

### Rayleigh optical depths used by Brewer

Rayleigh coefficients used by Brewer are given in Table 1 as BE values. How these coefficients enter Brewer programs and how they are used can be found in INIT.RTN and MAIN.RTN. Relevant excerpts of these routines are listed at the end of this document.

Rayleigh optical depth (in sense of Beer-Lambert law) can be obtained from BE values after taking into account scaling used by Brewer:

$$\tau_R = BE/P4/\log_{10}(e)$$

where  $P4=10^4$ . We compare these values with Rayleigh optical depth from formulas of Hansen-Travis (1974) and Bodhaine et al. (1999):

$\tau_R = 0.008569 * (\mu m)^{-4} * (1 + 0.0113 * (\mu m)^{-2} + 0.00013 * (\mu m)^{-4})$	Hansen-Travis (1974)
$\tau_R = 0.002152 * (1.0455996 - 341.29061 * (\mu m)^{-2} - 0.90230850 * (\mu m)^2)$ $\tau_R = \tau_R / (1 + 0.0027059889 * (\mu m)^{-2} - 85.968563 * (\mu m)^2)$	Bodhaine et al. (1999)

Both formulas apply for sea level and are valid for 1013.25mb pressure. The results of comparisons are in Table 1 and Figure 1.

Table 1 Rayleigh optical depth comparisons

i	$\lambda_i$	BE	$\tau$ -Brew	$\tau$ -HT	$\tau$ -Bod	HT-Brew	Bod-Brew	$\lambda_i - 1.07$	$\tau$ -HT
2	306.3	4870	1.1213	1.1051	1.1122	-0.002013	0.000045	305.23	1.1217
3	310.1	4620	1.0637	1.0485	1.0548	-0.001008	0.000221	309.03	1.0641
4	313.5	4410	1.0154	1.0010	1.0066	-0.000189	0.000382	312.43	1.0157
5	316.8	4220	0.9716	0.9574	0.9625	0.000000	0.000000	315.73	0.9713
6	320.1	4040	0.9302	0.9163	0.9208	0.000256	-0.000257	319.03	0.9294

We observe that Rayleigh optical depth according to Brewer is larger by about 0.015OD than Hansen-Travis and by about 0.01OD larger than Bodhaine.

Brewer uses signals  $F_2, \dots, F_6$  from slits  $i=2, \dots, 6$  and then calculates differences  $F_i - F_5$  with respect to the slit 5. So, Rayleigh optical depth enters as differences  $\tau_R(\lambda_i) - \tau_R(316.8)$ . These differences are compared in columns “HT-Brew” and “Bod-Brew”:

$$HT-Brew = [ \tau_R(\lambda_i) - \tau_R(316.8) ]_{HT} - [ \tau_R(\lambda_i) - \tau_R(316.8) ]_{Brew}$$

$$Bod-Brew = [ \tau_R(\lambda_i) - \tau_R(316.8) ]_{Bod} - [ \tau_R(\lambda_i) - \tau_R(316.8) ]_{Brew}$$

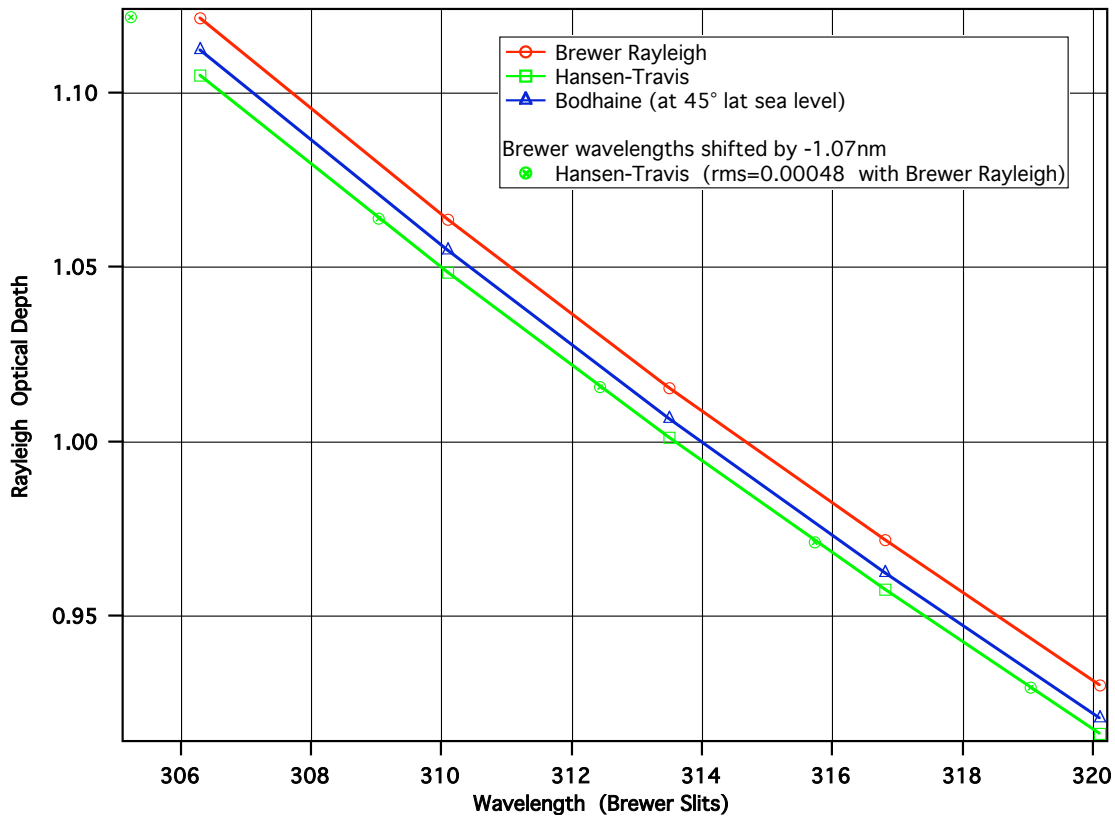


Figure 1. Rayleigh optical depth comparisons

The relative differences from Bodhaine (rms=0.00022) are 5 times smaller than for Hansen-Travis (rms=0.001). This implies that however small slope and nonlinearity differences that exist within the 306.3nm and 320.1nm range in  $\tau_R(\lambda)$  as function of wavelength, the differences are better replicated by Bodhaine than by Hansen-Travis. This is good news for Brewers as Bodhaine formula is considered to be more accurate than Hansen-Travis formula.

Now we calculate the effect on ozone retrieval of Rayleigh coefficients using Brewer formulas. We use the array of weights,  $W_{O_3} = \{0.0, -1.0, 0.5, 2.2, -1.7\}$  and Rayleigh optical depths  $\Delta R = \{\Delta \tau_R(\lambda_i)\}$ .

We calculate  $\Delta O_3$  as follows:

$$\Delta O_3 = \text{SUM}(W_{O_3} * \Delta R) * P_4 * \log_{10}(e) * (M_3/M_2) / (10 * A_1)$$

for  $M_2 = M_3 = 1$ . When ozone airmass  $M_2 = 4$  (SZA=76.3094°) which is maximum for Brewer MKIV, then the  $\Delta O_3$  error slightly increases (by  $M_3/M_2 = 1.04261$  times).  $A_1$  was assumed to be 0.33.  $\Delta \tau_R(\lambda_i)$  are differences between Rayleigh optical depth by Brewer and Hansen-Travis or Bodhaine. The results:

$$\begin{aligned}\Delta O_3 \text{ (Hansen-Travis)} &= -0.63 \text{ DU} \\ \Delta O_3 \text{ (Bodhaine)} &= -0.54 \text{ DU}\end{aligned}$$

The negative signs in the errors indicate that ozone retrieved by Brewer will be underestimated. These errors can be approximately scaled by pressure factor P/1013, so they would be smaller at higher elevations.

We conclude that incorrect values of Brewer Rayleigh coefficients have a negligible effect on ozone retrieval. However, it is important to remember that Brewer's Rayleigh optical depth should not be used in retrievals of aerosol optical depth as significant errors of 0.01-0.015 OD will occur.

We note that Brewer utilizes only three digits out of available four when encoding Rayleigh coefficients. Also we note that smoothing of  $\tau_R(\lambda)$  with slit function will have negligible effect as the slit functions are almost symmetric and  $\tau_R(\lambda)$  is practically linear over 2\*FWHM range. So the discrepancy is not the effect of smoothing. We also observed that for wavelengths shifted by negative 1.07nm (see last two columns in Table 1) Hansen-Travis formula provides almost identical value as Brewer (rms=0.00048 OD). We rather doubt that this kind of error or a leftover from earlier design, when wavelengths were different, has occurred. Anyway the origin of Brewer's Rayleigh optical depths values remains unknown.

### Sensitivity to aerosols

Note that

$$\Delta O_3 = \text{SUM}(W_{O_3} * BE) * (M3/M2) / (10 * A1)$$

is only 0.3DU. This means that Rayleigh correction implemented in Brewer procedures (line 8330 in MAIN.RTN) has negligible effect on the end result. Whether the pressure P=1013mb or P=0mb is entered into Brewer calculations the results differ only by 0.3DU. We found it interesting that for Rayleigh optical depth the MS9 parameter is so small. So we decided to calculate values of  $\Delta O_3$  error for various aerosols modeled with Angstrom law  $AOD(\lambda) = \beta \lambda^{-\alpha}$ . The results are in Table 2.

In all cases  $\Delta AOD = AOD(310.1) - AOD(320.1)$  is either 0.1 or -0.1 which is less than for Rayleigh where  $\tau_R(310.1) - \tau_R(320.1) \approx 0.13$ . Some values of  $\alpha$  are unrealistically large but they approximate Rayleigh as for Rayleigh  $\alpha > 4$  in this narrow spectral range. On the other hand, for a small  $\alpha$  the value of  $\Delta AOD = \pm 0.1$  is unrealistically large. Departure from linearity is in the 3<sup>rd</sup> column and it is defined as difference between maximum and minimum residuals from linear fit in 306.3-320.1 range using the five nominal Brewer wavelengths. Assuming that we did not make a sign error in calculations and its interpretation,  $\alpha > 0$  produces negative ozone error and  $\alpha < 0$  positive ozone error. The

largest errors are when AOD is linear with respect to wavelength ( $\alpha=-1$ ). If  $\Delta AOD$  is other than  $\pm 0.1$ , the ozone error can be scaled proportionally.

Table 2. Effect of aerosols on ozone retrieval at one airmass

Angstrom Coefficient $\alpha$ $AOD(\lambda) = \beta\lambda^{-\alpha}$	AOD(310.1)- AOD(320.1) [OD]	Residuals from linear fit: Res <sub>max</sub> -Res <sub>min</sub> [OD]	$\Delta O_3$ [DU]
Hansen-Travis $\alpha \approx 4.25^*$	0.1	0.0042	-0.70
Bodhaine $\alpha \approx 4.29^*$	0.1	0.0043	-0.63
Brewer Rayleigh $\alpha \approx 4.24^*$	0.1	0.0047	-0.23
$AOD(\lambda) = \beta\lambda^{-\alpha} \quad dAOD(\lambda)/d\lambda < 0$			
4.5	0.1	0.0043	-0.55
4	0.1	0.0039	-1.16
3.5	0.1	0.0035	-1.78
3	0.1	0.0031	-2.40
2.5	0.1	0.0027	-3.02
2	0.1	0.0023	-3.64
1.5	0.1	0.0019	-4.26
1	0.1	0.0015	-4.88
0.5	0.1	0.0011	-5.50
0.25	0.1	0.0010	-5.81
Linear $\alpha = -1$	0.1	0.0000	-7.37
$AOD(\lambda) = \beta\lambda^{-\alpha} \quad dAOD(\lambda)/d\lambda > 0$			
-0.25	-0.1	0.0006	6.43
-0.5	-0.1	0.0004	6.75
Linear $\alpha = -1$	-0.1	0.0000	7.37
-1.5	-0.1	0.0004	7.99
-2	-0.1	0.0008	8.62
-2.5	-0.1	0.0011	9.25

It should be noted that the sensitivity to aerosols also arises during Langley calibrations. When calibrations are performed at Mauna Loa the effect of aerosols is small. However it would be beneficial to have Langley calibration performed by instruments at their actual locations that often have high turbidity. The results of Langley would be greatly stabilized if aerosol desensitization was performed and more accurate ETC value would be obtained. It is possible that the prevailing aerosol conditions may bias ETC estimate. This bias might be different for different instruments as their slit wavelengths sets are

\*  $\alpha$  was obtained from fitting  $\ln(\tau_r)$  vs.  $\ln(\lambda)$  linear fit at five nominal wavelengths of Brewer given in Table 1.

slightly different. The wavelengths in Table 1 are nominal only. We haven't studied the problem of different wavelengths, yet.

If indeed, as Table 2 shows, aerosols with negative Angstrom coefficient overestimate ozone, this fact may shed some light on results of Jaroslowski et al. (2003) and the counter arguments by Arola and Koskela (2004) that dealt with the cases of negative Angstrom coefficients in UV. The cases of  $dAOD(\lambda)/d\lambda > 0$  are physically possible (lack of small particles in aerosol particle size distribution) and were observed for example by Lenoble et al. (2002).

### Optimal weights in Brewer algorithm issue

Our final question is whether the ozone weights  $W_{O_3}$  were selected to minimize the effect of Rayleigh extinction or was it the side (spandrel) effect of desensitization requirements with respect of other parameters? Savastiouk (2005) does not answer this question, though he discusses the issue of weights selection and uses it to minimize ozone profile temperature dependence. Savastiouk and McElroy (2005) did optimize weigh coefficients of one Brewer to make it insensitive to aerosols with  $\alpha=1$ . The issue of weights was touched upon in Kiedron et al. (2008), where Monte-Carlo method was used to study stray light effects.

Rayleigh can be well corrected with knowledge of pressure and wavelengths, so one does not need to waste one degree of freedom in weight selection for Rayleigh desensitization. It would be more useful, to use the weight in the minimization with respect to effects from realistic aerosols for larger range  $\alpha$ , say 0.8-1.5. In real world the  $\Delta AOD$  and Angstrom coefficients  $\alpha$  correlate, so the desensitization should be done using non-linear constraints that call for a non-linear method. The Monte-Carlo method might be the most adaptable method to optimization problems with non-linear constraints.

Brewer instruments have slightly different wavelength slit sets. Each Brewer's sensitivity to aerosols might be different while they use the same weight in retrieval algorithm. The results in Table 2 may not apply to all Brewers. They were calculated for nominal wavelengths set. Each Brewer to perform optimally should has its own optimal weight set. This was suggested by Savastiouk (2005). This approach has not been implemented. The ramification of this approach on Brewer networks calibration and keeping the "Brewer ozone scale" would need to be investigated.

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## References

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## Excerpts from Brewer Routines

INIT.RTN
12060 FOR I=2 TO 6:READ BE(I):NEXT:REM read Rayleigh coeffs
12070 DATA 4870,4620,4410,4220,4040

INIT.RTN
12110 P4%=10000:P3%=1000

MAIN.RTN
8330 IF C\$="ds" OR C\$="fz" OR C\$="sc" OR C\$="fm" THEN F(I)=F(I)+BE(I)*M3*PZ%/1013:REM rayleigh

MAIN.RTN
8315 F(I)=LOG(VA)/CO*P4%:J=I:IF J=0 THEN J=7

MAIN.RTN
8710 FOR I=4 TO 6:MS(I)=F(5)-F(I-2):NEXT:MS(7)=F(6)-F(5):REM single ratios
8715 MS(8)=MS(4)-3.2*MS(7):REM SO2 ratio
8720 MS(9)=MS(5)-.5*MS(6)-1.7*MS(7):REM O3 ratio