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Methodology for validation of Brewer spectrophotometers collected data

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A B S T R A C T

The National Institute for Space Research, INPE/Brazil, monitors the fluxes of the Solar Ultraviolet Radiation (R-UV) on ground, since 1990, through a network of Brewer Spectrophotometers located at Brazil, Bolivia, Chile and Antarctica. This spectrophotometer is recognized by the World Meteorological Organization (WMO) and the Global Atmosphere Watch (GAW) Program as the standard instrument for ozone and R-UV measurements. The objective of this work is to describe and evaluate the operation of Brewer in the R-UV collecting process, at the same time that it presents a methodology developed for data validation for the period from 1997 to 2012 in the cities of La Paz, Bolivia and Natal, Brazil. It is also presented an evaluation of the optical assembly operation with highlight in the Standard Lamps (SL) of Spectrophotometers. Operational wear were observed in all instruments. The mathematical model of radiative transference named Tropospherical Ultraviolet Visible Model (TUV) was used to simulate an IUV database. By means of linear regression analysis between the two bases, the time series of the Brewer (predictor variable) was adjusted by means of the TUV time series (response variable). This review presents an algorithm for validation of its records and a routine for the pre-analysis of the Brewer collected data.

Keywords: Ultraviolet Radiation, Brewer Spectrophotometer, Tropospherical Ultraviolet Visible Model.

Metodologia para validação de dados coletados por espectrofotômetros Brewer*

R E S U M O

O Instituto Nacional de Pesquisas Espaciais (INPE) monitora fluxos da Radiação Ultravioleta (R-UV), em solo, desde 1990, através de uma rede de espectrofotômetros *Brewer* no Brasil, Bolívia, Chile e Antártida. O espectrofotômetro é reconhecido pela Organização Mundial de Meteorologia (OMM) e pelo programa "*Global Atmosphere Watch*" (GAW) como padrão para medições de ozônio e R-UV. O objetivo deste trabalho é descrever e avaliar o funcionamento do instrumento no processo de coleta da R-UV, ao mesmo tempo em que apresenta metodologia desenvolvida para validação de dados referentes ao período de 1997 a 2012 nas cidades de La Paz, Bolívia e Natal, Brasil. Avaliou-se o funcionamento da parte óptica com destaque nas Lâmpadas Padrão (SL) dos espectrofotômetros. Observaram-se desgastes naturais no funcionamento dos instrumentos. Utilizou-se o modelo matemático de transferência radiativa TUV "*Tropospherical Ultraviolet Visible Model*" para simular uma base de dados do índice de radiação ultravioleta (IUV). Por meio de análise de regressão linear entre as duas bases, realizou-se o ajuste da série temporal do *Brewer* (variável preditora) por meio da série temporal do TUV (variável resposta). Este *review* apresenta algoritmo para validação dos registros e um roteiro para a pré-análise dos dados coletados.

Palavras-chave: Radiação Ultravioleta, Espectrofotômetro Brewer, Tropospherical Ultraviolet Visible Model.

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Introduction

The Brewer Spectrophotometer is a sophisticated instrument designed to measure the intensity of ultraviolet radiation (R-UV), concentration of total ozone (O_3), nitrogen dioxide (NO2) and sulfur dioxide (SO2) (Kirchhoff, 2000; Silva, 2002). It is recognized by the "*World Meteorological Organization*" (WMO) and by the "*Global Atmosphere Watch*" (GAW) program as a standard instrument for ozone and R-UV measurements (SCI-TEC, 1995; SCI-TEC, 1999; Zamorano, 2003).

a

b

Figure 1. Brewer Spectrophotometer: (a) at La Paz–Bolivia, In the Physics Laboratory of the *"Universidad Mayor de San Andrés*" and (b) at Natal – RN, Brazil, in the Laboratory of the Nacional Institute for Space Research in Northeastern Regional Center.

In the internal structure of the instrument, all aluminum parts are anodized in black to minimize the dispersion of light. In addition, there is a heating and/or ventilation system and a humidity sensor that allows better performance and precision in the operation of the equipment, regulating its internal temperature and allowing the use under different environmental conditions

The spectrophotometer consists of three parts: 1) the optical, represented by a set of lenses, diffraction grating, filters and standard lamps; 2) the electronic/electrical, represented by control panels that monitor and adjust the optical part, and 3) the computational, represented by an operative part that translates electrical signals into binary numbers and stores them in database files in the datalogger. The solar radiation is collected by the side window and the quartz dome on the top of the instrument; these surfaces are covered with a special enamel to ensure durability and minimize radiative heating. (Figure 1).

One type of measurement obtained by the Brewer is the direct solar radiation - ds, collected exclusively through the side window. A prism, with a right angle to the zenith, directs the incident light from the Sun to the optical axis of the instrument; in the sequence a second prism is driven, controlled by a microprocessor operating in a domain up to 270 degrees of rotation. This system automatically identifies the solar zenith angle. The zenith-stepper is mounted on the front of the optical arrangement and is controlled by the main electronic board (SCI-TEC, 1995).

A quartz-halogen lamp provides a light source that is used as a reference for intensity measurements. This is powered by a DC current source of 1.5 A. The lamp filament is located at the focal point of a convex double lens so that the lamp light is directed by the optical axis given by the main prism. Below the halogen lamp is the mercury lamp that provides a light source for calibrating wavelengths. In this way, they are referred to as standard lamps. The light is then directed to the foreoptics or front optical system, consisting of an iris diaphragm and two motor-operated cylinder filters, integrated into the main electronic board, controlled by a microprocessor, and, connected to an electrical source. Each cylinder is enclosed in a carton that has six 25.4 mm diameter holes, spaced in 60-degree intervals, arranged on a wheel. Each hole can be selected to cross the optical axis by rotating on fine filter gears. The filter wheel is used to automatically adjust the level of light entering the spectrometer. After passage of light through the main optical system, the beam continues through the secondary or posterior optical system, consisting of a lens with a flat and convex portion; (SCI-TEC, 1995), the flat surface is directed to the entrance slot in the ultraviolet spectrometer (SCI-TEC, 1995).

The optical subassembly of the spectrophotometer receives light through the entrance slit and disperses it in a high quality spectrum along the focal plane in the exit slit. Six diffraction slits are positioned along the exit focal plane at the operating wavelengths. One of them corresponds exclusively to the wavelength of Mercury (302nm). The wavelength is adjusted by rotating the grid with the stepper motor that drives a micrometer. The automatic wavelength calibration procedure is capable of measuring or adjusting the wavelengths to an accuracy of 0.01 nm. The output of the slits is given in five operational wavelengths: 306.3 nm; 310.1 nm; 313.5 nm; 316.8 nm and 320.1 nm (Zamorano, 2003).

Light that passes through the diffraction slits is collected at the cathode of a detector and is converted into photon pulses; these are amplified, broken down and divided before being transmitted to a meter. The resulting photon count is recorded in the wavelength channels. Thus, the microprocessor is programmed to operate according to the commands of the instrument's own software installed on an external computer that executes the commands and receives the raw data that is saved to the hard disk drive in real time (SCI-TEC, 1995; SCI-TEC, 1999). You can schedule the collection time, the number of daily, monthly or annual observations, and the interval between collections.

The Verifying that the instrument is working properly is the first step before performing any data collection and / or analysis. This procedure is done in three steps namely: 1) Calibration of the instrument by the manufacturer. For this purpose, since 1990, the International Ozone Services Inc (IOS) Laboratory performs calibrations in the Brewers that operate in South America, in some countries of Europe and Asia, covering different latitudes and longitudes; 2) Internal and external calibrations with standard lamps performed by local operators during data collection; and 3) Verification of the information collected by Fortran software calculations. With the help of the program designed by Martin Stanek, in 1998, the original data can be operated in Windows environment outside the instrumentation so that the data can be organized in ASCII or data files (SCI-TEC, 1999).

The calibration procedure mainly consists of evaluating the operation of the optical and electrical part of the equipment, specifically the internal lamps (Standard Lamp "SL" and Mercury Lamp "HG"). This procedure is done by comparing with standard lamps tested in the laboratory, working simultaneously with the internal lamps of the instrument. In this way, the Brewer's diffraction grating is adjusted to perform simultaneous readings of the irradiance of the bulbs, performing power measurements every 3.5 nm with scanning of each wavelength in a higher to shorter direction. The measurements of the two sets of lamps are saved in a file named QLdddyy ##. All files receive this coding by the instrument's operational form, where "ddd" is the day, "yy" is the year and "##" is the identification number of the instrument. During Brewer normal operation, other files, commands and tests with the same encoding are also generated (SCI-TEC, 1999; Zamorano, 2003).

The National Institute for Space Research (INPE) has been monitoring R-UV fluxes, on ground, since the early 1990s through a network of Brewer spectrophotometers installed in some states of Brazil, Bolivia, Chile, and the region sub Antarctica. Within this monitoring network, the cities of La Paz (16º29 'S, 68º08' W, 3600 m), capital of Bolivia, and Natal, located in the northeast region of Brazil (NEB) (05º47 'S, 35º2' W , 31 m), because they are characterized by registering ultraviolet (UVI) rates considered as "extreme" according to the classification of the World Health Organization (WHO) throughout the year (Kirchhoff, 2000; Rodriguez, 2011; Corrêa, 2015). In addition, these locations are also part of the network because of their importance in measuring the global distribution of O_3.

The Brewer spectrophotometer requires extensive technical knowledge from the operator to ensure proper operation. In the literature there is little published research that discloses the way the instrument is operated. These include: Brewer (1973); Sci-Tec (1995); Bais (1997); Fioletov et al. (1997); Fioletov et al (1998); Sci-Tec (1999); Carvalho & Henriques (2000); Zamorano (2003). Although these surveys describe how the intensity of solar radiation is measured in wavelengths through the optical and electrical system of the equipment, these publications do not provide the care and considerations one should have before using the information collected. In this sense, this work, in addition to providing information on the proper operation of the Brewer spectrophotometer, according to international standards, guides the care in its handling and discusses the pre-analysis and analysis of the information obtained by the instrument.

During the development of this research, there were observed bad function in the optical part of the Brewers of La Paz and Natal, mainly in the intensity of the SL and HG lamps reflected in IUV record failures. For this reason, the main objective of this study was to describe and evaluate the operation of Brewer in the process of collecting R-UV information, and through the use of mathematical models to correct possible natural failures of Brewer spectrophotometers. In this way, to obtain a database, with scientific consistency.

The mathematical model of the Tropospherical Ultraviolet Visible (TUV) radiative transfer developed by Mandronich (1992) is used to calculate the spectral flux, dissociation coefficients and biological irradiance between the lengths of 120 and 750 nm with a resolution of 0,01nm

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Materials and methods

This work was developed with information obtained from the instruments of the cities of La Paz, Bolivia (16º29 'S, 68º08' W, 3600 m) and Natal, Brazil (05º47 'S, 35º2' W, 31 m). The analysis period for the two localities corresponds to the interval of the year from 1997 to 2012 with hourly databases, with some periods without information because there was a replacement of the instrument, like in the case of La Paz, and / or internal calibrations by the operators. The methodology of Brewer spectrophotometer operation is given in three procedures as shown in Figure 2 which summarizes the whole process of obtaining and evaluating the informations. Thus the current work refers to the 3rd procedure divided into two stages.

The first step is a descriptive one about the operation of the Brewer spectrophotometer, from the entry of the solar radiation to the conversion of its intensity, in each selected wavelength, in binary numbers and later storage in files in the database.

The second stage concerns the pre-analysis of the data collected through the use of executable programs that evaluate the monthly UVI; (SL and HG) monthly and daily for standard lamps. A TUV model was used with IUV simulations under clear sky conditions and a regression analysis, t test, Chapiro test to correct possible faults in the optical part of the instruments for validation and scientific consistency of the information, for further analysis (Figure 2).

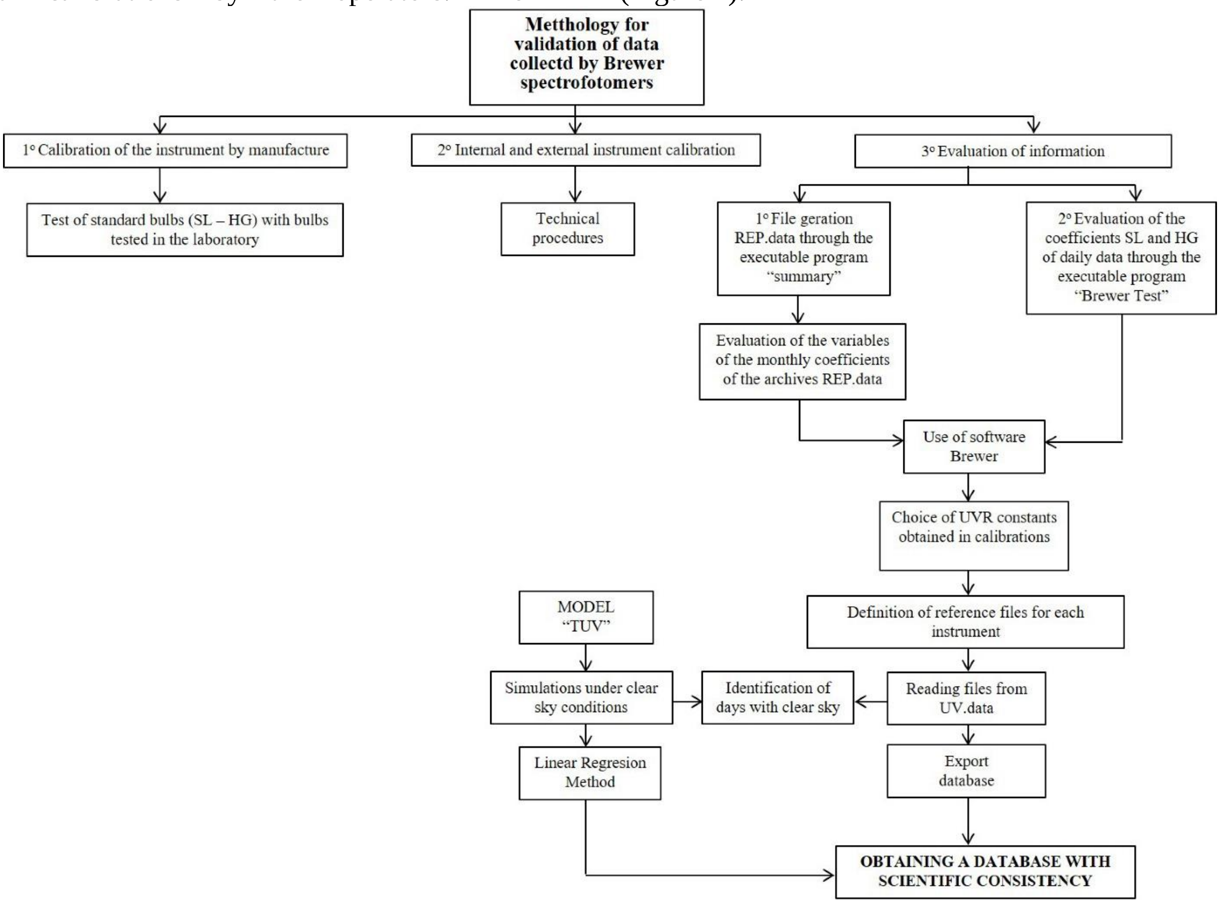


Figure 2: Flowchart of the methodology in the evaluation of R-UV information by Brewer

In the measurements made, all informations are stored by the software in a consistent database that needs a general evaluation of the variables and coefficients. In order to facilitate the manipulation of information, in 2003, the INPE researcher Felix Zamorano developed a "summary" executable program that works with the "AVG.dat" files, which contain the original information and from them is extracted the "REP.dat" file containing a summary of the main variables of the daily maxima and information on the lamps and operating conditions of the Brewer (SCI-TEC, 1995). In the specific case of the city of La Paz, two instruments, REP110.dat, REP056.dat and for Natal, only one, REP073, were operated during the time interval analyzed here.

According to the information processing standards established by IOS, the variables and coefficients of the hourly daily data also obtained from the "AVGs.dat" files should be evaluated by means of the Brewer Test executable program (Stanek, 1998). This check allows you to evaluate the operation of the Standard Lamp (SL - HG) and other parameters. In this way, the AVG data were analyzed using the SLOAVG files for SL, to evaluate the total optical and electrical system of the equipment and the concentration of the total ozone column (O_3); (NO2) and HGOAVG for HG which refers to the mercury lamp that monitors the internal temperature of the instrument and the ultraviolet (R-UV) radiation flux.

Among the main commands on the main menu of the Brewer software:

1) “*Response*” this command directs the constant that performs the calculations to generate the answer file to be exported;

2) “*Initialization*” defines the reference files for each instrument. These files must be defined after the installation of the program and saved in the file "UVBrewer.ini";

3) “*Setup*” or “*Scan Setting*” refers to the correction, if necessary, of some parameters of the R-UV range, as well as the calculation of irradiance and integrated dose rates. Corrections are given for all parameters by means of mathematical calculations performed by the software itself;

4) “*Export*” the export, in this research was carried out on a monthly basis in order to avoid saturation in the program. Thus, output folders were created for Brewer 056, 110 and 073 comprising the period from 1997 to 2012.

Next, one must choose the UVRdddyy constant generated from the QL files in the validation process. Within the information of each constant is information organized in two columns, the first refers to each wavelength in units of Angstrom (10-10m), and the second refers to the response in counts / m / mWm2 / nm (SCI-TEC, 1999). This information allows the calculations made by the program itself to minimize possible errors in the variability of records corresponding to R-UV. Therefore, the constant closest to the period to be analyzed must be chosen.

Like Brewer requires periodic maintenance, since, as a rule, it is subject to the natural elements that can generate changes in the synchronization between the optical and electrical parts, affecting the records of the collected informations, a second validation of the information of R -UV by means of the mathematical model of radiative transfer "Tropospherical Ultraviolet Visible Model (TUV)" (Mandronich, 1992).

The TUV considers visible radiation, RUV-A (315 <λ <400 nm), RUV-B (280 <λ <315 nm) and RUV-C (100 <λ <280 nm) and take into account the coefficients of photolysis and biologically active irradiation (IUV, DNA damage, Vitamin D production, etc.). Since the optical properties of the atmosphere varies with the altitude or optical depth, in the TUV, atmosphere is divided into 50 adjacent and homogeneous layers. In each one it is assumed that the dispersion and absorption properties are constant, but may be different from layer to layer. The calculation of the radiative fluxes are simulated by the radiative transference equation and discrete ordinate algorithms (DISORT) developed by Stamnes et al. (1988) considering the factors that interfere in the R-UV that reaches the terrestrial surface.

In the case of this study, it was chosen to perform simulations under clear sky conditions, since the simulation in the presence of cloudiness does not provide reliable results. This is due to the fact that the TUV considers only homogeneous and stratified layers to represent the cloudiness, that is, a condition quite distinct from the space-time variability observed in nature.

Since the TUV model was adjusted to calculate the IUV only under clear sky conditions, through Brewer, the days under these conditions were identified. In this way, two time series with the same quality and consistency of information were obtained. A simple regression analysis was performed considering the method of least squares estimation. Considering two variables X and Y generating n pairs (X1, Y1), ... (Xn, Yn), where Y is a linear function of X, one can establish a simple linear regression whose statistical model corresponds:

$$Y_i + \beta_0 + \beta_{1Xi} + \varepsilon_i \qquad \text{para i = 1, ..., n,}$$

Since Yi corresponds to the IUV data of the TUV model;

Xi represents the independent variable that refers to Brewer IUV data;

εi represents the residual error;

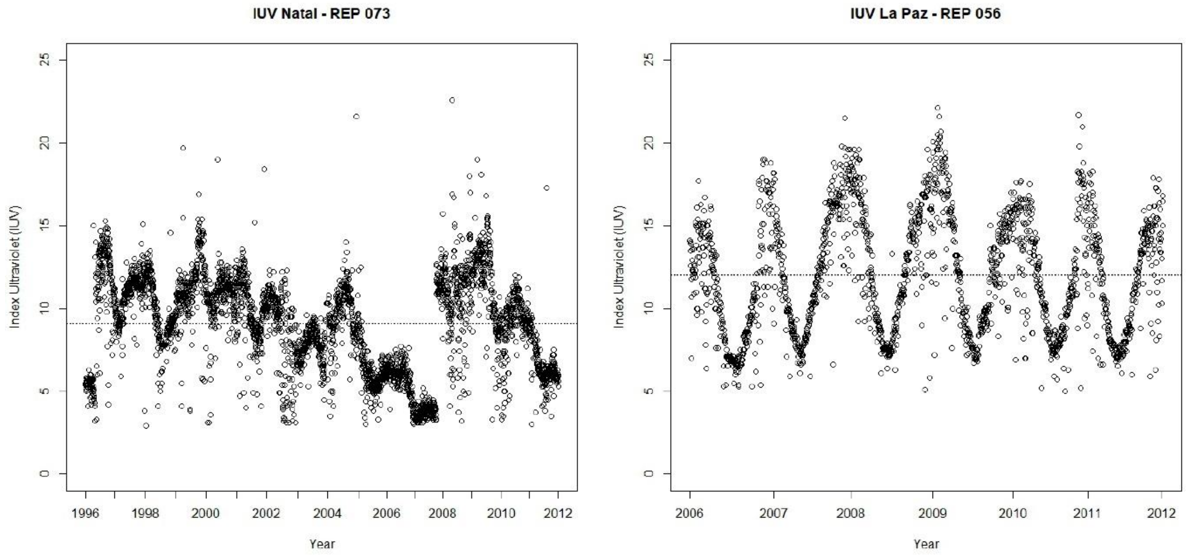
β0 and β1 correspond to the parameters of the model to be estimated.

The coefficient of determination R^2 was calculated to verify the quality of adjustment between the values of the Brewer instruments (predictive variable) and those of the TUV (response variable). The R^2 ranges from 0 to 1, indicating, in percentage, how much the model can explain the observed values. When closer to 1, it better captures the variability of the data.

In order to obtain a better response of the model, this analysis was performed in shorter periods, because in the calculation of the Brewer time series, constants are chosen that generate the information and according to international standards it is advisable to perform in periods close to those of the constants. In addition, in La Paz there was an equipment exchange in the year of 2004.

Results and discussion

Figure 3 presents the time series of the IUV daily maximums for the cities of Natal and La Paz of the REP files. The Christmas time series corresponds to the period from 1996 to 2012, in which a significant number of "extreme" IUV registries (28%) were observed in the interval, according to WHO classification. Throughout the time series, we have observed records that reached IUV values up to 23 years. It is also worth noting a drop in registrations of up to 30% highlighting the years of 2006 and 2007. All these facts in the time series show imperfections in the functioning of the part optical and / or electric brewer. As for the time series of the city of La Paz corresponding to the period from 2006 to 2012 (item b in figure 3), a seasonal behavior was observed, with an average IUV of 11.8 (straight dotted line) and 56% of the records higher than the "extreme" scale of the IUV (WHO, 2003). It is worth noting that the city of La Paz is above 3,600m altitude, which is decisive for the high percentage of extreme IUV. Research has shown that at each kilometer of altitude the intensity of IUV increases from 5% to 7% (Okuno, 1996; Rivas, 2002; Corrêa, 2003; McKenzie, 2003). In addition, during the summer, values up to 22 were recorded, corresponding to 11 units above the value established as "extreme" by WHO. These values are similar to measurements performed in other researches in the city of La Paz, where IUV = 24.0 (Zaratti, 2003) and IUV = 19.7 (Rodriguez, 2011).



(a) **(b)**

Figure 3 Time series of daily IUV (a) of the REP073.dat files - from Natal - Brazil for the period from 1996 to 2012 and (b) REP056 from La Paz - Bolivia for the period from 2006 to 2012.

Within the informations of REP file, there are also those of the calibration coefficients (R5, R6 and F1) which refer to the operation of the intensity of the Standard Lamp (SL). Figure 4 shows the time series of the coefficients of the Brewer # 056 spectrophotometer from La Paz corresponding to the period from 2006 to 2012. The scales of each coefficient correspond to dimensionless values and the parameters are established in the calibrations performed by the manufacturers. The last available IOS calibration report was for year 2004, which at the time were within the parameters (SCI-TEC, 1999; Zamorano, 2003). As the series correspond to longer periods, it is observed that the standard lamp intensities became unstable over the years. The dotted straight lines correspond to the averages of each time series. In the time series of the coefficients SL (R5) and (R6) similar behaviors are observed with some descending peaks throughout the year of 2007, emphasizing the instability in the intensity of the standard lamps.

The time series of the SL coefficient (F1), which refers to the intensity of the Standard Lamp, shows a fall in the registers in the year 2010. This behavior in the time series of the standard lamps shows that it is necessary to make an adjustment in the optical part or even a lamp replacement

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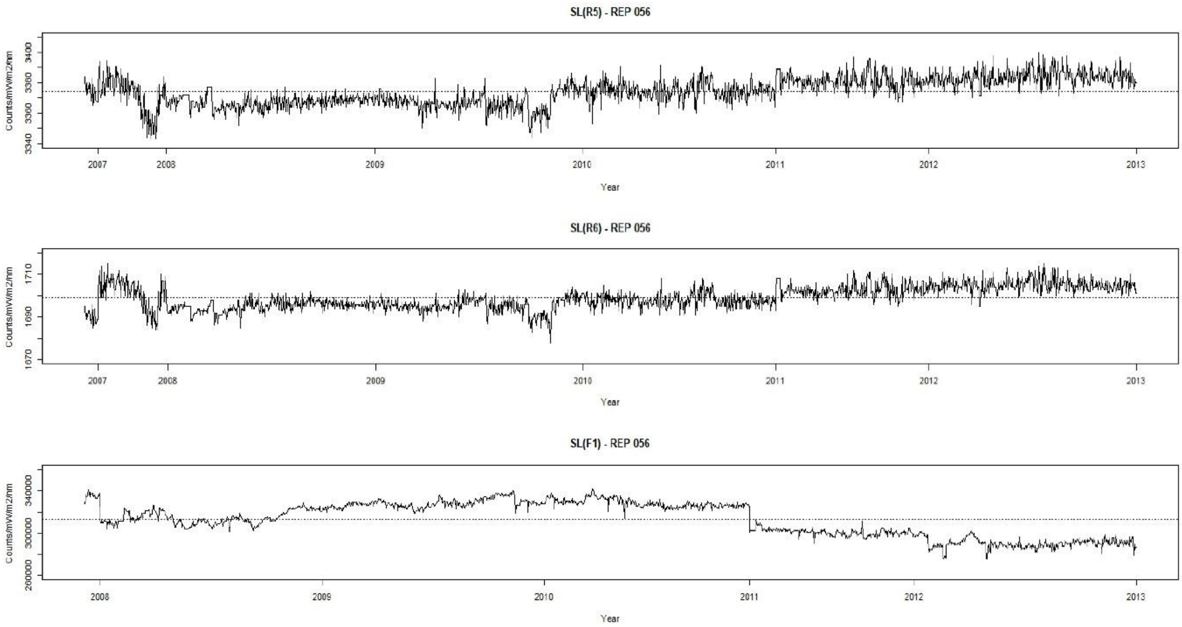
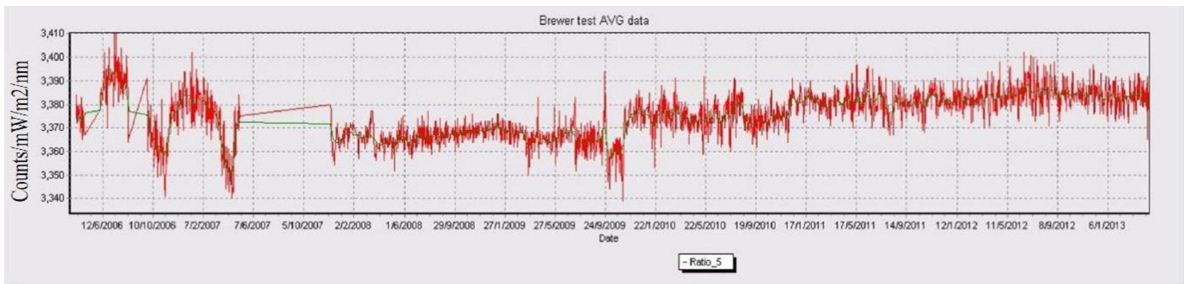


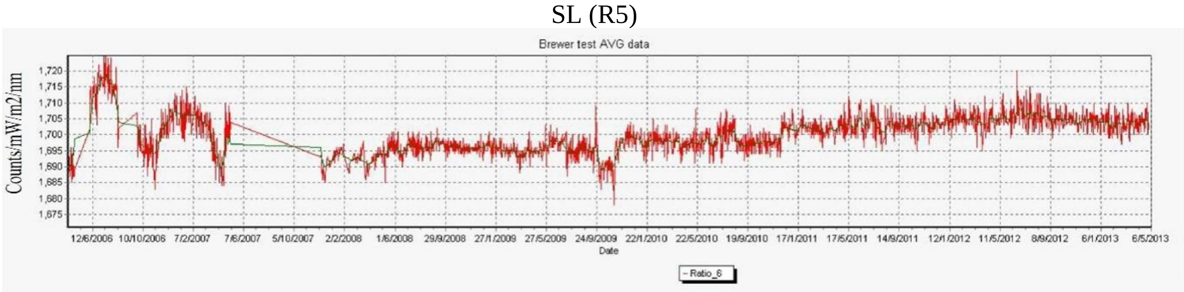
Figure 4. Calibration coefficients of the Brewer 056 of Standard Lamp from the city of La Paz - Bolivia

After evaluation of the REP file, the following procedure includes the evaluation of the same variables in hourly form. For this purpose, the "Brewer Test" program, which works with the AVG files, is used, that contains all the original informations. Figure 5 shows the hourly time series of the SL (R5) and SL (R6) coefficients of Brewer 056 of La Paz referring to the period from 2006 to 2012. The red line represents the time series, the green line corresponds to a smoothing of the series made by calculations of the program itself.

Due to technical maintenance procedures, during the period from October 2006 to December 2007, the records were not continuous. There are standard lamp mismatches in the intensity and transmission of sunlight in the optical part. This is reflected in arbitrary records considered as outliers in databases. Therefore, consideration should be given to adjusting or changing the optical axis of the lamps.



SL (R5)



SL (R6)

Figure 5**.** Calibration coefficients R5 and R6 of the Brewer Standard Lamp 056 correspond to the period 2006 to 2013 of the city of La Paz - Bolivia

Figure 6 shows the daily time series of the corresponding constants SL (R5) and SL (R6) in the period of 1996 and 2012 of the Natal Brewer. A defect in the optical part of the instrument may be due to: 1) the operation of the intensity of the lamps, 2) the change in the filter located in the posterior optical part, 3) the reduction of the gain of the amplifier photo, or 4) Humidity problems inside the instrument. Any defect of any of these parts or of the four is reflected by a change in the variation of the records throughout the time series with structural break, decrease in trend, variability and interruption/data failure. This fact shows a decrease in instrument sensitivity since the registers are outside the parameters established in official calibrations by IOS in the years 2000, 2004 and 2009 stating that the instrument came to operate with some periods of instability in the Standard Lamp decreasing its sensitivity in 16%. This indicates that the information collected is without consistency, with errors in the measurements, since according to IOS, a margin of error between 5% and 10% is acceptable. According to IOS recommendations, it is necessary to generate a new REP file or replace the lamps

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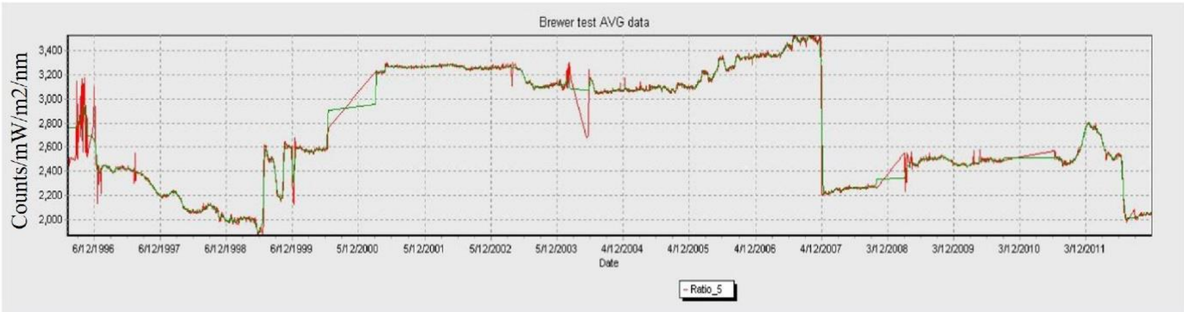
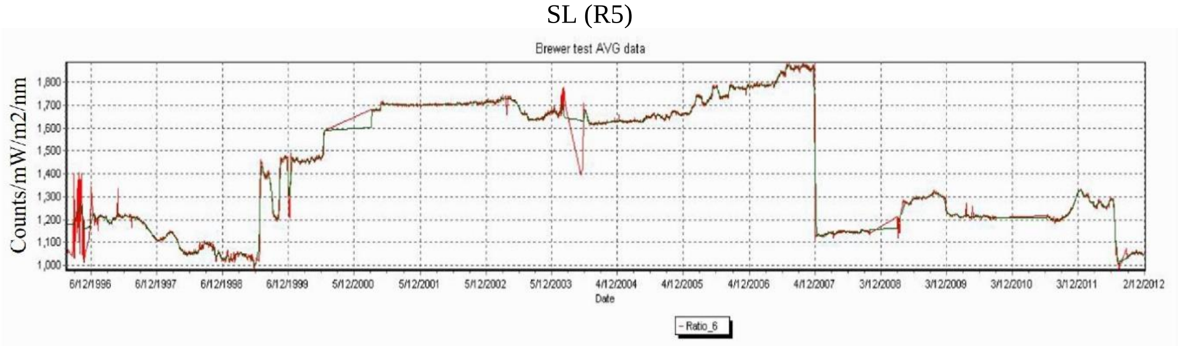


SL (R5)



SL (R6)

Figure 6. Calibration coefficients R5 and R6 of Brewer Standard Lamp 073 corresponding to the period from 1996 to 2012 of the city of Natal - Brazil

Another very important variable in the evaluation of the Brewer operation corresponds to the "HG", which refers to the conduction of the light to the micrometer and to the diffraction grating that disperses the sunlight in five wavelengths of operation to five output slots (SCI -TEC, 1999). The information is extracted from the HGOAVG file. In addition, it also records the internal temperature of the instrument by means of three sensors (thermocouples). Figure 7 shows the time series of the HG mercury lamp registers of the Natal Brewer 073. It is observed that in the analyzed period the internal temperature of the equipment oscillated between 25ºC to 48ºC. In La Paz, HG records ranged from 20ºC to 45ºC. According to IOS, the Brewer is capable of operating between -50 ºC to 50 ºC (Zamorano, 2003). Thus, it was verified that there were no changes outside the operating domain, in the internal temperature of the equipment, discarding the hypothesis that the observed changes in the intensity of SL were caused by this reason.

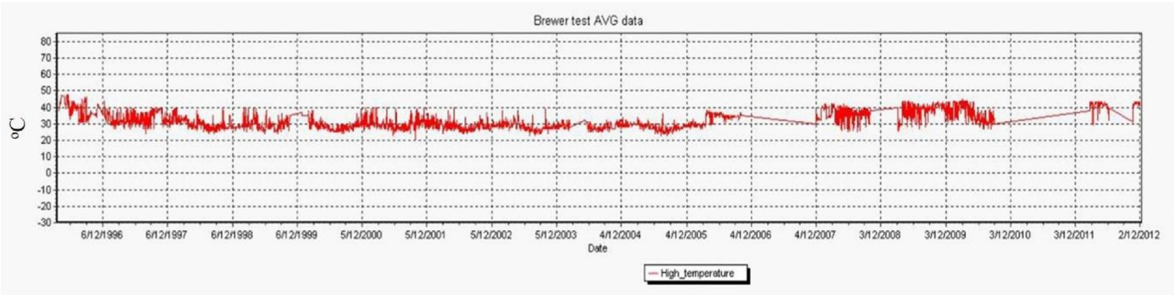
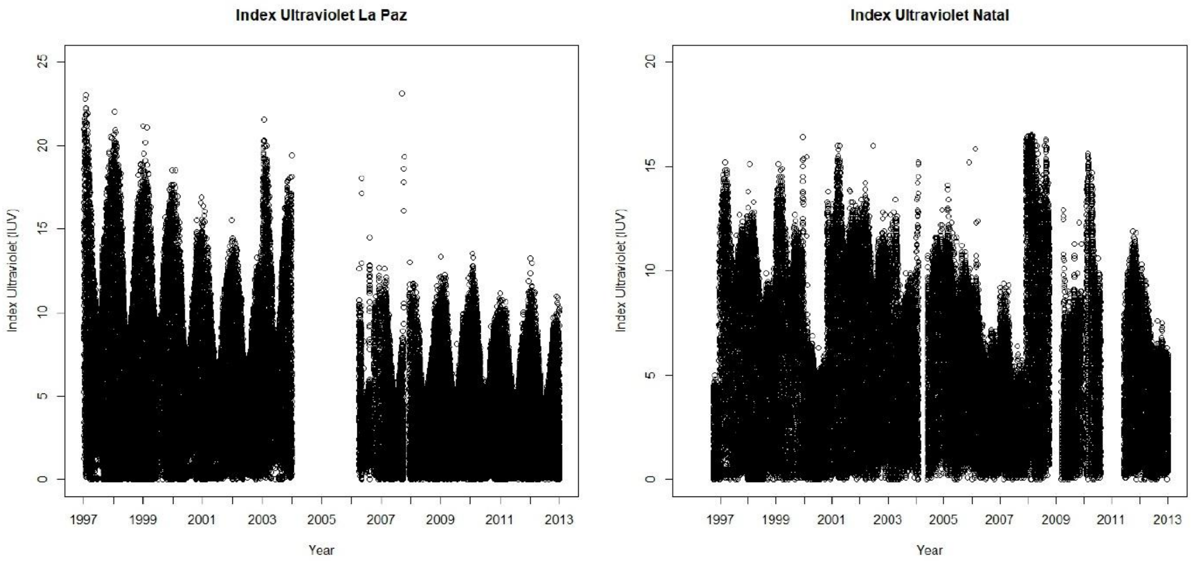


Figure7. Temporary temperature equipment series of measurement extracted from the Brewer constant HG 073 corresponding to the period 1996 - 2012 in the city of Natal - Brazil.

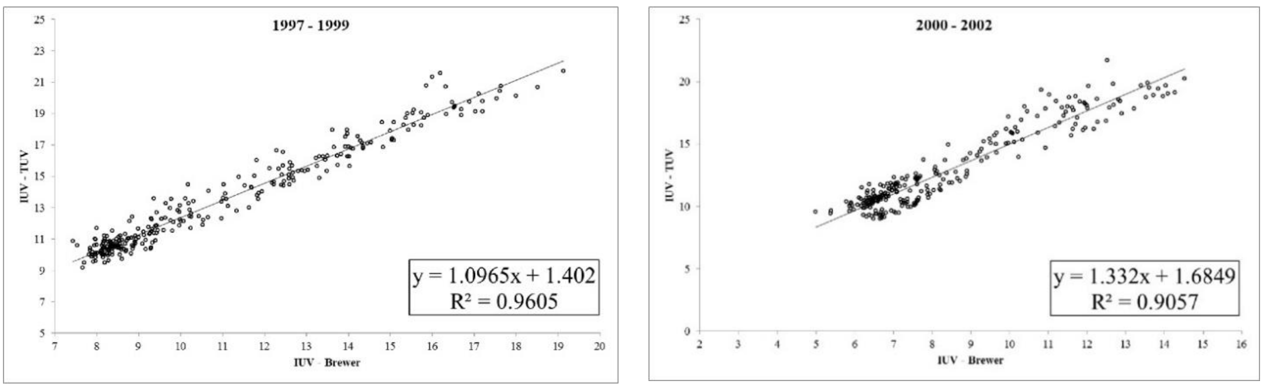
Figure 8 shows the hourly time series of IUV of the cities of La Paz and Natal. As expected, the time series of the two localities have faults and both have a decreasing trend in the records.



(a) **(b)**

Figure 8. IUV hourly temporal series of the Brewer from cities of La Paz and Natal refers to the period of 1997 to 2012

In order to correct the discrepancies observed in the series, the IUV simulation was performed by the TUV model and compared to the measurements performed on clear sky days. The correlation analysis allowed us to determine the adjustment equations. To illustrate, Figure 9 shows the correlation analysis in short periods as explained in the methods with the calculation of the equations and the value of the coefficient of determination for the city of La Paz. R^2 values above 0.90 were obtained for both cities.



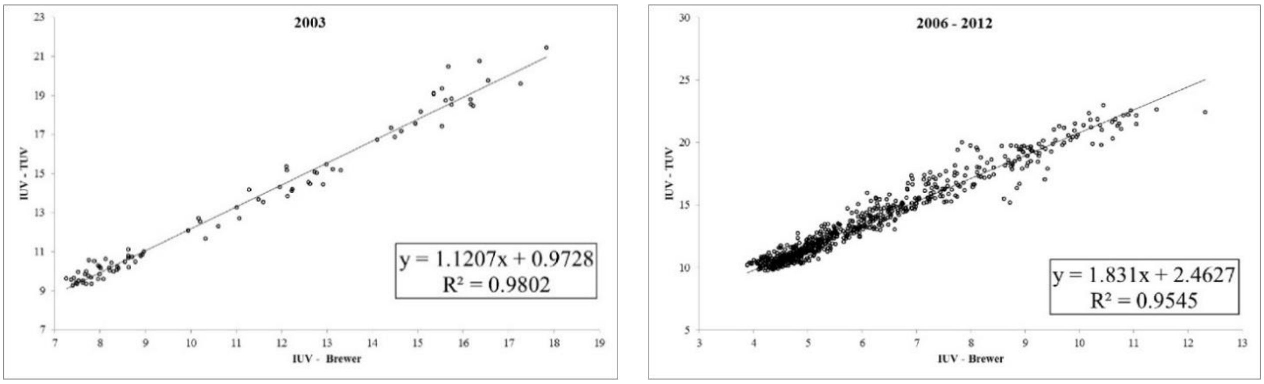


Figure 9. Correlation analysis between the Brewer and the TUV model for the city of La Paz - Bolivia

Conclusions

The cities of La Paz, Bolivia and Natal, Brazil have geographical and latitudinal characteristics that are the main factor for "extreme" IUV records according to WHO classification. For this reason, since the 1990s, INPE has monitored the fluxes of R-UV, in soil, in these locations with a Brewer spectrophotometer. As it was presented, this instrument demands a rigorous control in the acquisition, the treatment and the analysis of the data. There is an international procedure for data validation that must be followed using specific programs. Thus, the present study described the most important considerations, procedures and care to be taken into consideration before any analysis of information provided by the spectrophotometers, following the standards established by IOS and instrument manuals, pointing out characteristics in the time series of data that indicate faults in the operation of the equipment, specifically in its optical part, constituting the main problem for the scientific use of the information collected.

During the evaluation, periods of instability were observed in the Standard Lamp (SL) and the Mercury Lamp (HG), also reported in the IOS reports in the calibrations in the years 2000, 2004 and 2009 which indicated that there was a decrease in lamp intensity in up to 16%, and the allowed is 5% to 10%. These faults in the optical part of the instruments were verified in the changes of the temporal series of the files REP with the daily maximums and in the AVG files with daily and hourly data.

Through the TUV model and correlation analysis, the discrepancies were corrected in the spectrophotometer databases for the two localities, which could be made available for further analysis, now presenting scientific consistency (data validation process).

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3. Monitoring the Ozone Layer and UV radiation in South America and Antarctica (ATMANTAR). Process CNPq n°52.0182/2006-5

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