Problems in the Use of Interference Filters for Spectrophotometric Determination of Total Ozone

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ABSTRACT

An analysis of the use of ultraviolet narrow-band interference filters for total ozone determination is given with reference to the New Zealand filter spectrophotometer under the headings of filter monochromaticity, temperature dependence, orientation dependence, aging, and specification tolerances and nonuniformity. Quantitative details of each problem are given, together with the means used to overcome them in the New Zealand instrument. The tuning of the instrument's filter center wavelengths to a common set of values by tilting the filters is also described, along with a simple calibration method used to adjust and set these center wavelengths.

1. Introduction

The idea of using optical filters to select the ultraviolet bands used in the spectrophotometric determination of atmospheric total ozone is an appealing one since optical filters, in principle, allow the construction of a small, rugged and relatively inexpensive spectrophotometer. Such an instrument would be well suited to field use and would be a viable alternative to the widely used standard instrument in total ozone determination, the Dobson spectrophotometer. The Dobson is a quartz prism double monochrometer (Dobson, 1957), and as such, is relatively cumbersome and requires careful calibration, operation and maintenance.

Several instruments using the glass absorption type of optical filter have been constructed, the most notable being the two-filter Russian M-83 spectrophotometer [Gushchin (1963), also described in English by Khrgian (1973)], but none has gained acceptance as an equal to the Dobson spectrophotometer. The basic reason is that glass absorption filters have broad transmittance bands, often about 20–30 nm wide, which do not permit the use of the convenient monochromatic Lambert-Beer attenuation law. Correction schemes can be devised, but they require an accurate knowledge of the ozone absorption spectrum, and they cannot adequately cope with the unknown atmospheric particulate scattering. For example, Bojkov (1969) found systematic differences between the M-83 and Dobson spectrophotometer ozone values of up to 30%, and the work of Osherovich *et al.* (1974) suggests even greater discrepancies.

Fortunately, the problem of obtaining sufficiently narrow bandwidths has now been solved with the development of a radically different type of filter, the interference filter, whose wavelength band selection arises from wave interference rather than from any absorption process. These filters are essentially Fabry-Perot etalons, but use dielectric cavity spacers and multilayer dielectric reflectors, and may consist of more than one cavity unit. The development of UV filters has lagged somewhat behind that of visible filters, but now narrow-band filters of a quality suitable for ozone spectrophotometry are commercially available.

The first interference filter ozone spectrophotometer was described by Osherovich *et al.* (1969), and since then its use has been reported by Osherovich *et al.* (1974) and Steblova (1975). The New Zealand interference filter spectrophotometer, in its Mark I form, was first described by Matthews (1971), while the Mark II version was later described by Matthews *et al.* (1974) and Basher (1975). Further improvements have led to the current Mark III model, shown in Fig. 1, to which this paper mostly refers.

It should not be thought that the use of interference filters is without difficulty. The purpose of this paper is to describe the characteristic problems of interference filters when used for ozone spectrophotometry, and outline the means used by the authors to overcome these problems in the New Zealand filter instrument.

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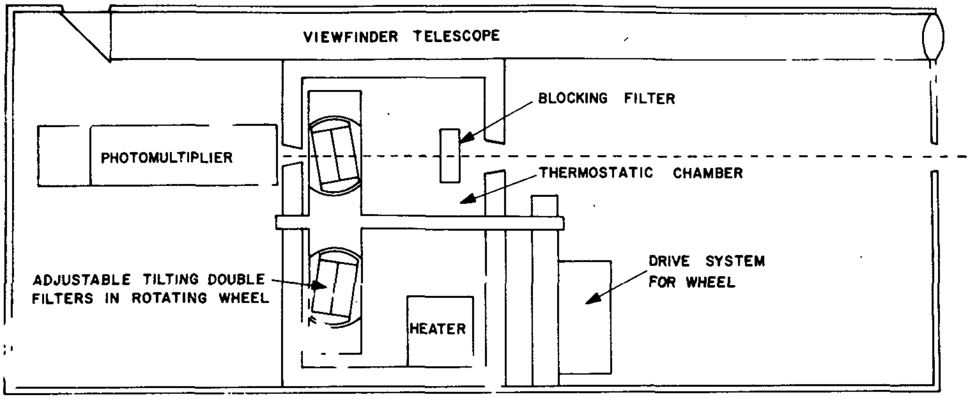

FIG. 1. Schematic of Mark III filter ozone spectrophotometer design, illustrating temperature control, tilting filters, and other features discussed in article.

2. Interference filter characteristics

This section looks at each of the five major problem areas in the use of ultraviolet interference filters for total ozone determination, assessing the significance of each in turn.

a. Filter monochromaticity

There are three aspects of filter monochromaticity which must be given careful attention for satisfactory filter instrument performance: 1) passband narrowness, or half-bandwidth, 2) passband sharpness or steep-sidedness, and 3) absence of contaminating leakage bands. As is described by Basher (1977) in a companion paper, each contributes to the "bandwidth effect," the effect on intensity measurements, and consequently on total ozone measurements, due to imperfect monochromaticity.

First, half-bandwidths (the bandwidth between half peak transmittance points) of 1 to 3 nm, similar to the Dobson instrument slitwidths, are desirable and are now available in custom-built commercial filters. Such bandwidths are sufficiently narrow to keep the "bandwidth effect" within manageable levels, yet are sufficiently wide to allow sizeable radiation flux transmission, and to provide solar intensity stability, with respect to filter center wavelength variation, by a broad averaging of the highly variable spectrum of the sun.

Second, it is not enough to just have narrow half-bandwidths; the tenth-, hundredth-, thousandth-, etc., bandwidths must also be as narrow as possible, especially for the shorter wavelength filters for which the gradient of incident solar intensity with wavelength is very high. Although most manufactured filters are inadequate in this respect, it has been realized that a significant improvement can be achieved simply by putting two filters of the same wavelength in tandem to produce a "double filter," as illustrated in Fig. 2. The closer approximation of the monochromatic ideal by the double filter is numerically confirmed by a significant reduction in its bandwidth effect down to levels of about ±2% (Basher, 1977). The improvements come at the expense of reduced peak transmittance, but this can usually be compensated for in other ways. It should be noted that the double filter spectrum is represented here by the mathematical product of two single filter spectra as the true spectrum cannot be adequately measured outside the central passband region; consequently, because of multiple reflections between the two filters, its transmittance may be underestimated by perhaps up to 20% and its passband sharpness may be a little overestimated.

Third, transmittance "leakage" bands, such as that shown in Fig. 2 at 345 nm, must be minimized in order to produce an acceptable level of monochromacity. Leakage bands are the residues of the transmittance sidebands which have been only partly suppressed by the manufacturer's blocking filters, and in the authors' UV filters, they commonly appear in the 340–370 nm near-ultraviolet region and in the 700–1200 nm near-infrared region. Only those bands falling within the bounds of the atmosphere's UV cutoff at 290 nm and the instrument long-wavelength sensitivity cutoff are of any significance.

Leakage bands can be blocked by additional selective absorption or interference blocking filters, or by doubling a filter. Doubling a filter is an effective means only if the leakage band is small compared to the passband, i.e., the transmittance rejection ratio is small, as in Fig. 2, for example. Actually, the "flux" or energy ratio, the ratio of the product of transmittance and half-bandwidth, is a better measure of a leakage band, as Fig. 3 illustrates.

It is obvious that, relative to the filter passband, the broad near-infrared leakage bands of Fig. 3 will contribute a large amount of radiation, even when the filter is doubled, and that the problem will be exacerbated by the atmosphere's preferential attenuation of UV radiation, especially at large values of airmass. The solution to such leakages lies with IR

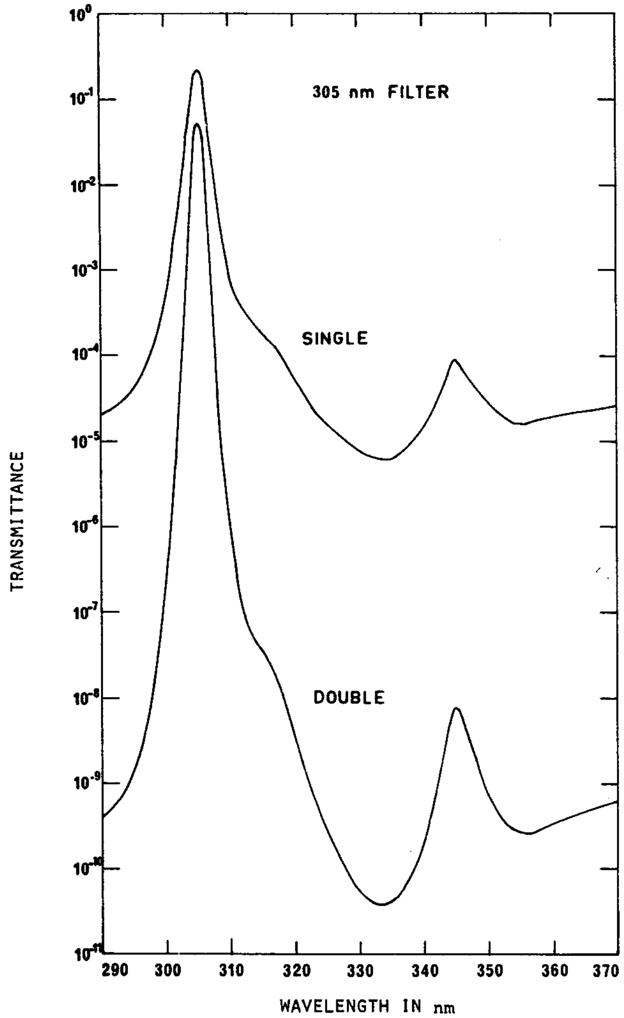

FIG. 2. Spectral transmittance of single and double 305 nm filters, illustrating the better monochromaticity of double filters.

insensitive photomultipliers such as the S5 or similar types, and good IR blocking filters. The blocking filter currently used in the filter instrument consists of a slice of nickel sulphate hexahydrate crystal sandwiched between two plates of Corning CS 7-54 glass, and provides a 10^6 blocking to the IR leakage bands as well as to the near-ultraviolet leakage bands, yet still transmits a sizeable 50% at passband wavelengths. As is shown by the linear Langley plots of Fig. 4, this combination of double filters, photomultiplier and blocking filter provides the monochromaticity required for the filter instrument.

b. Temperature dependence

Regular changes in the optical characteristics of interference filters occur with temperature owing to the temperature dependences of the refractive indices and thicknesses of the filters' dielectric layers. The most significant change is a positive linear shift in center wavelength, with values ranging up to 0.005% $(^\circ\mathrm{C})^{-1}$ being observed by Blifford (1966) and Furman and Levina (1971). Values of this order are quite significant. For example, a 0.015% or 0.05 nm shift in the 305 nm filter's center wavelength will change the filter's ozone absorption coefficient by about 1%. (The 305 nm filter is used as an example because its behavior has the greatest effect on the final total ozone value determined.) The measurements displayed in Fig. 5 give a representative value of 0.0105 ± 0.0005 nm $(^\circ\mathrm{C})^{-1}$ in center wavelength shift for the filter instrument's filters. To overcome this with Mark III instruments the filters are enclosed in a thermostatically controlled environment kept at $40 \pm 5^\circ\mathrm{C}$ for an ambient temperature range of -10 to $35^\circ\mathrm{C}$. The nickel sulphate blocking filter is also placed in this environment to overcome its temperature dependence

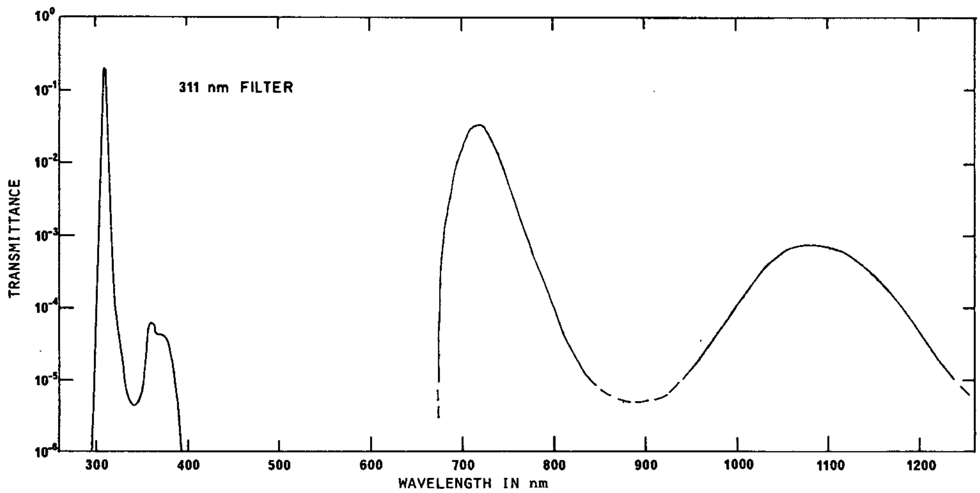

FIG. 3. Extended spectrum of the 311 nm filter transmittance showing ultraviolet and large infrared leakage bands.

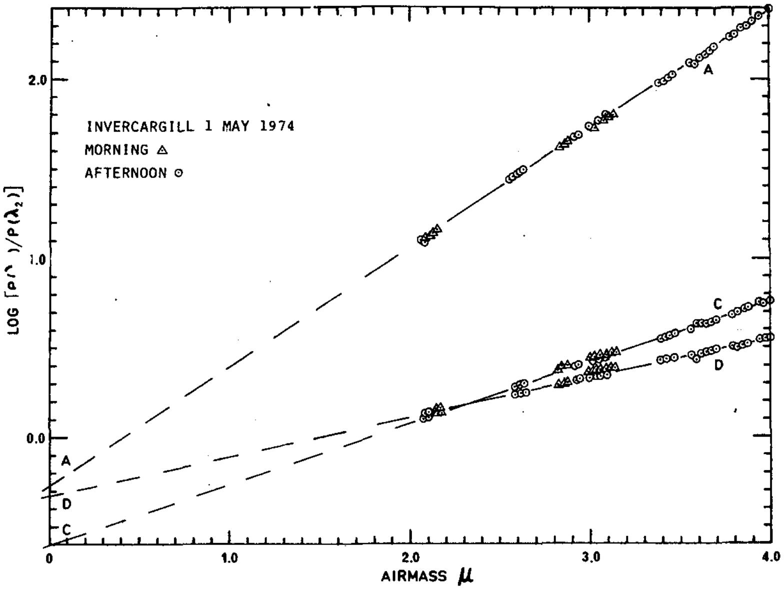

FIG. 4. Langley plots, or log response ratio versus airmass, for the filter instrument's A, C and D wavelength pairs.

which is most noticeable at the longer wavelength bands.

c. Orientation dependence

An interesting, and, as shall be seen later, very useful effect is the dependence of interference filter spectral characteristics on the angle of incidence of incoming radiation. With increasing angle, Blifford (1966) observed a shifting of the filter passband to shorter wavelengths, accompanied by decreasing peak transmittance and increasing half-bandwidth. Some changes of this sort are to be expected, of course, since interference phenomena are angle dependent.

The measurements illustrated in Figs. 6 and 7 show similar behavior for the filter instrument's filters, the most significant effect being the shift in center wavelength. It can be seen that for angles of incidence $\theta < 15°$, the shift in center wavelength $\Delta\lambda$ fits the $\Delta\lambda \propto \theta^2$ theoretically based formula of Lissberger and Wilcock (1959). Another conclusion of Lissberger and Wilcock which is useful is that an axially symmetric convergent or divergent beam of semi-angle α and with axis normal to the filter, results in precisely half the center wavelength shift produced by tilting the filter through α with respect to a parallel beam.

Two situations need considering. First, calibration errors can arise in measuring filter spectra if the calibrating instrument's beam through the filte

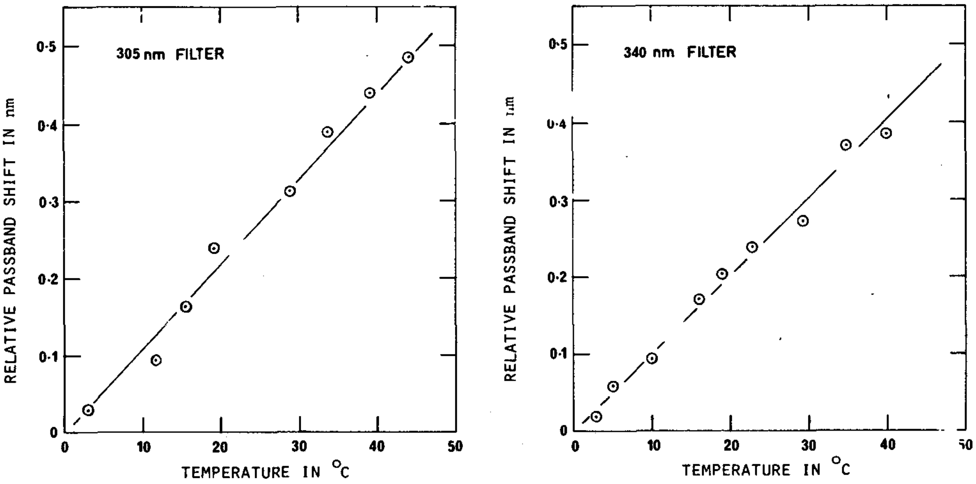

FIG. 5. Temperature dependence of filter center wavelengths. A positive linear shift is shown.

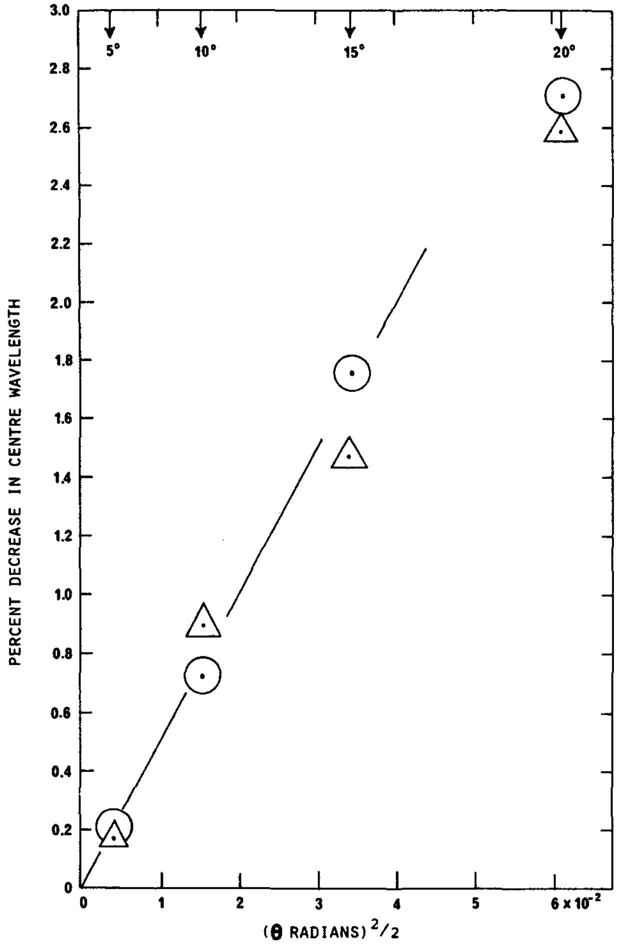

FIG. 6. Dependence of filter center wavelengths on radiation angle of incidence.

sample converges or diverges. For example, the sample beam in the Cary 14 recording spectrophotometer converges in two mutually perpendicular planes at semi-angles of about 4° and 1.4°, and thus can reduce the filter instrument's filter center wavelengths by about 0.06%, with a consequent error in the 305 nm filter's ozone absorption coefficient of almost 4%. Fortunately, this problem can be largely circumvented by simply masking the outermost divergent parts of the beam.

Second, center wavelength reductions can accompany actual measurements. With diffuse sources such as zenith skylight, the 1.2° semi-angle field of view of the Mark III filter instrument results in a reduction of only 0.005%, or 0.3% in the ozone absorption coefficient of the 305 nm filter. Only the one field of view is used. With direct sun measurements, the dominating direct solar radiation is subtended at a semi-angle of only 0.3° and thus causes negligible center wavelength shift, provided the filters' alignments with respect to the solar beam are sufficiently constant. For this purpose, the filter instrument is equipped with a telescope alignment system.

d. Aging

The optical characteristics of interference filters are known to age, i.e., change with time, the most important change being a gradual shift in center wavelength. Furman and Levina (1971) contend that moisture absorbed by or dessicated from the filters is the primary cause of center wavelength shift. They derive an approximate relation between the shift and a filter's water content which suggests that the filter instrument's hermetically sealed filters are stabilized against moisture effects to 0.01 nm or less in center wavelength. This figure is quite adequate for the purposes of total ozone measurement. Furman and

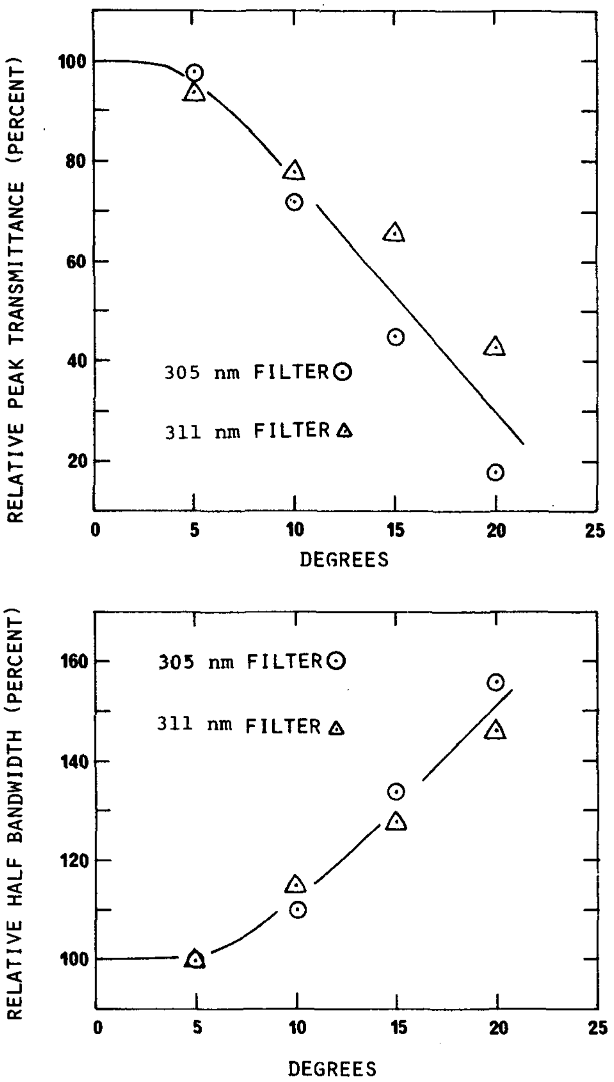

FIG. 7. Dependence of filter peak transmittance and half-bandwidth on radiation angle of incidence.

Levina also indicate that changes in peak transmittance and half-bandwidth are negligibly small.

Moisture is not strictly an aging agent since its effects are reversible. It is also not the sole type of aging effect. In another comprehensive study, Title *et al.* (1974) and Title (1974) show that the thermal and irradiation histories of their visible region filters affected the filters' aging. With respect to thermal histories, they found, first, that filters kept at less than 38°C exhibited quite variable center wavelength reductions of from 0.01 to 0.10 nm per year, and second, that this aging effect could be accelerated by baking the filters at 100°C for several months. The important point about baking is that although the cumulative shift becomes large (up to 1.0 nm), the rate of the shift decreases, sometimes by an order of magnitude. The "thermal" behavior of the filter instrument's UV filters is at present unknown and the filters are not baked. However, any shifts of 0.1 nm per year or less can be adequately countered by the calibration methods described later.

With respect to irradiation-induced aging, Title found that the band of solar radiation between 340 and 500 nm caused reductions in his filter center wavelengths of the order of 0.1 nm per hundred hours of exposure. He concludes from a study of the materials and construction of the filters that the shift is a direct result of radiation absorption by the filters' zinc sulphide layers. The UV filters of the New Zealand filter instrument do not contain this material, but it is possible that the materials which are used do have absorption bands which behave is a similar fashion, and as a simple precaution, the blocking filter described in Section 2a is now placed in front of the interference filters.

It should be borne in mind that since aging is a chemical process, it is very dependent on the chemical characteristics of the particular dielectric materials used in the filter. Confident assessment of the aging behavior of one type of filter from the behavior of another is therefore rather difficult, and the possible existence of other significant aging effects must be acknowledged. However, measurements made so far indicate a total aging shift of less than 0.1 nm year^{-1} for the filter instrument's filters.

e. Specification tolerances and nonuniformity

Because of the difficulty of accurately depositing the many very thin layers that comprise an interference filter, it is not possible to construct filters to the level of precision, repeatability or uniformity ideally desired for the filter instrument. The following tolerances in the main optical characteristics are typical: ±0.5 nm in center wavelength, ±0.3 nm in half-bandwidth and peak transmittances of from 5 to 25%.

The variability in center wavelength is a major drawback, since it means that each set of filters must have its ozone absorption coefficients separately calculated using an absorption spectrum, probably the Vigroux (1953) spectrum, whose accuracy is known to be inadequate both relatively and absolutely. Hence, the results of individual filter instruments will differ among themselves as well as differing with the Dobson instrument, such differences perhaps amounting to 5% in total ozone.

The second major difficulty is optical nonuniformity across each filter. The worst case experienced by the authors exhibited variations of over 20% in peak transmittance and 1.0 nm in center wavelength. Such variations can be reduced by a uniformity specification, but at present the limit appears to be about ±5% in the product of peak transmittance and half-bandwidth (this product is approximately proportional to the flux transmitted per unit area), and ±0.2 nm in center wavelength.

The main effect of variability in peak transmittance and half-bandwidth is to give variable extraterrestrial constants. By contrast, the main effect of variability in center wavelength is to give variable ozone absorption coefficients. Both types of variation mean that the area of a filter used in its calibration must correspond to the area used operationally, yet in practice this is difficult to achieve because the calibrating instrument and filter instrument usually have dissimilar beam geometries. In order to maintain the constancy of a calibration, the filters must be kept in fixed positions in the filter wheel.

An important improvement in the Mark III instrument with respect to nonuniformity has been the placement of the filter wheel as close as possible to the photomultiplier. With the Mark II instrument the combination of filter nonuniformity, a photomultiplier and filter separation of 20 cm and variability in instrument alignment gave rise to variations in measured direct sun intensitities of several percent. At different alignments the photomultiplier "saw" the sun through different areas of the filters.

3. Calibration

In summary of the last section, it can be said that for the purpose of total ozone measurement, interference filters can be made which are sufficiently narrow in bandwidth, and which can be readily defended from the effects of leakage bands, temperature, orientation, moisture-induced aging and transmittance variability. The remaining problems are essentially those of calibration: how to easily determine the ozone absorption coefficients for each filter set, how to best ensure consistency between calibration of different filter sets, and how to check for and correct possible aging effects. These problems have been overcome in the New Zealand filter instrument by means of the following two techniques: filter tilting and "discriminator" calibration. (The filter instrument's extraterrestrial constants are found with the same methods used with the Dobson instrument.)

a. Filter tilting

By making use of the dependence of filter center wavelength on orientation (Fig. 6), it is possible to "tune" the varying center wavelengths of different filter sets to predetermined and common values. The tuning of filters has several advantages.

1) With all filter sets tuned to a common set of center wavelengths, only one set of ozone absorption coefficients needs to be calculated, and the possible lack of filter instrument comparability, due to inaccuracies in the individual sets of absorption coefficients needed for individual filter sets, is eliminated.

2) With suitable specification, the filters can be tilted to match the standard Dobson wavelengths, thus ensuring comparability between the filter and Dobson instruments and continuity in total ozone data.

3) Any aging drifts in center wavelength can be corrected simply by retuning the filters.

A quantitative idea of the filters' tuning capabilities can be gained from Fig. 6. It can be seen that a 10° maximum tilting angle will provide a 2.5 nm tuning range in center wavelength. This will allow compensation for a ±0.75 nm tolerance range in center wavelength, plus adjustment for a possible cumulative aging shift of 1.0 nm.

Fig. 7 shows that tilting will alter a filter's peak transmittance and half-bandwidth, especially for angles $>5°$, and thus may alter the instrument's extraterrestrial constants. Any adjustment of the tilt, therefore, requires a subsequent check of the constants by means of a standard lamp type of test. There will also be an increase in the bandwidth effect (see Basher, 1977), approximately in proportion to bandwidth. A secondary spreading effect occurs with zenith type measurements owing to the distribution of angles of incidence within the instrument's 2.4° field of view. Tilting also increases the sensitivity of the filter center wavelengths to instrument alignment on the sun, in proportion to tilt angle. At the maximum 10° tilt angle, a ±0.05° alignment precision is needed to keep the center wavelength to within an acceptable ±0.025 nm.

b. Discriminator calibration

The "discriminator" calibration method, currently being developed by the authors, is addressed to the question of how to determine the tilt angle needed to accurately set the filters to the desired center wavelengths. The tilting calibrations can, of course, be carried out using a good quality spectrophotometer such as a Cary 14, but this procedure suffers from the following disadvantages: the need for an accessible and expensive calibrating spectrophotometer and the need to remove the filter wheel from the filter instrument, together with the requirements discussed in earlier sections, i.e., a parallel calibrating beam, calibration of the same area of filter as is used operationally, and maintenance of the filters at operational temperature (40°C).

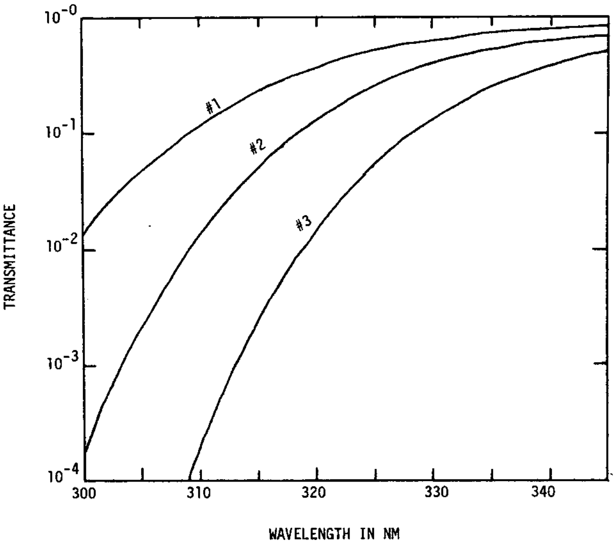

FIG. 8. Spectral transmittance of discriminator filters used in calibrating the filter instrument.

The new method is expected to overcome virtually all the above disadvantages. It makes use of "discriminator filters"—spectrally well-calibrated filters whose transmittance, as shown in Fig. 8, decreases sharply and monotonically with decreasing wavelength over the near-ultraviolet region. If the transmittance of the discriminator is measured directly with the filter instrument and a light source, the one-to-one relationship between glass transmittance and wavelength will provide a unique transmittance measurement for each of the six filter bands, each transmittance corresponding to the filter's center wavelength. The filters can therefore be calibrated *in situ* with the discriminator acting as the wavelength standard.

In practice, the transmittance measurements are made by a discriminator in and out sequence of intensity measurements and are compared to calculations of the discriminator transmittance weighted by the spectrum of the particular source used and the appropriate filter passbands. The accuracy of the method appears limited to ±0.1 nm in center wavelength. Although a laboratory calibration using a UV lamp will probably yield the best accuracy, the interesting possibility of using the sun as a source is being presently investigated since it would enable the simple field calibration of the filter instrument. Table 1 lists the characteristics of the two thicknesses of soda

TABLE 1. Discriminator characteristics.

Wavelength band (nm)	305	311	317	325	331	340
Glass thickness (mm)	1.0	1.0	1.0	4.0	4.0	4.0
Transmittance (%)	6.0	17.6	31.2	10.7	26.6	54.3
Gradient ($\%\ \text{nm}^{-1}$)	23	13	9	23	11	5

glass discriminators used to cover the 300 to 340 nm spectral range.

4. Conclusion

The above analysis of the New Zealand filter instrument's interference filter characteristics shows that interference filters, as distinct from absorption type filters, are very suitable for use in the spectrophotometric determination of total ozone provided certain precautions are taken. Overall, it can be concluded that the net uncertainty is about 5%, the largest part of this being due to center wavelength uncertainty from calibration and aging, and to uncertain stability in the transmittance spectra of the interference and blocking filters. To assess the instrument's long-term behavior, intercomparisons with Dobson spectrophotometers are being undertaken by the New Zealand Meteorological Service and by NASA Wallops Flight Center. A version of the instrument is commercially available.

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