

# Comparison of column ozone retrievals by use of an UV multifilter rotating shadow-band radiometer with those from Brewer and Dobson spectrophotometers

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The U.S. Department of Agriculture UV-B Monitoring Program measures ultraviolet light at seven wavelengths from 300 to 368 nm with an ultraviolet multifilter rotating shadow-band radiometer (UV-MFRSR) at 25 sites across the United States, including Mauna Loa, Hawaii. Column ozone has been retrieved under all-sky conditions near Boulder, Colorado (40.177 °N, 105.276 °W), from global irradiances of the UV-MFRSR 332- and 305-nm channels (2 nm FWHM) using lookup tables generated from a multiple-scattering radiative transfer code suitable for solar zenith angles (SZA's) up to 90°. The most significant sources of error for UV-MFRSR column ozone retrievals at SZA's less than 75° are the spectral characterizations of the filters and the absolute calibration uncertainty, which together yield an estimated uncertainty in ozone retrievals of  $\pm 4.0\%$ . Using model sensitivity studies, we determined that the retrieved column ozone is relatively insensitive ( $<\pm 2\%$ ) to typical variations in aerosol optical depth, cloud cover, surface pressure, stratospheric temperature, and surface albedo. For 5 months in 1996–1997 the mean ratio of column ozone retrieved by the UV-MFRSR divided by that retrieved by the collocated Brewer was 1.024 and for the UV-MFRSR divided by those from a nearby Dobson was 1.025. The accuracy of the retrieval becomes unreliable at large SZA's of more than 75° as the detection limit of the 305-nm channel is reached and because of overall angular response errors. The UV-MFRSR advantages of relatively low cost, unattended operation, automated calibration stability checks using Langley plots, and minimal maintenance make it a unique instrument for column ozone measurement.

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## 1. Introduction

Ozone is a trace gas with largest concentrations in the stratosphere. Because of its strong absorption of harmful solar UV radiation it is essential to life on

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the Earth's surface. Its absorption of UV and absorption and emission of infrared radiation make ozone of key importance to the radiative balance and hence the dynamics of the troposphere and stratosphere. With the recent dramatic ozone destruction in the Antarctic, the lesser but significant Arctic declines,<sup>1</sup> and the small decreases noted at mid-latitudes,<sup>2,3</sup> it becomes more important to monitor ozone abundances over extended time periods and over large spatial areas. Although satellite retrievals provide excellent spatial coverage of column ozone and minimize instrument-to-instrument biases through use of a single platform, ground-based ozone retrievals provide the finer spatial and temporal resolution necessary to determine trends. In addition, the instruments are easier to recalibrate and check for stability. Ground-based and satellite instruments complement each other by allowing ongoing comparison of each sensor's retrievals.

The National Oceanic and Atmospheric Administration Climate Monitoring Diagnostics Laboratory

(NOAA CMDL) Dobson network (nine sites located in North America), the U.S. Environmental Protection Agency (EPA) Brewer network (17 sites in North America), and the Canadian Environmental Service Brewer network (13 North America stations) routinely make ground-based column ozone measurements. The U.S. Department of Agriculture (USDA) UV-B Monitoring Program, established in 1992, has recently installed the ultraviolet multifilter rotating shadow-band radiometer (UV-MFRSR, Yankee Environmental Systems, Turners Falls, Mass.) at 25 sites across the United States including Mauna Loa, Hawaii, with the intent of determining the UV climatology and possible temporal trends.<sup>4</sup> In this paper we describe a method to retrieve column ozone using UV-MFRSR global irradiances. In Section 2 we provide an experimental description of the three spectral instruments used to retrieve column ozone in this study. In Section 3 we present a comparison of UV-MFRSR ozone retrievals from 5 months in 1996–1997 with those from collocated Brewer and nearby (19 km south) Dobson spectrophotometers. Section 4 consists of a description of the radiative transfer method to determine column ozone from the UV-MFRSR data along with a discussion of the sensitivity of column ozone retrievals to atmospheric variables and instrumental sources of error. Finally, in Section 5 we provide conclusions.

## 2. Experimental Description

### A. Introduction

For the comparison, 5 months (October–December 1996 and May–June 1997) of column ozone values were compared using data from both the UV-MFRSR and the EPA Brewer at Table Mountain, Colorado (40.177° N, 105.276° W), and from the nearby (19 km to the south) Dobson at Boulder, Colorado, operated by the NOAA CMDL. For all these instruments the data for solar zenith angles (SZA's) greater than 75° were considered unreliable and therefore excluded from the comparison.

### B. Ultraviolet Multifilter Rotating Shadow-Band Radiometer

The UV-MFRSR<sup>4</sup> consists of a common diffuser above seven separate ion-assisted-deposition interference filter photodiode detector combinations and is similar in design to the visible shadow-band radiometer described by Harrison *et al.*<sup>5</sup> The wavelengths are nominally 300, 305, 311, 317, 325, 332, and 368 nm (2 nm FWHM), and the radiometer returns direct, global, and diffuse irradiances. The shadow-band blocks the direct beam to give the diffuse irradiance whereas the direct beam is determined by subtracting the diffuse from the unblocked total and dividing by the cosine of the SZA. Cosine corrections were made on the direct but not the diffuse measurements. The temperature of the head containing the diffuser, filters, photodiodes, and preamplifiers was maintained at  $45^\circ \pm 0.5^\circ \text{C}$ . Measurements were taken

every 20 s, aggregated into 3-min averages, and recorded in an onboard data logger.

The algorithm used to retrieve column ozone from the UV-MFRSR and the sources of error of the retrievals are discussed in Section 4. In this study only the global (total horizontal) irradiances were employed to retrieve column ozone. Data from each day under all-sky conditions were utilized.

### C. Brewer Spectrophotometer

The Brewer single-grating spectrophotometer used in this study (serial no. 101) is a model MK IV, as are the rest in the U.S. EPA network. It measures the global UV irradiance from 286.5 to 363 nm through a horizontally positioned diffuser and the total column ozone by measuring the direct beam through a sloping side quartz window.<sup>6–8</sup> Movements of its zenith prism and azimuth tracker enable the Brewer to operate in an automated mode with a user-defined schedule. Two types of ozone measurement are made routinely by the Brewers in the network. For direct Sun (DS) measurements, the zenith prism points directly to the Sun. For the zenith sky (ZS) measurements, the prism faces straight up and a polarizer selects the weakly polarized component of the zenith skylight. Like the Dobson spectrometer, the Brewer measures repeatedly at several wavelengths: 306.3, 310.1, 313.5, 316.8, and 320.0 nm. The relative intensities at these wavelengths is then used to calculate the total column ozone. Because the radiation at 306.3 nm is absorbed strongly by SO<sub>2</sub> as well as by ozone, the DS scan is also used to compute the total column SO<sub>2</sub>, thereby improving the accuracy of the ozone retrievals. The wavelength 306.3 nm was chosen because of the relatively strong SO<sub>2</sub> absorption and weak ozone absorption in this region. The Brewer ozone retrievals utilize the Bass and Paur<sup>9</sup> ozone absorption coefficients at a constant temperature of 228.3 K. The Brewer is not temperature stabilized but employs temperature correction coefficients measured by the manufacturer. An internal lamp check is used to monitor the Brewer's relative spectral calibration stability. For the period of 1 May to 30 June 1997 the change in spectral calibration was within 1.3%. No angular correction is required because both Brewer DS or ZS scans utilize a small field of view.

Fioletov *et al.*<sup>10</sup> report on a method that establishes a relationship between total column ozone and spectral UV global irradiances as a means of retrieving column ozone. The method shows good agreement for clear skies with Brewer DS measurements with a standard deviation of approximately 3%.

The Brewer ozone data used for this intercomparison are the daily average values from DS and ZS scans at SZA less than 75°. As the Sun gets lower, scattered light becomes comparable to the direct component, which renders the DS result unreliable. For the cloudy days, no valid data come from DS scans. Although the ZS may provide some meaningful data on cloudy days, its empirical method makes it much less accurate than the DS scan. Each ZS retrieval is

the average of five column ozone retrievals made within a scan. When the standard deviation of these individual column ozone retrievals exceeds 2.5 Dobson unit (DU), that ZS scan is rejected. This resulted in occasional days with missing data when none of the scans passed the test.

#### D. Dobson Spectrophotometer

The Dobson ozone spectrophotometer is a double-prism monochromator that obtains total column ozone by measuring the relative intensities at pairs of wavelengths in the UV region, specifically from 305.5 to 453.6 nm. The wavelength pairs are chosen such that one of the wavelengths is relatively unaffected by ozone absorption whereas the other is absorbed. By means of a calibrated optical attenuator (the wedge), the intensity of the less absorbed of the wavelength pair is reduced to match the intensity of the more strongly absorbed wavelength, and the value on the r-dial that relates to the position of the wedge is taken to be the relative intensity of the wavelengths being measured. Use of two different wavelength pairs for each observation allows the scattering by air molecules and aerosols to be corrected. All the measurements are referenced to a standard instrument (Dobson serial no. 83) through intercomparison. The theoretical basis for these measurements is described by Dobson.<sup>11</sup>

Measurements are made on both DS and ZS that may be clear or cloudy. Observational details, necessary calculations, and methods of calibration are summarized by Komhyr.<sup>12</sup> DS column ozone amounts are calculated directly from observed quantities. However, ZS-derived ozone amounts require use of statistical methods and lookup tables that are based on a series of quasi-simultaneous measurements of DS versus clear ZS measurements made with the specific instrument at its normal operating site. Cloud correction charts are based on a similar series of observations made on days when the sky was partly clear and partly cloudy. The influence that was due to SO<sub>2</sub> absorption is not considered here but is expected to be small at Boulder. Komhyr and Evans<sup>13</sup> estimated that at Boulder during 1978, the observed SO<sub>2</sub> annual mean mixing ratio of 0.011 parts per million by volume resulted in an annual mean error in Dobson ozone retrieval of approximately 0.6%.

For well-maintained and well-calibrated Dobson instruments, DS column ozone measurements are estimated to be reproducible to within 1%. The reproducibility of zenith blue sky measurements is also approximately 1% and that of zenith cloudy sky measurements approximately 3% with properly constructed correction charts.<sup>14</sup> The accuracy is harder to gauge as it involves the absolute accuracy of the ozone absorption coefficients, their temperature dependence, and the atmospheric temperature profile. The accuracy of the direct and zenith blue sky measurements is estimated to be approximately  $\pm 3\%$  and zenith cloudy  $\pm 5\%$ .<sup>14</sup> Like the Brewer spectrophotometer, the total ozone amounts are processed using

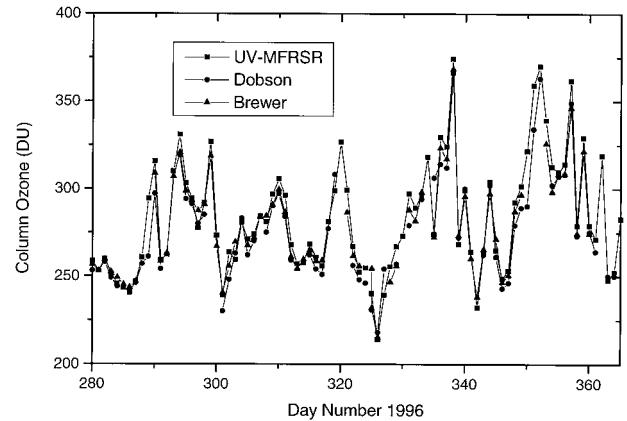


Fig. 1. Comparison of column ozone retrieved by UV-MFRSR, Dobson, and Brewer for 3 months in 1996 near Boulder, Colorado. The mean ratio of the UV-MFRSR divided by the Dobson was 1.021, and the mean ratio of the UV-MFRSR divided by the Brewer was 1.010.

the Bass and Paur<sup>9</sup> 1985 absorption coefficients as recommended by Mateer and Deluisi.<sup>15</sup> The coefficients are based on air mass  $\mu = 2$  and an ozone-weighted mean temperature of 227 K (as opposed to 228.3 K for the Brewer) as described by Komhyr *et al.*<sup>16</sup>

### 3. Comparison Results of Column Ozone Retrievals

Column ozone was retrieved from UV-MFRSR data for each day from 5 October through 31 December 1996 when the minimum noon SZA ranged from 44.8° to 63.5°. To study retrievals when the Sun was higher in the sky, the study was extended to include from 1 May to 30 June 1997 with the minimum noon SZA between 25.0° and 16.5°. The UV-MFRSR was calibrated by means of the Langley technique<sup>17,18</sup> based on 15 events within the air-mass range 2–6 using the objective algorithm of Harrison and Michalsky.<sup>19</sup> The average zero air-mass voltage intercepts of a Langley plot for both the 305- and the 332-nm channels were determined and used with the extraterrestrial flux from VanHoosier *et al.*<sup>20</sup> and the measured spectral response function (SRF) of the two channels to obtain the calibration factors. Ozone was retrieved as described below in Section 4 as the average of the four measurements taken on each day for the smallest SZA at 5° increments (e.g., 55°, 50°, 50°, and 55°). These retrievals were compared with those from a collocated Brewer and a nearby Dobson spectrophotometer. There is no Dobson data on weekends, and there are occasional missing days for the Brewer because of broken clouds.

The results of these comparisons are shown in Figs. 1 and 2 and summarized in Table 1. For the first period October–December 1996, the mean ratio of the UV-MFRSR column ozone retrievals divided by those from the Brewer was 1.010 with a standard deviation (s.d.) of 0.0189 and for UV-MFRSR retrievals divided by those of the Dobson the mean ratio was 1.021 with a s.d. of 0.0325. The mean ratio of the Brewer to the

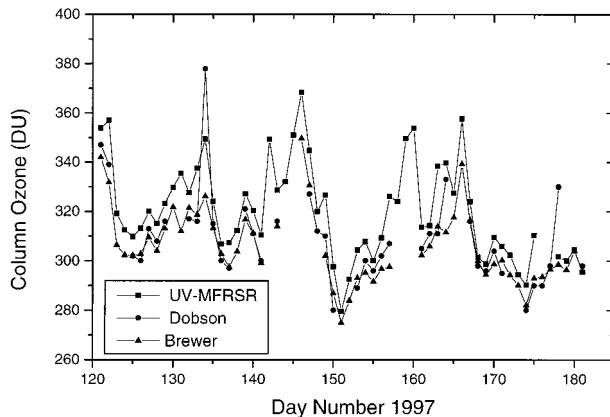


Fig. 2. Comparison of column ozone retrieved by the UV-MFRSR, Dobson, and Brewer for May and June 1997. The mean ratio of the UV-MFRSR divided by the Dobson was 1.028 and the mean ratio of the UV-MFRSR and the Brewer was 1.037.

Dobson during this period was 1.011 with a s.d. of 0.0224. For the second period from May–June 1997, the mean ratio UV-MFRSR retrievals divided by the Brewer retrievals was 1.037 with a s.d. of 0.0219 and the mean ratio of retrievals of the UV-MFRSR divided by the Dobson was 1.028 with a s.d. of 0.0321. The mean ratio of the Brewer to the Dobson ozone retrievals during this second period was 0.990 with a s.d. of 0.0298. Possible reasons for the observed differences are discussed below. These results of the UV-MFRSR in relation to the Brewer and the Dobson compare favorably to the mean ratio of 1.038 for the Toronto Brewer column ozone retrievals divided by those from a collocated Dobson during a 5-yr period reported by Kerr *et al.*<sup>8</sup> It should be noted that in the Kerr *et al.* study different ozone absorption coefficients were used by each instrument which accounts for some of the observed bias.

#### 4. Column Ozone Retrievals with the Ultraviolet Multifilter Rotating Shadow-Band Radiometer

##### A. Radiative Transfer Algorithm Description

Stamnes *et al.*<sup>21</sup> describe an algorithm to retrieve ozone column from the ratio of global spectral irradiances (0.6-nm resolution) at 340 and 305 nm. Using simulations with clouds, they show that ozone retrievals employing global irradiances are less prone to errors because of clouds than retrievals such as the Dobson and Brewer that use ZS irradiances when the Sun is obscured. However as Mayer *et al.*<sup>22</sup> demonstrate, optically thick clouds with large vertical extent (for example, from thunderstorms) cause increased photon path length through the tropospheric ozone resulting in enhanced absorption of the shortest wavelengths. Under these conditions, the ozone retrievals of the UV-MFRSR, the Brewer, and the Dobson will all be biased high. Stamnes *et al.*<sup>23</sup> discuss how clouds affect Dobson ZS ozone retrievals. Mayer and Seckmeyer<sup>24</sup> verify that more-accurate ozone retrievals from spectral measurements are achieved if the measurements around 340 and 305

nm are smoothed by passing a 2.0-nm FWHM triangular-shaped filter over the measured irradiances centered at these wavelengths instead of using the two individual spectral irradiances themselves as was done in Stamnes *et al.*<sup>21</sup> Booth<sup>25</sup> and Dahlback<sup>26</sup> use the global irradiances measured by a UV filter radiometer (10 nm FWHM) along with the Stamnes *et al.*<sup>27</sup> model to determine column ozone. The present study takes a similar approach. More background material may be found in Basher and Matthews<sup>28</sup> who discuss retrievals of ozone from DS measurements using a UV filter radiometer as do Flynn *et al.*<sup>29</sup> and Labow *et al.*<sup>30</sup> who also present a thorough analysis of errors.

The radiative transfer model used in this study is also the multiple-scattering discrete ordinate method of Stamnes *et al.*<sup>27</sup> modified for spherical geometry by Dahlback and Stamnes<sup>31</sup> allowing irradiance calculations for SZA of up to 92°. The model's interface has been modified by Madronich<sup>32</sup> which simplifies the computations. The atmosphere is divided into 50, 1-km layers with the temperature of each layer taken from the U.S. Standard Atmosphere and utilizes the temperature-dependent ozone cross sections of Molina and Molina,<sup>33</sup> the U.S. Standard Atmosphere ozone profile, and the extraterrestrial irradiance of VanHoosier *et al.*<sup>20</sup> For the UV-MFRSR ozone retrievals,  $N$  values were computed.  $N$  is the ratio of simulated global irradiances from the sensor at the 332- and 305-nm channels computed by the integral multiplication of the SRF of these channels,  $F_2$  and  $F_1$ , respectively, times the global irradiances  $I$  from 300 to 338 nm in 0.1-nm increments.

$$N = \frac{\int F_2(\lambda)I(\lambda)d\lambda / \int F_2(\lambda)d\lambda}{\int F_1(\lambda)I(\lambda)d\lambda / \int F_1(\lambda)d\lambda}.$$

The model was run over a range of SZAs from 5° to 90° (in 5° steps) and with column ozone from 220 to 450 DU (in 10-DU steps), and lookup tables of the  $N$  values were constructed. The measured ratio of UV-MFRSR global irradiances of these two channels was determined at the same 5° SZA intervals, and the column ozone was determined by linear interpolation. No aerosols or clouds were introduced in the model. The elevation was set to 1.524 km and the surface albedo to 0.05.

Table 1. Summary of Ozone Retrieval Comparison Results

Ratio	UV-MFRSR/ Dobson	UV-MFRSR/ Brewer	Brewer/ Dobson
Mean October–December 1996	1.021	1.010	1.011
Standard deviation	0.0325	0.0189	0.0224
Mean May–June 1997	1.028	1.037	0.990
Standard deviation	0.0321	0.0219	0.0298

## B. Sensitivity Studies

### 1. Methodology

To investigate the biases in UV-MFRSR ozone retrievals that are due to changing optical properties of the atmosphere and potential instrument errors, a number of tests were performed using the discrete ordinate method. Computation time of the tests was reduced by running a test of the model at 1.0 nm rather than the 0.1-nm increments with a fixed SZA of 45° and column ozone of 300 DU. Using a 1.0-nm increment, we computed the  $N$  value (the ratio of global irradiances at 332 and 305 nm). This  $N$  value was within 1.2% of the  $N$  value obtained when the model was run at 0.1-nm increments with all input parameters remaining the same, corresponding to a difference in column ozone of 1.3 DU. Additional model tests using the 1.0-nm increments established that the variation of  $N$  values with SZA and ozone column had the same functional dependence as with 0.1 nm, thus justifying the faster test.

### 2. Atmospheric Optical Effects

The effects of variations in atmospheric pressure, aerosol loading, and cloud cover on ozone retrievals were studied by varying one model parameter at a time. A comparison of the column ozone values that corresponded to the resulting  $N$  values formed the basis of the evaluation. Variation of surface pressure by  $\pm 30$  mbars, typical of the extremes in pressure because of synoptic weather patterns, resulted in a variation in retrieved ozone column of only  $\pm 1.5$  DU. It was found, however, that the ozone retrievals are sensitive to the differences in surface elevations that typically occur within the USDA network.

Increasing the total aerosol optical depth at 340 nm from 0 to 0.2 using the aerosol profile of Elterman<sup>34</sup> (1968), characteristic of the greatest expected turbidity at rural sites where all the USDA sites are located, had a +2-DU effect on ozone column retrievals. The asymmetry factor ( $g$ ), a measure of the forward-scattering properties of the aerosols, was set to 0.61. The single-scattering albedo ( $\omega$ ) that is the ratio of scattering to extinction was set to 0.99. The aerosol optical depth was assumed to have a  $\lambda^{-1}$  wavelength dependence. The reason that ozone retrievals are little affected by moderate aerosol loading is because the aerosol attenuation factor is nearly constant with wavelength,<sup>35</sup> and nonabsorbing aerosols increase the ratio of diffuse to direct irradiances without significantly influencing the global irradiance.<sup>36</sup>

Changing the surface albedo from 0.0 to 0.2 resulted in an overestimation of ozone column of +1 DU. However changing the albedo from 0.0 to 0.95, as might well happen after a fresh layer of snow, resulted in ozone column overestimation of +4 DU. Table 2 summarizes these results from which it can be concluded that ozone retrievals are relatively insensitive (<1.5%) to variations in surface pressure, surface albedo, and moderate aerosol loading.

**Table 2. Sensitivity of the UV-MFRSR Ozone Retrievals to Changes in Atmospheric Properties<sup>a</sup>**

Pressure	Temperature Profile	Aerosol Optical Depth	Albedo
$\pm 30$ mbars	$\pm 10$ K	$\tau=0\text{--}0.2$	0–0.2
$\pm 1.5$ DU	$\pm 4$ DU	+2 DU	+1 DU

<sup>a</sup>SZA, 45°; column ozone, 300 DU; albedo, 0.05;  $z$ , 1.524 km;  $\Delta\lambda$ , 1.0

### 3. Cloud Effects

The sensitivity of ozone retrievals to clouds is more difficult to study because of the need for three-dimensional radiative transfer models and the problems in quantifying the optical properties of the complex multiphase cloud fields found in nature.<sup>37</sup> To simplify the computations, plane-parallel clouds were used to study this sensitivity. To a first approximation, clouds can be considered as gray bodies, that is spectrally neutral, because they are essentially nonabsorbing in the UV. With this assumption, clouds would have no effect on ozone retrievals in the UV that utilize either global irradiances or ZS radiances. However, Mayer *et al.*<sup>22</sup> report a twofold overestimation of column ozone retrievals using the Stammes *et al.*<sup>21</sup> technique with global spectral irradiance measurements made under an optically and geometrically thick cloud during a thunderstorm. A second effect of clouds causes an underestimation of column ozone resulting from the redirection of photons scattered within the cloud and emerging downward from its base. Consider the case of the Sun at a SZA of 70° with an optically thick cloud between 4 and 5 km. Photons emerge from the bottom of the optically thick cloud with nearly isotropic direction. In such a case the average angle of the downward cosine-weighted isotropic irradiance is 45° regardless of the SZA. The average path length through the remaining ozone beneath the cloud is thus shorter than the clear sky case. The magnitude of the two competing effects is governed by SZA, cloud height, optical thickness, geometric thickness, and the tropospheric ozone profile. All the errors that are due to clouds will affect scattered-light ozone retrievals made with the Dobson, the Brewer, and the UV-MFRSR. Another source of error in these column ozone retrievals is attributable to absorption that is due to aerosols within the cloud.<sup>22</sup> This is not addressed in this study but could be important under thick clouds with heavy loadings of absorbing aerosols.

The errors in ozone retrievals that are due to clouds were estimated by computing  $N$  values for clouds of various heights, and optical thicknesses, at two different SZA's, and for four column ozone amounts. For these clouds, forward scattering was specified by setting  $g$  equal to 0.85 and the absorption properties of cloud droplets defined by specifying a value of  $\omega$  of 0.9999. Low, middle, and high clouds of a geometric thickness of 1 km (altitude was 1–2, 4–5, 9–10 km,

**Table 3. Worst-Case Sensitivity of the UV-MFRSR Ozone Retrievals to Change in Cloud Height and Optical Depth<sup>a</sup>**

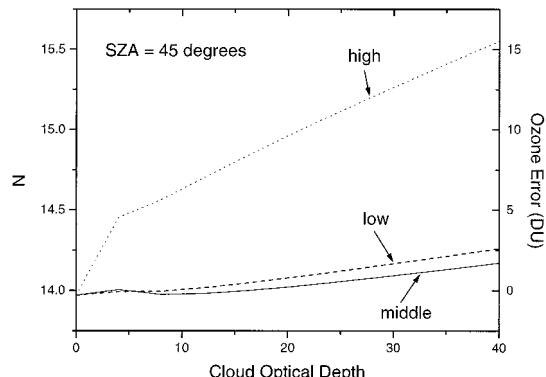
SZA (deg)	Column Ozone (DU)	Cloud Height	Cloud Height	Cloud Height
		Low (1–2 km) (DU)	Middle (4–5 km) (DU)	High (9–10 km) (DU)
45	300	+3	+2	+15
70	300	-2	-4	-5
45	100	-5	-5	-2
70	100	-5	-5	-5
45	450	+10	+10	+25
70	450	-5	-6	-6

<sup>a</sup> $\tau$ , 0–40; albedo, 0.05;  $z$ , 1.524 km;  $\Delta\lambda$ , 1.0 nm.

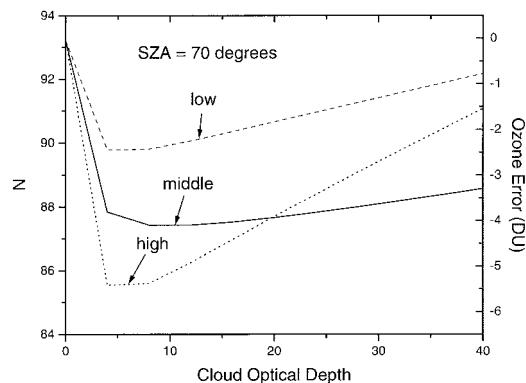
respectively) composed of water were placed in the model, and the cloud optical depths varied from 0 to 40. The results of these tests are summarized in Table 3.

For 300 DU and a SZA = 45°, the dependence of  $N$  values and ozone retrievals on cloud optical depth for a 1-km-thick cloud at altitude ( $z$ ) = 1–2 km (low), 4–5 km (middle), 9–10 km (high), respectively, is shown in Fig. 3. In this case clouds at each height result in an overestimate of the ozone by as much as 5 DU. For a SZA of 70°, Fig. 4 shows that the retrievals underestimate ozone by as much as 6 DU for all clouds. In Fig. 4 the two competing effects at low Sun of photon redirection beneath the cloud and absorption due to ozone within the cloud are apparent. The  $N$  value reverses its downward trend as the photon path through the cloud increases with cloud optical depth (making  $N$  larger), countering the effect of the photon redirection (which makes  $N$  smaller) that has already saturated once the cloud is optically thick (optical depth >5).

The errors in retrieved ozone caused by variations in cloud optical depth and height are somewhat different for large or small column ozone amounts. With a column ozone amount of only 100 DU for a SZA of 45°, the ozone amount will be underestimated



**Fig. 3.** Differences in  $N$  value (the 332-nm/305-nm ratio) and associated error in retrieved ozone that is due to varying the cloud optical depth for low (1–2-km), middle (4–5-km), and high (9–10-km) clouds. The computations were performed for 300 DU and SZA of 45°.



**Fig. 4.** Same as Fig. 3 except the computations were performed for SZA of 70°.

by as much as 5 DU for all cloud heights. For 100 DU and a SZA of 70°, the ozone amount will again be underestimated by as much as 5 DU for all cloud heights. With large column ozone amounts the errors that are due to clouds are somewhat larger. At 450 DU for a SZA of 45°, the ozone amount will be overestimated by as much as 10 DU for a low and middle cloud and +25 DU for the unlikely case of a high cloud of optical depth up to 40. For a SZA of 70° with the same column ozone, the ozone amount will again be underestimated by as much as 6 DU for all clouds at each height.

#### 4. Effects that are Due to Different Ozone Absorption Coefficients and Stratospheric Temperatures

Ozone absorption coefficients change in response to atmospheric temperature that varies with altitude, season, and location. The model for UV-MFRSR column ozone retrievals uses the U.S. Standard Atmosphere profile composed of 50 layers each with a separate temperature. The ozone-weighted average temperature of the model is 225.0 K. The Dobson and the Brewer use ozone-weighted temperatures of 227.0 and 228.3 K, respectively. We choose the Molina and Molina (MM) cross sections because they were used in the Stammes *et al.*<sup>21</sup> study. Table 4 summarizes the differences in the ozone absorption coefficients averaged over the bandpass ( $\text{cm}^{-1}$ ) of the 305- and 332-nm channels with the Bass and Paur (BP) and MM measurements at 225.0 and 227.0 K. For the BP absorption coefficients, the difference in

**Table 4. Comparison of Ozone Absorption Coefficients  $\alpha$  used by Dobson and Brewer (Bass and Paur) and UV-MFRSR (Molina and Molina) Averaged over the Filter Bandpass**

Filter Center Wavelength (nm)	T(K)	$\alpha$ (Bass and Paur) ( $\text{cm}^{-1}$ )	$\alpha$ (Molina and Molina) ( $\text{cm}^{-1}$ )
305.4	227	4.4724	4.5940
332.5	227	0.0778	0.0618
305.4	225	4.4601	4.5815
332.5	225	0.0714	0.0615

Table 5. Effects of Instrument Uncertainties on Ozone Retrievals

CW 305 nm	CW 332 nm	Calibration Factor at 305 nm	Calibration Factor at 332 nm
$\pm 0.2$ nm	$\pm 0.2$ nm	$\pm 5\%$	$\pm 5\%$
$\pm 7$ DU	$\mp 4$ DU	$\mp 7$ DU	$\pm 5$ DU

absorption coefficients that is due to the slightly different average temperatures is  $<0.3\%$ . However, at the same temperature the BP ozone absorption coefficients are 2.7% smaller than the MM for the 305-nm channel. Calculations of  $N$  values at  $45^\circ$  and  $70^\circ$  with 300 DU show that if the BP absorption coefficients at an ozone-weighted temperature of 227.0 K were used in the model instead of the MM at 225.0 K that were used in this study, approximately +3 DU more ozone would be retrieved from the UV-MFRSR. This would worsen the agreement with the Dobson and the Brewer. This bias has been added to the uncertainty of the UV-MFRSR retrievals.

The effect of changing the ozone-weighted atmospheric temperature on ozone retrievals was studied by perturbing the 225 K average by  $\pm 10$  K. This value was chosen because it is larger than the difference between the monthly mean temperature at 50 mbars for 40 °N zonally averaged for January (215 K) and July (220 K) found in the *Middle Atmospheric Program Handbook*.<sup>38</sup> The altitude of the largest ozone concentration is found near 50 mbars, so the temperature at this height is representative for stratospheric ozone. The  $\pm 10$  K temperature perturbation caused a difference in retrieved ozone of  $\pm 4$  DU. If an average ozone-weighted temperature of 215 K (instead of 225 K) were adopted in the model, the retrieved ozone from the UV-MFRSR would be closer to that of the Dobson and the Brewer. Because use of the same ozone absorption coefficients would worsen the agreement between the UV-MFRSR and the Brewer and the Dobson shown below, there must be a calibration error with the UV-MFRSR causing the bias.

##### 5. Instrumental Effects

Changes in the spectral response of the filters or absolute errors in the instrument calibration will bias the ozone retrievals. A wavelength shift (or error in characterization) of  $\pm 0.2$  nm for the 305-nm channel will cause an error in ozone column of approximately  $\pm 7$  DU. The same shift in the 332-nm channel results in a column ozone error of  $\mp 4$  DU. A calibration error of  $\pm 5\%$  in the 305-nm channel assuming no error in the measurement of the spectral response will cause an ozone retrieval error of  $\mp 7$  DU and at 332 nm  $\pm 5$  DU. These results are summarized in Table 5. It is critical for accurate ozone retrievals using the UV-MFRSR that accurate calibrations and characterizations of bandpasses be maintained. For this reason the USDA program has instituted Langley plot stability checks<sup>39</sup> to determine filter and calibration stability. Initial analysis of nearly a

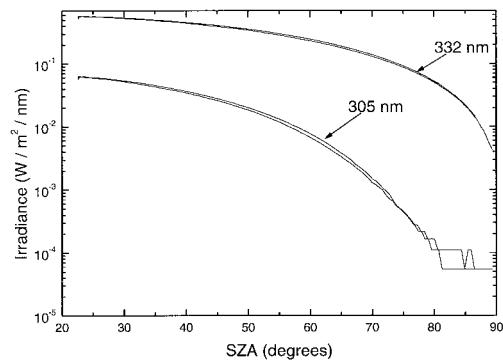


Fig. 5. Time series of the UV-MFRSR global irradiances for 9 May 1997 at Table Mountain, Colorado. At SZA more than  $75^\circ$ , the 305-nm channel has reached its detection limit.

year's data each from of 15 UV-MFRSR detectors indicate few cases of filter degradation.<sup>40</sup> This study is ongoing and will be the subject of a future paper.

Another possible instrumental error will occur if the signal-to-noise ratio of either of the two channels becomes too small, making the ratio of the two irradiances inaccurate. This is illustrated in Fig. 5, which shows a plot of calibrated UV-MFRSR irradiances on the clear day 9 May 1997. The 305-nm channel reaches its detection limit by SZA of  $80^\circ$  whereas the 332-nm channel maintains a good signal-to-noise ratio even at SZA of  $90^\circ$  as shown in Fig. 5. Figure 6 shows the ozone retrieved from these measurements at each  $5^\circ$ . The large divergence in the A.M. and the P.M. values demonstrate that the retrieval is unreliable for SZA more than  $75^\circ$ . Similar signal-to-noise ratio limitations might arise even at SZA less than  $75^\circ$  under thick clouds which could attenuate the signal at 305 nm so much that the ratio of 332–305-nm channels was not useful for ozone retrievals.

The divergence in the ozone retrievals in Fig. 6

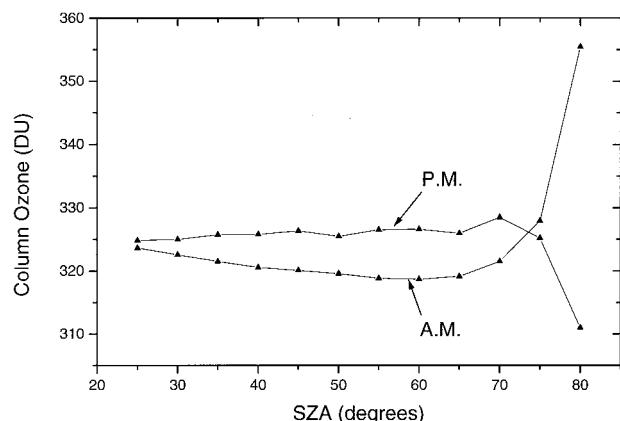


Fig. 6. Time series of UV-MFRSR ozone retrievals for 9 May 1997. At SZA less than  $75^\circ$ , the values are within  $\pm 5$  DU of the average of the  $30^\circ$ ,  $25^\circ$ ,  $25^\circ$ , and  $30^\circ$  results. After the detection limit of the 305-nm channel is reached for SZA more than  $75^\circ$ , the ozone retrievals become unreliable. This plot is typical of many other days.

could also be due to the angular response of the detector. Ideally the detector responds to radiation at all angles in proportion to the cosine of the polar angle (0° being at the zenith). Deviations from this ideal response of the UV-MFRSR are routinely measured to be from 0% at polar angles at 0° to greater than 10% at 80°. Because the diffuse component is not corrected, it is possible that the actual angular response will bias the global irradiances and thereby the retrieved ozone. Because the measured angular response errors are small (less than 10% for SZA less than 70°), these errors, which will bias the global irradiance, are expected to be insignificant at SZA less than 70°.

## 5. Conclusions

The UV-MFRSR measurements of column ozone agree under all sky conditions with the Brewer and Dobson instrument retrievals within the combined estimated uncertainties of these three instruments. Sensitivity studies demonstrate that the UV-MFRSR ozone retrievals are relatively insensitive (<2%) to typical changes in cloud cover, aerosol loading, surface pressure, and albedo. However, serious overestimations of column ozone are likely under geometrically and optically thick clouds. The column ozone retrievals from the UV-MFRSR are sensitive to the SRF characterization, absolute calibration accuracy, and stability of each channel. Considering the instrumental uncertainties of the UV-MFRSR ( $\pm 0.1$  nm for the SRF characterization of the filters and  $\pm 3\%$  for the accuracy of the Langley calibrations), the different cross sections used by the UV-MFRSR and the Brewer and the Dobson, as well as the sensitivity to atmospheric effects, the uncertainty in column ozone retrievals is estimated to be  $\pm 4\%$  for SZA less than 70°. The UV-MFRSR shows a consistent high bias versus the Brewer and the Dobson (mean ratios range from 1.010 to 1.037), suggesting possible SRF or calibration errors in the two channels used for the UV-MFRSR retrievals.

Because the UV-MFRSR is automated, it returns data more frequently than the Dobson and does not need operator attention. Because it is a filter instrument it is less expensive and has so far been easier to maintain than the Brewer or the Dobson. The UV-MFRSR determines ozone by using global irradiances, making the retrievals less sensitive to cloud effects when the direct beam is obscured than those from the Brewer or the Dobson which utilize zenith irradiances. Thus the UV-MFRSR is accurate and has advantages that make it unique for routine, unattended column ozone measurement.

The Tropospheric Ultraviolet and Visible Radiation Model (TUV v3.9) used for these computations is available at <http://www.acd.ucar.edu>, follow the Modeling link.

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