6 The Brewer Spectrophotometer

James B. Kerr

Scientist Emeritus of Environment Canada
4396 Kingscote Road, V0R 1N2
Cowichan Bay, British Columbia
E-mail: jbkerr@shaw.ca

Abstract   In the late 1960s and early 1970s, concerns were raised regarding the vulnerability of stratospheric ozone to anthropogenic activities and the consequential increase of ultraviolet-B (UVB) radiation at the earth's surface. These concerns prompted the development of new scientific instrumentation for monitoring the state of the ozone layer and levels of surface UV radiation. Included in the list of instrumentation is the ground-based Brewer spectrophotometer. The Brewer spectrophotometer has now been in operation at some sites for more than 25 years and has participated in numerous specialized field campaigns. Site instruments have been stable over long periods of time and function reliably in unattended operation for periods of several days under a wide range of operating conditions. The Brewer spectrophotometer has proven to be a valuable scientific tool that has made significant contributions to our understanding of the ozone layer and the dependence of surface UV radiation on stratospheric ozone and other atmospheric variables. This chapter discusses the history of the development of the Brewer spectrophotometer, describes the design and operation of the instrument, outlines the methods and algorithms used to measure the geophysical variables, and reviews some scientific results of operational and specialized measurements.

Keywords   atmospheric ozone, ultraviolet radiation, radiation instrumentation, measurement techniques

6.1   Introduction

The Brewer spectrophotometer is a modified Ebert grating spectrometer that has been designed to measure the intensity of radiation at targeted UV and visible wavelengths. Pointing capabilities of the instrument allow the measurement of

direct irradiance, global irradiance, or sky radiance from a specified direction, including the zenith. The column amount of atmospheric constituents that absorb or scatter solar or lunar radiation can be determined using differential optical absorption spectroscopy (DOAS) techniques. Atmospheric gases that are measured using their absorption properties include ozone, sulfur dioxide (SO_2), and nitrogen dioxide (NO_2). In addition, aerosol optical depth can be determined from measurements of direct solar irradiance.

Today nearly 200 Brewer instruments have been manufactured and are operating in about 40 countries. The early instruments have operated almost continuously for about 25 years at some sites. Instruments operate unattended outdoors under a wide range of weather conditions encountered at tropical, high latitude, and high altitude sites. Ozone measurement records spanning up to 25 years have provided a wealth of valuable information that has contributed toward our understanding of the changing ozone layer. Measurement records of spectral UV radiation are more than 15 years in length at several sites and allow analysis for long-term changes in UV radiation. Brewer instruments account for about 75% of spectral UV data reported to global and regional databases (WMO, 2007).

6.2   History

An early version of a grating spectrometer was developed at Cambridge University, UK and used by David Wardle in the winter of $1963-1964$ to make measurements of total column ozone during the polar night at Resolute, Canada using stellar radiation as a light source (Wardle, 1965). The instrument was later brought to the University of Toronto where subsequent versions of grating spectrometers were developed with Alan Brewer, Jim Kerr, and Tom McElroy. These instruments were used for short-term research projects that demonstrated the capability of grating spectrophotometers for measuring atmospheric ozone (Brewer and Kerr, 1973; Kerr, 1973) and nitrogen dioxide (Brewer et al., 1973). Brewer (1973) proposed that a grating spectrophotometer could be developed with the goal of supplementing the Dobson ozone spectrophotometer (Dobson, 1957) and the M-83 filter ozonometer (Gustin et al., 1985), which were the only ground-based operational instruments in use at the time. Kerr, McElroy, and Wardle moved to the Atmospheric Environment Service (AES) of Environment Canada in Downsview, Ontario in the early 1970s where the goal of developing an operational grating instrument to measure surface UV irradiance and atmospheric ozone was kept alive.

One major consideration regarding the development of a viable instrument with potential for widespread use as an operational network instrument was commercialization. It was realized that it would be necessary for the instrument to be manufactured commercially by a company capable of making specialized

scientific equipment and supporting it over a long period of time. During the later part of the 1970s, the first pre-production prototype instruments (Mark Ⅰ) were developed and manufactured by SED Systems of Saskatoon, Canada.

The Mark Ⅰ prototype instruments were tested in operational use over a period of several months, and in field intercomparison experiments (Kerr et al., 1981; Parsons et al., 1981). Significant information regarding the calibration, stability, and reliability of the instruments was acquired during this period of operation. Much of what was learned regarding the possible improvements that were needed to address shortcomings was noted and included in the development of the production version (Mark Ⅱ), which has the same optical layout and configuration as the earlier version.

The design and development of the Mark Ⅱ version was carried out jointly by AES and SED Systems and focused mainly on providing fully automatic operation. Full automation of the instrument was considered to be important because the general trend for monitoring geophysical variables was evolving toward automatic measurement in order to reduce manpower and increase data volume. The Dobson spectrophotometer is not automated, and the introduction of a fully automated instrument would offer a distinct advantage.

There were several aspects that needed to be considered to enable unattended operation over different time periods over several days. The first consideration was that of data recording. The first commercial prototype provided a serial port that could output data to a printer. However, manual operations were required to align the instrument, set it up, and then initiate an observation. The requirement for manual operation was addressed by installing several stepping motors to make mechanical adjustments, which would otherwise require manual setup. About this time, personal computers were becoming available, offering a means to fulfill data recording and mechanical positioning requirements at a relatively low cost. The first "control computer" for the automated Brewer instrument was the Commodore PET, which was programmed to schedule and carry out sequences of measurements and tests. The advent of modern day personal computer technology and communication technology has significantly improved and simplified the reliability of data management tasks such as data storage, reporting, and analysis.

In the early 1980s, Brewer instruments were manufactured (by a new company called Sci-Tec Instruments Inc.) and commenced operation at Canadian sites as well as several sites operated by foreign institutes. Three Brewer instruments were established as the calibration "triad" in Downsview (Kerr et al., 1985), and the same three instruments comprise the triad today (Fioletov et al., 2005). Brewer instruments replaced the existing five Dobson instruments in the Canadian ozone-monitoring network after an overlap period of at least three years (Kerr et al., 1988). In addition, the Canadian network expanded to 12 sites beginning in the late 1980s (Kerr, 1994). Around the same time, Brewer instruments were upgraded to measure spectral UV irradiance and appropriate calibration facilities and standards were developed to allow this measurement on an absolute scale.

The Brewer instrument proved to be stable on an absolute scale over long periods of time (Kerr and McElroy, 1993). UV spectral measurement records using Brewer instruments commenced at several sites around the world in the early 1990s (Bais et al., 1994; Ito et al., 1994; Vandersee and Köhler, 1994).

During this time, two new versions of the Brewer instrument were developed: the Mark Ⅲ and the Mark Ⅳ. The Mark Ⅲ is a double monochromator, which was developed to reduce stray light that can be a problem in single monochromators. The Mark Ⅳ has a modified grating, which allows the option to measure radiation at visible wavelengths to determine atmospheric NO_2, as well as the standard UV wavelengths used to determine ozone, SO_2, and spectral UV irradiance. In the late 1990s, a Mark Ⅴ version of the instrument was developed to measure radiation at wavelengths in visible red light (600 nm – 650 nm) where ozone is measured using the Chappuis absorption bands. This instrument can measure ozone at low sun angles ($< 10°$ solar elevation) and is particularly suitable at high latitude locations (WMO, 2006; Tanskanen et al., 2007).

Since 1990, workshops for users of Brewer instruments have been held about every two years. These meetings have been hosted by agencies in Europe, North America, and Asia. In addition, the developers from AES (now the Meteorological Service of Canada, MSC) and manufacturers of the instrument, and the commercial companies that service and calibrate field instruments, also attend these workshops. The purpose of the workshops is to offer interested users a platform to present results and experiences from using Brewer instruments. The meetings also allow users and supporting groups the opportunity to interact with each other. The workshops are organized as a series of seminars under various topics, such as measurement type (e.g., UV, total ozone, etc.), calibration procedures, data analysis, and data archiving. Results presented at the workshops are formally published as WMO reports (e.g., WMO, 1994; WMO, 2006).

In 1996, Sci-Tec Instruments Inc. merged with Kipp and Zonen Inc. and production of the instruments was later transferred to Delft, Holland. Today only the Mark Ⅲ version of the instrument is manufactured, and the Mark Ⅱ and Mark Ⅳ instruments are no longer produced. However, technical service and support is still provided for these existing instruments.

6.3   The Instrument

The optical components of the Brewer spectrophotometer are comprised of three parts: (1) the fore-optics, (2) the spectrometer, and (3) the photomultiplier housing, as illustrated in Fig. 6.1 (from Fig. 2.5 of the Brewer Instruction Manual, courtesy of Kipp and Zonen). Additional information regarding the optical components can be found in Fig. 2.4 of the Brewer Instruction Manuals. The fore-optics direct incoming radiation onto the entrance slit of the spectrometer. The

spectrometer disperses and focuses a spectrum of the incident radiation across a set of exit slits. For the Mark Ⅱ and Mark Ⅳ instruments, the photomultiplier counts photons of radiation that pass through the exit slits. The Mark Ⅲ version of the instrument has a second spectrometer (recombining spectrometer) that mirrors the dispersing spectrometer of the Mark Ⅱ and Mark Ⅳ versions.
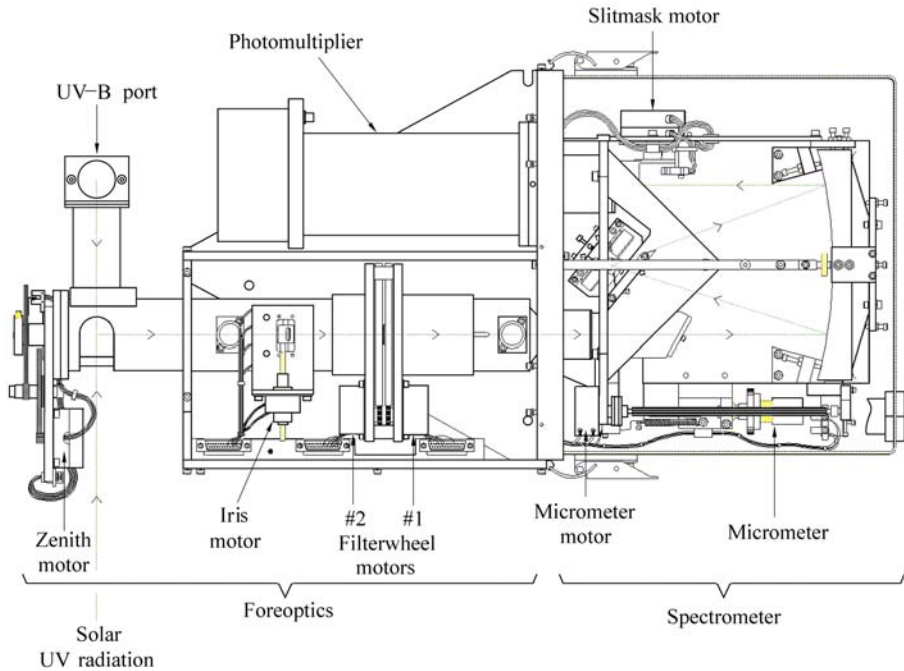
Figure 6.1 Optical layout of the single monochromator (Mark Ⅱ and Mark Ⅳ) versions of the Brewer Spectrophotometer. This diagram shows the foreoptics, the spectrometer, and the photomultiplier components of the instrument. For the Mark III double monochromator, the dispersing spectrometer is the same as that shown here and the recombining spectrometer is the mirror image located behind (beneath) the base plane of the spectrometer illustrated above. The photomultiplier housing for the Mark Ⅲ is located beneath the foreoptics. (Illustration from Brewer Instruction Manual, courtesy of Kipp and Zonen)

A photograph of the Mark Ⅲ version is shown in Fig. 6.2. The optical components and supporting electronics of the Brewer instrument are enclosed in a weatherproof container that is painted white to minimize radiative heating. The cover for the instrument has a sloping quartz window to allow UV radiation onto the fore-optics of the instrument for direct sun, direct moon, and zenith sky measurement. Mounted on the top of the instrument is a Teflon diffuser covered by a quartz dome for measurements of global irradiance. The enclosed instrument sits on top of an azimuth drive box, which rotates the instrument in azimuth with

a precision of about 0.025°. Normally the azimuth drive aligns the instrument so that the quartz window faces the sun.

Figure 6.2   Photograph of the Mark Ⅲ version of the Brewer Spectrophotometer (Courtesy of Kipp and Zonen)

6.3.1   The Fore-Optics

A 45° fused quartz prism is located at the head of the fore-optics tube and reflects incoming radiation (by total internal reflection) at right angles along the horizontal optical path of the instrument. The zenith prism plays an important role in selecting the appropriate source of radiation for lamp tests, sky measurements, direct sun or moon measurements, or UV spectral measurements. The prism rotates about the optical axis of the fore-optics so that radiation originating from zenith angles between 0° and 90° can be directed along the axis. In this mode, the instrument measures the radiance at the respective zenith angle. Rotation of the zenith prism is done by a computer controlled stepping motor (called the zenith motor), which acts through a set of reducing gears to position the desired direction with a precision of 0.128°.

A lamp housing containing a mercury lamp and a quartz iodine lamp is located below the zenith prism. When the zenith prism is directed so that it points downward (zenith angle of 180°), radiation from the lamps is directed along the optical path. The mercury lamp is used to check the wavelength setting of the instrument and adjust it if necessary. The quartz iodine lamp provides a radiation source to check the relative wavelength response of the instrument.

Radiation incident on a horizontal Teflon diffuser on top of the cover is viewed by rotating the zenith prism to view horizontally towards the UV port shown in Fig. 6.1. The UV port consists of another 45° prism that is mounted on the fore-optics tube and positioned directly below the horizontal diffuser. The UV port prism reflects radiation transmitted through the horizontal diffuser at right angles toward the zenith prism, which in turn, reflects radiation at right angles along the optical path. In this mode, the instrument measures global irradiance.

Radiation passing along the fore-optics axis then passes through a lens that focuses radiation from infinity onto the plane of an iris. The iris is used for only direct sun or moon measurement. When the azimuth and zenith are aligned toward the sun or moon, the focused image of the target passes through the aperture of the iris, which is closed to about five solar diameters (e.g., Cede et al., 2003). This prevents most of the scattered sky radiation around the solar or lunar disk to pass through to the spectrometer. Scattered sky radiation can become important when the sun is low, or at relatively large aerosol or cloud optical depths. For all other measurements, the iris remains open and does not block any radiation passing along the optical axis.

After passing through the plane of the iris, radiation is collimated by a second lens and then passes through two filter wheels which can both hold up to six filters. The first wheel consists of an open position and neutral density filters with increasing optical depth in the five remaining positions. Progressive filter positions decrease radiation by a factor of about 3. A second six-position filter wheel inserts filters that include ground quartz for direct sun measurements and polarization filters. The ground quartz filter is used to diffuse direct sun radiation, which reduces errors that may result from the effects of slight misalignment. After passing by the filter wheels, radiation is then focused onto the entrance slit of the spectrometer.

6.3.2   The Spectrometer

The Brewer instrument uses a modified Ebert grating spectrometer (Fastie, 1952) to disperse incoming radiation into a spectrum. The first optical element of the spectrometer is a tilted quartz lens. The purpose of the lens is to correct for optical aberrations, which are inherent in an Ebert spectrometer. Both of the lens surfaces correct for an aberration. An off-axis spherical concave surface of the lens compensates for coma due to the asymmetry of the Ebert spectrometer. The second surface is cylindrical convex and is used to correct for astigmatism.

The optical path continues to a spherical mirror where radiation is collimated and directed toward the grating. Radiation is dispersed at the grating and directed toward the spherical mirror where the spectrum is focused on the plane of the exit slits.

There are six exit slits that are approximately evenly spaced across the focal plane. The shortest wavelength slit is for wavelength calibration using a grouping of mercury emission lines near 302.1 nm or the single emission line at 296.68 nm.

The other five slits correspond to wavelengths that take advantage of the structure of both the ozone and SO_2 absorption spectra at UV wavelengths. Figure 6.3 shows the wavelength positions of the six slits with the absorption spectra of ozone and SO_2. The absorption spectrum of ozone differs from that of SO_2 and, as a result, it is possible to quantify both absorbers (Kerr et al., 1981).
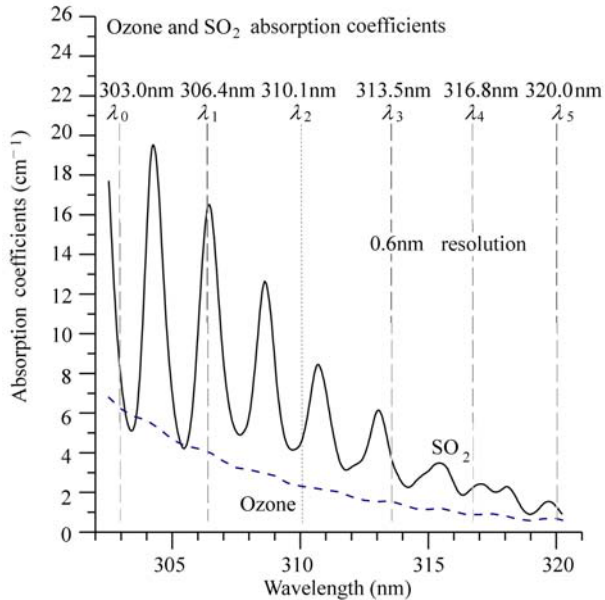
Figure 6.3   Absorption coefficients for ozone and SO_2 smoothed to the resolution of the Brewer instrument. Operational wavelengths of the Brewer Spectrophotometer (λ_1 to λ_5) and the wavelength used for special applications (λ_0) are shown. The absorption features for SO_2 are significantly different than those for ozone, making it possible to measure both constituents simultaneously. It should be noted that under polluted conditions, column SO_2 is usually less than 5 Dobson Units (DU), and stratospheric ozone values typically range between 200 and 500 DU. The amount of UV-B absorbed by SO_2 is therefore generally less than 5% that of ozone. However, absorption by SO_2 can be significant under plumes from major volcanic eruptions (Kerr et al., 1982; Krueger, 1983). Absorption coefficients are those of Bass and Paur (1985) at $-45°C$, and the coefficients for SO_2 are those of McGee and Burris (1987) at $-63°C$

The slits are covered by a cylindrical mask with openings that are positioned by a stepping motor to open one slit at a time. In operation, the time required to switch from one wavelength to another is about 0.016 sec, and the sampling time at each wavelength position is seven times the switching time (about 0.115 sec). A sampling cycle progresses from a lower wavelength (e.g., wavelength 1) to an upper wavelength (say wavelength 5) and back. The range of the sampling cycle and the number of sampling cycles in a sample are programmable.

The cylindrical mask also contains a position that blocks all slits as well as opening two slits at a time. The purpose of the blocking position is to provide a quick sample of the instrument's dark count (i.e., the signal that the instrument registers without any radiation). Dark count is normally measured as part of the sampling sequence and is subtracted from the counts registered at each wavelength channel. The purpose of the double slit opening is to allow a quick measurement of the instrument's dead time. Dead time is measured by comparing the photon counts when both slits are opened with the sum of photon counts when the two slits are opened individually. This test is done quickly and automatically as part of the daily operational schedule.

An 1,800 line/mm holographic grating is used in the second order for the Mark Ⅱ instrument and a 1,200 line/mm grating is used in the third order for the Mark Ⅳ instrument. The grating is mounted on a set of cross-springs that serves as a frictionless bearing to allow the control of rotation with virtually no hysteresis over the operational wavelength range. Rotation of the grating is controlled by a stepping motor which drives a micrometer acting at the end of a lever arm. The drive between the stepping motor to the micrometer is geared so that one motor step is equivalent to a shift of about 0.007 nm of the spectrum across the exit slit plane. For the existing design of the Brewer instrument, the mechanical limits of the grating rotation allow for a range of wavelengths spanning from about 285 nm (measured on the shortest slit) to 365 nm (measured using the longest slit). Extension of this wavelength range without loss of hysteresis and wavelength precision is difficult. The wavelength setting can be measured to about 0.1 micrometer step (Gröbner et al., 1998; Kerr, 2002), but the wavelength positioning is limited to 1.0 micrometer steps.

The double monochromator (Mark Ⅲ) uses basically the same dispersion spectrometer as that of the Mark Ⅱ and Mark Ⅳ with a 3,600 line/mm holographic grating used in the first order. The main difference is that a 45° mirror is placed ahead of the cylindrical slit mask to reflect radiation 90° downward onto the horizontal focal plane where radiation passes through the exit slits and into the recombining spectrometer, which is the mirror image of the dispersing spectrometer. Both gratings (holographic with 3,600 line/mm) for the Mark Ⅲ are individually controlled to allow automatic measurement and adjustment of the wavelength alignment of the two spectrometers. Further descriptions of the double monochromator regarding wavelength stability (Gröbner et al., 1998) and spectral characteristics (Bais et al., 1996; Wardle et al., 1997) are reported in the literature.

6.3.3 The Photomultiplier Housing

A light proof, hermetically sealed, dehumidified cylindrical housing houses the photomultiplier with electronics for high voltage power and for the high-speed amplifier for photon counting. High voltage DC power to operate the photomultiplier

is usually set at a voltage between 1,200 and 1,400 volts, depending on tube characteristics. A photon arriving at the light sensitive cathode initiates a burst of electrons that cascades and is amplified as is passes through the various stages of the tube. The burst of electrons arriving at the anode is then amplified to yield a pulse that is counted in the counting register. A discriminator level is set at about 30 milli-volts to filter out low voltage pulses, which are more likely electronic noise and not light signal.

An order-blocking filter is placed between the exit slits and the cathode of the photomultiplier to remove radiation from grating orders that are not used. For the Mark II instruments, the second order radiation ($\sim$280 nm $-$ 350 nm) is used and the first order ($\sim$560 nm $-$ 700 nm) is blocked by a nickel sulfate/UG-11 filter combination. In the Mark IV, the first order ($\sim$840 nm $-$ 1,050 nm) is not used and a filter wheel inserts an order-blocking filter. Second order visible radiation ($\sim$420 nm $-$ 525 nm) for measurements of NO_2 is selected with a BG-12 filter, and third order ($\sim$280 nm $-$ 350 nm) for measurements of ozone, SO_2, and spectral UV radiation is selected by a nickel sulfate/UG-11 filter combination. An order-blocking filter is not used in the Mark III instruments that are equipped with gratings operating in the first order.

6.3.4   Support Electronics

An on-board microcomputer coordinates the movement of the six (Mark II and Mark III) or seven (Mark IV and Mark V) stepping motors located in the instrument as well as the azimuth drive located in the mounting box beneath the instrument. This microcomputer provides the time base for coordinating the movement of the slit mask and the accumulation of photon counts in appropriate memory registers. It also controls the switching of the lamps, and monitors various supply voltages and temperature readings at different locations inside the instrument. Wired communication with a separate control computer, which is usually located indoors, is done through an RS-232 communication port. The microcomputer accepts ASCII commands, executes each command task, and signals the task completion back to the control computer. Multiple commands can be sequenced and executed in order of sequence.

Instruments operating in cold climates are heated to limit the lower range of operation. Should the temperature drop below a specified value (between 5℃ and 20℃), a thermostat switches on the heaters inside the instrument box. Some Brewer instruments have been modified to operate in a thermally regulated (both heated and cooled) environment that allows minimal temperature variability.

Other electronics inside the instrument include power supplies for several components of the instrument. These components include the mercury and standard lamps, the high voltage for the photomultiplier, drive supplies for the stepping motors, and the heaters.

6.3.5 The Control Computer

The control computer is a personal desktop or laptop computer that communicates directly with the microcomputer on the Brewer instrument via a RS-232 serial link. The control computer allows operation of the Brewer instrument either manually by entering commands from a menu or automatically by entering a sequence of commands that is scheduled as a function of solar zenith angle (SZA) or time of day. Nearly all of the data collected by Brewer instruments is collected during automatic operation. The manual mode is used mainly for setup, special tests, or debugging operations.

The control computer is programmed using GWBasic allowing users of the instrument to develop customized measurements or tests. Versions of the control program have been developed that use other computer languages, i.e., Matlab; however, these programs are not in general use. Preliminary results of measurements are calculated and summarized in real time allowing quick identification of instrumental problems.

Many operators automatically retrieve a daily file of raw data remotely (usually overnight) from field instruments using communication links such as telephone or the internet. Daily data files are typically 100 KB to 200 KB in size depending on observation schedule, location, and time of year, and are often archived into a central database on a day-to-day basis. Preliminary data results are reported in near real time for use in applications, such as UV Index forecast or public distribution of real time total ozone and UV Index values. In addition, programs can be uploaded remotely to the Brewer control computer allowing schedule changes or special tests to be carried out without on-site intervention.

6.4 Corrections Applied to Data

There are a number of corrections that are applied during the processing of the photon count data. The requirements for corrections arise from the unique characteristics of each instrument. Corrections include those for dark count, dead time, stray light, temperature response, neutral density filter attenuation, cosine response, and polarization effect.

6.4.1 Dark Count

Correction for the dark count is fairly straightforward and involves the subtraction of the dark count from the signal count. Dark counts arise from thermal noise and are generated spontaneously in photomultiplier tubes. The dark count is temperature dependent and varies from tube to tube. The dark count can also change with

time and is dependent on the history of light exposure. As mentioned earlier, the dark count is measured as part of a sample and is stored on all data records.

6.4.2 Dead Time

The correction for dead time is required because the photon counting process is non-linear. A photon pulse generated by the photomultiplier and amplifier has a finite width of about 30 nanoseconds (ns). Thus, two or more photons arriving within 30 ns merge into a single pulse, which is registered as one count. The probability for missed counts increases with the count rate, and as the count rate increases, the registered counts eventually saturate. The maximum operating count rate for the Brewer instrument is limited to about 2 million counts per second (MHz). Under this condition, the average photon spacing is about 15 times the photon pulse width, and correction for dead time can be accurately made. Prior to every measurement, targeted radiation is sampled, and if the count rate is too high, the appropriate neutral density filter is inserted to reduce the count rate below 2 MHz. If the count rate is low (<0.5 MHz), the thickness of the neutral density is reduced, if possible.

The correction assumes the following model:

$$N = N_o \exp(-t N_o) \tag{6.1}$$

where N is the measured photon count rate.

N_o is the corrected photon count rate.

t is the dead time.

With knowledge of t, it is possible to solve iteratively for N_o from N. At maximum measured count rate ($N = 2$ MHz), the correction required is about $+6.5\%$ for an instrument with dead time of 30 ns.

As discussed in Section 6.3.2, the slit mask of the Brewer spectrophotometer is designed to measure dead time quickly and automatically by using a mask position where two slits (slit #2 and slit #4) are opened together. This allows a two-source linearity measurement by counting the photons with two slits opening individually, as well as with both opening together. Three equations are described for N_2, N_4 and N_{2+4}, where N_2 = number of photons counted with slit #2 opened, N_4 = number of photons counted with slit #4 opened, and N_{2+4} = number of photons counted with both slits opened. From these three equations, three unknowns (N_{o2}, N_{o4}, and t) can be solved iteratively since it is known that $N_{o2} + N_{o4} = N_{o2+4}$. Results of this internal two-source test compare very well with conventional, but more cumbersome, tests using two external radiation sources.

In operation, the dead time is measured and recorded on a daily basis using two intensity settings, and the results are used as an indicator of instrument performance. Measured dead times for the two intensity levels should agree and should remain fairly stable with time. These tests are useful to warn operators of

possible problems associated with the setting or stepping of the slit mask, as well as photon counting circuitry.

6.4.3 Stray Light

Stray light is an inherent problem with spectrometers. Stray light is light that arrives at the focal plane at a wavelength position shifted from the primary wavelength position. The amount of stray light generally decreases with the difference between the shifted wavelength and the primary wavelength (Wardle et al., 1997). Use of holographic gratings reduces this problem; however, for single monochromators, stray light from nearby wavelengths is typically 10^{-3} to 10^{-4} times that of the primary wavelength.

Stray light is an important consideration for making UV measurements. The rapid increase of ozone absorption with decreasing wavelength (Fig. 6.3) causes UV radiation at the earth's surface to increase by several orders of magnitude over a relatively short wavelength range, particularly when the sun is low in the sky. This means that stray light from longer wavelengths can make up a significant fraction of the signal measured at shorter wavelengths where there is relatively little radiation.

It is possible to apply a correction for the stray light present in a single monochromator (Kerr, 2002). This is done by measuring the distribution of light from a monochromatic source (laser) that is dispersed in the spectrometer and scattered to nearby wavelengths from the primary wavelength. Once this dependence is known, it is possible to calculate the spectrum of stray light and subtract it from the measured spectrum.

The problem of stray light is significantly reduced with the double Brewer monochromator. In this case, the second pass through the recombining spectrometer effectively reduces stray light to about 10^{-7} to 10^{-8} times that of the primary wavelength (Wardle et al., 1997). Use of the double Brewer instrument increases the accuracy of ozone and UV measurements and extends the range of operation to lower sun angles.

6.4.4 Temperature Response

Brewer instruments are sensitive to temperature. The temperature dependence is mainly due to the transmission properties of the nickel sulfate filter, which is used as part of the order-blocking filter combination for UV operation and is necessary to reduce stray light in the spectrometer. The temperature dependence is linear; however, it increases non-linearly with increasing wavelength (Kerr, 2002). Temperature of the instrument near the nickel sulfate filter is measured, so the response can be determined and corrections can be made. Sensitivity to

temperature is measured both under controlled cold chamber conditions as well as field operational conditions. Typical temperature sensitivities range from about $-0.5\%/^{\circ}C$ to $+0.1\%/^{\circ}C$ and vary from instrument to instrument. Temperature response corrections have been routinely made to ozone measurements prior to submission and analysis of data records. Temperature response has also been measured and applied to spectral UV data (Weatherhead et al., 2001; Siani et al., 2003; Garane et al., 2006). Uncertainty of the temperature corrections is about $\pm 0.05\%/^{\circ}C$. The double monochromator Mark Ⅲ version of the Brewer instrument has significantly less stray light, and the nickel sulfate filter is not required for order blocking. Temperature response of the Mark Ⅲ is therefore less of a problem.

6.4.5   Neutral Density Filters

A series of five neutral density filters is located in a filter wheel of the fore-optics and can be inserted into the optical path should the intensity of incoming radiation require reduction. The filters increase in density by factors of about 3 up to a density of about 300 (Kerr, 2002). For operational measurements of ozone using the standard DOAS technique (described in Section 6.5), there is no need to account for the presence of a filter. This is because the filters are nearly neutral, so they attenuated all wavelengths nearly equal, and there is essentially zero differential optical absorption from wavelength to wavelength. In reality, the filters are not exactly neutral; however, optical density gradients are linear with wavelength and any effects linear with wavelength are removed by the Brewer DOAS technique for measuring ozone (see Section 6.5).

   Knowledge of the attenuation characteristics of the neutral density filters is essential for absolute spectroscopy applications and for measurements of aerosol optical depth. Absolute applications include the measurement of global or direct spectral UV irradiance. Routine measurements are made of global spectral UV irradiance (Kerr and McElroy, 1993) and special measurements have been developed to measure direct irradiance (Bais, 1997; Gröbner and Kerr, 2001). For measurements of aerosol optical depth (e.g., Bais, 1997; Kerr, 2002), accurate knowledge of the optical thickness of the neutral density filters is crucial since it is difficult to distinguish between the nearly neutral optical depth of a filter with that of atmospheric aerosols.

6.4.6   Cosine Response

Traditionally, the measurement of surface radiation has been made to quantify the downward flux incident on a horizontal surface. This is used for studies involving the radiative transfer of flux through the atmosphere and at the earth's surface.

The downward flux is the total radiation integrated over the celestial hemisphere weighted with the cosine of the zenith angle.

Most radiation monitoring instruments, including the Brewer, are designed to replicate the cosine response to incident radiation. The Teflon diffuser of the Brewer approximates the cosine response; however, at large zenith angles, the response falls below the cosine function (Fioletov et al., 2002). Measurements of global irradiance are therefore in error by values that range up to -10% depending on wavelength, SZA (solar zenith angles), and clarity of the sky. The cosine response is instrument dependent (Bais et al., 2005) and, with proper measurement, correction for the departure from the cosine response is applied to the data with the aid of a radiative transfer model or another parameterization technique (Bais et al., 1998; Fioletov et al., 2002). The uncertainty of the corrected values is about 2%. Also, work has been carried out to improve the cosine response of the sensor (Gröbner, 2003), and these new diffusers are available.

6.4.7 Internal Polarization

It has been demonstrated that there is a sensitivity dependence on SZA for measurements of direct radiation due to polarization effects between components of Brewer spectrophotometers (Cede et al., 2004; 2006a). Unpolarized radiation from direct sun becomes increasingly polarized as the incident angle through the quartz window increases from normal transmission (SZA = 35°), and the direction of enhanced polarization is along the axis parallel to the length of the window. This polarization interacts with the grating, which is more sensitive to radiation polarized on the axis perpendicular to the grating grooves. At SZA = 0°, the polarization axis of the grating is aligned parallel to the polarization axis transmitted through the window. With increasing SZA, the angle between the two axes of polarization increases. Thus, for window transmission normalized to SZA = 35°, the apparent transmission is enhanced for SZA < 35° and reduced for SZA > 35°.

Corrections can be applied to direct radiation data provided the degree of polarization of the grating sensitivity is known. It should be noted that the degree of polarization is not necessarily the same for all instruments. Calculations by Cede et al. (2004; 2006a) assume 100% polarization (extreme case) for the grating response. In general, the degree of polarization for the grating is less than 100%, and for single spectrometers (Mark Ⅱ and Mark Ⅳ), the polarization is significantly less than 100% since there is only one grating.

Corrections can also be achieved by the use of hardware modifications. Use of a cylindrical quartz window with the axis centered on the axis of rotation for the zenith prism would ensure that direct radiation always passes through the window at right angles. Also, a depolarizer inserted in the fore-optics removes the polarization effect (Cede et al., 2006a). Use of a Teflon diffuser instead of the ground quartz diffuser for measurements of direct radiation also avoids this effect since the

Teflon has been found to be an effective depolarizer, whereas the ground quartz removes very little polarization.

The internal polarization effects do not impact the operational measurements of ozone and other atmospheric gases that use DOAS techniques. These techniques measure the relative absorption at different wavelengths and the wavelength dependence of the polarization effect was found to be negligible (Cede et al., 2006a). However, corrections for the polarization effects should be applied for absolute measurements of the extraterrestrial spectra, aerosol optical depth, aerosol single scattering albedo, and estimates of actinic flux (Webb et al., 2002). Measurements of global UV irradiance are not affected since the Teflon diffuser on top of the instrument has been found to be an effective depolarizer.

6.5   Measurement of Total Ozone

The second most important atmospheric variable affecting surface UV radiation after cloud cover is total column ozone. Ozone strongly absorbs radiation in the UV and accounts for the sharp cutoff of the solar spectrum at about 290 nm. The most common measurement made by Brewer instruments is that of total column ozone, which is the amount of ozone in a column of the atmosphere compressed to standard temperature (STP $= 273\,°K$ and pressure $= 1{,}013.25$ mb). Column ozone is measured in Dobson Units (DU $= 10^{-3}$ cm ozone at STP). Total ozone measurements are routinely reported to the World Ozone and UV Data Centre (WOUDC) in Toronto. Direct sun measurements are the preferred measurement type because they are the most accurately defined. Measurements are also made using zenith sky radiance, global irradiance, and direct irradiance from the moon.

6.5.1   Measurement Technique

The standard algorithm used for determining total ozone with the Brewer instrument is a DOAS technique using radiation measured at four of the operational UV wavelengths, (λs shown in Fig. 6.3): 310.1 nm ($\lambda = 2$), 313.5 nm ($\lambda = 3$), 316.8 nm ($\lambda = 4$), and 320.0 nm ($\lambda = 5$). Bandpasses for the slits are approximately triangular in shape (Gröbner et al., 1998) with a full-width-half intensity (FWHI) of about 0.6 nm (Kerr, 2002). The DOAS method for measuring total ozone is based on the following equation (Kerr et al., 1981), which quantifies the intensity of direct solar radiation at the earth's surface:

$$\log(I_\lambda) = \log(I_{o\lambda}) - \beta_\lambda m \times p/p_o - \tau_\lambda \sec(\text{SZA}) - \alpha_\lambda O_3 \mu \tag{6.2}$$

where I_λ is the measured intensity of radiation at wavelength λ.

$I_{o\lambda}$ is the extraterrestrial intensity at wavelength λ.

β_λ is the Rayleigh scattering coefficient at λ.

m is the effective pathlength of direct radiation through air.

p is the pressure at the station.

p_o is standard pressure (1,013.25 millibars).

τ_λ is the aerosol optical depth at λ.

sec (SZA) is the secant of the solar zenith angle (SZA).

α_λ is the ozone absorption coefficient at λ.

O_3 is the column amount of atmospheric ozone.

μ is the ratio of the effective pathlength of direct radiation through ozone to the vertical path.

The intensity of radiation at the four operational wavelengths over the 10 nm range is represented by the 4 I_λ values shown in Eq. (6.2). The measurement of ozone takes advantage of the curvature of ozone absorption as a function of wavelength over the wavelength range (Fig. 6.3). The four equations ($\lambda = 2-5$) are linearly combined and rearranged to yield the following:

$$F + \Delta\beta m = F_o - \Delta\tau\sec(\text{SZA}) - \Delta\alpha O_3\mu \qquad (6.3)$$

where $F = \log(I_2) - 0.5\log(I_3) - 2.2\log(I_4) + 1.7\log(I_5)$

$F_o = \log(I_{o2}) - 0.5\log(I_{o3}) - 2.2\log(I_{o4}) + 1.7\log(I_{o5})$

$\Delta\beta = \beta_2 - 0.5\,\beta_3 - 2.2\,\beta_4 + 1.7\,\beta_5$

$\Delta\tau = \tau\delta_2 - 0.5\,\tau\delta_3 - 2.2\,\tau\delta_4 + 1.7\,\tau\delta_5 \sim 0$

$\Delta\alpha = \alpha_2 - 0.5\,\alpha_3 - 2.2\,\alpha_4 + 1.7\,\alpha_5$

The linear combination is weighted to minimize effects of small shifts in wavelength (i.e., $\Delta F_o/\Delta\lambda$ is near a stationary point) and to eliminate SO_2 absorption. The weighting also makes any function linear with wavelength equal to zero (i.e., $\lambda_2 - 0.5\lambda_3 - 1.7\lambda_4 + 2.2\lambda_5 = 0$). Thus aerosol scattering ($\Delta\tau\delta$), which is approximately linear with wavelength over the relatively small wavelength range, becomes negligible in Eq. (6.3). The effects of Rayleigh scattering ($\Delta\beta m$) in Eq. (6.3) are calculated using the Rayleigh scattering coefficients of Bates (1984). The amount of total ozone is then readily calculated from the equation using $O_3 = (F_o - F - \Delta\beta m)/\Delta\alpha\mu$ provided values for F_o and $\Delta\alpha$ are known. The precision over a long period of time for a direct sun measurement made with a well-calibrated and well-maintained Brewer instrument is demonstrated to be better than $\pm 1\%$ (Fioletov et al., 2005). Values of F_o and $\Delta\alpha$ (calibration constants) are unique for each instrument and depend on the detailed band passes of the slits of each instrument. All instruments in operation require the determination of the calibration constants. Determination of the calibration constants is discussed further in Section 6.5.2.

The Brewer instrument is also used to derive total ozone from measurements of polarized radiation scattered from the zenith sky. The zenith radiation measured at the four wavelengths is weighted to yield the value F_{zs}, in the same manner as F for direct sun shown in Eq. (6.3). Many pairs of direct sun and zenith sky observations taken over a period of more than a year are used to establish a statistical relationship that relates F_{zs} as a function of F_o, total ozone (derived from direct sun data), and

airmass (μ). The measurement pairs are made under a wide range of total ozone and airmass values. Once the relationship is established, total ozone can be determined from a measurement of F_{zs} made when the sun is not available.

The precision of the zenith sky measurement is not as good as that for the direct sun (Dobson, 1957; Brewer and Kerr, 1973) and is observed to be about $\pm 2\%$ under most conditions without heavy clouds provided the zenith sky algorithm has been derived for the specified instrument and location. Radiation polarized parallel to the solar plane is used since it has been shown that this radiation is less sensitive to the presence of thin clouds (Brewer and Kerr, 1973). When heavy convective clouds are present, the apparent total ozone can increase substantially (Fioletov et al., 1997; Mayer et al., 1998; Kerr and Davis, 2007). This is likely caused by enhanced absorption due to multiple scattering through ozone within the clouds.

Total ozone derived from zenith sky measurements also depends on the vertical distribution of ozone, particularly when the SZA is large. For example, the majority of zenith radiation passes vertically through a layer of ozone near the ground since most of the radiation is scattered above the layer. However, for a layer near the top of the atmosphere, the effective pathlength is relatively longer since most of the scattering occurs below the layer and radiation from the sun that is scattered toward the instrument passes through the layer obliquely.

Total ozone is also derived from measurements of global radiation (Fioletov et al., 1997; Kerr and Davis, 2007) and measurements using the focused sun (Josefsson, 1992) or moon (Kerr, 1989a) as a light source. Measurements using global irradiance are useful for situations when the direct sun is not available. Focused sun measurements are used at high latitudes at times of the year when the solar elevation does not reach 15°. Measurements using the moon as a light source are useful for obtaining data when the sun is below the horizon. This is particularly beneficial for obtaining data from high latitudes during winter when the sun is absent most of the time.

6.5.2 Calibration

Calibration of an instrument requires the determination of the calibration constant F_o and the effective ozone absorption coefficient $\Delta\alpha$ as discussed in the previous section. Determination of $\Delta\alpha$ is done for all instruments by applying laboratory measurements of the slit transmission functions to the ozone absorption coefficient spectrum. The absorption spectrum of Bass and Paur (1985) has been used operationally since this is used by other operational ground-based (Dobson) and satellite-based (Total Ozone Mapping Spectrometer (TOMS)) instruments. Other ozone absorption spectra are available (e.g., Molina and Molina, 1986; Brion et al., 1993), and if these spectra are applied to the Brewer instrument, differences of up to a few percent in total ozone result.

The slit transmission functions are determined by measuring the signal of emission lines at accurately known wavelengths as they are scanned individually across each exit slit by moving the micrometer. Emission lines from mercury, cadmium, neon, and other elements are used (Gröbner et al., 1998). The known wavelengths are then used to determine the wavelength setting as a function of micrometer step for each slit, and the shape of the transmission as a function of wavelength is accurately determined for each slit. Operational measurements involving wavelength scans (e.g., global UV scans) use the wavelength dispersion function to select wavelength settings during the scans.

There are two methods to determine the extraterrestrial calibration constant (F_o from Eq. (6.3)): (1) the primary calibration method, and (2) the calibration transfer method. Primary calibrations are done by use of the Langley plot technique, also called the zero airmass extrapolation technique (Kerr et al., 1985). If the aerosol term ($\Delta\delta$ (SZA)) in Eq. (6.3) is ignored then, the measured value (F), plus the calculated Rayleigh term ($\Delta\beta m$) is a linear function of airmass (μ) with the value F_o as the intercept. Therefore, if measurements are made under a range of μ (e.g., $1 < \mu < 3.5$) throughout a day when ozone remains constant, then a plot of ($F + \Delta\beta m$) versus μ would yield a straight line with intercept F_o.

Extraterrestrial calibrations of Brewer instruments are carried out regularly at Mauna Loa Observatory (MLO), Hawaii (19.5°N, 155.6°W, 3400 m above sea level). This site offers stable observing conditions required for the calibrations and a low μ value at noon ($\mu < 1.2$) for most of the year. The high altitude of MLO is above most tropospherical contamination and the tropical location ensures minimal day-to-day variability of stratospheric ozone. In reality, ozone does not remain constant during the day at MLO and typically varies by about ± 2 DU ($1 - \sigma$) throughout any given day (see Kerr, 2002), resulting in an uncertainty of F_o that would cause an error in total ozone of about 1.5%. Calibrations are therefore averaged over a 10-day period to reduce the effects of daytime ozone variability. The calibrations are done in two parts. The results of the first part are applied to past data and those of the second part are used for future data. Any changes or upgrades to the instrument (e.g., realignment, replacing or cleaning optical components, etc.) are carried out between the first and second parts.

The calibration reference for the global Brewer network is a triad of instruments based in Toronto. These instruments have been calibrated independently from the basic physical principles described above. There are three instruments to ensure the integrity and continuity of the reference. For example, if one instrument should develop a problem, the problem instrument is quickly identified as the outlier and measures are taken to correct the problem promptly. Historically since 1982, there has been at least one of the three instruments in operation at all times, fulfilling the objective of providing the continuous availability of a calibration reference. Normally, all three instruments are operating together and analysis of their long-term records shows agreement between the instruments comprising the triad better than 1% over a 20 year period (Fioletov et al., 2005).

The second method for determining F_o for an instrument is by the calibration transfer method, which uses an instrument with a known F_o. Simultaneous direct sun measurements are made with the calibrated instrument and one or more uncalibrated instruments. The total ozone value (O_3) from the calibrated instrument is used to determine the F_o of the uncalibrated instrument using $F_o = F + \Delta\beta m + \Delta\alpha O_3 \mu$ (from Eq. (6.3) with the $\Delta\delta$ sec (SZA) set equal to zero). In practice, F_o is determined from the results of many side-by-side measurements made over the period of one or two days to provide a large range of airmass.

Calibration of operational field instruments is done by use of a traveling standard. This process uses an instrument, which is calibrated using the primary standard triad in Toronto. This traveling instrument is then transported to a site where it is used as the calibration reference for the field instrument. In practice, several regional field instruments are calibrated in one trip. After calibration of the field instrument(s), the traveling standard returns to Toronto for a follow-up calibration check. This operational process has the advantage that both the triad reference, as well as the field instruments, remain in operation continuously and are not subject to any risks involved with transporting an instrument.

Another method by which field instruments are calibrated is through intercomparison field campaigns. This method has been used traditionally for Dobson instruments, and Brewer instruments have often participated in these Dobson intercomparisons to ensure agreement between Brewer and Dobson references (e.g., Komhyr et al., 1989). Also, in some situations, it is more efficient for several field Brewer instruments to be calibrated by a traveling standard during a regional intercomparison campaign. Overall, the intercomparison campaign method is less desirable than the one-on-one site calibration method since the absence of field instruments during the intercomparison leaves gaps in the data records at field sites and instruments are subject to damage during transport to and from the intercomparisons.

6.6   Measurement of Spectral UV Radiation

The Brewer Mark II instrument measures global spectral irradiance (mW/m^2/nm) incident on the horizontal Teflon diffuser for wavelengths between 290 nm and 325 nm at a resolution of about 0.58 nm and a sampling interval of 0.5 nm (Kerr and McElroy, 1993). Later versions of the instrument have extended the wavelength range to include irradiance at wavelengths up to 365 nm (Bais, 1997; Gröbner et al., 1998).

For the short scans (290 nm – 325 nm), the shortest operational exit slit (normally set a 306.3 nm for ozone measurements) is used. The grating is rotated via the micrometer stepping motor to locate radiation centered at the specified wavelength on slit 1. Samples progress from 290 nm to 325 nm and then back to 290 nm.

Radiation is sampled for about one second at each wavelength setting, and the grating is repositioned to the next wavelength setting 0.5 nm away. A complete scan takes about three minutes. The extended scan (290 nm − 365 nm) takes longer, but is usually sampled in one direction: from the shortest to longest wavelength. The extended scan also switches to the longest wavelength slit part way through the scan to allow coverage to 365 nm.

Measurement of spectral UV irradiance is an absolute measurement, which is intrinsically more difficult than the DOAS measurement method used for total ozone. Calibration and data processing therefore require additional attention in order to obtain high quality spectra that are accurate on an absolute scale. Data processing should include corrections for dark count, dead time, neutral density filters, stray light, temperature response, and cosine response as discussed in Section 6.4.

Spectral UV data measured by Brewer instruments are regularly reported to the WOUDC (http://www.msc-smc.ec.gc.ca/woudc/) as well as the European Ultraviolet Database (EUVDB; http://uv.fmi.fi/uvdb). Here the data are archived, checked for quality, and flagged should there be any problems. These data are readily available to the scientific community.

Calibration on an absolute scale is carried out using 1,000 W quartz lamps with known irradiance output traceable to a national standards institute, such as the National Institute for Standards and Technology (NIST) in the United States. Calibrated lamps are supplied with known emissivity as a function of wavelength with an estimated accuracy of about ±2% on an absolute scale. Typically, several primary (supplied by a standards institute) and secondary lamps (calibrated by comparison to a primary) are used for periodic calibrations. Analysis of the long-term calibration records for some Brewer instruments has shown that the output stability and degradation with age varies significantly from lamp-to-lamp. Calibration results vary by as little as ±1.5% for some lamps and as much as ±4% for others. Newly calibrated primary lamps usually agree to within ±2%; however, some degrade very rapidly with age and others have remained constant for many hours of operation over the period of several years.

For instrument calibration, the power to a lamp is accurately controlled to ensure that it is operated at the specified current and voltage. The lamp is placed vertically above the horizontal diffuser at an accurately determined distance inside a blackened housing or a dark room to block external radiation and to minimize radiation reflected from the lamp. From the lamp emissivity data and the geometric setup, it is possible to determine the irradiance at the location of the diffuser. Scans of the lamp are made and, using the known irradiance, the responsivity of the Brewer instrument as a function of wavelength is determined. The responsivity is determined for radiation arriving vertically downward from the zenith. Additional measurements must be made to determine the responsivity as a function of zenith angle. Correction for the departure of the responsivity from the cosine function can be applied to data.

Generally the lamp irradiance is significantly less than that seen with the instrument exposed to full sunlight. It is therefore important to ensure that the instrument responds linearly to radiation over the range that encompasses both calibration and measurement. The frequent testing of the linearity (as discussed in Section 6.4.2), and its application during data processing, ensure the linear response of the instrument and the accuracy of the data.

The pointing capabilities of the Brewer instrument also allow for the absolute measurement of direct irradiance provided absolute calibration is carried out for the direct sun port (Bais, 1997; Gröbner and Kerr, 2001). This calibration is not done as part of a routine operation of field instruments. However, special methods have been developed to determine the responsivity of the direct measurement by using lamps viewed through the pointing prism, or by comparison of a direct measurement through the prism with a direct measurement on the diffuser (Kazadzis et al., 2005). Careful consideration must be made for neutral density filter transmission, instrument temperature, internal polarization, and stray light.

Absolute measurements of direct irradiance can be used to determine the absolute intensity of the solar spectrum using the Langley extrapolation method. Extrapolated measurements of the solar spectrum using well-calibrated Brewer instruments have shown agreement to within $\pm 3\%$ compared with spectral measurements made from a satellite (Bais, 1997; Gröbner and Kerr, 2001).

Brewer instruments have participated in many intercomparison campaigns for UV instruments. Instrument intercomparisons are often used as a check to quantify differences between individual instruments and various instrument types (e.g., Thompson et al. 1997; Bais et al., 2002). During intercomparisons, individual instruments are calibrated using their normal operating procedures and then used to measure global irradiance simultaneously with other calibrated instruments. With the participation of several instruments, all measuring the same signal, it is possible to determine measurement uncertainty from differences between instruments and to identify problem instruments. Intercomparisons have been used to standardize calibration and operational procedures and, overall, the quality of UV measurements has improved significantly with time as a result of knowledge gained through the intercomparisons.

6.7   Measurement of Other Atmospheric Variables

In addition to total ozone and spectral UV radiation, the Brewer instrument is capable of measuring other atmospheric variables that affect the wavelength distribution and angular distribution of surface UV radiation through absorption and scattering processes. These variables include the vertical profile of ozone, column sulfur dioxide (SO_2), column nitrogen dioxide (NO_2), aerosol optical depth, and effective temperature of atmospheric ozone.

6.7.1   Vertical Profile of Ozone

The traditional method used to derive the vertical profile of ozone is the Umkehr method (Gotz et al., 1934), which has been adapted for use with the Brewer instrument (Mateer et al., 1985; McElroy and Kerr, 1995). Measurements are made of radiation scattered from the zenith sky at twilight during sunrise or sunset for solar zenith angles between 90° and about 75°. Zenith sky radiation as a function of wavelength depends on total ozone, the solar zenith angle, and the vertical distribution of ozone. It is therefore possible to determine the vertical profile of ozone from measurements made as the SZA passes between 90° and 75°. It takes between one and three hours to cover this SZA range depending on latitude and time of year. One condition for good quality Umkehr measurements of the vertical profile of ozone is that the sky remains clear during the observing period. The fully automated capabilities of the Brewer instrument allow measurements to be attempted every morning and every evening during twilight. Good quality measurements can be selected during the analysis of the data set.

6.7.2   Atmospheric SO$_2$

Surface UV radiation is affected by the presence of atmospheric SO$_2$, which has strong absorption bands at UV wavelengths (Fig. 6.3). Sources of atmospheric SO$_2$ are both manmade and natural. Measurements of SO$_2$ are important for tracking and assessing impacts of emissions from pollution sources, such as coal burning power plants. Measurements are also important for tracking and quantifying naturally occurring SO$_2$ emitted by volcanoes. Pollution sources typically result in a few DU of column SO$_2$ unless observations are made near a source. Column SO$_2$ in the vicinity of a volcanic eruption can be more significant (Kerr et al., 1982; Krueger et al., 1995). Ground-based measurements of atmospheric SO$_2$ using the Brewer instrument have played an important role in the development and validation of satellite-based SO$_2$ measurements (Schaefer et al., 1997) used primarily for detecting and tracking volcanic emissions.

The SO$_2$ absorption spectrum at UV wavelengths has significantly more structure than that of ozone as shown in Fig. 6.3. The differences in structure allow the measurement of SO$_2$ in addition to ozone. The presence of SO$_2$ in the atmosphere can add a false signal to total ozone measured with the Dobson instrument (Kerr et al., 1985). However, the operational total ozone algorithm for the Brewer instrument (Eq. (6.3)) is insensitive to SO$_2$. The Brewer algorithm for measuring SO$_2$ uses the peak absorption feature at 306.3 nm (Fig. 6.3) and is described in detail by Kerr et al. (1985). Column SO$_2$ is usually measured using the direct sun method since it the most accurate method and values are reported to the WOUDC

when available. SO_2 can be seen on zenith sky measurements if values are significantly large, particularly during the passage of debris from a volcanic eruption (e.g., Kerr et al., 1982).

6.7.3   Atmospheric NO_2

Surface UV radiation is also affected by atmospheric NO_2, which absorbs at UV wavelengths. Atmospheric NO_2 typically absorbs a small percentage of global radiation at the earth's surface. Sources of atmospheric NO_2 are both manmade and natural. Pollution from sources such as automobiles and aircraft account for NO_2 near the ground, in addition to regions in the troposphere and lower stratosphere. NO_2 occurs naturally in the stratosphere and plays an important role in the photochemistry of stratospheric ozone. Measurements of NO_2 are therefore important for both pollution studies, as well as in the study of the stratosphere.

NO_2 absorbs radiation in the visible as well as the UV region of the spectrum. Its absorption in the UV has little structure and is nearly linear with wavelength, so it does not interfere with UV ozone measurements. However, at visible wavelengths between 420 nm and 450 nm, NO_2 absorption is highly structured with wavelength allowing its measurement (Brewer et al., 1973). Several researchers now monitor NO_2 routinely using DOAS techniques with the visible absorption features (Hofmann et al., 1995, and references therein). The Brewer Mark IV instrument uses the set of five wavelengths positioned at wavelengths in the visible and an algorithm weighted to optimize NO_2 absorption as described in detail by Kerr (1989b).

6.7.4   Aerosol Optical Depth

Atmospheric aerosols play an important role in scattering and absorbing radiation as it passes through the atmosphere. The intensity and angular distribution of surface radiation are affected by the aerosols' optical depth (τ in Eq. (6.2)), vertical distribution, and absorption and scattering characteristics. Aerosol optical depth (τ) is comprised of two components: absorbing and scattering (i.e., $\tau = \tau_{abs} + \tau_{scat}$). Aerosols typically reduce surface UV irradiance by a few percent and can reduce surface irradiance by more than 50% in some cases.

There are a number of sources of atmospheric aerosols. Natural sources include volcanoes, dessert dust, and smoke from forest fires. Manmade sources include pollution from industrial activity (smog). The measurement of aerosols is important for several scientific applications ranging from local to global issues. Local issues include the prediction of smog alerts in the vicinity of cities and tracking of smoke from forest fires. Regional issues include transport of pollution across

borders. Global issues include the impact of widespread manmade aerosols on our changing climate and the impact of volcanic aerosols on the ozone layer.

The Brewer instrument is capable of determining τ using measurements of direct solar radiation provided the extraterrestrial response of the instrument is accurately known and appropriate corrections are applied. Measurements must be made at several wavelengths in order to quantify and correct for the absorption of absorbing atmospheric gases such as ozone, SO_2, and NO_2.

Extraterrestrial values (log ($I_{o\lambda}$) terms in Eq. (6.2)) are determined by making measurements of log (I_λ) (in Eq. (6.2)) at a clean site (e.g., MLO) to determine the values of log (I_λ)$+\beta_\lambda m+\alpha_\lambda O_3 \mu$ from many measurements made throughout a day. A plot of these values against sec (SZA) yields a straight line with intercept log ($I_{o\lambda}$). Intercept values made at several wavelengths averaged over a period of several days are used as the extraterrestrial reference for the particular instrument. Once the extraterrestrial values are known, it is possible to determine τ_λ from measurements made at a field site using Eq. (6.2).

Corrections that must be applied to the measurements include dark count, dead time, instrument temperature, neutral density filter, internal polarization, and stray light (if required). These corrections must be applied both to the calibration measurements as well as to the field site measurements. Further details of the methods of instrument calibration and the method for measuring τ are discussed in Kerr (2002) and Arola and Koskela (2004). Results of optical depth measurements using the Brewer instrument have been reported by many researchers (Bais, 1997; Kerr, 1997; Carvalho and Henriques, 2000; Jaroslawski and Krzyscin, 2000; Jaroslawski and Krzyscin, 2005; Meleti and Cappellani, 2000; Gröbner et al., 2001; Kirchhoff et al., 2001; Kerr, 2002; Cheymol and De Backer, 2003; Gröbner and Melita, 2004; Kazadzis et al., 2007).

6.7.5 Effective Temperature of Atmospheric Ozone

The temperature of atmospheric ozone influences the amount of UV radiation reaching the surface. The absorption of radiation by ozone in the UV is temperature dependent and generally increases with temperature. The effective temperature of atmospheric ozone (i.e., average temperature of column ozone weighted by ozone concentration) can vary by up to 20℃ depending on latitude and season. Over this temperature range, ozone absorption can change by up to 10% at some wavelengths.

It is possible to measure the effective temperature of ozone since the spectrum of the temperature dependence has features that can be used as a dependent vector in a DOAS analysis. The methods used to measure effective ozone temperatures and the multiyear records of the effective ozone temperatures at Toronto are reported by Kerr (2002) and Kerr and Davis (2007).

6.8   The Brewer Spectrophotometer as a Powerful Research Tool

The original development of the Brewer spectrophotometer and subsequent upgrades have provided users with pre-programmed routines for making a suite of the most common types of operational measurements, set-up, tests, and calibrations. Pre-programmed routine measurements include global UV scans, Umkehr measurements, measurements of total ozone, SO_2, and NO_2 using direct sun, zenith sky, or global radiation. Operational tests include standard lamp and mercury lamp tests to set wavelength, wavelength shutter motor test, and dead time test. Calibrations include the slit function dispersion measurement and responsivity calibration for global measurements.

Software operating on the control computer offers interested users the opportunity to develop customized programs to carry out specialized types of measurements and support tests. Customized measurements take advantage of the fact that all operational mechanical adjustments are controlled with stepping motors. Depending on the objective of a specialized measurement, some hardware modification may be required. However, most hardware modifications are relatively minor and fairly easy to implement. For example, a custom filter may replace or supplement an existing filter in one of the three filter wheels. Some of these specialized measurements have been discussed in pervious sections (Bais, 1997; Wardle et al., 1997; Gröbner et al., 1998; Gröbner and Kerr, 2001; Kerr, 2002; Kerr and Davis, 2007). Other customized measurements include that developed to measure NO_2 using an advanced scanning technique (Cede et al., 2006b) and a new method developed to measure tropospheric and stratospheric ozone profiles using sky radiance measurements at multiple viewing angles (Tzortziou et al., in press).

There is further potential for use of the Brewer instrument to explore other possible scientific applications. Pointing capabilities allow the investigation of the dependence of spectral irradiance as a function of direction. Measurement of radiation in the first order of the Mark II instrument (600 nm – 650 nm) could allow the measurement of ozone using the Chappuis band. Measurements could then be made at low solar elevations since ozone absorption is smaller and Rayleigh scattering is significantly less at these wavelengths than those in the UV. A new scan type, called the "group-scan method," has recently been developed (Kerr, 2002) and could be applied to the measurement of NO_2 at visible wavelengths, resulting in improved accuracy for measurements of NO_2.

Brewer instruments have also participated in numerous scientific field campaigns that are intended to study various aspects regarding atmospheric composition and surface UV radiation. Measurements made by Brewer instruments provide important input to detailed investigations of photochemical and physical processes involved in our understanding of the ozone layer and surface UV radiation. In some cases, special measurements and schedules are developed to ensure critical measurements

are made at appropriate times. Contributions made to campaigns include measurements of atmospheric variables such as total ozone (e.g., Kerr et al., 1994; Margitan et al., 1995), aerosol optical depth (e.g., Gröbner et al., 2001), or surface UV radiation (e.g., Bais et al., 2001).

6.9 Summary

The Brewer spectrophotometer has been in operation at some sites almost continuously for up to 25 years. It has also been proven reliable in numerous specialized field campaigns and intercomparisons. In general, the instruments have proven to be quite stable over long periods of time and function reliably in unattended operation for periods of several days under a wide range of operating conditions.

The Brewer spectrophotometer is a valuable scientific tool that has made significant contributions to our understanding of the ozone layer and the dependence of surface UV radiation on stratospheric ozone and other atmospheric variables. Several dozen papers have been published that focus on the instrument itself, and several hundred papers have been published reporting scientific results that include data from Brewer spectrophotometers.

Acknowledgements

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