Direct spectral measurements with a Brewer spectroradiometer: absolute calibration and aerosol optical depth retrieval

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We present three different methods for the absolute calibration of direct spectral irradiances measured with a Brewer spectroradiometer, which are shown to agree to within ±2%. Direct irradiance spectra derived by Brewer and Bentham spectroradiometers agree to within 4 ± 3%. Good agreement was also found by a comparison of the aerosol optical depth and Angstrom exponent retrieved by the two instruments and a multifilter rotational shadowband radiometer. The spectral aerosol optical depth (300−365 nm) derived from six years of direct irradiance measurements at Thessaloniki shows a distinct seasonal variation, averaging to ~0.3 at 340 nm in winter and ~0.7 in summer.

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1. Introduction

Measurements of solar UV radiation gained considerable importance during the past decade due to the observed ozone depletion.[1,2] The intensity of solar UV radiation reaching the Earth's surface has important implications for human health, UV-sensitive ecosystems, atmospheric chemistry, and agriculture.[3] Until now most of the scientific efforts have been put into the irradiance received in a horizontal surface (global irradiance). The instruments performing such measurements reached a high level of accuracy during the past decade, as a result of continuous technical improvements, standardization of operational and quality control procedures, and international collaboration.[4–6] Several intercomparisons were organized since the early 1990s[7–12] to investigate the accuracy and the limitations of instruments measuring solar UV radiation. In the last comparison held in Thessaloniki, Greece, in 1997 the majority of the 19 participating instruments agreed to better than ±5%.[13]

Spectral measurements of the direct irradiance are important for many atmospheric science applications. They are used to determine the aerosol optical depth (AOD),[14] as well as the columnar abundance of atmospheric species absorbing in the UV.[15,16] Moreover, various modeling studies benefit from such measurements since their parameterization is much easier than that of global or diffuse radiation.[17] Lately, direct irradiance spectral measurements were used to determine the actinic flux in combination with global irradiance[18–20] measurements. They are also useful to calculate correction factors for the deviation of global irradiance measurements from the ideal angular response, known as cosine correction factors.[21,22] Finally, they can be used to determine the spectrum of the extraterrestrial solar flux from ground-based measurements.[23,24]

Despite their usefulness, spectral measurements of direct solar irradiance in the UV are included in only a few observational programs.[25] One reason was the need for a Sun-pointing system adaptable to the already existing spectroradiometers. However, instruments like the Brewer spectrophotometers can measure the direct spectral irradiance with the existing pointing system that is used for the total column ozone measurements. A second important

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reason was the lack of reliable methodologies for the absolute calibration of the direct solar irradiance measurements. Although significant improvements have been made during the past years,[23,24] some of the uncertainties in the calibration and measurement methodologies have not yet been eliminated.

The absorption and scattering of solar irradiance by aerosols is an important parameter for climate studies. The reduction of UV irradiance reaching the Earth's surface by aerosol over polluted areas can become even larger than the increase of UV due to the ozone reduction.[26,27] Thus the determination of the AOD in the UV region is of great importance. Use of the AOD in the visible to calculate the UV attenuation induced by aerosols[28] may not be sufficient because of the strong spectral dependence of AOD in the UV.[29]

Most of the efforts used to retrieve the AOD from the Brewer spectrophotometers' direct Sun measurements were based on the Langley technique.[30–33] One of the main advantages of this method is that there is no need to calibrate the measured direct irradiance signals (e.g., counts or current). The irradiance at the top of the atmosphere is calculated by extrapolation to zero air mass and is expressed in the same units with the measurements.

The Langley technique could be used to calibrate the direct spectral irradiance measurements by use of satellite-derived extraterrestrial solar spectra. However, the natural variability of the measured extraterrestrial irradiance is large for the achievement of the absolute calibration function with an accuracy better than ±5%, and a large number of Langley data sets is required in an ideal atmospheric environment with constant optical depth and a large range of solar zenith angles.[24] Such criteria cannot be fulfilled in most of the UV monitoring stations worldwide. Moreover, possible instrument sensitivity changes over short time periods should also be considered when such data sets are analyzed.

In this paper we present different methodologies for the determination of the absolute calibration function for the direct irradiance spectral measurements recorded with a Brewer spectroradiometer. One of our objectives is to investigate the possibility for a laboratory-based calibration methodology that is applicable to similar instruments. We validate the results by performing synchronous direct spectral measurements with a different type of spectroradiometer (Bentham DTM 300). Measurements of the AOD and the Angstrom exponent obtained by the two spectroradiometers and by a multifilter shadowband radiometer are compared. Finally, AOD measurements derived from direct irradiance spectral measurements during the past six years in Thessaloniki, Greece (40°38′ N, 22°57′ E), are presented.

2. Instrumentation and Measurements

Two double-monochromator UV spectroradiometers were used to measure the direct solar spectral irradiance and to derive the AOD: a Brewer MKIII and a Bentham DTM 300. In the frame of the influence of clouds on the spectral actinic flux in the lower troposphere (INSPECTRO) project, a Bentham DTM 300 spectroradiometer operated by the University of Innsbruck, Institute of Medical Physics, was installed at the University of Thessaloniki, Greece, where a Brewer MKIII spectroradiometer operates regularly, for a period of five months (March–July 2003). The Bentham was performing regular spectral measurements of actinic flux and global irradiance during the entire period. Occasionally, the Brewer and the Bentham instruments performed synchronized direct Sun spectral measurements.

The Brewer spectroradiometer is a double monochromator consisting of two identical spectrometers equipped with holographic diffraction gratings (3600 lines/mm) operating in the first order. The operational spectral range of the instrument is 287.5−366.0 nm, and its spectral resolution is 0.55 at full width at half-maximum (FWHM). The sampling interval is normally 0.5 nm. The wavelength calibration is achieved by scanning the emission lines of spectral discharge lamps, and the absolute calibration is maintained by scanning every month a 1000-W quartz–halogen tungsten lamp of spectral irradiance, traceable (through Optronic Laboratories Inc.) to the National Institute of Standards and Technology standards. According to the provider, the uncertainty of the 1000-W calibrated lamps is within ±2.5% (1σ), whereas an additional ±2% should be expected from the transfer of the calibration to our working standards. The later uncertainty was estimated from a series of measurements in the laboratory. A set of five 50-W lamps is used weekly to track the stability of the instrument.

For the direct irradiance measurements, a rotating prism directs the incoming radiation into the fore optics of the instrument. The whole system follows the Sun through the rotation of the prism but also the rotation of the whole instrument about its vertical axis. The field of view (FOV) of the instrument is controlled by an iris, which can be set between ~2° (used regularly for the direct Sun measurements) and 10°. Five neutral-density filters with increasing attenuation of $\sim 10^{0.5}$ can be inserted into the beam path to protect the photomultiplier from overexposure to sunlight. The spectral transmission of these filters is known to better than ±1% from measurements in the laboratory with a 1000-W lamp.

The Bentham DTM 300 consists of a double monochromator with a 300-mm focal length and two sets of holographic gratings with 1200 and 2400 lines/mm, respectively, which can be chosen through the software. With the 2400-lines/mm grating, the spectral resolution is 0.48 nm (FWHM) and the wavelength setting uncertainty is less than 0.1 nm. The usual operational wavelength range is between 280 and 500 nm. The photomultiplier is operated at 600 V, which gives a lower limit for irradiance of $\sim 10^6\ m^{-2}\ nm^{-1}$. The absolute calibration of the spectroradiometer is based on a 1000-W halogen lamp, traceable to the Physikalisch Technische Bundesanstalt. The Bentham instrument also measures the direct irradiance by a telescope with a FOV of ~1.5°. The measurements of direct spectral irradiance allow the determination of the total column ozone and AOD in the wavelength range of 290–500 nm.[15] For the absolute calibration of the direct spectral irradiance, a 1000-W calibrated lamp is positioned to a horizontal distance of 4 m. To obtain the irradiance output of the lamp at this distance, the irradiances from the calibration certificate are scaled by the inverse distance square law.[34]

A multifilter rotating shadowband radiometer (MFR-7; Yankee Environmental System Inc., Turner Falls, Massachusetts) has operated at the Laboratory of Atmospheric Physics at Thessaloniki since February 2001 providing 1-min averages of AOD at five wavelengths (415, 501, 615, 675, and 867 nm). Measurements are usable only when recorded under clear-sky conditions. Gaps in the time series of this instrument are mainly associated with overcast conditions, which are more frequent during the fall–winter period. Details on the methodology used for the calculation of the AOD from the MFR-7 measurements is given in Gerasopoulos *et al.*[35]

3. Calibration of Direct Sun Spectra

For the majority of the monitoring stations that use Brewer spectroradiometers for UV spectral measurements, the global irradiance calibration procedure is more or less standardized and the associated uncertainties can be sufficiently quantified.[36,37] On the contrary, the absolute calibration of direct irradiance measurements has not yet reached a similar level of standardization.

The only difference in the light path inside the instrument between the direct and the global irradiance measurements is use of different entrance optics. Actually a Teflon diffuser and a director prism are the two extra optical components used in global irradiance measurements. On the basis of our experience with the Brewer spectrophotometer, we believe that the stability of the diffuser is fairly good for relatively long periods (of the order of a year), and therefore we do not expect to contribute significantly to the short-term variability of the absolute calibration. Indeed, sensitivity changes can be attributed to changes or degradation of the photomultiplier or changes of the spectrometer components, both as a result of aging and temperature variations. Therefore, instead of measuring the absolute calibration for the direct irradiance measurements independently, one could use a factor that would adjust the global irradiance calibration to be used for the calibration of the direct irradiance measurements. This dimensionless factor, which is a function of wavelength, is defined as the spectral ratio of the direct irradiance measured through the direct irradiance port (director prism) of the Brewer and the direct irradiance as measured through the UV port (diffuser), hereafter denoted as the calibration transfer function (CTF). The determination of this factor can be repeated every few months to account for possible degradation of the instrument's diffuser.

Measurements of direct irradiance with Brewer spectroradiometers can be influenced by the polarization of incoming radiation on different optical components, such as the external tilted window, the prisms, and the gratings, which may also affect the absolute calibration. To our knowledge, these effects have not been studied extensively. An investigation that was performed in the laboratory[38] concluded that polarization effects on Brewer direct irradiance measurements are more evident at large solar zenith angles, leading to an underestimation of the measured irradiances from 2% to 6%, respectively, for zenith angles between 60° and 75°. These changes were attributed mainly to polarization of radiation from the tilted quartz window of the instrument. Further research is needed to confirm these laboratory results, involving also solar measurements with different types of spectroradiometers, especially at large solar zenith angles.

In Subsections 3.A–3.C we discuss the three methods used to determine the CTF and in which we use either the solar radiation or the radiation from a lamp in the laboratory.

A. First Indirect Method (Shadowing Disk)

We performed quasi-simultaneous measurements of the direct irradiance using the direct port and the global and diffuse irradiances through the global port from 290–365 nm in steps of 5 nm. To measure the diffuse irradiance, the direct radiation is blocked by a shadowing disk with a 3 cm radius, positioned between the Sun and the diffuser (1.27 cm radius) at a distance of 41.5 cm. Thus the FOV of the shadowing disk is ~8° with a slope angle of 2.5°. The FOV of the instrument with the iris closed (standard mode for the Brewer direct irradiance measurements) was measured to ~2°. The difference between direct irradiance measurements performed with the iris closed and open (FOV ~ 10°) may provide an estimate of the forward-scattered direct radiation. Such measurements for various solar zenith angles on a cloudless, but turbid, day showed that the forward-scattered irradiation was less than 2% of the direct irradiance. Because it was so small, we could not determine whether this scattered radiation was wavelength dependent, although it would be expected as such. In less turbid environments, the fraction of the scattered light would be much smaller. Similar results were reported by Groebner and Kerr.[24] Finally it should be mentioned that the characterization of another Brewer MKIII spectroradiometer (Brewer 171[38]) resulted in a FOV of ~2.7° for a closed iris and 8.5° for an open iris.

The spectral CTF for the direct spectral measurements, $f_{CT}(\lambda)$, can be calculated from

$$f_{CT}(\lambda) = \frac{E_b(\lambda)\cos(\theta)}{E(\lambda) - E_d(\lambda)}, \tag{1}$$

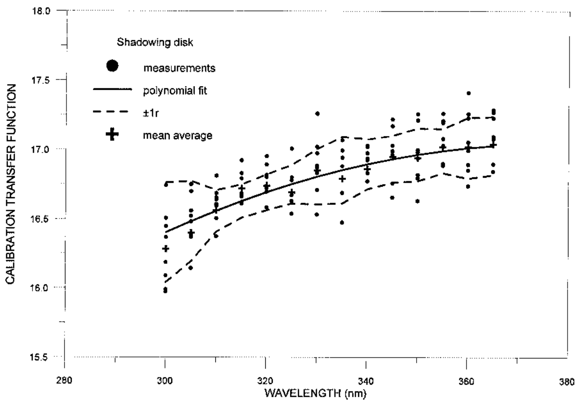

Fig. 1. Spectral CFT used to convert the Brewer spectral response for global irradiance measurements to that applicable to direct irradiance measurements, as calculated from measurements with the shadowing disk. Circles represent measurements performed in three different days, and crosses are their average at each wavelength. The solid curve is a second-degree polynomial fit on the averages, and the dashed curves are the 1σ uncertainty envelope.

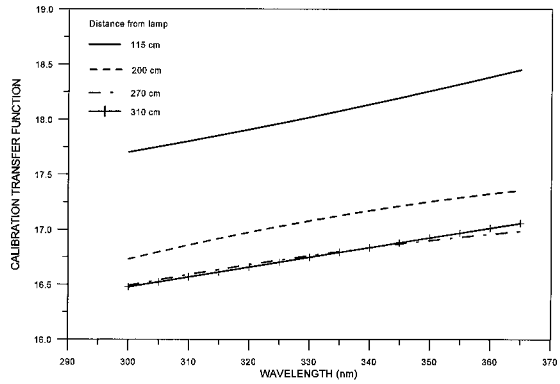

Fig. 2. Spectral CTF derived from the Brewer spectrophotometer direct irradiance measurements of a 1000-W DXW quartz–halogen lamp at distances of 115, 200, 270, and 310 cm.

where E_b, E, and E_d are, respectively, the direct (normal to the beam), global, and diffuse spectral irradiance signals (uncalibrated measurements, or counts) measured by the spectroradiometer; and θ is the solar zenith angle. The limitations and the uncertainties of these measurements are described in Bais.[23] Measurements to determine the CTF are usually per formed at small solar zenith angles and under cloud-free and low aerosol conditions to avoid overestimation of the diffuse irradiance, especially at UV-*B* wavelengths due to the already mentioned FOV difference. The uncertainty of the CTF, based on the scatter of all eight measurements that were performed during June and July 2003, is estimated to within ±1% (Fig. 1). Therefore the total uncertainty of the direct irradiance calibration (including the uncertainty of the global irradiance calibration and the FOV difference) is within ±4% (1σ).

B. Second Indirect Method (Box)

A second indirect method was tested to check independently the calibration factors determined from the first. The idea was taken from Groebner and Kerr[24] and Alaart.[39] A specially designed box with a hole on its top surface was placed above the diffuser of the spectroradiometer. The hole allows the direct solar radiation from a certain direction only (in our case corresponding to a solar zenith angle $\theta_0 = 30°$) to reach the diffuser. A small portion of diffuse radiation also enters through the hole, but it is weak enough, compared with the direct radiation, to be considered negligible. The FOV for this setup was ~10°, i.e., similar to the solid angle subtended by the shadowing disk used in the previous method. With this setup, the Brewer spectroradiometer could measure almost simultaneously (within ~30 s) the direct solar irradiance through both the diffuser ${}^{d}E_b(\lambda)$ and the direct port $E_b(\lambda)$. The first could be calibrated absolutely since it is measured through the global irradiance port. Finally, the CTF could be calculated from

$$f_{\mathrm{CT}}(\lambda) = \frac{{}^{d}E_b(\lambda)\cos(\theta_0)}{E_b(\lambda)}. \tag{2}$$

Measurements of these two quantities were performed for solar zenith angles between 29° and 31° under clear skies and low aerosol conditions, in steps of 10 nm. The differences found in the CTFs determined by the two methods were within ±2%.

C. Calibration in the Laboratory

We performed the third method in the laboratory using a 1000-W DXW quartz–halogen lamp of spectral irradiance. We performed measurements of the lamp's spectral irradiance at various distances from the Brewer by directing the pointing system of the instrument toward the lamp. The angle of the zenith prism when pointing at the lamp varied from 30° to 45° (relative to the vertical, upward-pointing position) for all the measured distances. A black surface was placed behind the lamp to eliminate direct scattered light reaching the entrance prism. Because of the size of the lamp's filament, distances longer than 270 cm were used to better match the actual geometry of the direct solar irradiance measurements. At ~270 cm, the apparent size of the filament as seen by the input optics of the Brewer is almost equal to the apparent size of the Sun (~0.5°). The distances were measured from the center of the filament to the front surface of the prism situated at the Brewer's entrance optics (4 cm behind the sloped quartz window). We calculated the irradiance of the lamp at these distances from its irradiance calibration certificate (with reference to a 50-cm distance) using the inverse distance square law.

The results of this laboratory experiment are presented in Fig. 2, which shows the CTF derived from lamp measurements at various distances. The curves are second-degree polynomials fitted on the actual measurements. Evidently the curves corresponding to 270 and 310 cm are very close each other, suggest-

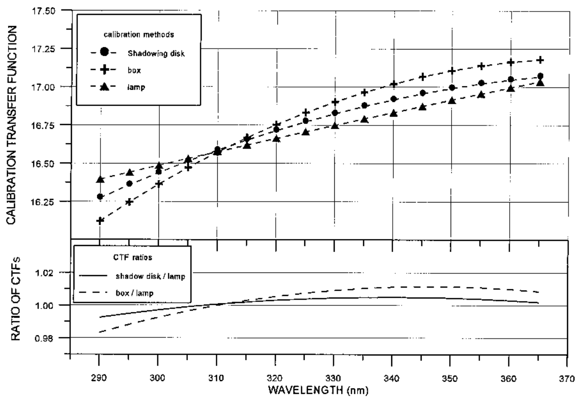

Fig. 3. Upper panel: spectral CTFs smoothed by polynomial fits for direct irradiance measurements as derived from the three different methods. Lower panel: spectral ratio of CTF determined indirectly from solar irradiance measurements (shadowing disk, solid curve; box, dashed curve) to that determined from lamp measurements in the laboratory.

ing that at these distances the lamp can be regarded as a point source and that the measurements can be safely used to determine the CTF for the direct irradiance. At shorter distances, even though the filament of the lamp falls into the FOV of the instrument, its size is large with respect to the distance and therefore the measured irradiance is overestimated. Consequently, the calibration factor for the direct irradiance derived from measurements at distances shorter than 270 cm would be systematically overestimated (by ~4% and 10%, respectively, for the two short distances in our example).

The uncertainty due to photon-counting statistics for the measurements at 310 cm is approximately ±2% at 305 nm and ±1% at 340 nm. The total uncertainty of this method is estimated to ±5.5% at 305 nm and ±5% at 340 nm and is a result of the uncertainties due to the calculation of the lamp irradiance at these distances with the inverse distance square law, the exact definition of the point at the Brewer direct port for measuring the distance from the lamp (approximately ±3 cm), the inhomogeneity of the lamp irradiance at the measuring angle, and the lamp calibration certificate and transfer to the lamp working standards.

Second-degree polynomial fits applied on the wavelength-dependent CTFs derived from the above three methods are shown in the upper panel of Fig. 3. The CTFs derived from the indirect methods are lower in the UV-*B* and higher in the UV-*A* compared with those derived from the measurements in the laboratory. This could be because we overestimated the direct irradiance measurements (due to forward-scattered light from the Sun's direction) or underestimated the diffuse irradiance measurements with either the shadowing disk or the box. In both cases the errors are wavelength dependent, resulting in higher values of the CTF in the UV-*A*. Theoretically, these spectral differences could also depend on the turbidity of the atmosphere, with the UV-*B* scattered light underestimated because of the above-mentioned FOV difference. The differences between the three methods are shown in the lower panel of Fig. 3. In general the agreement is within ±2%. This result is better than would be expected because the uncertainty estimates of each method are not less than ±4%, as already discussed.

D. Calibration with the Langley Method

A fourth independent measurement approach used to test the direct irradiance calibration results and also to retrieve the AOD was employed by the Langley calibration method.[40] For the determination of the extraterrestrial solar irradiance (I_0), 16 half-days during 2003 were chosen, which satisfied the following criteria:

- more than ten direct irradiance spectra yielding a correlation in the Langley plots of better than 0.99;
- at least ten measurements corresponding to air masses between 1.5 and 3.5; and
- standard deviation of ozone and AOD columns of less than 2.5 D.U. (Dobson units) and 0.04, respectively, during the Langley calibration day.

Results from the Langley plots for these 16 days are shown in Table 1 for three selected wavelengths. They include the average of the derived extrapolated extraterrestrial irradiances (I_0, in counts), the associated standard deviations, and the resulting uncertainty in AOD retrieval.

On the basis of the irradiance at the top of the atmosphere derived from the Langley plots, ln I_0 in Table 1, and using the airborne tunable laser absorption spectroscopy 3 (ATLAS 3) extraterrestrial spectrum (convoluted with the Brewer slit function), we calculated new spectral calibration factors for the direct irradiance. The differences with the calibration factors calculated from the CTF derived by the shadow disk technique, which is the one regularly

Table 1. Summary of Langley Plot Parameters

Parameter	Wavelength (nm) 320	340	350
ln I_0 (counts)	17.9906	18.1424	18.0649
Standard deviation of ln (I_0)	0.0757 (0.42%)	0.0865 (0.48%)	0.0867 (0.48%)
Error in AOD	0.0189	0.0184	0.0185
Calibration factors difference (%)	−4.40	−0.28	0.86

used for our measurements, are shown in the last row of Table 1.

The results showed that maximum differences in the UV-*A* are within 3%, whereas in the UV-*B* differences can reach 10%. As discussed in Section 1, this approach for the absolute calibration of direct spectral irradiance is more uncertain because of the uncertainties in the determination of I_0, especially in the UV-*B*. However, the calculated CTFs, especially in the UV-*A*, are in agreement with those produced from the above-discussed three methods.

4. Aerosol Optical Depth Retrieval

Retrievals of AOD from ground-based sensors generally employ the Langley plot calibration method[41,42] or measurements of absolute spectrally resolved solar irradiance with a calibrated spectroradiometer.[14,15] In this study, following the methodology described in Marenco *et al.*,[14] we used direct irradiance spectral measurements in the range of 290−365 nm and in steps of 0.5 to retrieve the total column of the AOD. The method that was used to calibrate the direct irradiance spectra is the first of the three methods presented in Section 3. Moreover, we used the ATLAS 3 extraterrestrial solar spectrum[43] that was convoluted with the slit function of the Brewer spectroradiometer and adjusted to account for the seasonal variation of the Sun–Earth distance. The Rayleigh optical depth was calculated according to Hansen and Travis,[44] and the ozone cross sections were taken from Bass and Paur.[45] Both the ozone and SO_2 columns used were measured by the Brewer instrument.

The experimental error (1σ) on the AOD is estimated to within 0.07 in the UV-*B* and 0.05 in the UV-*A* for measurements at solar zenith angles between 15° and 75°.[13] This error is the result of the propagation of errors due to the direct irradiance measurement and calibration uncertainties, the determination of the extraterrestrial spectrum, and the measurement of ozone and SO_2. Using a power law for the dependence of AOD on wavelength,[46] we determined the Angstrom exponent α for each direct irradiance scan by applying a least-squares fit on the optical depth data between 330 and 365 nm. This wavelength region was chosen because below 330 nm the effect of ozone is strong, and thus small uncertainties may cause significant deviations and introduce errors in the determination of α. In addition, at the low UV-*B* wavelengths, the uncertainty increases because of the weak measurement signals, especially at large solar zenith angles.

We followed the same methodology for the AOD retrieval with the Bentham DTM 300 instrument, using its direct spectral irradiance measurements that were calibrated independently.

5. Comparison of Brewer and Bentham Measurements

A. Comparison of Direct Spectral Irradiances

Direct irradiance spectral measurements recorded simultaneously by the Brewer and the Bentham spectroradiometers on three nonconsequent cloud-free days, during the four-month period that the two instruments were measuring in parallel, are compared. For both instruments, different calibrations were used in each of the three days due to the long time intervals between them.

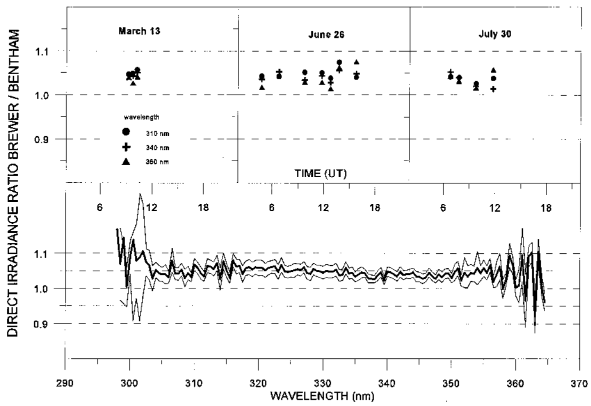

Fig. 4. Upper panel: Brewer-to-Bentham direct irradiance ratios at 310, 340, and 360 nm (circles, crosses, and triangles). Lower panel: mean spectral ratio (thick curve) and standard deviation (light curves) from all scans performed in the three reported days.

Because of differences in the instruments' slit functions, all measurements were passed through the SHICrivm algorithm,[47] which corrects possible wavelength shifts and transforms the measured spectra to standardized ones, with a spectral resolution of 1 nm FWHM (triangular slit function). In addition, the spectra were adjusted to account for differences in the calibration sources used by the two instruments, which are traceable to Physikalisch Technische Bundesanstalt and National Institute of Standards and Technology, respectively, for the Bentham and Brewer instruments. We determined this correction factor by measuring both primary sources in a dark room at the end of the measurement campaign. It is interesting to report that the differences found in the lamp irradiance calibrations were up to 8% at 300 nm, decreasing to 3% at 365 nm. The reasons for these differences are not discussed here since they fall outside the scope of this paper.

The upper panel of Fig. 4 shows the comparison of spectral irradiances at three selected wavelengths during the three days, covering a range of solar zenith angles from 17° to 72°. The plot in the lower panel presents the average spectral ratios, together with the 1σ envelope. The marked structure in the wavelength region above 353 nm is an effect from the application of the SHICrivm algorithm, which cannot take into account the change in the slit function of the Brewer at this wavelength. It appears that the two instruments differ by $\sim 4 \pm 3\%$ (1σ) during all three days for wavelengths higher than 305 nm. At shorter wavelengths the ratio is noisier due to smaller irradiance signals and to the remaining effects of the different slit functions. The systematic differences can be attributed to different calibration procedures

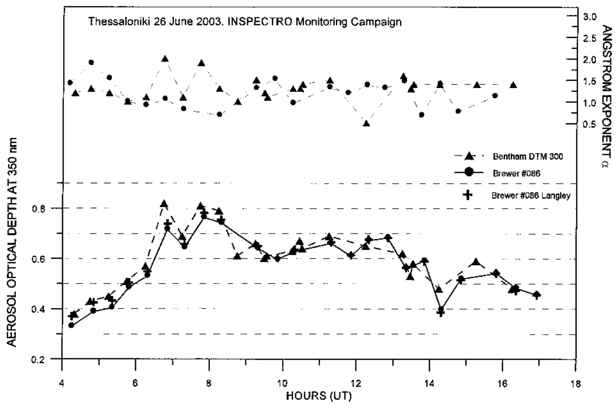

Fig. 5. Upper panel: comparison of the Angstrom coefficients retrieved from the AOD measurements derived from the Bentham (triangles) and the Brewer (circles) spectroradiometers on 26 June 2003. Lower panel: diurnal course of AOD at 350 nm derived from the two instruments. Crosses represent the AOD derived from the Brewer by use of the extraterrestrial irradiance derived from Langley plots.

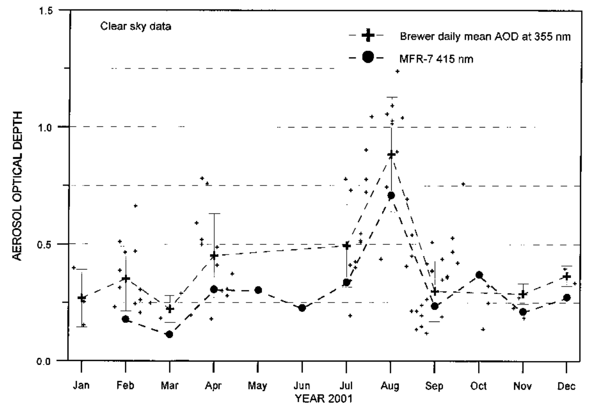

Fig. 6. Monthly mean AOD at 355 nm (crosses) and 415 nm (circles) measured with the Brewer and the MFR-7 instruments, respectively. Smaller crosses represent the daily averages of AOD at 355 nm, measured by the Brewer.

followed for each instrument and to small differences in the FOV (the FOV of the Brewer is ~0.5° larger). Finally, a small effect can be expected from the different measurement principles, as, for example, the Sun tracking. The Brewer follows the Sun by calculating its position whereas the Bentham aims for the Sun position by scanning the sky to find the position of maximum irradiance.

Given that the three days are several weeks apart, the stability of the ratio with time is satisfactory, with mean daily averages within ±1%. Similar agreement, 0.98 ± 0.04 (1σ), was found in a comparison of global irradiances, which were recorded by the two instruments during a period of approximately three months. Synchronous global irradiance measurements were more frequent than the direct measurements during this period. It is worth mentioning that this is one of the few comparisons of direct spectral irradiances in the UV with instruments that were primarily designed for global irradiance measurements.

B. Comparison of Retrieved Aerosol Optical Depth and Angstrom Exponents

On 26 June 2003, a cloud-free day, more than 20 direct solar irradiance spectra were measured simultaneously by the Brewer and the Bentham spectroradiometers, from which the spectral AOD and the Angstrom exponent were calculated. The diurnal variation of the AOD at 350 nm during this day ranged between 0.3 and 0.8, and the results of the intercomparison are shown in Fig. 5.

The mean optical depth and Angstrom exponent as derived from the Brewer were, respectively, 0.56 ± 0.11 and 1.18 ± 0.32, whereas the Bentham measured, respectively, 0.60 ± 0.11 and 1.30 ± 0.30. The maximum difference in AOD was 0.07, and in most cases the Bentham reported higher values. This is a result of the systematic (~4%) difference in the direct irradiance measurements between the two instruments, shown in Fig. 4. In addition, we used the Brewer direct irradiances to calculate the AOD using the extraterrestrial irradiance derived from Langley plots on other clear days, as described in Subsection 3.C, which agrees well the optical depth calculated from direct irradiances calibrated with the shadowing disk procedure. The result is encouraging, taking into account the different theoretical and experimental approaches of the two algorithms and also the uncertainties related with the Brewer AOD retrieval, especially in the UV-*B* part of the spectrum.[48,49]

During 2001, additional measurements of the AOD and the Angstrom exponent were performed in Thessaloniki with an MFR-7 instrument, which are compared with measurements from the Brewer spectroradiometer, although the operational spectral range of the two instruments is different. The MFR-7 operates in the visible whereas the Brewer operates in the UV. Figure 6 shows the comparison of monthly means of AOD at 415 nm measured by the MFR-7 with those measured by the Brewer at 355 nm under cloud-free days only. Both show a peak that is observed during August 2001. There is strong evidence that Thessaloniki was at that time influenced by biomass burning aerosols originating from the northern coast of the Black Sea.[35,50] The systematic absolute difference of ~0.15 can be explained by the different wavelengths used. To verify this hypothesis, the Angstrom exponent as retrieved from the MFR-7 was used to extrapolate the AOD measured by the same instrument to 355 nm by use of the Angstrom formula. This extrapolated AOD from the MFR-7 is compared with that measured with the Brewer at the same wavelength in Fig. 7.

The correlation coefficient r^2 of the two data sets is 0.968. Mean values calculated for one year's measurements were 0.48 ± 0.29 and 0.49 ± 0.33 for the Brewer and the MFR, respectively. The observed deviation and dispersion could be mainly a result of the different approaches used by the two instruments to derive the AOD. In addition, the applied extrapola-

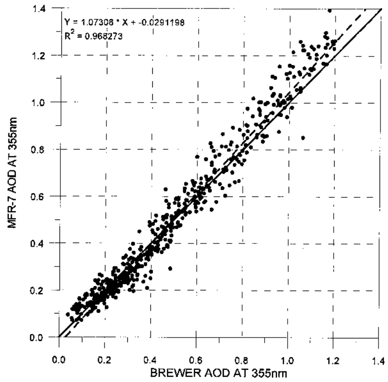

Fig. 7. Comparison of AOD at 355 nm as measured by the Brewer and as derived through extrapolation of the MFR-7 measurements.

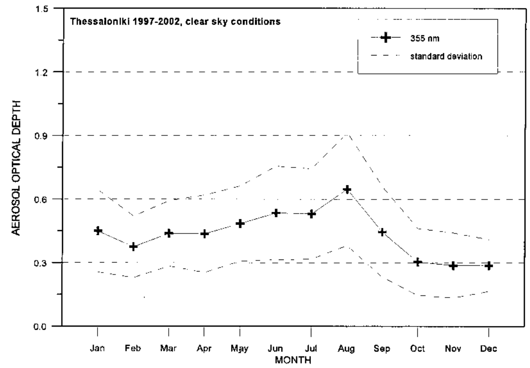

Fig. 9. Mean annual variation of monthly AOD at 355 nm measured at Thessaloniki during the period 1997–2003 (crosses). The envelope of dashed curves represents the 1σ departures from the mean.

tion may introduce some uncertainty, although the AOD difference between 355 and 415 nm is expected to be relatively small.

6. Aerosol Optical Depth Measurements at Thessaloniki, Greece

Spectral measurements of the direct solar irradiance have been conducted in Thessaloniki since 1994 with the double-monochromator Brewer spectroradiometer MKIII, but only since 1997 have regular calibrations been included in the operational procedures. We calibrated these spectra using the shadowing disk procedure (transfer of calibration from the global to the direct port) as described above and the global irradiance calibrations that are regularly made. New CTFs are calculated on a two to three month basis by choosing cloudless and low-turbidity days. From the calibrated spectra recorded under clear-sky conditions, the spectral AOD was retrieved for the period 1997–2003. For the selection of the cloud-free days, we used (a) the hourly cloud cover observations from the National Meteorological Service at Thessaloniki airport, selecting cloud coverage of less than 2 octas and (b) the methodology described in Vasaras *et al.*,[51] which is based on the variability of collocated pyranometer data and on comparisons of 8-min averages with clear-sky model calculations. Daily averages of AOD at 355 nm for the period of study are shown in Fig. 8. The gaps in the series are either missing data due to the absence of the Brewer in experimental campaigns, to operational problems, or to the absence of clear-sky days.

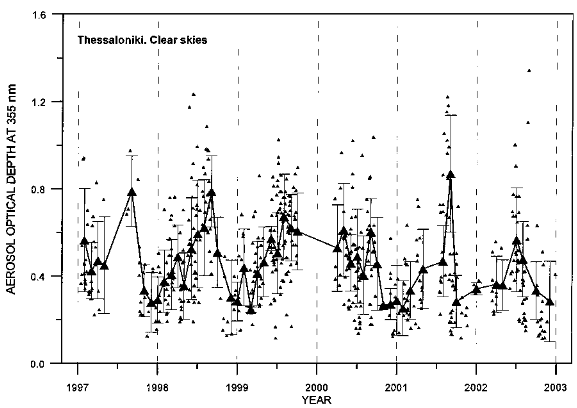

Fig. 8. Daily averages of AOD at 355 nm (small triangles) at Thessaloniki under clear skies for the period 1997–2003. Large triangles represent monthly averages with their standard deviation (1σ).

The AOD over the urban area of Thessaloniki shows a systematic annual variability with values of around 0.3 in the winter and 0.6 in the summer. The seasonal variability of the AOD is mainly related to the seasonal characteristics of the production, transport, and removal processes of aerosols over the region. Many studies[35,52,53] reported a summer peak for the AOD in the Eastern Mediterranean. In 2001 the observed summer peak of 0.85 at 355 nm was the maximum observed during the six years of measurements and occurred in August.

Figure 9 shows the mean annual variation of AOD at 355 nm over Thessaloniki, ranging from 0.3 in December to 0.7 in August. The observed seasonality can be attributed to various local parameters, such as the enhanced evaporation and high temperatures in the summer that increase the turbidity, the absence of significant wet removal of aerosols, and the transboundary transportation of particles from eastern directions. The later is confirmed by the consistency of backtrajectories.[35,54] In addition, local northern winds are dominant during the winter time, which lead to a cleaning of the atmosphere and thus to lower AOD values.

7. Conclusions

Three different methods were proposed for the calibration of the direct spectral measurements of a Brewer spectroradiometer. The expected uncertainty of each method varies between ±4% and ±5.5%. However, the derived CTFs agree within ±2%.

The different approaches for the direct spectral irradiance calibration were investigated with the aim to quantify the level of accuracy of each method. Moreover, an attempt was made to compare the currently used calibration techniques with a procedure that takes place in the laboratory. Although the calibration methodologies were tested and applied in a double-monochromator Brewer spectroradiometer, the same principles can be followed for the calibration of single-monochromator Brewers, taking into account, however, the stray-light rejection problem.

Direct solar spectral irradiance measurements from two independently calibrated spectroradiometers, a Brewer MKIII and a Bentham DTM 300, agreed to within $4 \pm 3\%$ during three different days, which were more than one month apart, and for solar zenith angles ranging between 17° and 72°.

AOD derived by these two instruments under clear skies agreed to within 0.1 at 355 nm. Good agreement was also found in calculated values of the Angstrom exponent. The optical depths derived from the Brewer measurements with different calibration procedures for the direct irradiance are also in good agreement.

Significant correlation ($r^2 = 0.968$) was found between one year of simultaneous AOD measurements performed at Thessaloniki with a Brewer spectroradiometer and a MFR-7.

AOD measurements at Thessaloniki from 1997 to 2003 show an annual variation with higher values during summer and a distinct maximum in August. These results were verified by the independently calibrated MFR-7 instrument, which measured the AOD in the visible range.

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