The Brewer reference triad

V. E. Fioletov, J. B. Kerr, C. T. McElroy, D. I. Wardle, V. Savastiouk, and T. S. Grajnar
Environment Canada, Toronto, Ontario, Canada

Received 28 July 2005; revised 25 August 2005; accepted 19 September 2005; published 26 October 2005.

[1] It has been more than 20 years since the Brewer reference triad was established by Environment Canada at Toronto. The triad serves as a reference for traveling standard instruments that are used to calibrate Brewer spectrophotometers around the world. The members of the triad are calibrated on a regular basis at Mauna Loa, Hawaii. Regular tests made with an internal quartz halogen lamp make it possible to track the instrument response between the calibrations. A new analysis of available column ozone data records indicates that the uncertainty in the daily values derived from each instrument is approximately 0.6%. The random errors of individual observations are within ±1% for 90% of all measurements. Sources of potential errors in the individual Brewer measurements as well as quality control tools are also discussed. **Citation:** Fioletov, V. E., J. B. Kerr, C. T. McElroy, D. I. Wardle, V. Savastiouk, and T. S. Grajnar (2005), The Brewer reference triad, *Geophys. Res. Lett.*, *32*, L20805, doi:10.1029/2005GL024244.

1. Introduction

[2] The Brewer spectrophotometer was developed in the early 1980s as an instrument for the precise measurement of total ozone [*Kerr et al.*, 1981]. It is widely used by the Global Atmosphere Watch (GAW) program run under the auspices of the World Meteorological Organization (WMO) to measure column ozone, SO_2, and spectral UV irradiance. There are now more than 180 instruments installed around the world. To maintain measurement stability, instrument characteristics are regularly measured using tests based on standard light sources. In addition, instruments are regularly calibrated against the reference instrument(s). Calibration is done by comparing a field instrument to a traveling standard [*Kerr et al.*, 1985]. The traveling standard itself is calibrated against the set of three Brewer instruments located in Toronto and known as the Brewer reference triad. The triad comprises three Brewer instruments (serial numbers 8, 14, and 15) and was established in 1984. Each of the triad Brewers is independently calibrated at Mauna Loa, Hawaii, every 2–6 years (Table 1). The absolute calibration of a Brewer instrument requires the determination of the principal instrument-specific characteristics: the weighted ozone absorption coefficient and the extra-terrestrial calibration (ETC) values as well as additional characteristics such as the temperature dependence of the instrument sensitivity. All these characteristics except for the ETC value can be determined from a set of tests on the instrument using standard sources of light as described in the Brewer manual. Regular tests made with an internal quartz halogen lamp make it possible to track the instrument response between the calibrations and ETC values are adjusted accordingly.

[3] The long-term stability of Brewer network instruments is determined by the stability of the triad and the accuracy of the transfer of the calibration information from the triad to the travelling standard and from the travelling standard to the field instruments. The performance of the triad therefore affects the performance of the entire Brewer network. In this study, a 20-year long record of direct sun (DS) total ozone measurements by the triad Brewers in Toronto is examined. The input data are only the ozone values derived by the processing algorithm described below and the corresponding times of observations. The discrepancies between the ozone values from the instruments are used to quantify the instrument precision. As well, the discrepancies in measured ozone values are resolved into their two components namely the error in the assignment of ETCs and ozone absorption coefficients.

2. Data and Analysis

2.1. Processing Algorithm

[4] The Brewer instrument measures the intensity of direct sunlight at five wavelengths between 306 nm and 320 nm, the four longest of which are used to calculate the column ozone (Ω) using the following expression [*Evans et al.*, 1987]:

$$F + \Delta\beta \cdot m = F_o - \Delta\alpha \cdot \Omega \cdot \mu \qquad (1)$$

where m and μ are the slant paths for air and ozone and F_o is the ETC. F, $\Delta\alpha$, and $\Delta\beta$ are scalars formed respectively from the intensities I_i at the four wavelengths, the corresponding ozone absorption coefficients α_i and the Rayleigh scattering coefficients β_i. Specifically

$$F = \sum_{i=1}^{4} w_i \cdot \log I_i, \quad \Delta\alpha = \sum_{i=1}^{4} w_i \cdot \alpha_i, \quad \Delta\beta = \sum_{i=1}^{4} w_i \cdot \beta_i$$

The precise wavelengths (310.1, 313.5, 316.8, and 320 nm) and weighting coefficients (1.0, −0.5, −2.2, and 1.7) have been chosen to minimize the effect of SO_2 and small shifts in wavelength on the measurement and to suppress variations that change linearly with wavelength. Once the values $\Delta\alpha$ and F_o are known, it is possible to determine total ozone from F. The actual wavelength settings are slightly different from instrument to instrument. The coefficient $\Delta\alpha$ is determined for each individual instrument from a set of tests, where the exact values of the instrument wavelengths are measured using spectral lamps. The weighted ozone absorption coefficient $\Delta\alpha$ is calculated for these wavelengths using Bass-Paur ozone absorption coefficients [*Bass and Paur*, 1985]; F_o values can be either

0094-8276/05/2005GL024244$05.00

Table 1. Calibrations of the Triad Brewers at Mauna Loa Observatory, Hawaii

Brewer 8	Brewer 14	Brewer 15
May 1983	July 1984	January 1984
March 1987	November 1991	November 1991
February 1992	March 1997	October 1994
October 1994	March 2000	March 2002
March 1999		

transferred from the reference Brewer or determined directly by the Langley plot method. The latter was done for the triad Brewers.

[5] Instrument properties change with time. An internal quartz halogen lamp is used to track these changes in instrument response. If the characteristics of the internal lamp remain the same, the measured intensity of the lamp signal reflects changes in the instrument sensitivity and can be used to adjust F_o as described below. In fact, the lamp characteristics are also changing with time, but these changes have little dependence on the wavelength. The weighted ratio used for ozone is insensitive to changes of intensity that are linear functions of the wavelength, and therefore is not very sensitive to the lamp degradation. The lamp characteristics are also monitored and lamps are replaced if changes of their characteristics are substantial.

[6] There were typically from 2 to 8 measurements of the lamp intensity per day, known also as "standard lamp tests" or "SL tests". The weighted intensity of lamp emission was averaged over a two-week period following the calibration and was used as a reference (L_o). The median value (L) of daily weighted averages from all SL tests within 2 weeks prior to and after a particular day was used as a reference for the instrument state for that day. The median value, instead of the mean, was used to avoid the influence from individual erroneous SL tests. The adjusted ETC value $F_o' = F_o - L_o + L$ was used to calculate column ozone for that day.

[7] The procedure described above reduces the effect of long-term changes of instrument characteristics on measured ozone. There are, however, short-term changes caused by internal instrument temperature (T) fluctuations. To compensate for these changes, the ETC value is further adjusted: $F_o'' = F_o' + \tau \cdot (T - T_o)$, where T_o is the instrument temperature at the time of ozone calibration and τ is the temperature coefficient, estimated from a set of SL tests taken typically as a part of the calibration procedure at a wide range of temperatures (0° to 30°C).

[8] Each Brewer DS measurement is based on a group of 5 sub-measurements, each of which is used to calculate a total ozone value. The average of these 5 values is reported as the ozone value for a DS measurement and their standard deviation is also reported as the measurement standard deviation (MSD). The MSD is used to determine the acceptability of each measurement. The normal acceptance criteria for DS measurements, used also in this study, are MSD $\leq$ 3 DU and $\mu \leq 3.5$. The number of accepted DS measurements per day depends very much on season and weather. There could be as many as 90 accepted DS measurements per day reported by Brewer 8 on a sunny summer day in recent years. This number is lower for Brewer 14 (up to 40 measurements) and Brewer 15 (up to 60) because these instruments take a substantial number of spectral UV observations leaving less time for DS measurements. The total number of individual DS measurements used in this study is about 100,000 for Brewers 8 and 15 and about 70,000 for Brewer 14 from 5542 days.

2.2. Instrument Uncertainties and Random Errors

[9] Previous analyses of triad data [*Kerr et al.*, 1998] have been based on discrepancies between operational daily ozone values defined as averages of all satisfactory (see later) DS measurements for each instrument. Because the results apply strictly to the operational values, they include the effects of ozone changes during the day combined with differences in the timing and number of measurements by each instrument. In this analysis, the contribution of ozone changes is suppressed and the results apply primarily to instrumental performance. The following statistical model was applied to the data from each day:

$$\Omega = A_8 \cdot I_8 + A_{14} \cdot I_{14} + A_{15} \cdot I_{15} + B \cdot (t - t_0) + C \cdot (t - t_0)^2 \quad (2)$$

Ω is an ozone measurement by any instrument, t is the corresponding time of the measurement and t_0 is the time of local solar noon. I_8 is an indicator function for Brewer 8. It is set to 1 if the ozone value Ω is measured by Brewer 8 and to 0 otherwise. I_{14} and I_{15} are indicator functions for Brewers 14 and 15 respectively. The coefficients A_8, A_{14}, A_{15}, B and C were estimated by the least-squares method.

[10] The coefficient A_8, (or A_{14}, A_{15}) for a particular day can be interpreted as an average of all measurements on that day from Brewer 8 (or 14, 15) with diurnal ozone variations relative to the noon ozone value removed. The average of the three coefficients $A = (A_8 + A_{14} + A_{15})/3$ can be used as a benchmark to estimate the performance of individual instruments. Figure 1 shows the difference between the coefficients A_8, A_{14}, and A_{15} of individual triad Brewers and the average A.

[11] Figure 1 shows that the instrument deviations are typically within 1%. The standard deviations of the 3-month averages plotted in Figure 1 are 0.40 %, 0.46%, and 0.39% for Brewers 8, 14, and 15, respectively, or about $\sigma = 0.42\%$ on average. From this, assuming that the instrument errors are independent, the standard uncertainty (δ) can be estimated as $\sqrt{1.5}\sigma$, or about 0.51% for 3-month averages. The numbers for daily averages are just slightly higher, σ = 0.47% and δ = 0.58%, suggesting that the instrument

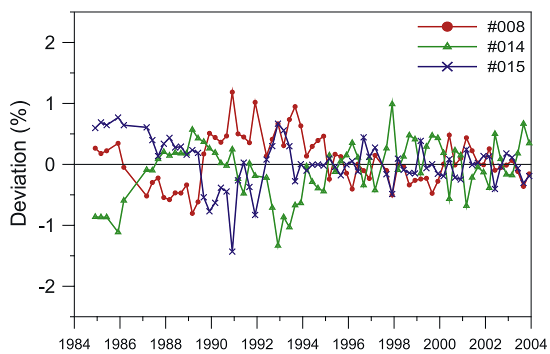

Figure 1. Deviations of ozone values of individual triad Brewers from the mean of the three instruments. Each point on the graph represents a 3-month average.

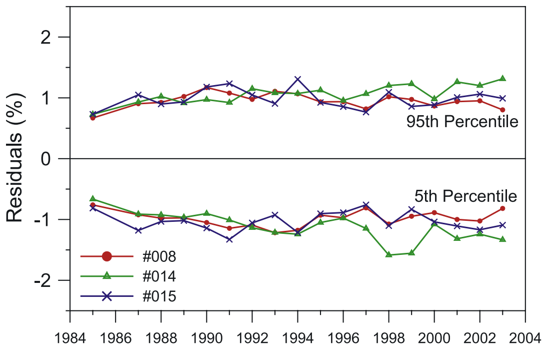

Figure 2. The 5th and 95th percentiles of the residuals of the statistical model (1). Each point on the plot is based on one year of data. The residuals represent how well individual DS measurements agree with diurnal ozone variations approximated by a quadratic function when instrument-specific systematic errors are removed.

uncertainty is mostly related to long-term instrument drifts, specifically longer than 3 months.

[12] Slow diurnal variations in total ozone and long-term uncertainties of the Brewers are reflected by the parameters of the statistical model. The residuals of the model include short-term fluctuations in ozone and some remaining instrument uncertainties. The latter include, for example, uncertainties caused by instrument temperature fluctuations and by differences in the characteristics of the neutral density filters. The standard deviation of the residuals of the statistical model is about 2 DU or 0.65%. About 90% of all residuals are between −1% and +1% (Figure 2).

[13] The residual standard deviations necessarily include contributions from the variability of each Brewer's measurements which is traced and reported as the measurement standard deviation (MSD), and which is used to determine the acceptability of each measurement. Figure 3 (top) shows the distribution of the MSD values versus the slant paths (μ). This is primarily the result of the MSD (of Ω) being proportional to that of the measured quantity F divided by μ, equation (1), and of the variability F not being much influenced by μ except at very large μ. Figure 3 (bottom) shows the mean, 5th and 95th percentiles of the residuals of the model (2) with the data binned by the MSD values. With MSD $\leq$ 3 DU, which is the normal acceptance criterion, the 5th and 95th percentiles are located at about −1% and 1% respectively, confirming that about 90% of all residuals are within ±1%.

[14] The spread of the residuals becomes wider with MSD > 3 DU. Figure 3 demonstrates that the 95th percentile remains at the +1% level, while 5th percentile and the mean values decline with increasing MSD. This indicates that there is a fraction of systematically low ozone observations that grows with increasing MSD.

[15] Knowledge of the ozone changes during the day, as provided by the coefficients A, B and C, allows estimation of errors in the assignments of the two instrument constants for each of the three instruments. In other words, if the actual ozone value for each measurement is known, we can determine what values of the instrument constants would give the best agreement between the actual and measured ozone values for each instrument. Of course, the actual ozone values are not known, but its best estimate from the 3 triad Brewer instruments can be used instead. This in turn allows the deviations shown in Figure 1 to be resolved into contributions from errors in the ETCs and from errors in the composite ozone absorption coefficients ($\Delta\alpha$). The following statistical model was adopted:

$$F + \Delta\beta \cdot m = \left(F_o'' + \mathrm{X}\right) + \left(\mathrm{A} + \mathrm{B} \cdot (\mathrm{t} - \mathrm{t_0}) + \mathrm{C} \cdot (\mathrm{t} - \mathrm{t_0})^2\right) \cdot \mu \cdot (\Delta\alpha + \mathrm{Y}) \quad (3)$$

where F is the measured weighted average of logarithms of measured light intensities at the four wavelengths, F_o'' and $\Delta\alpha$ are the instrument's constants (i.e. the assigned values), the expression within the second set of parentheses is the ozone amount, μ is the ozone slant path and X and Y are assignment errors to the F_o'' and $\Delta\alpha$ values. X and Y were estimated for each of the three Brewers using the least squares method for each 3-month season (Figure 4). The scale on the left of the upper panel of Figure 4 represents the error corresponding to X when μ = 2. One interesting indication from Figure 4 is that during 1997–2000 there were significant errors in the assignment of both ETC and absorption coefficients to Brewer 14 relative to the mean of the 8 and 15 assignments. However, the effects of these errors on ozone values largely compensate for each other and are not evident in Figure 1.

2.3. Comparison With TOMS

[16] Satellite ozone measurements and particularly data from Total Ozone Mapping Spectrometer (TOMS) are

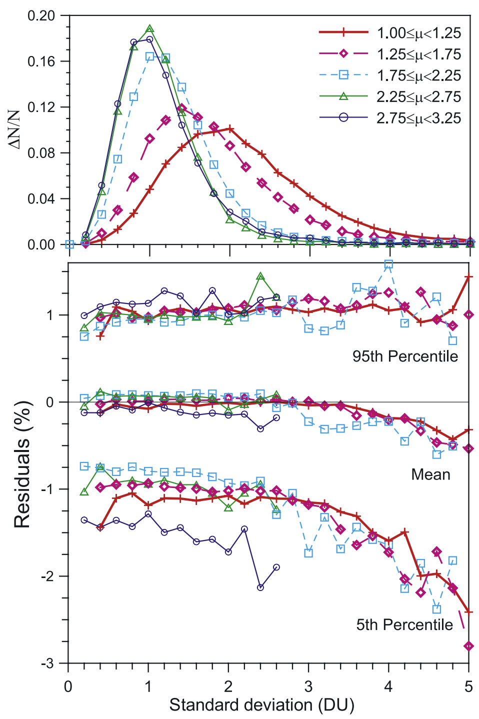

Figure 3. (top) The distribution of the standard deviations of individual DS measurements as a function of air mass value. (bottom) The mean, 5th and 95th percentiles of the residuals of the model (2) where the data are binned by the standard deviation of 5 individual Brewer measurements comprising a single DS observation.

commonly used for verification of ground-based measurements [e.g., *Fioletov et al.*, 1999; *Labow et al.*, 2004]. Figure 5 shows the mean and standard deviation of the difference between TOMS data version 8 and the triad Brewers at Toronto. The comparison with TOMS demonstrates the same features in individual Brewer performance as were seen in Figure 1: Brewer 14 data are lower than the data from the other instruments in 1984–1985 and in 1992–1993, but were relatively high in 2003. Brewer 15 data were relative low in 1989 and 1990. Standard deviations of the Brewer-TOMS daily differences are less than 2% in about half of all seasons and they exceed 3% only in recent years of Earth Probe operation and during the first months of the triad operation. Figure 5 also suggests that the offset between Earth Probe TOMS and Brewer data is slightly different from those between Nimbus 7 TOMS and Brewer data at Toronto. *Labow et al.* [2004], reported a similar result when they compared data from 30 northern hemisphere stations with TOMS. This suggests that the difference in offsets is caused by the TOMS instruments.

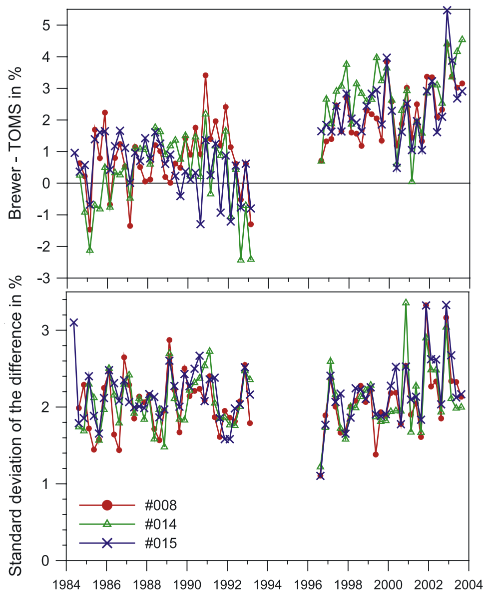

Figure 5. The mean and standard deviation of the difference between TOMS and the triad Brewers in percent. Each point represents a 3-month average. Only measurements within ±2 hours from the TOMS overpass time and only overpasses within 50 km from the Brewer location were used for this comparison.

3. Summary

[17] The Brewer triad has been in operation for twenty years and has been the source of the calibration reference for Brewer network instruments. It is estimated that the standard uncertainty is about 0.58% for daily averages. Long-term instrumental drifts are slightly smaller: the standard uncertainty for 3-month averages is only 0.51%. These numbers confirm that the triad instruments meet the GAW requirement to measure long-term changes in ozone with a precision better than 1%. It was also found that the random errors of individual observations are within ±1% in about 90% of all measurements. Comparison of the triad data with TOMS overpass data demonstrated that the standard deviation of the difference between satellite and ground-based measurements can be less than 2% and seldom exceeds 3%.

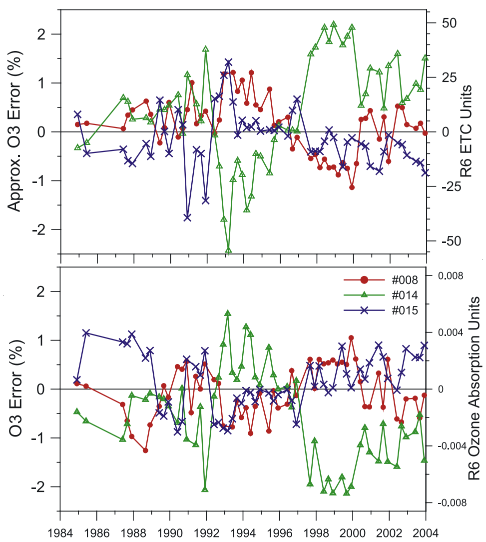

Figure 4. Relative systematic errors in ETCs and effective ozone absorption estimated using the statistical model (2). The vertical axes on the right represent the values in the units used in the actual Brewer algorithm (“R6 ratio units”). The vertical axis on the left demonstrates the % value of these errors in total ozone values. Each point on the graph represents a 3-month average.

References

Bass, A. M. and R. J. Paur (1985), The ultraviolet cross-sections of ozone, I. The measurements, in *Atmospheric Ozone: Proceedings of the Quadrennial Ozone Symposium Held in Halkidiki, Greece, 3–7 September 1984*, edited by C. S. Zerefos and A. Ghazi, pp. 606–610, Springer, New York.

Evans, W. F. J., H. Fast, A. J. Forester, G. S. Henderson, J. B. Kerr, R. K. R. Vupputori, and D. I. Wardle (1987), Stratospheric ozone science in Canada: An agenda for research and monitoring, *Internal Rep. ARD-87-3*, 128 pp., Atmospheric Environment Service, Toronto, Ont., Canada.

Fioletov, V. E., J. B. Kerr, E. W. Hare, G. J. Labow, and R. D. McPeters (1999), An assessment of the world ground-based total ozone network performance from the comparison with satellite data, *J. Geophys. Res.*, *104*, 1737–1748.

Kerr, J. B., C. T. McElroy, and R. A. Olafson (1981), Measurements of ozone with the Brewer spectrophotometer, in *Proceedings of the Quadrennial International Ozone Symposium*, edited by J. London, pp. 74–79, Natl. Cent. for Atmos. Res., Boulder, Colo.

Kerr, J. B., W. F. J. Evans, and I. A. Asbridge (1985), Recalibration of Dobson field spectrophotometers with a traveling Brewer spectrophotometer standard, in *Atmospheric Ozone: Proceedings of the Quadrennial Ozone Symposium Held in Halkidiki, Greece, 3–7 September 1984*, edited by C. S. Zerefos and A. Ghazi, pp. 381–386, Springer, New York.

Kerr, J. B., C. T. McElroy, and D. I. Wardle (1998), The Brewer instrument calibration centre 1984–1996, in *Atmospheric Ozone*, *Proceedings of the Quadrennial Ozone Symposium*, edited by R. D. Bojkov and G. Visconti, pp. 915–918, Parco Sci. e Technol. d'Abruzzo, L'Aquila, Italy.

Labow, G. J., R. D. McPeters, and P. K. Bhartia (2004), A comparison of TOMS and SBUV version 8 total column ozone data with data from ground stations, in *Proceedings of the Quadrennial International Ozone Symposium*, edited by C. S. Zerefos, pp. 123–124, Int. Ozone Comm., Athens, Greece.

V. E. Fioletov, T. S. Grajnar, J. B. Kerr, C. T. McElroy, V. Savastiouk, and D. I. Wardle, Environment Canada, Ottawa, ON, Canada M3H 5T4. (vitali.fioletov@ec.gc.ca)