduce the difference between the clear sky and cloudy sky measurements due to this component. They reported encouraging results using the Brewer grating spectrophotometer and subsequently Dobson (in Walshaw, 1975) and Mateer et al. (1977) supported the method's use with the Dobson instrument. However, Dziewulska-Losiowa's (1978) experiments with it were quite unsuccessful, and the method is not described in the WMO Dobson Operations Handbook (Komhyr, 1980b).

Owing to the difficulty of properly accounting for all the known sources of systematic error and for the uncertainties of observational practice, it would seem that the best means of assessing the accuracy of cloudy-sky measurements, and possibly also zenith blue sky measurements and focussed-image measurements, is by analysis of actual data sets, such as was done by Komhyr (1960 - see Appendix A also), and Dobson and Normand (1962). It is likely that further studies of this sort already exist in unpublished form. Bearing in mind the large contribution of these measurement types to the column ozone data archives, it is highly desirable that any such existing studies be reviewed and circulated, and that further studies be initiated by those familiar with the data and with good access to suitable data sets. Better methods or improvements to the old methods might also be devised.

10.5 Summary

(i) Although the physics of atmospheric scattering processes is well known, the great temporal and spatial variations of aerosol and cloud characteristics prevent the exact calculation of their effects on column ozone measurements. Instead, empirical methods must be used.

(ii) The current debate about the accuracy of the Rayleigh scattering coefficients needs to be quickly resolved. The coefficients now used with the Dobson instrument are probably accurate to 1%, which gives negligible error for the AD and CD ozone estimations and perhaps up to 0.5% error for the C ozone estimation.

(iii) The standard sea level Rayleigh scattering coefficients need to be corrected in proportion to a station's mean pressure altitude, and to its daily pressure variations. Usually this is only important for single bandpair combinations.

(iv) The RMS accuracy of the AD ozone estimations derived from measurements of zenith skylight is at best 0.005 atm cm, or about 1.5%, and may in general be twice this value.

(v) Maximum ozone errors for direct sun and zenith sky estimations due to aerosol extinction alone, and for the particularly hazy conditions of $\delta = 0.5$ are about 0.022, 0.048, 0.106 and 0.009 atm cm respectively for the A, C, D and AD band combinations. Very few sites ever experience such strong haziness and certainly for averages of one month or more the errors in AD estimations will be less than 1%.

(vi) The use of non-linear representations of the aerosol extinction spectrum, and hence of combinations of the A, B, C and D bandpairs which are more elaborate than the standard AD combination, leads to the magnification of experimental errors and is rarely, if ever, justified by the expected magnitude of the aerosol extinction error.

(vii) The RMS accuracy of the AD ozone estimation derived from measurements of the cloudy zenith sky is at best about 0.010 atm cm, or 2 to 3 per cent, and will be greater under thick or variable cloud. Under cumulonimbus clouds, and in the vicinity of thunderstorms, very large deviations, of up to 0.200 atm cm or over 50% may be encountered, but this may be due to a real ozone increase rather than to any error.

(viii) There is little readily accessible information on the accuracy of the zenith blue and cloudy zenith sky methods. It is desirable that any relevant unpublished atmospheric modelling studies or data analyses be circulated and that further studies be initiated. The

possibility of improvements to the methods should be considered.

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Forward to Interfering Absorption and Emission

11. INTERFERING ABSORPTION AND EMISSION

11.1 Introduction

Ozone provides by far the most dominant absorption in the near UV spectrum, which is as it should be, of course, if we are to measure ozone with any accuracy in this region. At the same time, there are other atmospheric gases which absorb in the near UV, and hence which can interfere with the measurement, as it is defined by equation 1.4. The most important of these are sulphur dioxide (SO_2), and nitrogen dioxide (NO_2) (Komhyr and Evans, 1980). There also exists, in principle, the possibility of interference from UV emissions by atmospheric gases and particles.

The effect of an interfering absorbing gas depends on its spectral absorption cross sections, and on the gas column amount and its spatial and temporal variation. For most atmospheric gases these quantities are not sufficiently well known for our purposes. In general, the spectral cross sections will be less accurately known than those for ozone, i.e., will have uncertainties of >>10%, and probably even larger uncertainties will be present for the relative absorption coefficients of paired bands. A coefficient in atm-cm^{-1} is multiplied by 3.722 x 10^{-20} to give the equivalent cross section in cm^2, and by 1/0.4462 to give the equivalent in m^{2}mol^{-1}.

The spatial distributions of gases range from being uniform, as occurs for globally diffuse sources or unreactive species, to being very variable, as occurs for point sources and reactive species. An interfering gas may be of natural origin or of anthropogenic origin. The effect at any site due to a nearby point source, such as a factory, city or volcano, will depend on the direction and the horizontal turbulent dispersion characteristics of the prevailing wind, and on any chemical loss (or gain) processes within the plume. The vertical extent of dispersion is of no direct interest since our concern is only with column amounts of the gas, i.e., height integrated amounts. However, column amounts can be deduced from concentration measurements if sufficient information on the height profile of the gas is available. For example, in urban situations, concentration data on various species are often available, and the scale height of the gas, or the height of the inversion layer which generally accompanies urban air pollution episodes, can be found from meteorological observations. The column amount x_2 of a well mixed layer of gas is related to the mean concentration C in ppmv and the inversion height z by

$$x_2 \text{ (atm cm)} = \frac{(1 - \exp(-z/H))}{1.251} \cdot C(\text{ppmv}) \qquad (11.1)$$

where H is the atmosphere's scale height, which equals 8.49 km for a layer at 17°C.

Extremely high column amounts of an interfering gas can occur close to its source under conditions of very small horizontal dispersion, but of course these will have only very limited spatial extent, by definition. When a large number of point sources are spread over an extended region they may constitute an "area source", within which the wind direction and dispersion have little effect on the column amount experienced.

The primary source of anthropogenic SO_2 is the burning of sulphur-bearing fuels at large oil refineries, smelters, coal and oil fired electric power plants, and at other smaller industrial plants. Domestic coal and oil use may be a problem in some areas. The production of anthropogenic NO_2, and the consequent local photochemical production of ozone is largely due to motor vehicle exhausts and is thus largely confined to urban areas. The production of other industrial waste gases, such as H_2O_2, is also confined largely to industrial and urban areas. The significance of large scale burnings of forest and of crop detritus, which occurs throughout the tropical and temperate land areas, is as yet unknown.

The ozone error, ΔX, due to an interfering absorption is:

α_2

$$\Delta X \text{ (atm cm)} = \frac{}{\alpha_1} x_2 \text{ (atm cm)} \qquad (11.2)$$

(Komhyr and Evans, 1980), where α_1 and α_2 are the respective absorption coefficients of the ozone and the interfering gas for the particular band or band combination of interest. Thus the errors will not show any airmass dependence, except if the amount of interfering gas has a diurnal variation, which it well might.

If absorption interference due to point sources is a persistent problem, then it will almost always be possible to relocate the Dobson instrument to a site distant from, and predominantly upwind of, the offending source. A shift of even 10 km may have a significant effect, though to avoid the plum of a city a shift of 100 km or more may be needed (Komhyr and Evans, 1980). Each Dobson site needs to be considered individually for its pollution potential. When the problem is an area source, it may be necessary to correct for the interference by means of supplementary chemical and meteorological measurements.

Some general considerations show that the effects of atmospheric radiation emissions in the UV will be very small. Fluorescence derives its energy from the absorption of more energetic photons, i.e., from light of shorter wavelength. However, light of wavelengths less than 300 nm will not penetrate the ozone layer to reach the bulk of the atmosphere where presumably the bulk of any fluorescing species will reside. Any fluorescence from above the ozone layer necessarily will be weak and will be absorbed in passing through the ozone layer to an extent similar to that for extraterrestrial sunlight. Also, the fluorescent energy is emitted into a full 4π steradian field, only a small part of which is received by the Dobson field of view, and fluorescence (and luminescence) is not an efficient energy conversion process. Luminescence (airglow) is generally very weak, as is evidenced by the degree of blackness of the rural night sky.

Although it is possibly out of context here, it is worth mentioning the so-called Ring effect, which refers to the reduction in the depth of the deep and very narrow Fraunhofer lines in the near UV and visible skylight relative to the same lines in direct sunlight. The effect amounts to a filling in of a few percent (Brinkman, 1968). A number of explanations have been proposed, including airglow, aerosol fluorescence and Raman scattering, but none is as yet generally accepted (Kattawar et al., 1981). The important consideration for our problem is that any effect on the flux for the relatively broad 1 nm Dobson bands will be very small, almost certainly less than 0.5%.

11.2 Interfering absorption

Dobson (1963) briefly discussed the question of interfering absorption and concluded that only SO_2 would be a problem, and that even then, its effect was negligible for his instrument at Oxford. Komhyr and Evans (1980) studied the effects of a range of anthropogenic pollutants known to have UV absorption bands, namely SO_2, NO_2, N_2O_5, H_2O_2, HNO_3, acetaldehyde, acetone, acrolein, and locally produced ozone. For each pollutant they estimated, firstly, the absorption coefficients at the Dobson bands, and secondly, the likely column amounts from surface concentration data and mean mixing height or inversion height estimates. Only SO_2 and NO_2 showed any significant effects. In clean air their column amounts are of the order of 0.0001 atm cm, but in the most extreme cases their concentrations can approach 1 ppm, which if present throughout a 0.5 km layer, would result in column amounts of 0.046 atm cm. For this most extremely polluted air, Komhyr and Evans (1980) calculate errors in the AD ozone estimation of 25% and 5% respectively for SO_2 and NO_2, and corresponding errors in the CD ozone estimation of 45% and 11%.

The above worst-case errors are very large, but in practice their occurrence will be very limited. Most Dobson instrument sites are not subject to high pollution, and the time averages of the errors, say over a month, will be considerably less than the peak values. For example, Komhyr and Evans (1980) estimate for a site 16 km from Denver, in an area near two oil refineries and an electrical generating plant, that AD errors due to SO_2 would have a maximum of 15% (three hour average), would exceed 3% on perhaps four days per year, and would amount to only about 0.6% when averaged over the year. Similarly, they estimate for Pasadena, 16 km from Los Angeles, that AD errors due to NO_2 would have

a maximum of 3% (one hour average), and would amount to 0.8% for the annual average of the daily maximum, and to 0.5% for the annual average of all the data. Thus, even for such chronically polluted sites, the errors in long term AD ozone data due to urban SO_2 and NO_2 will be only about 1%.

Komhyr and Evans (1980) show that the combined error contribution of N_2O_5, H_2O_2, HNO_3, acetaldehyde, acetone and acrolein for highly polluted air is less than 0.3% and is therefore negligible. Photochemically produced ozone in polluted air is part of the ozone column, but it is not part of what one might consider to be "background" or "naturally produced" ozone, and it certainly could interfere with efforts to understand long term variations of stratospheric ozone amounts. Komhyr and Evans (1980) estimated that in very extreme pollution, this locally produced ozone could add about 0.025 atm cm, or about 8%, to the ozone column amount, but that the time-averaged errors for even chronically polluted sites are probably less than 1%. Most sites will never be affected.

Direct measurements of column amounts of SO_2 have been made by Evans et al. (1981) and Kerr et al. (1981) using the Brewer spectrophotometer. With measurements from its five bands, it is possible to simultaneously solve for the ozone column amount, the SO_2 column amount, and the local spectral gradient of aerosol attenuation, provided, of course, that there is no other interfering absorption present. Measurements for the period September 1979 to June 1980 at Toronto showed daily average values of SO_2 of up to 0.010 atm cm and a long term average of about 0.003 atm cm. Using Komhyr and Evans (1980) absorption coefficients, these imply AD ozone errors of about 5% and 1.5% respectively. These are very approximately twice those estimated for anthropogenic SO_2 at Denver by Komhyr and Evans (1980).

Evans et al. (1981) had the good fortune to experience on 20 and 21 May 1980, the overhead passage of the Mt. St. Helens eruption plume, and to thereby measure its elevated column amounts of SO_2. The maximum amount measured was in excess of 0.050 atm cm, which would have resulted in an error in the AD ozone estimate in excess of 0.075 atm cm. The SO_2 column amount for this event could also be estimated from the Dobson instrument measurements and these SO_2 estimates agreed well with those from Brewer instrument measurements. Also, the Dobson ozone estimates, when corrected for the SO_2 interference, agreed well with the (implicitly corrected) Brewer ozone estimates. Overall, the work of Evans et al. (1981) and Kerr et al., (1981) provides a picture of SO_2 interference which is consistent, at least within the uncertainties inherent in the measurement techniques.

The Mt. St. Helens measurements have led some investigators to the view that small but important levels of interference will be present due to stratospheric SO_2 and its periodic replenishment by volcanic eruptions, since although the volcanic emissions of SO_2 are small relative to anthropogenic SO_2 emissions (e.g. Sigurdsson (1982) quotes yearly values of 2.8×10^5 tons and 1.3×10^8 tons respectively), the residence times of SO_2 in the stratosphere are greater than those in the troposphere. Thus there may be globally distributed stratospheric SO_2 levels of the order of 0.005 atm cm with residence times of the order of many months. This implies slowly varying errors in the Dobson AD ozone estimates of the order of 1%. This view is supported by an analysis of Brewer instrument measurements made before and after the recent January 1982 stratospheric "Mystery Cloud" (W.F.J. Evans, personal communication) and by the intense and widespread interference observed in the satellite SBUV/TOMS ozone estimates in April 1982 (A.J. Krueger, personal communication) in the vicinity of the plume of the erupting Mt. El Chichon in Mexico.

The significance of a volcanic event depends on the amount of sulphur injected into the stratosphere and hence upon the sulphur content of the erupting rock and the degree to which the eruption penetrates the tropopause. These factors will vary considerably but probably they could be estimated for the major eruptions of this century. A large part of the initial sulphur input could be in the form of sulphur compounds other than SO_2. The effect of some eruptions may be considerably larger than that of Mt. St. Helens. For example, it seems that the El Chichon eruption was much larger, and Sigurdsson (1982) reports that the massive Laki eruption of 1783 produced 5×10^7 tons of SO_2, which

was approximately 300 times the Mt. St. Helens SO_2 production.

The effects, if any, of other atmospheric gases on the Dobson measurements have not been studied explicitly it seems. The work of Thompson et al. (1963) and the review of Hudson (1974) imply that CO_2, CO, O_2, H_2O, N_2O, NH_3, and NO have no absorption bands in the 300 to 350 nm region. The chlorofluorocarbons CF_2Cl_2, $CFCl_3$, and CCl_4, and presumably also their bromocarbon counterparts, do not absorb at ultraviolet wavelengths greater than 290 nm (Molina, 1980). There are a number of trace constituents, such as BrO, $ClONO_2$, and HOCl which do absorb in this wavelength range (Molina, 1980), but in these cases it is quite probable that their column amounts are too small to cause any significant interference. The possibility of interfering absorption from molecular complexes, ranging from dimers to aerosol particles, has yet to be properly considered. The dimer $(NO_2)_2$ is known to absorb in the UV (Molina, 1980), as is the collision pair $(O_2)_2$ (Perner and Platt, 1980). The UV absorption of aerosols is much smaller than their infrared absorption (Toon and Pollack, 1976), but it should not be neglected as a potential source of interference.

Anomalous spectral features have been found in various UV spectral intensity measurements and have given rise to speculation as to possible interfering species. Kerr (1973) discussed nitrogen hydride, NH, as a possible candidate for explaining anomalies at Dobson and Brewer bands, though at that time NH concentrations were unknown and since then no further work has been reported. Krueger (1969) considered the effect of excited oxygen molecules in an attempt to explain discrepancies in his high altitude rocket optical ozone measurements. DeLuisi (1980) and McPeters and Bass (1982) note the possibility of absorption interference in seeking to explain anomalies in their UV spectra of transmitted radiation and satellite backscattered radiation respectively. It must be pointed out, however, that all these measurements will be limited by the uncertainties in the ozone absorption spectra used in analysing the intensity spectra.

The only firm direct evidence of significant absorption interference is that for SO_2, but at the same time there is a multitude of atmospheric gases whose absorption spectra and column amounts are at best poorly known. Even with SO_2, the absorption coefficients used for Dobson bandpairs are uncertain to 30% (Evans et al., 1981) and are probably temperature dependent, and our knowledge of its column amounts are still very limited. Clearly, there is a great need for more comprehensive studies of the problem. Particular emphasis should be given to the analysis of high quality transmission or backscattered spectra, of the sort done by DeLuisi (1980) and McPeters and Bass (1982), and using the new Bass and Paur (1981) absorption coefficients. Transmission spectra for long horizontal paths would also be very useful. Emphasis should also be given to the study of the effects of volcanic eruptions, and possibly also of large scale fires of forests and crop material.

11.3 Interfering emission

Very little has appeared in the literature on the subject of atmospheric emissions in the near UV region, which is probably indicative of its overall insignificance. As was discussed in the Introduction, 11.1, there are fundamental reasons why this is likely to be so.

Kulkarni (1968) discusses the question of UV airglow interfering with Dobson B bandpair measurements made on the moon and concluded that the Herzberg band of molecular oxygen and the hydroxyl radical, OH, are possible sources. In their search for explanations for anomalous backscattered UV spectral features, McPeters and Bass (1982) suggested NO emission as the cause for a band at 272 nm, but they considered that the only possible source for emission in the 300 to 310 nm region was oxygen, and even then the intensities required would be unreasonably large. Aerosols might possibly be a source of fluorescent emission. The backscattering of night lighting by aerosols and air molecules, though not an emission, might be a small source of interference to moonlight measurements, especially when the ground is snow covered. In total, the above evidence is weak and does not point to any significant interference.

11.4 Summary

(i) Absorption by atmospheric constituents other than ozone can interfere with the accuracy of Dobson ozone estimations. Of the multitude of anthropogenic, volcanic and background gases or particles, only a few are thought at present to interfere in any significant way, but our knowledge of the relevant column amounts and absorption cross sections is far from complete.

(ii) Column amounts of anthropogenic SO_2 in extremely polluted air may cause overestimates approaching 25% in AD ozone estimates. However, even at chronically polluted sites, the errors would exceed 5% on only a few days per year and would average to 1% or less over a year.

(iii) Column amounts of anthropogenic NO_2 in extremely polluted air may cause overestimates approaching 5% in AD ozone estimates. However, even at chronically polluted sites, the errors would exceed 3% on only a few days per year and would average to 1% or less over a year.

(iv) In very polluted air, the total error in AD ozone estimates due to maximum amounts of the anthropogenic known UV absorbers N_2O_2, H_2O_2, HNO_3, acetaldehyde, acetone and acrolein is less than 0.5%. The presence of other interfering species cannot be ruled out. The effect of large scale anthropogenic burnings of forest and crop detritus is unknown.

(v) Photochemically produced ozone in polluted urban air can interfere with the measurement of the "background" column ozone amount. On occasion it may rise to 8% of the column total, but even at chronically polluted sites the long term contribution will be less than 1%.

(vi) Volcanic eruptions may produce sufficient SO_2 to cause errors of 30% or more to AD ozone estimates made beneath the plume up to some hundreds of kilometres from the volcano. Also, sufficient SO_2 may be injected into the stratosphere by volcanic eruptions to cause AD ozone errors of 1 to 2% over regional or global scales which decay slowly over periods of many months.

(vii) The combination of theoretical and experimental evidence indicates that UV radiation emission within the atmosphere is a negligible source of error.

(viii) Overall, the error due to interfering absorption for yearly average AD ozone estimates is likely to be less than 2% for chronically polluted sites and less than 0.5% elsewhere. Spatially averaged errors will tend to be even less. Errors for the CD estimation are approximately twice those of the AD combination.

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Forward to Airmass Accumulation

12. AIRMASS CALCULATION

12.1 Introduction

The "airmass" as a general term, describes the ratio of the amount of an attenuating medium integrated along a slanted path through the atmosphere to the amount integrated along a vertical path. It enables the amount of the medium in a vertical column to be derived from measurements of attenuation along the slanted path. In the ozone measurement equations, equation 1.1 and the following equations, three attenuating media are described, ozone, air molecules and aerosol, and each has a slightly different airmass, owing principally to their different height distribution and the sphericity of the atmosphere. However, all are approximately equal to secant Z, where Z is the solar zenith angle at the observing site.

Aerosols are concentrated near the ground and the appropriate airmass is taken to be sec Z, though generally the aerosol term and hence its airmass are neglected. The airmass for scattering by air molecules, m, can be calculated to account for the atmosphere's sphericity and for atmospheric refraction, and has been empirically expressed by Kasten (1966) as:

$$m = (\cos Z + 0.1500\,(93.885 - Z)^{-1.253})^{-1} \qquad (12.1)$$

where Z is in degrees. The airmass appropriate to the ozone layer, μ_h, is taken as the secant of the zenith angle at the mean height of the ozone layer, and the mean height has been traditionally assumed to be 22 km (Dobson, 1957a). Figure 12.1 illustrates the geometry of the situation, and from this it is not difficult to show that:

$$\mu h = (\cos(\arcsin(l \sin Z)))^{-1} \qquad (12.2)$$

or

$$\mu h = (1 - l2 \sin^2 Z)^{-1/2} \qquad (12.3)$$

where

$$l = (R + r)/(R + h) \approx 1 - (h - r)/R \qquad (12.4)$$

As shown in Figure 12.1, h is the mean ozone layer height above mean sea level and r is the altitude of the observing station. Note that h depends on the difference of these, i.e., on h-r, and not on h alone. If h-r = 22 km and R = 6370 km, then l= 0.99655.

Incidentally, the solar zenith angle Z is expressed as:

$$\cos Z = \cos\varphi \cos\delta \cos\theta + \sin\varphi \sin\delta \qquad (12.5)$$

where φ is the station latitude (negative in the Southern Hemisphere), δ is the solar declination (negative from about September 21 to about March 21), and θ is the local hour angle of the sun at the observing station (zero at local apparent noon). Komhyr (1980b) gives a full account of how to determine these parameters, and hence Z and μ_h, not only for the sun but also for the moon.

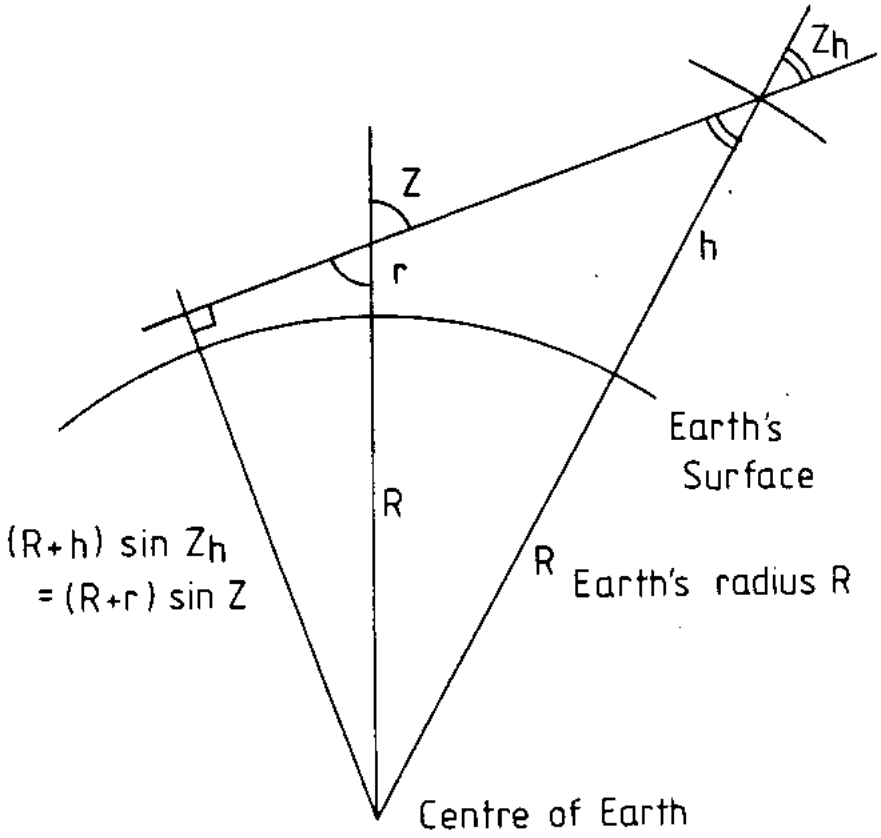

Figure 12.1 Geometry for finding the expression for airmass μ_h of a mean ozone layer at height h when observed from a site at altitude r.

12.2 Error analysis

It is useful to compare the three airmass terms: this is done in Table 12.1. The table shows that the differences among the airmass terms are small for small solar zenith angles, but become increasingly important beyond an airmass of 2.

TABLE 12.1

Comparison of sec Z, m and μh, for h-r = 22 km.

Z	sec Z	m	μ_h
10	1.0154	1.0148	1.0153
60	2.0000	1.9928	1.9797
70	2.9238	2.8999	2.8508
75	3.8637	3.8081	3.6911
80	5.7587	5.5803	5.2117
83	8.2054	7.7278	6.8009
85	11.4735	10.3229	8.3292
87	19.1069	15.2186	10.2112

In particular, the use of sec Z in place of μ_h would contribute errors of 1% at an airmass of 2 and 5% at an airmass of 4. Errors in airmass μ_h transfer to ozone estimates in direct proportion. The air molecule scattering terms in the ozone estimates for double wavelength pairs, equations (1.10) and (1.11), are so small that they may, for convenience, be replaced by μ_h. However for single wavelength pair determinations, this substitution can be unsatisfactory, since the resulting percent ozone errors for the A, B, C and D bandpairs, respectively, are 0.2, 0.3, 0.5 and 1.0 times the percent difference between m and μ_h. For example, an error of about 1.5% could be expected for a single C bandpair measurement at an airmass of 3.8.

The ozone airmass μ_h depends on the mean height of the ozone layer. This varies over the range of about 13 to 30 km, but is usually between 17 and 27 km (Khrgian, 19751 WMO, 1981). It is highest and least variable in the tropics, and lowest and most variable at high latitudes and at high mid latitudes.

It is now recommended by Komhyr (1980b) that approximate climatological mean layer heights be used for h in the computation of μ_h in order to avoid mean biases. The values recommended may be expressed as h = (26 - φ/10) km, where φ is the magnitude of the latitude. The effect of station altitude is not great since the highest stations are at about 3 km in altitude and most are below 1 km, but at the same time, it can be of significance for high airmass measurements and the altitude should be included in equation (12.4). The small variation of R around the globe has negligible effect on the accuracy of μ_h.

The dependence of μ_h on h-r is illustrated in Table 12.2 in terms of the percentage difference relative to the case of h-r = 22 km.

TABLE 12.2

Difference, in percent, of airmass at various values of h-r, relative to h-r = 22 km.

	h-r = 14	18	22	26	30	km
Z = 60°	0.4	0.2	0	-0.2	-0.4	%
75°	1.6	0.8	0	-0.8	-1.5	%
80°	3.4	1.7	0	-1.6	-3.1	%
83°	6.2	3.0	0	-2.7	-5.2	%

The table shows that if the value of h-r is fixed at 22 km, as was customary until recently (see Dobson 1957a), there will arise significant errors for high airmass measurements when the layer mean height is very high or very low. This is of particular significance for high latitude sites since these sites normally are subject to both low mean layer heights and high airmass values. Mid latitude sites are also affected in the winter since the zenith angle listed above, 60°, 75°, 80° and 83°, correspond to the noon airmass at winter solstice at latitudes of 37°, 52°, 57° and 60° respectively.

The use of the recommended climatological mean layer heights will significantly reduce the above mentioned error in climatological ozone data. However some error will remain owing to the uncertainty in the climatological mean layer heights, and to the correlation of ozone amount with layer height. Errors in airmass, and therefore ozone amount, due to day to day and seasonal variations in mean layer height may be estimated from Table 12.2. The sensitivity to such variations is approximately 0.05, 0.2, 0.4 and 0.7% km respectively at the zenith angles 60°, 75°, 80° and 83°. Since variations in mean height can be of the order of 2 km, day to day ozone errors of over 0.5% may be common for measurements made at airmasses over 4. The measurement types recommended (Komhyr, 1980b) for the higher airmass ranges, the CD focussed image and zenith sky measurement types, are those principally affected.

The sensitivity of airmass calculations to errors in timing of observations and to errors in the latitude and longitude assumed for a site may be readily found by differentiating equation (12.5). The percentage airmass error, ε_p, due to timing and longitude errors, at the times of the equinoxes, is given by:

$$\varepsilon_p = -100 \tan\theta \Delta\theta \qquad (12.6)$$

where Δθ (in radians) is the hour angle error or equivalent longitude or timing error. The airmass error is greatest at large hour angles and is independent of latitude for any given hour angle. The error values listed in Table 12.3 below show that in order to keep such errors below a few tenths of a percent, the timing of observations should be accurate to about 10 seconds, and the site's longitude should be accurate to about 2 minutes of arc, which is equivalent to a distance in the east-west direction of about 3.5 km at the equator. Similar east-west distance accuracies hold for higher latitudes also, owing to the compensation there of the smaller distance per degree of longitude by the generally smaller hour angles at which measurements are made. Note that systematic timing and longitude errors will tend to cancel in daily data which are the means of morning and afternoon observations taken at similar airmasses.

TABLE 12.3

Percentage airmass errors due to timing or longitude errors, at the equinoxes, as a function of hour angle θ.

Error Δθ (radians)		= 2.91 x 10-4	2.91x 10-3	1.75 x 10-2
(deg. min.sec.)		1'	10'	1°
(time)		4 sec	40 sec	4 min
(distance atequator)		1.8 km	18 km	111 km
Sec θ = 2	θ = 60.0°	0.05%	0.5%	3.0%
3	70.5°	0.08%	0.8%	4.9%
4	75.5°	0.11%	1.1%	6.8%
5	78.5°	0.14%	1.4%	8.6%

The percentage airmass error due to latitude error, at the times of the equinoxes, is given by:

$$\varepsilon_p = -100 \tan\varphi \Delta\varphi \qquad (12.7)$$

where Δφ is the latitude error in radians. The airmass error therefore is greatest at high latitudes and is independent of hour angle. The errors listed in Table 12.4 below show that in order to keep the airmass error to less than a few tenths of a percent, the site's latitude should be accurate to about 5 minutes of arc for low and middle latitude sites, and to about 2 minutes of arc for high latitude sites.

TABLE 12.4

Percentage airmass errors due to latitude errors, at the equinoxes.

Error Δφ =		1'	10'	1°
Latitude =	50°	0.03	0.3	2.1%
	60°	0.05	0.5	3.0%
	70°	0.08	0.8	4.8%
	80°	0.16	1.6	9.9%

Modern surveying methods are well able to provide the latitude and longitude accuracies required, though this does not necessarily mean that all sites achieve these accuracies. Similarly, there are few places in the world where timing accuracies of 10 seconds are not possible, but this alone does not guarantee 10 second accuracies in routine operations.

12.3 Summary

(i) The airmass for ozone absorption, μ_h, depends on the altitude difference between the ozone layer mean height and the observing station, as well as on the solar zenith angle. Errors in the calculation of μ_h transfer to ozone estimates in direct proportion.

(ii) Mean ozone layer heights range from about 13 to 30 km, are greatest in the tropics and in the summer and autumn, and are smallest and most variable at high latitudes and in the winter and spring.

(iii) Climatological average mean layer heights should be used when calculating μ_h. The mean height of 22 km traditionally assumed may give rise to ozone errors of typically up to -1% in the tropics and up to +5% in high latitudes. The errors are negligible up to an airmass of 2, but then rise rapidly.

(iv) Even when climatological yearly average heights are used, residual day to day and seasonal variations will give rise to errors of over 0.5% for airmasses over 4.

(v) Generally, since measurements at high airmasses are required only at high and middle latitudes, the airmass errors will amount to less than 0.5% in the tropics almost always, but may rise to a few percent at high latitudes, especially during winter.

(vi) The airmass appropriate to air molecule (Rayleigh) scattering, m, may be safely approximated by μ_h for any double wavelength pair ozone estimate, but the proper value is required for single wavelength pair ozone estimates above an airmass of 2.

(vii) Airmass errors due to observation timing errors and to site latitude and longitude errors vary, principally with airmass and latitude. Overall, they will be held to less than a

few tenths of a percent if the observation times are accurate to 10 seconds and the site's latitude and longitude are accurate to 2 minutes of arc.

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Forward to Solar Constancy

13. SOLAR CONSTANCY

13.1 Introduction

The variation of ozone amount in response to solar activity and solar variations on various time scales is of great intrinsic interest, and as well, provides valuable tests of atmospheric chemistry models, especially their radiation components. It is important therefore to consider to what extent the ozone measurement method itself is affected by, and is in error owing to, these solar variations. This discussion concerns the Dobson instrument only, but the problem also affects satellite ozone instruments which use extraterrestrial intensities or intensity ratios which are fixed between periodic recalibrations.

The accuracy of Dobson instrument ozone estimates depends on the constancy of solar extraterrestrial irradiance through the expression:

$$dX_k = \frac{d(L_{ok})}{\mu_h \Delta\alpha_k} \qquad (13.1)$$

which is derived from equation (1.8). Constancy in absolute irradiance is of no significance of course. Constancy is demanded only for the irradiance ratios of bandpairs, or for the ratio of irradiance ratios when a double bandpair method, such as the AD method, is used. Note that, once again, the double bandpair practice tends to reduce the susceptibility to error. The ozone uncertainty described by equation (13.1) depends inversely on the airmass and the relative absorption coefficient, whose product in normal practice ranges from about 1.5 to 4.5 atm-cm^{-1}. All instruments are affected in the same way, but there will be a tendency to find larger values of $\mu_h \Delta\alpha_k$ at higher latitude sites, and hence smaller effects there.

If the ozone uncertainty is to be kept to 0.0015 atm cm, i.e., about 0.5%, then the uncertainty in the intensity ratio must be less than about 0.5% also. The constancy of 0.5% is required only over the interval between the periodic recalibration of the instrument's extraterrestrial constants. These intervals are typically two to five years, but may be much longer. Constancy is always assumed, but the evidence to support the assumption is rather limited.

13.2 Solar spectral irradiance variations

The visible and near UV parts of the solar spectrum are emitted by the sun's photosphere, the apparent "surface" of the sun. The absorption of upwelling radiation within the photosphere by overlying gas restricts the perceived emitting region to a relatively shallow layer. The radiation emitted toward Earth from the outer parts of the solar disc is subjected to more absorption along its slanted photospheric path and therefore comes from higher and cooler layers and is less bright. This relative darkening near the disc periphery is known as limb darkening. It is spectrally dependent and is most marked in the near UV. Subsequent absorption by highly ionised material in the sun's chromosphere imposes strong and spectrally dense absorption lines, known as Fraunhofer lines, on the near UV spectrum (see Figure 5.1). Overall, the near UV spectrum incident at Earth is roughly similar to that of a 5700°K blackbody.

The sun rotates with a period which varies from about 27 days at its equator to about 24 days at its poles. Large darker and cooler areas of the sun's surface, known as sunspots, appear from time to time and rotate across the disc. These are magneto-hydrodynamically active zones whose numbers and size vary in a cyclical fashion with a period of about 11 years. The maximum of the last cycle occurred about 1979.

Considerable efforts have been made, especially in recent decades, to measure the solar spectrum and its variations. (For an extensive summary of the field, see White, 1977). In the UV, visible, and near IR regions, these efforts have concentrated mainly on the following:

firstly, the measurement of the solar constant (the total irradiance at mean Earth distance) to high accuracy (better than 1%);

secondly, the measurement of the spectral distribution of this energy to moderate accuracy (about 2 to 5% in the near UV);

thirdly, the measurement of the middle UV spectral fluxes which are of importance to aeronomy, to accuracies of 10% to 50%.

Thus, most of the available spectral data can only resolve variations greater than 5%, which is not sufficient for our problem. There are many experimental difficulties. The long term stability of calibrations is always difficult to maintain. Measurements made on the centre of the solar disc and corrected for limb darkening may differ from full-disc measurements. The Fraunhofer line structure in the 300 to 350 nm region can result in intensity gradients of up to 40% nm^{-1} for 1 nm spectrometer bands, which means that wavelength accuracy is very important, and it can result in significant measurement differences between instruments of different bandwidths. Despite these limitations, a brief summary of the relevant available data is attempted as follows.

A variety of measurements of the solar constant made since 1976 agree to within 0.3% of their mean result (Frohlich, 1982). Individual measurement methods indicate small trends, of the order of 0.03% yr^{-1}, and satellite measurements show continual variations on the time scale of days and weeks, mainly dips of the order of a few tenths of percent. These appear to be due largely to sunspots, which are considered to block part of the outgoing flux. The energy thus not radiated appears to be stored in a very large reservoir of very long time constant, and hence to contribute to very small long-term variations (Frohlich, 1982). The wavelength dependence of these variations is unknown. Some wavelength dependence of such sunspot-related variations should be expected owing to the wavelength dependences of limb darkening and of the emission with solar altitude.

Livingston's (1978) measurements of temperature-sensitive Fraunhofer lines at 538 nm imply a 6°K decrease in photospheric temperature in 1977, in parallel with the rise in sunspot number that year. However, Heath (1980) states that Livingston's subsequent measurements showed that this decrease continued right through the sunspot maximum, and that there were corresponding increases for other upper photospheric layers. It can be noted that any overall photospheric temperature increase of greater than 6°K would produce total flux changes which would be inconsistent with the known stability of the solar constant since 1976.

Heath and Thekaekara's (1977) summary of solar ultraviolet measurements showed a variation apparently related to the 11 year sunspot cycle, with amplitudes decreasing smoothly from about 50% at 160 nm to 10% at 300 nm. However, Simon (1978) considers that experimental uncertainties preclude the drawing of such a conclusion, and Nicolet (1980) states that there is no astrophysical basis for any significant variation above 175 nm. Moreover, Cooper's (1982) analysis of the semi-diurnal (12 hr) Earth atmospheric tide indicates that the UV band absorbed by ozone (approximately 200 to 300 nm), which provides the tide's forcing, varies by less than 2% over the sunspot cycle. Simon et al. (1982) conclude that the irradiance at 300 nm is known to ±5%. Heath and Thekaekara (1977) show that the irradiance variations associated with the 27 day solar rotation are less than 1% at 300 nm.

A more recent review of UV flux variability (Heath, 1980), especially as measured by satellite instruments, indicates a number of systematic variations in spectral irradiance. Among other things described are: firstly, differences between active and inactive parts of the 27 day cycle amounting to several percent below 285 nm but less than 0.5% above 300 nm; secondly, a variation over a fourteen month period which amounted to about 8% at 200 nm, 3% at 300 nm and less than 0.5% at 350 nm, and which, if real, would contribute a 0.06% yr^{-1} decrease to the solar constant (the possibility of instrument spectral drift was noted, however), thirdly, a long-term 15% amplitude variation in the 340 to 380 nm flux, relative to the 390 nm flux, deduced from ground-based Langley method measurements in 1931 and 1951 and satellite measurements in 1978. Frohlich and Wehrli (1982) give evidence of UV irradiance variations of the order of hundredths of a percent over periods of minutes and hours, which indicate that the amplitudes of the variations at 368, 500 and 778 nm are in the ratios of 4:2:1

approximately.

Some upper limits to the variation of the solar UV irradiance ratios may be determined from the measurements of the Dobson instrument itself. On very clear days with settled synoptic conditions, AD ozone estimates may be made which are repeatable to 0.5%, which suggests that variations in the irradiance ratio for the AD band combination are less than about 0.5% over the periods of tens of minutes for which repeatability holds good. Over longer periods it is necessary to exclude the effects of the atmosphere by studying the experimentally determined extraterrestrial constants as a function of time. The instrument component of the constants is checked by reference to standard lamps: thus the constancy of the solar intensity ratio is calibrated, in effect, against the constancy of the lamps' intensity ratio. Day to day variations in extraterrestrial constants during a period of their determination at Mauna Loa (Dobson and Normand, 1962) showed the solar irradiance ratios were constant over this period to at least 1%. It is possible that some institutions have maintained standard lamps with documented histories for many years and that from these the long term constancy of their Dobson extra-terrestrial intensity ratios could be determined. Such studies would be very valuable.

Incidentally, the long-term behaviour of ozone data can be used to set upper limits to the longer term variations of the irradiance ratios, though of course these limits are of no use in assessing the long-term accuracy of the ozone data. For example, yearly average ozone amounts for the world generally lie within 2% of the long term mean (WMO, 1981), which suggests that year to year variations in the irradiance ratios are less than approximately 4%. This estimate is complicated by the direct effect of any UV flux changes on ozone amounts, however.

The discussion of near UV solar flux variations given above is neither extensive nor conclusive. The independent evidence from balloon, rocket and satellite instruments does suggest that there are small variations on a variety of time scales, but generally the available data have large uncertainties, are uncorroborated, and are lacking in firm astrophysical explanation. Furthermore, the measurements available do not have the combination of spectral resolution and irradiance accuracy required to meet our specific needs. Dobson instrument measurements apply to the right bands and have sufficient precision, and do provide some estimates of the limits to the variations, but they are limited by uncertainties in instrument calibrations and atmospheric attenuation. Further advances with the problem must await the results of currently deployed or planned satellite instrumentation.

Overall, the evidence points to variations in the solar irradiance ratios for the Dobson bandpairs of less than 1%, and hence to resulting variations (errors) in the ozone estimates of less than 1%. However, the possibility of much larger variations must be acknowledged.

13.3 Summary

(i) The Dobson measurement method assumes that the solar irradiance ratios for its bands are constant (to less than about 0.5%) for the duration of the interval between recalibrations of extraterrestrial constants. The standard AD double bandpair method is insensitive to any irradiance change which is spectrally linear.

(ii) Solar radiation in the 300 to 350 nm region is of photospheric origin, but is overlaid with strong chromospheric Fraunhofer absorption lines. The solar constant, which is also largely photospheric in origin, is known to 0.3%, but varies by a few tenths of a percent over daily and weekly time scales (probably in response to sunspot variations), and may have a long term trend of a few hundredths of a percent per year.

(iii) Measurements from satellites, rockets, balloons and ground-based spectrophotometry indicate that any near UV flux variations are of the order of a few percent or less. These data do not have the spectral resolution or accuracy needed for this study of the Dobson instrument.

(iv) Dobson instrument measurements indicate that irradiance ratios are constant to 1% or better over periods of minutes to days, and are probably constant to at least 4% on a year to year basis. Further study of Dobson instrument data and calibration records to assess

solar variability would be very desirable.

(v) The evidence available at present has many uncertainties, but overall, it indicates that errors in ozone estimates due to UV flux variability are most unlikely to be greater than 1%.

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14. CONCLUSION

14.1 Introduction

How accurate is the Dobson instrument? What variance may be ascribed to instrument uncertainties in the ozone data? These basic questions are simple, but their answers are not. As has been shown in preceeding sections, there is a great variety of error sources, there are large variations in the effect of the error sources from instrument to instrument, and the many factors upon which errors are dependent are often not well known. The combining of the error estimates into a single "representative" value is difficult for present day measurements, and is very difficult for measurements made in the past. For most of the errors, especially the larger ones, there is no a priori basis for their representation as variances. Thus there are significant difficulties in assessing the reduction of the errors in data from a time series or from an ensemble of instruments.

Despite the difficulties, some answers must be given, and it is the purpose of this last section to attempt the generalisations required. It should be understood that these involve a certain amount of subjective judgement. It is recommended that the numerical error estimates given be used with caution and only after reference has been made to the accompanying text.

Finally, at the end of the section, there is given a summary and discussion of ways of improving the accuracy of both the instrument and the network as a whole.

14.2 Summary and discussion of errors

Most of the individual error estimates have been given in the summaries to be found at the end of each section. A grand summary of them, for just the AD direct sun ozone estimation, is given in Table 14.1 below. In the table, estimates are made for two loosely defined categories, "typical good instrument or situation", and "typical bad case". The first category describes the errors expected when proper procedures of maintenance and operation are faithfully carried out and when adverse factors, such as stray light, heavy haze, high pollution or high airmass, are not significantly affecting the measurements. The second category describes the typical errors expected on occasion, or at some sites, or with some instruments, in situations when the error concerned is large.

The proportions of instruments falling in and between these categories depend on the particular error source. A very rough overall estimate is that at present half the network's instruments will meet most of the "typical good" category estimates all or most of the time and that perhaps ten to twenty percent of the network will be affected by some of the larger "typical bad case" category estimates all or most of the time. In the past, the proportion meeting most of the "typical good"

Three broad generalisations can be made on the basis of Table 14.1. Firstly, the aggregate of the instrument-related error sources is greater than the aggregate of all the other error sources. Secondly, the largest of the instrument-related error sources concern the extra-terrestrial constants, stray light and optical adjustment. Thirdly, atmosphere-related error sources (excluding the absolute accuracy of the ozone absorption coefficient scale) are small except for a few sites affected by severe air pollution. These generalisations have been largely understood and accepted, if not explicitly demonstrated, by instrument specialists for some time.

The error estimates in each column of Table 14.1 cannot be simply added or RMS added, but some form of aggregation is called for. It seems as if suitable measures of accuracy for present day daily AD direct sun ozone estimations, relative to the current ozone absorption coefficient absolute scale, are about 3% for instruments mostly meeting the "typical good" category requirements, and about 5% to 10% for instruments which suffer from the larger errors listed in the "typical bad" category. Overall, the author risks the guess that two thirds of recent years' AD direct sun ozone estimations have an accuracy of 3% or better relative to the current absolute scale. This is reasonably consistent with the 1979 comparison of Dobson stations with the BUV-TOMS satellite instrument reported in WMO (1982).

TABLE 14. 1

Summary of error sources for individual daily standard AD direct sun ozone estimates.

Error source	Error estimates		Comments
	Typical good instrument or situation	Typical bad case	
Instrument sources:			
Temperature dependence	<1%	2%	Depends on climate and operator care.
Mechanical deformation	<1%	?	Inadequate information.
Stray light	<1%?	5%?	Inadequate information. Very variable. Rapid increase for airmasses > 3.
Wavelength adjustment	1%	2%	Better results in recent years generally.
Other optical problems	<1%	10%?	Inadequate information. Some may be accounted for in other error source entries.
Wedge calibration	0.5%	2%	Modern equipment needed for best results.
Bandwidth effect	<0.5%	<0.5%	Larger values for other band combinations.
ETC determination	1%	5%	Best results from direct intercomparison. Langley method error often about 5%.
ETC stability	1.5%	4%	Drift over 2 to 5 years between intercomparisons.
Electronics	<0.5%	1%?	Inherently small.
Operational precision	<1% RMS	<2% RMS	Depends on skill, atmospheric stability, airmass.
Atmospheric sources:			
Ozone absorption			
(i) absolute coefficient	3%?	3%?	Good prospects for 1 to 2% in near future.
(ii) relative coefficient	1.5%	1.5%	Due to stratospheric temperature variation.
Aerosol extinction	<0.2%	3%	Worst case requires extremely turbid sky.
Interfering absorption	<0.5%	5%	Only bad near cities, volcanoes etc., on occasion.
Other sources:			
Airmass calculation	<0.2%	<5%	Only bad at high latitudes with "22 km" assumption.
Solar variability	<1%?	<1%?	Inadequate information. Is zero when ETC is set.
Sampling biases	<0.5%	3%	Proportional to temporal and spatial variability.

Analyses of archived Dobson column ozone data often use only the AD direct sun observations. However, if all the ozone data are used, then the accuracies of the other observation types must be considered. What little is known of these is summarised for the main types in Table 14.2. All observation types suffer from the error sources listed for the AD direct sun observation in Table 14.1, and usually so to a greater extent. The error estimates listed in Table 14.2 represent approximate accuracies relative to the standard AD estimation. The usefulness of the non-standard observations depends on their information contribution relative to the otherwise available data and to the expected natural variation. In some instances an observation of 10% accuracy may be very useful.

TABLE 14.2

Summary of errors for the main non-standard estimation methods. These errors are additional to those in Table 14.1 for the standard AD direct sun method,

and are rather approximate.

Estimation method	Error estimate: Typical good instrument or situation	Error estimate: Typical bad case	Comments
AD zenith blue and information.	2% RMS	5% RMS?	Depends on accuracy of empirical method charts. Little
AD zenith cloud on density and	3% RMS	10% RMS?	As above. Also depends cloud's type, temporal variation.
CD direct sun to three	2%	5%?	Errors generally two times those for AD direct sun.
C direct sun mainly inter-	3%	10%?	Additional errors from aerosols and fering absorption.
Focussed image information. instrument and	4%?	20%?	Very little Depends on on operator skill.

The question of the detectability of trend in ozone data is of great topical interest. Table 14.3 isolates those error sources which could conceivably contribute trend-like error to archived data, and it gives for each source an estimate of the possible trend in the daily AD direct sun observation of an individual instrument. This shows that erroneous trends of up to about 10% per decade can be expected for some instruments. This sets a significant limitation to the trend detection capability of the data. It is particularly ironic that the considerable efforts which have been made over the past decade to upgrade the adjustment and calibration of instruments are themselves a source of some of the largest potential erroneous trends.

TABLE 14. 3

Summary of error sources which could exhibit trend-like behvaiour, with estimates of potential erroneous trend for an individual instrument's AD direct sun observations.

Error source	Likely maximum trend percent per decade 1973-1983	Comment
Optical adjustments and their historical improvement	5%	Due to changes to instruments and periodic calibrations especially upgradings over last ten years.
ETC determinations	5%	Due to changes to instruments and periodic calibrations especially upgradings over last ten years.
Instrument drift	2%	Effect is reduced by frequent calibrations.
Ozone layer temperature	0.5%?	No substantial evidence for this.
Aerosol extinction	1%	Requires heavy and changing haze.
Interfering absorption	2%	Only significant near sources.
Airmass calculation	1%	Due to change from fixed 22 km layer to climatological mean heights.

Solar variability	<1%?	Inadequate information.

It is not clear to what extent the nett erroneous trends of instruments in a group will be correlated. In Reinsel's (1981) statistical study, the trends at individual stations for the one to two decades before 1979 were found to range from about -4% per decade to about +8% per decade. These values are consistent with the estimated magnitudes of possible erroneous trends given in Table 14.3. Although the detected trends may reflect some real ozone changes, their scatter within a region, especially the -2 to +8% per decade scatter found for Europe, indicates that other factors, probably instrument?related errors, are the main cause.

Any systematic reduction of the effects of stray light (see Section 4) over the last decade or so would have contributed an upward erroneous trend with a total change of possibly up to 10% for the particular instruments concerned. The results of the instrument intercomparisons should provide some information on any predominance of positive or negative corrections and therefore any nett erroneous trends. The calibration histories reported in WMO (1982) for the instruments (mostly United States instruments) which have undergone repeated intercomparisons, show a tendency for successive corrections to be of the same sign. This indicates systematic long term drifts in each instrument's response. Interestingly, seven of the nine instruments show predominantly negative corrections, i.e., positive drifts. The corrections are generally in the range of 1 to 3%, and give nominal drifts generally in the range of 1.5 to 5% per decade. The significance of the drifts will depend on the time intervals elapsing between intercomparisons and hence between corrections. A cursory examination of the international intercomparison results given in Section 7 shows no predominance of positive or negative corrections, though this deserves further study.

The possible errors for an individual daily ozone estimation listed in Table 14.1 can be large, but the nett errors in statistical means of estimations will be less, of course. In the daily mean for a large number of instruments, or for a large region, many of the errors will reduce as if part of a random distribution. Systematic error components will be present though, the largest being those due to the determination and stability of extraterrestrial constants, to stray light effects and to other optical adjustments or problems, and altogether these might amount to an error of up to say 3%. The combined effect of aerosol extinction and interfering absorption may amount to a bias of 1 to 2% under extensive urban haze and pollution, such as is common, for example, over large areas of Europe and north eastern United States during the summer, or following large volcanic events, but otherwise it should be less than about 0.5%. The combination of biases due to the bandwidth effect, the airmass calculation, solar irradiance variability and sampling biases are likely to be negligible.

At an individual station the errors in time averages, viz, monthly, seasonal and yearly means, will also reduce, to the extent that they are random over time. However, there will remain some significant relative biases, in particular, those from errors of adjustment and calibration, which may cause seasonally dependent errors of up to 10% and which may show step changes due to periodic re-adjustment or re-calibration. Interfering absorption can also cause biases at some sites which might amount to say 2% for some monthly data. The total relative bias in yearly mean data, at a guess, might lie at 3% or less for most individual instruments at present, but would have been greater in the past. This is also moderately consistent with the results of the Dobson-BUV TOMS comparison results (WMO, 1982). The ultimate and more hazardous guess is that the yearly mean global ozone column data might have relative accuracies of about 1 to 2%. This guess is obviously open to debate.

An important point is that statistical trend analyses of historical data series, if properly done, will show up any step changes in the data record, together with any systematic variations or excesses in the quasi-random components of the record. Indeed, such analyses may in fact be more useful for the detection of data irregularities than for the original purpose of trend detection.

Clearly, in order to extract the most information from any Dobson ozone data set, it is essential for statisticians and instrument specialists to jointly examine the data set, preferably on a station by station, or instrument by instrument basis. To simply use assessed typical error estimates, such as those given here, may result in large overestimates or underestimates of errors for a particular instrument, as

well as a missed opportunity to detect, and hence correct, obvious data errors.

An instructive example of the joint approach is the re-evaluation of the 1963 to 1979 Dobson record for Bismark, North Dakota by Komhyr et al. (1981b). They carefully examined the calibration and test histories of the instrument and determined corrections for various factors for the whole record of daily data. The most significant correction component arose from changes to the extraterrestrial constants. The corrections showed a seasonal cycle superimposed on a long term drift, with magnitudes typically in the 1 to 3% range. Only about 2% of the data needed a correction greater than 5%. The largest errors, from 10-18%, occurred either in the early few years, or as the result of two instances of data processing error. This particular instrument is regarded by Komhyr et al. as a very stable one. The authors subsequently carried out trend analyses on both the uncorrected and corrected sets, and found the resulting trend estimates to be different by about 1% per decade, though this was smaller than the statistical uncertainty in the estimates.

14.3 Summary and discussion of recommendations

Various suggestions and recommendations have been made throughout this review with a view to improving the accuracy of the Dobson instrument and the observational network. Many of the recommendations have been made before by others, but have yet to be implemented satisfactorily. Most have already been listed in the section summaries, but they are drawn together here, under three categories, according to whether they are principally physical factors, instrument factors, or operational factors.

The physical factors concern ozone absorption coefficients, interfering absorption, and solar irradiance variability. A thorough re-evaluation of the Dobson ozone absorption coefficients based on the work of Bass and Paur (1981) is already being undertaken by an ad hoc committee of the International Ozone Commission and should be completed by the end of 1983. The real significance of interfering absorption by volcanic SO_2 and by other less well known trace species, especially those of industrial origin, will require further research. Some surveillance of the literature on atmospheric chemistry for new or newly discovered potentially interfering species would be desirable. The question of the effect of any solar UV variations will be difficult to resolve owing to the requirements of spectral resolution and high accuracy over periods of years. Satellite mesurements will be essential, though there is some prospect of using Dobson instrument calibration records to assess past variability.

Instrument factors form potentially large error sources. The principal items needing attention are stray light and certain aspects of the optical design. Stray light is undoubtedly a serious problem for some instruments and should be subject to further detailed research. The fact that its effect varies noticeably among instruments suggests that its solution should not be difficult. There are other intrinsic optical characteristics, in particular internal reflections and lens aberrations, whose effects need further careful examination, possibly by means of ray tracing techniques. There are likely to be some associations between stray light, optical problems and inadequate adjustment of the instrument. The dependence of photomultiplier relative spectral sensitivity on temperature and applied voltage deserves further study. Further research into the instrument causes of the larger of the drifts in extraterrestrial constants would also be very desirable.

Recommendations about operational factors are the most numerous of the three categories considered. This is partly due to the nature of operational observational programmes and their need for continual attention to operational detail. The most important, essential recommendation is that the intercomparison of instruments, both by multiple instrument international intercomparisons and by travelling reference instruments or reference standard lamps, be continued on a regular scheduled basis, and be extended as quickly as possible to include all of the instruments in the network. Only in this way will the large errors due to inaccurate extraterrestrial constants be avoided. It would also be very prudent to strengthen the World Dobson Spectrophotometer Standard by representing it as the result of not just one, but three primary reference instruments.

The current efforts to extend to all instruments the quality of adjustments and operations being achieved at the major laboratories should also be continued. Serious consideration should be given to establishing international and regional training programmes for station observers. The possibility of a

newsletter to disseminate, in timely fashion, views and techniques relating to the network and its accuracy should also be encouraged. A newsletter could also provide a vehicle for the many useful small studies, for example studies similar to the papers of G.M.B. Dobson (Walshaw, 1975) which otherwise might not be published.

There is a need to further explore the accuracy of the non-standard observation types, e.g., the cloudy sky method, and to seek improvements to these observation types. The development and exploitation of automated Dobson measurement systems should be given every encouragement. Further studies of sampling errors and their impact should be done, an important issue being to better define the ratio of scientific benefit to financial cost for the establishment of any new stations. There are regular calls for new stations in the remote oceanic and southern hemisphere regions, but so far few countries have shown any willingness to financially support them.

Overall, it seems that in order to have the world's Dobson instruments function optimally as a network, there is a need for further coordination and leadership. Some of the additional responsibilities could be shared throughout the network, but probably most would be best done by, or under the umbrella of, the Central Dobson Spectrophotometer Laboratory. Ideally the management of the network should be based on an agreed-to quality assurance plan which defines the procedures required to actively ensure that the desired standards are reached in ail aspects of the network's operation. The instrument's Operations Handbook (Komhyr, 1980b) already goes a long way to meeting the objectives of quality assurance. Serious consideration will need to be given to increasing the resources available to implement the various recommended components of any quality assurance plan, especially the relatively costly tasks of international intercomparisons and international staff training exercises.

Error analyses and error reduction efforts are usually very worthwhile, but their success inevitably advances the point of diminishing returns, where only small improvements in accuracy are gained for large efforts. At present there remain several large potential error sources, of the order of 5%, which definitely require further attention. However, once these are generally under control, our efforts should then increasingly concentrate on ensuring the successful routine operation of the network at this sustainable minimum error level, which for individual instruments in the Dobson network might eventually be, overall, about 2% relative uncertainty, plus the 1 to 2% absolute uncertainty due to the uncertainty in any new standard ozone absorption coefficients.

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APPENDIX A

Extract, courtesy of W.D. Komhyr, from:

CANADIAN
METEOROLOGICAL MEMOIRS
No. 6

MEASUREMENTS OF ATMOSPHERIC OZONE
AT MOOSONEE CANADA - JULY 1 1957
TO JULY 31 1960 * : * W. D. KOMHYR

DEPARTMENT OF TRANSPORT
METEOROLOGICAL BRANCH

TORONTO ONTARIO
1960

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6. ZENITH SKY OBSERVATIONS.

6.1. ADZB Observations.

By comparing 177 nearly simultaneous X^{DS}_{AD} and X^{ZB}_{AD} values measured over a wide range in μ and X since July, 1957, it was possible to correct empirically the chart supplied by Beck, Ltd., from which estimates of ozone amount are made from measurements on the blue zenith sky. The corrected chart I_{AD}, shown in Figure 2, gave excellent results. After application of the new chart to the 177 comparison values, the following error frequencies resulted.

Error	≤ 1%	≤2%	≤3%
Frequency	54%	78%	95%

The new chart was used in the reduction of the entire body of ozone measurements made since July, 1957, on the clear zenith sky.

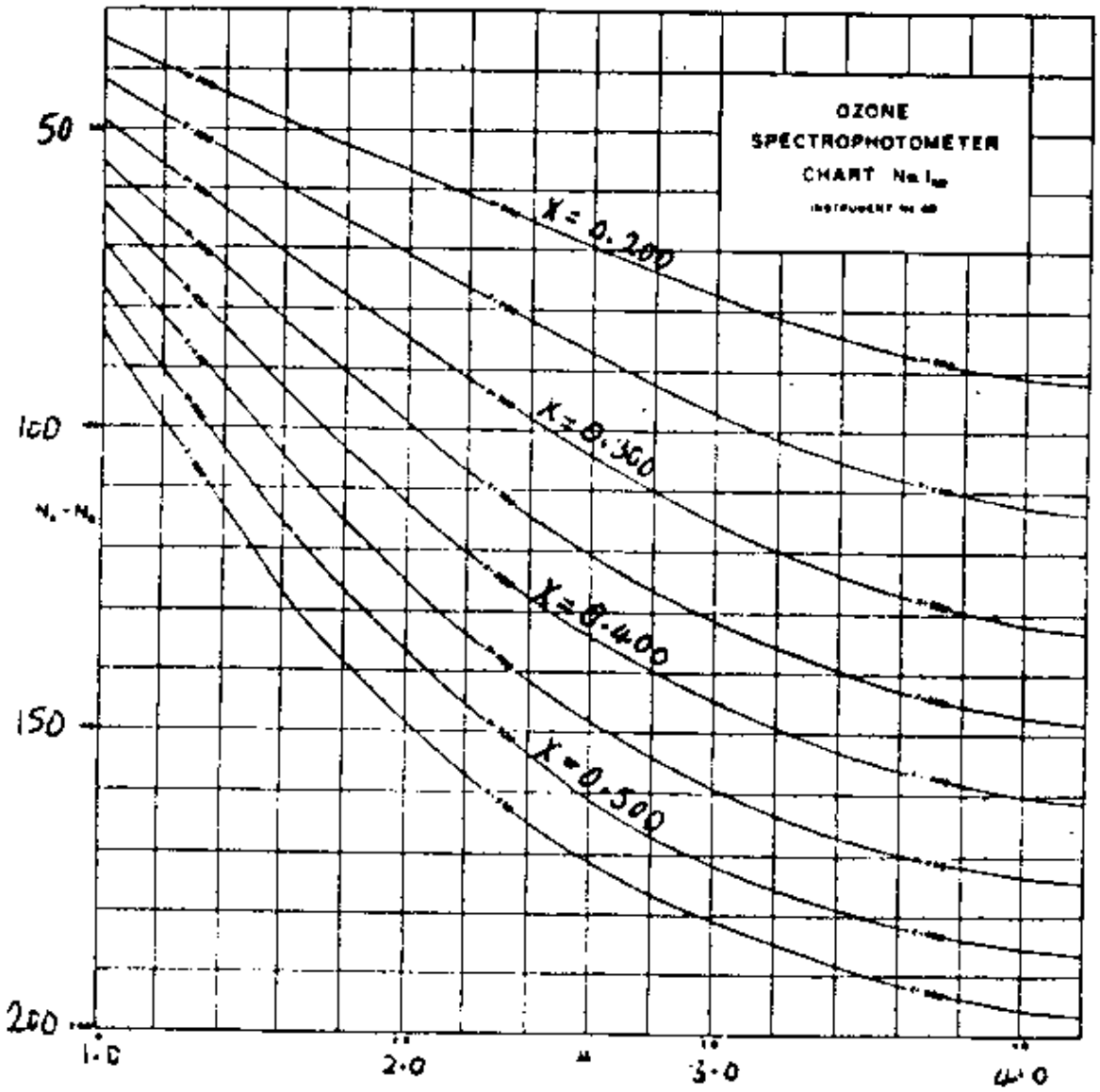

Fig. 2

6.2. Use of Chart I_{AD} on Cloudy Zenith Sky Observations.

A total of 137 ozone measurements made on the cloudy zenith sky were compared with direct sun measurements taken within 3 hours of the cloudy sky observations. The values of X^{ZC}_{AD}, read off Chart I_{AD}, represented a wide range of X, while μ varied from about 1.1 to 2.4. It as immediately apparent that the X^{ZC}_{AD} values were large when compared with the direct sun total ozone amounts, especially when μ and X were high. On the basis of the data in hand, a tentative cloud correction table (Table 14) was, therefore, drawn up to be used in conjunction with Chart I_{AD}. Also, an arbitrary cloud density scale was established consisting of the numbers 1 to 10. A cloud density of 10 implies extremely thick cloud, while figure 5 refers to cloud of medium thickness. Cloud of density 3 just obscures the sun's disc. Cloud corrections are to be applied to X^{ZC}_{AD} values deduced from Chart I_{AD} only when the cloud density is greater than 3.

For the 136 finally corrected cloudy zenith observations that were compared with direct sun observations, the following error frequencies were found:

Error	≤ 1%	≤ 2%	≤ 3%	≤ 4%
Frequency	32%	55%	76%	91%

The result is very gratifying in view of the fact that the comparison observations were made several hours apart in many instances and, therefore, represent, at least in part, real changes in ozone amount. It appears likely, in general, that the errors In the values of X^{ZC}_{AD} coded in the IGY/AGI Forms 0-1 are less than about

3%.

6.3. CC' Wavelength Observations on Blue Zenith Sky.

Nearly simultaneous observations on ADDS and CC'ZB were available for 201 cases. These observations were used to determine corrections to the Chart I_C supplied by the manufacturer. The corrected chart, applicable to measurements at Moosonee, is shown In Figure 3. In using the new chart to evaluate CC'ZB observations, haze corrections are applied by using the cloud correction chart shown in Figure 5. In re-working the 201 cases used to construct the new chart, the following error frequencies were found:

Error	≤ 1%	≤ 2%	≤ 3%
Frequency	60%	82%	92%

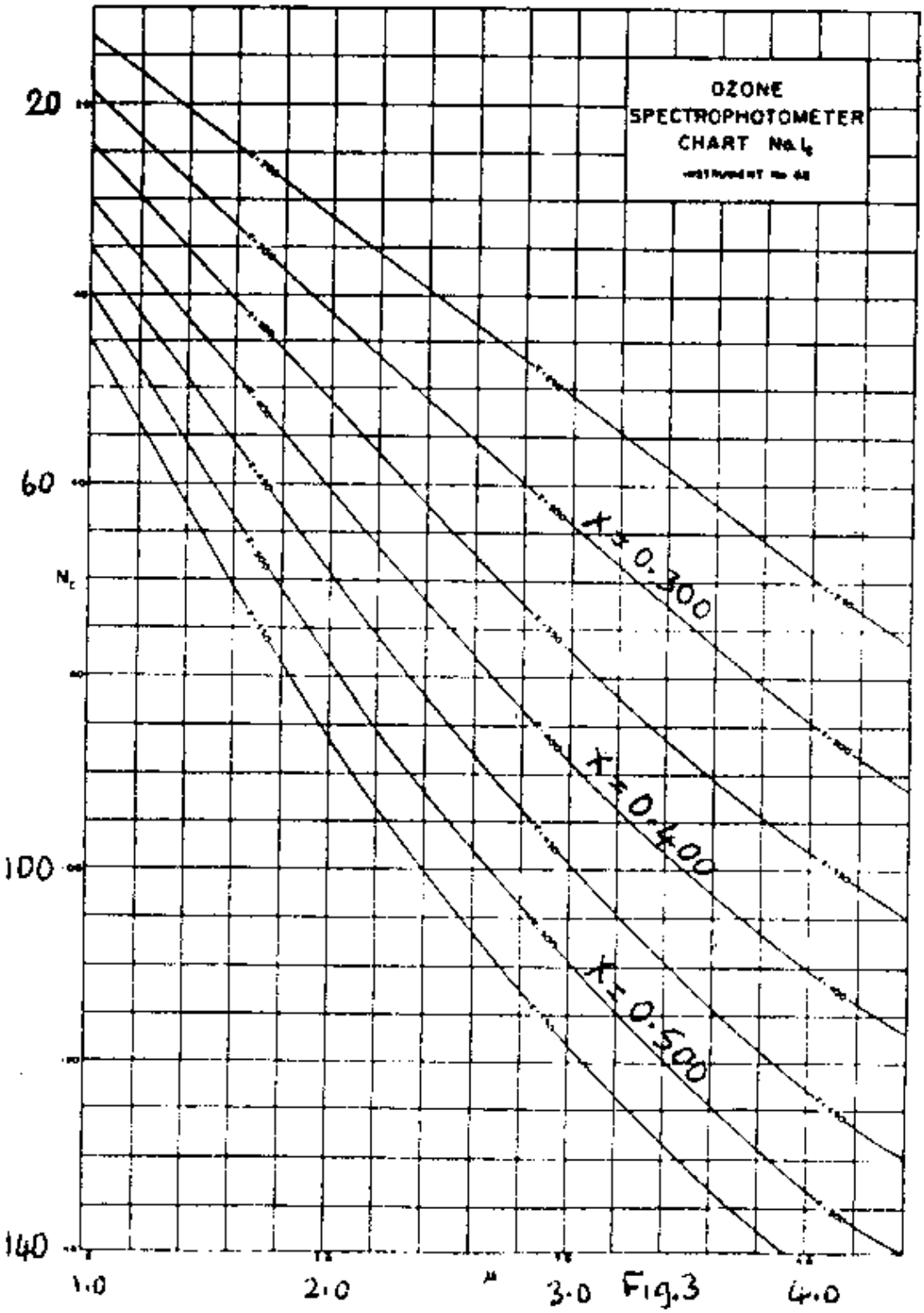

Fig.3

6.4. CC' Wavelength Observations on Cloudy Zenith Sky.

The Oxford technique for evaluation of CC'ZC observations involves the use of two auxiliary charts to determine corrections to be applied before use of Chart I_C. First, in Chart II, isopleths of constant X are plotted against coordinates $N^{ZB}_{C'}$ and μ. One guesses the probable value of X and reads off $N^{ZB}_{C'}$, applicable to exceptionally clear conditions. Next, one enters chart III with $N^{ZB}_{C'} - N^{ZC}_{C'}$ and μ to get ΔN_C. This correction, ΔN_C, is then subtracted from N^{ZC}_{C}. Chart I_C is entered with corrected N^{ZC}_{C} and μ to get X. If this X differs appreciably from the value assumed initially, the whole process is repeated using the new X.

In examining the observations at Moosonee, little justification was found for constructing more than one curve on the $N^{ZB}_{C'}$ vs μ chart. Experimental data are plotted in Figure 4, the empty circles represent individual points and the solid circles are average points representing groups based on various X and μ ranges. The final curve, representative of all X values, is drawn just below the highest values plotted. It is interesting to note the reversal of this curve at low μ. The Oxford curves retain a negative slope through the entire μ range. For comparison, the Oxford curve for.350 cm is shown (dashed) in Figure 4. The reason for this reversal is not completely clear. A similar reversal has been found in the analysis of data from Edmonton. Possibly it represents a climatological rather than physical effect. That is to say, increased atmospheric scattering due to water vapour and haze may cause the reversal at low μ.

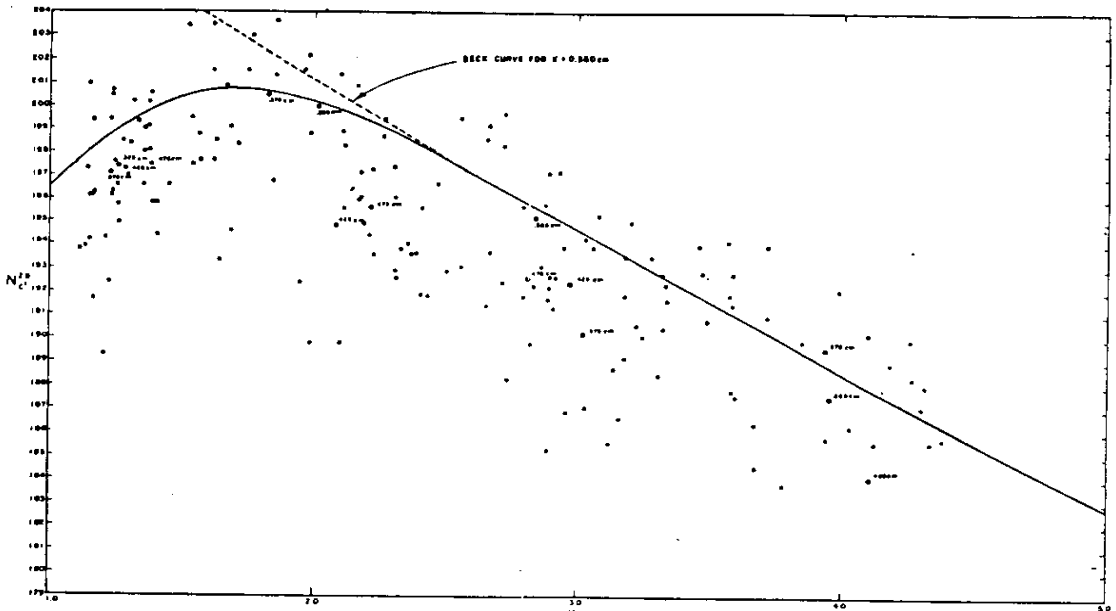

Fig. 4. Spectrophotometer Observations on Blue Zenith Sky using the C' Wave Lengths

Using the curve of Figure 4, new cloud correction charts were constructed using approximately 300 comparison observations taken throughout the period of record. In this analysis $X^{ZC}_{CC'}$, values were compared with "correct" X^{DSGQP}_{AD}, X^{ZB}_{AD} and X^{ZC}_{AD} values. The bulk of the comparisons were made with X^{ZC}_{AD} values. Because the data plotted on Figure 4 were represented on a single curve, it was possible to combine the Oxford Charts II and III into a single chart which is shown in Figure 5.

The analysis suggested that the effect of cloud height on the observations was considerably less than indicated by the Oxford charts. Indeed, in preparing the final coded data, only the Low Cloud Correction Chart was used. A close examination of the final coded data later suggested that the middle and high cloud data were possibly a little low, perhaps by as much as 0.010 cm. Tentative middle and high cloud corrections have been incorporated in Figure 5 and these will be used in reducing future data on a provisional basis.

In applying the CC' charts (Figure 3 and 5) to the 300 comparison values, the following error frequencies were found:

Error	≤ 1%	≤ 2%	≤ 3%	≤ 4%
Frequency	33%	66%	81%	89%

The 11% of the values having an apparent error greater than 4% include several observations where the total ozone is either increasing or decreasing or where light precipitation is falling. The result is encouraging when we consider that most comparisons were made against ADZC values which have a similar error frequency.

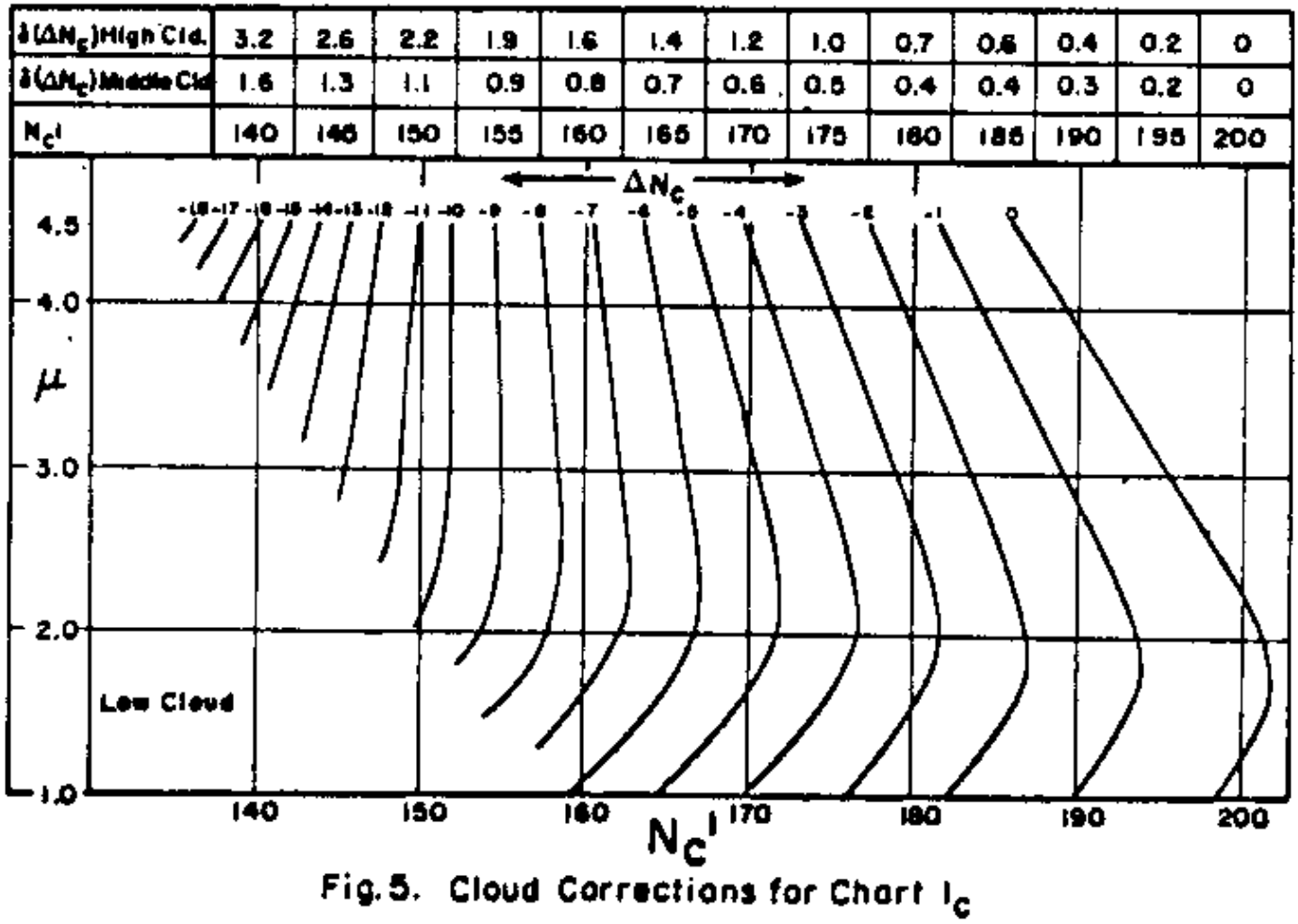

Fig. 5. Cloud Corrections for Chart I_c

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