List of changes on "Study on the effect of instrumental temperature on Brewer total ozone column measurements".

Alberto Berjón et al.

We would like to thank the three referees for the suggestions which definitely help to improve this paper. We include below our point-by-point response to the referees comments and a version of the paper with all changes highlighted.

Response to Vladimir Savastiouk

The revised text of the paper addressed many of the concerns raised in the initial review and it reads much better now. I did find other areas where the paper can be improved, some of them are very important.

1. The title sounds as if the paper investigates the Brewer ozone calculation temperature dependence in general, but the content is mostly a comparison of 2 different experiments on 2 different Brewers plus a mentioning of variability of temperature coefficient values among the Brewers in EUBREWNET. I am not sure any general statements can be definitively drawn from this. A title similar to “An investigation of TC determination in EUBREWNET Brewers” can be more precise,

> **As shown in the results, the temperature coefficients (τ_b and τ'_b) can be very different depending on the method used to obtain it, but the effect on ozone (τ_{R6}) does not depend on the used method. We think this result can be extended to other instruments since it seems to be due to the linear combination used in the Brewer algorithm. Therefore the title proposed by the referee does not meet the aims of this work. Nevertheless, in order to clarify the object of the study, the title of the work has been modified as: “Study on the effect of instrumental temperature on Brewer total ozone column measurements”**

P1 L20 Push rod doesn’t really control the movement of the diffraction grating. Suggest not going into this details and say “materials used in the monochromator are selected to minimize the effect of the internal temperature changes on the spectrum position relative to the exit slits.”

> **We have replaced the sentence suggested by the referee.**

I will repeat my comment in the initial review: the paper does not clearly differentiate between two completely different temperature effects in the Brewer: the positioning of the spectrum and the changes in the spectral sensitivity. Some paragraphs refer to both effects that is extremely confusing. Moreover, the paper doesn’t actually investigate anything relating to the spectral shifts and so it is unclear why the authors even go into this area. A simple statement that is in page 1 is more than enough and I feel that no mentioning of this should be anywhere in the paper after that.

> **To clarify this point we have modify the second and third paragraphs of the introduction. The main idea is to introduce the effects by which temperature can modify the Brewer measurements. But as changes in wavelength selection are of special relevance for the ozone determination, we introduce the mechanism already used in the brewer to avoid this effect.**

P2 L5 “During the test, the diffraction grating is positioned such that the operating wavelengths are dispersed onto the appropriate exit slits” - please rephrase as this sentence doesn’t describe much.

We think this sort description of the HG test is enough for the scope of this paper. It is slightly modified from the “BREWER COMMAND SUMMARY” (pag. 95) of the “MKIII OPERATOR’S MANUAL” (http://www.kippzonen.com/Download/207/Brewer-MkIII-Operator-s-Manual). We include this reference in the revised manuscript for those interested in more details about this test.

P2 L14 TC are calculated for all operating wavelengths, not just those used for ozone

The sentence is modified as “Temperature coefficients in a linear approximation are determined during this characterization for all Brewer operating wavelengths.”

P2 L25 replace “the” with “some” in “quartz window and the neutral density filters”

This is replaced.

P3 L7 remove double “an”

This is removed.

P3 L15 it’s not really an “alternative”, it’s the same

“but can be alternatively defined” is modified as “but can be also written”

P3 L19 I refuse to accept your explanation that since you’ve already used this notation for the slit numbering in another paper and this makes it ok to use it again. It is wrong to use unconventional terminology, Many papers before yours used it correctly.

We agree with the referee that the numbering assigned to the slit may not be the standard even if it can be found widely in the bibliography. We change the nomenclature to slit2 -> 310.0 nm, slit3 -> 313.5 nm, slit4 -> 316.8 nm and slit5 -> 320.0 nm.

P6 L10-18 Should not be in this paper.

This section is removed.

P7 L18 Have you looked at the fact that Brewers have at least three different PMT types and that can contribute to the differences in the TC? If you did, what was the result? If not, why not?

This is one of the reasons we have carried out a statistical analysis of the temperature sensitivity of the different Brewer models. However, we have not seen significant differences beyond the differences shown between the models.

P7 L22,25 The order filter in not just NiSO4 crystal, but a combination filter with two UG11 glass filters.

We rename “$NiSO_4$ filter” by “$NiSO_4$/UG11 filter”

P10 L20 *** An important point!!! *** : did you calculate the slopes and their uncertainties using the averages for each temperature? It very much looks like you did and then your uncertainty is incorrect as you forgot that each point (each average) has an uncertainty associated with it already (a very large standard deviation in fact). You should re-calculate those uncertainties using each point or propagate the uncertainties of the averages to that of the slopes. When you do this you will likely find that the uncertainty is larger than 100% for most of your slopes, which brings back my original point from the initial review: if for each temperature you have a spread of R6 so large that is close to the spread between R6 at extreme temperatures you cannot actually correct or improve such data. Whatever you do you will still have that spread. So, the question then is can you even trust such a data for determining TC?

> **We are very confident in the TC shown in the present work. Even if not all the data variation is explained by the temperature, as it is clearly shown by the R^2 values, the dependence of the data with the temperature is clearly shown in the plots.**
>
> **The linear regressions were done using the averages for each temperature. This was done to prevent a overrepresentation of those temperatures with a higher number of measurements. Nevertheless, in order to avoid any doubt, we have now included a second analysis with the results when linear regressions are done using individual measurements. The results show no strong differences between the standard error from both methods, as it depends on the number of measurements we are using in the linear regression. But in a few cases, some overrepresentation is detected when using individual values. All these considerations are included in the manuscript.**

P11 L1 I am not sure I understand why you are saying "in spite of robustness of the TOC calculation algorithm". The algorithm clearly works. It was the instrument (the hardware) that didn't.

> **We try to emphasize that it is not possible to obtain correct results if the internal halogen lamp varies greatly. Nevertheless, the sentence is removed from the revised manuscript to avoid any confusion.**

P11 L5 You may consider stating clearly that it is imperative to schedule SL tests throughout the day to cover the different temperatures inside the Brewer.

> **We agree with the referee and we included in the Conclusions section the following sentence: "In order to apply this method it is advisable to schedule SL tests throughout the day to record as wide a range of temperature variation as possible."**

Response to Referee #3

GENERAL COMMENTS

This paper addresses an important issue for the Brewer users and ozone communities, since an accurate assessment of the Brewer temperature dependence is essential to ensure reliable TOC measurements. It is also generally well written. However, some issues should be solved prior to publication.

SPECIFIC COMMENTS

1. The main issue, from my point of view, is the reliability of the measurements in the frame of the experimental setups. For example, the authors state that "The analysis of the internal lamp measurements in PTB1 shows a very marked nonlinear behaviour when using slit 5 and 6 relative to slit 2" (p. 9) and ascribe this behaviour to the internal halogen lamp. However, also the external lamp (slit 5-6) charts in Fig. 7 show some curvature above 40°C, which cannot be ascribed to the halogen lamp. Furthermore, looking at Fig. 6, I cannot understand the inconsistency of the results at PTB2 (internal lamp measurements show hysteresis, while external lamp measurements do not) and K&Z (vice-versa). It would be desiderable for the reader to have these issues explained better, in order to trust the results of the experiments (were the external lamps stable? Were temperatures measured reliably? Etc.)

> **Two main issues considered as responsibles of the failed result in the first experiment at the PTB are the halogen internal lamp and the alignment of the external light source with the direct entrance port. As described in the text , in PTB1 "A Hamamatsu model LC8 UV source with a built-in Xe lamp and equipped with a quartz fiber bundle as a light guide was used to illuminate simultaneously both global and direct input ports of the Brewer". But in PTB2 "On this second occasion, referred to as PTB2, the external lamp was aligned with the direct entrance port.". We have rewritten Results and Conclusions sections to reinforced this idea.**
>
> **The inconsistencies shown in Figure 6, in spite of using a stabilized external lamp, as in the K&Z experiment, or correcting the observed variations through monitors, as in the case of PTB experiments, reflect the difficulty of determining absolute temperature coefficients. In Figure 6 it should be noted that the total variation of the measurements F(310.1nm) is around 1% when temperature change more than 50 °C. One of the main points of this work is to show how the combination of the measurements at different wavelengths, specially when combining the four channels, reduces the possible uncontrolled effects and allow us to determine the temperature sensitivity of the Brewer. The results and conclusions are rewritten to clearly show this point.**

2. I could have missed this information, but was the wavelength alignment ("hg tests") checked during the chamber experiments? It should be explained whether the final temperature sensitivity takes the wavelength shifts into account;

> **The standard procedure to correct wavelength shifts was applied in every cycle. We write in the manuscript: "In all cases, each measurement cycle included an HG test, repositioning the micrometer of the diffraction grating to locate the 302.15nm line of the mercury discharge lamp."**

3. I cannot understand why tau_R6 (linear combination) is much more stable than the relative coefficients. Does this mean that F(306.3) is not a good reference? Or that noise is lower when combining the irradiances at 4 wavelengths compared to only 2 wavelengths?

> **The combination of the four wavelengths clearly increase the stability in both experiments. When combining the irradiances at 4 wavelengths any linear effects with wavelength is suppressed (Equation 5). But this not happened when combining only 2 wavelengths. We clarify this point in the Conclusions as follows:**
>
> **"The calculated τ_{R6} are very much stable. The combination of the four wavelengths clearly increase the stability in all the experiments. This is probably because the linear combination**

removes any linear effect with the wavelength, as it verify Equation 5. Instead, the relative coefficients does not verify this property."

4. It is stated that "The conclusions of this work cannot be extended to MkII and MkIV models" due to presence of NiSO4 filter. I agree with the authors that the temperature coefficients may vary between MkIII and other Brewer types, but why the main outcome of the paper (i.e. that the standard lamp can be effectively used to track the Brewer sensitivity to temperature changes) should be compromised?

The main source of thermal sensitivity in the MKII and MKIV models seems to be due to the NiSO4 filter. Therefore, we prefer no to generalize a result that has not been validated in our experiment. We rewrite the sentence to clarify this point:

"Therefore, the conclusions of this work may not be directly applicable to the MKII and MKIV models. Further studies are necessary in order to analyze these specific models."

5. Regarding the very last paragraph, recommending a change of the reference temperature, I am not sure whether this would reduce the uncertainty of the temperature correction. Indeed, since the correction is assessed based on experimental data, small measurement errors at ~22-23°C would result in lower deviations of the angular coefficient if the reference point is farther (0°C) from the reference. Instead, some issues could arise if the temperature dependence is locally linear about ~22-23°C, but globally not linear. In that case, I agree that changing the reference temperature would be a benefit.

The reduction in uncertainty should be understood in the total data set when considering the uncertainty of the temperature coefficient. The majority of the data of the different Brewer are measured at an internal temperature close to 22 °C, but very few are measured near 0 °C. At the end of the Results section we now include a study of how such a change could affect the uncertainty derived for the data set in the EUBREWNET network.

6. Finally, according to the data usage rules of EUBREWNET, an acknowledgement to the PI's providing the data used in the paper (e.g., Fig. 1) should be included. I would suggest the authors to include the statement recommended on the EUBREWNET website: "We thank the European Brewer Network (http://rbcce.aemet.es/eubrewnet/) for providing access to the data and the PI investigators and their staff for establishing and maintaining the "#" sites used in this investigation".

We modify the acknowledgments to include the Eubrewnet recommendation.

"We thank the European Brewer Network (http://rbcce.aemet.es/eubrewnet/) for providing access to the data and the PI investigators and their staff for establishing and maintaining the 32 sites used in this investigation. We further acknowledge the support of the Fundación General de la Universidad de La Laguna."

TECHNICAL CORRECTIONS

- check usage of "internal lamp" vs more rigorous "internal halogen lamp" or "standard lamp" thoughout the paper. Indeed, two internal lamps are available in the Brewer (mercury and halogen);

"internal lamp" is replaced by "internal halogen lamp"

- p. 1 line 18, "temperature-compensated" is not clear here, but the concept is explained in the following lines. Simply remove "temperature-compensated";

We will keep the term "temperature-compensated" in the text as is the term used in the cited reference (McElroy, 2014). We think this term faithfully describe the monochromator designed for the Brewer, and as the concept is explained in the following lines it should be clear enough.

- p.2 line 28, "studied by different authors": please add bibliographic references;

Three relevant references about that issue are now included: (Weatherhead et al., 2001; Siani et al., 2003; Fountoulakis et al., 2017).

- p. 3 line 20-24: rewrite this paragraph splitting the two points: 1) the weightings are chosen to minimise influence of SO_2, linear effects and constant term; 2) the wavelengths are chosen to maximise sensitivity to ozone and to minimise small shifts in wavelengths (sun scan test);

The sentence is rewritten to clearly split the two points:

"The wavelengths, λ_i, used in Equations 2 and 3 have been especially selected to minimize any small shift in wavelength (Fioletov et al., 2005). Moreover, coefficients ω_i have been determined to suppress any influence of the aerosol and the SO_2 in the ozone retrieval (Dobson, 1957; Kerr et al., 1981). In general any linear effects with wavelength is also suppressed, as λ_i and ω_i verify Equations 4 and 5."

- p. 4 Eq. 8: it is a common error. To comply with the Lambert-Beer-Bouguer equation, either Eq. 1 should read ETC – R6 or the cross section should be – sum(w_i alpha_i). Since the Brewer weightings give a negative differential cross section, it would look better if Eq. 8 had a "minus" sign;

We correct the error in Equation 1 writing ETC-R6.

- p. 6 line 1: "it" → "they";

The typo is corrected.

- p. 6 line 17: define "Cte" (did you mean "constant"?)

We replaced "Cte" by "constant"

- p. 6 line 18, "constant" → "constant over all wavelengths" (not in time);

We replaced "constant" by "constant over all wavelengths"

- p. 7 line 17 and line 28: "Figure" → "Fig."

We keep "Figure" in these two cases as it is the term used all along the text.

- p. 10 line 20: why the diurnal, and not the annual, variation was chosen to provide an idea of the internal temperature changes?

We clarify this point with the following sentence:
"As the mean diurnal variation is close to 10°C, that value can be considered the diurnal uncertainty due to the temperature correction. This result is important when we try to distinguish between different operating issues that may generate diurnal cycles, as wrong temperature coefficients or incorrect values of ETC."

Response to Referee #4

General comments:

The article provides a complete characterization of thermal sensitivity of the Brewer spectrophotometers in total ozone measurements. Although the topic addressed in the paper is very important for Brewer users, the issue of the temperature correction and the experimental procedure to investigate the temperature effect on ozone measurements can be also used for other instruments.

The paper is well-structured, all sections are well interrelated, and the objectives are clearly identified.

Specific comments:

Pag 1 L15: The authors should specify which kind of environmental parameters the instruments are exposed outdoors.

> **The present work focuses on the analysis of the effect of temperature on measurements, and therefore at this point we refer exclusively to temperature. To avoid ambiguities, the paragraph is rewritten as follows:**
>
> **"To be able to make this measurements, this equipment should be suitable for outdoor use. Moreover, this instrument should operate at any temperature, since it is installed on a wide range of environments, from subtropical deserts to polar zones."**

Pag 1 L20: which kind of changes are produced in the measured spectrum?

> **The paragraph has been rewritten to address the comments of other referees, but we have include the following sentence that may response to this question:**
>
> **"Changes in temperature may affect the Brewer in two different ways: changing its sensitivity and causing a spectrum shift."**

Pag 2 L4: How the internal temperature is measured should be specified here.

> **The sentence describing how the internal temperature is measured is moved from Pag 7 to Pag 2, and the sentence is rewritten as:**
>
> **"Thus the Brewer operational procedure recommends to perform an internal Hg-lamp test (HG test) when the internal temperature, which is registered for each ozone measurement by a sensor located near the PMT, varies more than 3°"**

Pag2 L12: typo "approxiamation"

> **The typo is corrected.**

Pag 2 L15: for readers not familiar with TOC measurements with Brewer it needs to specify what is the "routine operation" and what are "the original coefficients".

> **The sentence is rewritten to clarify the procedure of determining the temperature coefficients during the calibration campaigns:**
>
> **"If an appreciable temperature dependence in the retrieved ozone is detected during the calibration campaigns, the temperature coefficients are corrected using the in-field data of the internal halogen lamp measurements along the diurnal temperature variation (Redondas and Rodríguez-Franco, 2015)."**

Pag2 L28: Include some references about that issue.

Three relevant references about that issue are now included: (Weatherhead et al., 2001; Siani et al., 2003; Fountoulakis et al., 2017).

Pag2 L 30: the acronym "EMRP ENV59" should be explained.

The acronym EMRP (European Metrology Research Programme) is now explained in the text. The project identification (ENV59) is removed as the project is clearly identified by the tittle. The sentence is rewritten as:

"On this basis, the validation of the procedures for the retrieval of the temperature coefficients was included as one of the objectives of the "Traceability for atmospheric total column ozone" (ATMOZ) project of the European Metrology Research Programme (EMRP)."

Pag 2 L 34: Specify the places of PTB (Physikalisch-Technische Bundesanstalt) and at Kipp &Zonen facilities

The places of both facilities are now included and the sentence is rewritten as:

"For this purpose, we have made measurements with #185 and #233 MKIII Brewer spectrophotometers respectively at PTB (Physikalisch-Technische Bundesanstalt) in Braunschweig, Germany, and Kipp &Zonen in Delft, Netherlands."

Fig1: specify at least in the legend what is the line inside the box, the top and bottom of each box are the 25th and 75th percentiles of the samples, and which values are set the whiskers.

A description of the different elements is included in the figure legend as follows:

"Median temperatures are represented by lines within boxes determined by the 1st and 3rd quartiles. Whiskers represent Tukey's limits."

Pag 7 L17: Typo "EUBRENET", include brackets to "(Figure 3)"

The typo is corrected.

Pag. 7 L 28: why did the authors use only MKIII and not also MKII or MKIV which have shown higher $\tau R6$ than MKIII?

We have included the following sentence in the Conclusions to clarify this point:
"We have prioritized the MKIII model in this study since it is the most extended model and generally used as reference, as in the case of the RBCC-E."

Pag 9 : typo in "this clearly observed behaviors"

The typo is corrected.

Pag 9: Acknowledgements. As reported in Recommended guidelines for data use and publication of

Eubrewnet data, the authors should write :" We thank the European Brewer Network (http://rbcce.aemet.es/eubrewnet/) for providing access to the data and the PI investigators and their staff for establishing and maintaining the "#" sites used in this investigation."

We modify the acknowledgments to include the Eubrewnet recommendation.

“We thank the European Brewer Network (http://rbcce.aemet.es/eubrewnet/) for providing access to the data and the PI investigators and their staff for establishing and maintaining the 32 sites used in this investigation. We further acknowledge the support of the Fundación General de la Universidad de La Laguna.”

~~Characterization of~~ Study on the ~~instrument temperature dependence~~ effect of instrumental temperature on Brewer total ozone column measurements

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Abstract. The instrumental temperature correction to be applied to the ozone measurements by the Brewer spectrophotometers is derived from measurements of the irradiance from an internal halogen lamp in the instrument. These characterisations of the Brewer instruments can be carried out within a thermal chamber, varying the temperature from -5°C to +45°C, or during field measurements, making use of the natural change in ambient temperature. However, the internal light source used to determine the thermal sensitivity of the instrument could be affected in both methods by the temperature variations as well, which may affect the determination of the temperature coefficients. In order to validate the standard procedures for determining Brewer's temperature coefficients, two independent experiments using both external light sources and the internal halogen lamps have been performed within the ATMOZ Project. The results clearly show that the traditional methodology based on the internal halogen lamps is not affected by possible temperature ~~effects on the internal lamps~~affecting the light source. The three methodologies yielded equivalents results, with differences in total ozone column below 0.08% for a mean diurnal temperature variation of 10°C.

1 Introduction

The Brewer spectrophotometer has been used for decades as a reference instrument to retrieve total ozone column (TOC) and for validation of satellite-based measurements. TOC is retrieved from direct sun measurements at four wavelengths in the ultraviolet (UV), from 310.1 nm to 320.1 nm. ~~In order to perform this type of~~ To be able to make this measurements, this equipment ~~operates outdoor and therefore it is exposed to environmental changes~~should be suitable for outdoor use. Moreover, this instrument ~~operates in all climatic and weather conditions~~should operate at any temperature, since it is installed on a wide range of environments, from subtropical deserts to polar zones. ~~This exposure to weather makes it necessary to develop~~

a mechanism that prevents the measurement results from being affected by changes in ambient temperature . Changes in temperature may affect the Brewer in two different ways: changing its sensitivity and causing a spectrum shift.

Prevent changes in wavelength selection are of special relevance for the ozone determination and different strategies are already applied to minimize this problem. Therefore, the impact of temperature on the spectrum shift is expected to be minimal. The spectrophotometer consists of a temperature-compensated monochromator that allows accurate measurements in the UV range (?). Due to temperature changes the monochromator expands or contracts, which produces changes in the measured spectrum. To avoid this effect, the material of the push rod that controls the movement of the diffraction grating is selected so that its contraction and expansion causes the opposite effect on the spectrum, thus minimizing Materials used in the monochromator are selected to minimize the effect of the temperature on the measurementsinternal temperature changes on the spectrum position relative to the exit slits. Nevertheless, mechanical tolerances in the manufacturing may cause imperfections in this temperature compensation. Thus the Brewer operational procedure recommends to perform an internal Hg-lamp test (HG test) when the internal temperature, which is registered for each ozone measurement by a sensor located near the PMT, varies more than 3°C (?). The HG test uses a mercury discharge lamp (line 302.15 nm or 296.73 nm) to check the stability of the wavelength calibration during Brewer operations. During the test, the diffraction grating is positioned such that the operating wavelengths are dispersed onto the appropriate exit slits . Moreover, other elements in the spectrophotometer, such as the photomultiplier tube, can also be affected by temperature changes and, therefore, in order to ensure the accuracy of the measurements, it is necessary to characterize the thermal sensitivity of the spectrophotometer in order to correct its effect (?). Finally, the wavelength used to determine TOC are selected at stationary points in the solar spectrum to minimize the effect of any residual spectrum shift (?).

The Brewer spectrophotometer quality assurance protocol includes the thermal characterization of the instrument. This characterization is initially carried out inside a thermal chamber at Kipp & Zonen, manufacturer of the Brewer spectrophotometer, by measuring the output of an internal halogen lamp while varying the temperature of the chamber from -5°C to +45°C during a period of 72 hours. Temperature coefficients in a linear approxiamation are determined during this characterization for each of the channels used for the determination of TOCall Brewer operating wavelengths using a linear approximation.

If an appreciable temperature dependence in the retrieved ozone is detected during the routine operation, the original calibration campaigns, the temperature coefficients are corrected using the in-field data of the internal halogen lamp measurements along the diurnal temperature variation . This procedure is normally applied during intercomparison campaigns (?). A drawback of this method is the narrower temperature range that is available for the field measurements compared with the thermal chamber method. However, the natural ambient temperature variation applies to the instrument during its normal operation mode, which generally yields acceptable temperature coefficients.

The determination of the thermal sensitivity of the instrument by means of the internal halogen lamp, used in both described procedures, implies that the internal halogen lamp lamp itself and the power supply circuit are also subjected to temperature changes and they can also exhibit some temperature sensitivity. This can potentially modify the lamp irradiance or its alignment, hampering the determination of the temperature coefficients. In addition, there are different elements involved in the direct sun measurements but not in the measurement of the internal halogen lamp, such as the quartz window and the neutral density filters, which can make the results of the characterization to be ineffective when applied to the operational measurements.

While the temperature effect over the global UV measurements of the Brewer spectrophotometer has been studied by different authors (???), so far no validation of the temperature sensitivity of the TOC retrieved from the Brewer measurements has been reported. On this basis, the validation of the procedures for the retrieval of the temperature coefficients was included as one of the objectives of the EMRP ENV59 project "Traceability for atmospheric total column ozone" (ATMOZ) project of the European Metrology Research Programme (EMRP).

In this work, we report on a comparative study of the temperature coefficients retrieved using the standard procedures (using the internal halogen lamp in a thermal chamber and during field measurements) and two alternatives setups employing external lamps for thermal chamber measurements. For this purpose, we have made measurements with #185 and #233 MKIII Brewer spectrophotometers respectively at PTB (Physikalisch-Technische Bundesanstalt) and at in Braunschweig, Germany, and Kipp&Zonen facilities, respectivelyin Delft, Netherlands. Field data from the EUBREWNET (COST Action ES1207) database is also used (**?**).

2 Principle of measurement of the Brewer spectrophotometers

In order to understand how the temperature correction is applied to the measurements by the Brewer spectrophotometers we review in this section the basic measurement principles that are used to obtain the TOC from this instrument. A comprehensive description of the Brewer instrument and the TOC calculation from the results of the measurements can be found in **?**.

TOC is the main product derived from solar direct irradiance measurements by the Brewer spectrophotometers. The direct irradiance measurement is performed by pointing the direct entrance port normally to the sun based on an an azimuth tracker and a rotating quartz prism which follows the sun's elevation. These measurements are made through a quartz window covering the direct port. To select the different wavelengths used in the calculation, the Brewer spectrophotometer maintains a fixed position of the diffraction grating and uses a rotating slit mask to select successively each wavelength. The rapid movement of the slit mask assures that all wavelengths are measured almost simultaneously. TOC, in Dobson units (DU) or milli-atm-cm, is obtained from Equation 1 (following manufacturer's nomenclature):

$$TOC = \frac{R_6 - ETC - B}{A\mu}\frac{ETC - R_6 - B}{A\mu} \tag{1}$$

where R_6 is usually defined on the basis of double ratios between intensity measurements, $I_c(\lambda_i)$, at certain wavelengths (**?**), but can be alternatively defined it can be also written as the linear combination of the common logarithm of the intensity:

$$R_6 = \sum_{i=1}^{4} \omega_i F_c(\lambda_i) \tag{2}$$

$$F_c(\lambda_i) = 10^4 log(I_c(\lambda_i)) \quad (3)$$

The coefficients, ω_i, take values of -1.0, 0.5, 2.2 and -1.7 for the wavelength of 310.1 nm, 313.5 nm, 316.8 nm and 320.1 nm respectively. These wavelengths correspond to slits 3 to 6 2 to 5 in the rotating slit mask of the monochromator. $I_c(\lambda_i)$ are obtained from the Brewer raw intensity after dark count, dead time, temperature and filter transmittance corrections. The wavelengths, λ_i, and coefficients, ω_i, used in Equations 2 and 3 have been especially selected to suppress minimize any small shift in wavelength (?). Moreover, coefficients ω_i have been determined to suppress any influence of the aerosol and the SO_2 effects in the measured signal in the ozone retrieval (??). In general any linear effects with wavelength is also suppressed, as λ_i and ω_i verify Equations 4 and 5. This also allows to minimize any small shift in wavelength and the influence of sulfur dioxide on the ozone retrieval (?).

$$\sum_{i=1}^{4} \omega_i = 0 \quad (4)$$

$$\sum_{i=1}^{4} \omega_i \lambda_i \approx 0 \quad (5)$$

ETC is a linear combination (Equation 6) of the extraterrestrial constant of the instrument, $F_{ext}(\lambda_i)$, which can be obtained from a comparison with a calibrated instrument or from the Langley plot method (?).

$$ETC = \sum_{i=1}^{4} \omega_i F_{ext}(\lambda_i) \quad (6)$$

B is a linear combination of the Rayleigh transmittance of the air, $\beta(\lambda_i)$, corrected by the Rayleigh air mass, ν, and the ratio between the pressure at the observation position, p, and the standard pressure at sea level, p_0.

$$B = \nu \frac{p}{p_0} \sum_{i=1}^{4} \omega_i \beta(\lambda_i) \quad (7)$$

A is a linear combination of the ozone absorption coefficients, $\alpha(\lambda_i)$.

$$A = \sum_{i=1}^{4} \omega_i \alpha(\lambda_i) \quad (8)$$

Both the Rayleigh air mass, ν, and the ozone air mass, μ, are calculated assuming an effective altitude of 5 km and 22 km respectively (?).

R_6 is derived from the intensity ratios, or equivalently from Equation 2, and therefore it has no units, just like ETC and B.

3 Temperature correction

Most photo-detectors have some sensitivity to temperature. If the sensitivity can be linearly approximated, the intensity I $[c/s]$ measured at different temperatures T $[°C]$, while the detector is illuminated with a stable light source, can be expressed as:

$$I = I_c - \tau_0(T - T_0) \tag{9}$$

,

where T_0 is the reference temperature, I_c is the intensity of the source measured at the reference temperature, and τ_0 is the variation rate of the intensity with the temperature $[c/s°C]$. We can rewrite this expression as:

$$I_c = \frac{I}{1 - \tau(T - T_0)} \tag{10}$$

where $\tau = \tau_0 / Ic$ is the temperature coefficient having units of $1/°C$. This last expression has an advantage that, while τ_0 depends on the intensity of the light source, τ is independent and we can use it to determine the intensity of the source at the reference temperature. This process is generally referred to as temperature correction.

The temperature coefficient is usually determined in a laboratory measuring a stable light source while the detector temperature is varied. τ is calculated from the linear regression between measured intensity and the temperature. From the previous equation and applying the natural logarithm, we can write:

$$ln(I_c) = ln(I) - ln(1 - \tau(T - T_0)) \tag{11}$$

For Brewer Spectrophotometers $\tau \approx 10^{-3}\ °C^{-1}$, then ~~$\tau_0(T - T_0) \ll 1$~~ $\tau(T - T_0) \ll 1$ and we can approximate the natural logarithm $ln(1 + x)$ to the first order term of its Taylor expansion:

$$ln(I_c) = ln(I) + \tau(T - T_0) \tag{12}$$

In the Brewer data processing, this expression is multiplied by 10^4, the natural logarithm is replaced by common logarithm and T_0 is set to $0°C$.

$$10^4 log(I_c) = 10^4 log(I) + \tau_b T \tag{13}$$

Where $\tau_b = 10^4 log(e) \tau$ is the Brewer temperature coefficient. Using Equation 3 we can rewrite this expressed as:

$$F_c = F + \tau_b T \tag{14}$$

We can define a Brewer relative temperature coefficient, $\tau'_b(\lambda_i)$, by subtracting the reference coefficient from coefficients derived for other spectral channels. Usually the reference coefficient is the one corresponding to the wavelength $\lambda_0 = 303.2nm$. In terms of the Brewer temperature coefficient we can express the relative coefficient as:

$$\tau'_b(\lambda_i) = \tau_b(\lambda_i) - \tau_b(\lambda_0) \tag{15}$$

Since the weights used in the common Brewer algorithm to calculate ozone are chosen to verify Equation 4, we can write the Equation 2 as:

$$R_6 = \sum_{i=1}^{4} \omega_i F_c(\lambda_i) = \sum_{i=1}^{4} \omega_i F(\lambda_i) + T \sum_{i=1}^{4} \omega_i \tau_b(\lambda_i) = \sum_{i=1}^{4} \omega_i F(\lambda_i) + T \sum_{i=1}^{4} \omega_i \tau'_b(\lambda_i) \tag{16}$$

Equation 16 shows that we can use interchangeably $\tau_b(\lambda_i)$ or $\tau'_b(\lambda_i)$ to calculate R_6 and therefor TOC.

The relative temperature coefficients, $\tau'_b(\lambda_i)$, can be calculated from Equation 15, but ~~it~~ they can also be experimentally retrieved by the linear regression between the ratio of intensities, expressed as $F(\lambda_i) - F(\lambda_0)$, and the temperature:

$$\begin{aligned} F(\lambda_i) &= F_c(\lambda_i) - \tau_b(\lambda_i) T \\ F(\lambda_i) - F(\lambda_0) &= F_c(\lambda_i) - F_c(\lambda_0) - (\tau_b(\lambda_i) - \tau_b(\lambda_0)) T \\ F(\lambda_i) - F(\lambda_0) &= F_c(\lambda_i) - F_c(\lambda_0) - \tau'_b(\lambda_i) T \end{aligned} \tag{17}$$

The relative coefficients have the advantage that they can be reliably derived even if the illumination condition is not stable. The only requirement for the determination of the relative coefficients is that the change of the light source is proportional at all wavelengths.

Furthermore, from the previous Equations we can see that the temperature effect over R_6 can be reduced to the lineal combination of the temperature coefficients, τ_{R6}.

$$\tau_{R6} = \sum_{i=1}^{4} \omega_i \tau_b(\lambda_i) \tag{18}$$

Where $\tau_b(\lambda_i)$ can refer indistinctly to the Brewer temperature coefficients or to the relative temperature coefficients. τ_{R6} is expected to be more robust to changes in the light source than the relative coefficients $\tau'_b(\lambda_i)$. Since w_i verify Equation 5, τ_{R6} can be correctly determined not only if the change of the light source is proportional at all wavelengths, but also if the change is linear with the wavelength.

~~As discussed earlier, the temperature changes may affect the Brewer's monochromator by slightly modifying the wavelength of the measurement.~~

$$F(\lambda_i + \Delta\lambda) = F(\lambda_i) + \Delta\lambda \left.\frac{\partial F}{\partial \lambda}\right|_{\lambda=\lambda_i}$$

$$R_6 = \sum_{i=1}^{4} \omega_i F(\lambda_i + \Delta\lambda) = \sum_{i=1}^{4} \omega_i F(\lambda_i) + \sum_{i=1}^{4} \omega_i \Delta\lambda \left.\frac{\partial F}{\partial \lambda}\right|_{\lambda=\lambda_i}$$

From Equation ?? we can see that the variation of R_6 will depend on how different is the derivative of the irradiance between the selected wavelengths. This effect is minimized by selecting the wavelengths at stationary points in the solar spectrum (?) where $\partial F/\partial\lambda \sim 0$. In the case of the lamps used to characterize the temperature sensitivity, the spectrum is smooth enough to consider $\partial F/\partial\lambda = Cte$ in a short wavelength interval. This has the same effect and the second term of the right-hand side of the Equation ?? is cancelled as $\Delta\lambda$ is constant or proportional to λ.

4 Operating temperature

4 Operating temperature and thermal sensitivity in EUBREWNET

In order to determine the most suitable temperature range for the experiments, we have made a study on the operating temperature of the Brewer. The standard operating ambient temperature range provided by the manufacturer of the Brewer spectrophotometer is from 0$°C$ to +40$°C$. This limitation comes from the operating temperature range of the photomultiplier tube (PMT), from 0$°C$ to +50$°C$. As the heat dissipated by the internal electronics increases the temperature in the instrument by about 5$°C$, the operating temperature range of the Brewer has a safety margin of 5$°C$.

In the case that the ambient temperature drops below 0$°C$ the equipment should be operated using an internal heater that allows to extend the operating ambient temperature range to -20$°C$ - +40$°C$. In practice, the internal heater is activated when instrument temperature drops below 10$°C$ or 20$°C$ depending of the instrument configuration. Additionally, a cold-weather cover is furnished by the manufacturer for extreme weather conditions, which allows operating the instrument at ambient temperatures as low as -50$°C$.

From the EUBREWNET database (http://rbcce.aemet.es/eubrewnet) we have studied the Brewer spectrophotometer internal temperatures at which the ozone measurements have been made in 32 measurement stations from 1996 to 2017. The temperature inside the instrument is registered for each ozone measurement by a sensor located next to the PMT. For this analysis, 4.2 million recorded temperatures were used. The stations involved in the study are mainly in Europe, but there are also data from Greenland, Australia, Uruguay and Algeria. They are, therefore, a very representative sample of the different environmental conditions under which the Brewer spectrophotometers are measuring throughout the world. Figure 1 shows a boxplot for all the stations. The median temperature values for all the stations are between 16$°C$ and 32$°C$, while the 1st and 3rd quartiles are always above 11$°C$ and below 39$°C$ respectively. The mean diurnal temperature variation is 12$°C$. Figure 2 shows a histogram with data from all stations together. Considering all the data, the mean temperature value is 23.0$°C$ and a median value is 22$°C$, with a standard deviation of 16.6$°C$. The 1 and 99 percentiles are estimated to correspond to 5$°C$ and

44°C. Only a small number of measurements (0.04%) are outside the safety limits for the PMT that we discussed earlier (0°C, 50°C).

We have also analyzed the thermal sensitivity, τ_{R6}, of 44 Brewer spectrophotometers at the ~~EUBRENET~~ EUBREWNET database, Figure 3. These values range from -0.9°C^{-1} to 4.0°C^{-1}. Two different distribution clearly appears related to the different Brewer models. MKIII model has a mean τ_{R6} value of 0.20°C^{-1} and a standard deviation of 0.52°C^{-1}. But in the case of MKII and MKIV the mean value rises to 1.54°C^{-1} and the standard deviation is 0.70°C^{-1}. While Brewer MKIII has a double monochromator to assure a low stray light influence in UV, MKII and MKIV have a single monochromator, so that they use a $NiSO_4$/UG11 filter in front of the PMT to eliminate the effect of visible light on the measurements, i.e., to reduce the stray light in the UV range. The higher temperature dependence observed in the single-monochromator Brewers is commonly attributed to this $NiSO_4$/UG11 filter (**??**).

5 Experimental setups

To study the temperature sensitivity of Brewer spectrophotometers by using external lamps, two different experimental setups have been used: a first one at PTB in Braunschweig, Germany and a second at Kipp & Zonen in Delft, Netherlands (both shown in Figure 4). For these studies, MKIII Brewers #185 and #233 were chosen. These instruments are the traveling master ~~istrument of the~~ instrument of the Regional Brewer Calibration Center for Europe (RBCC-E) triad at the Izaña observatory of the Spanish National Meteorological Agency (AEMET) and a research instrument of Kipp & Zonen, respectively.

During the experiments the internal heater was turned off, but the air circulation fan was left on to evenly distribute the air inside the Brewer, allowing a uniform heating up and cooling down of the internal components.

For the Brewer #185 characterization, a dedicated climate chamber at PTB was used to provide the necessary conditions. The schematic of the measurement system is presented in Figure 5 (left). The temperature and humidity of the chamber was monitored using the built-in sensors of the chamber and two extra sensors, one PT-100 thermometer and one Almemo humidity and temperature sensor. A Hamamatsu model LC8 UV source with a built-in Xe lamp and equipped with a quartz fiber bundle as a light guide was used to illuminate simultaneously both global and direct input ports of the Brewer. The light guide was terminated with light-shaping-diffuser (LSD) to provide uniform illumination. To monitor the output stability of the UV source, a set of monitor detectors were placed close to the Brewer input ports. Those included two SiC photodiodes and a calibrated spectrometer. One of the SiC photodiodes was located inside the chamber and the other one outside. To direct the UV-radiation onto the external SiC diode a similar light guide was used as for the Xe lamp system. For optimal irradiation conditions the internal SiC photodiode and the entrance optics of the spectrometer included special quartz-based Primusil diffusers. For the external SiC photodiode, no diffuser was used to compare the readings with the diffuser-covered detectors and register any possible change of the diffuser transmittance due to the change of temperature or relative humidity in the chamber during the experiment. The Brewer observations consisted of alternately measuring the internal and the external lamps. The external Xe lamp was continuously on during the whole cycle of the characterisations while the internal halogen lamp was turned on and off for each measurement. The drift of the Xe source irradiance at the Brewer entrance port was corrected by using the calculated mean of the normalized integrated spectral data from the monitor spectroradiometer and the temperature-corrected SiC detector readings.

The experiment was done twice at the PTB facilities. On the first occasion in January 2016, refered in the results as PTB1, the quartz fiber bundle was used to illuminate simultaneously both global and direct input ports of the Brewer. The temperature of the climate chamber was varied between -5$°C$ to +40$°C$ over a 70 hours period. Separate cycles were used above and below 0$°C$ to achieve better control over temperature and humidity. Due to some inconsistencies in the retrieved results of the first experiment, the temperature characterisations were repeated at the PTB facilities in February 2017. On this second occasion, refered to as PTB2, the external lamp was aligned with the direct entrance port. The global port was not used for the measurements. In addition, the internal halogen lamp was replaced since anomalous behavior was observed during its operation at the time of the first measurements in January 2016 and later also at the RBCC-E. Two different temperatures cycles were used at different temperature change rate. First, the temperature of the climate chamber was varied between 8$°C$ and 45$°C$ over a 64 hours period with a temperature change rate of 1.2$°C/h$. A second cycle was done varying the temperature from -8$°C$ to 30$°C$ over 50 hours with a temperature change rate of 2.8$°C/h$.

The experimental set up for characterizing Brewer #233 is shown in Figure 5 (right). The temperature in the chamber was varied from -5 to +45 during a period of 72 hours. A Laser Driven Light Source (LDLS) Energetiq EQ-99, from Dutch Metrology Institute (VSL), was used as an external lamp. By means of an optical fibre bundle, the light was guided into the chamber, collimated by a 25 mm lens and then illuminated the Brewer's quartz window at normal incidence. The collimated beam illuminated the rotating prism, which was aligned in accordance with the incoming light. During the external lamp measurements, no lamp monitor was used, as one of the main characteristics of the LDLS is its high stability (**?**). The other components in the beam delivery part were assumed to be stable and independent of temperature. Two separated experiments were performed using the internal halogen lamp in the first case and the external LDLS via the quartz window in the second case. The respectively lamps were continuously turned on during each experiments.

In all cases, each measurement cycle included an HG test, repositioning the micrometer of the diffraction grating to locate the 302.15nm line of the mercury discharge lamp.

Since different instruments have been used in each experiment (#185 at PTB and #233 at K&Z) the differences in results may be due not only to the differences of the experiment setup, but also to the different Brewer instrument.

In this work we also include an analysis of the measurements based on the internal ~~lamps~~ halogen lamp during field measurements at dates close to the characterizations in the temperature chambers.

6 Results

Results from the experiments carried out at the PTB and at Kipp & Zonen, as well as the analysis of field measurements, are presented in this section.

In Figure 6 we show results of the Brewer measurements of both the external and the internal halogen lamp at different temperatures. For the sake of brevity, only the data for 310.1 nm wavelength are shown. The measurements at the other wavelengths show a very similar behavior. The first evident thing apparent in the figures is the difficulty of assuming a linear behavior in these measurements. Despite using different experimental setups and instruments, the results are not as expected. Only the relation between the measurement results of the internal halogen lamp and the temperature in the K&Z experiment can be considered linear. Nevertheless, some behaviors are repeated in the two experiments at the PTB, which makes us assume that they are probably due to real changes in the behavior of lamps, detectors or the different mechanical elements during the experiments. One of this these clearly observed behaviors is the presence of hysteresis cycles. This is possibly related to an inhomogeneous temperature distribution within the instrument. In any case, it is difficult to extract information from the data presented in this way.

The total variation shown in the plots in Figure 6 is only about 1% for a temperature change of more than $50°C$ over near three days. In these conditions it is difficult to ensure sufficient stability of the light sources and the required precision in the alignment. Any uncontrolled effect during the measurements may negatively impact the determination of the absolute temperature coefficients. These results reflect the difficulty of determining absolute temperature coefficients for the Brewer.

As stated in section 3, relative coefficients are intended to be more robust against variations of the experimental conditions. Figures 7, 8 and 9 show results of the relative analysis of the measurements presented versus temperature and the relative temperature coefficients derived from both the external and the internal lamps in the three experiments. The analysis of the internal halogen lamp data from field measurements is also presented. Since the number of measurements for certain temperatures is much higher than for others

We can clearly see the improvement when using the relative analysis. We show two different linear regressions for each data sets. In the first one we use the individual measurements and in the second, the linear regression has been performed with respect to the average values at each temperature. We can clearly see the improvement when using the relative analysisThis is done to avoid overrepresentation of any of the temperatures since the number of measurements for certain temperatures is much higher than for others. The result summary for both linear regressions methods are shown in Tables 1 and 2.

The analysis of the internal halogen lamp measurements in PTB1 shows a very marked nonlinear behavior when using slit intensities 5 and 6 relative to slit intensity 2. Due to this, only data below 30°C have been used to make the linear regression used to obtain the relative temperature coefficient. This behavior is not repeated in PTB2. This change in the behaviour must could be due to the replacement of the internal halogen lamp between both experiments. One week before the PTB1 experiment, the internal halogen lamp was burned out and it had to be replaced. However, this replaced lamp used in the PTB1 experiment did not show a stable behaviour also during later field measurements. Therefore, it was replaced again in March 2016. This is also the reason why we have only a few number of measurement points to make the field data analysis shown in Figure 7. This Moreover, differences between external lamp measurements in PTB1 and PTB2 are may be due to the alignment changes of the external lamp and the direct entrance port. All these problems makes us to consider Brewer #185 not stable during the PTB1 experiment and, therefore, its results will not be included in the final analysis.

On the other hand, the PTB2 experiment (Figure 8) shows more consistent results. In this case, the relations between the relative measurements and the temperature are mainly linear, although some non-linearity is observed for both the internal and the external lamp measurements between 40°C and 50°C. This non-linearity for high temperatures may be explained by the photomultiplier tube behaviour at this temperatures. Figure 10 shows the dark signals for Brewers #185 and #233 measured during PTB2 and K&Z experiments. They demonstrate different behaviour in the operating temperature range. However, for temperatures between 40°C and 50°C both show an increase in the dark signals. Additionally, dark signals of #185 show two different behaviours between 40°C and 50°C along the whole experiment time. From the data sets of the EUBREWENET data base we can see that the most usual behavior corresponds to the one shown by #233.

The K&Z experiment gives also a linear relation between the relative data and the temperature for both the internal and the external lamp measurements, Figure 9.

From ~~Table ??~~ Tables 1 and 2 we can see that the determined relative temperature coefficients present important differences depending on the used data set (thermal chamber measurements with internal halogen lamp and external lamp or field measurements with internal lamp) in both PTB2 and K&Z experiments. However, when calculating τ_{R6} the differences ~~disappear~~ are strongly reduced and very similar values are obtained, as shown in Figure 11.

~~The differences~~ Differences between the τ_{R6} values retrieved from the internal and the external lamps are ~~0.05 and 0.01 respectively in the~~ less than 0.06 for both PTB2 and K&Z experiments, independently if the linear regression is done using individual values or mean values for each temperature. Including the field data retrieval, ~~the~~ differences are within about 0.08 in both PTB2 and K&Z experiments ~~. As the~~ when the linear regression is done using mean values for each temperature. For the regression using individual values, difference rise to 0.14 and 0.07 for the PTB2 and K&Z data sets respectively. The higher coefficient show in the case of the PTB2 field data set when the linear regression is done using individual values, indicates that the greatest number of measurements taken at lower temperatures has a negative impact on the estimated coefficient.

The typical value of the numerator in Equation 1, ~~$R_6 - ETC - B$~~ $ETC - R_6 - B$, is about 1000 for an optical airmass of 1, ~~the~~ thus differences in τ_{R6} of 0.08 represent a 0.08% of TOC for a ~~diurnal~~ temperature variation of 10°C. As the mean diurnal variation is close to 10°C, that value can be considered the diurnal uncertainty due to the temperature correction. This result is important when we try to distinguish between different operating issues that may generate diurnal cycles, as wrong temperature coefficients or incorrect values of ETC.

Note that the uncertainty associated to the different coefficients in ~~Table ??~~ Tables 1 and 2 correspond to the standard uncertainty of the slopes from linear regressions in Figures 7, 8, 9 and 11. τ_{R6} coefficients can ~~be calculated from~~ also be calculated as a linear combination of the relative coefficients ~~in Table ??~~ or directly from the linear regressions in Figure 11. But to derive the associated uncertainty of τ_{R6} from the uncertainties of the relative coefficients we should assume they are not independent variables. Therefore, the calculation of τ_{R6} uncertainty is more direct from the linear regressions.

It is worth to note that temperature correction is usually applied to measurement data using a reference temperature close to the most frequent operation temperature. A reference temperature close to the mean operational temperature means that the applied temperature correction is most of the time small and thus a low accurate estimation of the temperature sensitivity will not have a high effect over the TOC retrieval. However, this is not the case with the Brewer spectrophotometer, which use a reference temperature of 0°C while the mean operation temperature is 23°C and a median value of 22°C. Considering negligible the uncertainty of the temperature measurement, we can write the uncertainty associated with the temperature correction as $\delta\tau_{R6}(T - T_0)$, where $\delta\tau_{R6}$ is the uncertainty associated to the coefficient τ_{R6}. Figure 12 shows a estimation of the uncertainties of the temperature correction for the measurements in EUBREWNET database using the distribution of temperature previously shown in Figure 2 and the mean value of $\delta\tau_{R6} = 0.08°C^{-1}$ that we have obtained from the differences between the methods. As we can see, the estimated uncertainties are close to zero for most of the cases when $T_0 = 22°C$ and the maximum uncertainty would only be half the maximum uncertainty in the case of $T_0 = 0°C$. While a change of temperature reference form $T_0 = 0°C$ to $T_0 = 22°C$ may increase the uncertainty associated with some measurements made at low temperatures, in general it would result in a reduction of uncertainty.

7 Conclusions

Two experiments were conducted at the PTB (January, 2016 and February, 2017) and the Kipp & Zonen (October, 2016) facilities to validate the standard methods for the determination of the temperature dependence of the Brewer MKIII measurements used to retrieve atmospheric TOC.

~~These experiments confirm that the characterisations performed in a thermal chamber using either the internal lamp of the Brewer instrument or an external lamp as well as those carried out with the internal lamp during field measurements lead to small differences in the retrieved τ_{R6}. This is so even though the values of the relative coefficients are obtained using different types of lamps. The obtained results are in agreement because the algorithm used to retrieve TOC removes any linear effect with the wavelength~~We have prioritized the MKIII model in this study since it is the most extended model and generally used as reference, as in the case of the RBCC-E.

~~However, in spite of the robustness of the TOC calculation algorithm, the first experiment~~The first experiment, performed at PTB in January 2016 with a non-stable spectrophotometer, led to unsuccessful results but it shows that it is necessary to guarantee a good performance of the Brewer instrument before carrying out the temperature sensitivity analysis. This highlights the importance of the method based on the internal halogen lamp measurement data in the field since it presents the best way to ensure the correct functioning of the spectrophotometer throughout its operation.

~~While the behavior of the relative measurements are approximately linear with temperature, absolute measurements exhibit behaviors such as hysteresis that may become difficult to model. This implies that the temperature coefficients used in the determination of TOC should not be directly used to correct the Brewer temperature sensitivity in AOD or UV measurements, which should be analyzed separately (?)~~In order to apply this method it is advisable to schedule SL tests throughout the day to record as wide a range of temperature variation as possible.

The ~~difficulty of obtaining absolute coefficients from the measurements in the thermal chamber is~~ absolute measurement obtained through the different methods present important inconsistencies that prevent its use to derive absolute temperature coefficients. These problems are probably due to the ~~way the temperature changes affects the different elements in the Brewer spectrophotometer. Thermal expansion in the fore optics affects the alignment of the system causing a proportional change in all wavelengths. The effect on the monochromator causes small changes in the wavelength. Also the temperature affects the photomultiplier causing a nonlinear response mainly at high temperatures~~difficulties to control the whole system with the required precision. The total variation of the measurements is only about 1% with a temperature change of more than 50°C. Uncontrolled effect during the measurements may negatively impact the determination of the absolute temperature coefficients.

The relative measurements seems to be more robust against uncontrolled effects, and they present an approximately linear behavior with the temperature. However, the derived relative coefficients show important differences depending on the data used for their calculation. However, the

The calculated τ_{R6} are very much stable. The combination of the four wavelengths clearly increase the stability in all the experiments. This is probably because the linear combination removes any linear effect with the wavelength, as it verify Equation 5. Instead, the relative coefficients does not verify this property.

Better results are found when the linear regression are done using the mean value for each temperature. The TOC differences due to the method used to calculate the temperature coefficients τ_{R6} are below 0.08% for a mean diurnal temperature variation of 10°C.

These experiments confirm that the characterisations performed in a thermal chamber using either the internal halogen lamp of the Brewer instrument or an external lamp as well as those carried out with the internal halogen lamp during field measurements lead to small differences in the retrieved τ_{R6}. This is so even though the values of the relative coefficients are obtained using different types of lamps.

The analysis of the EUBREWNET data shows some temperature sensitivity differences between Brewer MKIII model and the MKII and MKIV models, may be related with $NiSO_4$/UG11 filter. Therefore, the conclusions of this work can not be extended may not be directly applicable to the MKII and MKIV models. Further studies are necessary in order to analyze these specific models.

Finally, it is worth to note that temperature correction is usually applied to measurement data using a reference temperature close to the most frequent operation temperature . A reference temperature close to the mean operational temperature means that the applied temperature correction is most of the time small and thus a low accurate estimation of the temperature sensitivity will not have a high effect over the TOC retrieval. However, this is not the case with the Brewer spectrophotometer, which use a reference temperature of advisable to consider a change in the temperature reference from the actual 0°C while the mean operation temperature is 23°C and a median value of to 22°C. A change of the reference temperature will reduce the TOC While this could increase the uncertainty associated with the uncertainty of some measurements made at low temperatures, in general it would result in a reduction in the uncertainty associated with the temperature correction.

Competing interests. The authors declare that they have no conflict of interests.

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Network (http://rbcce.aemet.es/eubrewnet/) for providing access to the data and the ~~EUBREWNET data access and the support by~~ PI investigators and their staff for establishing and maintaining the 32 sites used in this investigation. We further acknowledge the support of the Fundación General de la Universidad de La Laguna.

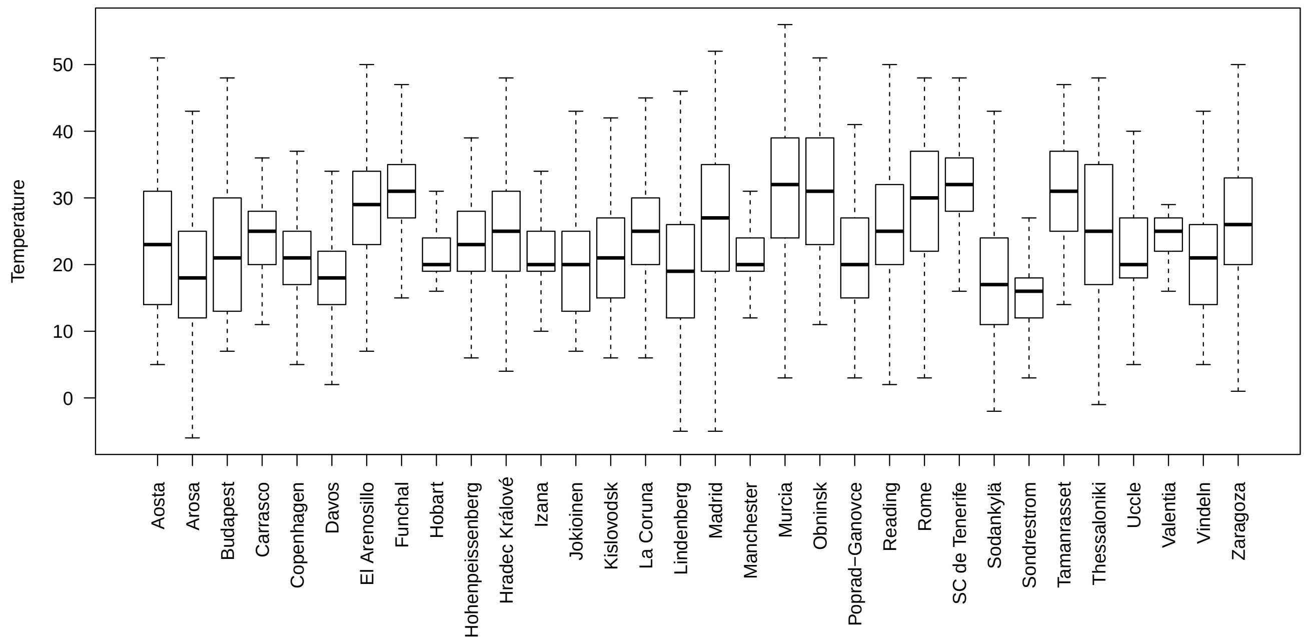

Figure 1. Statistics of each of the 32 stations used for the analysis of the operational instrumental temperatures. Median temperatures are represented by lines within boxes determined by the 1st and 3rd quartiles. Whiskers represent Tukey's limits. The 1st and 3rd quartiles are always above 11$°C$ and below 39$°C$ respectively.

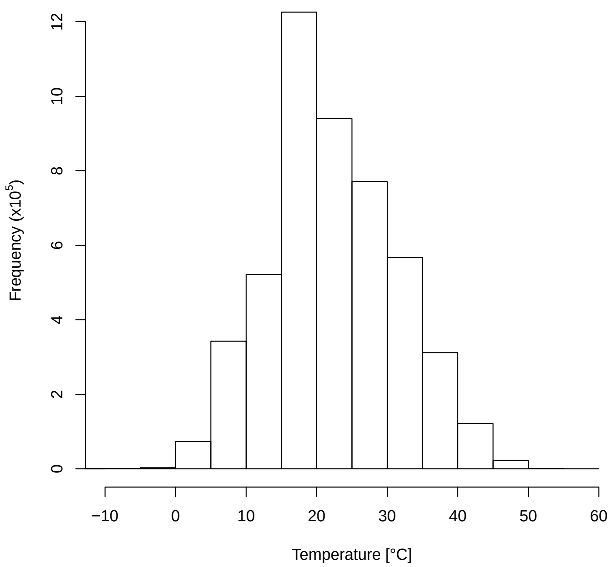

Figure 2. Frequency distribution of instrument temperatures from EUBREWNET database. 4.2 million temperature data points have been used. Only a 0.04% of measurements are outside the recommended limits ($0^{\circ}C$ and $50^{\circ}C$).

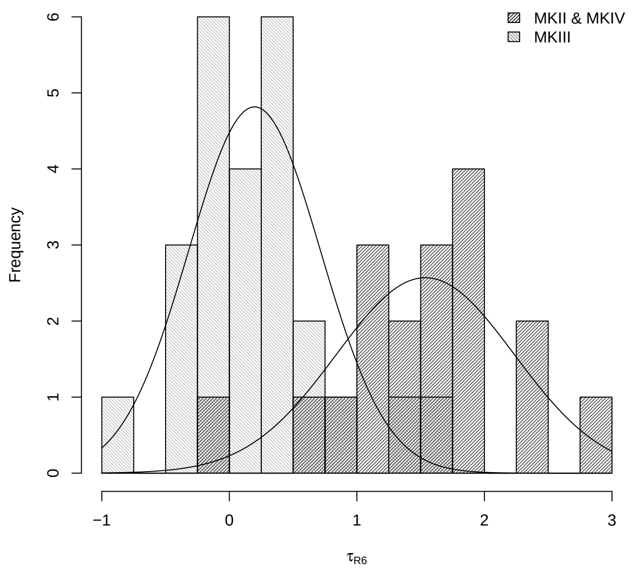

Figure 3. Temperature sensitivity of the different Brewer models.

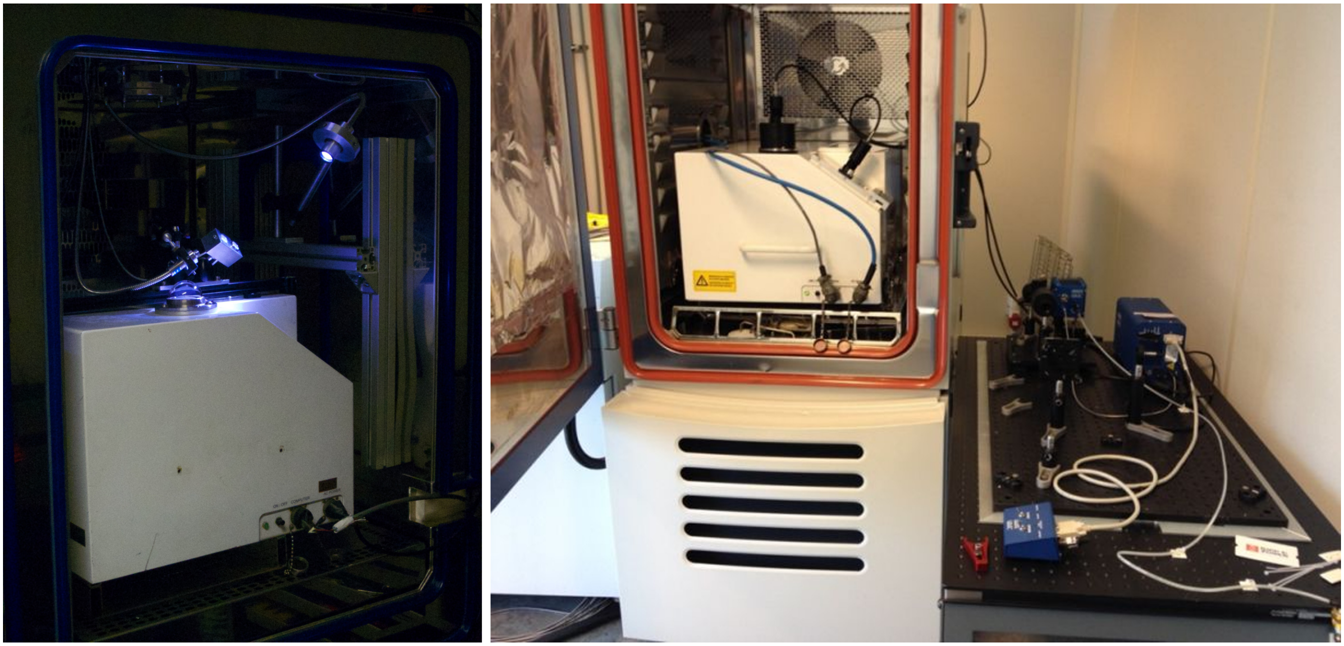

Figure 4. Pictures showing Brewer instruments in the controlled environment chambers for the measurements at the PTB (left) and at the Kipp & Zonen facilities (right).

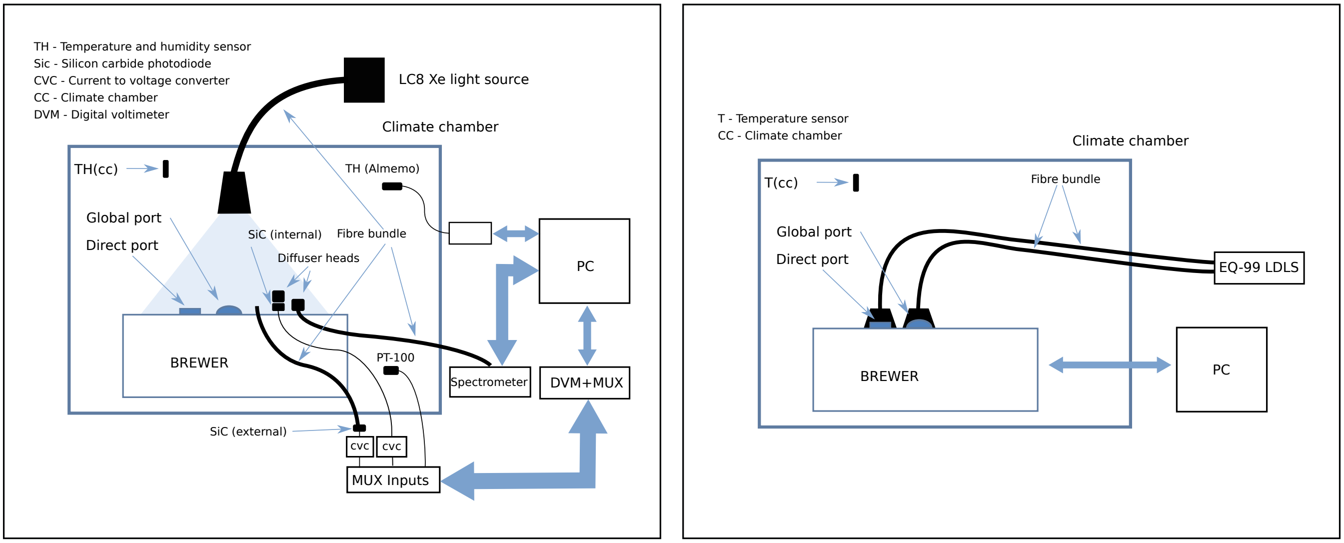

Figure 5. Measurement setups for used for the Brewer characterizations at PTB (left) and at Kipp & Zonen (right).

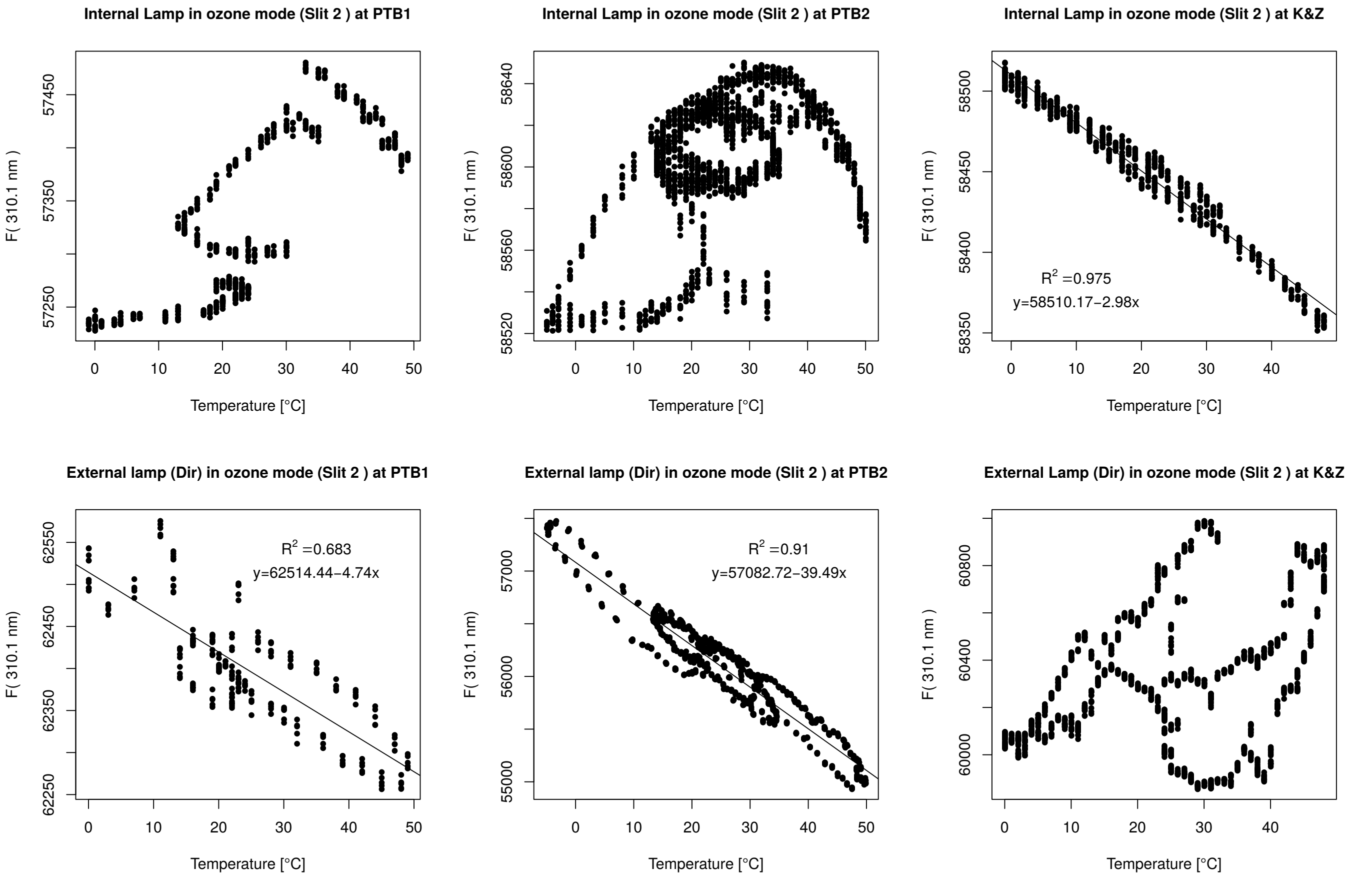

Figure 6. Scatter plot of Brewer measurement data (Slit ~~3~~2) versus temperature in the temperature chambers from PTB1, PTB2 and K&Z experiments when illuminating with the internal (upper plots) and the external lamps (lower plots).

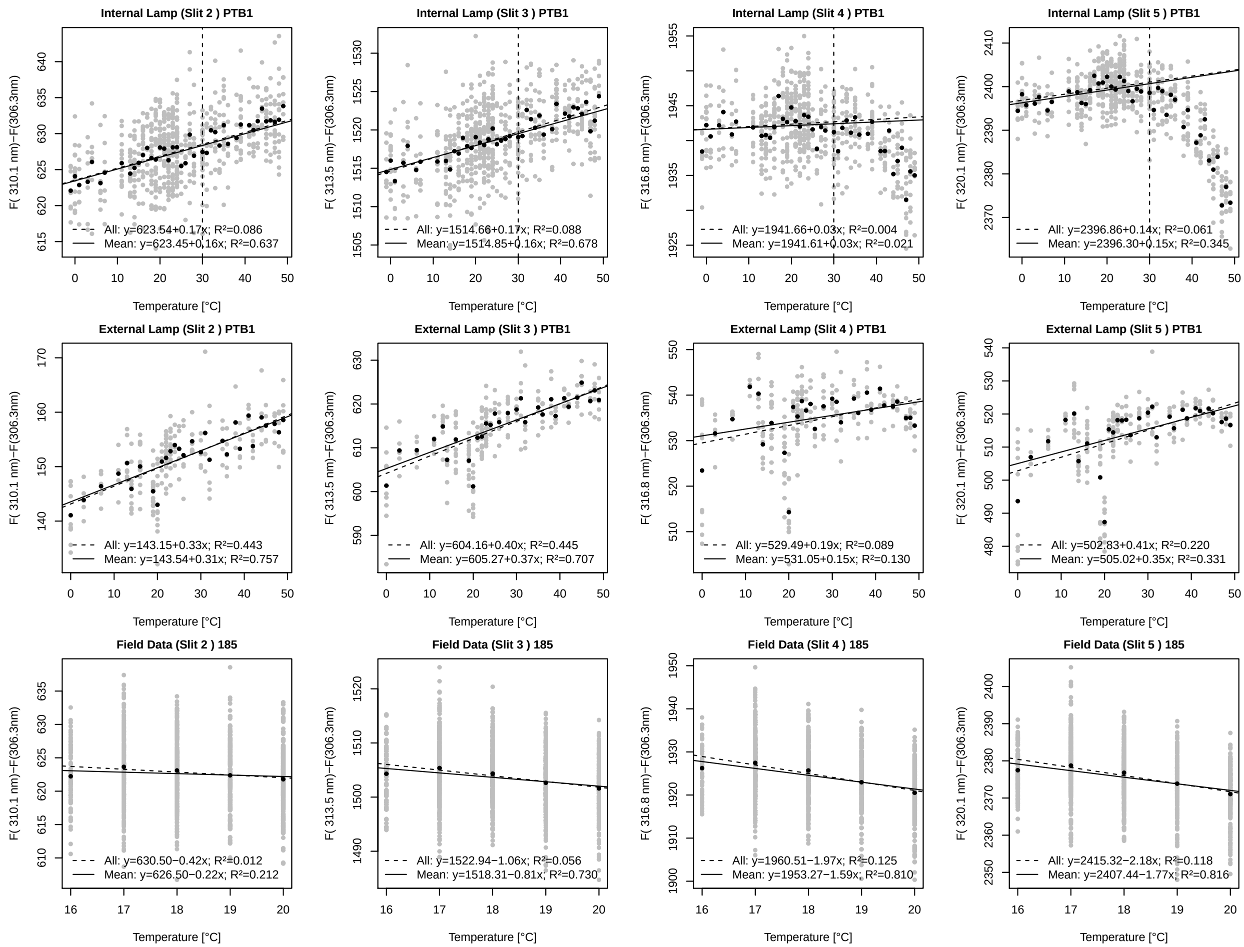

Figure 7. PTB1 experiment. Linear ~~regression~~ regressions between relative Brewer data (Slit 2, 3, 4 ~~, 5~~ and ~~6~~ 5 relative to Slit ~~2~~1) and temperature coefficients determined from internal and external lamp measurements in the temperature chamber and from field data. ~~Dark~~ Linear regression using individual measurements (grey points) is represented by dashed lines, while solid lines represent the linear regression when using average values at each temperature.

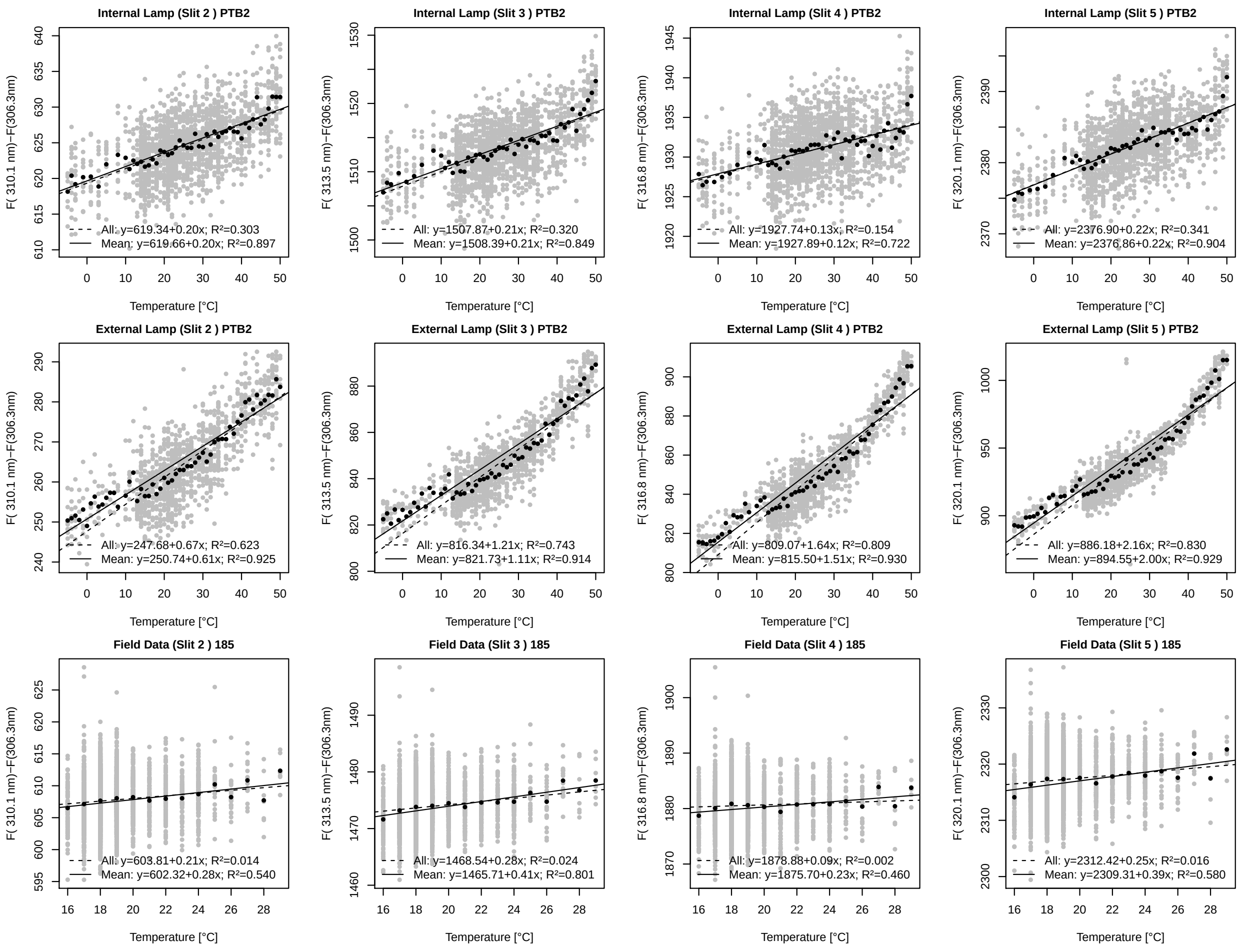

Figure 8. PTB2 experiment. Linear regression between relative Brewer data (Slit 2, 3, 4 ~~, 5~~ and ~~6~~ 5 relative to Slit ~~2~~1) and temperature coefficients determined from internal and external lamp measurements in the temperature chamber and from field data. ~~Dark~~ Linear regression using individual measurements (grey points) is represented by dashed lines, while solid lines represent the linear regression when using average values at each temperature.

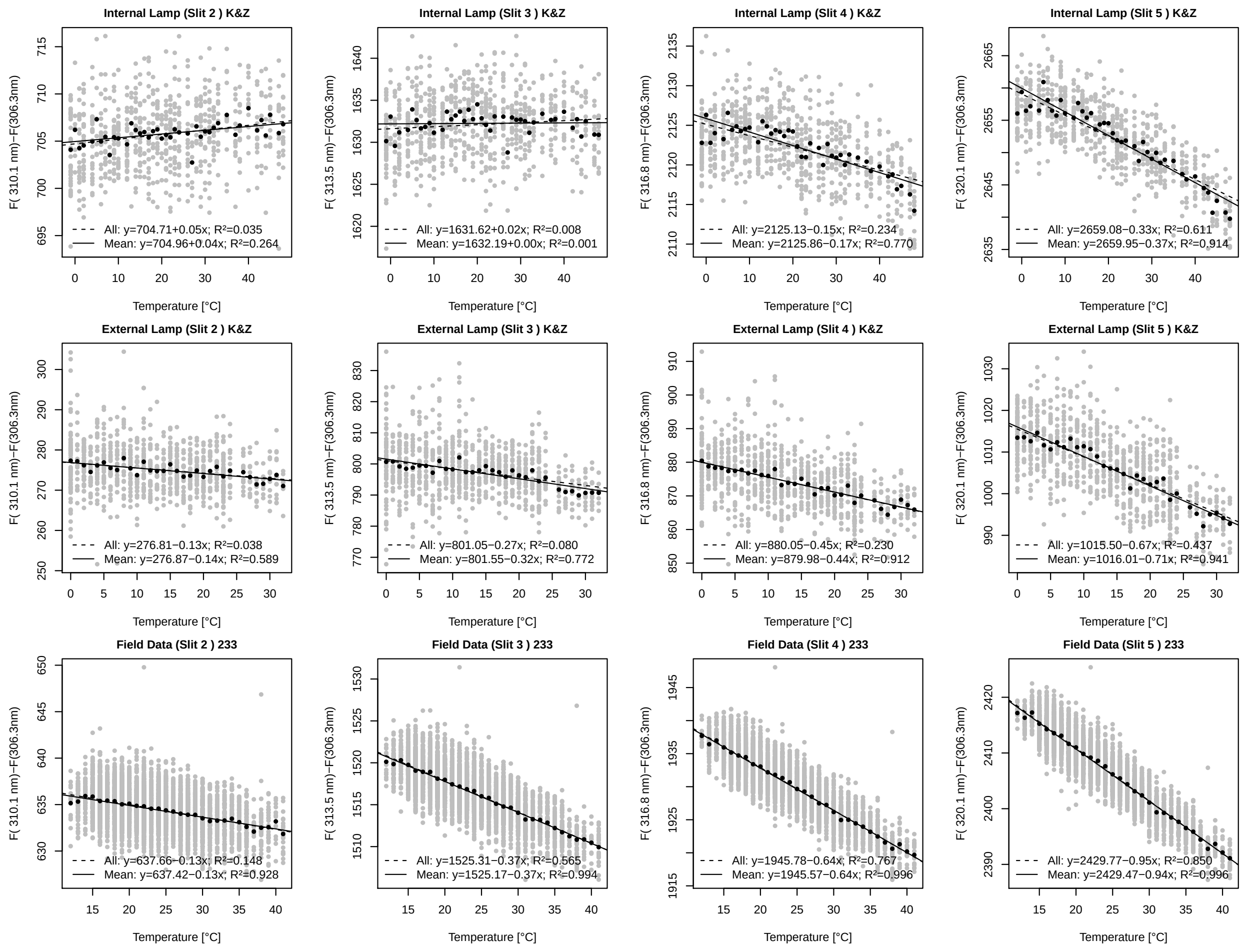

Figure 9. K&Z experiment. Linear regression between relative Brewer data (Slit 2, 3, 4 ~~, 5~~ and ~~6~~ 5 relative to Slit ~~2~~1) and temperature coefficients determined from internal and external lamp measurements in the temperature chamber and from field data. ~~Dark~~ Linear regression using individual measurements (grey points) is represented by dashed lines, while solid lines represent the linear regression when using average values at each temperature.

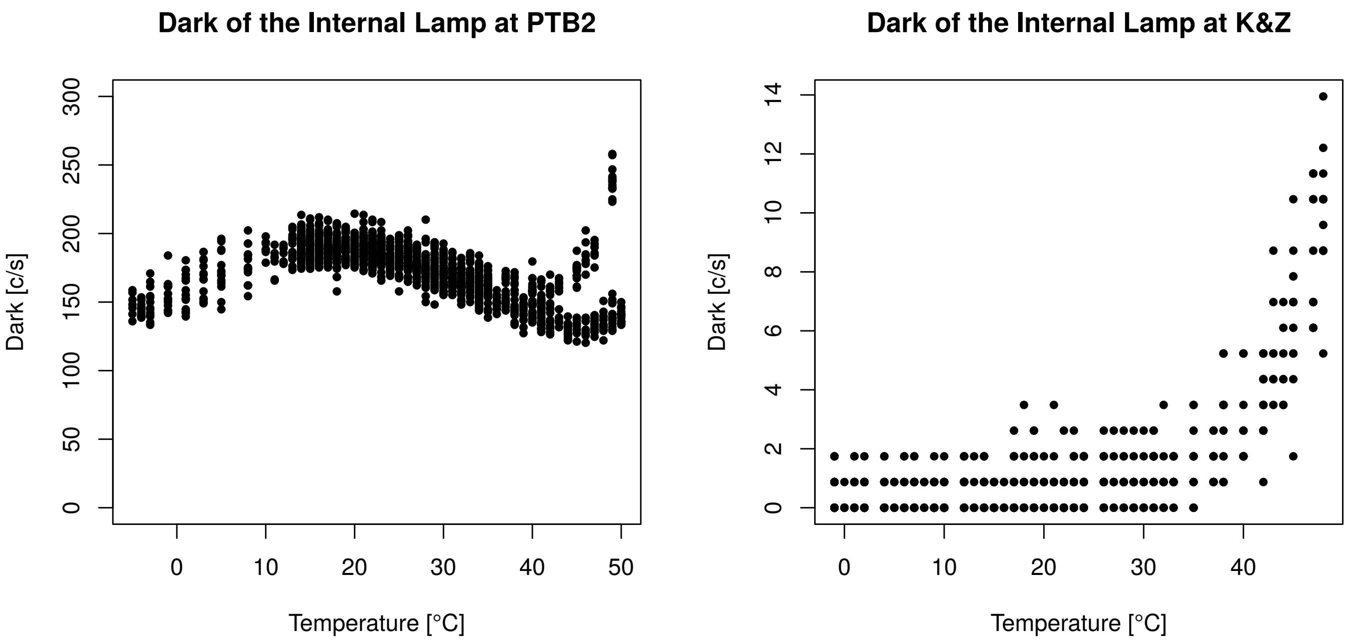

Figure 10. Dark signal values during the PTB2 and the K&Z experiments.

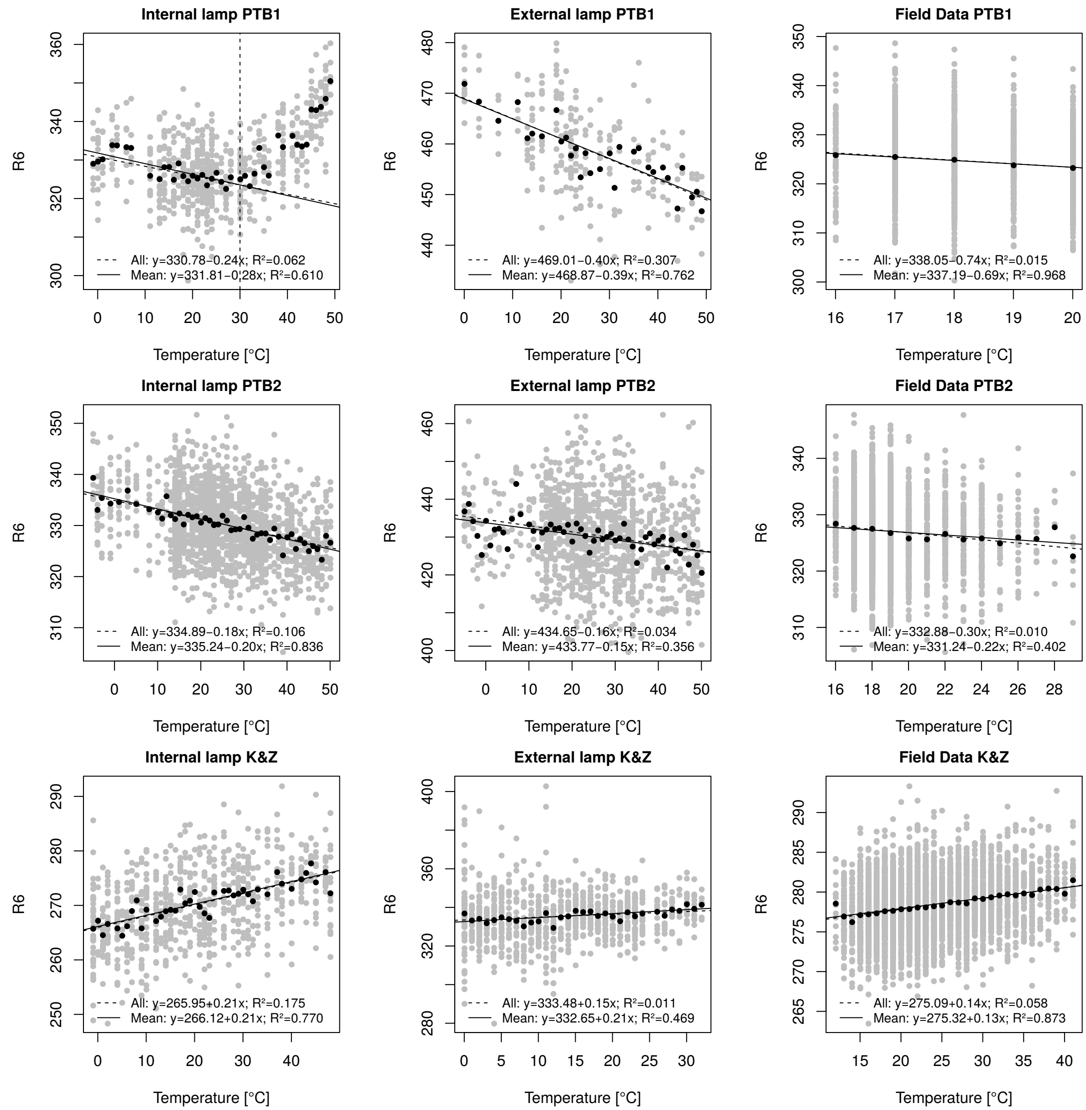

Figure 11. Linear regression between τ_{R6} and temperature for PTB1, PTB2 and K&Z experiments using internal and external lamp in the temperature test chamber and from field data. ~~Dark~~ Linear regression using individual measurements (grey points) is represented by dashed lines, while solid lines represent the linear regression when using average values at each temperature.

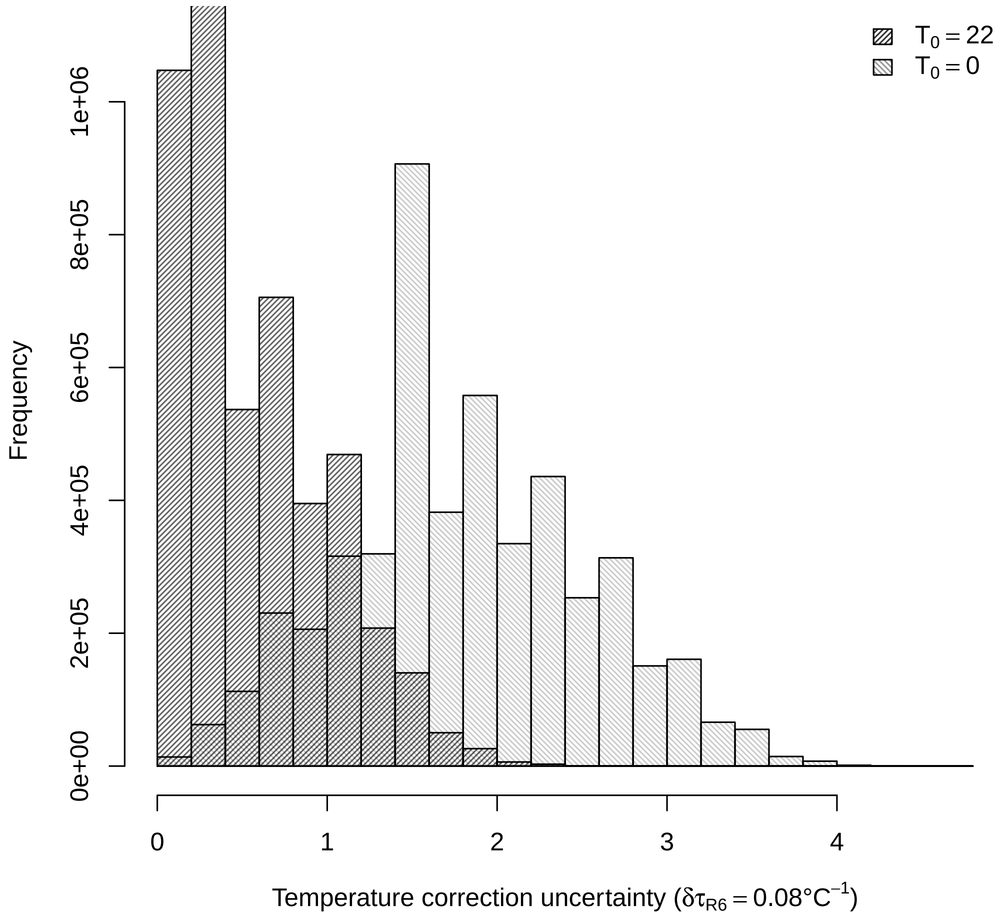

Figure 12. Distribution of the temperature correction uncertainties using $\delta\tau_{R6} = 0.08°C^{-1}$ for the reference temperature $T_0 = 0°C$ and $T_0 = 22°C$.

Table 1. Temperature coefficients obtained from the linear regression of the individual measurements, for slit 2, 3, 4 , 5 and 6 5 retrieved from Brewer measurements relative to slit 2 1 (τ_b') and temperature coefficient for R_6 (τ_{R6}). Rows are grouped in three blocks representing the tree experiments (PTB1, PTB2 and K&Z). For each experiment, results from external (top row) and internal (middle row) lamp measurements in the temperature chamber, and derived from field data (bottom row) are shown.

Experiment	$\tau_b'(310nm)$ [$°C^{-1}$]	$\tau_b'(313nm)$ [$°C^{-1}$]	$\tau_b'(316nm)$ [$°C^{-1}$]	$\tau_b'(320nm)$ [$°C^{-1}$]	τ_{R6} [$°C^{-1}$]
PTB1 Ext.Lamp	-0.33 ± 0.02	-0.40 ± 0.03	-0.19 ± 0.04	-0.41 ± 0.05	0.40 ± 0.04
PTB1 Int.Lamp	-0.17 ± 0.03	-0.17 ± 0.03	-0.03 ± 0.03	-0.14 ± 0.03	0.24 ± 0.05
PTB1 Field	0.42 ± 0.11	1.06 ± 0.12	1.97 ± 0.15	2.18 ± 0.18	0.74 ± 0.18
PTB2 Ext.Lamp	-0.67 ± 0.02	-1.21 ± 0.02	-1.64 ± 0.02	-2.16 ± 0.03	0.16 ± 0.03
PTB2 Int.Lamp	-0.20 ± 0.01	-0.21 ± 0.01	-0.13 ± 0.01	-0.22 ± 0.01	0.18 ± 0.01
PTB2 Field	-0.21 ± 0.03	-0.28 ± 0.03	-0.09 ± 0.03	-0.25 ± 0.03	0.30 ± 0.05
K&Z Ext.Lamp	0.13 ± 0.02	0.27 ± 0.03	0.45 ± 0.03	0.67 ± 0.03	-0.15 ± 0.05
K&Z Int.Lamp	-0.05 ± 0.01	-0.02 ± 0.01	0.15 ± 0.01	0.33 ± 0.01	-0.21 ± 0.02
K&Z Field	0.13 ± 0.01	0.37 ± 0.01	0.64 ± 0.01	0.95 ± 0.01	-0.14 ± 0.01

Table 2. Temperature coefficients obtained from the linear regression of the mean values for each temperature, for slit 2, 3, 4 and 5 retrieved from Brewer measurements relative to slit 1 (τ'_b) and temperature coefficient for R_6 (τ_{R6}). Rows are grouped in three blocks representing the tree experiments (PTB1, PTB2 and K&Z). For each experiment, results from external (top row) and internal (middle row) lamp measurements in the temperature chamber, and derived from field data (bottom row) are shown.

Experiment	$\tau'_b(310nm)$ [$^\circ C^{-1}$]	$\tau'_b(313nm)$ [$^\circ C^{-1}$]	$\tau'_b(316nm)$ [$^\circ C^{-1}$]	$\tau'_b(320nm)$ [$^\circ C^{-1}$]	τ_{R6} [$^\circ C^{-1}$]
PTB1 Ext.Lamp	-0.31 ± 0.03	-0.37 ± 0.05	-0.15 ± 0.07	-0.35 ± 0.09	0.39 ± 0.04
PTB1 Int.Lamp	-0.16 ± 0.03	-0.16 ± 0.02	-0.03 ± 0.04	-0.15 ± 0.04	0.28 ± 0.05
PTB1 Field	0.22 ± 0.24	0.81 ± 0.29	1.59 ± 0.45	1.77 ± 0.49	~~0.70 ± 0.07~~ 0.69 ± 0.07
PTB2 Ext.Lamp	-0.61 ± 0.02	-1.11 ± 0.05	-1.51 ± 0.06	-2.00 ± 0.08	0.15 ± 0.03
PTB2 Int.Lamp	-0.20 ± 0.01	-0.21 ± 0.01	-0.12 ± 0.01	-0.22 ± 0.01	0.20 ± 0.01
PTB2 Field	-0.28 ± 0.07	-0.41 ± 0.06	-0.23 ± 0.07	-0.39 ± 0.09	0.22 ± 0.08
K&Z Ext.Lamp	0.14 ± 0.02	0.32 ± 0.03	0.44 ± 0.03	0.71 ± 0.03	-0.21 ± 0.04
K&Z Int.Lamp	-0.04 ± 0.01	-0.00 ± 0.01	0.17 ± 0.01	0.37 ± 0.02	-0.21 ± 0.02
K&Z Field	0.13 ± 0.01	0.37 ± 0.01	0.64 ± 0.01	~~0.95 ± 0.01~~ 0.94 ± 0.01	-0.13 ± 0.01