

Atmospheric Ozone : Determination by Chappuis-Band Absorption

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ABSTRACT

Ozone content in the atmospheric column above Mauna Loa Observatory, Hawaii, was determined in experiments by measuring the attenuation of sunlight in the visible spectrum Chappuis bands (500 nm $<\lambda<$ 700 nm wavelength). The dominant source of uncertainty in such determinations is the accuracy with which the magnitude of the published Chappuis-band absorption coefficients are known. Values of ozone (for 42 clear days) obtained by using Vigroux's absorption coefficients differed systematically, and were 17.6% smaller than those derived simultaneously in time and space with a Dobson spectrophotometer. The agreement with the Dobson values improves, but is not perfect, when Inn and Tanaka's absorption coefficients are used in the data analysis. Until more accurate information becomes available on ozone absorption coefficients, spectrophotometric-derived values of atmospheric ozone must be considered uncertain to 10–20%.

1. Introduction

Ozone absorbs light in the yellow and red Chappuis-band continuum, at specific wavelength bands in the infrared (at 4.7, 9.6 and 14.1 μ), and at ultraviolet wavelengths (Goody, 1964; Hudson, 1971). The column amount of atmospheric ozone has historically been investigated by measuring the absorption of sunlight by ozone with photoelectric spectrophotometers operating in the ultraviolet regions. In this regard, the Dobson spectrophotometer has been most extensively used; it has provided a coherent record of amounts and variability of O_3 in the atmospheric column for half a century [for an interesting historical account see Dobson (1968)]. Today, modernized versions (Komhyr and Grass, 1972) of the Dobson are the primary instruments in the worldwide O_3 network, though the Dobson technique may have certain systematic errors associated with its use. This paper reports on a study which was done to see if systematic errors in measuring O_3 by Chappuis-band absorption could be made comparable with or smaller than those affecting the Dobson determinations of ozone.

2. Systematic errors associated with the Dobson spectrophotometer

The determination of ozone amounts with a Dobson, or with other instruments operating in the UV, are uncertain because of the possibility of systematic error. One cause of error, though normally less than 1 or 2%,

is the temperature and pressure dependence of the absorption coefficients in the UV (Holland and Thomas, 1975).

A second, and possibly more important, source of error in the Dobson is related to an assumption made about long-term stability of incoming solar radiation at the operating wavelengths. Heath and Thekaekara (1977) reported finding evidence that solar UV radiation fluctuates in association with active regions on the sun. The fluctuations are of the order of 1% over a single solar rotation, but can perhaps reach several percent over the course of an 11-year cycle of solar activity. What is of real concern in ozone work is that the sun's spectral irradiance may fluctuate differently at closely spaced UV wavelength bands in response to changing solar Fraunhofer absorption-line strengths. Line blanketing at Dobson wavelengths is $\sim 40\%$ and photospheric temperature increments of the order 10 K can cause substantial (several percent) alterations in the strengths of different photospheric absorption lines through the Boltzman-Saha relationship. Livingston (1978) reported seeing variations in the relative strengths of Fraunhofer lines corresponding to a 6 K photospheric temperature change; if they prove to be real, such variations would possibly introduce errors into Dobson-derived ozone values. Ozone derived from spectrophotometry in the ultraviolet may appear to fluctuate simply from changes in the solar output. It is therefore desirable to develop an independent method to measure O_3 amount. The Chappuis bands offer an alternate possibility.

3. Ozone absorption in the Chappuis bands

The error sources inherent in a UV instrument can be reduced by measuring optical absorption of sunlight in the *visible* Chappuis-band semicontinuum. The solar output in these bands is thought to be constant, probably to better than 1% (Labs and Neckels, 1968). In addition, stray light in instruments is lower and simpler to deal with at visible wavelengths than at ultraviolet wavelengths, and optical absorption in the Chappuis bands does not depend on the gas temperature or pressure.

The above remarks must be tempered with the realization that the absorption of light in the Chappuis bands is small, only a few percent, hence it is difficult to measure accurately. The O_3 absorption coefficient at the peak of the Chappuis bands (600 nm) is only one-sixth what it is at 320 nm. If systematic errors were equal in the visible and UV, one could undoubtedly determine O_3 more accurately by operating in the ultraviolet, as Dobson chose to do. But the systematic errors differ for the ultraviolet and visible-band situations and one cannot say *a priori* that a Dobson-type instrument would be more accurate than a Chappuis-band-type instrument. The remainder of this paper is devoted to the study of the Chappuis-band method of deriving O_3 .

4. Theory

Chappuis-band absorption occurs in a quasi-continuum; there are no strong peaks in the absorption spectrum. In the ultraviolet, on the other hand, there is considerable structure in the ozone absorption spectra, allowing one to choose two closely spaced wavelengths, one absorbing strongly, the other lightly, to derive aerosol corrections. The shorter of the ACD Dobson wavelength pairs are in the smoother region of the ozone absorption spectra. The aerosol corrections become more involved, however, when measurements are attempted in the Chappuis bands.

In the Chappuis band study, the following strategy was used to correct for aerosols: 1) the extinction of light was measured at 10 individual narrow wavelength regions, five of which were influenced by the Chappuis bands, the others being outside the bands, and 2) an amount of ozone was chosen to minimize the deviations between computed and observed Chappuis-band absorptions. If the optical absorption coefficient for the Chappuis bands is $A(\lambda)$ per STP cm of ozone amount, then one can calculate a value of x (the column amount of ozone in STP cm) to minimize the quadratic form

$$Q = \sum_{i=1}^n (\tau_i - xA_i - \tau_{D,i})^2, \quad (1)$$

where the index i is used to specify different wavelengths λ_i . The τ_i are the corresponding measured ozone-plus-aerosol optical thicknesses through the atmosphere

(they are obtained by subtracting Rayleigh optical depth from measured total optical depth) and $\tau_{D,i}$ represent estimated *aerosol* optical thickness values. Since aerosol optical depth varies smoothly with wavelength, one may approximate the optical depth from aerosols by, say, the first two terms of a Taylor series expansion about an arbitrary mid-visible wavelength λ_0 , i.e.,

$$\tau_D = a_0 + a_1(\lambda - \lambda_0) + a_2(\lambda - \lambda_0)^2, \quad (2)$$

and rewrite Eq. (1) as

$$Q = \sum_{i=1}^n [\tau_i - xA_i - a_0 - a_1(\lambda - \lambda_0) - a_2(\lambda - \lambda_0)^2]^2. \quad (3)$$

The technique works because aerosol optical thickness always varies slowly and gradually with wavelength over the Chappuis-band region (Deirmendjian, 1968). The ozone amount x and the coefficients a_0 , a_1 and a_2 are determined from Eq. (3) by applying regression theory on measurements of τ_i made at n different wavelengths. A variation in the method involving the weighting of measured values of extinction to place more emphasis on the most accurate ones is described by King and Byrne (1976).

Regarding the accuracy of the ozone amount x determined by Eq. (3), it depends on the uniqueness of the values a_0 , a_1 and a_2 , and to some extent on the choice of λ_0 . The Taylor expansion of the aerosol extinction spectrum [Eq. (2)] is most accurate when carried out around a wavelength near the center of the region sample ($400 < \lambda < 850$ nm); λ_0 was therefore taken at 600 nm. Of the 10 wavelength bands used, three were blueward and two were redward of the Chappuis bands and were not affected by O_3 at all. It is important to realize that the extinction in these five bands had provided the greatest weight in determining the constants a_0 , a_1 and a_2 . This was verified by running the analysis for the five wavelengths blueward and redward of the Chappuis bands; the values of a_0 , a_1 and a_2 were identical within the limit of allowable error to those obtained when analyzing all 10 wavelengths. It is concluded that the values of the constants a_0 , a_1 and a_2 are uniquely determined, and hence the values of x is also known unambiguously. The residuals $R_i = \tau_i - xA_i - \tau_{D,i}$ were in the range 0.001–0.004.

Another approach to the problem of deriving ozone from the Chappuis bands is to assume a power law relationship for aerosol extinction of the form (Shaw *et al.*, 1973)

$$\tau_D = C\lambda^{-n}. \quad (4)$$

Analyses were made on the data using the power law relationship and the derived values of O_3 were found to be identical with those from Eq. (2) within the limits of allowable error. The determination of O_3 with the power law relationship, may also be carried out graphically on log τ vs log λ paper. The graphical

approach has the advantage of incorporating human pattern recognition ability; bad points can be quickly identified and removed or corrected. Numerical values of the constants C and n , which pertain to the aerosol characteristics at Mauna Loa, are described in a separate paper (Shaw, 1979).

5. Experimental procedures

The experiments were carried out at Mauna Loa Observatory using a photometer incorporating well-blocked (maximum leakage $< 10^{-5}$) interference filters and a silicon photoelectric detector. The signals were recorded to a precision of $1:10^4$ and the instrument was calibrated with the Langley method for 110 days (Shaw *et al.*, 1973). Drifts in instrumental sensitivity occurred and were 1% per year at blue wavelength and 0.2% per year at red wavelengths. The optical thicknesses of the atmosphere at all ten wavelengths was derivable to unusually good accuracy because of the excellent atmospheric conditions at Mauna Loa and because of the inherent stability of the silicon diode detector.

6. Results

The Chappuis-band method is accurate at a station like Mauna Loa because of the small amounts of contaminating aerosol. The aerosols caused only 1–2% extinction of sunlight when the sun was near the zenith, compared to 10–30% extinction found at rural continental locations (Flowers *et al.*, 1969). Fig. 1 shows a representative aerosol-plus-ozone extinction spectrum at Mauna Loa, and the least-squares estimate (dotted line) of aerosol optical thickness derived with Eq. (4). Intercomparisons with the Dobson at Mauna Loa was possible for 42 days.

A finding of some importance in this study was that the mean values of O_3 deduced by Chappuis-band spectrophotometry differed systematically and were 17.5% lower than those derived from Dobson spectrophotometry when Vigroux's (1953) absorption coefficients were used in the data analysis. When Inn and Tanaka's (1953) values of absorption coefficients for O_3 were employed in the analysis procedure the mean column amounts of ozone agreed more accurately. The standard deviation of the ratio $x(\text{Chappuis})/x(\text{Dobson})$, after multiplying the derived values of O_3 by 1.175, was 0.04. Values of ozone determined by the Chappuis band and Dobson methods are given in Table 1.

7. Error analysis

An analysis to model the experimental procedure identified sources of systematic errors affecting the determination of ozone by the Chappuis-band method. One error source is stray light leaking through the filters out of their passband. This was investigated by measuring the filter blockage with monochromatic light from

argon and dye lasers and was found to be negligible contributing at most a few tenths of 1% uncertainty in the derived values of O_3 . Systematic errors could also come about from the use of a wrong atmospheric air mass function (it depends on the vertical profile of ozone), or from diurnal variations of aerosol optical thickness. These sources of error introduced uncertainties into the optical thickness of $\delta\tau = \pm 0.002$, and at most an uncertainty in the derived O_3 of 4%. At Mauna Loa the aerosol optical thickness was small, an order of magnitude smaller than at most rural observatories, and even if the aerosol loading changed by a factor of 2 through the morning hours at Mauna Loa, it would introduce an error in ozone amount of only a few percent (Russell and Shaw, 1975).

In summary, the expected errors in deriving O_3 by the Chappuis band method is strongly dependent on the magnitude of the aerosol optical thickness. Though the error in deriving O_3 was 4% at Mauna Loa, it would be larger at an observatory with higher aerosol content. The implication is that if ozone is to be measured using the Chappuis band method to anywhere near the accuracy obtainable with a Dobson spectrophotometer, the experiments would have to be made from high-altitude locations with low turbidity.

8. Conclusions and discussion

The mean atmospheric column ozone amounts at Mauna Loa, determined by the Chappuis-band method and with the Dobson method, disagreed with each other by 17.5% when Vigroux's Chappuis-band absorption coefficients were employed in the analysis. The disparity was smaller, however, when Inn and Tanaka's (1953) absorption coefficients were used. But it is to be noted that there is an internal discrepancy in Inn and Tanaka's paper on the Chappuis-band coefficients. The authors, unfortunately, did not tabulate their coefficients: they graphed them against wavelength. Inn and Tanaka claim in the *text* of their paper that their coefficients are 20% different from Vigroux's, yet their graph (Fig. 3) only indicates about a 10% difference. Our study, assuming that the Dobson is measuring correct O_3 amounts (an assumption that could be in error), indicates that the "correct" Chappuis-band absorption coefficients are 17.6% lower than those tabulated by Vigroux. Inn and Tanaka's values give closer agreement than Vigroux's, but neither should be adopted until additional work is done in refining the accuracy of the Chappuis band coefficients.

The Chappuis-band absorption coefficients have also been measured at one wavelength (577 nm) by Hearn (1961) who indicated agreement with Inn and Tanaka's coefficients to 2% and by Griggs (1968) who, on the other hand, found agreement with Vigroux's values! Clearly, more work needs to be done on resolving these discrepancies in the Chappuis-band absorption coefficients.

TABLE 1. Comparison of derived ozone with Dobson measurements at Mauna Loa Observatory, 1976.

| Day no. (1976) | Chappuis O ₃ * | Dobson O ₃ | $R = \frac{O_{3C}}{O_{3D}}$ |
|-------------------|---------------------------|-----------------------|-----------------------------|
| 107 | 0.269 | 0.268 | 1.002 |
| 128 | 0.297 | 0.303 | 0.980 |
| 131 | 0.270 | 0.290 | 0.929 |
| 133 | 0.269 | 0.290 | 0.926 |
| 134 | 0.267 | 0.283 | 0.942 |
| 135 | 0.263 | 0.271 | 0.969 |
| 146 | 0.301 | 0.307 | 1.020 |
| 156 | 0.282 | 0.300 | 0.941 |
| 163 | 0.286 | 0.289 | 0.990 |
| 166 | 0.296 | 0.300 | 0.987 |
| 168 | 0.285 | 0.289 | 0.987 |
| 170 | 0.279 | 0.290 | 0.963 |
| 173 | 0.272 | 0.275 | 0.991 |
| 174 | 0.275 | 0.277 | 0.994 |
| 175 | 0.271 | 0.277 | 0.980 |
| 177 | 0.268 | 0.277 | 0.966 |
| 181 | 0.292 | 0.286 | 1.021 |
| 183 | 0.288 | 0.283 | 1.018 |
| 184 | 0.286 | 0.281 | 1.018 |
| 189 | 0.282 | 0.288 | 0.980 |
| 191 | 0.274 | 0.281 | 0.976 |
| 194 | 0.284 | 0.273 | 1.041 |
| 195 | 0.276 | 0.278 | 0.994 |
| 196 | 0.274 | 0.273 | 1.005 |
| 197 | 0.286 | 0.275 | 1.041 |
| 198 | 0.281 | 0.274 | 1.026 |
| 202 | 0.297 | 0.279 | 1.064 |
| 203 | 0.284 | 0.269 | 1.056 |
| 204 | 0.293 | 0.268 | 1.094 |
| 205 | 0.281 | 0.271 | 1.038 |
| 208 | 0.285 | 0.270 | 1.056 |
| 211 | 0.279 | 0.271 | 1.031 |
| 212 | 0.270 | 0.267 | 1.013 |
| 216 | 0.272 | 0.276 | 0.987 |
| 217 | 0.273 | 0.278 | 0.984 |
| 218 | 0.282 | 0.272 | 1.038 |
| 219 | 0.283 | 0.282 | 1.005 |
| 223 | 0.283 | 0.275 | 1.030 |
| 224 | 0.295 | 0.306 | 0.964 |
| 226 | 0.389 | 0.276 | 1.090 |
| 231 | 0.291 | 0.277 | 1.051 |
| 235 | 0.280 | 0.275 | 1.019 |

Standard deviation in the ratio R: 0.038

* Note: Vigroux's Chappuis-band absorption coefficients have been divided by 1.176 to put the mean Chappuis value in agreement with the Dobson.

Error analysis of the Chappuis-band technique predicts that the *precision* of day-to-day ozone determinations should be $\sim 2\%$ for the Mauna Loa data. The observed standard deviation in the ratio of Chappuis to Dobson-derived O₃ values was 3.5%, after the Chappuis O₃ values were multiplied by 1.175 to trim the mean values into agreement. One can conclude that the Dobson measurements and Chappuis measurements at Mauna Loa tracked each other to a precision of a few percent over the one-year period of comparison in 1976. It is recommended that similar comparisons be made at the times of maximum solar

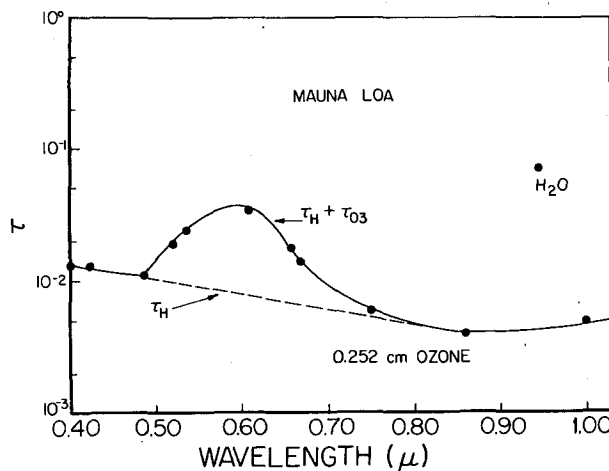


FIG. 1. Solid line: measured wavelength dependence of aerosol-plus-ozone optical thickness at Mauna Loa Observatory. Dotted line: estimated wavelength dependence of aerosol optical thickness.

activity and minimum solar activity to see if variation in the solar blanketing changes the ratio of Dobson ozone values to Chappuis ozone values.

At stations not having the low turbidities and stable conditions found at Mauna Loa, the Chappuis-band method would lose accuracy. The uncertainties of instrument calibration (by the Langley method) are, to first order, directly proportional to the aerosol optical depth itself. Thus ozone could only be inferred to 10% or even 20% accuracy by the Chappuis-band method for monitoring stations having aerosol optical depths of 0.1–0.2, which would be typical values for low-elevation rural locations. When done at high-altitude, low-turbidity stations the Chappuis-band method of deriving atmospheric ozone can apparently be performed to an accuracy quite comparable with Dobson spectrophotometry. But there is a crucial need to resolve the discrepancies in the published ozone absorption coefficients before one can accept *any* estimates of column ozone determined by Dobson or by the Chappuis band method.

Note added in proof: After submitting this paper the author learned that independent measurements of ozone at Mauna Loa by R. Angione and R. Rossen (personal communication) disagreed with the Dobson by 18%—to be compared with our reported discrepancy of 17.6%.

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