REGIONAL BREWER CALIBRATION CENTER EUROPE RBCCE

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Davos 2021

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Contents

1 Introduction

This Fifteenth campaign was a joint exercise of the Regional Brewer Calibration Center for Europe (RBCC-E) and the World Radiation Center with the support of MeteoSwiss and the Global Atmosphere Watch (GAW) program of the World Meteorological Organization (WMO). The following operations were performed by the RBCC-E during the intercomparison:

1. Ozone calibration against the RBCC-E travelling reference (B#185).
2. Compilation of the calibration histories of the instruments.
3. Evaluation of the Level 2 Eubrewnet ozone data for the period between intercomparisons.

During this intercomparison, the RBCC-E transferred its own absolute ozone calibration, obtained by the Langley method at the Izaña Observatory (IZO). A discussion about the calibration of the reference instrument (B#185) is presented in Sec.3. All the participating instruments were provided with a provisional calibration at the end of the campaign, which can be considered final calibration constants for most of them. A detailed calibration report for each instrument is available online. A calibration history of the Brewers which have participated in previous campaigns was also included in this document. A participant's list is presented in Table 1-1.

The results of the blind comparison with the reference instrument Brewer #185 showed very satisfactory results , all instruments shows an agreement better than 1% with 66% with an agreement better than 0.5% range (see Fig. 1-1). A good agreement with the reference instrument Brewer #185 using the final calibration constants, within the range ±0.5%, is achieved.

Table 1-1 – Participant List at Davos 2021 campaign.

INSTITUTION	IP	BREWER	COUNTRY
MeteoSwiss	F. Zeilinger	040	Switzerland
MeteoSwiss	F. Zeilinger	072	Switzerland
MeteoSwiss	F. Zeilinger	156	Switzerland
Kipp & Zonen	P. Babal	158	The Netherlands
PMOD/WRC	L. Egli	163	Switzerland
RBCC-E / State Meteorological Agency of Spain	A. Redondas	185	Spain
Kipp & Zonen	P. Babal	245	The Netherlands

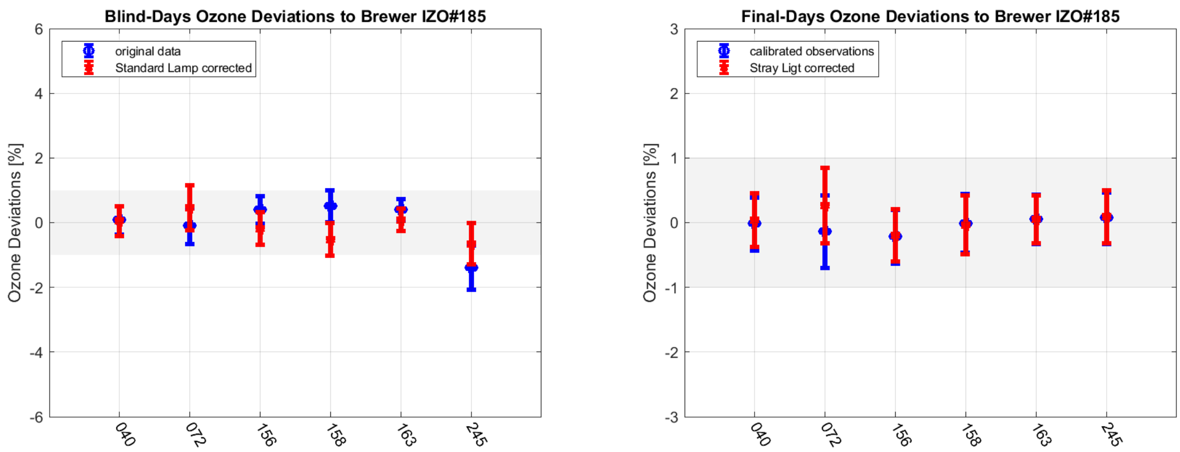

Figure 1-1 – Ozone relative percentage differences of all Davos 2021 participating instruments to RBCC-E travelling standard IZO#185. Ozone measurements collected during the blind period upper panel are reprocessed using the original calibration constants, with (red) and without (blue) Standard Lamp correction. Final days on the lower panel were reprocessed using the final calibration constants after the maintenance, with (red stars) and without (blue dots) Stray Light correction on single brewer. Error bars represent the standard deviation.

2 Summary

2.1 Campaign conditions and schedule

The weather conditions during the campaign at the The Physical Meteorological Observatory in Davos (1860 m.a.s.l.) were not ideal for calibration with rain during the second half of the campaign. For the instruments with no maintenance we have around 150 near simultaneous measurements with the reference instrument Brewer #185 but for those with maintenance we only have around 40 measurements, when we recommend to have a minimum of 100 near-simultaneous direct sun ozone measurements for a reliable calibration (Fig. 2-2).

As shown in Fig. 2-3, total ozone content during the campaign ranged between 290 and 350 DU. Most observations ($\approx$ 75%) were within the 350-600 DU ozone slant column (OSC) range, see Fig. 2-4. The internal temperature was approx. 20$\pm$10°C, see Fig. 2-5

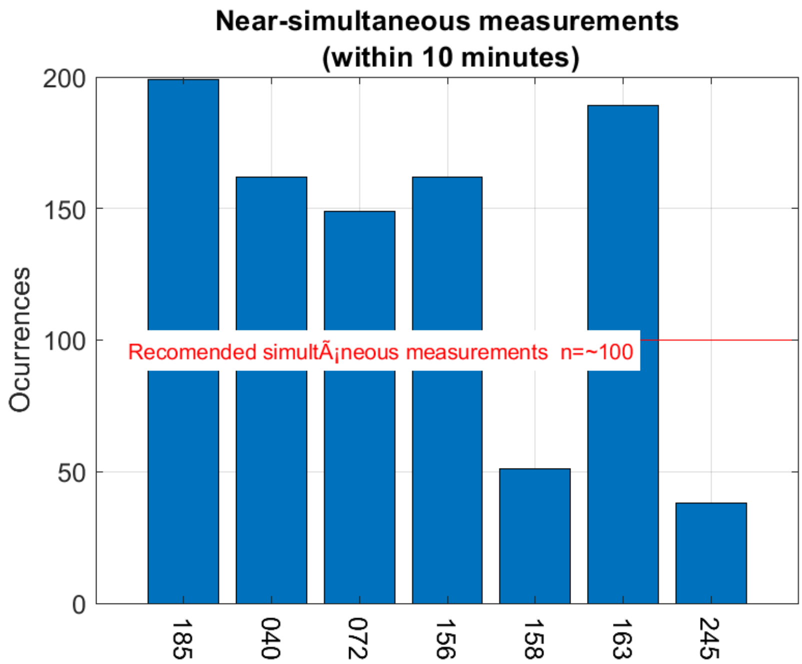

Figure 2-2 – Number of near-simultaneous ozone measurements.

The actions carried out each day of the campaign are shown in Table 2-2. The first day is dedicated to the installation of the instrument. The next two/three days (depending on the weather conditions) will be “blind”. During blind days any manipulation of the instrument that can produce a change on the initial calibration should be avoided. After that, the routine schedule can be interrupted to perform whatever maintenance tasks are needed to be done (dispersion tests, lamp calibrations, etc). In this campaign, the service of Kipp&Zonen experts were performed in 2 of the participants, this actions are summarised on the maintenance sheet.Finally, the programmed UV day measurements are considered as blind and final days for UV and ozone measurements, respectively.

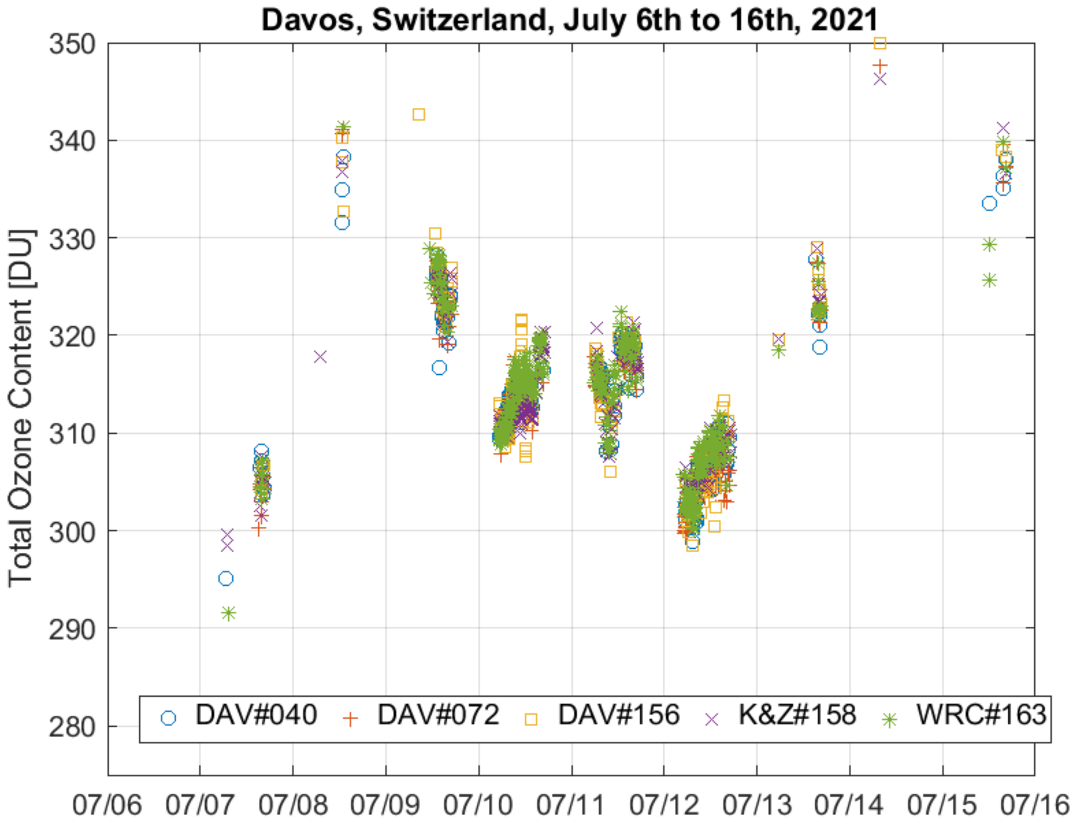

Figure 2-3 – Total ozone for the campaign, for instruments which didn't require maintenance.

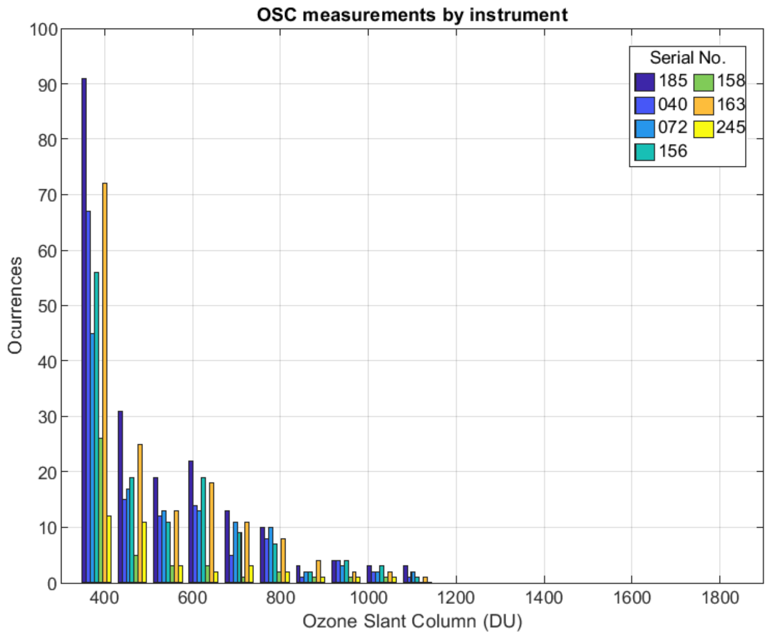

Figure 2-4 – Frequency distribution of ozone slant column ranges.

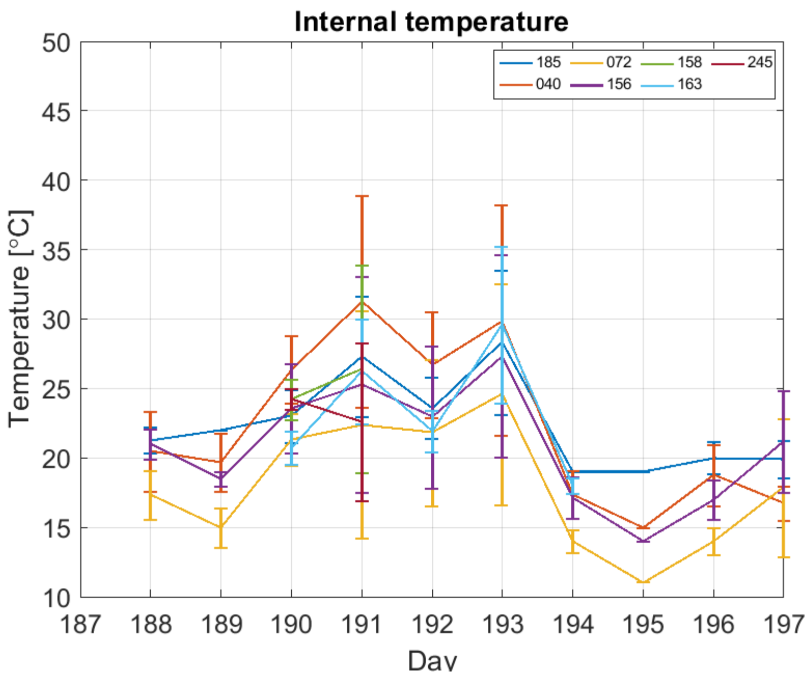

Figure 2-5 – Internal temperature of participating Brewer instruments.

DAY	ACTION	NOTES
Mon June 17th (168)	Installation	
Tue June 18th (169)	O_3 mesaurements	Blind days
Wed June 19th (170)	O_3 mesaurements	Blind days
Thu June 20th (171)	O_3 mesaurements / O_3 services	Service days
Fri June 21st (172)	O_3 mesaurements / O_3 services	Service days
Sat June 22nd (173)	O_3 mesaurements / O_3 services	Service days
Sun June 23rd (174)	O_3 mesaurements / O_3 services	Final ozone days / ATMOZ field campaign
Mon June 24th (175)	O_3 mesaurements	Final ozone days / ATMOZ field campaign
Tue June 25th (176)	O_3 mesaurements / UV	Final ozone days / UV comparison with QASUME
Wed June 26th (177)	O_3 mesaurements / UV	Final ozone days / UV comparison with QASUME
Thu June 27th (178)	O_3 mesaurements / UV	Final ozone days / UV comparison with QASUME
Fri June 28th (179)	Packing	

Table 2-2 – Davos 2021 campaign schedule.

2.2 Blind Comparison

During the blind period, the instruments are working with their home calibration and the ozone is calculated using these calibration constants. An initial comparison with the reference Brewer gives us an idea of the initial status of the instrument, i.e. how well the instrument performed using the original calibration constants (those operational at the instrument's station). Moreover, it is possible to detect changes of the instrument response due to the travel from internal tests, such as the Standard Lamp one, performed before and after the travel.

The Standard Lamp (SL) test is an ozone measurement using the internal halogen lamp as a source. In the local station, this test is performed routinely to track the spectral response of the instrument and therefore the ozone calibration. A reference value for the SL R6 ratio is provided as part of the calibration of the instrument. The ozone measurement is routinely corrected assuming that deviations of the R6 value from the reference value are the same that changes in the Extraterrestrial Constant (ETC). This is the so-called Standard Lamp correction. Hence, it is reasonable to investigate if the observed R6 changes are related with similar changes in the calibration constant. If this were the case, then the ETC constant should be corrected by the same change in SL R6 ratio as $ETCnew = ETCold - (SLref - SLmeasured)$.

Figure 2-6 and Table 2-3 show the difference between the calculated and reference R6 values, and as it can be observed, most of the Brewers presented variations of ±10 units which suggests that the instruments have remained stable from their last calibration. Note that Brewer #075 do not perform Standard Lamp measurements during blind days and #228 shows a huge change due to maintenance.

	brw	SL_blind_Reference	mean_SL	difference	std_table_blind_sl	mean	std_t1	mean_slc	std_slc	SL_correction
DAV#040	40	1738	1739	-1	2	0	0.4	0	0.5	0
DAV#072	72	1960	1952	8	2	0	0.5	0.6	0.6	0
DAV#156	156	440	450	-10	2	0.4	0.4	-0.2	0.5	0
K&Z#158	158	541	557	-16	2	0.5	0.5	-0.5	0.5	0
WRC#163	163	278	283	-5	1	0.4	0.3	0.1	0.4	0
IZO#185	185	353	353	0	2	0	0	0	0.1	0
K&Z#245	245	438	426	12	3	-1.4	0.6	-0.7	0.6	0

Table 2-3 – Standard Lamp record during blind days with comparison with the reference value, mean total ozone deviation with the reference for the blind days without and with correction (SLC), the last column shows the the Standard Lamp correction improves the comparison with the reference.

However, the comparison with a reference instrument is the only way to assess whether the SL measurements properly track changes on the calibration constants or if the change observed is due to an emission spectrum change. We have to note that no all the instrumental changes are properly tracked by the Standard Lamp. For example, filter deterioration or linearity problems are not detected by the Standard Lamp measurement.

The results of the blind comparison with the reference instrument Brewer #185 showed very satisfactory results. With better agreement than in previous campaigns, 4 of 6 instruments shows an agreement better than 0.5%: DAV#040, DAV#072, DAV#156, and WRC#163. These instruments represent the 66% of all the participating Brewers. Moreover, 100% of the instruments show an agreement inside the 1% range. The Standard Lamp results for the blind days are summarized in Fig. 2-7.

The stray light effect observed in the single Brewers can be seen in Fig. 2-8, with a prominent ozone slant column dependence in ozone measurements. The stray light correction implemented on the final calibration is explained in detail in the next section.

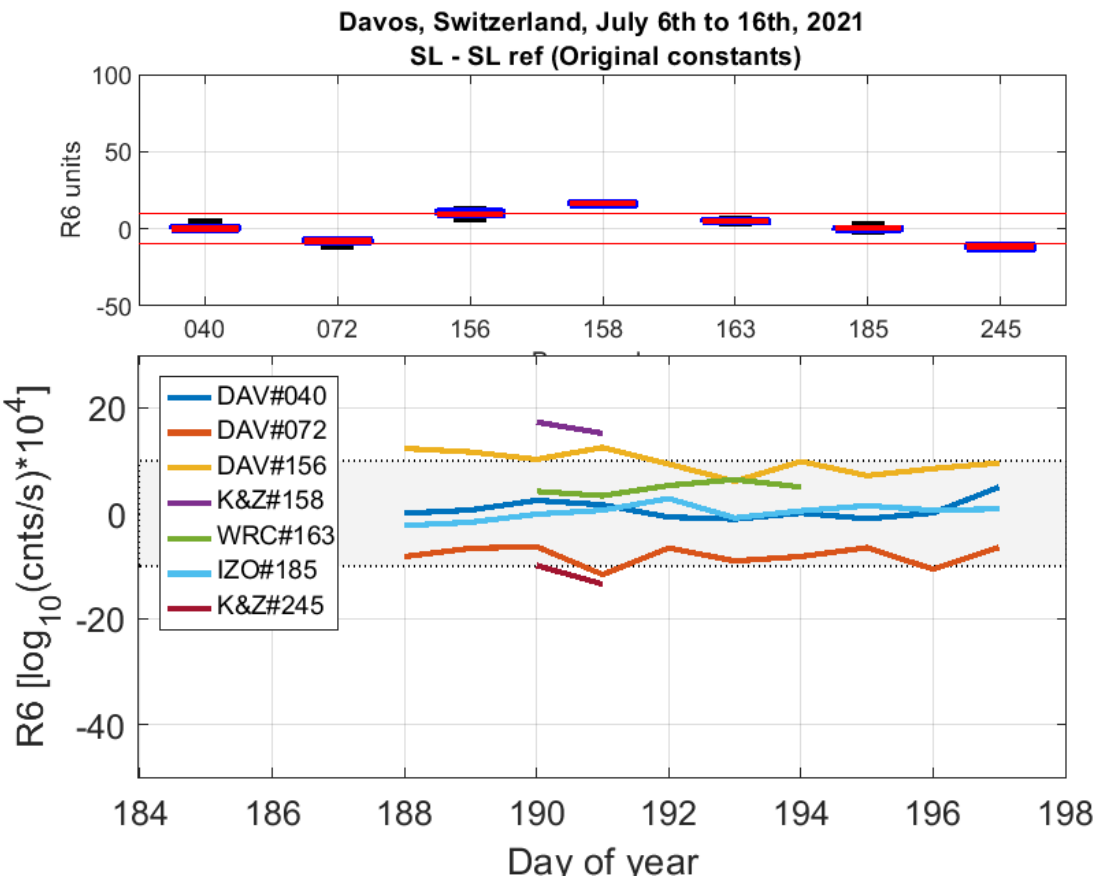

Figure 2-6 – Standard lamp R6 difference to R6 reference value from last calibration during the blind days, before the maintenance. Variations within the ±10 range (≈ 1% in ozone) are considered normal, whereas larger changes would require further analysis of the instrument performance.

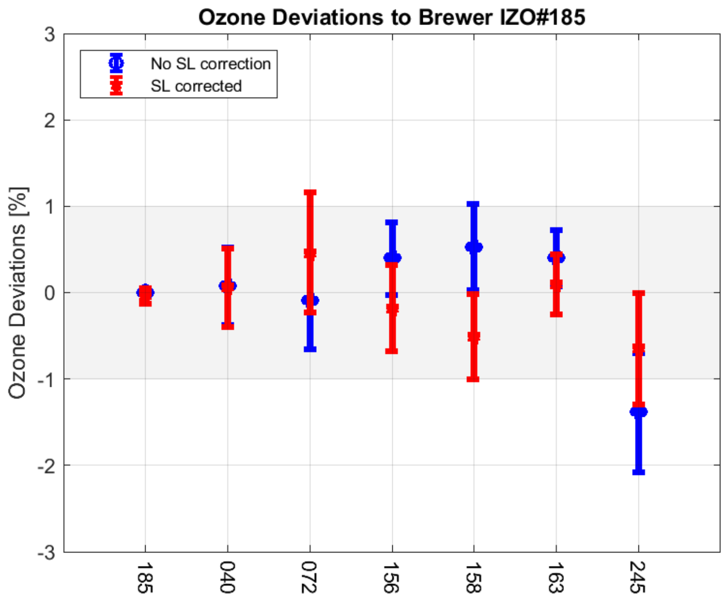

Figure 2-7 – Ozone relative percentage differences of all Davos 2021 participating instruments to RBCC-E travelling standard IZO#185. Ozone measurements collected during the blind period are reprocessed using the original calibration constants, with (red) and without (blue) Standard Lamp correction. Error bars represent the standard deviation.

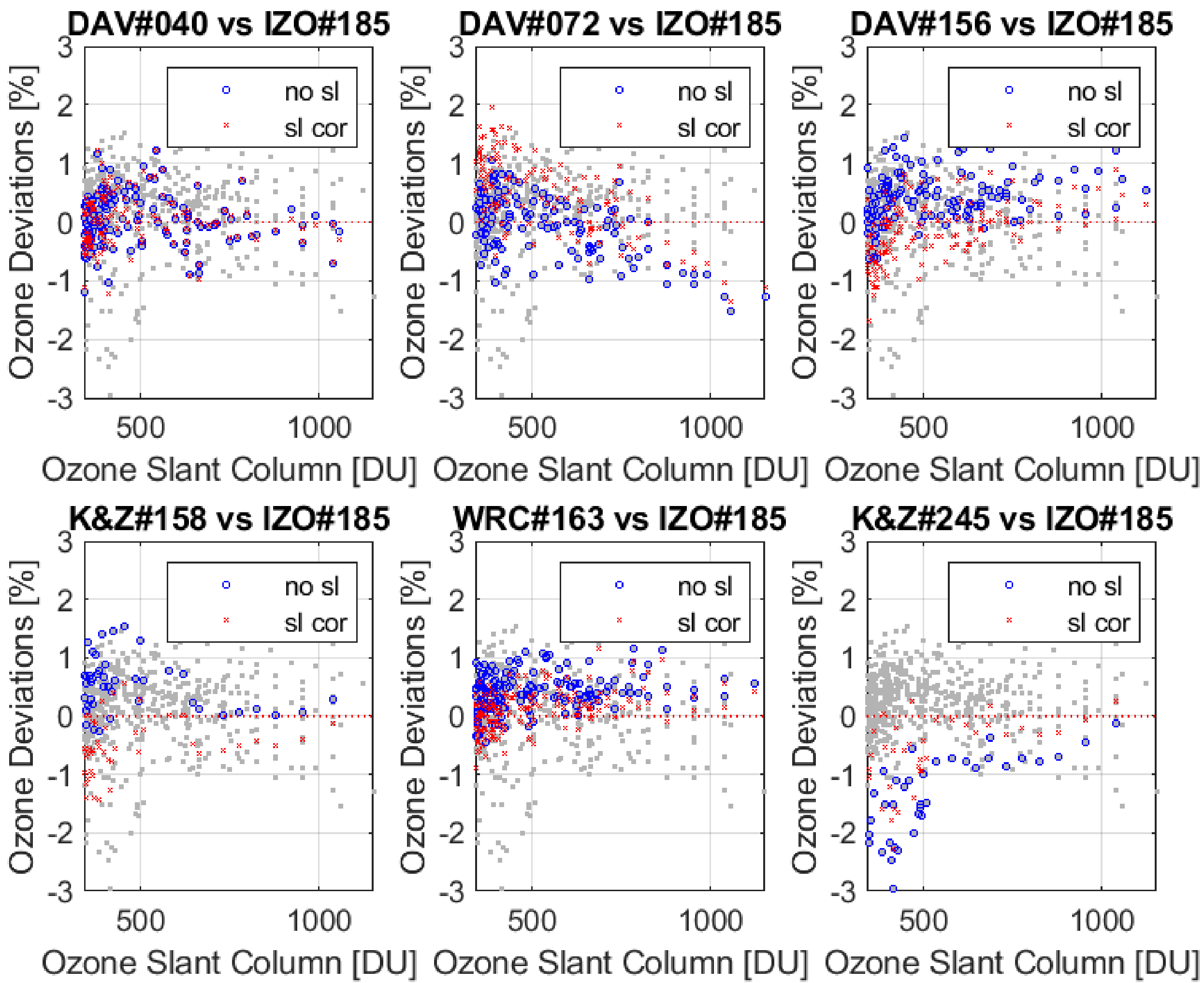

Figure 2-8 – Blind-days ozone relative differences (percentage) of all Davos 2021 Brewer instruments with respect to the RBCC-E travelling standard Brewer #185. Ozone measurements collected during the blind period (before the maintenance) were reprocessed using the original calibration constants, with (red stars) and without (blue stars) standard lamp correction. Grey dots mean ozone deviations for all participating instruments.

2.3 Final Calibration

We define the final days as those available after the maintenance work has been finished for each participating instrument. These days are used to calculate the final calibration constants, so we tried not to manipulate the instruments during this period. Furthermore, the SL R6 value recorded during the final days is normally adopted as the new reference value. It is also expected that this parameter will not vary more than 5 units during this period.

Figure 2-9 shows the differences between the daily standard lamp R6 ratio and the proposed R6 reference value during the final days. As expected, the recorded SL values did not vary more than 5 units during this period,

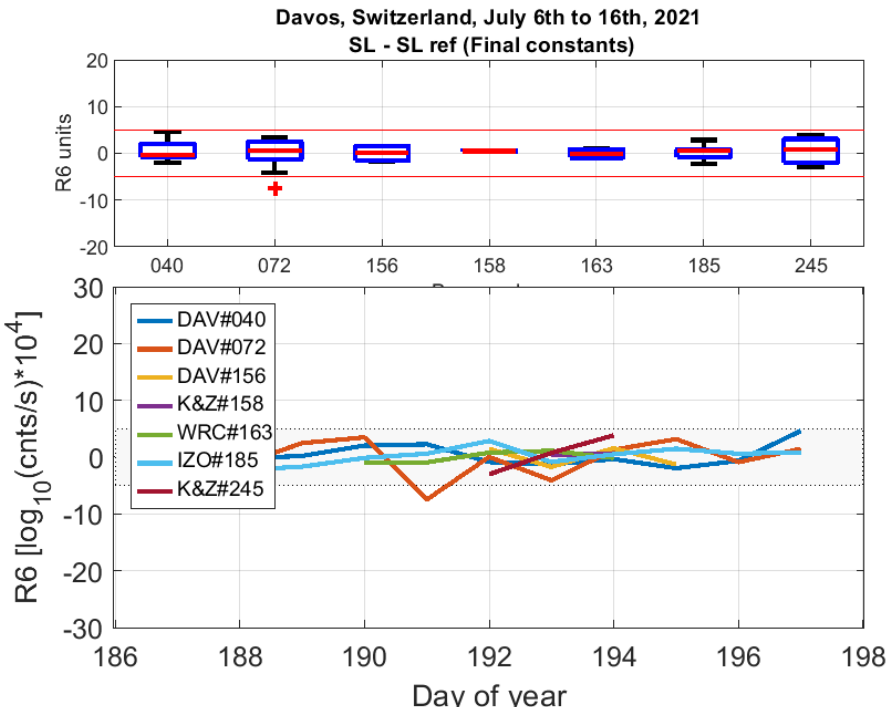

Figure 2-9 – Standard lamp R6 ratio to R6 reference from last calibration differences during the final days grouped by Brewer serial number (above) and as a function of time (below). The shadow area represents the tolerance range (±5 R6 units).

Deviations of ozone values for all the participating instruments from the RBCC-E travelling standard Brewer IZO#185 are shown in Fig. 2-10. We have recalculated the ozone measurements using the final calibration constants, with and without Stray Light correction in the case of single Brewer instruments. The ozone underestimation due to the effect of the Stray Light in single Brewers and the correction applied by the model are depicted in Fig. 2-11, details of these corrections are found in Redondas et al. [2018].

All Brewers were calibrated using the One Parameter ETC transfer method, i.e., the ozone absorption coefficient was derived from the wavelength calibration (dispersion test) and only the ozone ETC constant is transferred from the reference instrument. The two parameters calibration method is also used as a quality indicator. For all the instruments the one and the two parameters ETC transfer methods agreed

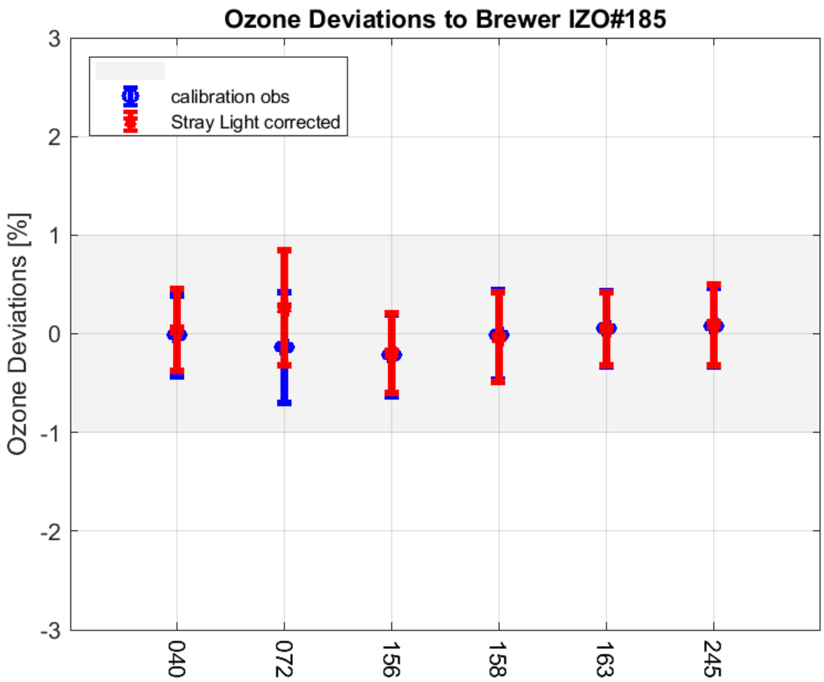

Figure 2-10 – Ozone relative percentage differences of all Davos 2021 participating instruments with respect to the RBCC-E travelling standard IZO#185. Ozone measurements collected during the final period are reprocessed using the proposed calibration constants, with (red plots) and without (blue plots) Stray Light correction. Error bars represent the standard deviation.

with each other within the ±10 units limit for ETC constants and ±0.001 atm/cm for the ozone absorption coefficient (one micrometer step), which indicates the quality of the calibration provided. With these tolerance limits, a good agreement with the reference instrument Brewer #185 using the final calibration constants, within the range ±0.5%, is achieved.

In Table 2-4 we summarize the mean differences, with and without applying the Stray Light correction, respect to the reference instrument. The ozone was calculated using the final calibration of the instrument.

	mean (no stray-l corr.)	std (no stray-l corr.)	mean (stray-l corr.)	std (stray-l corr.)
DAV#040	0	0.4	0	0.4
DAV#072	-0.1	0.5	0.3	0.6

Table 2-4 – Ozone deviation with respect to the reference calculated with the final calibration.

Finally, in Fig. 2-12 we show the individual differences, with and without applying the Stray Light correction, with respect to the reference instrument.

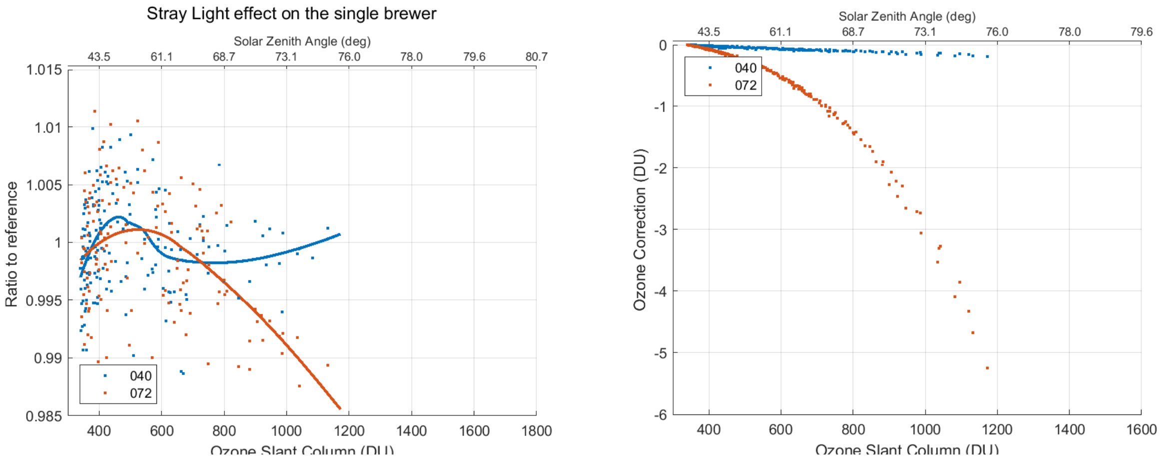

Figure 2-11 – Ozone relative percentage differences of the single Brewers at Davos 2021 with respect to RBCC-E travelling standard IZO#185, showing the underestimation of the Ozone measurements for solar Zenith angle above 70° (left) and the correction applied by the model in Dobson Units (right).

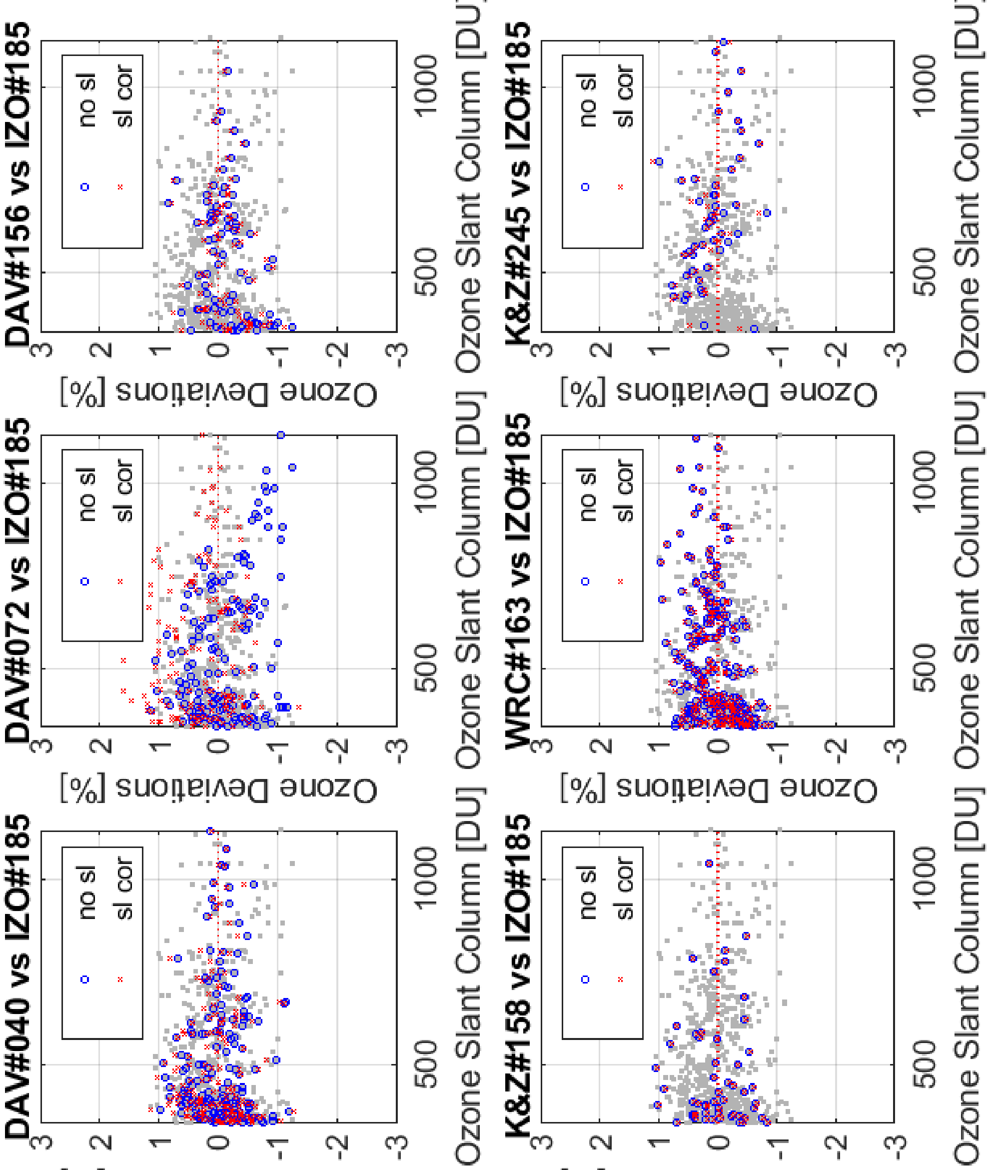

Figure 2-12 – Final-days ozone relative differences (percentage) of all Brewer instruments at Davos 2021 with respect to the RBCC-E travelling standard Brewer #185. Ozone measurements collected during the final period (after the maintenance) were reprocessed using the final calibration constants, with (red stars) and without (blue stars) Stray Light correction. Grey dots mean ozone deviations for all participating instruments.

References

Alberto Redondas, Virgilio Carreño, Sergio F. León-Luis, Bentorey Hernández-Cruz, Javier López-Solano, Juan J. Rodriguez-Franco, José M. Vilaplana, Julian Gröbner, John Rimmer, Alkiviadis F. Bais, Vladimir Savastiouk, Juan R. Moreta, Lamine Boulkelia, Nis Jepsen, Keith M. Wilson, Vadim Shirotov, and Tomi Karppinen. EUBREWNET RBCC-E Huelva 2015 Ozone Brewer Intercomparison. *Atmospheric Chemistry and Physics*, 18(13):9441–9455, July 2018. ISSN 1680-7316. doi: https://doi.org/10.5194/acp-18-9441-2018. URL `https://www.atmos-chem-phys.net/18/9441/2018/acp-18-9441-2018.html`.

3 RBCC-E Brewer Reference

The RBCC-E was established at the Izaña Atmospheric Research Centre in 2003. It comprises three MkIII Brewer spectrophotometers: a Regional Primary Reference (Brewer #157), a Regional Secondary Reference (Brewer #183) and a Regional Travelling Standard (Brewer #185). The WMO scientific advisory group (WMO-SAG) on Ozone authorised in 2011 the RBCC-E to transfer its own ozone absolute calibration.

The IZO-CCL (Central Calibration Laboratory) reference transferred to the campaigns is the mean of the three independently calibrated Brewer instruments. This methodology can be summarised in three steps:

1. Instrumental characterisation : Determination of linearity Fountoulakis et al. [2016] , temperature coefficients Berjón et al. [2018] and filter attenuation Redondas et al. [2018b].
2. The Absorption coefficient is determined by measurements of the spectral lamp emission lines using the methodology of Gröbner et al. [1998] and Redondas et al. [2018a].
3. The ETC is onsite determined by Langley Method (León-Luis et al. [2018]; Redondas [2003], Ito et al. [2014], Redondas et al. [2014].

The points 1 and 2 of this methodology were tested and validated with the cooperation of Metrology Institutes during the ATMOZ project (Gröbner et al. [2017]), in which the RBCC-E participated together with the Dobson World and Brewer European Calibration Centres. Finally, the methodology used to calculate the ETC is described in Redondas [2003], Redondas et al. [2018b], Ito et al. [2014]. The current status and maintenance of the RBCC-E is discussed in León-Luis et al. [2018].

Regarding the IZO CCL is worth to highlight that:

- The three instruments are calibrated independently. The Langley calibration is performed continuously onsite.
- The methodology, code and data used on the calibration are publicly available on the web, so are reproducible. This includes the QA/QC protocol (http://rbcce.aemet.es/svn/iberonesia/RBCC_E) and the Triad Langley calibration (http://rbcce.aemet.es/svn/iberonesia/RBCC_E/Triad).
- There is continuous assessment of the triad based on the comparison with the total ozone observations at Izaña Observatory provided with the FTIR, DOAS and ECC Ozone Sondes techniques, which are recognised as part of the NDACC program. This makes Izaña a supersite for ozone measurement.

The calibration of the RBCC-E triad against the World Brewer Triad (WBT) was established by a yearly comparison with the travelling standard Brewer #017 operated and maintained by International Ozone Services Inc. (IOS) and checked at the station by means of the Langley extrapolation method. In addition, during the RBCC-E Brewer intercomparison campaigns, the travelling standard #185 is compared with other reference instruments when it is possible. These reference instruments are: IOS travelling reference #017, Brewer #145 – operated by Environment and Climate Change Canada (ECCC) – and the Kipp & Zonen travelling reference #158. The first two instruments provide a direct link to the WBT: a report of the comparison between references can be found in Redondas et al. [2018b]. As suggested by WMO-SAG the link to the WBT will be conducted by joint Langley campaigns at Mauna Loa or Izaña stations, but this Langley intercomparisons has not been possible since 2014.

Ref. checklist: B#185	Description	Passed?	Value	Comments
Calibration data				
Ref. of travelling standard	RBCC-E B#185			Own Langley
Is the standard calibrated?		Y		
% difference before travel			0.077	
% difference after travel			0.074	
Calibration data				
HP/HG	test repeteable within 0.2 steps?	Y		
SH	shutter delay is correct?	-		
RS	test within $\pm$ 0.003 from unity for illuminated slits and between 0.5 and 2 for the dark counts	Y		
Dead time	Is it between 28 and 45 ns for multiple-board Brewers and 16 and 25 ns for single-board ones?	N	28	
Standard lamp	SL ratio R6 is within 5 units from calibration?	Y	353	
Standard lamp	SL ratio R5 is within 10 units from calibration?	Y	490	

Table 3-1 – Calibration and instrument checklist of Brewer#185.

The intercomparison campaign scheduled for summer 2020 in Davos 2021 , Switzerland, was suspended due to restrictions imposed by the situation arising from COVID-19. Finally this campaign was held in the summer of 2021, on July 6th to 16th, 2021. This same summer, the campaign in El Arenosillo, Huelva (Spain), was also held on September 6th to 17th, 2021. Brewer #185 It was used in both campaigns as a reference, and it remained at the El Arenosillo station between both campaigns. Therefore, the validation of the reference after the campaign has been carried out later than on other occasions. However, as shown in the following sections, the instrument remains stable from several months before the campaign until a month after the return to Izaña, when its annual maintenance was carried out.

3.1 RBCC-E Brewer Reference spectrometer calibration

As a preliminary and subsequent task during all the intercomparison campaign, the reference instrument (Brewer #185) is analysed in detail. So, its instrumental parameters – dead time (DT), temperature dependence, filter characterisation as well as its ozone absorption coefficient calculated from a dispersion test – are compared with the values recorded prior and after the campaign. A summary with the main parameters of Brewer #185 checked before the instrument departed for the campaign is presented in Table 3-1. A detailed instrumental report is available at Redondas et al. [2021].

However, the Langley technique is the best procedure to detect if the calibration of the instrument has changed. The stability of the instruments of the Triad are analysed in periods determined by events than can affect the calibration, during this periods the Langley Plot are averaged to obtain the ETC. The

	Date	SL	se	N
"SL cable isolation"	14-Aug-2020	353.3	0.1	310
"DAV2021"	28-Jun-2021	353.4	0.5	11
"At huelva"	18-Jul-2021	352.4	0.2	46
"ARE2021"	06-Sep-2021	349.4	0.6	11
"At Izana"	23-Sep-2021	348.9	0.2	34

Table 3-2 – Standard Lamp R6 ratio, for the reference instrument. SL refers to the mean of the R6 ratio, se to its standard error and N to the number of data used to make the statistics.

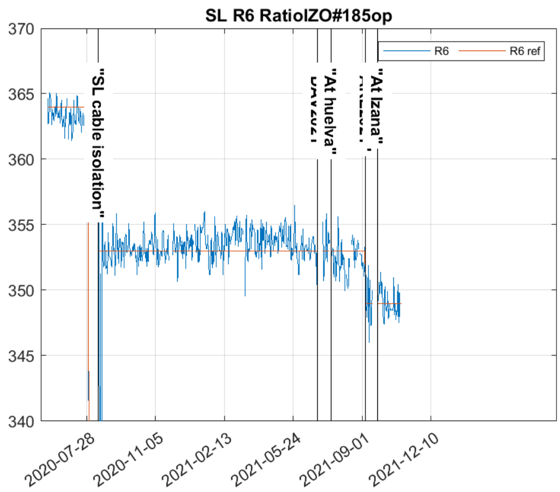

Figure 3-1 – Standard lamp R6 measurements for Brewer #185 during the year. The vertical lines indicate relevant events in the instrument's operation.

events associated to Brewer#185 are summarised at Table 3-2 and plotted as vertical lines on the figure of the Standard Lamp record, Figure 3-1. These events include an instrument ground adjustment in August 2020, as well as the travel to the intercomparison campaigns as possible events. We can see how the value of the SL measure varies slightly, about 4 units, on September 6, 2021. This change is related to the replacement of the zenith motor origin detection diode, but it has not effect either in the Langleys or in the comparison with the other Brewers of the Triad before and after the campaign. Therefore, the observed change is considered to only affect the standard lamp and does not reflect a change in the instrument. It should be noted that this change is so small that it would not be applied as a correction on Eubrewnet, where corrections of less than 6 units are not considered.

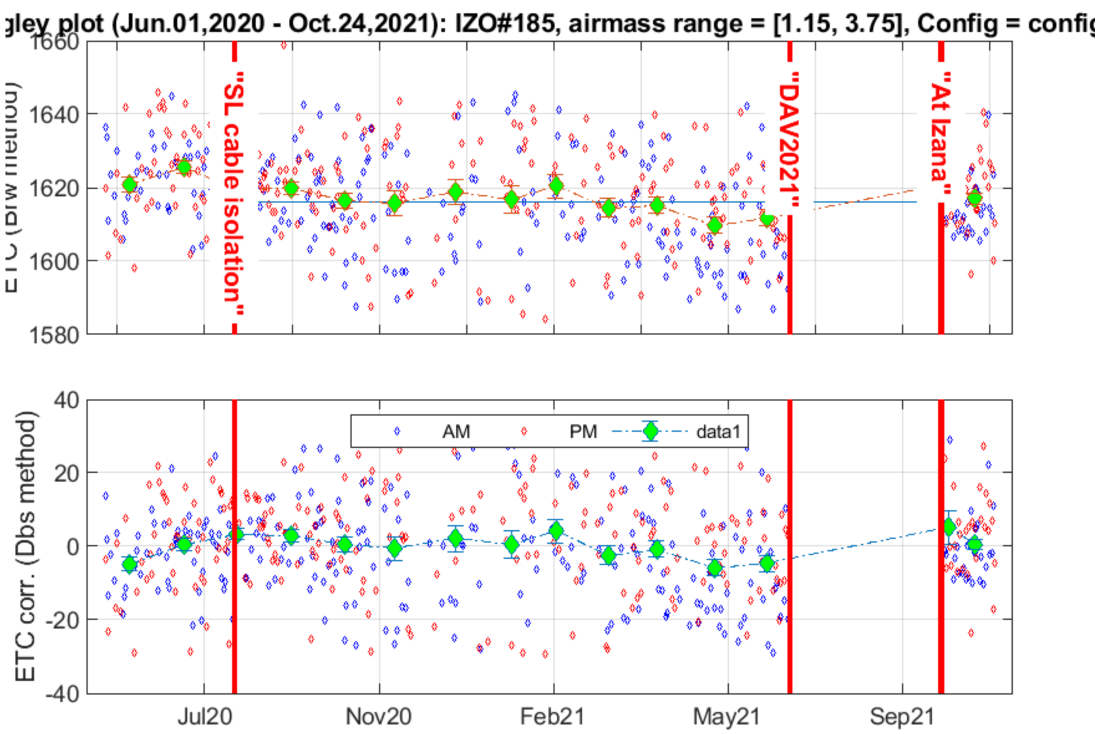

Figure 3-2 – Langley ETC calculation for Brewer #185 during the year. In the upper panel, the Brewer Langley (standard) is plotted, and in the lower panel the Langley using the Dobson Method, which gives the ETC correction. The blue (red) dots correspond to Langley results derived from AM (PM) data. The dashed line represents monthly means of both AM and PM Langley results, . The vertical red lines indicate relevant events in the instrument's operation.

Figure 3-2 shows the Langley values calculated before and after the campaign from the morning and afternoon observations made during this year, summarised on Table 3-3. As it can be observed, the ETC values obtained before and after the campaign are in agreement with the reference ETC in the operational setting. This value is also confirmed using the Dobson Langley plot method (Dobson and Normand [1958], Kiedron and Michalsky [2016]).

The stability of Brewer#185 can also be checked comparing it with the two Brewers of the RBCC-E Triad which remain at IZO, Brewers #157 and #183. This comparison is performed for two date ranges: before the campaign, using data from 2021-04-15 to 2021-06-25, and after the campaign, using data from 2021-09-24 to 2021-10-25. Fig. 3-3 shows the daily relative difference with respect to the Triad's mean for the ozone observations of the three instruments before and after the intercomparison campaign. Fig. 3-4 and Tables 3-6 and 3-7 further show the relative differences with respect to the Triad's mean by OSC range. The average differences between brewer #185 and the Triad before and after the campaign are 0.077% and 0.074% respectively, which can be considered negligible. It is important to note that it is the mean of Triad instruments which is transferred during the Davos 2021 campaign (Table 3-4). But, as it is showed, in this case it coincides with the value of the travelling reference #185.

	labels	ETC	brw	std	dbs	std2	N
14-Aug-2020	Before Campaign	1616	1616	14.2	0	14	331
23-Sep-2021	After Campaign	1616	1618	10.5	1	10.5	53

Table 3-3 – Extraterrestrial constant of Brewer#185 (ETC) and the mean values and standard deviations and number of Langley events (N) before and after El Arenosillo campaing, using the standard langley method (brw) and Dobson method (dbs).

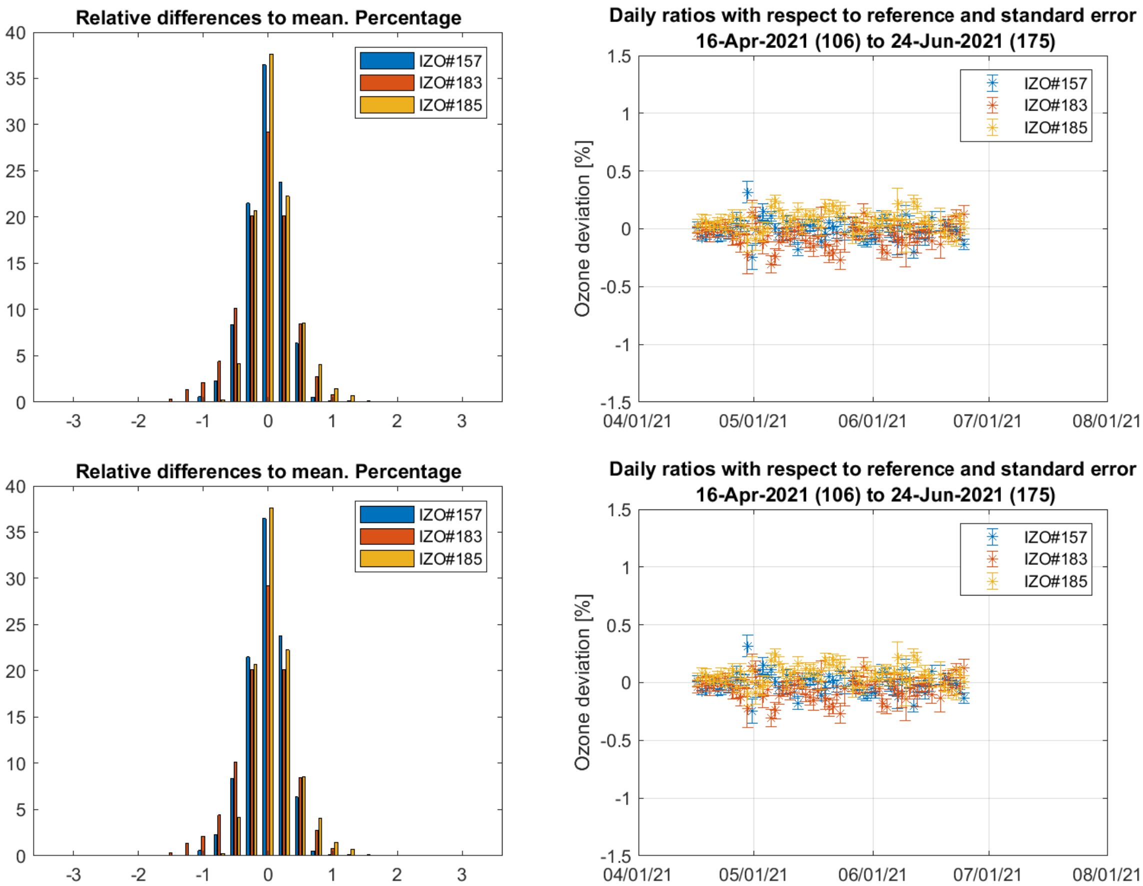

Figure 3-3 – Deviations of near-simultaneous ozone measurements of RBCC-E Brewers (serial nos. #157, #183 and #185) to the Triad's mean (left) and temporal evolution of daily mean deviation of near-simultaneous ozone measurements (right). The upper part shows the data before the intercomparison, while the lower part shows the subsequent data.

Table 3-4 – Instrument constant file for Brewers #185 in the campaign.

	ICF22720.185
o3 Temp coef 1	0
o3 Temp coef 2	0
o3 Temp coef 3	0
o3 Temp coef 4	0
o3 Temp coef 5	0
Micrometer steps/deg	0
O3 on O3 Ratio	0.3415
SO2 on SO2 Ratio	2.35
O3 on SO2 Ratio	1.15
ETC on O3 Ratio	1616
ETC on SO2 Ratio	80
Dead time (sec)	2.8e-08
WL cal step number	1020
Slitmask motor delay	14
Umkehr Offset	2423
ND filter 0	0
ND filter 1	4370
ND filter 2	10250
ND filter 3	14150
ND filter 4	21800
ND filter 5	26400
Zenith steps/rev	2972
Brewer Type	0
COM Port #	0
o3 Temp coef hg	0
n2 Temp coef hg	353
n2 Temp coef 1	490
n2 Temp coef 2	0
n2 Temp coef 3	5
n2 Temp coef 4	8
n2 Temp coef 5	0
O3 Mic #1 Offset	0
Mic #2 Offset	0
O3 FW #3 Offset	242
NO2 absn Coeff	0
NO2 ds etc	114858349
NO2 zs etc	92010460
NO2 Mic #1 Offset	151909779
NO2 FW #3 Offset	155024648
NO2/O3 Mode Change	170169377
Grating Slope	1
Grating Intercept	-10
Micrometer Zero	1733
Iris Open Steps	250
Buffer Delay (s)	0
NO2 FW#1 Pos	64
O3 FW#1 Pos	256
FW#2 Pos	0
uv FW#2 Pos	0
Zenith Offset	0
Zenith UVB Position	2216

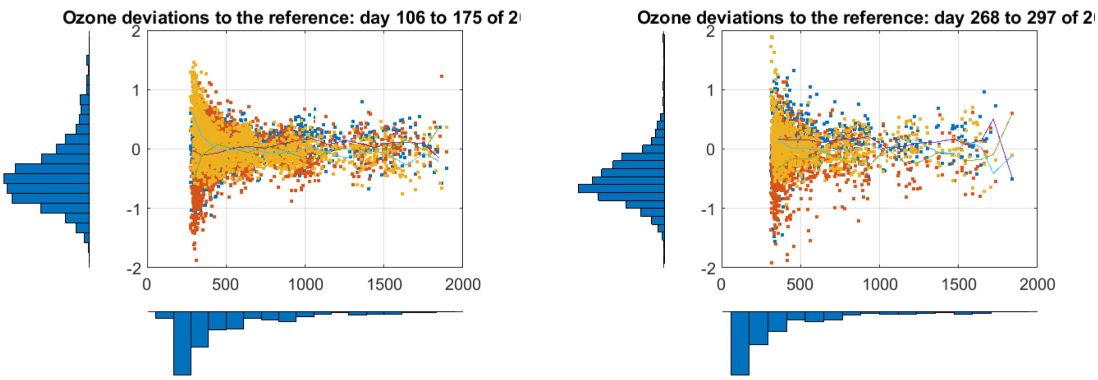

Figure 3-4 – Deviation of near-simultaneous ozone measurements by OSC. Data before (left) and after (right) the intercomparison.

Table 3-6 – Deviation of near-simultaneous ozone measurements by OSC. Data before the intercomparison.

	B#157	**B#183**	**B#185**
All	0 +/-0.29	-0.1 +/-0.41	0.1 +/-0.32
< 350	-0.1 +/-0.38	-0.3 +/-0.58	0.4 +/-0.39
< 500	-0.1 +/-0.28	0.1 +/-0.38	0 +/-0.27
< 700	0 +/-0.2	0 +/-0.26	0 +/-0.2
< 1000	0.1 +/-0.18	0 +/-0.24	-0.1 +/-0.17
< 1200	0.1 +/-0.18	-0.1 +/-0.23	0 +/-0.17
> 1200	0.1 +/-0.23	0 +/-0.26	-0.1 +/-0.24

Table 3-8 shows the ETC values calculated from 1-point and 2-point methods when Brewer #185 is calibrated from the other two instruments of the RBCC-E Triad. These results can be compared to the operative values of the ETC and ozone absorption coefficient, which are also included in Table 3-8. This calibration shows a very good agreement between the independent calibrations obtained by Langley and the cross-calibration between the reference instruments, especially for the 1P calibration, where the differences obtained are below 5 units. For the 2P comparison, the differences are slightly greater, mainly due to the difference with the absorption coefficient obtained from the dispersion tests.

Finally, to check the stability of the Brewers which remained in IZO during the campaign, the ozone measured by the two instruments is compared since 2021-04-15 to 2021-10-25. Fig. 3-5 and Table 3-9 show the daily relative difference of #157 and #183 with respect to their mean. Differences between these two instruments are below 0.2% for the whole period.

Table 3-7 – Deviation of near-simultaneous ozone measurements by OSC. Data after the intercomparison.

	B#157	B#183	B#185
All	0.2 +/-0.35	-0.2 +/-0.43	0.1 +/-0.32
< 350	0.2 +/-0.46	-0.5 +/-0.44	0.3 +/-0.43
< 500	0.1 +/-0.37	-0.2 +/-0.46	0 +/-0.28
< 700	0.1 +/-0.25	-0.1 +/-0.34	0 +/-0.19
< 1000	0.2 +/-0.21	-0.2 +/-0.33	0 +/-0.23
< 1200	0 +/-0.19	-0.1 +/-0.32	0.1 +/-0.24
> 1200	0.1 +/-0.29	-0.2 +/-0.34	0 +/-0.32

Table 3-8 – ETC values calculated from comparison between the RBCC-E instruments.

	Initial Date	Final Date	ETC Operative	O_3 Abs. Coeff. Op.	ETC 1P	ETC 2P	O_3 Abs. Coeff. 2P
157	15-Apr-2021	25-Jun-2021	1616.0	0.3415	1617.9	1625.6	0.340
183	15-Apr-2021	25-Jun-2021	1616.0	0.3415	1618.0	1626.3	0.340
157	24-Sep-2021	25-Oct-2021	1616.0	0.3415	1614.4	1621.7	0.340
183	24-Sep-2021	25-Oct-2021	1616.0	0.3415	1620.3	1629.5	0.339

3.2 Summary

As a summary, the analysis of RBCC-E Brewer reference shows the following:

- During the Davos 2021 campaign, the calibration trasferred is the mean of te triad reference of the RBCC-E. As it is showed, in this case it coincides with the value of the traveling reference #185.
- The ETC values for Brewer #185 obtained using the Langley plot method before and after the campaign, coincide with each other.
- Comparison of the #185 calibration against the other two Brewers of the RBCC-E Triad shows differences of less than 5 units from the reference ETC before and after the Davos 2021 intercomparison campaign.

Table 3-9 – Relative differences from ozone mean value for Brewers #157 and #183 from 2021-04-15 to 2021-10-25.

	Initial Date	Final Date	Mean O_3 diff [%]	Std O_3 diff [%]	Num.
157 vs 183	25-Jun-2021	24-Sep-2021	0.03	0.01	3375

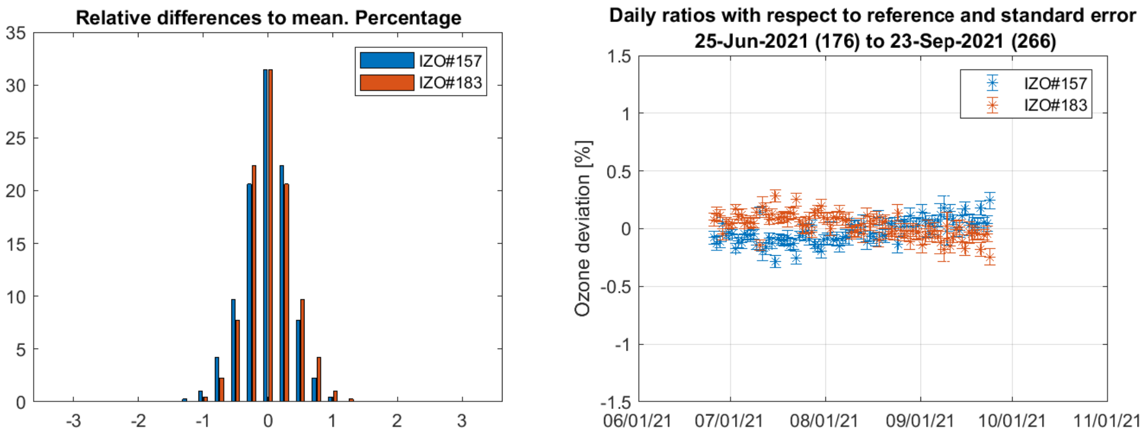

Figure 3-5 – Deviations from near-simultaneous ozone measurements of Brewers #157 and #183 with respect to their mean (left) and temporal evolution of daily mean deviation of near-simultaneous ozone measurements (right). In the latter figure, the error bars represent the standard error. Data covers the campaign period.

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4 Brewer DAV#040

4.1 Calibration Summary

The Fifteenth Intercomparison Campaign of the Regional Brewer Calibration Center Europe (RBCC-E) was held from July 6th to the 16th, 2021, at the Physikalisch-Meteorologisches Observatorium PMOD (Davos, Switzerland).

Brewer DAV#040 participated in the campaign in the period from July 6th to 16th. The campaign days of Brewer DAV#040 correspond to Julian days 187 – 197.

For final calibration purposes, we used **257** simultaneous DS ozone measurements taken from day **188** to **197**. As no maintenance was required for Brewer DAV#040, we used the same data set for the evaluation of the initial status as for the final calibration.

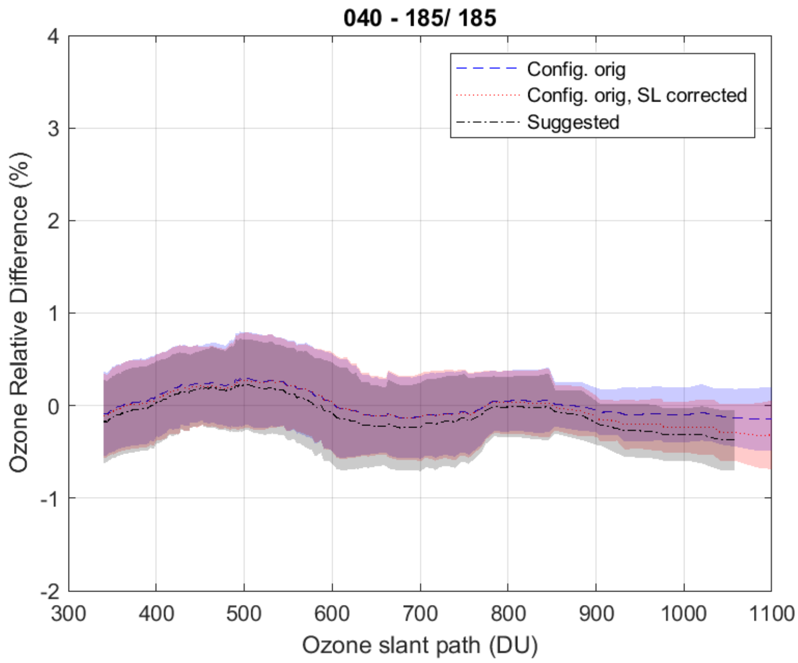

Figure 4-1 – Mean DS ozone column percentage difference between Brewer DAV#040 and Brewer IZO#185, plotted as a function of the ozone slant path. Results for the current (issued in the previous calibration campaign) configuration are show in blue; the red dotted line corresponds to the same configuration, but with the standard lamp correction applied; the black line corresponds to results obtained with the updated configuration proposed in the current campaign. The shadow areas represent the standard deviation of the mean. The plot corresponds to the final days of the campaign.

As shown in Fig. 4-1, the current ICF (ICF21018.040, blue dashed line) produces ozone values with an average difference of around 0% with respect to the reference instrument. This is a rather small difference, and highlights the stability of Brewer DAV#040. The SL correction (Fig. 4-1, red dotted line) does not improve the comparison with Brewer IZO#185 during this campaign. However, due to the peaks of the R6 standard lamp measurements, which are also observed in the HV measurements, we recommend applying the SL correction from the 2018 calibration to the current one.

Being a Mk. II model, Brewer DAV#040 measurements are typically affected by stray light. However, as show in Fig. 4-2, the ozone slant path during the campaign barely exceeds 1000 DU, which is a low value for which the effect of stray light is small, and the errors when characterizing the stray light are very high. We recommend therefore to continue using the stray light coefficients determined in the last Intercomparison Campaign.

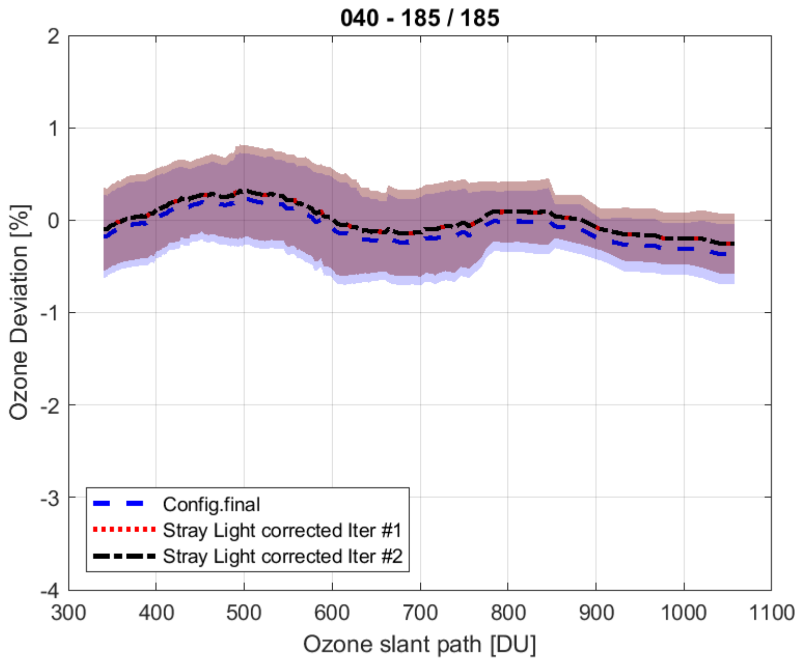

Figure 4-2 – Mean DS ozone column percentage difference between Brewer DAV#040 and Brewer IZO#185, plotted as a function of the ozone slant path. Results for the final (issued in this calibration campaign) configuration are show in blue; the red dotted line corresponds to the same configuration, but with the stray light correction obtained after 1 iteration; the black line corresponds to results obtained after 2 iterations. The shadow areas represent the standard deviation of the mean. The plot corresponds to the final days of the campaign.

The dead time (DT) shows a difference of 1 ns between the current value and the measured during the campaign, respectively $3.7{\cdot}10^{-8}$ and $3.6{\cdot}10^{-8}$. Despite being a very small change, its effect can be significant for single Brewers, and therefore we recommend updating the DT value.

We appreciate a small but clear temperature dependence in the standard lamp observations, which indicates the temperature coefficients can be improved.

The neutral density filters didn't show nonlinearity in the attenuation's spectral characteristics. We have not applied any correction to filters.

We suggest continuing to use the current Ozone Absorption Coefficient, with a value of 0.335.

All the other parameters analyzed (run/stop tests, Hg lamp intensity, CZ & CI files,...) show reasonable results.

Taking into account all this, we suggest some changes to the configuration of Brewer DAV#040.

4.2 Recommendations and Remarks

1. The R6 standard lamp test results from Brewer DAV#040 have been stable most of the time during the last 3 years. The old R6 reference value was 1738 and, although the difference is within the acceptable error of ± 5, it could be updated to **1739**.
2. We suggest a new R5 reference value of **3275**.
3. We suggest updating the DT to **3.6·10**$^{-8}$ seconds, which is one units less than the value proposed in the last intercomparison.
4. We have found that new temperature coefficients improve the behaviour of the instrument, and we include them in the final ICF for the campaign.
5. The neutral density filters show the same behaviour as in the previous campaign, and we suggest retaining the same correction factors.
6. Brewer DAV#040 measurements taken at large ozone slant paths are affected by stray light. We suggest applying the stray light correction, with the parameters obtained in the 2018 campaign.
7. Finally, we suggest updating the ETC value from **2963** to **2965**.

4.3 External links

Configuration File

http://rbcce.aemet.es/svn/campaigns/dav2021/bfiles/040/ICF18821.040

Calibration Report

https://docs.google.com/spreadsheets/d/12-4EoZzJkJDv5Pgpdt3PNZlZLXahvdlubhqOyijRack/edit#gid=1368862599

Calibration Reports Detailed

Historic and instrumental

http://rbcce.aemet.es/svn/campaigns/dav2021/latex/040/html/cal_report_040a1.html

Temperature & Filter

http://rbcce.aemet.es/svn/campaigns/dav2021/latex/040/html/cal_report_040a2.html

Wavelength

http://rbcce.aemet.es/svn/campaigns/dav2021/latex/040/html/cal_report_040b.html

ETC transfer

http://rbcce.aemet.es/svn/campaigns/dav2021/latex/040/html/cal_report_040c.html

4.4 Instrument History: Analysis of Average files

4.4.1 Standard Lamp Test

As shown in Figure 4-3 and 4-4, the standard lamp test performance is quite stable most of the time since the last calibration. However, There are some changes that are also observed in the HV. To prevent these events may affect the ozone, we recommend to apply the standard lamp correction. After the campaign, the mean R6 and R5 values are respectively 1739 and 3275.

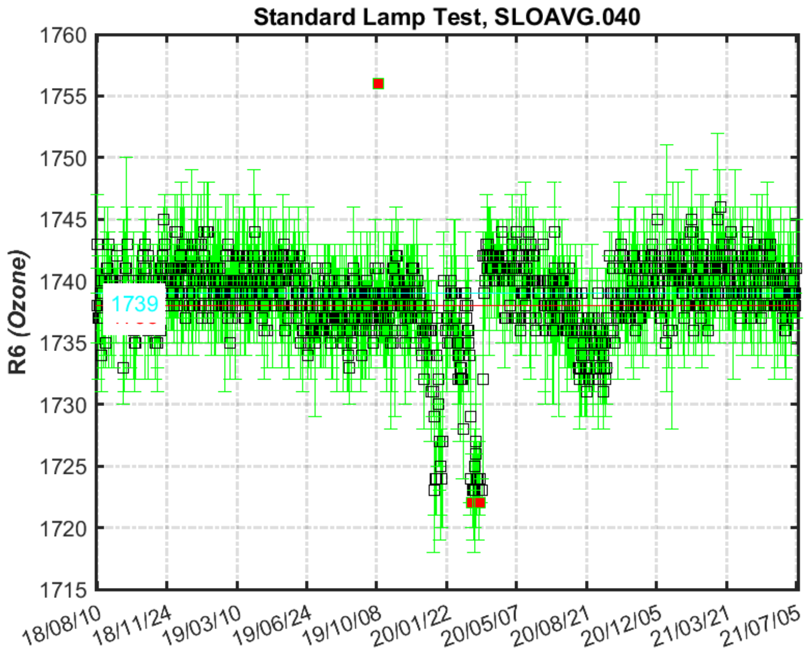

Figure 4-3 – **Standard Lamp test R6 (Ozone) ratios. Horizontal lines are labeled with the original and final reference values (red and blue lines, respectively)**

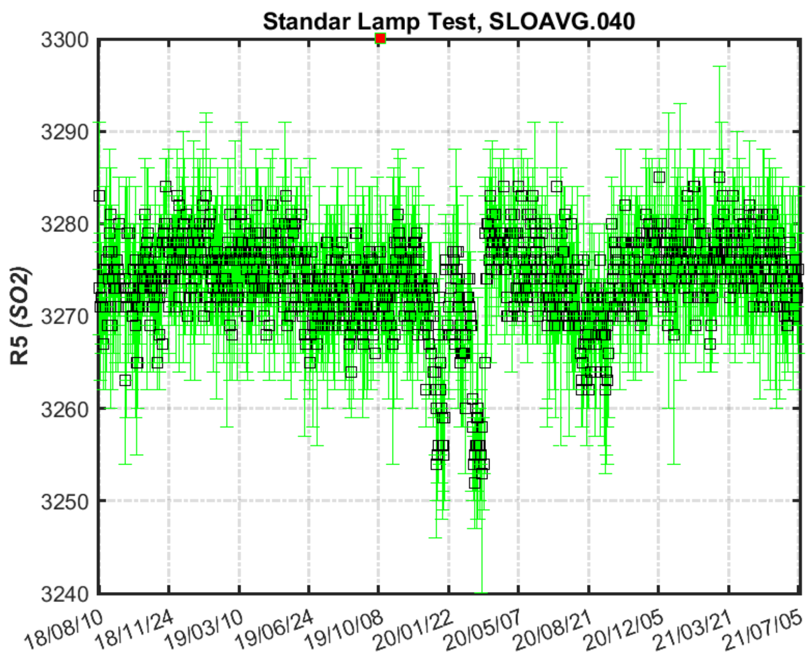

Figure 4-4 – **Standard Lamp test R5 (SO_2) ratios**

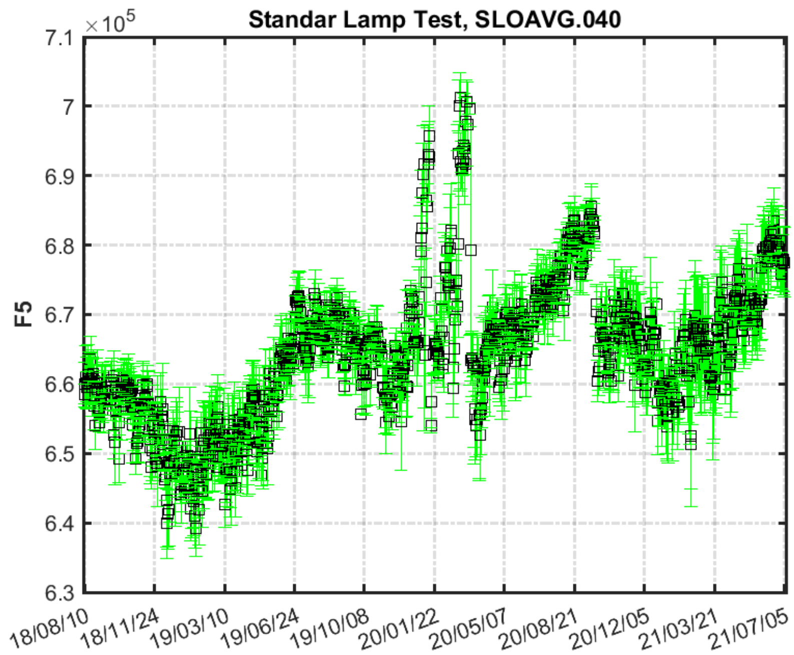

Figure 4-5 – **SL intensity for slit five.**

4.4.2 Run Stop and Dead Time

Run stops test values are within the test tolerance limits, see Fig. 4-6. The Hg slit is the noisier, but within the normal range of this slit.

As shown in Fig. 4-7, the current DT reference value of $\mathbf{3.7{\cdot}10}^{-8}$ seconds is just 1 ns larger than the value recorded during the calibration period, $\mathbf{3.6{\cdot}10}^{-8}$ s. This change, while small, is significant for single Brewers as DAV#040. Therefore, this new value has been used in the new ICF

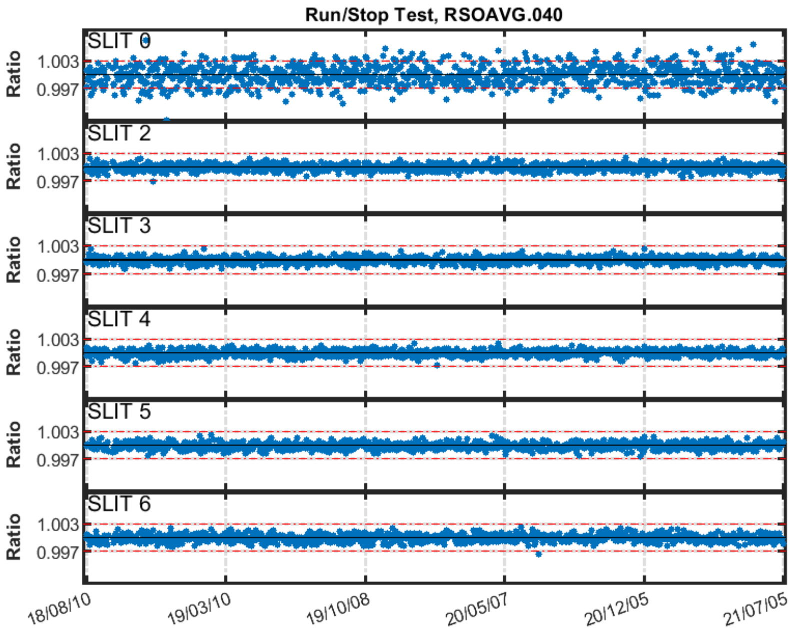

Figure 4-6 – **Run/stop test**

4.4.3 Analog Test

Fig. 4-8 shows that the high voltage has remained almost constant around at **1497** over the last three years, except for the first months of 2020. This change at the beginning of 2020 has also been observed in the R6 parameter, calculated from the SL measurements, but it is neither observed in the current nor the voltage of the SL.

4.4.4 Mercury Lamp Test

The intensity of the internal mercury lamp was reduced and stabilised as of May 2020, after an adjustment in the filter wheel #2. No other noticeable events have been observed in the last three years.

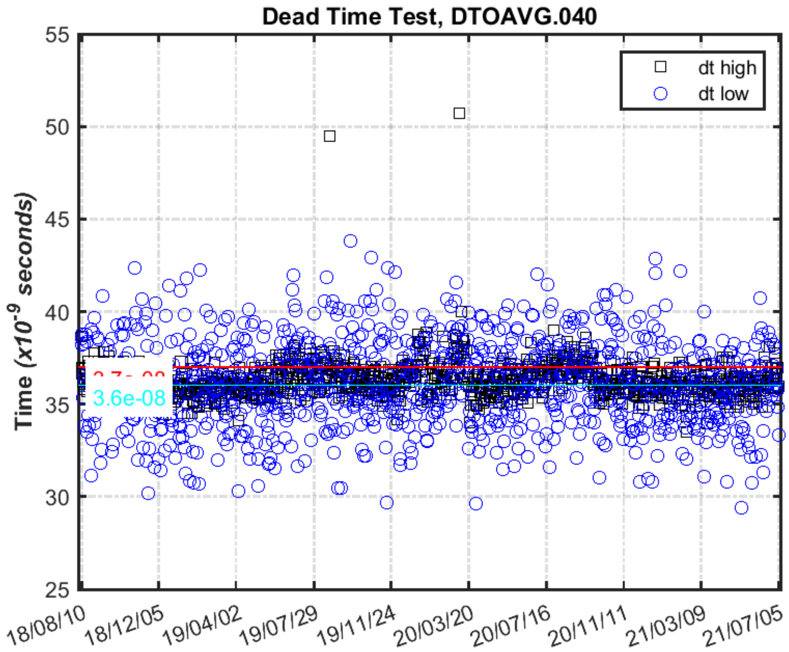

Figure 4-7 – Dead Time test. Horizontal lines are labelled with the current (red) and final (blue) values.

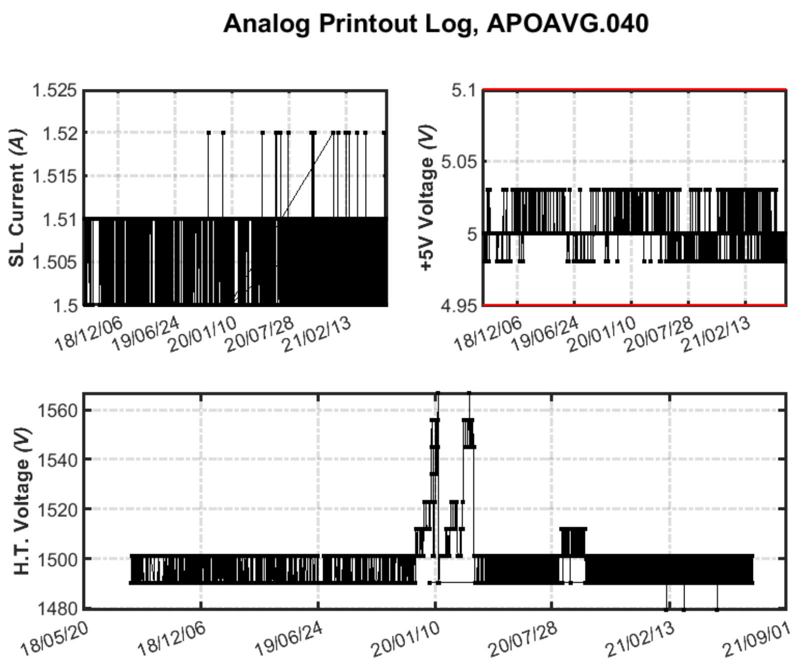

Figure 4-8 – Analog voltages and intensity.

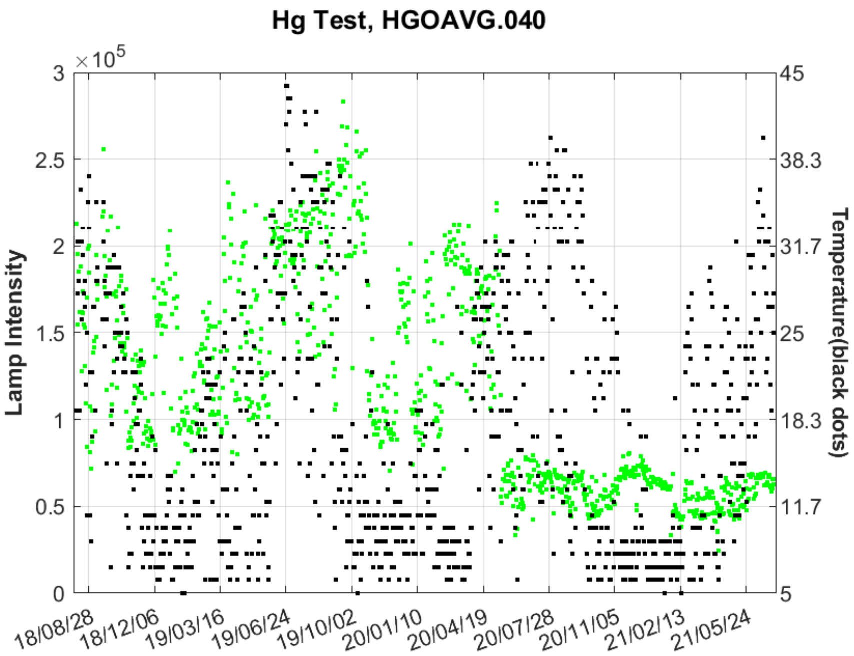

Figure 4-9 – Mercury lamp intensity (green squares) and Brewer temperature registered (black dots). Both parameters refer to maximum values for each day.

4.4.5 CZ scan on mercury lamp

We analyzed the scans performed on the 296.728 nm mercury line, in order to check both the wavelength settings and the slit function width. As a reference, the calculated scan peak, in wavelength units, should be within 0.013 *nm* from the nominal value, whereas the calculated slit function width should be no more than 0.65 *nm*. Only a few scans have been done since the last calibration for Brewer **DAV#040** as can be seen in Fig. 4-10. The analysis of these scans and those performed during the campaign show that the measured wavelength of the mercury line is slightly out of the accepted tolerance range, so we suggest reviewing the Dispersion Calibration File. Regarding the slit function width, results are good, with FWHM parameter lower than 6.5 Å.

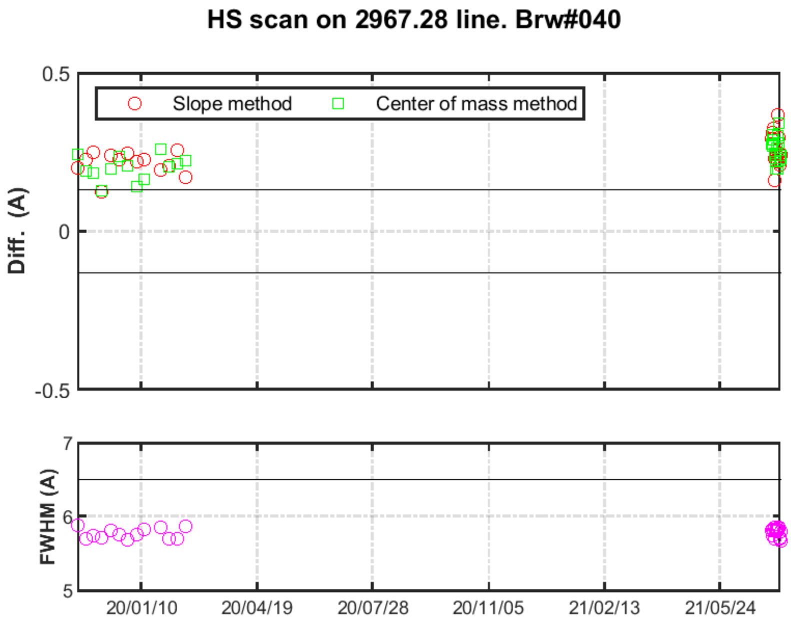

Figure 4-10 – CZ scan on 296.728 *nm* Hg line. Upper figure shows differences with respect to the reference line (solid lines represent the limit ±0.013 *nm*) as computed by two different methods: slopes method (red circles) and center of mass method (green squares). Lower figure shows Full Width at Half Maximum value for each scan performed. Solid line represents the limit 0.65 *nm*

4.4.6 CI scan on internal *SL*

CI scans of the standard lamp recorded at different times can be compared to investigate whether the instrument has changed its spectral sensitivity. We shown in Fig. 4-11 percentage ratios of the Brewer **DAV#040** CI scans performed during the campaign relative to the scan CI18821.040. As it can be observed, the lamp intensity has varied respect to the reference spectrum around 1%. Similar variation have been observed in the daily R6 and R5 values. This is a nice behavior for a SL lamp.

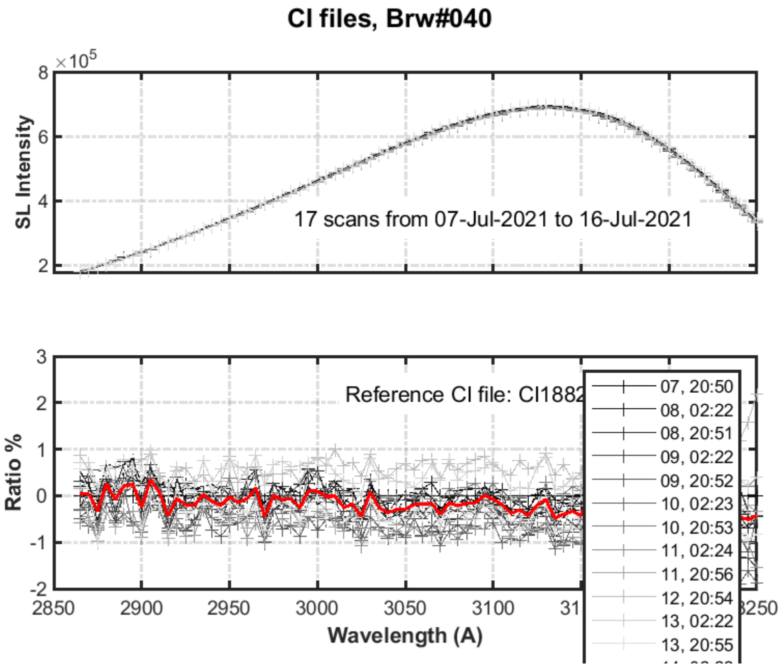

Figure 4-11 – **CI scan of Standard Lamp performed during the campaign days. Scans processed (upper panel) and relative differences with respect to a selected reference scan (lower panel). Red line represents the mean of all relative differences**

4.5 Absolute Temperature Coefficients

Temperature coefficients are determined using the standard lamp test. For every slit, the raw counts corrected for zero temperature coefficients are used in a linear regression against temperature with the slopes representing the instrument's temperature coefficients. From this we obtain the corrected *R6* and *R5* ratios to analyze the new temperature coefficients' performance.

As shown in Fig. 4-12, the current coefficients correct the effect of temperature similarly than the coefficients calculated using the data from this campaign (temperature range from **8**$^\circ$ **C** to **37**$^\circ$ **C**). The values of the coefficients are summarized in Table 4-1.

We have also extended our analysis using the data recorded since the previous campaign. As shown in Figs. 4-13 and 4-14, these new coefficients perform slightly better than the current coefficients. For this reason, we have used the new coefficients in the final ICF.

Table 4-1 – Temperature Coefficients. The final coefficients are calculated using the data recorded since the previous campaign. Coefficients are normalized to slit#2

	slit#2	**slit#3**	**slit#4**	**slit#5**	**slit#6**
Current	0.0000	-0.2600	-0.4700	-0.9600	-2.0400
Calculated	0.0000	-0.3000	-0.6500	-1.2000	-2.5200
Final	0.0000	-0.2418	-0.4848	-0.9968	-2.1730

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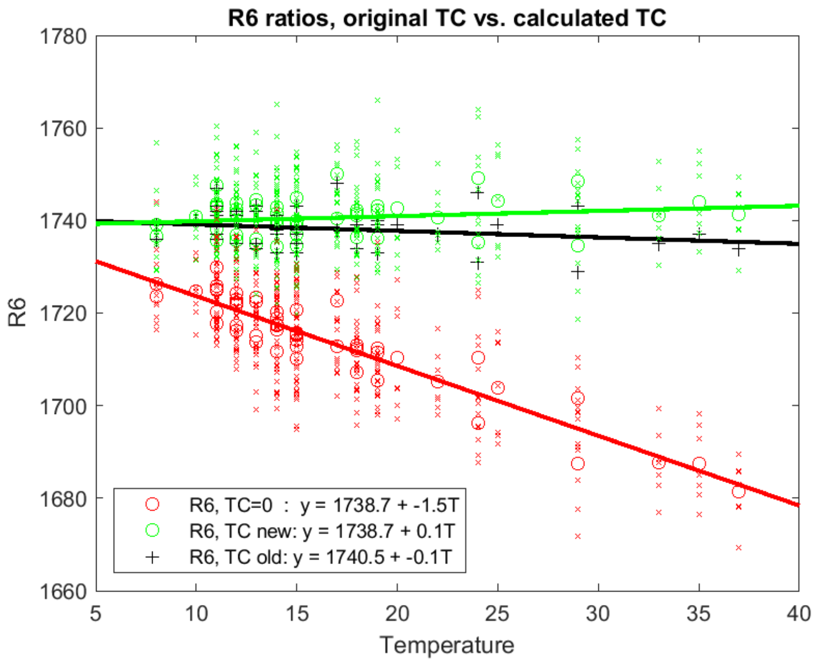


Figure 4-12 – Temperature coefficients' performance. Red circles represent standard lamp R6 ratios calculated from raw counts without temperature correction (temperature coefficients set to 0). Black crosses and green circles represent standard lamp R6 ratios corrected with original and calculated temperature coefficients, respectively. Data corresponds to the present campaign.

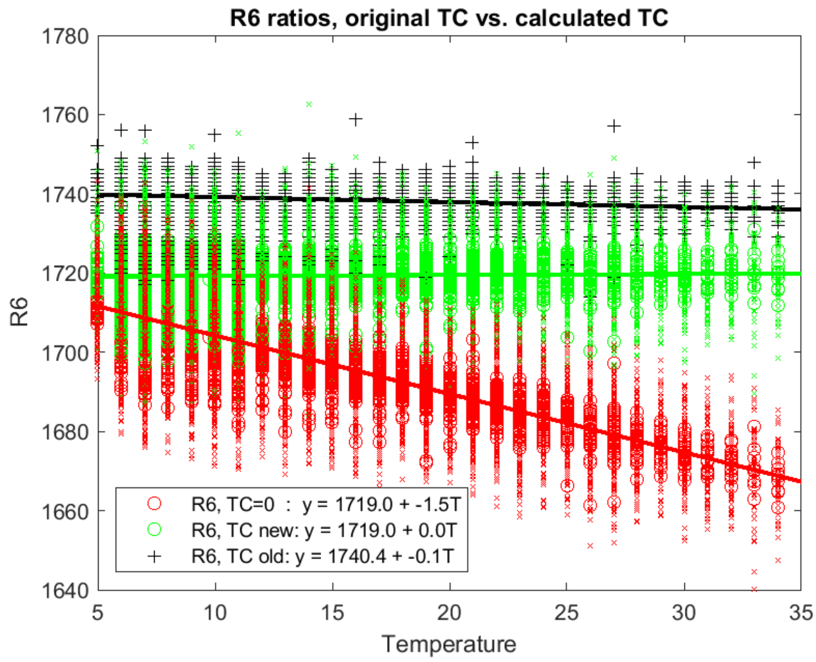


Figure 4-13 – **Same as Fig. 4-12 but for the whole period between calibration campaigns.**

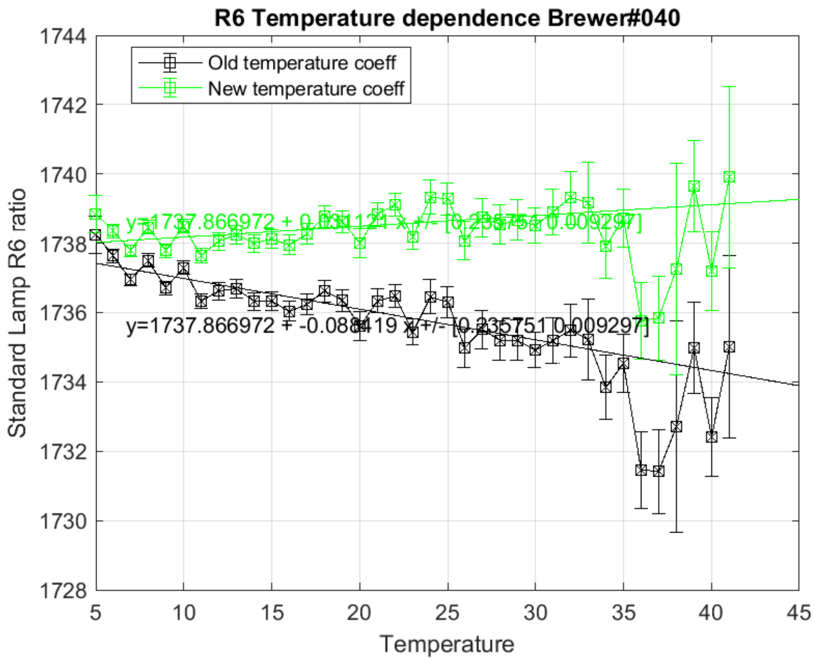


Figure 4-14 – **Standard lamp R6 (MS9) ratio as a function of temperature. We plotted R6 ratio recalculated with the original (black) and the new (green) temperature coefficients**

4.6 Attenuation Filter Characterization

4.6.1 Attenuation Filter Correction

The filter's spectral dependence affects the ozone calculation because the Brewer software assumes that their attenuation is wavelength-neutral. We can estimate the correction factor needed for this non-linearity by multiplying the attenuation of every filter and every wavelength by the ozone weighting coefficients.

During the calibration period, a total of **46** FI tests were analyzed to calculate the attenuation for every filter and slit. Fig. 4-15 shows the results of these tests, and Table 4-2 shows the calculated ETC corrections for each filter.

The FI analysis shows a different behaviour for filters 1 and 4. However, filter 1 is used only at large optical masses, where the non-linearity of the filters has no effect, and filter 4 is rarely used. Taking this into account, we recommend continuing with no filter correction on the ETC.

Table 4-2 – **ETC correction due to Filter non-linearity. Median value, mean values and, 95% confidence intervals are calculated using bootstrap technique**

	filter#1	filter#2	filter#3	filter#4	filter#5
ETC Filt. Corr. (median)	-2	-25	-18	10	-22
ETC Filt. Corr. (mean)	-3	-14.9	-19	9.7	-16.1
ETC Filt. Corr. (mean 95% CI)	[-14.1 8.7]	[-26.9 -2.1]	[-29.3 -6.5]	[-1.3 21]	[-37.6 4.7]

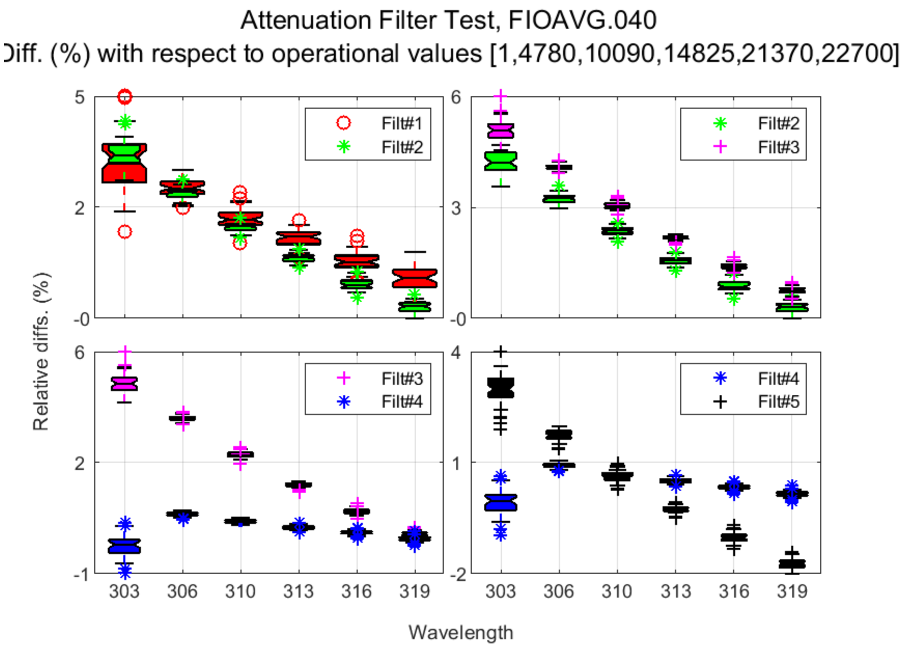


Figure 4-15 – Notched box-plot for the calculated attenuation relative differences of neutral density filters with respect to operational values. We show for each subplot relative differences corresponding to correlative filters (color box-plots). Solid lines and boxes mark the median, upper and lower quartiles. The point whose distance from the upper or lower quartile is 1 times larger than the interquartile range is defined as outlier.

4.7 Wavelength Calibration

4.7.1 Cal-Step determination

The sun scan routine takes DS ozone measurements by moving the micrometer about 15 steps below and above the ozone reference position (wavelength *Calibration step-number*). A Hg test is required before and after the measurement to assure the correct wavelength setting during the *sun scan* test. Ozone *versus* step number ideally shows a parabolic shape with a maximum at the ozone reference position. With this choice, small wavelength shifts ($\approx \pm 2$ steps) do not affect the ozone value. This optimal micrometer position is a near-linear function of the ozone slant path at the time of the scan, see Fig. 4-16

Previous to the campaign, 32 sun-scan (SC) tests covering a ozone slant path range from 400 to 1200 DU were collected, see Fig. 4-17)). No additional SC measures are required during the campaign as Brewer DAV#040 routinely operates from Davos station. The calculated Cal-Step Number (CSN) was about 2 step lower than the value in the current configuration: **941** *vs.* **943**. Taking this into account, we suggest keeping the current CSN, **943**.

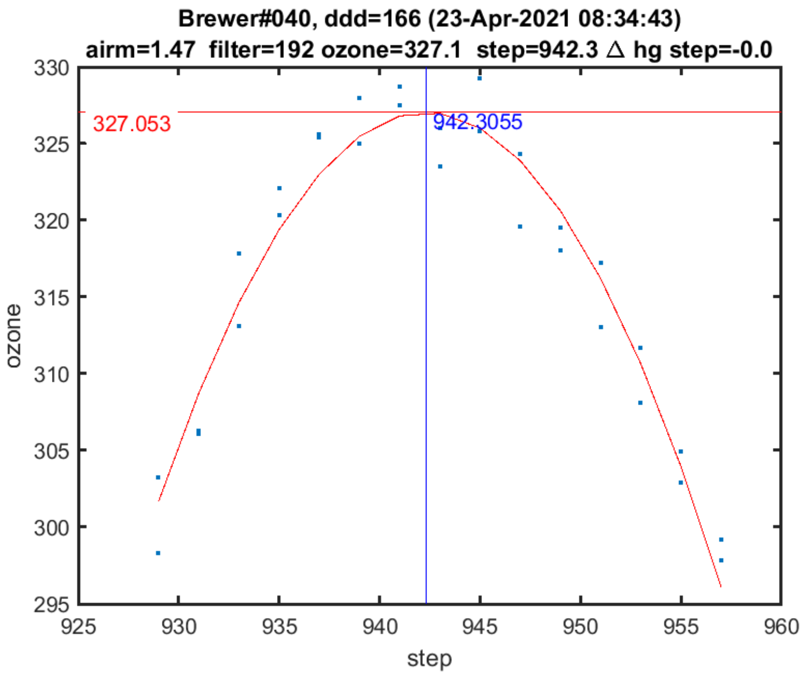


Figure 4-16 – **Ozone measurements moving the micrometer 15 step around the operational CSN defined in the initial configuration**

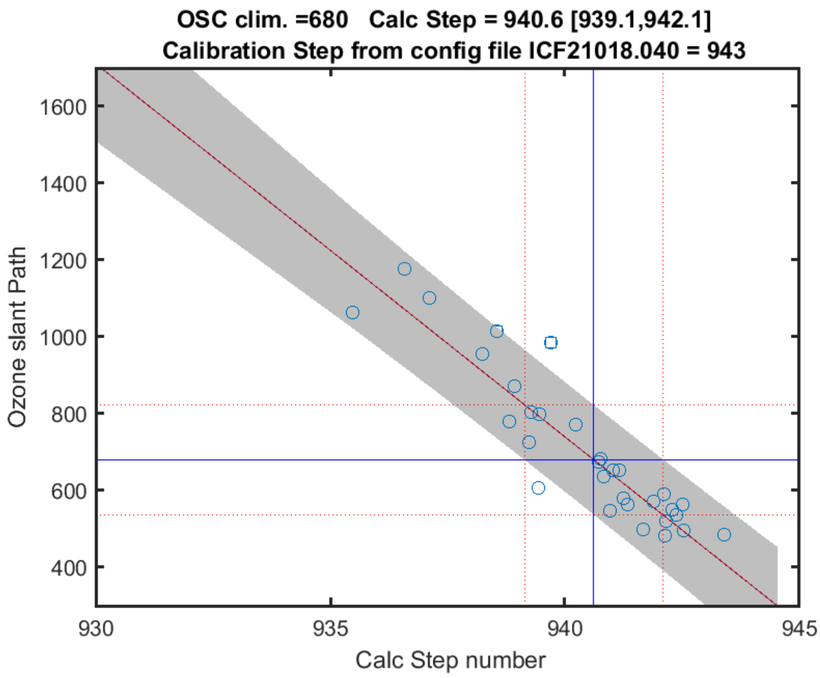


Figure 4-17 – Ozone Slant Path *vs* Calc – Step number. Vertical solid line marks the calculated *Cal Step Number* for a climatological OSC equal to 680 (horizontal solid line). Grey area represents a 95% confidence interval

4.7.2 Dispersion Test

We analyzed the dispersion tests carried out in the previous and present calibration campaigns. For all of them, we processed data from Mercury and Cadmium spectral lamps, using cubic functions to adjust the micrometer step number to wavelength positions. The results of this historical analysis are summarized in Table 4-3.

In particular, for the current campaign, Fig. 4-18 shows that the cubic fitting was good for all the dispersion tests, with residuals being lower than 0.1 Å in most of the slits. For the dispersion tests, Table 4-4 provides individual wavelength resolution, ozone absorption coefficient, sulfur dioxide absorption coefficient, and Rayleigh absorption for the operational CSN and those at ± 1 step.

An absorption coefficient equal to **0.335** is suggested in the final configuration.

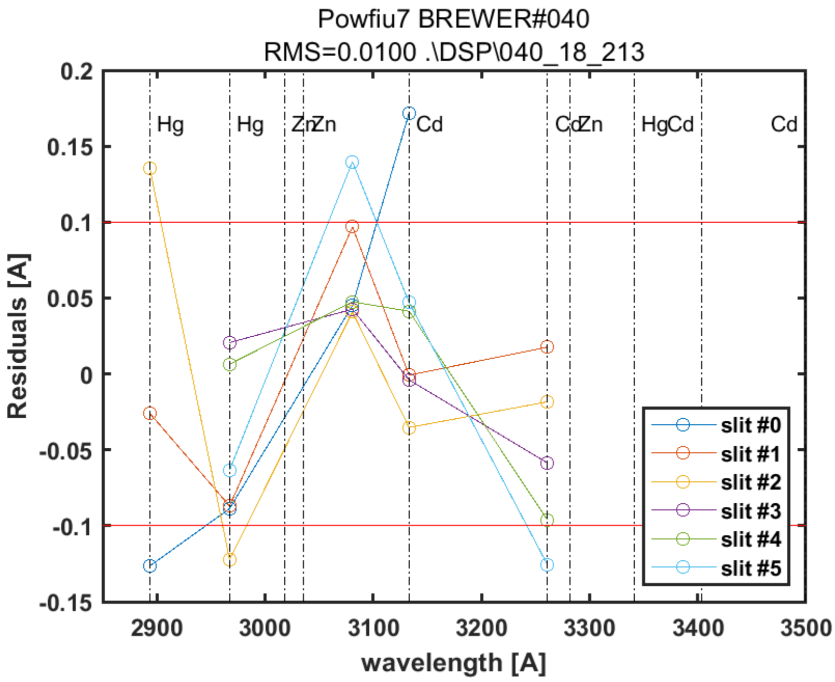


Figure 4-18 – 2021 residuals of cubic fit

Table 4-3 – **Absorption coefficients from the cubic fitting**

	Calc-step	O3abs coeff.	SO2abs coeff.	O3/SO2
Current	943	0.3350	2.3500	1.1415
06-Jul-2016	943	0.3375	3.1187	1.1375
10-Jul-2016	943	0.3377	3.1271	1.1384
19-Jul-2017	943	0.3370	3.1188	1.1370
01-Aug-2018	943	0.3332	3.1285	1.1259
05-Aug-2018	943	0.3376	3.1228	1.1356
18-Nov-2020	943	0.3327	3.1305	1.1257
21-Jun-2021	943	0.3331	3.1511	1.1238
14-Jul-2021	943	0.3371	3.1424	1.1347
Final	943	0.3350	2.3500	1.1415

Table 4-4 – **2021 dispersion derived constants from the cubic fitting**

step= 942	slit#0	slit#1	slit#2	slit#3	slit#4	slit#5
WL(A)	3022.79	3063.03	3100.66	3135.14	3168.04	3200.12
Res(A)	4.1305	5.7135	5.5947	5.7953	5.6908	5.4846
O3abs(1/cm)	3.0592	1.7787	1.004	0.67427	0.37539	0.29245
Ray abs(1/cm)	5117.0844	4832.0841	4583.7188	4370.293	4178.3254	4001.3955
SO2abs(1/cm)	8.2833	5.6247	2.4314	1.8791	1.0549	0.60657
step= 943	slit#0	slit#1	slit#2	slit#3	slit#4	slit#5
WL(A)	3022.86	3063.1	3100.73	3135.2	3168.1	3200.19
Res(A)	4.1304	5.7134	5.5946	5.7952	5.6907	5.4845
O3abs(1/cm)	3.056	1.7772	1.0037	0.67394	0.37542	0.29195
Ray abs(1/cm)	5116.5734	4831.6149	4583.2854	4369.89	4177.9494	4001.0441
SO2abs(1/cm)	8.2645	5.6435	2.4396	1.8685	1.056	0.60439
step= 944	slit#0	slit#1	slit#2	slit#3	slit#4	slit#5
WL(A)	3022.93	3063.17	3100.79	3135.27	3168.17	3200.25
Res(A)	4.1303	5.7133	5.5945	5.7952	5.6905	5.4844
O3abs(1/cm)	3.0525	1.7757	1.0034	0.67352	0.37544	0.29142
Ray abs(1/cm)	5116.0624	4831.1458	4582.8522	4369.4871	4177.5735	4000.6927
SO2abs(1/cm)	8.2425	5.6621	2.4477	1.8576	1.057	0.60219
step	O3abs	Rayabs	SO2abs	O3SO2Abs	Daumont	Bremen
942	0.33815	86287.2351	3.1352	1.1379	0.34874	0.34012
943	0.33714	86266.2497	3.1424	1.1347	0.34777	0.33913
944	0.3361	86245.2699	3.1495	1.1314	0.34677	0.33811

4.7.3 Umkehr

For the Umkehr calibration, only the lines shorter than 3400 Å were used. The Umkehr offset is calculated by forcing the wavelength of slit #4 at the ozone position to be the same as on slit #1 at the Umkehr setting. The Umkehr offset calculated is **2424**. Table 4-5 summarizes the dispersion test for umkehr: wavelength, resolution and ozone absorption coefficient.

Table 4-5 – **2021 Umkehr dispersion constants**

step= 943	slit#0	slit#1	slit#2	slit#3	slit#4	slit#5
WL(A)	3023	3063	3101	3135	3168	3200
Res(A)	4.1304	5.7134	5.5946	5.7952	5.6907	5.4845
O3abs(1/cm)	3.056	1.7772	1.0037	0.67394	0.37542	0.29195
Ray abs(1/cm)	0.51166	0.48316	0.45833	0.43699	0.41779	0.4001
step= 2424	slit#0	slit#1	slit#2	slit#3	slit#4	slit#5
WL(A)	3125	3164	3200	3233	3265	3296
Res(A)	3.9804	5.5924	5.4642	5.6905	5.4616	5.3259
O3abs(1/cm)	0.69542	0.39527	0.29208	0.12183	0.060993	0.033408
Ray abs(1/cm)	0.4433	0.42025	0.40011	0.38275	0.36709	0.35263

4.8 ETC Transfer

Based on the Lambert-Beer law, the total ozone column in the Brewer algorithm can be expressed as:

$$X = \frac{F - ETC}{\alpha\mu} \tag{1}$$

where F are the measured double ratios corrected for Rayleigh effects, α is the ozone absorption coefficient, μ is the ozone air mass factor, and ETC is the extra-terrestrial constant. The F, α and ETC parameters are weighted functions at the operational wavelengths with weighting coefficients $w = [0, 1, -0.5, -2.2, 1.7]$ for slits 1 to 5, with nominal wavelengths equal to $[306.3, 310.1, 313.5, 316.8, 320.1]$ nm.

The transfer of the calibration scale (namely ETC) is done side by side with the reference instrument. Once we have collected enough near-simultaneous direct sun ozone measurements, we calculate the new extraterrestrial constant after imposing the condition that the measured ozone will be the same for simultaneous measurements. In terms of the previous equation for ozone, this leads to the following condition:

$$ETC_i = F_i - X_i^{reference}\alpha\mu \tag{2}$$

For a good characterized instrument, the ETC determined values show a Gaussian distribution and the mean value is used as the instrument constant. One exception to this rule is the single monochromator Brewer models (MK-II and MK-IV) which are affected by stray light.

For single monochromator Brewers, the ETC distribution shows (see Fig.4-20) a tail at the lower ETC values for high Ozone Slant Column (OSC, the product of the total ozone content by the airmass). For this type of Brewer, only the stray-light free region is used to determine the ETC, generally from 300 to 900 DU OSC, depending on the instrument.

The stray light effect can be corrected if the calibration is performed against a double monochromator instrument, assuming that it can be characterized following a power law of the ozone slant column

$$F = F_o + k(X\mu)^s \tag{3}$$

where F are the true counts and F_o the measured ones.

$$ETC_i = ETC_o + k(X\mu)^s \tag{4}$$

where ETC_o is the ETC for the stray light free OSC region and k and s are retrieved from the reference comparison (Figure 4-22) . These parameters, determined in several campaigns, have been found to be stable and independent of the ozone calibration.

As the counts (F) from the single brewer are affected by stray light, the ozone is calculated using an iterative process:

$$X_{i+1} = X_i + \frac{k(X_i\mu)^s}{\alpha\mu} \tag{5}$$

Only one iteration is needed for the conditions of the intercomparison, up to 1500 DU. For ozone slant path measurements in the 1500–2000 DU range, two iterations are enough to correct the ozone.

Brewers are calibrated with the one parameter (1P) ETC transfer method: only the ozone ETC constant is transferred from the reference instrument. The so-called “two parameters calibration method” (2P), where both the ozone absorption coefficient and the ETC are calculated from the reference, is also obtained and serves as a quality indicator of the calibration. We consider a calibration optimal when both ETC values agree within 10 units, and the ozone absorption coefficient calculated from the dispersion tests and obtained with the 2P method agree within ± 2 micrometer steps, or approx. ± 0.002 atm.cm^{-1}. This range represents a total ozone difference of about 0.5% at airmass equal to 2, and total ozone of 300 DU.

The ETC is obtained by comparison with the reference brewer **IZO#185** using near-simultaneous measurements during **10** days (two measurements are considered near-simultaneous if they are taken less than **3.5** minutes apart). Measurements with airmass difference greater than 3% were removed from the analysis.

4.8.1 Initial Calibration

For the evaluation of initial status of Brewer DAV#040, we used the period from days **188** to **197** which correspond with **257** near-simultaneous direct sun ozone measurements. As shown in Fig. 4-19, the current calibration constants produce ozone values slightly higher than the reference instrument (0%). When the ETC is corrected taking into account the difference between the SL and R6 reference (SL correction), the results do not improve.

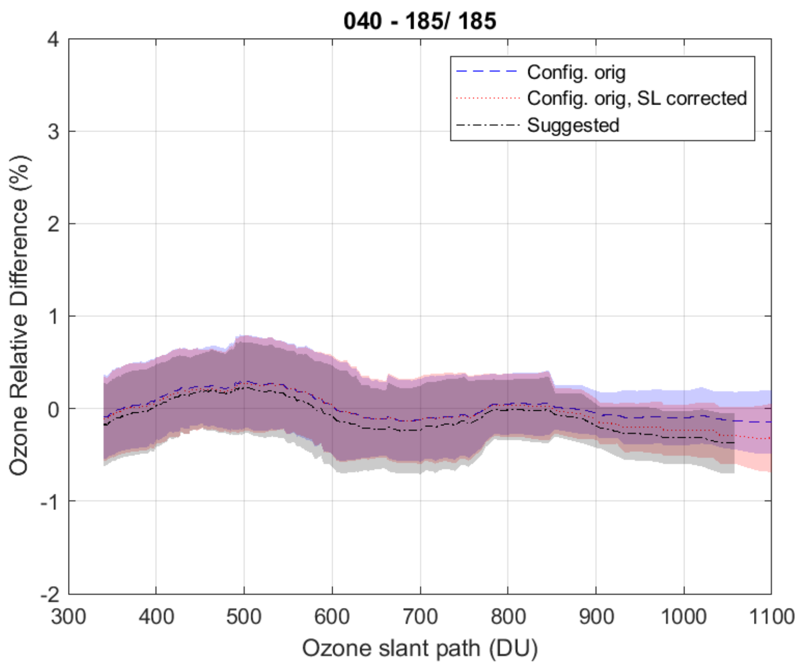


Figure 4-19 – Mean direct-sun ozone column percentage difference between Brewer DAV#040 and Brewer IZO#185 as a function of ozone slant path.

4.8.2 Final Calibration

A new ETC value has been calculated (see Fig. 4-20) also using the **257** simultaneous direct sun measurements from days **188** to **197**. The new value, calculated for OSC lower than 1, is 1 units higher than the current ETC value (**2963**). Therefore, we recommend using this new ETC, together with the new proposed standard lamp reference ratios, **1739** for R6. We updated the new calibration constants in the ICF provided. Of course, the new ETC has been calculated taking into account the new suggested dead time, **3.6**·**10**$^{-8}$, and temperature coefficients.

The ETC value in the final ICF corresponds to the 1P transfer. As shown in Table 4-6, the agreement between the 1P and 2P ETCs is only slightly above the maximum tolerance limit of 10 units.

Mean daily total ozone values and relative differences with respect to IZO#185 for the original and the final configurations are shown in Table 4-7.

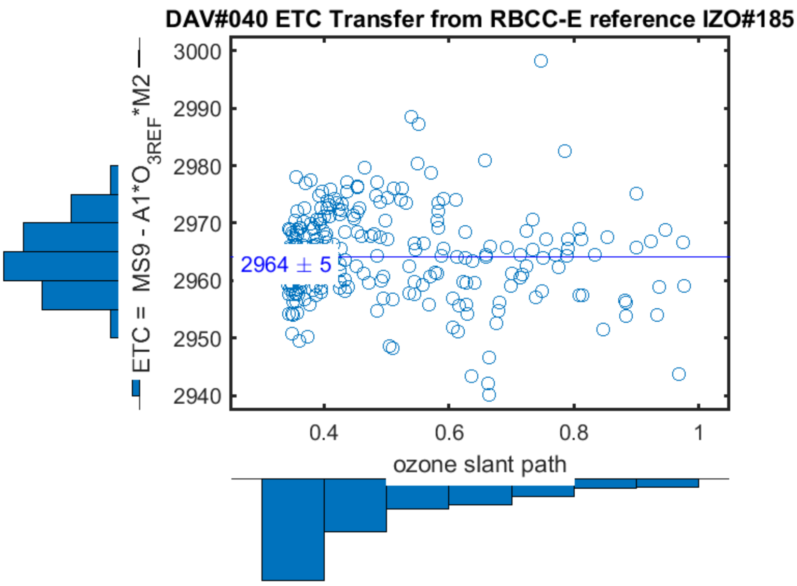


Figure 4-20 – **Mean direct-sun ozone column percentage difference between Brewer DAV#040 and Brewer IZO#185 as a function of ozone slant path, with OSC up to 1.**

Table 4-6 – **Comparison between the results of the 1P and 2P ETC transfer methods for the final days.**

	ETC 1P	ETC 2P	O3Abs final	O3Abs 2P
up to OSC=1	2964	2961	3350	3357
full OSC range	2964	2961	3350	3357

Table 4-7 – **Daily mean ozone and relative differences with respect to the reference, with the original and final (the latter, in the columns marked with a star) calibrations. Data from the final days.**

	Day	O3#185	std	N	O3#040	std	rd	O3(*)#040	std(*)	rd(*)
07-Jul-2021	188	305.2	1.4	6	306.2	1.8	0.3	305.9	1.7	0.2
08-Jul-2021	189	340.6	0	1	338.7	0	-0.6	338.3	0	-0.7
09-Jul-2021	190	323.9	2.1	22	324.5	2.6	0.2	324.1	2.4	0.1
10-Jul-2021	191	312.6	2.1	85	312.9	2	0.1	312.7	2	0
11-Jul-2021	192	315.6	3.3	49	316.9	3	0.4	316.6	3	0.3
12-Jul-2021	193	305.5	2.6	87	305	2.7	-0.2	304.8	2.9	-0.2
13-Jul-2021	194	322.5	0.3	6	321.8	1.5	-0.2	321.5	1.4	-0.3
14-Jul-2021	195	351.8	0	1	355.8	0	1.1	354.8	0	0.9
15-Jul-2021	196	338.5	1.9	2	337.3	0.8	-0.4	337.2	1.1	-0.4
16-Jul-2021	197	NaN	NaN	0	336.2	1	NaN	336.1	1	NaN

4.8.3 Stray light Correction

Stray light typically affect the ozone measurements of single-monochromator Brewers (models MK-II and MK-IV). To correct this effect, we use the following formula, which depended on the OSC.

$$X_{i+1} = X_i + \frac{k(X_i \mu)^s}{\alpha \mu} \tag{6}$$

Due to the location of the Davos station in a valley, the maximum OSC during the campaign barely exceed 1000 DU. For these OSC values, the stray light effect is small (see Fig. 4-22) and the uncertainties of k and s parameters are too high ($k = -3.9 \pm 2.7$ and $s = 1.43 \pm 7.53$). Therefore it has not been possible to determine the effect of stray light in this campaign, and we recommend continuing using the characterisation performed in the 2018 campaign.

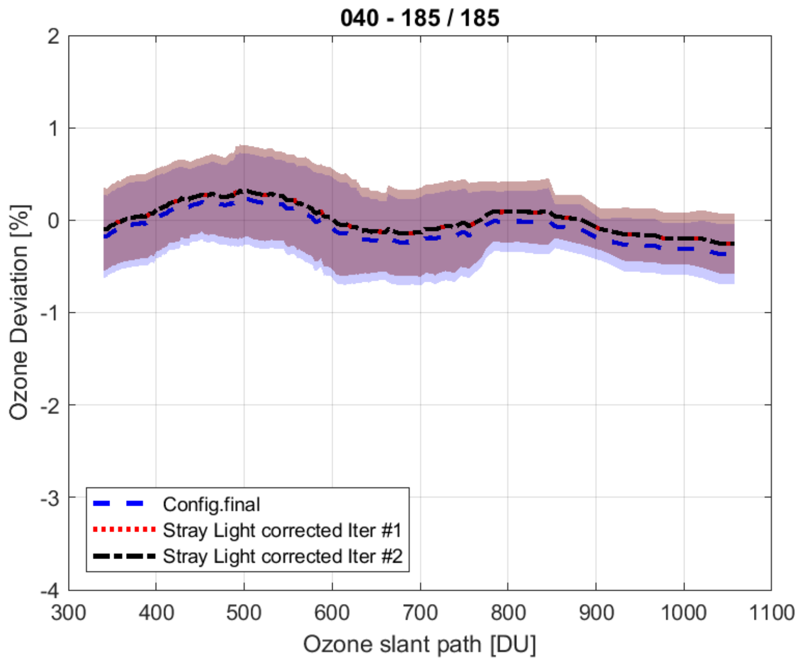


Figure 4-21 – Ratio respect to the reference when final constant are applied and stray light correction is introduced from empirical model is applied.

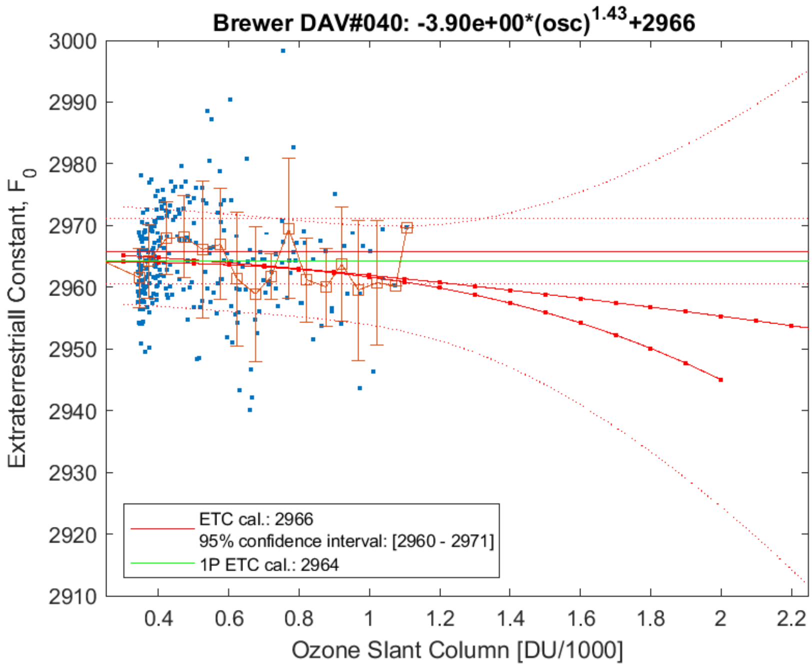
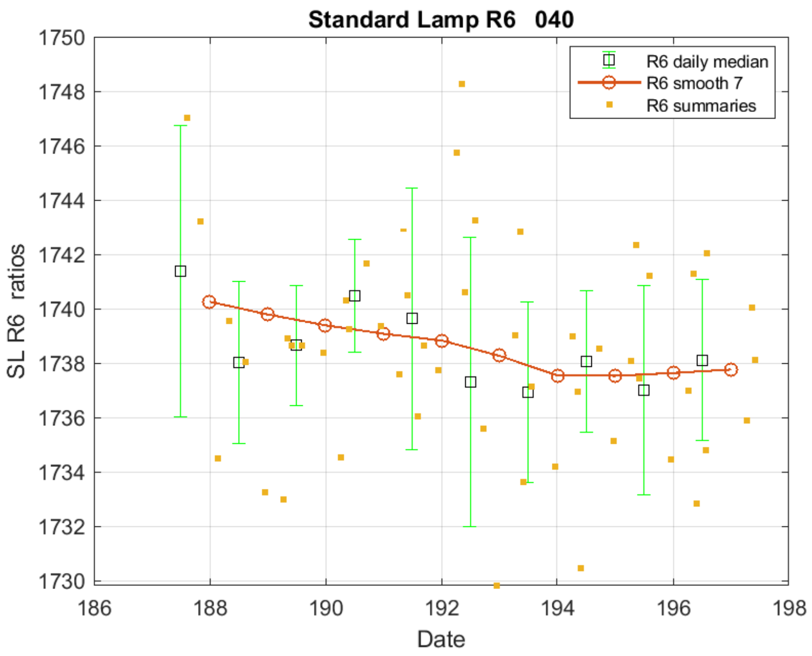


Figure 4-22 – **Stray light empirical model determination**

4.8.4 Standard Lamp Reference Values

The reference values of standard lamp ratios during the calibration period were **1739** for R6 (Figure 4-23) and **3275** for R5 (Figure 4-24).



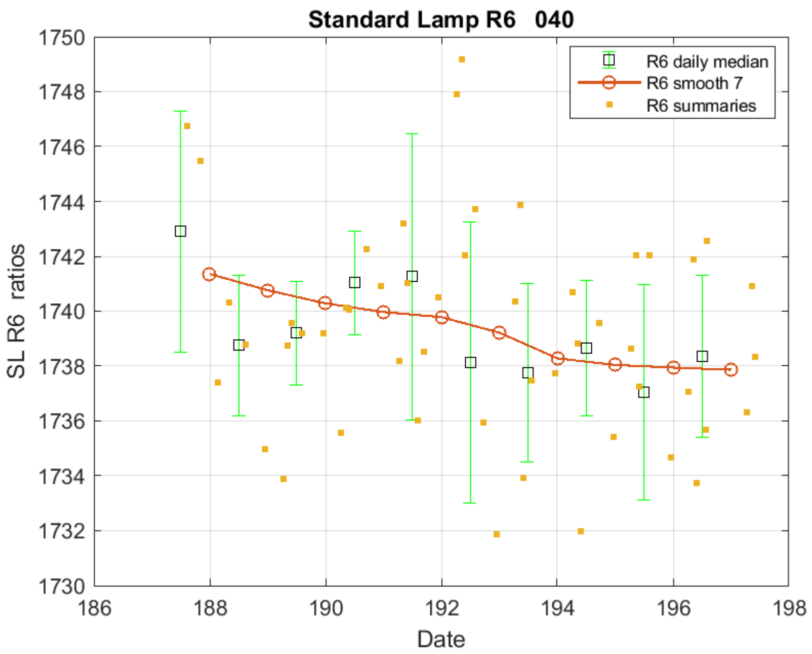
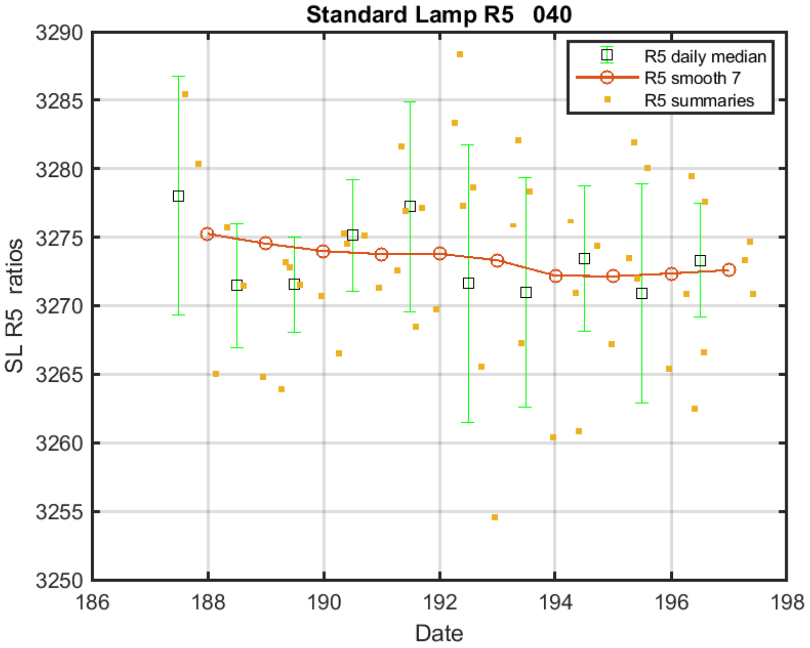


Figure 4-23 – Standard Lamp O_3 R6 ratios: daily mean and standard deviation (squares), seven day running mean (circle) and individual tests (black dots). Reprocessed using old (top) and new (bottom) instrumental constants



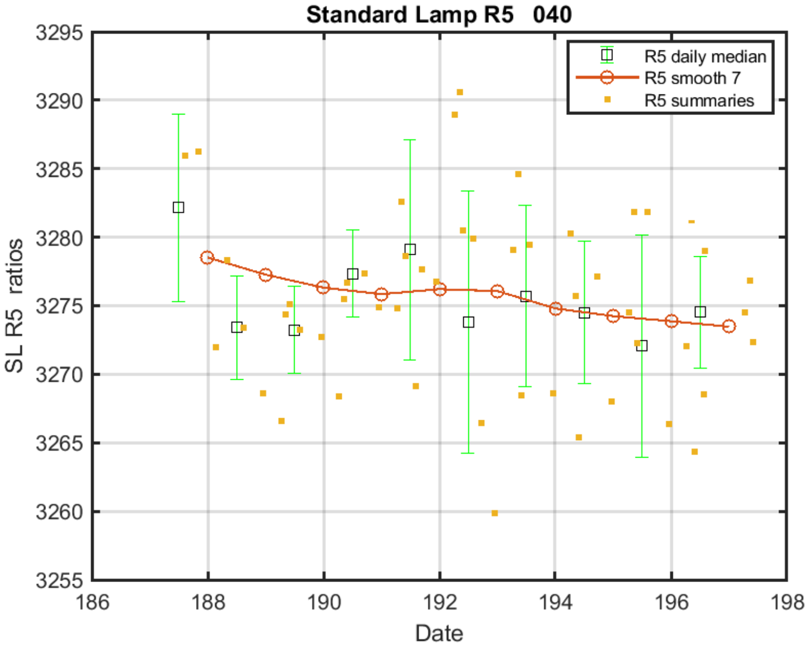


Figure 4-24 – Standard Lamp SO_2 R5 ratios: daily mean and standard deviation (squares), seven day running mean (circle) and individual tests (black dots). Reprocessed using old (top) and new (bottom) instrumental constants

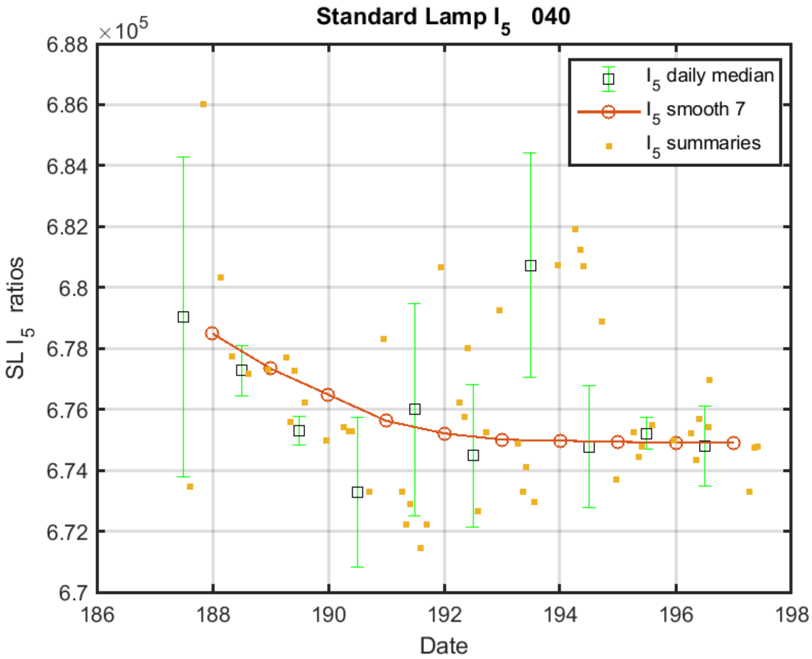


Figure 4-25 – Standard Lamp intensity: daily mean and standard deviation (squares), seven day running mean (circle) and individual tests (black dots)

4.9 Configuration

4.9.1 Instrument constant file

	Initial (ICF21018.040)	Final (ICF18821.040)
o3 Temp coef 1	0	0
o3 Temp coef 2	-0.26	-0.2418
o3 Temp coef 3	-0.47	-0.4848
o3 Temp coef 4	-0.96	-0.9968
o3 Temp coef 5	-2.04	-2.173
Micrometer steps/deg	0	0
O3 on O3 Ratio	0.335	0.335
SO2 on SO2 Ratio	2.35	2.35
O3 on SO2 Ratio	1.1415	1.1415
ETC on O3 Ratio	2963	2965
ETC on SO2 Ratio	2988	2988
Dead time (sec)	3.7e-08	3.6e-08
WL cal step number	943	943
Slitmask motor delay	74	74
Umkehr Offset	2424	2424
ND filter 0	0	0
ND filter 1	4780	4780
ND filter 2	10090	10090
ND filter 3	14825	14825
ND filter 4	21370	21370
ND filter 5	22700	22700
Zenith steps/rev	2816	2816
Brewer Type	2	2
COM Port #	1	1
o3 Temp coef hg	0	0
n2 Temp coef hg	1747	1747
n2 Temp coef 1	3283	3283
n2 Temp coef 2	0	0
n2 Temp coef 3	0	0
n2 Temp coef 4	0	0
n2 Temp coef 5	0	0
O3 Mic #1 Offset	3383	3383
Mic #2 Offset	0	0
O3 FW #3 Offset	0	0
NO2 absn Coeff	0	0
NO2 ds etc	0	0
NO2 zs etc	0	0
NO2 Mic #1 Offset	0	0
NO2 FW #3 Offset	0	0
NO2/O3 Mode Change	0	0
Grating Slope	0	0
Grating Intercept	0	0
Micrometer Zero	2686	2686
Iris Open Steps	250	250
Buffer Delay (s)	0.6	0.6
NO2 FW#1 Pos	0	0
O3 FW#1 Pos	256	256
FW#2 Pos	0	0
uv FW#2 Pos	64	64
Zenith Offset	28	28
Zenith UVB Position	2104	2104

4.10 Daily Summary report

Day	osc range	O3#185	std	N	O3#040	std	rd	O3(*)#040	std(*)	rd(*)
188	1000>osc>700	303.9	0	1	304.4	0	0.2	304.3	0	0.2
188	700>osc>400	305	1.5	5	306.5	1.8	0.5	306.2	1.7	0.4
189	osc<400	340.1	0	1	338.5	0	-0.5	338.3	0	-0.5
190	700>osc>400	323.1	1.8	16	323.1	2.3	0	323.4	2.3	0.1
190	osc<400	326.4	0.6	5	326.7	1	0.1	326.6	1	0.1
191	1500>osc>1000	309.3	0	2	309.7	0.3	0.1	309.6	0.2	0.1
191	1000>osc>700	310.5	2.2	12	310.2	1.9	-0.1	310.2	2	-0.1
191	700>osc>400	311.3	1.3	23	311.8	1.6	0.2	311.9	1.8	0.2
191	osc<400	314.4	1	41	313.8	1.1	-0.2	313.9	1.1	-0.2
192	1000>osc>700	315.4	0.3	3	316.8	2.5	0.4	316.5	2.5	0.4
192	700>osc>400	317	2.2	27	317.9	1.5	0.3	317.5	1.6	0.2
192	osc<400	315.6	4.2	15	316.3	4	0.2	315.7	4.1	0
193	1500>osc>1000	304.4	0	1	303.1	0	-0.4	302.7	0	-0.5
193	1000>osc>700	303.4	2.2	14	303.3	2.5	0	303	2.6	-0.1
193	700>osc>400	304.4	3	31	304.3	3.3	0	303.9	3.5	-0.1
193	osc<400	306.5	1.1	34	306.5	1.2	0	306.2	1.2	-0.1
194	1000>osc>700	322.7	0	2	322.6	0.4	0	322.4	0.4	-0.1
194	700>osc>400	322.5	0.3	4	321.4	1.8	-0.3	321.1	1.6	-0.4
195	osc<400	352.1	0	1	356.1	0	1.1	354.8	0	0.7
196	1000>osc>700	337.2	0	1	337.9	0	0.2	338	0	0.2
196	700>osc>400	339.9	0	1	336.8	0	-0.9	336.4	0	-1
197	1500>osc>1000	335.3	1	3	NaN	NaN	NaN	335.2	0.5	0
197	1000>osc>700	336.2	0.5	5	NaN	NaN	NaN	336.6	0.8	0.1

4.11 Summary Plots

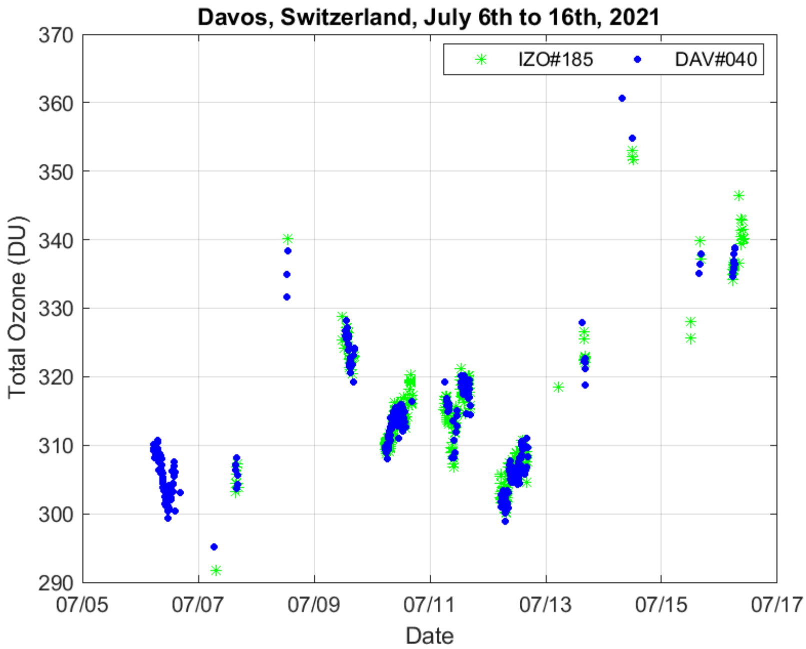
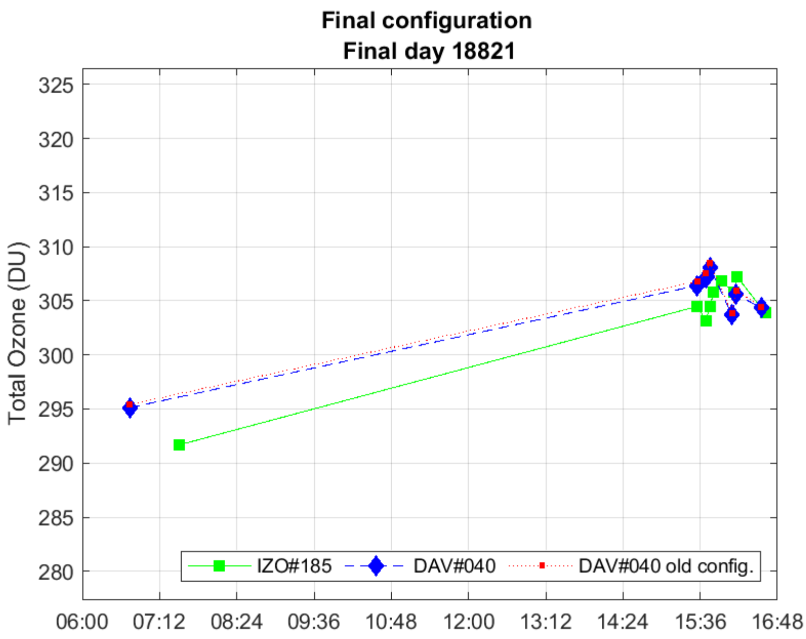
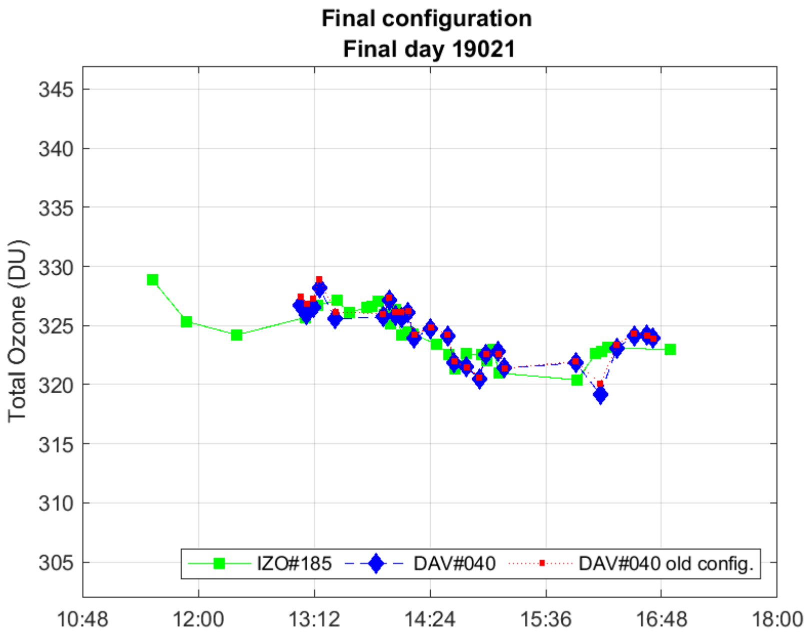
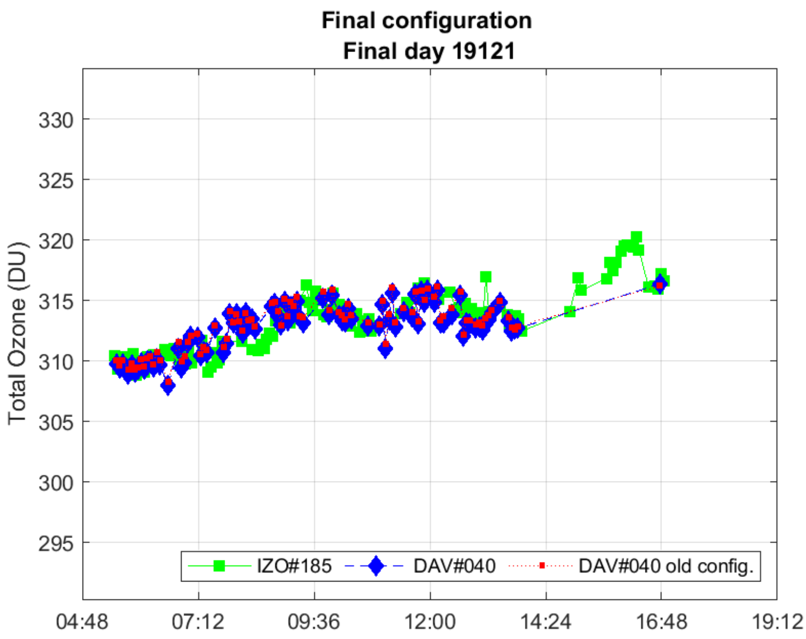
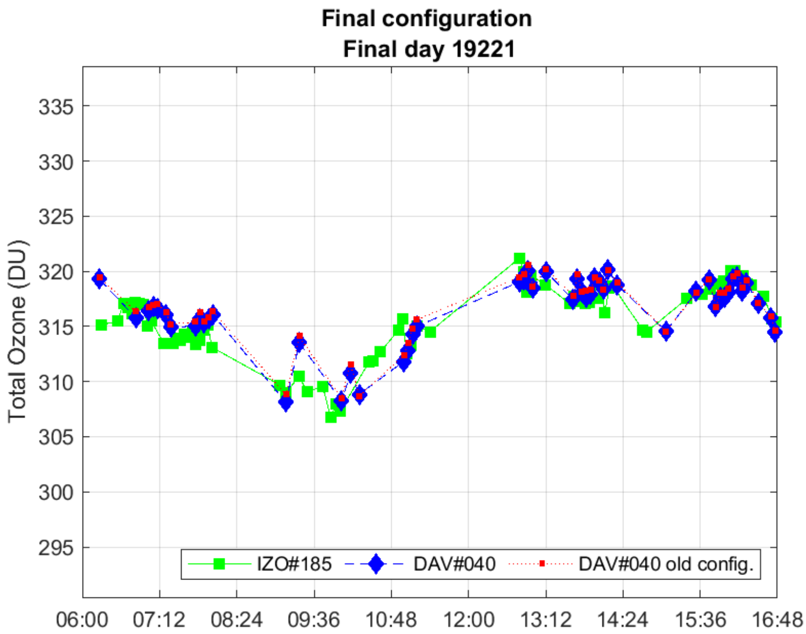


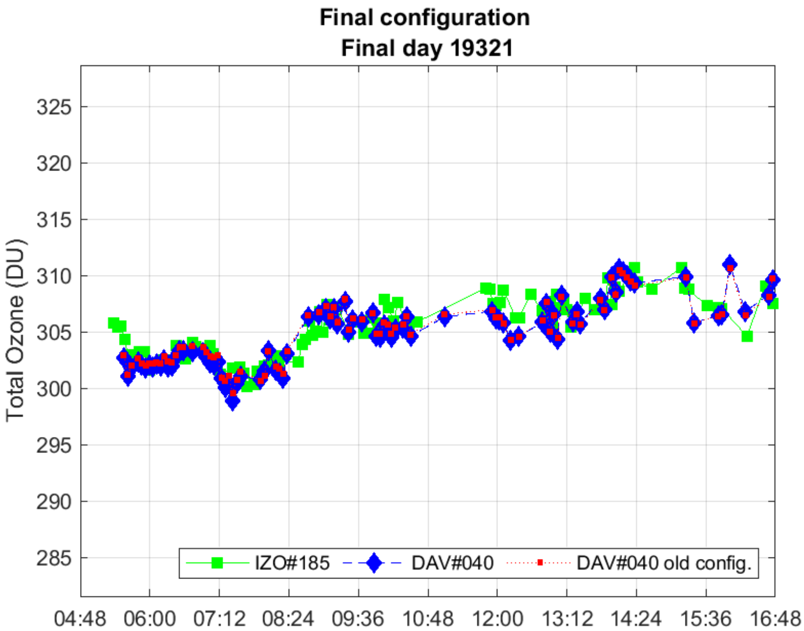
Figure 4-26 – Overview of the intercomparison. Brewer DAV#040 data are evaluated using final constants (blue circles)

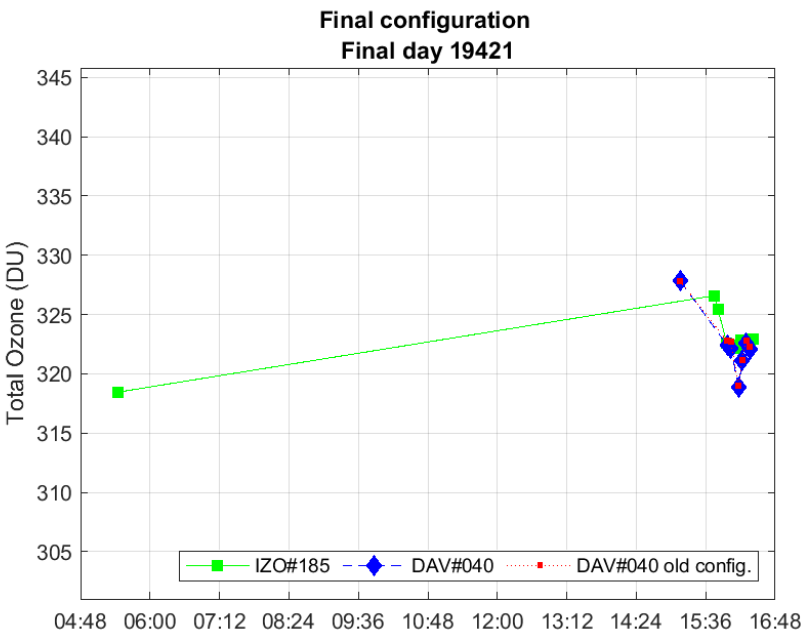

Final configuration
Final day 18821
Total Ozone (DU)
325
320
315
310
305
300
295
290
285
280
06:00
07:12
08:24
09:36
10:48
12:00
13:12
14:24
15:36
16:48
IZO#185
DAV#040
DAV#040 old config.

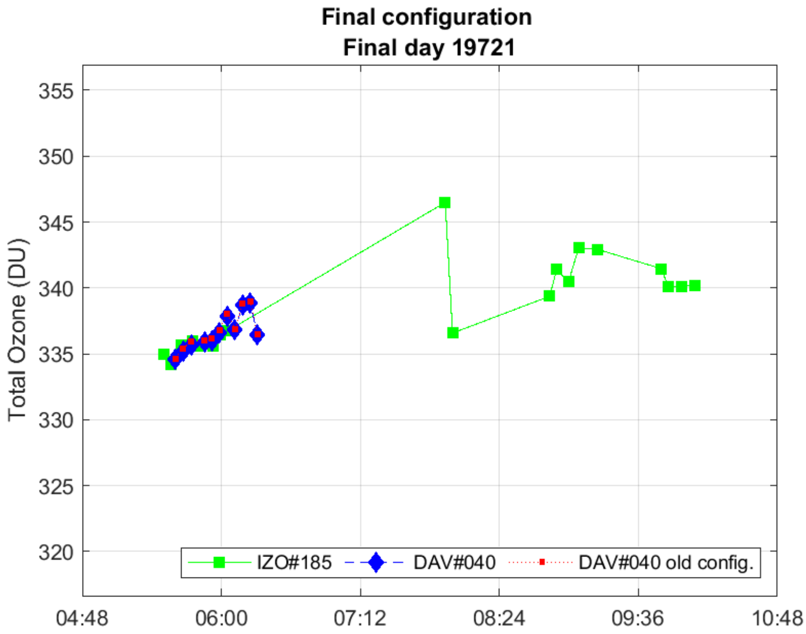

Final configuration
Final day 19021
Total Ozone (DU)
345
340
335
330
325
320
315
310
305
10:48
12:00
13:12
14:24
15:36
16:48
18:00
IZO#185
DAV#040
DAV#040 old config.


Final configuration
Final day 19121
330
325
320
315
310
305
300
295
Total Ozone (DU)
IZO#185
DAV#040
DAV#040 old config.
04:48
07:12
09:36
12:00
14:24
16:48
19:12


Final configuration
Final day 19221
335
330
325
320
315
310
305
300
295
Total Ozone (DU)
IZO#185
DAV#040
DAV#040 old config.
06:00
07:12
08:24
09:36
10:48
12:00
13:12
14:24
15:36
16:48


Final configuration
Final day 19321
Total Ozone (DU)
325
320
315
310
305
300
295
290
285
IZO#185
DAV#040
DAV#040 old config.
04:48
06:00
07:12
08:24
09:36
10:48
12:00
13:12
14:24
15:36
16:48


Final configuration
Final day 19421
Total Ozone (DU)
345
340
335
330
325
320
315
310
305
IZO#185
DAV#040
DAV#040 old config.
04:48
06:00
07:12
08:24
09:36
10:48
12:00
13:12
14:24
15:36
16:48



Final configuration
Final day 19721
Total Ozone (DU)
355
350
345
340
335
330
325
320
04:48
06:00
07:12
08:24
09:36
10:48
IZO#185
DAV#040
DAV#040 old config.

5 Brewer DAV#072

5.1 Calibration Summary

The Fifteenth Intercomparison Campaign of the Regional Brewer Calibration Center Europe (RBCC-E) was held from July 6th to the 16th, 2021, at the Physikalisch-Meteorologisches Observatorium PMOD (Davos, Switzerland).

Brewer DAV#072 participated in the campaign in the period from July 6th to 16th. The campaign days of Brewer DAV#072 correspond to Julian days 187 – 197.

For final calibration purposes, we used **176** simultaneous DS ozone measurements taken from day **188** to **197**. Power supply was replaced on day 192 (11th July) for Brewer DAV#072, but this change did not affected the measurement, therefore we used the same data set for the evaluation of the initial status as for the final calibration.

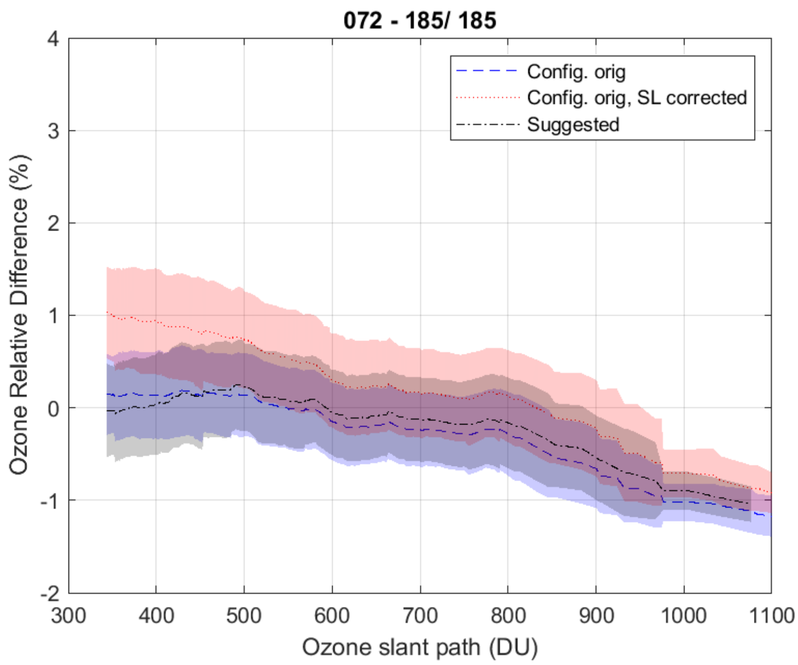


Figure 5-1 – Mean DS ozone column percentage difference between Brewer DAV#072 and Brewer IZO#185, plotted as a function of the ozone slant path. Results for the current (issued in the previous calibration campaign) configuration are show in blue; the red dotted line corresponds to the same configuration, but with the standard lamp correction applied; the black line corresponds to results obtained with the updated configuration proposed in the current campaign. The shadow areas represent the standard deviation of the mean. The plot corresponds to the final days of the campaign.

As shown in Fig. 5-1, the current ICF (ICF20018.072, blue dashed line) produces ozone values with an average difference of around −0.1% with respect to the reference instrument. This is a rather small difference, and highlights the stability of Brewer DAV#072. The SL correction (Fig. 5-1, red dotted line) does not improve the comparison with Brewer IZO#185 during this campaign. However, peaks have been observed both in R6 with HV with a good correlation. It has also been observed that these peaks are reduced when the equipment is turned off and then turned on. For this reason, the power supply was replaced on day 192 (11th July), and we recommend applying the SL correction from the 2018 calibration to the current one.

Being a Mk. II model, Brewer DAV#072 measurements are typically affected by stray light. However, as show in Fig. 5-2, the ozone slant path during the campaign barely exceeds 1000 DU, which is a low value for which the effect of stray light is small, and the errors when characterizing the stray light are very high. We recommend therefore to continue using the stray light coefficients determined in the last Intercomparison Campaign.

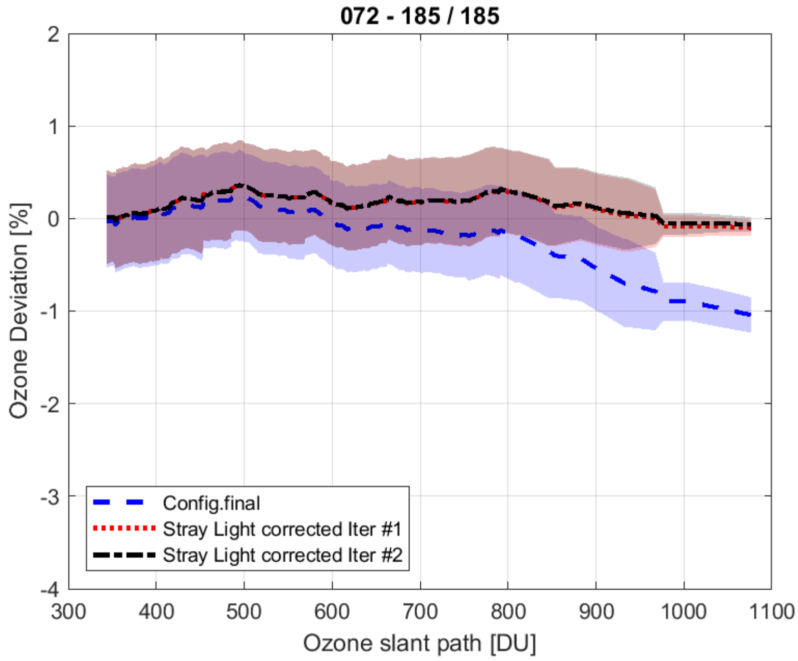


Figure 5-2 – Mean DS ozone column percentage difference between Brewer DAV#072 and Brewer IZO#185, plotted as a function of the ozone slant path. Results for the final (issued in this calibration campaign) configuration are show in blue; the red dotted line corresponds to the same configuration, but with the stray light correction obtained after 1 iteration; the black line corresponds to results obtained after 2 iterations. The shadow areas represent the standard deviation of the mean. The plot corresponds to the final days of the campaign.

The dead time (DT) shows a difference of 1 ns between the current value and the measured during the campaign, respectively $3.7{\cdot}10^{-8}$ and $3.8{\cdot}10^{-8}$. Despite being a very small change, its effect can be significant for single Brewers, and therefore we recommend updating the DT value.

We appreciate a small but clear temperature dependence in the standard lamp observations, which indicates the temperature coefficients can be improved. It's worth to note that for high temperatures, a non-linear effect is observed.

The neutral density filters didn't show nonlinearity in the attenuation's spectral characteristics. We have not applied any correction to filters.

The sun-scan tests (SC) before the campaign shows a clear difference with the operative cal step value. However, the historical results for this instruments showed that changing the CSN gets worse and hence we suggest keeping the current CSN.

We suggest continuing to use the current Ozone Absorption Coefficient, with a value of 0.3377.

All the other parameters analyzed (run/stop tests, Hg lamp intensity, CZ & CI files,...) show reasonable results.

Taking into account all this, we suggest some changes to the configuration of Brewer DAV#072.

5.1.1 Recommendations and Remarks

1. The R6 standard lamp test results from Brewer DAV#072 have been stable most of the time during the last 3 years. After updating the DT and temperature coefficients update, the old R6 reference value, 1960, can be updated to **1949**.
2. We suggest a new R5 reference value of **3722**.
3. We suggest updating the DT to $\mathbf{3.8{\cdot}10}^{-8}$ seconds, which is one units less than the value proposed in the last intercomparison.
4. We have found that new temperature coefficients improve the behaviour of the instrument, and we include them in the final ICF for the campaign.
5. The neutral density filters show the same behaviour as in the previous campaign, and we suggest retaining the same correction factors.
6. Finally, we suggest updating the ETC value from **3215** to **3210**.

5.1.2 External links

Configuration File

http://rbcce.aemet.es/svn/campaigns/dav2021/bfiles/072/ICF18821.072

Calibration Report

https://docs.google.com/spreadsheets/d/12-4EoZzJkJDv5Pgpdt3PNZlZLXahvdlubhqOyijRack/edit#gid=1901261701

Calibration Reports Detailed

Historic and instrumental

http://rbcce.aemet.es/svn/campaigns/dav2021/latex/072/html/cal_report_072a1.html

Temperature & Filter

http://rbcce.aemet.es/svn/campaigns/dav2021/latex/072/html/cal_report_072a2.html

Wavelength

http://rbcce.aemet.es/svn/campaigns/dav2021/latex/072/html/cal_report_072b.html

ETC transfer

http://rbcce.aemet.es/svn/campaigns/dav2021/latex/072/html/cal_report_072c.html

5.2 Instrument History: Analysis of Average files

5.2.1 Standard Lamp Test

As shown in Figure 5-3 and 5-4, the standard lamp shows some peaks over the last three years. These variations correlate with changes also observed in the HV. However, the current and voltage values of the standard lamp remain stable, so probably the observed peaks correspond to real changes in the instrument. After the campaign, the mean R6 and R5 values are respectively **1949** and **3722**.

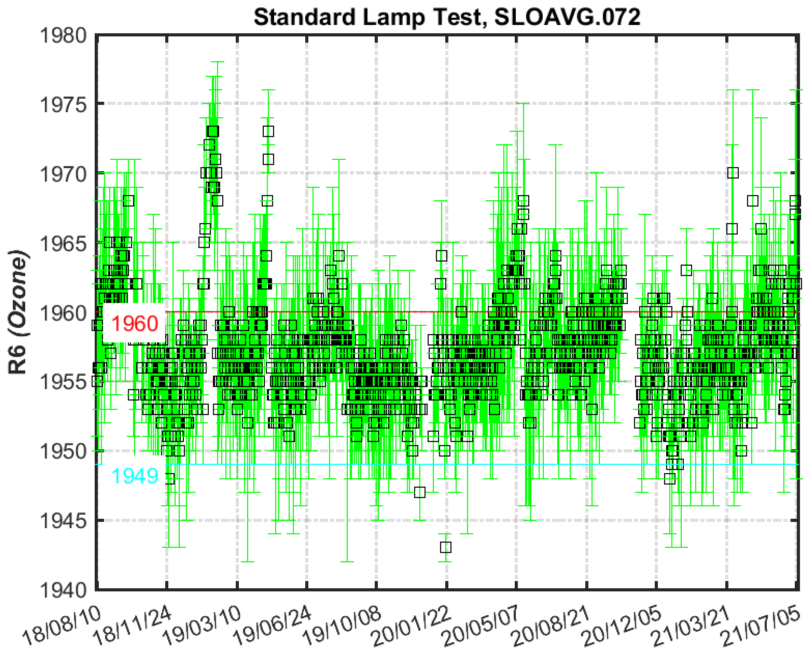


Figure 5-3 – Standard Lamp test R6 (Ozone) ratios. Horizontal lines are labeled with the original and final reference values (red and blue lines, respectively)

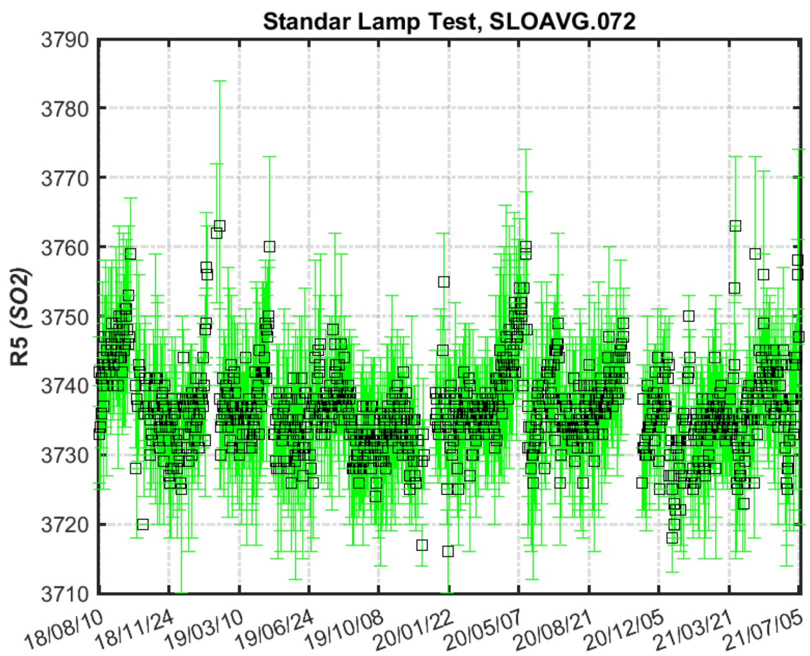


Figure 5-4 – **Standard Lamp test R5 (SO_2) ratios**

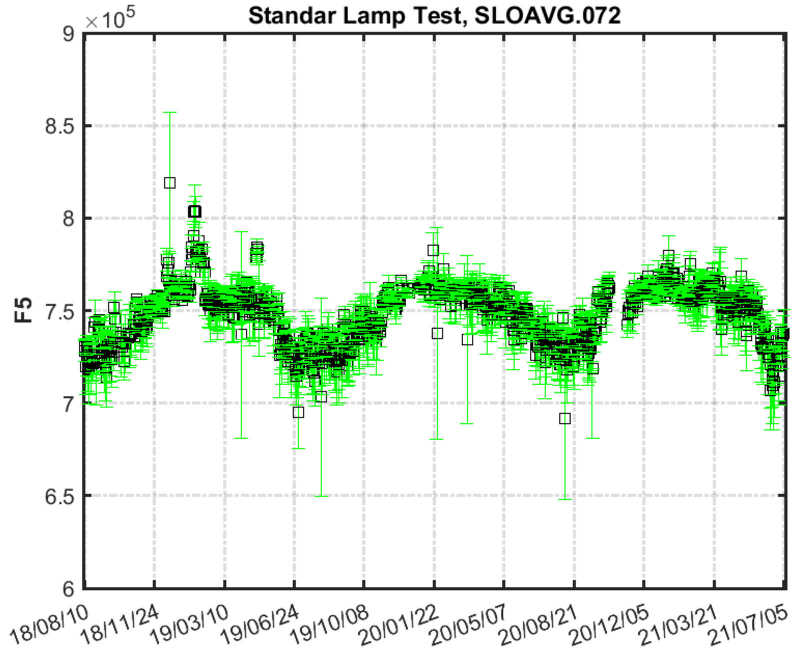


Figure 5-5 – **SL intensity for slit five.**

5.2.2 Run Stop and Dead Time

Run stops test values are within the test tolerance limits, see Fig. 5-6. The Hg slit is the noisier, but inside the normal range of this slit.

As shown in Fig. 5-7, the current DT reference value of $\mathbf{3.7{\cdot}10}^{-8}$ seconds is just 1 ns smaller than the value recorded during the calibration period, $\mathbf{3.8{\cdot}10}^{-8}$s. This change, while small, is significant for single Brewers as DAV#072. Therefore, this new value has been used in the new ICF.

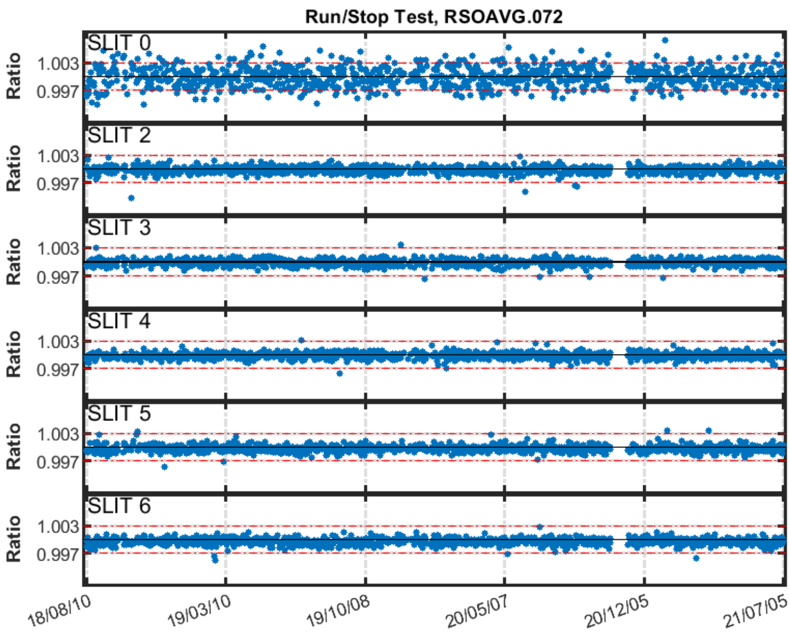


Figure 5-6 – Run/stop test

5.2.3 Analog Test

Fig. 5-8 shows some picks in HV since the last calibration. These picks have also been observed in the R6 parameter, calculated from the SL measurements, but they are neither observed in the current nor the voltage of the SL. It has also been observed that these peaks are reduced when the equipment is turned off and then turned on. For this reason, the power supply was replaced on day 192 (11th July), and we recommend applying the SL correction from the 2018 calibration to the current one.

5.2.4 Mercury Lamp Test

The intensity of the internal mercury lamp was reduced and stabilised as of May 2020, after an adjustment in the filter wheel #2, see Fig. 5-9. No other noticeable events have been observed in the last three years.

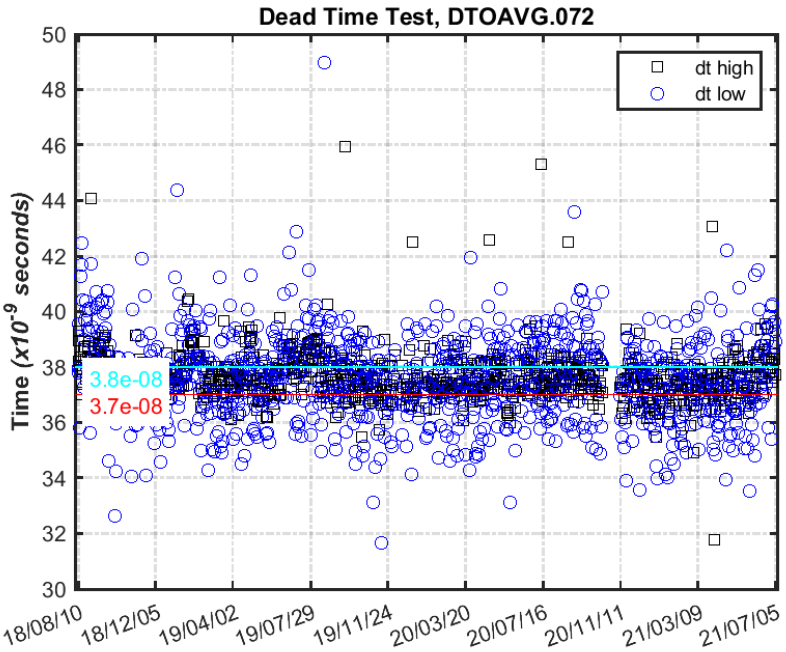


Figure 5-7 – **Dead Time test. Horizontal lines are labelled with the current (red) and final (blue) values.**

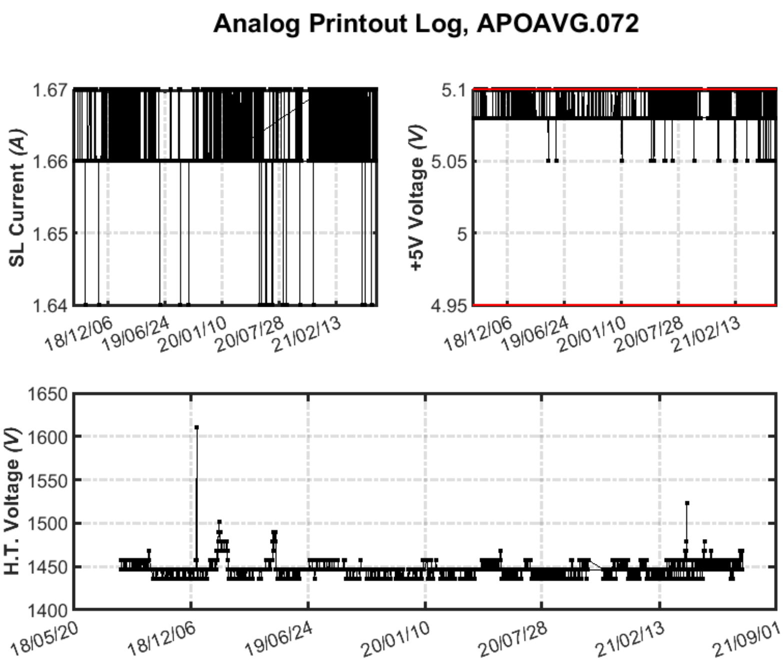


Figure 5-8 – **Analog voltages and intensity.**

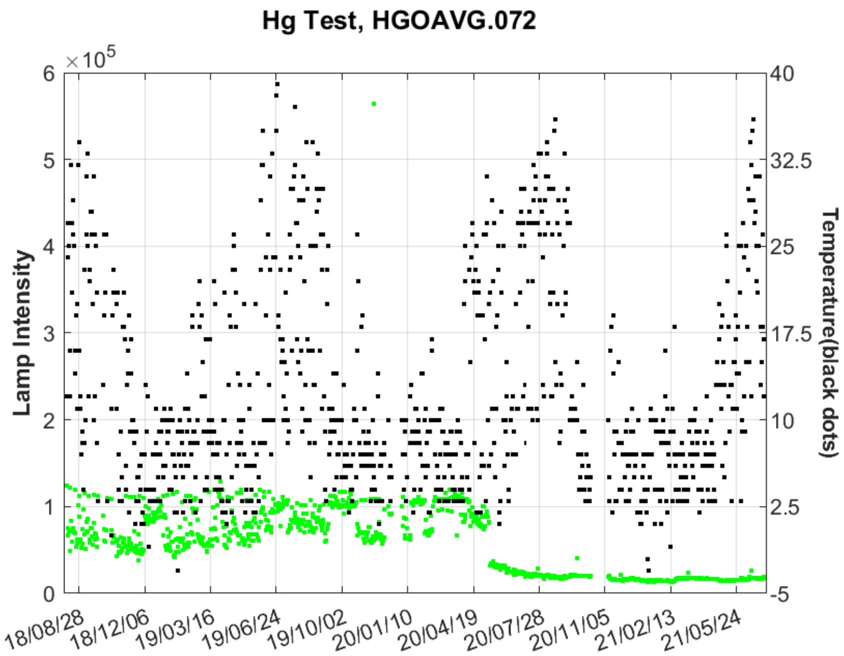


Figure 5-9 – Mercury lamp intensity (green squares) and Brewer temperature registered (black dots). Both parameters refer to maximum values for each day.

5.2.5 CZ scan on mercury lamp

We analyzed the scans performed on the 296.728 nm mercury line, in order to check both the wavelength settings and the slit function width. As a reference, the calculated scan peak, in wavelength units, should be within 0.013 *nm* from the nominal value, whereas the calculated slit function width should be no more than 0.65 *nm*. Analysis of CZ scans performed on Brewer **DAV#072** during the campaign show quite nice results, with the peak of the calculated scans within the accepted tolerance range. Regarding the slit function width, results are good, with FWHM parameter lower than 6.5 Å.

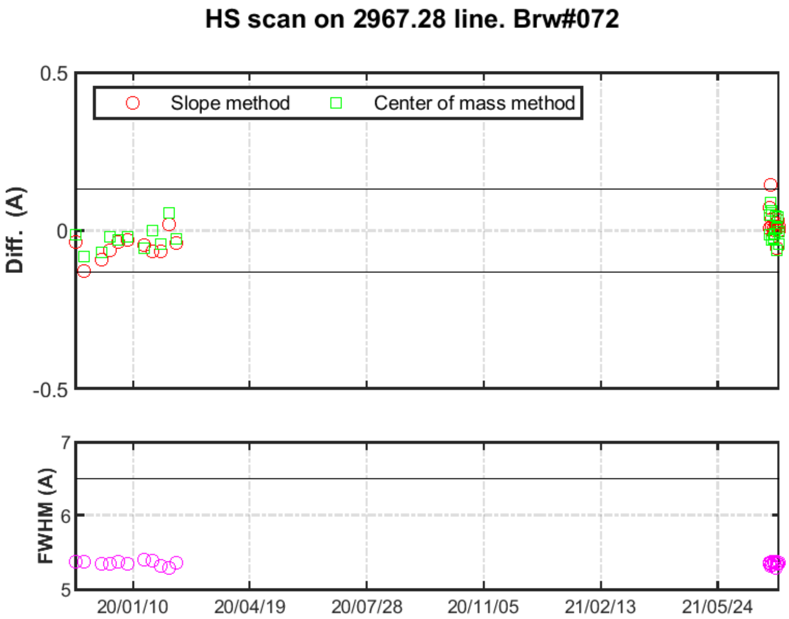


Figure 5-10 – CZ scan on 296.728 *nm* Hg line. Upper figure shows differences with respect to the reference line (solid lines represent the limit ± 0.013 *nm*) as computed by two different methods: slopes method (red circles) and center of mass method (green squares). Lower figure shows Full Width at Half Maximum value for each scan performed. Solid line represents the limit 0.65 *nm*

5.2.6 CI scan on internal *SL*

CI scans of the standard lamp recorded at different times can be compared to investigate whether the instrument has changed its spectral sensitivity. We shown in Fig. 5-11 percentage ratios of the Brewer **DAV#072** CI scans performed during the campaign relative to the scan CI18821.072. As it can be observed, the lamp intensity has varied respect to the reference spectrum around 2%. Similar variation have been observed in the daily R6 and R5 values. This behavior is normal for a SL lamp.

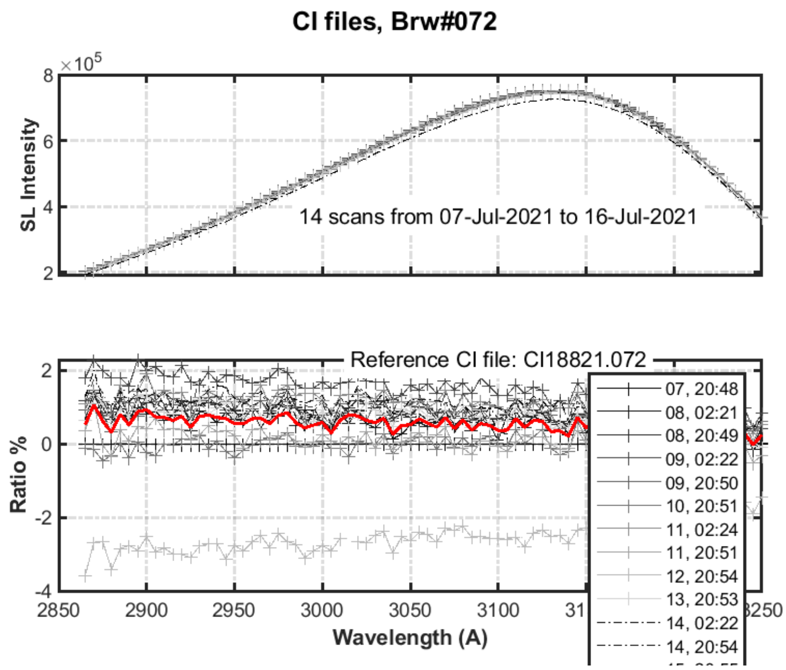


Figure 5-11 – **CI scan of Standard Lamp performed during the campaign days. Scans processed (upper panel) and relative differences with respect to a selected reference scan (lower panel). Red line represents the mean of all relative differences**

5.3 Absolute Temperature Coefficients

Temperature coefficients are determined using the standard lamp test. For every slit, the raw counts corrected for zero temperature coefficients are used in a linear regression against temperature with the slopes representing the instrument's temperature coefficients. From this we obtain the corrected *R6* and *R5* ratios to analyze the new temperature coefficients' performance.

As shown in Fig. 5-12, the current coefficients correct the effect of temperature similarly than the coefficients calculated using the data from this campaign (temperature range from **10**° **C** to **27**° **C**). The values of the coefficients are summarized in Table 5-1.

We have also extended our analysis using the data recorded since the previous campaign. As shown in Fig. 5-13 and 5-14, the new coefficients correct better the effect of temperature. Moreover, fig. 5-14 shows a non-linear behaviour at high temperatures. Only the linear part has been used to determine the temperature correction coefficients.

Table 5-1 – Temperature Coefficients. The final coefficients are calculated using the data recorded since the previous campaign. Coefficients are normalized to slit#2

	slit#2	slit#3	slit#4	slit#5	slit#6
Current	0.0000	-0.4968	-0.8072	-1.3838	-2.8861
Calculated	0.0000	-0.3000	-0.5000	-1.0000	-2.3000
Final	0.0000	-0.2400	-0.4900	-1.0000	-2.2600

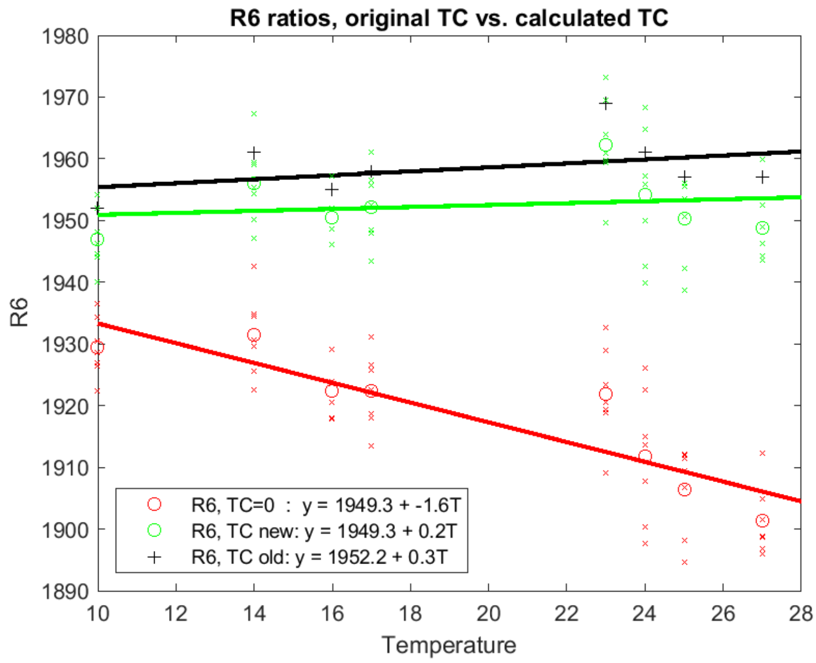


Figure 5-12 – Temperature coefficients' performance. Red circles represent standard lamp R6 ratios calculated from raw counts without temperature correction (temperature coefficients set to 0). Black crosses and green circles represent standard lamp R6 ratios corrected with original and calculated temperature coefficients, respectively. Data corresponds to the present campaign.

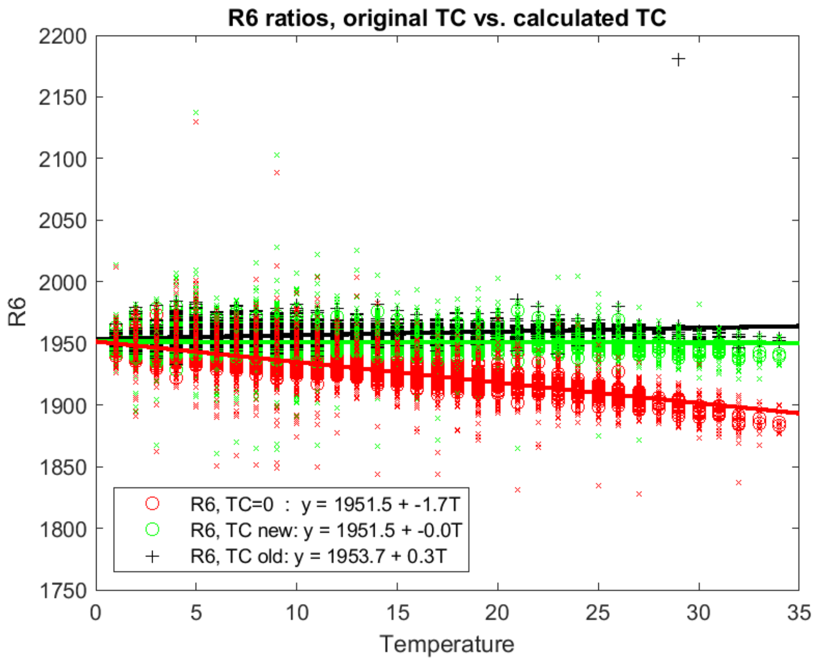


Figure 5-13 – **Same as Fig. 5-12 but for the whole period between calibration campaigns.**

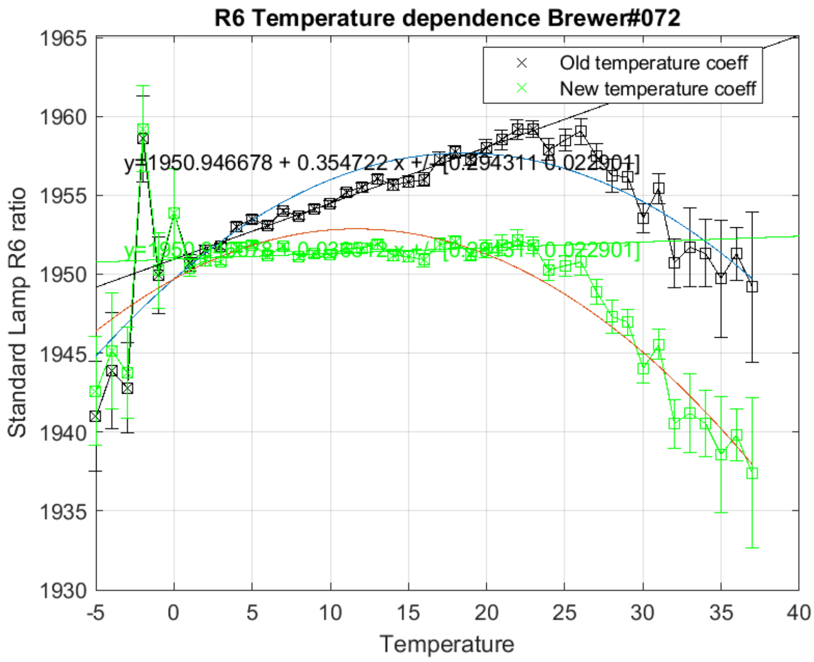


Figure 5-14 – Standard lamp R6 (MS9) ratio as a function of temperature. We plotted R6 ratio recalculated with the original (black) and the new (green) temperature coefficients

5.4 Attenuation Filter Characterization

5.4.1 Attenuation Filter Correction

The filter's spectral dependence affects the ozone calculation because the Brewer software assumes that their attenuation is wavelength-neutral. We can estimate the correction factor needed for this non-linearity by multiplying the attenuation of every filter and every wavelength by the ozone weighting coefficients.

During the calibration period, a total of **42** FI tests were analyzed to calculate the attenuation for every filter and slit. Fig. 5-15 shows the results of these tests, and Table 5-2 shows the calculated ETC corrections for each filter.

The FI analysis shows a different behaviour only for filter 5, which is rarely used. Despite this, the current ETC corrections perform well, and we recommend continuing with no filter correction on the ETC.

Table 5-2 – **ETC correction due to Filter non-linearity. Median value, mean values and, 95% confidence intervals are calculated using bootstrap technique**

	filter#1	filter#2	filter#3	filter#4	filter#5
ETC Filt. Corr. (median)	6	-3	1	2	-176
ETC Filt. Corr. (mean)	2.8	-2.9	-4.3	1.5	-170.7
ETC Filt. Corr. (mean 95% CI)	[-7.2 12.2]	[-13.5 7.1]	[-14.4 6.1]	[-8.1 11.3]	[-188.4 -151.1]

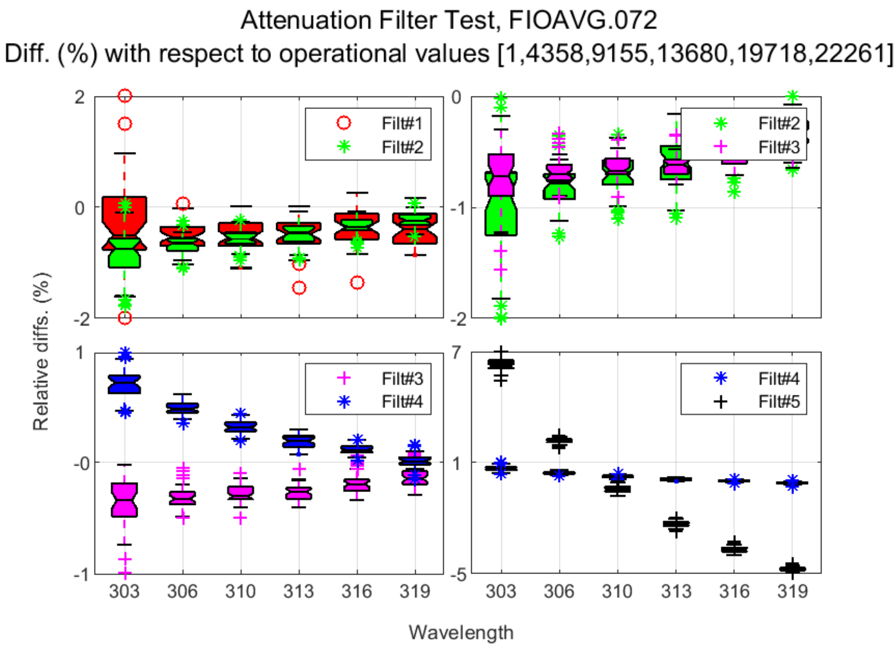


Figure 5-15 – Notched box-plot for the calculated attenuation relative differences of neutral density filters with respect to operational values. We show for each subplot relative differences corresponding to correlative filters (color box-plots). Solid lines and boxes mark the median, upper and lower quartiles. The point whose distance from the upper or lower quartile is 1 times larger than the interquartile range is defined as outlier.

5.5 Wavelength Calibration

5.5.1 Cal-Step determination

The sun scan routine takes DS ozone measurements by moving the micrometer about 15 steps below and above the ozone reference position (wavelength *Calibration step-number*). A Hg test is required before and after the measurement to assure the correct wavelength setting during the *sun scan* test. Ozone *versus* step number ideally shows a parabolic shape with a maximum at the ozone reference position. With this choice, small wavelength shifts ($\approx \pm 2$ steps) do not affect the ozone value. This optimal micrometer position is a near-linear function of the ozone slant path at the time of the scan, see Fig. 5-16

Previous to the campaign, 27 sun-scan (SC) tests covering a ozone slant path range from 400 to 1200 DU were collected, see Fig. 5-17)). The calculated Cal-Step Number (CSN) was 3 step lower than the value in the current configuration: **912** *vs.* **915**. However, the historical results for this instruments showed that changing the CSN gets worse and hence we suggest keeping the current CSN.

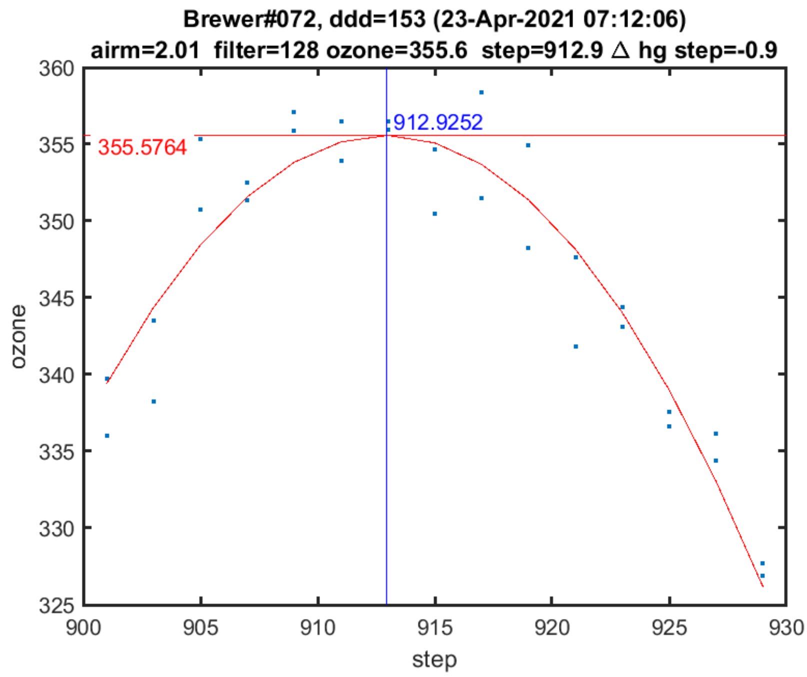


Figure 5-16 – Ozone measurements moving the micrometer 15 step around the operational CSN defined in the initial configuration

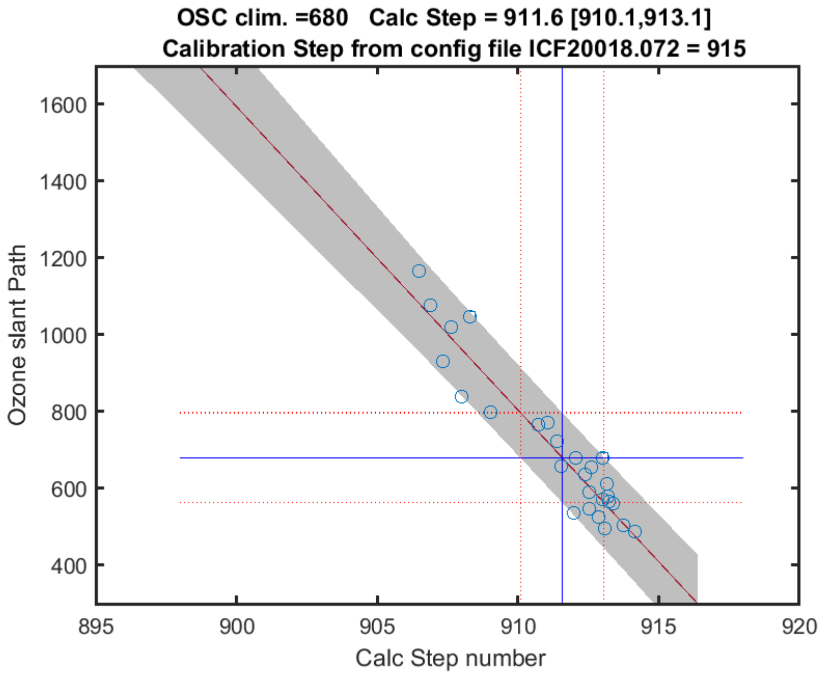


Figure 5-17 – Ozone Slant Path *vs* Calc – Step number. Vertical solid line marks the calculated *Cal Step Number* for a climatological OSC equal to 680 (horizontal solid line). Grey area represents a 95% confidence interval

5.5.2 Dispersion Test

We analyzed the dispersion tests carried out in the previous and present calibration campaigns. For all of them, we processed data from Mercury and Cadmium spectral lamps, using cubic functions to adjust the micrometer step number to wavelength positions. The results of this historical analysis are summarized in Table 5-3.

In particular, for the current campaign, Fig. 5-18 shows that the cubic fitting was good for all the dispersion tests, with residuals being lower than 0.1 Å in all slits. For the dispersion tests performed using the UV dome and the internal Hg lamp, Table 5-4 provides individual wavelength resolution, ozone absorption coefficient, sulfur dioxide absorption coefficient, and Rayleigh absorption for the operational CSN and those at ± 1 step.

An absorption coefficient equal to **0.3377** is suggested in the final configuration.

Table 5-3 – **Dispersion derived constants**

	Calc-step	O3abs coeff.	SO2abs coeff.	O3/SO2
Current	915	0.3377	2.3500	1.1415
27-Jun-2016	915	0.3381	3.2535	1.1353
19-Jul-2017	915	0.3373	3.2476	1.1331
01-Aug-2018	915	0.3398	3.2417	1.1406
12-Nov-2020	915	0.3410	3.2517	1.1420
21-Jun-2021	915	0.3386	3.2420	1.1359
14-Jul-2021	915	0.3397	3.2362	1.1411
Final	915	0.3377	2.3500	1.1415

Table 5-4 – 2021 dispersion derived constants

step= 914	slit#0	slit#1	slit#2	slit#3	slit#4	slit#5
WL(A)	3021.32	3063.02	3100.43	3134.96	3168.06	3199.95
Res(A)	3.6504	5.2824	5.229	5.5927	6.135	5.2756
O3abs(1/cm)	3.1273	1.7812	1.0054	0.67639	0.37615	0.29458
Ray abs(1/cm)	5127.8928	4832.1854	4585.1984	4371.3598	4178.2003	4002.311
SO2abs(1/cm)	8.4544	5.6886	2.3922	1.9083	1.0539	0.61369
step= 915	slit#0	slit#1	slit#2	slit#3	slit#4	slit#5
WL(A)	3021.39	3063.09	3100.5	3135.03	3168.13	3200.02
Res(A)	3.6504	5.2822	5.2289	5.5926	6.1343	5.2755
O3abs(1/cm)	3.1245	1.7797	1.0052	0.67604	0.37614	0.29412
Ray abs(1/cm)	5127.3764	4831.7128	4584.7617	4370.9537	4177.8216	4001.9568
SO2abs(1/cm)	8.4688	5.7098	2.3998	1.8973	1.0549	0.61152
step= 916	slit#0	slit#1	slit#2	slit#3	slit#4	slit#5
WL(A)	3021.46	3063.16	3100.56	3135.09	3168.19	3200.08
Res(A)	3.6504	5.2821	5.2287	5.5926	6.1336	5.2754
O3abs(1/cm)	3.1214	1.7783	1.0049	0.6757	0.37617	0.29366
Ray abs(1/cm)	5126.8601	4831.2402	4584.325	4370.5477	4177.4429	4001.6027
SO2abs(1/cm)	8.4808	5.7306	2.4074	1.8864	1.0558	0.60938
step	O3abs	Rayabs	SO2abs	O3SO2Abs	Daumont	Bremen
914	0.3405	114064.7741	3.226	1.144	0.3501	0.34167
915	0.33966	114039.7054	3.2362	1.1411	0.34934	0.34089
916	0.33874	114014.6432	3.2463	1.1381	0.34853	0.34005

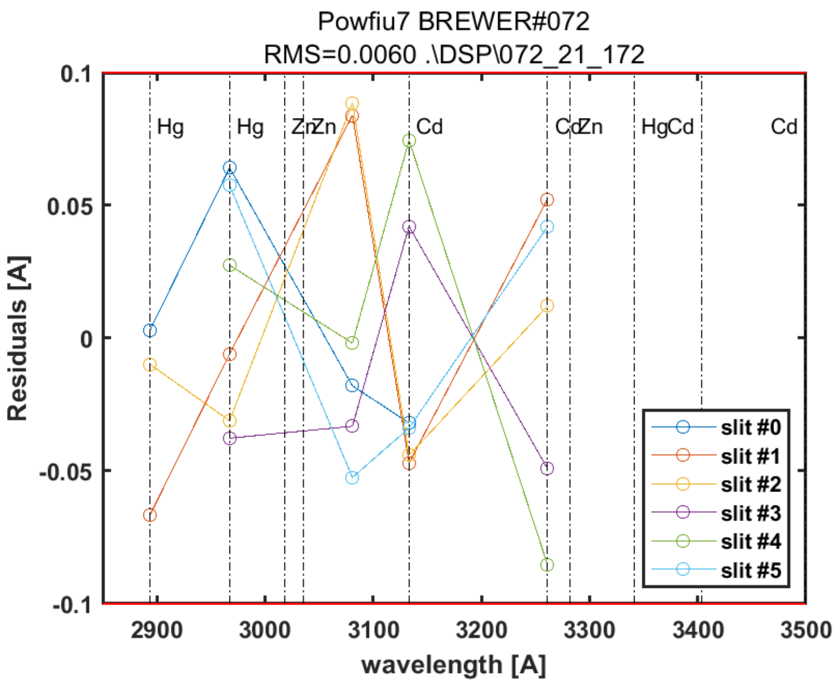


Figure 5-18 – 2021 residuals of cubic fit

5.5.3 Umkehr

For the Umkehr calibration, only the lines shorter than 3400 Å were used. The Umkehr offset is calculated by forcing the wavelength of slit #4 at the ozone position to be the same as on slit #1 at the Umkehr setting. The Umkehr offset calculated is **2387**. Table 5-5 summarizes the dispersion test for umkehr: wavelength, resolution and ozone absorption coefficient.

Table 5-5 – **2021 Umkehr dispersion constants**

step= 915	slit#0	slit#1	slit#2	slit#3	slit#4	slit#5
WL(A)	3021	3063	3100	3135	3168	3200
Res(A)	3.6504	5.2822	5.2289	5.5926	6.1343	5.2755
O3abs(1/cm)	3.1245	1.7797	1.0052	0.67604	0.37614	0.29412
Ray abs(1/cm)	0.51274	0.48317	0.45848	0.4371	0.41778	0.4002
step= 2387	slit#0	slit#1	slit#2	slit#3	slit#4	slit#5
WL(A)	3123	3164	3200	3233	3265	3296
Res(A)	3.6152	5.1126	5.0628	5.4911	5.1485	5.1567
O3abs(1/cm)	0.71458	0.39425	0.2952	0.12279	0.060413	0.033347
Ray abs(1/cm)	0.44413	0.42023	0.4002	0.38281	0.36706	0.35268

5.6 ETC Transfer

Based on the Lambert-Beer law, the total ozone column in the Brewer algorithm can be expressed as:

$$X = \frac{F - ETC}{\alpha\mu} \tag{1}$$

where F are the measured double ratios corrected for Rayleigh effects, α is the ozone absorption coefficient, μ is the ozone air mass factor, and ETC is the extra-terrestrial constant. The F, α and ETC parameters are weighted functions at the operational wavelengths with weighting coefficients $w = [0, 1, -0.5, -2.2, 1.7]$ for slits 1 to 5, with nominal wavelengths equal to $[306.3, 310.1, 313.5, 316.8, 320.1]$ nm.

The transfer of the calibration scale (namely ETC) is done side by side with the reference instrument. Once we have collected enough near-simultaneous direct sun ozone measurements, we calculate the new extraterrestrial constant after imposing the condition that the measured ozone will be the same for simultaneous measurements. In terms of the previous equation for ozone, this leads to the following condition:

$$ETC_i = F_i - X_i^{reference}\alpha\mu \tag{2}$$

For a good characterized instrument, the ETC determined values show a Gaussian distribution and the mean value is used as the instrument constant. One exception to this rule is the single monochromator Brewer models (MK-II and MK-IV) which are affected by stray light.

For single monochromator Brewers, the ETC distribution shows (see Fig.5-20) a tail at the lower ETC values for high Ozone Slant Column (OSC, the product of the total ozone content by the airmass). For this type of Brewer, only the stray-light free region is used to determine the ETC, generally from 300 to 900 DU OSC, depending on the instrument.

The stray light effect can be corrected if the calibration is performed against a double monochromator instrument, assuming that it can be characterized following a power law of the ozone slant column

$$F = F_o + k(X\mu)^s \tag{3}$$

where F are the true counts and F_o the measured ones.

$$ETC_i = ETC_o + k(X\mu)^s \tag{4}$$

where ETC_o is the ETC for the stray light free OSC region and k and s are retrieved from the reference comparison (Figure 5-22) . These parameters, determined in several campaigns, have been found to be stable and independent of the ozone calibration.

As the counts (F) from the single brewer are affected by stray light, the ozone is calculated using an iterative process:

$$X_{i+1} = X_i + \frac{k(X_i\mu)^s}{\alpha\mu} \tag{5}$$

Only one iteration is needed for the conditions of the intercomparison, up to 1500 DU. For ozone slant path measurements in the 1500–2000 DU range, two iterations are enough to correct the ozone.

Brewers are calibrated with the one parameter (1P) ETC transfer method: only the ozone ETC constant is transferred from the reference instrument. The so-called “two parameters calibration method” (2P), where both the ozone absorption coefficient and the ETC are calculated from the reference, is also obtained and serves as a quality indicator of the calibration. We consider a calibration optimal when both ETC values agree within 10 units, and the ozone absorption coefficient calculated from the dispersion tests and obtained with the 2P method agree within ± 2 micrometer steps, or approx. ± 0.002 atm.cm^{-1}. This range represents a total ozone difference of about 0.5% at airmass equal to 2, and total ozone of 300 DU.

The ETC is obtained by comparison with the reference brewer **IZO#185** using near-simultaneous measurements during **10** days (two measurements are considered near-simultaneous if they are taken less than **3.5** minutes apart). Measurements with airmass difference greater than 3% were removed from the analysis.

5.6.1 Initial Calibration

For the evaluation of initial status of Brewer DAV#072, we used the period from days **188** to **197** which correspond with **176** near-simultaneous direct sun ozone measurements. As shown in Fig. 5-19, the current calibration constants produce ozone values slightly higher than the reference instrument (-0.1%). When the ETC is corrected taking into account the difference between the SL and R6 reference (SL correction), the results do not improve.

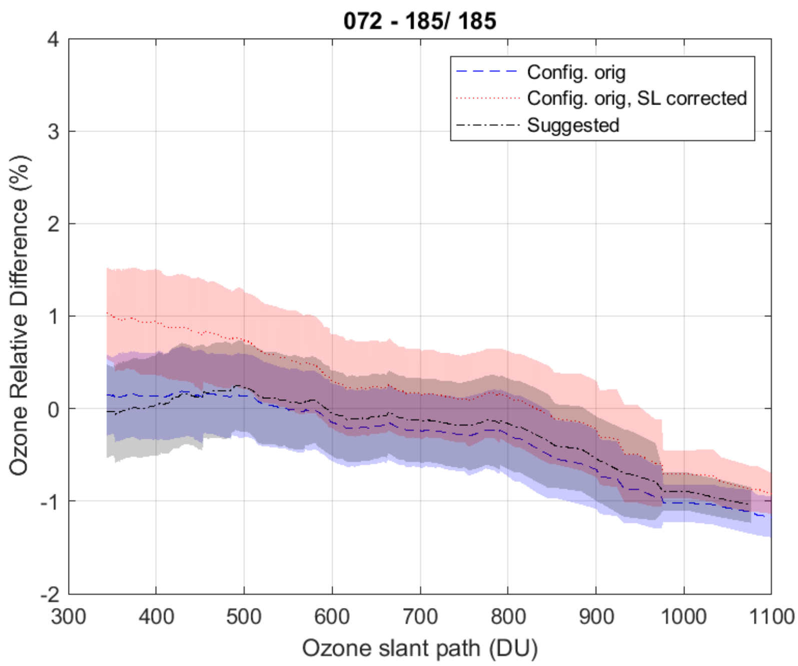


Figure 5-19 – Mean direct-sun ozone column percentage difference between Brewer DAV#072 and Brewer IZO#185 as a function of ozone slant path.

5.6.2 Final Calibration

A new ETC value has been calculated (see Fig. 5-20) also using the **176** simultaneous direct sun measurements from days **188** to **197**. The new value, calculated for OSC lower than 0.8, is 6 units higher than the current ETC value (**3215**). Therefore, we recommend using this new ETC, together with the new proposed standard lamp reference ratios, **1949** for R6. We updated the new calibration constants in the ICF provided. Of course, the new ETC has been calculated taking into account the new suggested dead time, **3.8**·**10**$^{-8}$.

The ETC value in the final ICF corresponds to the 1P transfer, and as shown in Table 5-6, the difference between 1P and 2P ETCs is below the maximum tolerance limit of 10 units.

Mean daily total ozone values and relative differences with respect to IZO#185 for the original and the final configurations are shown in Table 5-7.

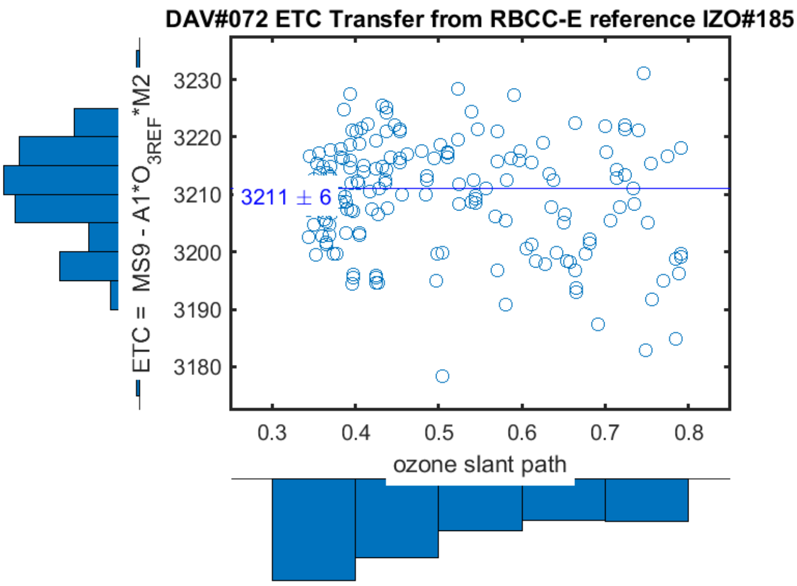


Figure 5-20 – **Mean direct-sun ozone column percentage difference between Brewer DAV#072 and Brewer IZO#185 as a function of ozone slant path, with OSC up to 0.8.**

Table 5-6 – **Comparison between the results of the 1P and 2P ETC transfer methods for the final days.**

	ETC 1P	ETC 2P	O3Abs final	O3Abs 2P
up to OSC=0.8	3211	3212	3377	3374
full OSC range	3210	3215	3377	3367

Table 5-7 – **Daily mean ozone and relative differences with respect to the reference, with the original and final (the latter, in the columns marked with a star) calibrations. Data from the final days.**

	Day	O3#185	std	N	O3#072	std	rd	O3(*)#072	std(*)	rd(*)
07-Jul-2021	188	304.2	0.6	6	304.1	1.1	0	304.6	1	0.1
08-Jul-2021	189	340.6	0	1	340.3	0	-0.1	340.7	0	0
09-Jul-2021	190	324	1.9	14	323.5	2.5	-0.2	323.5	2.4	-0.2
10-Jul-2021	191	312	2.1	59	312.7	2.5	0.2	312.7	2.1	0.2
11-Jul-2021	192	317.2	2.5	24	317.2	2.1	0	317.2	2	0
12-Jul-2021	193	305.3	2.7	75	304.6	2.7	-0.2	304.5	2.3	-0.3
13-Jul-2021	194	323.2	1.5	7	322.7	1.8	-0.2	323.2	2.1	0
15-Jul-2021	196	338.5	1.9	2	338.2	1.7	-0.1	338.4	1.5	0
16-Jul-2021	197	NaN	NaN	0	336.5	4.9	NaN	337	5.2	NaN

5.6.3 Stray light Correction

Stray light typically affect the ozone measurements of single-monochromator Brewers (models MK-II and MK-IV). To correct this effect, we use the following formula, which depended on the OSC.

$$X_{i+1} = X_i + \frac{k(X_i\mu)^s}{\alpha\mu} \tag{6}$$

Due to the location of the Davos station in a valley, the maximum OSC during the campaign barely exceed 1000 DU. For these OSC values, the stray light effect is small (see Fig. 5-22) and the uncertainties of k and s parameters are too high ($k = -32.7 \pm 2.7$ and $s = 4.11 \pm 7.53$). Therefore it has not been possible to determine the effect of stray light in this campaign, and we recommend continuing using the characterisation performed in the 2018 campaign.

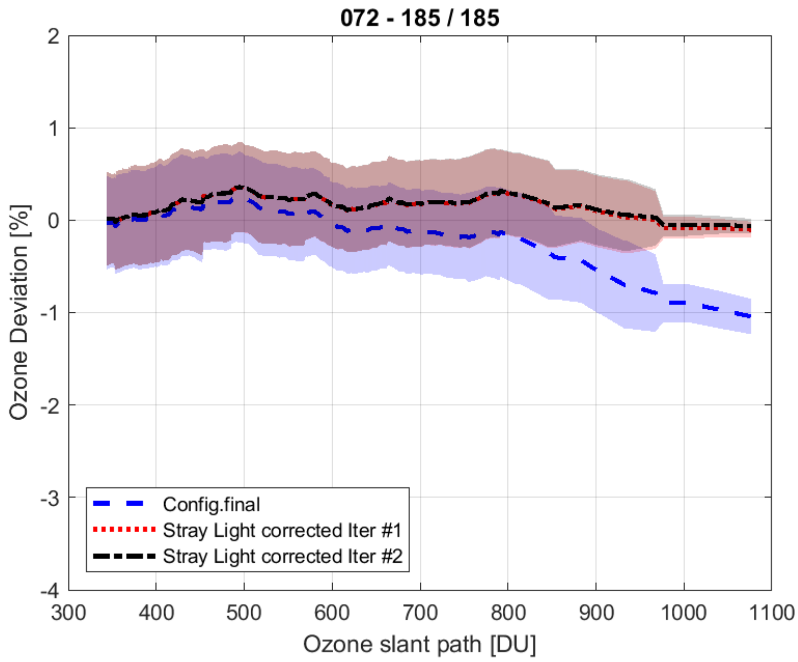


Figure 5-21 – Ratio respect to the reference when final constant are applied and stray light correction is introduced from empirical model is applied.

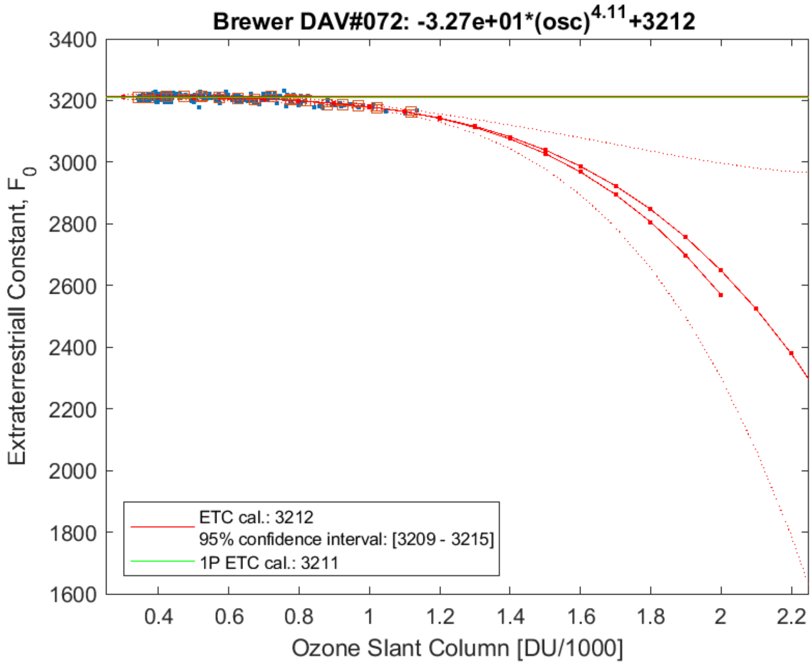


Figure 5-22 – **Stray light empirical model determination**

5.6.4 Standard Lamp Reference Values

The reference values of standard lamp ratios during the calibration period were **1949** for R6 (Figure 5-23) and **3722** for R5 (Figure 5-24).

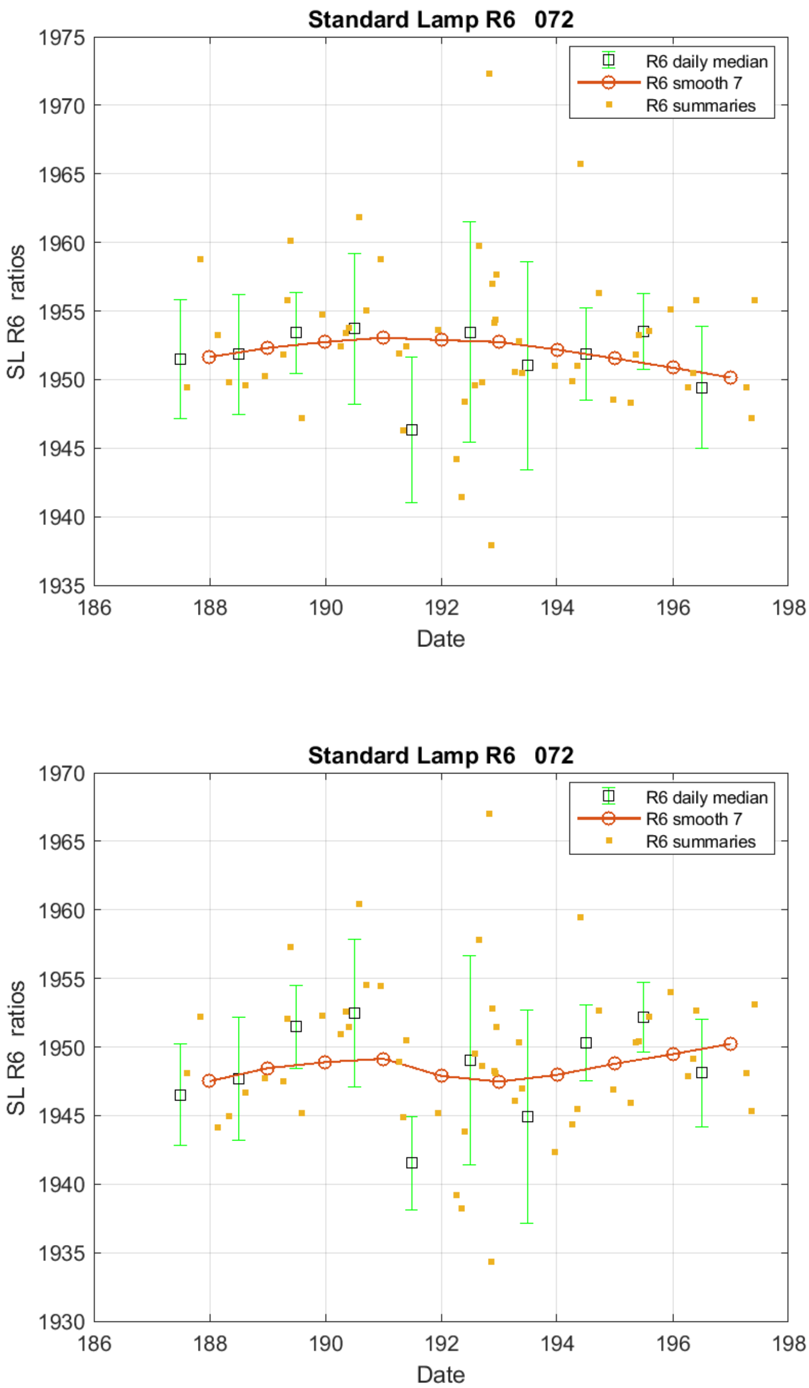
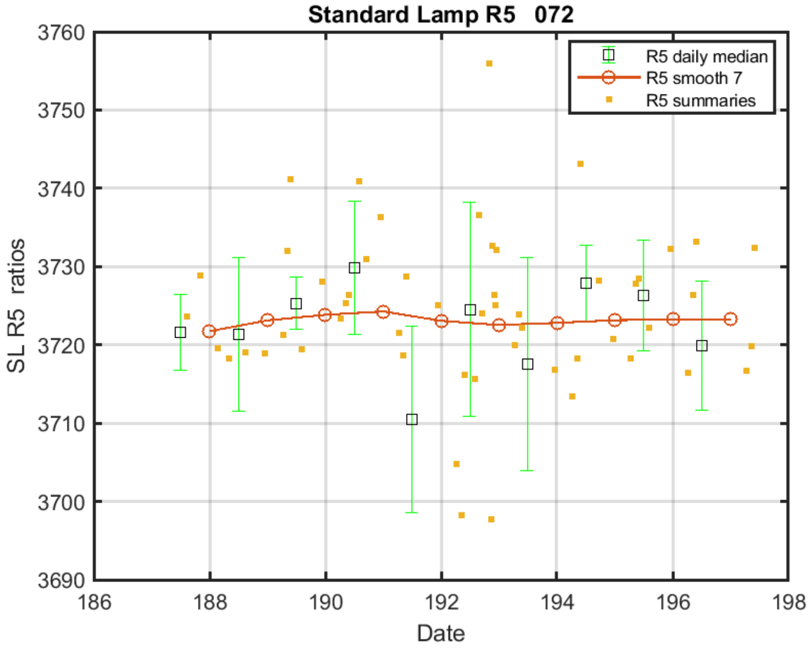


Figure 5-23 – Standard Lamp O_3 R6 ratios: daily mean and standard deviation (squares), seven day running mean (circle) and individual tests (black dots). Reprocessed using old (top) and new (bottom) instrumental constants



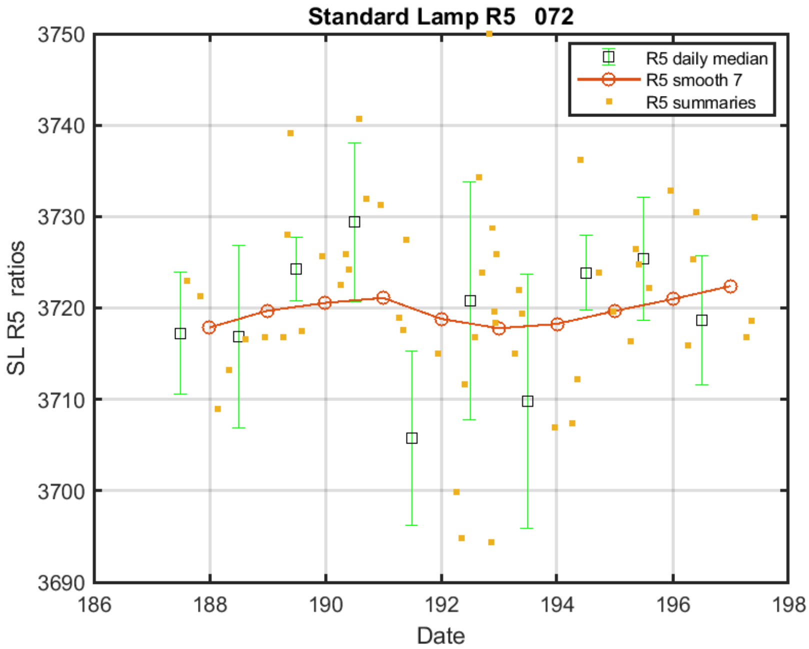


Figure 5-24 – Standard Lamp SO_2 R5 ratios: daily mean and standard deviation (squares), seven day running mean (circle) and individual tests (black dots). Reprocessed using old (top) and new (bottom) instrumental constants

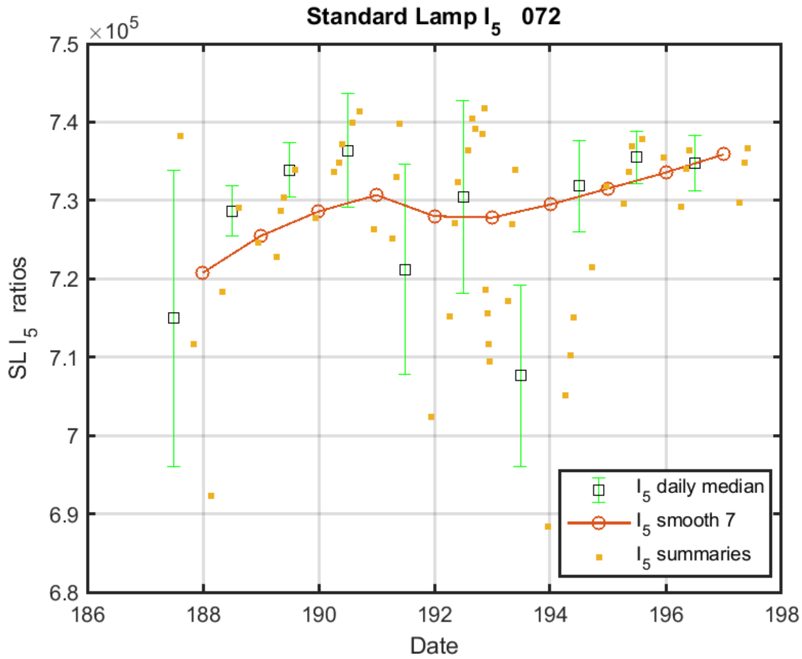


Figure 5-25 – Standard Lamp intensity: daily mean and standard deviation (squares), seven day running mean (circle) and individual tests (black dots)

5.7 Configuration

5.7.1 Instrument constant file

	Initial (ICF20018.072)	Final (ICF18821.072)
o3 Temp coef 1	0	0
o3 Temp coef 2	-0.4968	-0.24
o3 Temp coef 3	-0.8072	-0.49
o3 Temp coef 4	-1.3838	-1
o3 Temp coef 5	-2.8861	-2.26
Micrometer steps/deg	0	0
O3 on O3 Ratio	0.3377	0.3377
SO2 on SO2 Ratio	2.35	2.35
O3 on SO2 Ratio	1.1415	1.1415
ETC on O3 Ratio	3215	3210
ETC on SO2 Ratio	3262	3262
Dead time (sec)	3.7e-08	3.8e-08
WL cal step number	915	915
Slitmask motor delay	76	76
Umkehr Offset	2384	2384
ND filter 0	0	0
ND filter 1	4358	4358
ND filter 2	9155	9155
ND filter 3	13680	13680
ND filter 4	19718	19718
ND filter 5	22261	22261
Zenith steps/rev	2816	2816
Brewer Type	2	2
COM Port #	1	1
o3 Temp coef hg	0	0
n2 Temp coef hg	1960	1960
n2 Temp coef 1	3750	3750
n2 Temp coef 2	0	0
n2 Temp coef 3	0	0
n2 Temp coef 4	0	0
n2 Temp coef 5	0	0
O3 Mic #1 Offset	3865	3865
Mic #2 Offset	0	0
O3 FW #3 Offset	0	0
NO2 absn Coeff	0	0
NO2 ds etc	0	0
NO2 zs etc	0	0
NO2 Mic #1 Offset	0	0
NO2 FW #3 Offset	0	0
NO2/O3 Mode Change	0	0
Grating Slope	0	0
Grating Intercept	0	0
Micrometer Zero	2699	2699
Iris Open Steps	250	250
Buffer Delay (s)	0.2	0.2
NO2 FW#1 Pos	0	0
O3 FW#1 Pos	256	256
FW#2 Pos	0	0
uv FW#2 Pos	64	64
Zenith Offset	40	40
Zenith UVB Position	2096	2096

5.8 Daily Summary report

Day	osc range	O3#185	std	N	O3#072	std	rd	O3(*)#072	std(*)	rd(*)
188	1000>osc>700	303.9	0	2	305.9	0.7	0.7	304.9	0.8	0.3
188	700>osc>400	303.8	0.7	4	305.1	1.1	0.4	304.4	1.1	0.2
190	700>osc>400	323.4	1.6	10	324.2	2.6	0.3	322.9	2.2	-0.2
190	osc<400	326.5	0.7	3	327.3	2.3	0.2	325.9	2.3	-0.2
191	1000>osc>700	310.6	2.3	11	311.4	2.4	0.3	310.4	2.2	-0.1
191	700>osc>400	311.1	1.3	24	314.8	2.1	1.2	312.7	1.6	0.5
191	osc<400	314.4	1.1	19	318.3	1.7	1.2	314.1	1.7	-0.1
192	1000>osc>700	316.6	1.5	5	316.9	1.7	0.1	316	1.8	-0.2
192	700>osc>400	318.6	1.1	12	318.6	1.7	0	317.4	1.3	-0.4
192	osc<400	317.1	4.8	5	319.4	3.5	0.7	317.7	3.4	0.2
193	1500>osc>1000	304.9	0.8	2	302	0.2	-1	301.6	0.2	-1.1
193	1000>osc>700	303.7	2.4	15	302.6	2.5	-0.4	301.9	2.2	-0.6
193	700>osc>400	304.4	3	29	305.8	2.1	0.5	304.2	1.7	0
193	osc<400	306.5	1.2	22	308.8	1	0.8	306.2	1.2	-0.1
194	1000>osc>700	322.7	0	2	323.9	0.1	0.4	323.2	0.1	0.1
194	700>osc>400	323.6	2	4	324.1	2.6	0.1	323.4	2.9	-0.1
196	1000>osc>700	337.2	0	1	338.5	0	0.4	337.3	0	0
196	700>osc>400	339.9	0	1	341.1	0	0.4	339.5	0	-0.1
197	1500>osc>1000	335.1	0.8	3	NaN	NaN	NaN	331.5	1.5	-1.1
197	1000>osc>700	336.2	0.5	5	NaN	NaN	NaN	333.9	1	-0.7
197	700>osc>400	341.8	1.5	4	NaN	NaN	NaN	342.9	1	0.3
197	osc<400	340.2	0	2	NaN	NaN	NaN	343.1	2.3	0.8

5.9 Summary Plots

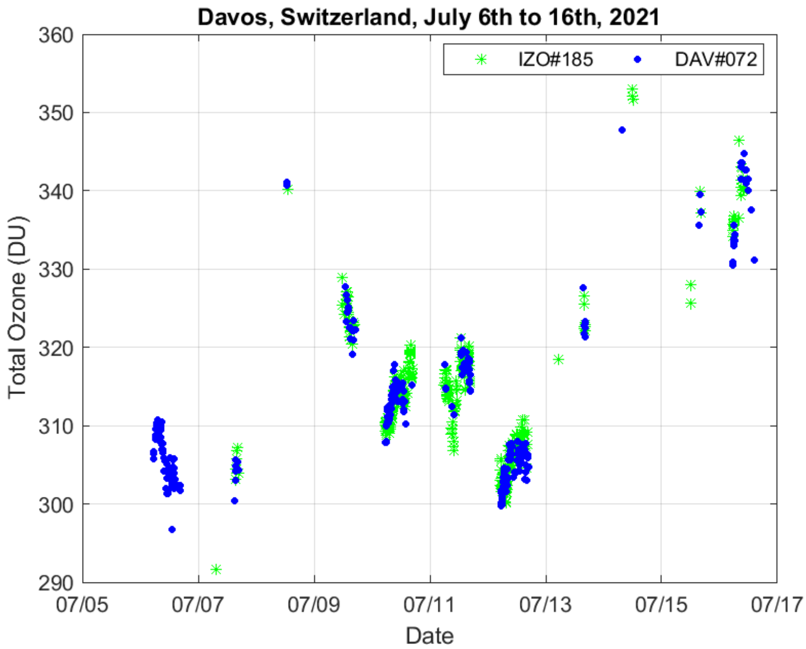
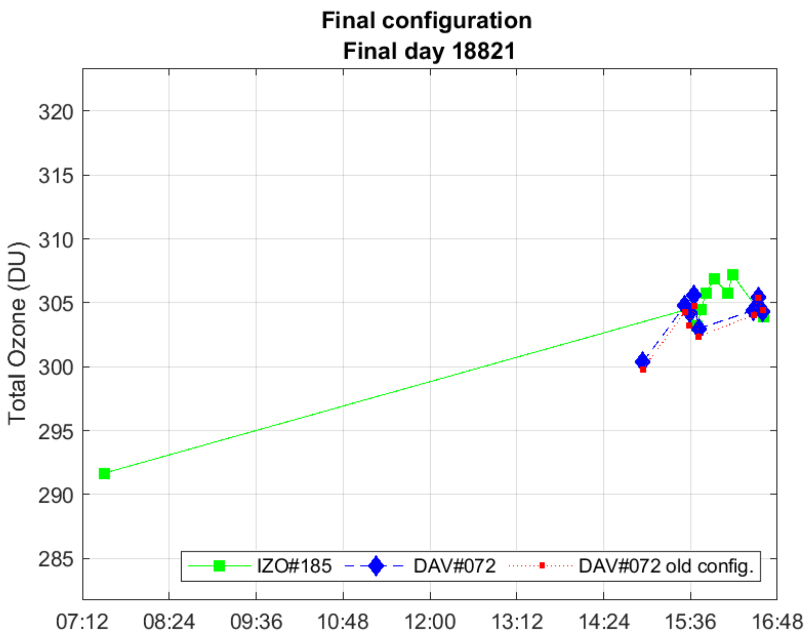
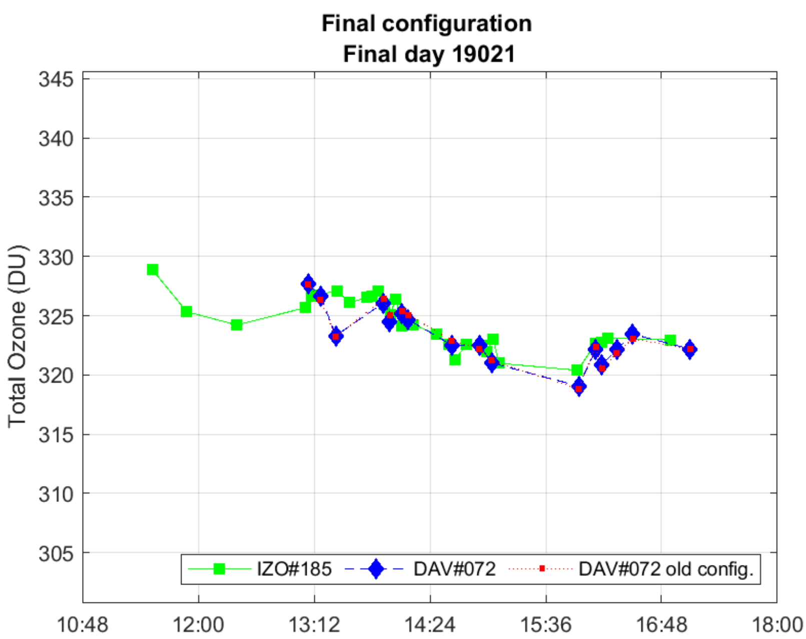
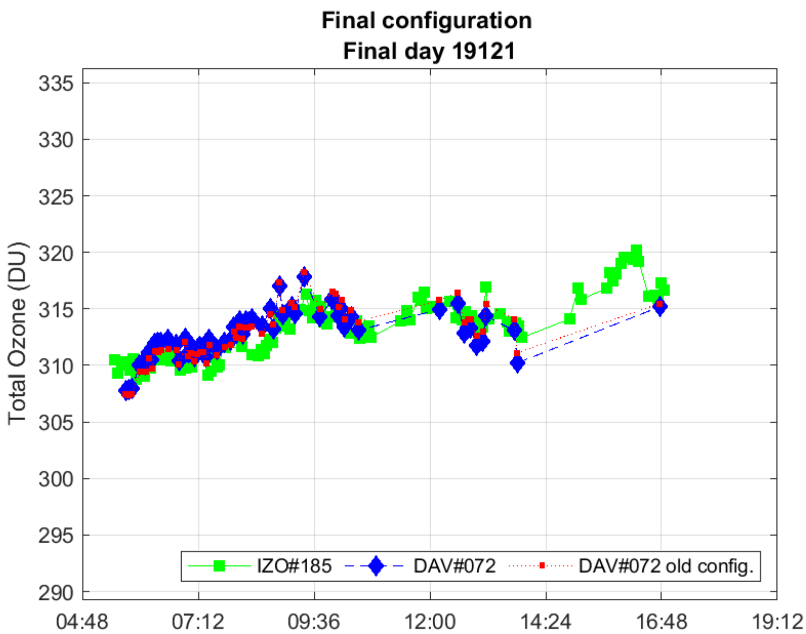
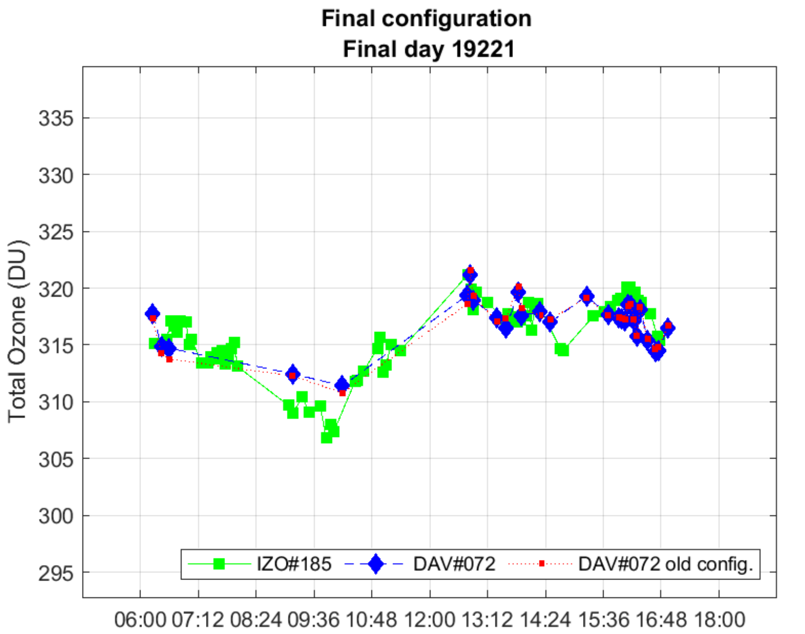


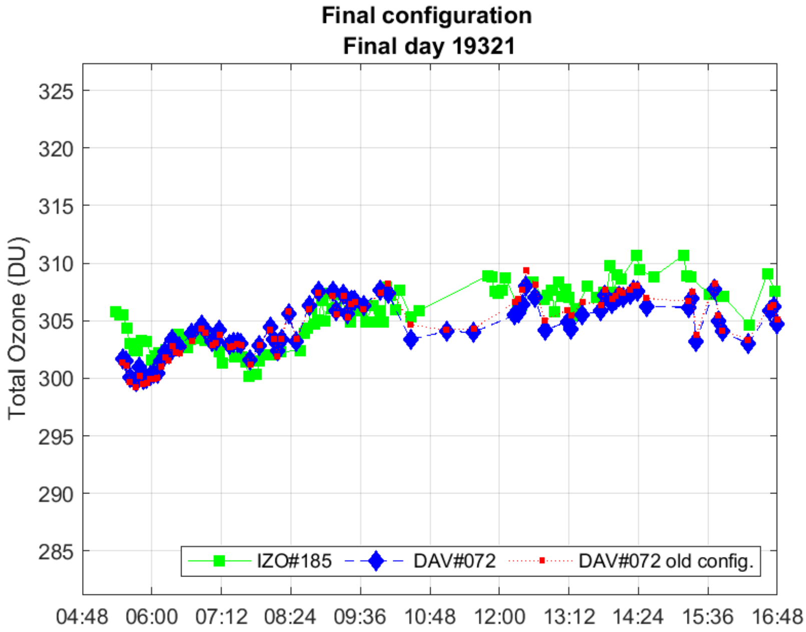
Figure 5-26 – Overview of the intercomparison. Brewer DAV#072 data are evaluated using final constants (blue circles)


Final configuration
Final day 18821
Total Ozone (DU)
320
315
310
305
300
295
290
285
07:12
08:24
09:36
10:48
12:00
13:12
14:24
15:36
16:48
IZO#185
DAV#072
DAV#072 old config.

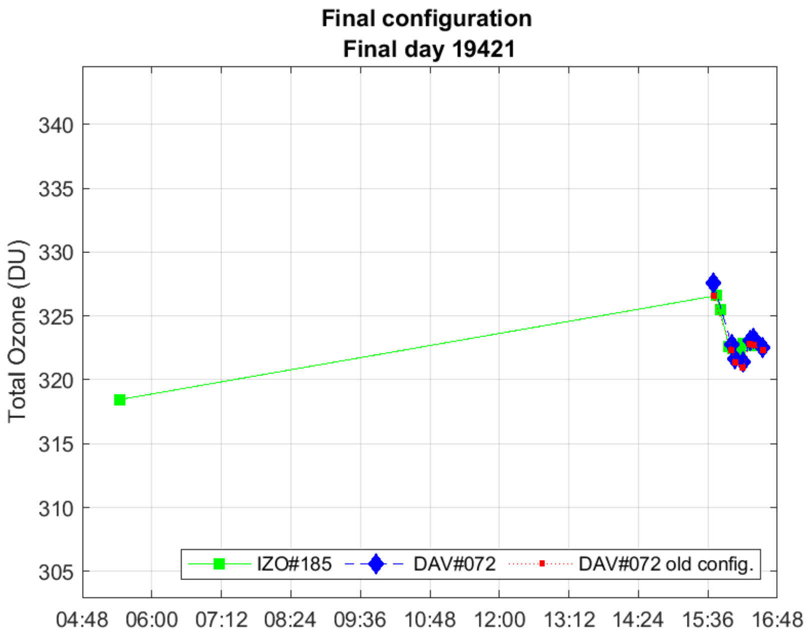

Final configuration
Final day 19021
Total Ozone (DU)
345
340
335
330
325
320
315
310
305
10:48
12:00
13:12
14:24
15:36
16:48
18:00
IZO#185
DAV#072
DAV#072 old config.


Final configuration
Final day 19121
Total Ozone (DU)
335
330
325
320
315
310
305
300
295
290
04:48
07:12
09:36
12:00
14:24
16:48
19:12
IZO#185
DAV#072
DAV#072 old config.

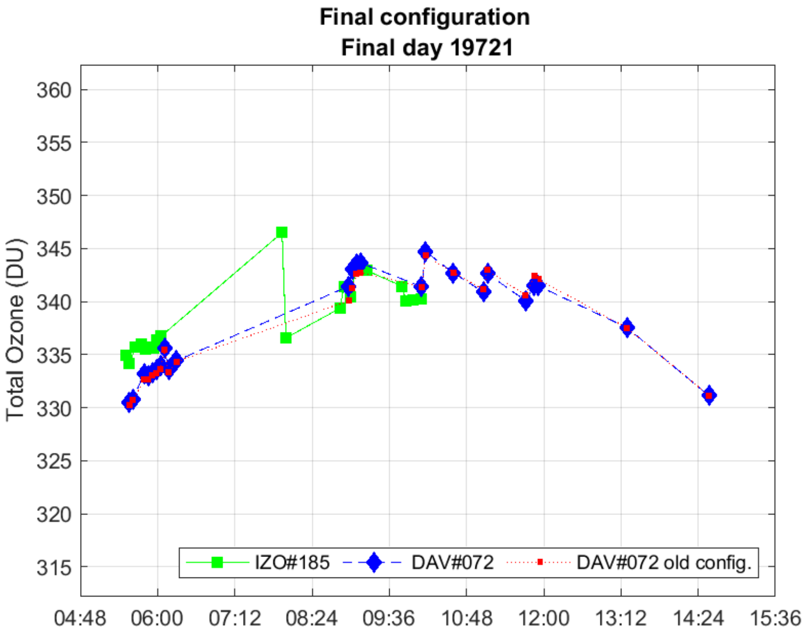

Final configuration
Final day 19221
Total Ozone (DU)
335
330
325
320
315
310
305
300
295
06:00 07:12 08:24 09:36 10:48 12:00 13:12 14:24 15:36 16:48 18:00
IZO#185
DAV#072
DAV#072 old config.



Final configuration
Final day 19321
Total Ozone (DU)
325
320
315
310
305
300
295
290
285
IZO#185
DAV#072
DAV#072 old config.
04:48
06:00
07:12
08:24
09:36
10:48
12:00
13:12
14:24
15:36
16:48



Final configuration
Final day 19421
Total Ozone (DU)
340
335
330
325
320
315
310
305
IZO#185
DAV#072
DAV#072 old config.
04:48
06:00
07:12
08:24
09:36
10:48
12:00
13:12
14:24
15:36
16:48



Final configuration
Final day 19721
Total Ozone (DU)
360
355
350
345
340
335
330
325
320
315
04:48
06:00
07:12
08:24
09:36
10:48
12:00
13:12
14:24
15:36
IZO#185
DAV#072
DAV#072 old config.

6 Brewer DAV#156

6.1 Calibration Summary

The Fifteenth Intercomparison Campaign of the Regional Brewer Calibration Center Europe (RBCC-E) was held from July 6th to the 16th, 2021, at the Physikalisch-Meteorologisches Observatorium PMOD (Davos, Switzerland).

Brewer DAV#156 participated in the campaign in the period from July 6th to 16th. The campaign days of Brewer DAV#156 correspond to Julian days 187 – 197.

For final calibration purposes, we used **137** simultaneous DS ozone measurements taken from day **192** to **195**. As no maintenance was required for Brewer DAV#156, we used the same data set for the evaluation of the initial status as for the final calibration.

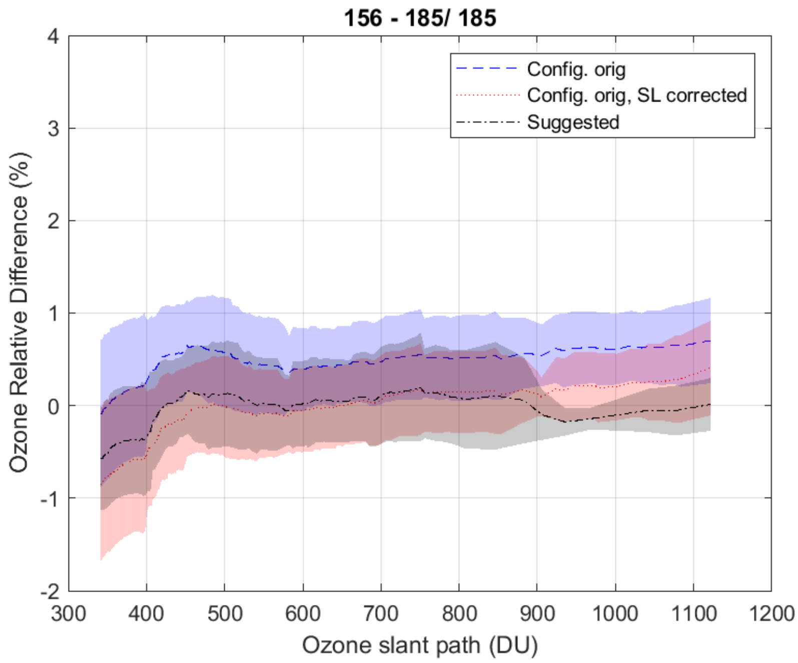


Figure 6-1 – Mean DS ozone column percentage difference between Brewer DAV#156 and Brewer IZO#185, plotted as a function of the ozone slant path. Results for the current (issued in the previous calibration campaign) configuration are show in blue; the red dotted line corresponds to the same configuration, but with the standard lamp correction applied; the black line corresponds to results obtained with the updated configuration proposed in the current campaign. The shadow areas represent the standard deviation of the mean. The plot corresponds to the final days of the campaign.

As shown in Fig. 6-1, the current ICF (ICF21018.156, blue dashed line) produces ozone values with an average difference of around 0.4% with respect to the reference instrument. This is a rather small difference, and highlights the stability of Brewer DAV#156. However, the SL correction (Fig. 6-1, red dotted line) improve the comparison with Brewer IZO#185, and we recommend applying the SL correction from the 2018 calibration to the current one.

We appreciate a small but clear temperature dependence in the standard lamp observations, which indicates the temperature coefficients can be improved.

The neutral density filters didn't show nonlinearity in the attenuation's spectral characteristics. We have not applied any correction to filters.

The sun-scan tests (SC) at the instrument's station before the campaign and those performed during the first days of the intercomparison, confirm the current cal step value (1020, within a step error of ±1).

We suggest continuing to use the current Ozone Absorption Coefficient, with a value of 0.341.

All the other parameters analyzed (run/stop tests, Hg lamp intensity, CZ & CI files, dead time,...) show reasonable results.

Taking into account all this, we suggest some changes to the configuration of Brewer DAV#156.

6.1.1 Recommendations and Remarks

1. The R6 standard lamp test from Brewer DAV#156 has increased around 10 units during the last 3 years. The old R6 reference value was 440. After changing the temperature coefficients the new recommended value is **451**.
2. We suggest a new R5 reference value of **1142**.
3. The DT value has evolved over the last three years, but always within ±2 ns that are acceptable for double Brewers. Therefore, the operative DT value in the new configuration file remains the same.
4. The neutral density filters show the same behaviour as in the previous campaign, and we suggest retaining the same correction factors.
5. We have found that new temperature coefficients improve the behaviour of the instrument, and we include them in the final ICF for the campaign.
6. Finally, we suggest updating the ETC value from **1743** to **1755**.

6.1.2 External links

Configuration File

`http://rbcce.aemet.es/svn/campaigns/dav2021/bfiles/156/ICF18821.156`

Calibration Report

`https://docs.google.com/spreadsheets/d/12-4EoZzJkJDv5Pgpdt3PNZlZLXahvdlubhqOyijRack/edit#gid=460789507`

Calibration Reports Detailed

Historic and instrumental

`http://rbcce.aemet.es/svn/campaigns/dav2021/latex/156/html/cal_report_156a1.html`

Temperature & Filter

`http://rbcce.aemet.es/svn/campaigns/dav2021/latex/156/html/cal_report_156a2.html`

Wavelength

`http://rbcce.aemet.es/svn/campaigns/dav2021/latex/156/html/cal_report_156b.html`

ETC transfer

http://rbcce.aemet.es/svn/campaigns/dav2021/latex/156/html/cal_report_156c.html

6.2 Instrument History: Analysis of Average files

6.2.1 Standard Lamp Test

As shown in Figure 6-2 and 6-3, R6 and R5 mean values are **447** and **1139**, but present a small increase during the last 3 years. R6 value has increased about 10 units from the last reference value, 440. After changing the temperature coefficients the new recommended value for R6 and R5 are respectively 451 and 1142.

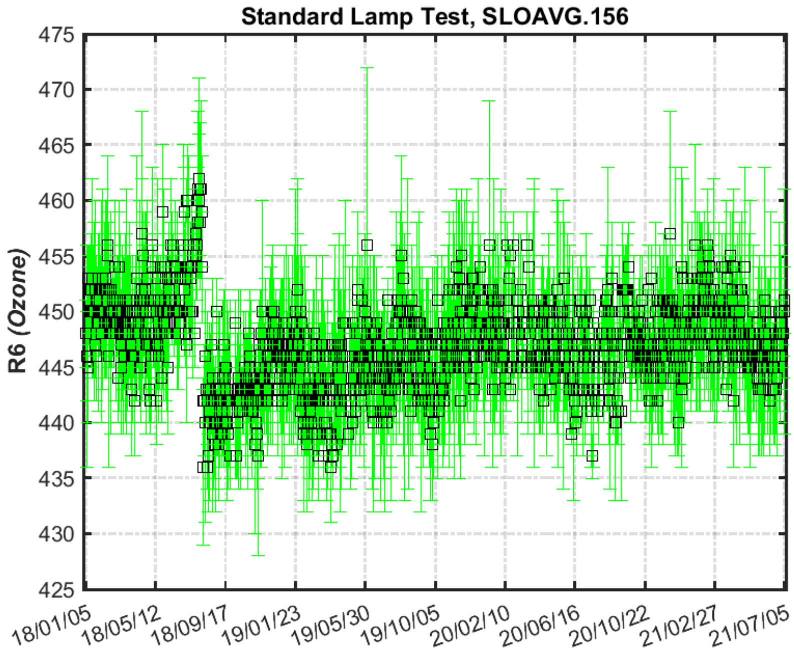


Figure 6-2 – **Standard Lamp test R6 (Ozone) ratios. Horizontal lines are labeled with the original and final reference values (red and blue lines, respectively)**

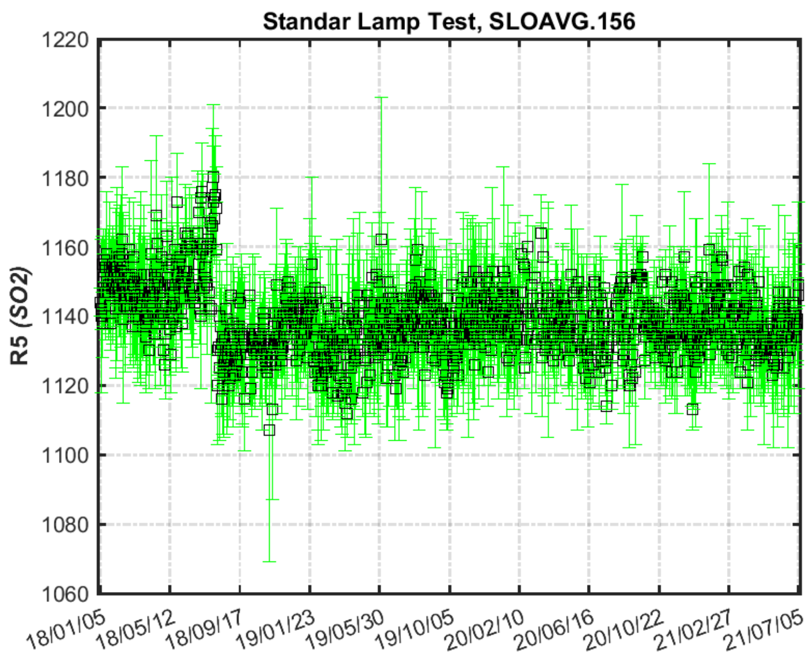


Figure 6-3 – **Standard Lamp test R5 (SO_2) ratios**

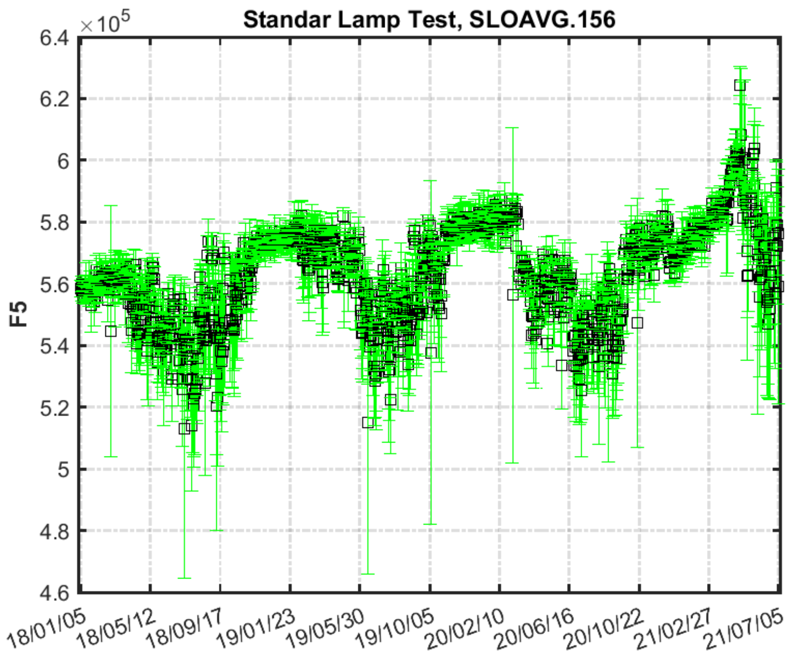


Figure 6-4 – **SL intensity for slit five.**

6.2.2 Run Stop and Dead Time

Run stops test values are within the test tolerance limits for all the slits with only a small number of outliers, as can be seen in figure Fig. 6-5.

As shown in Fig. 6-6, DT average is **2.7·10**$^{-8}$, but its value has evolved over the last three years. Differences with the reference value has been within ±2 ns from the current DT reference value, which is acceptable for double Brewers. Therefore the operative DT value in the new configuration file remains the same, **2.7·10**$^{-8}$ seconds.

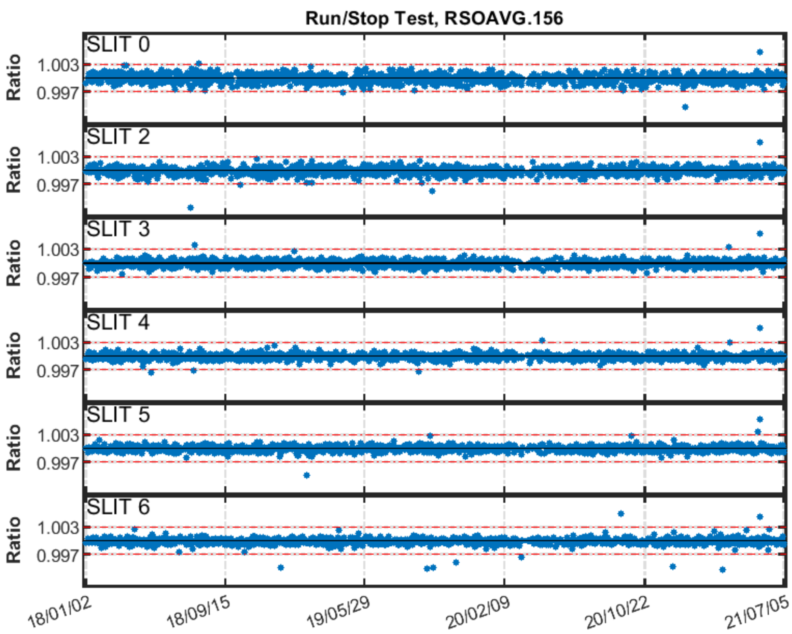


Figure 6-5 – Run/stop test

6.2.3 Analog Test

Fig. 6-7 shows that the high voltage has remained almost constant around at **1526** over the last two years. Furthermore, analog test values are within the test tolerance range.

6.2.4 Mercury Lamp Test

The intensity of the internal mercury lamp was reduced and stabilised as of May 2020, after an adjustment in the filter wheel #2. No other noticeable events have been observed in the last three years.

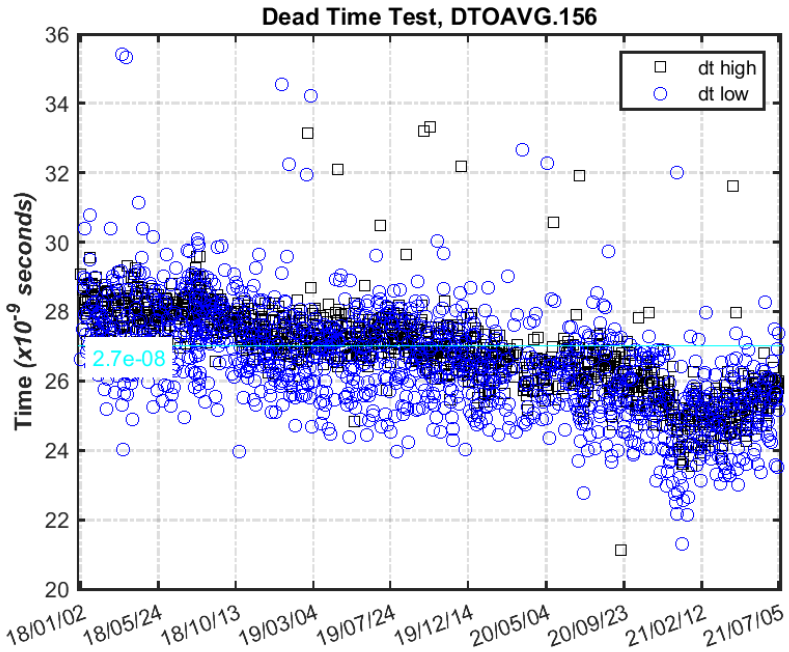


Figure 6-6 – **Dead Time test. Horizontal lines are labelled with the current (red) and final (blue) values.**

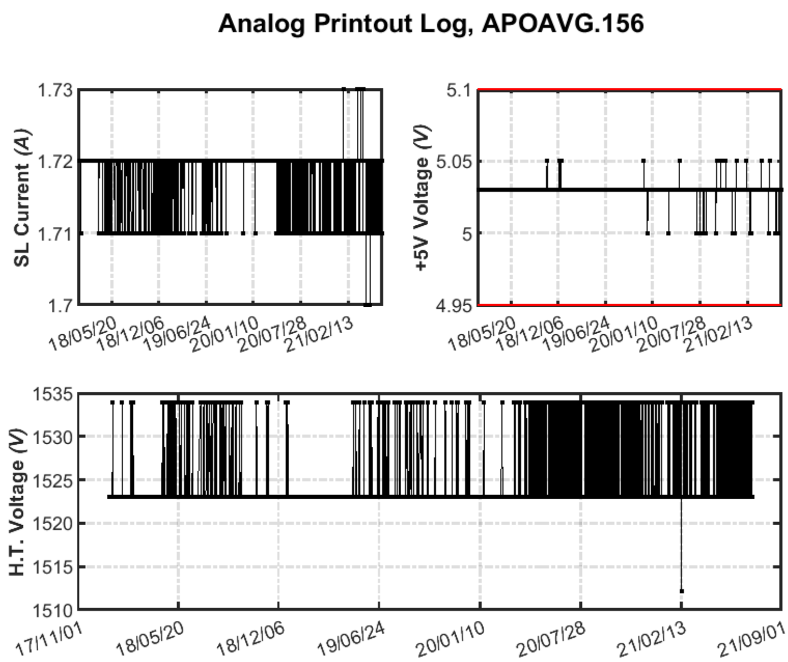


Figure 6-7 – **Analog voltages and intensity.**

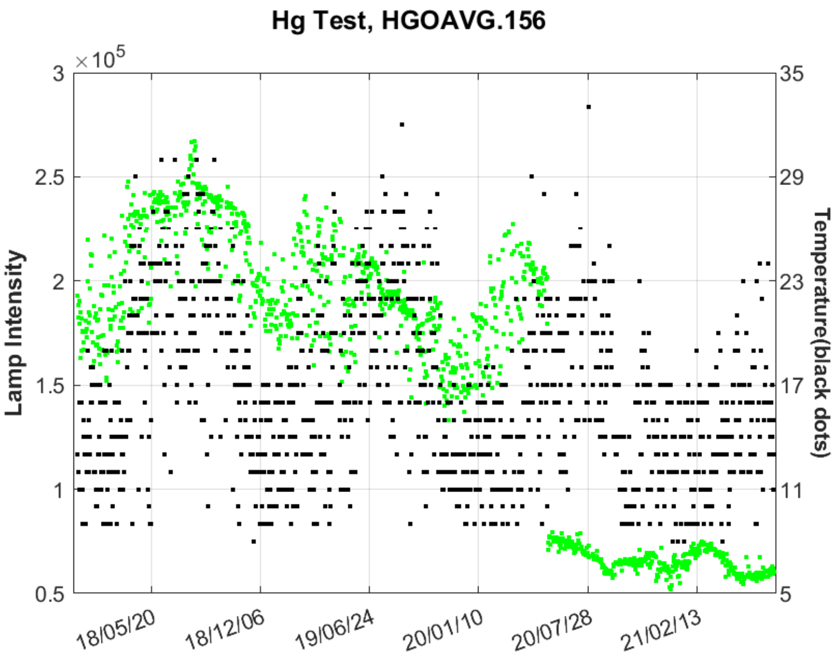
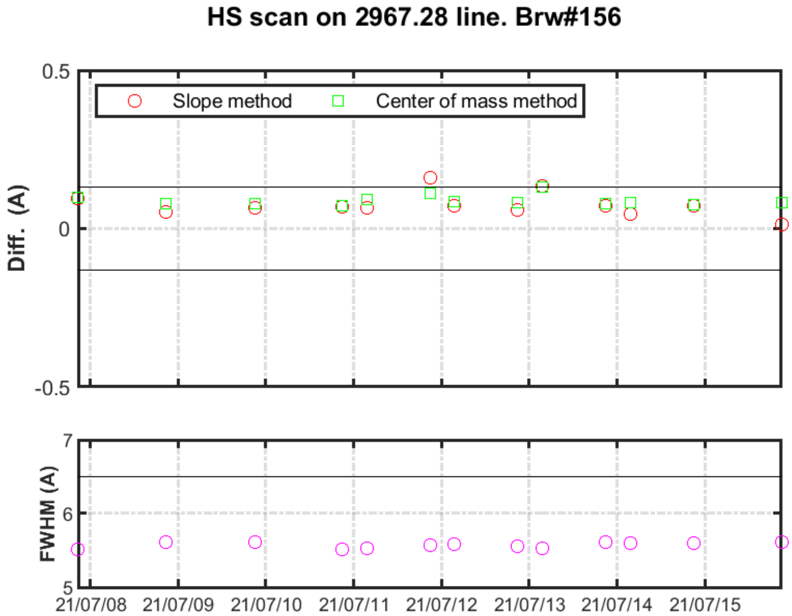


Figure 6-8 – Mercury lamp intensity (green squares) and Brewer temperature registered (black dots). Both parameters refer to maximum values for each day.

6.2.5 CZ scan on mercury lamp

In order to check both the wavelength settings and the slit function width, we analyzed the scans performed on the 296.728 nm, and 334.148 nm mercury lines, see Fig. 6-9. As a reference, the calculated scan peak, in wavelength units, should be within 0.013 *nm* from the nominal value, whereas the calculated slit function width should be no more than 0.65 *nm*. Analysis of the CZ scans performed on Brewer DAV#156 during the campaign show reasonable results, with the peak of the calculated scans close, although slightly below, the accepted tolerance range. Regarding the slit function width, results are good, with a FWHM lower than 6.5 Å.



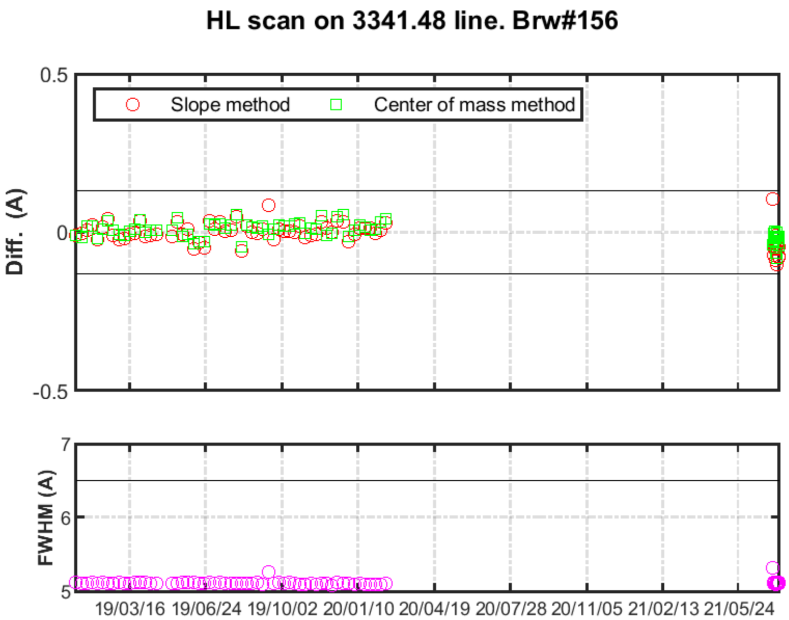


Figure 6-9 – CZ scan on Hg lines. The upper panels show differences with respect to the reference line (solid lines represent the limit ± 0.013 *nm*) as computed by the slopes (red circles) and center of mass (green squares) methods. Lower panels show the Full Width at Half Maximum value for each scan performed (solid lines represent the 0.65 *nm* limit

6.2.6 CI scan on internal *SL*

CI scans of the standard lamp recorded at different times can be compared to investigate whether the instrument has changed its spectral sensitivity. We shown in Fig. 6-10 percentage ratios of the Brewer **DAV#156** CI scans performed during the campaign relative to the scan CI18921.156. As it can be observed, the lamp intensity has varied respect to the reference spectrum around 5%. Similar variation have been observed in the daily R6 and R5 values. This behavior is normal for a SL lamp.

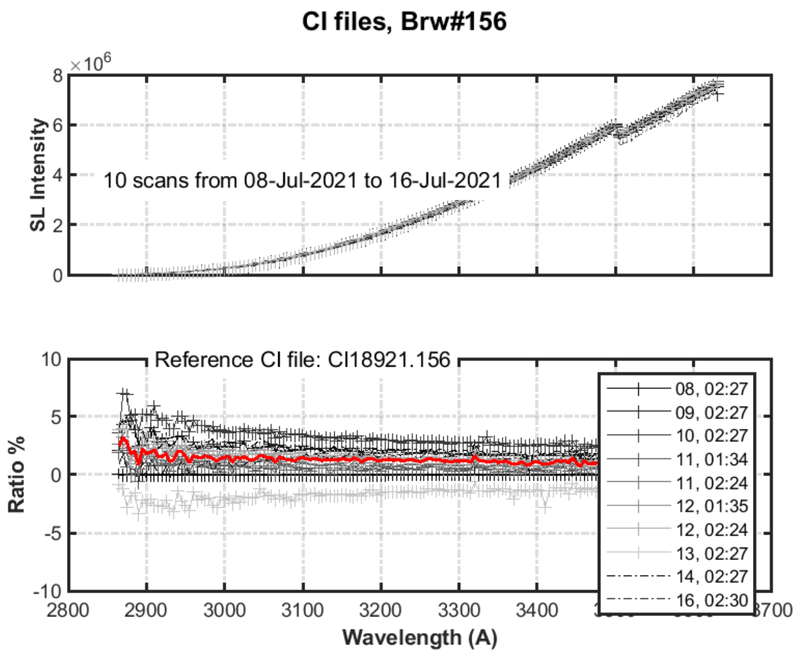


Figure 6-10 – CI scan of Standard Lamp performed during the campaign days. Scans processed (upper panel) and relative differences with respect to a selected reference scan (lower panel). Red line represents the mean of all relative differences

6.3 Absolute Temperature Coefficients

Temperature coefficients are determined using the standard lamp test. For every slit, the raw counts corrected for zero temperature coefficients are used in a linear regression against temperature with the slopes representing the instrument's temperature coefficients. From this we obtain the corrected *R6* and *R5* ratios to analyze the new temperature coefficients' performance.

As shown in Fig. 6-11 (temperature range from **9**° **C** to **33**° **C**, the current coefficients do an excellent job at reducing the temperature dependence, performing even better that the coefficients calculated using the data from the present campaign. The values of the coefficients are summarized in Table 6-1.

We have also extended our analysis using the data recorded since the previous campaign. As shown in Figs. 6-12 and 6-13, these new coefficients perform slightly better than the current coefficients. For this reason, we have used the new coefficients in the final ICF.

Table 6-1 – Temperature Coefficients. The final coefficients are calculated using the data recorded since the previous campaign. Coefficients are normalized to slit#2

	slit#2	slit#3	slit#4	slit#5	slit#6
Current	0.0000	-0.8100	-1.6500	-2.4800	-3.4100
Calculated	0.0000	-0.8700	-1.7300	-2.6100	-3.6600
Final	0.0000	-0.7800	-1.4700	-2.3500	-3.3200

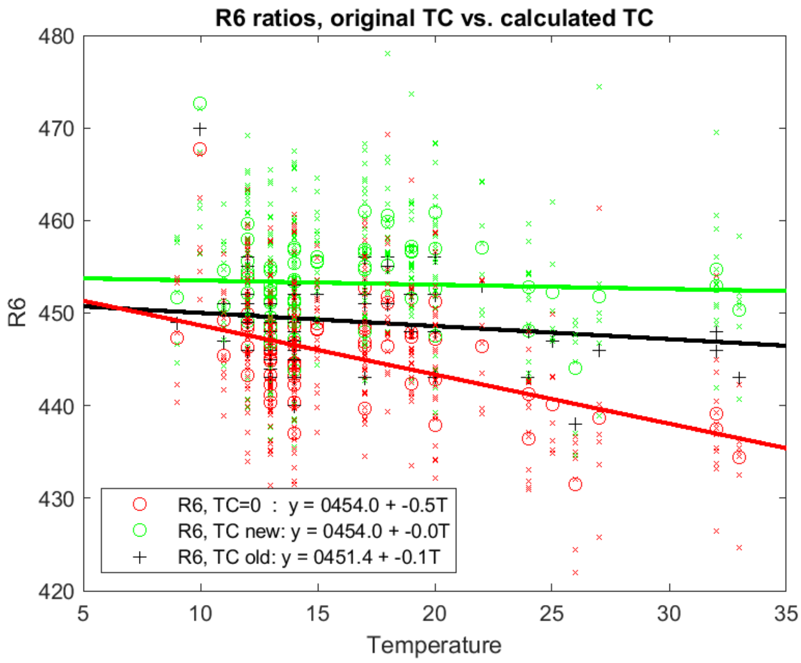


Figure 6-11 – Temperature coefficients' performance. Red circles represent standard lamp R6 ratios calculated from raw counts without temperature correction (temperature coefficients set to 0). Black crosses and green circles represent standard lamp R6 ratios corrected with original and calculated temperature coefficients, respectively. Data corresponds to the present campaign.

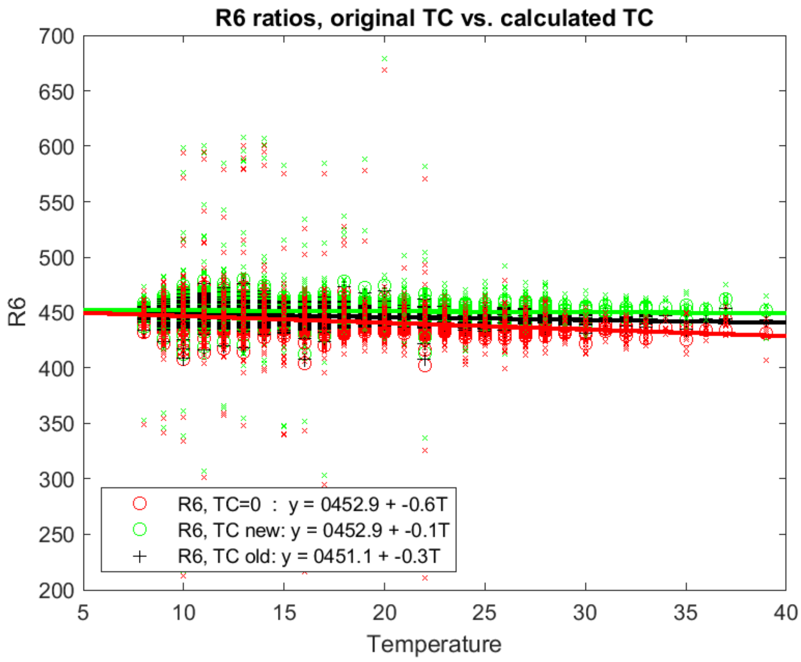


Figure 6-12 – **Same as Fig. 6-11 but for the whole period between calibration campaigns.**

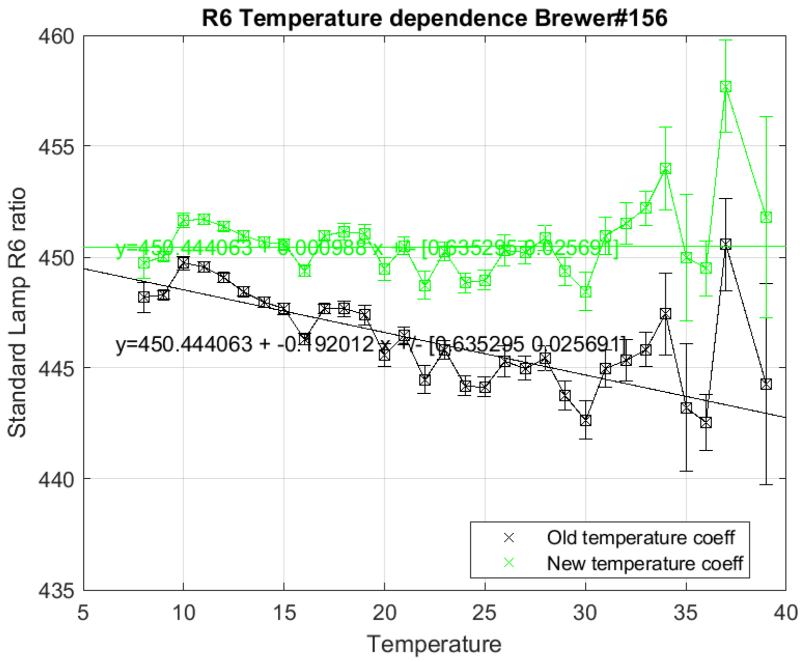


Figure 6-13 – **Standard lamp R6 (MS9) ratio as a function of temperature. We plotted R6 ratio recalculated with the original (black) and the new (green) temperature coefficients**

6.4 Attenuation Filter Characterization

6.4.1 Attenuation Filter Correction

The filter's spectral dependence affects the ozone calculation because the Brewer software assumes that their attenuation is wavelength-neutral. We can estimate the correction factor needed for this non-linearity by multiplying the attenuation of every filter and every wavelength by the ozone weighting coefficients.

During the calibration period, a total of **44** FI tests were analyzed to calculate the attenuation for every filter and slit. Fig. 6-14 shows the results of these tests, and Table 6-2 shows the calculated ETC corrections for each filter.

Table 6-2 – **ETC correction due to Filter non-linearity. Median value, mean values and, 95% confidence intervals are calculated using bootstrap technique**

	filter#1	filter#2	filter#3	filter#4	filter#5
ETC Filt. Corr. (median)	-4	-2	-4	-8	-2
ETC Filt. Corr. (mean)	-8.4	-2.8	-5.3	-5	2.7
ETC Filt. Corr. (mean 95% CI)	[-16.1 -0.4]	[-10.4 5]	[-12.1 1.7]	[-12.9 3.3]	[-17.6 21.9]

Calculated mean attenuation values for every filter are compared with operational values (see Table 6-2 and Figure 6-14), updating them (ICF file) when necessary. In the case of Brewer DAV#156 the observed transitions between successive filters are quite smooth in terms of attenuation (relative percentage differences lower than 10% when changing filter). Table 6-2 shows how most of the filters are affected similarly, except the filter #5, which is never used. Taking into account the relative ozone difference with respect to the reference Brewer IZO#185, we do not suggest the application of any ETC filter correction.

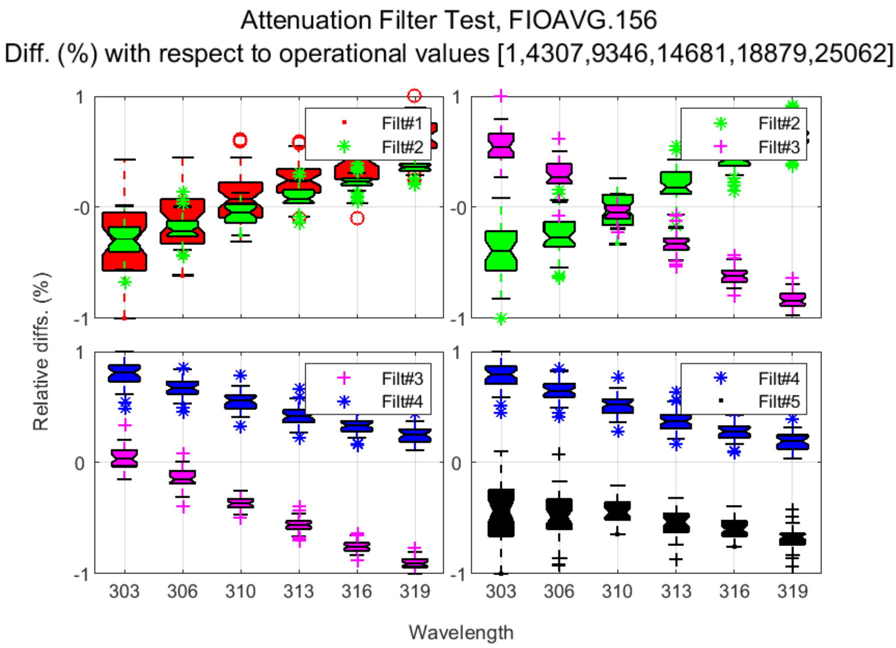


Figure 6-14 – Notched box-plot for the calculated attenuation relative differences of neutral density filters with respect to operational values. We show for each subplot relative differences corresponding to correlative filters (color box-plots). Solid lines and boxes mark the median, upper and lower quartiles. The point whose distance from the upper or lower quartile is 1 times larger than the interquartile range is defined as outlier.

6.5 Wavelength Calibration

6.5.1 Cal-Step determination

The sun scan routine takes DS ozone measurements by moving the micrometer about 15 steps below and above the ozone reference position (wavelength *Calibration step-number*). A Hg test is required before and after the measurement to assure the correct wavelength setting during the *sun scan* test. Ozone *versus* step number ideally shows a parabolic shape with a maximum at the ozone reference position. With this choice, small wavelength shifts ($\approx \pm 2$ steps) do not affect the ozone value. This optimal micrometer position is a near-linear function of the ozone slant path at the time of the scan, see Fig. 6-15

Previous to the campaign, 29 sun-scan (SC) tests covering a ozone slant path range from 400 to 1200 DU were collected, see Fig. 6-16)). No additional SC measures are required during the campaign as Brewer DAV#156 routinely operates from Davos station. The calculated Cal-Step Number (CSN) was about 1 step lower than the value in the current configuration: **1019** *vs.* **1020**. Taking this into account, we suggest keeping the current CSN, **1020**.

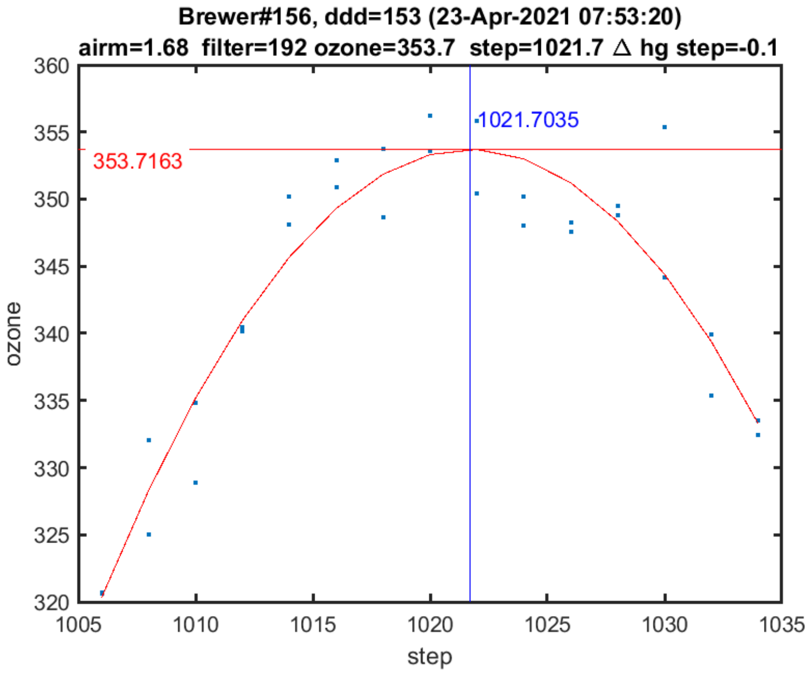


Figure 6-15 – **Ozone measurements moving the micrometer 15 step around the operational CSN defined in the initial configuration**

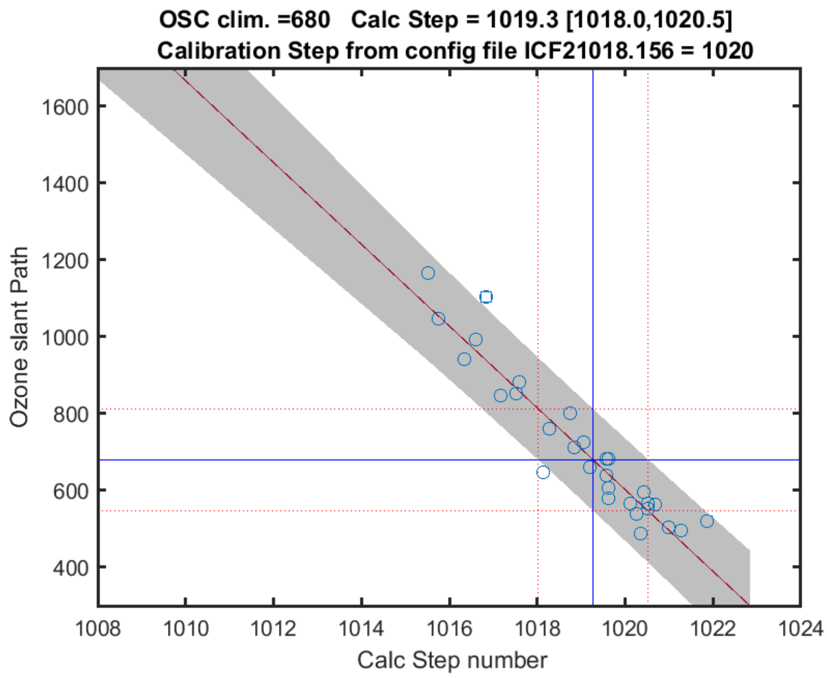


Figure 6-16 – Ozone Slant Path *vs* Calc – Step number. Vertical solid line marks the calculated *Cal Step Number* for a climatological OSC equal to 680 (horizontal solid line). Grey area represents a 95% confidence interval

6.5.2 Dispersion Test

We analyzed the dispersion tests carried out in the previous and present calibration campaigns. For all of them, we processed data from Mercury and Cadmium spectral lamps, using cubic functions to adjust the micrometer step number to wavelength positions. The results of this historical analysis are summarized in Table 6-3.

In particular, for the current campaign, Fig. 6-17 shows that the cubic fitting was good for all the dispersion tests, with residuals being lower than 0.1 Å in most of the slits. For the dispersion tests performed, Table 6-4 provides individual wavelength resolution, ozone absorption coefficient, sulfur dioxide absorption coefficient, and Rayleigh absorption for the operational CSN and those at ± 1 step.

An absorption coefficient equal to **0.341** is suggested in the final configuration.

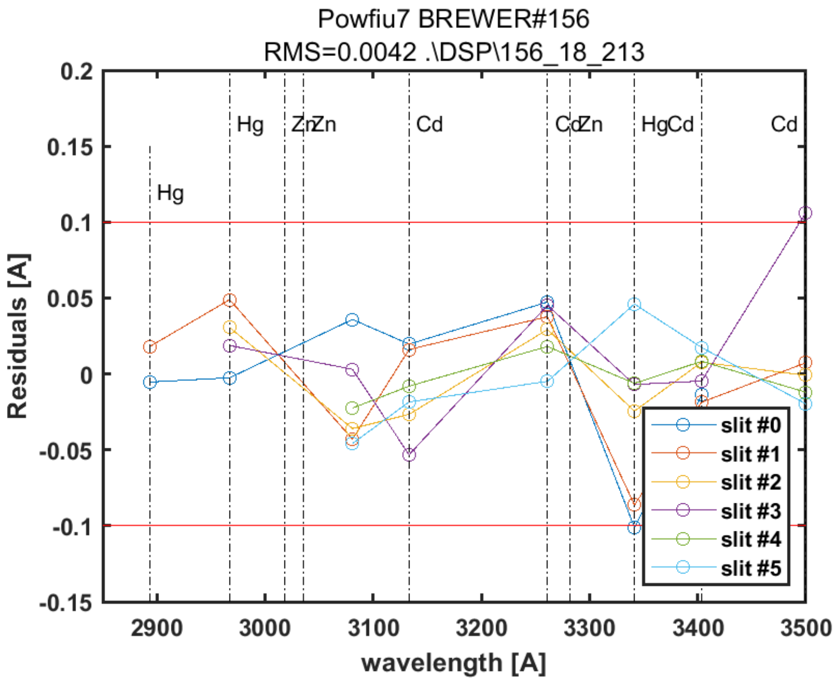


Figure 6-17 – 2021 residuals of cubic fit

Table 6-3 – **Dispersion derived constants**

	Calc-step	O3abs coeff.	SO2abs coeff.	O3/SO2
Current	1020	0.3410	2.3500	1.1653
07-Jul-2016	1020	0.3409	3.1274	1.1482
19-Jul-2017	1020	0.3399	3.1212	1.1449
01-Aug-2018	1020	0.3409	3.1360	1.1467
11-Nov-2020	1020	0.3417	3.1305	1.1497
22-Jun-2021	1020	0.3402	3.1437	1.1451
14-Jul-2021	1020	0.3409	3.1191	1.1479
Final	1020	0.3410	2.3500	1.1653

Table 6-4 – **2021 dispersion derived constants from the cubic fitting**

step= 1019	slit#0	slit#1	slit#2	slit#3	slit#4	slit#5
WL(A)	3031.68	3062.79	3100.38	3134.96	3168.01	3200.06
Res(A)	5.4242	5.4638	5.3331	5.495	5.346	5.2558
O3abs(1/cm)	2.6062	1.785	1.0054	0.677	0.37479	0.29388
Ray abs(1/cm)	5052.2859	4833.7253	4585.4983	4371.325	4178.4612	4001.7084
SO2abs(1/cm)	3.4706	5.5889	2.3911	1.9077	1.0556	0.61015
step= 1020	slit#0	slit#1	slit#2	slit#3	slit#4	slit#5
WL(A)	3031.76	3062.86	3100.45	3135.04	3168.08	3200.13
Res(A)	5.4241	5.4637	5.333	5.4949	5.346	5.2557
O3abs(1/cm)	2.6035	1.7835	1.0052	0.67664	0.37487	0.2934
Ray abs(1/cm)	5051.7569	4833.23	4585.0409	4370.8997	4178.0645	4001.3376
SO2abs(1/cm)	3.4527	5.6124	2.3988	1.8959	1.0568	0.6079
step= 1021	slit#0	slit#1	slit#2	slit#3	slit#4	slit#5
WL(A)	3031.83	3062.94	3100.52	3135.11	3168.15	3200.2
Res(A)	5.424	5.4636	5.3329	5.4948	5.3459	5.2557
O3abs(1/cm)	2.6008	1.782	1.0049	0.67624	0.37494	0.29289
Ray abs(1/cm)	5051.2279	4832.7347	4584.5835	4370.4744	4177.6678	4000.9668
SO2abs(1/cm)	3.435	5.6355	2.4064	1.8841	1.058	0.60555
step	O3abs	Rayabs	SO2abs	O3SO2Abs	Daumont	Bremen
1019	0.342	101255.4049	3.108	1.1513	0.35339	0.34461
1020	0.34093	101231.0073	3.1191	1.1479	0.35234	0.34352
1021	0.33985	101206.6165	3.1295	1.1445	0.35123	0.34239

6.5.3 Umkehr

For the Umkehr calibration, only the lines shorter than 3400 Å were used. The Umkehr offset is calculated by forcing the wavelength of slit #4 at the ozone position to be the same as on slit #1 at the Umkehr setting. The Umkehr offset calculated is **2432**. Table 6-5 summarizes the dispersion test for umkehr: wavelength, resolution and ozone absorption coefficient.

Table 6-5 – **2021 Umkehr dispersion constants**

step= 1020	slit#0	slit#1	slit#2	slit#3	slit#4	slit#5
WL(A)	3032	3063	3100	3135	3168	3200
Res(A)	5.4241	5.4637	5.333	5.4949	5.346	5.2557
O3abs(1/cm)	2.6035	1.7835	1.0052	0.67664	0.37487	0.2934
Ray abs(1/cm)	0.50518	0.48332	0.4585	0.43709	0.41781	0.40013
step= 2432	slit#0	slit#1	slit#2	slit#3	slit#4	slit#5
WL(A)	3134	3164	3200	3234	3265	3296
Res(A)	5.3406	5.3292	5.2118	5.3556	5.2381	5.1615
O3abs(1/cm)	0.67954	0.39486	0.29352	0.12057	0.060308	0.033384
Ray abs(1/cm)	0.43792	0.42025	0.40013	0.38272	0.36699	0.35256

6.6 ETC Transfer

Based on the Lambert-Beer law, the total ozone column in the Brewer algorithm can be expressed as:

$$X = \frac{F - ETC}{\alpha\mu} \tag{1}$$

where F are the measured double ratios corrected for Rayleigh effects, α is the ozone absorption coefficient, μ is the ozone air mass factor, and ETC is the extra-terrestrial constant. The F, α and ETC parameters are weighted functions at the operational wavelengths with weighting coefficients $w = [0, 1, -0.5, -2.2, 1.7]$ for slits 1 to 5, with nominal wavelengths equal to $[306.3, 310.1, 313.5, 316.8, 320.1]$ nm.

The transfer of the calibration scale (namely ETC) is done side by side with the reference instrument. Once we have collected enough near-simultaneous direct sun ozone measurements, we calculate the new extraterrestrial constant after imposing the condition that the measured ozone will be the same for simultaneous measurements. In terms of the previous equation for ozone, this leads to the following condition:

$$ETC_i = F_i - X_i^{reference}\alpha\mu \tag{2}$$

For a good characterized instrument, the ETC determined values show a Gaussian distribution and the mean value is used as the instrument constant. One exception to this rule is the single monochromator Brewer models (MK-II and MK-IV) which are affected by stray light.

Brewers are calibrated with the one parameter (1P) ETC transfer method: only the ozone ETC constant is transferred from the reference instrument. The so-called “two parameters calibration method” (2P), where both the ozone absorption coefficient and the ETC are calculated from the reference, is also obtained and serves as a quality indicator of the calibration. We consider a calibration optimal when both ETC values agree within 10 units, and the ozone absorption coefficient calculated from the dispersion tests and obtained with the 2P method agree within ± 2 micrometer steps, or approx. ± 0.002 atm.cm^{-1}. This range represents a total ozone difference of about 0.5% at airmass equal to 2, and total ozone of 300 DU.

The ETC is obtained by comparison with the reference brewer **IZO#185** using near-simultaneous measurements during **4** days (two measurements are considered near-simultaneous if they are taken less than **3.5** minutes apart). Measurements with airmass difference greater than 3% were removed from the analysis.

6.6.1 Initial Calibration

For the evaluation of initial status of Brewer DAV#156, we used the period from days **188** to **197** which correspond with **137** near-simultaneous direct sun ozone measurements. As shown in Fig. 6-18, the current calibration constants produce ozone values slightly higher than the reference instrument (0.4%). When the ETC is corrected taking into account the difference between the SL and R6 reference (SL correction), the results slightly improve.

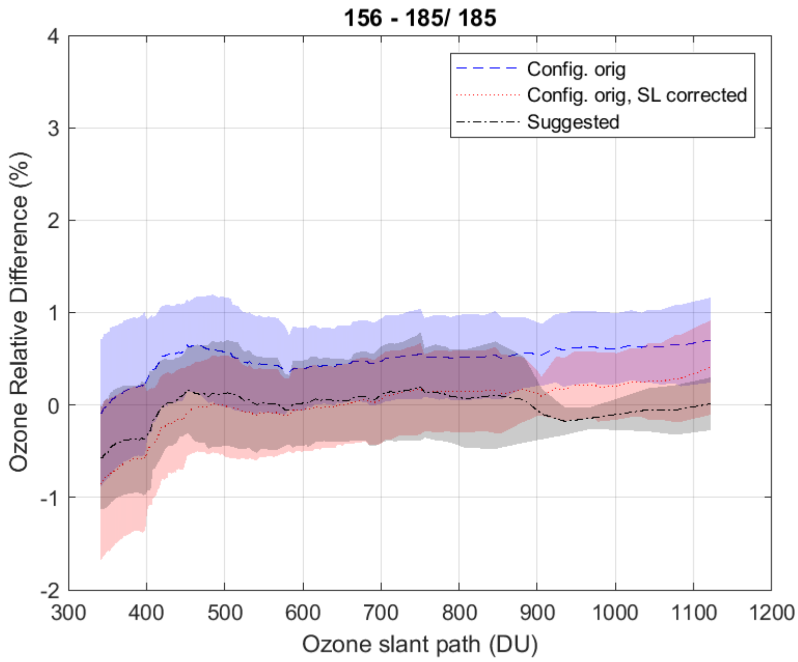


Figure 6-18 – Mean direct-sun ozone column percentage difference between Brewer DAV#156 and Brewer IZO#185 as a function of ozone slant path.

6.6.2 Final Calibration

A new ETC value was calculated (see Fig. 6-19) also using the **137** simultaneous direct sun measurements from days **192** to **195**. The new value, calculated using the full OSC range, is 10 units higher than the current ETC value (**1743**). Therefore, we recommend using this new ETC, together with the new proposed standard lamp reference ratios, **451** for R6. We updated the new calibration constants in the ICF provided.

The ETC value in the final ICF corresponds to the 1P transfer. As shown in Table 6-6, the agreement between the 1P and 2P ETCs is only slightly above the maximum tolerance limit of 10 units.

Mean daily total ozone values and relative differences with respect to IZO#185 for the original and the final configurations are shown in Table 6-7.

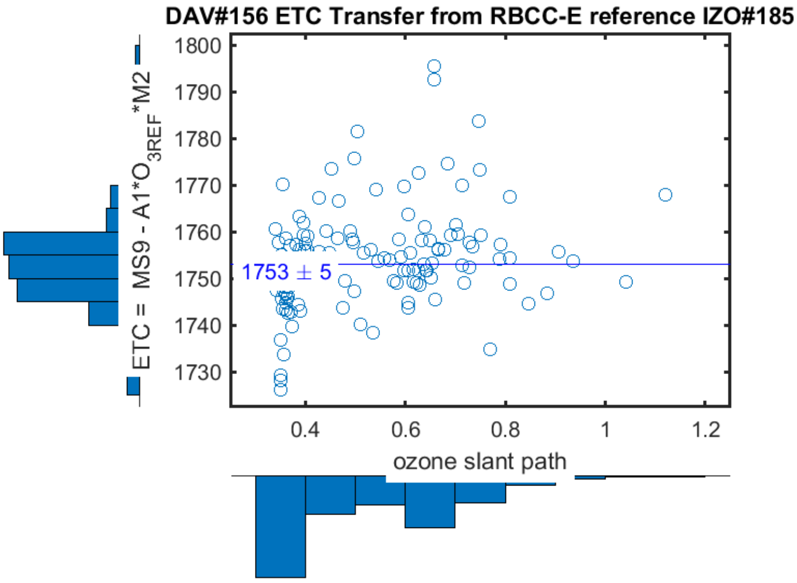


Figure 6-19 – **Mean direct-sun ozone column percentage difference between Brewer DAV#156 and Brewer IZO#185 as a function of ozone slant path.**

Table 6-6 – **Comparison between the results of the 1P and 2P ETC transfer methods for the final days.**

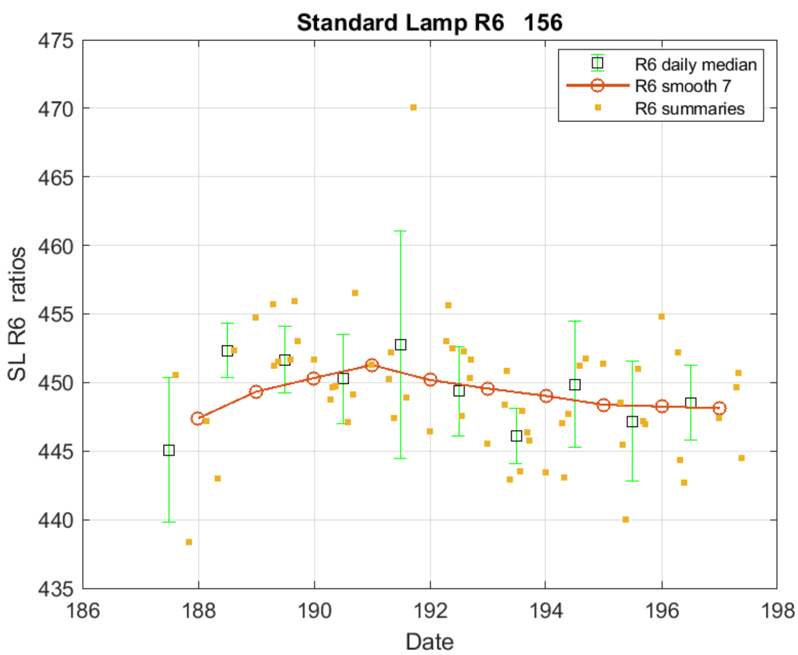
	ETC 1P	ETC 2P	O3Abs final	O3Abs 2P
full OSC range	1753	1754	3410	3402

Table 6-7 – Daily mean ozone and relative differences with respect to the reference, with the original and final (the latter, in the columns marked with a star) calibrations. Data from the final days.

	Day	O3#185	std	N	O3#156	std	rd	O3(*)#156	std(*)	rd(*)
10-Jul-2021	191	314.2	1	15	313.2	2.1	-0.3	311.8	2.2	-0.8
11-Jul-2021	192	315.7	3	43	317.5	2.9	0.6	316.2	3.1	0.2
12-Jul-2021	193	305	2.4	69	305.9	3	0.3	304.6	3	-0.1
13-Jul-2021	194	322.9	2.1	10	325.1	2.9	0.7	323.9	2.7	0.3

6.6.3 Standard Lamp Reference Values

The reference values of standard lamp ratios during the calibration period were **451** for R6 (Figure 6-20) and **1142** for R5 (Figure 6-21).



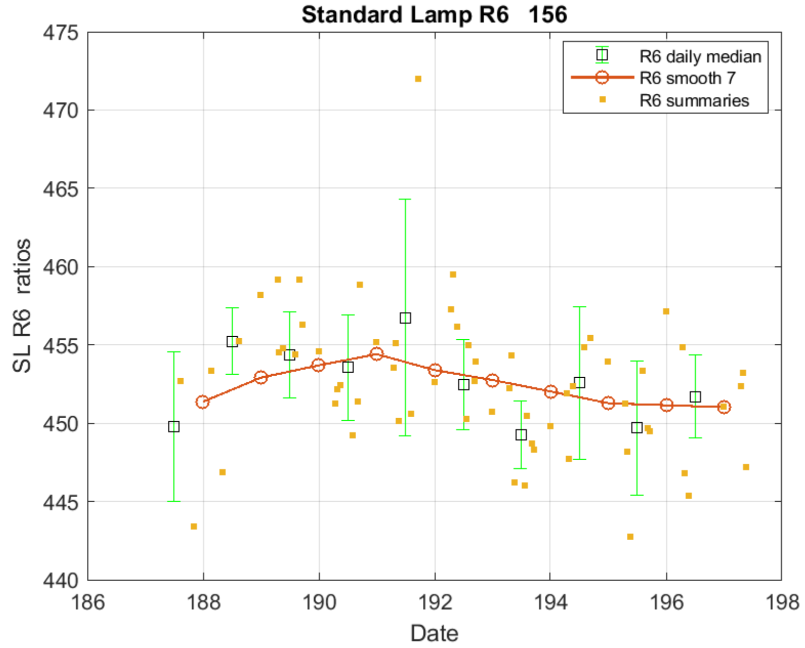
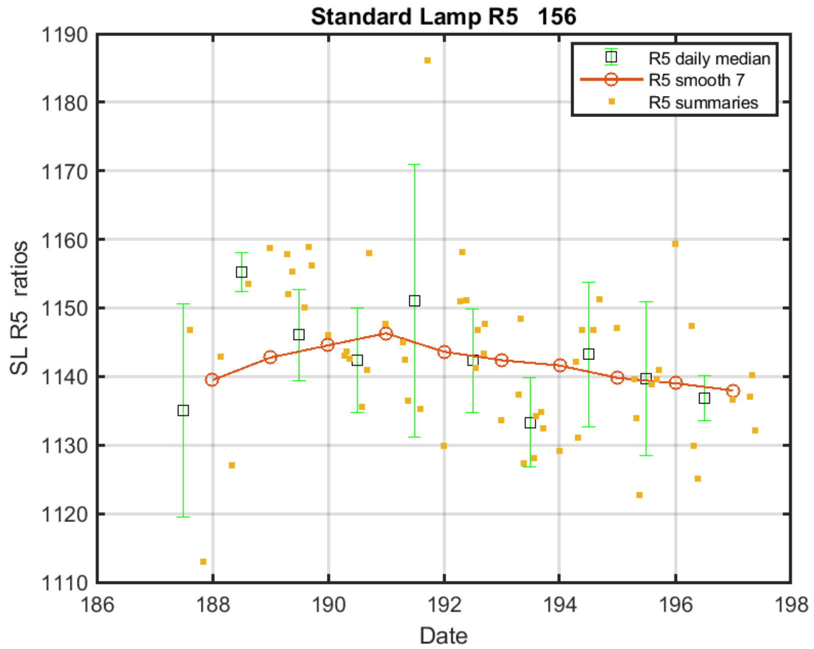


Figure 6-20 – Standard Lamp O_3 R6 ratios: daily mean and standard deviation (squares), seven day running mean (circle) and individual tests (black dots). Reprocessed using old (top) and new (bottom) instrumental constants



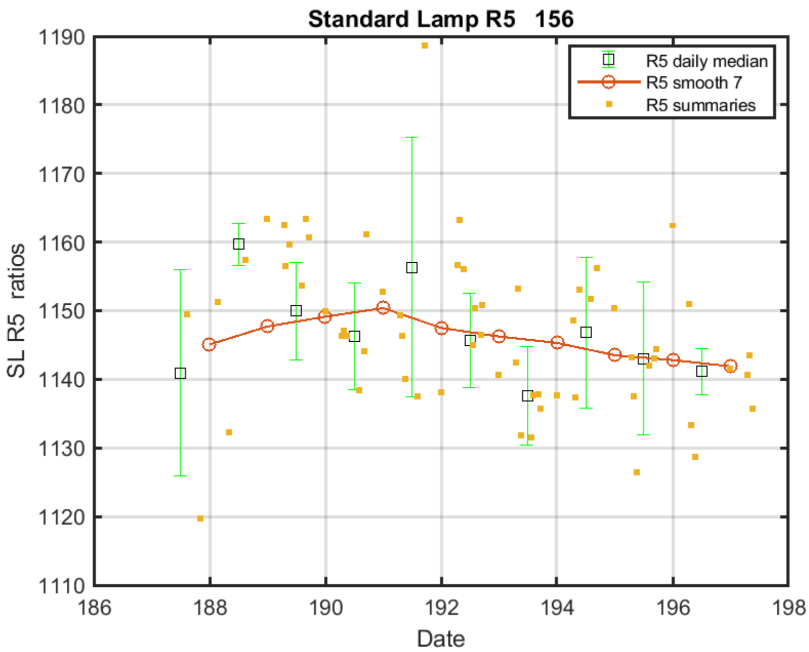


Figure 6-21 – Standard Lamp SO_2 R5 ratios: daily mean and standard deviation (squares), seven day running mean (circle) and individual tests (black dots). Reprocessed using old (top) and new (bottom) instrumental constants

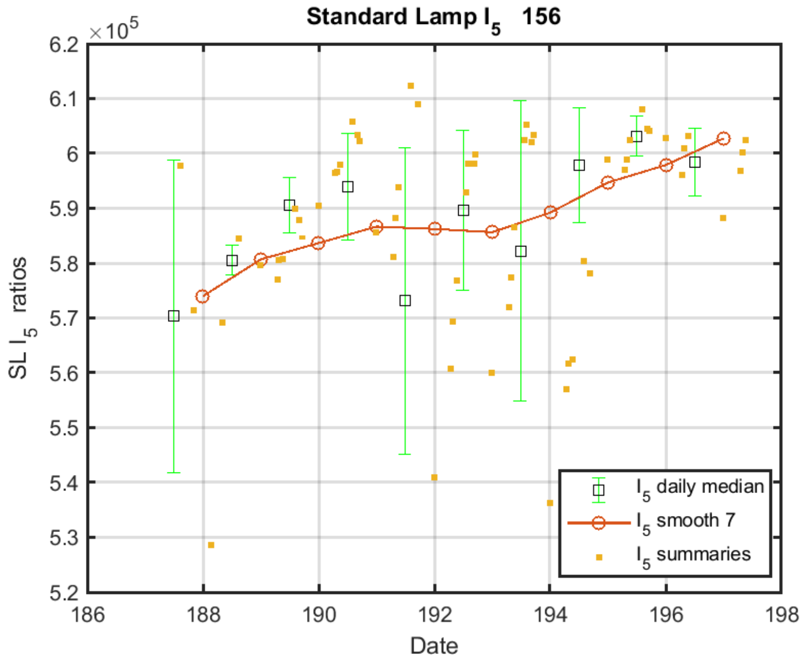


Figure 6-22 – Standard Lamp intensity: daily mean and standard deviation (squares), seven day running mean (circle) and individual tests (black dots)

6.7 Configuration

6.7.1 Instrument constant file

	Initial (ICF21018.156)	Final (ICF18821.156)
o3 Temp coef 1	0	0
o3 Temp coef 2	-0.81	-0.78
o3 Temp coef 3	-1.65	-1.47
o3 Temp coef 4	-2.48	-2.35
o3 Temp coef 5	-3.41	-3.32
Micrometer steps/deg	0	0
O3 on O3 Ratio	0.341	0.341
SO2 on SO2 Ratio	2.35	2.35
O3 on SO2 Ratio	1.1653	1.1653
ETC on O3 Ratio	1743	1755
ETC on SO2 Ratio	705	705
Dead time (sec)	2.7e-08	2.7e-08
WL cal step number	1020	1020
Slitmask motor delay	94	94
Umkehr Offset	2432	2432
ND filter 0	0	0
ND filter 1	4307	4307
ND filter 2	9346	9346
ND filter 3	14681	14681
ND filter 4	18879	18879
ND filter 5	25062	25062
Zenith steps/rev	2972	2972
Brewer Type	3	3
COM Port #	1	1
o3 Temp coef hg	0	0
n2 Temp coef hg	1125	1125
n2 Temp coef 1	441	441
n2 Temp coef 2	0	0
n2 Temp coef 3	0	0
n2 Temp coef 4	0	0
n2 Temp coef 5	0	0
O3 Mic #1 Offset	7412	7412
Mic #2 Offset	6150	6150
O3 FW #3 Offset	178	178
NO2 absn Coeff	-3	-3
NO2 ds etc	770	770
NO2 zs etc	740	740
NO2 Mic #1 Offset	8028	8028
NO2 FW #3 Offset	178	178
NO2/O3 Mode Change	2501	2501
Grating Slope	0.99875	0.99875
Grating Intercept	-17.5	-17.5
Micrometer Zero	1734	1734
Iris Open Steps	250	250
Buffer Delay (s)	0.6	0.6
NO2 FW#1 Pos	64	64
O3 FW#1 Pos	256	256
FW#2 Pos	0	0
uv FW#2 Pos	64	64
Zenith Offset	50	50
Zenith UVB Position	2234	2234

6.8 Daily Summary report

Day	osc range	O3#185	std	N	O3#156	std	rd	O3(*)#156	std(*)	rd(*)
188	1000>osc>700	303.9	0	1	306.2	0	0.8	NaN	NaN	NaN
188	700>osc>400	305.8	1	5	304.8	1.3	-0.3	NaN	NaN	NaN
189	osc<400	340.1	0	1	331.9	0	-2.4	NaN	NaN	NaN
190	700>osc>400	323.6	2.2	16	323.6	1.4	0	NaN	NaN	NaN
190	osc<400	326.4	0.6	3	326.3	1.4	0	NaN	NaN	NaN
191	1500>osc>1000	310.5	0	2	312.6	0.2	0.7	NaN	NaN	NaN
191	1000>osc>700	309.8	0.6	11	310.3	0.6	0.1	NaN	NaN	NaN
191	700>osc>400	311	1.2	24	310.2	1.7	-0.2	NaN	NaN	NaN
191	osc<400	314.4	1	30	311.1	2.1	-1.1	NaN	NaN	NaN
192	1000>osc>700	316.3	1.5	8	317.5	1.5	0.4	317.7	1.5	0.5
192	700>osc>400	316.9	2.1	62	316.3	2.3	-0.2	316.6	2.4	-0.1
192	osc<400	313.5	3.5	12	312.5	4.4	-0.3	313.1	4.6	-0.1
193	1500>osc>1000	305.5	0	2	305.3	0	-0.1	305	0	-0.2
193	1000>osc>700	302.9	1.9	26	303	2.6	0.1	302.7	2.7	-0.1
193	700>osc>400	303.7	2.3	48	304.7	3.4	0.3	304.5	3.5	0.2
193	osc<400	306.5	1.2	60	305.1	1.9	-0.5	305.2	1.9	-0.4
194	1500>osc>1000	318.5	0	2	319.4	0	0.3	319.5	0	0.3
194	1000>osc>700	322.8	0.1	8	323.1	1	0.1	323.3	1.1	0.1
194	700>osc>400	323.9	1.9	10	325.1	2.7	0.4	325.2	2.8	0.4
196	1000>osc>700	337.2	0	1	338.3	0	0.3	NaN	NaN	NaN
197	1500>osc>1000	335.6	0.1	2	NaN	NaN	NaN	NaN	NaN	NaN
197	1000>osc>700	336.2	0.5	5	NaN	NaN	NaN	NaN	NaN	NaN
197	700>osc>400	342.2	2	8	NaN	NaN	NaN	NaN	NaN	NaN
197	osc<400	340.2	0.1	2	NaN	NaN	NaN	NaN	NaN	NaN

6.9 Summary Plots

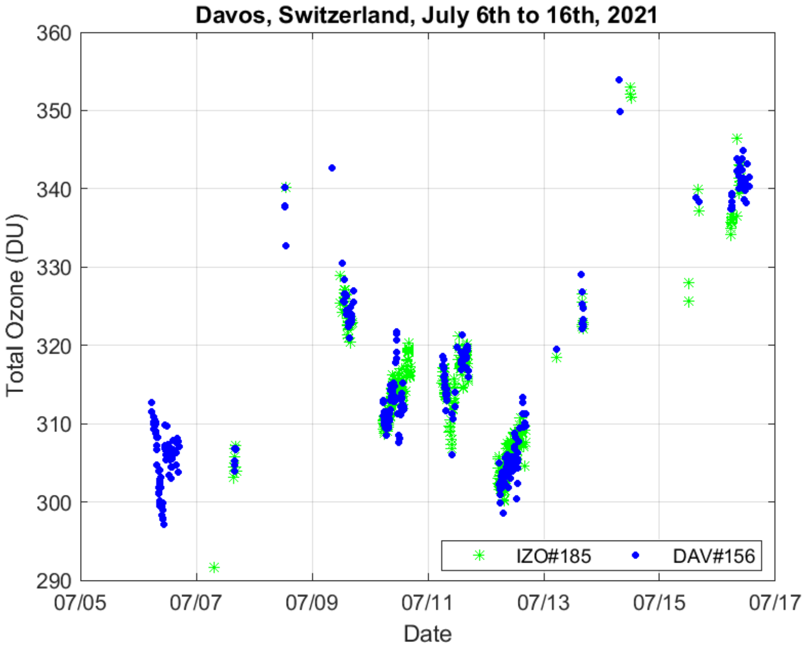
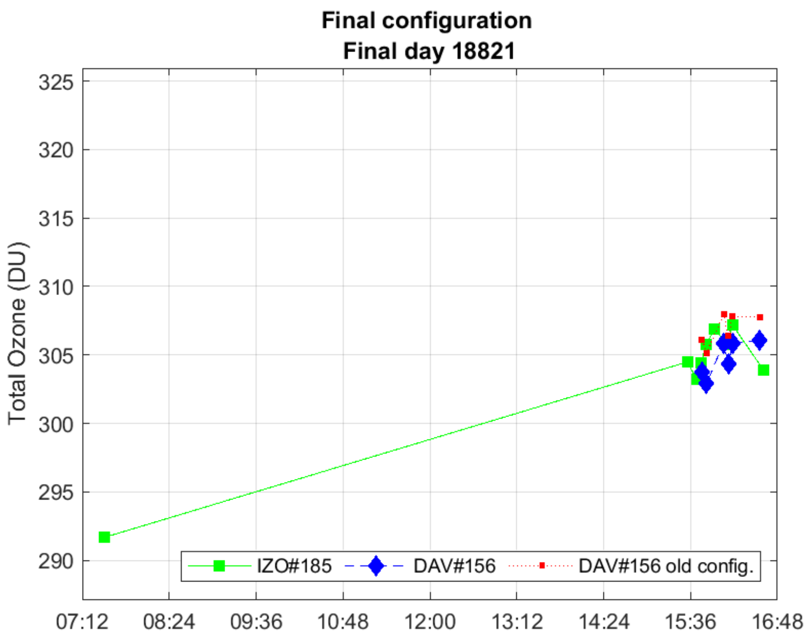
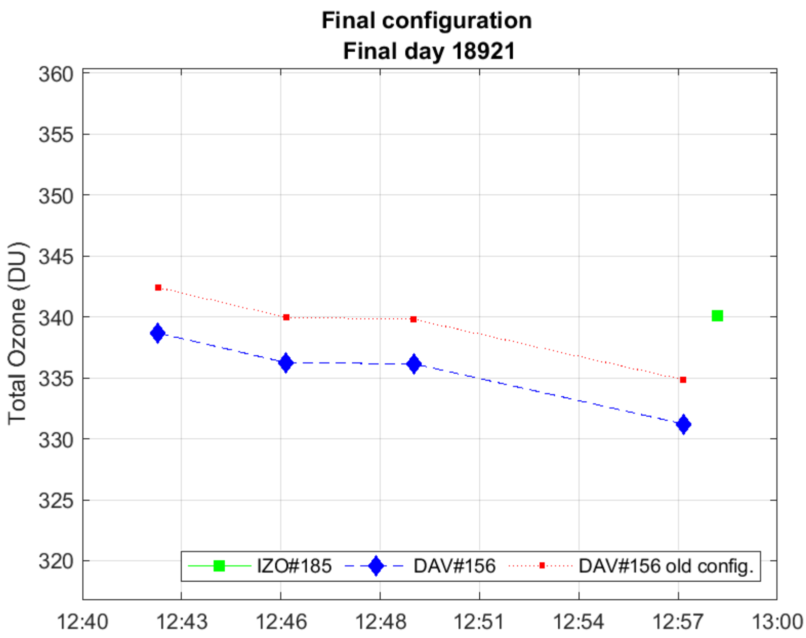
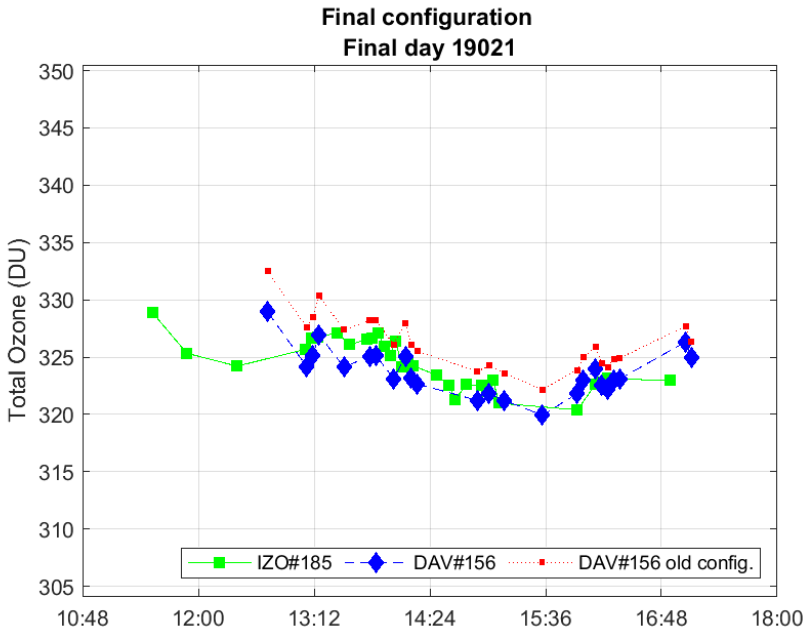
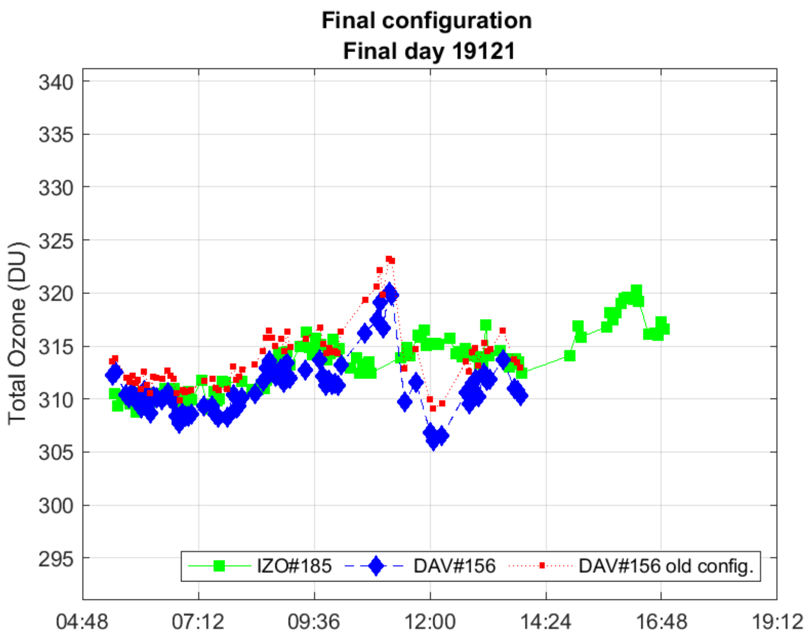


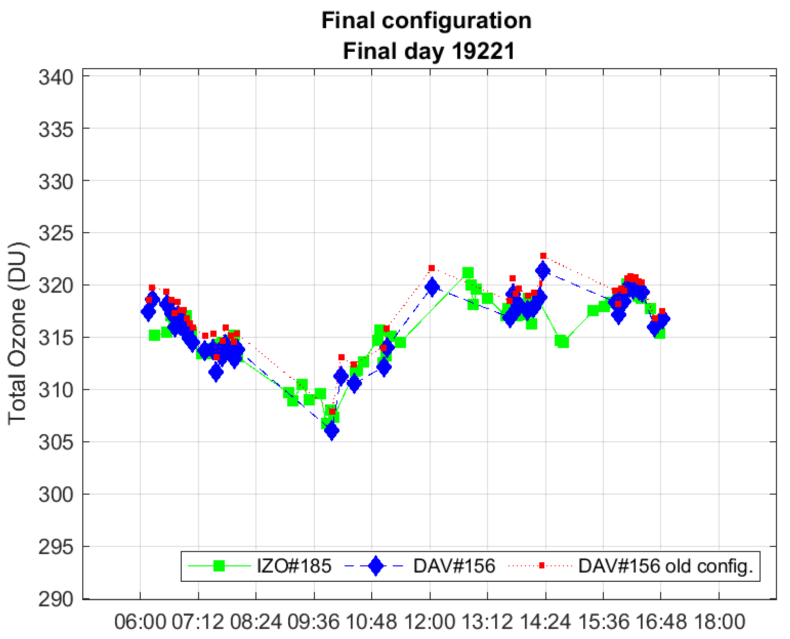
Figure 6-23 – **Overview of the intercomparison. Brewer DAV#156 data are evaluated using final constants (blue circles)**

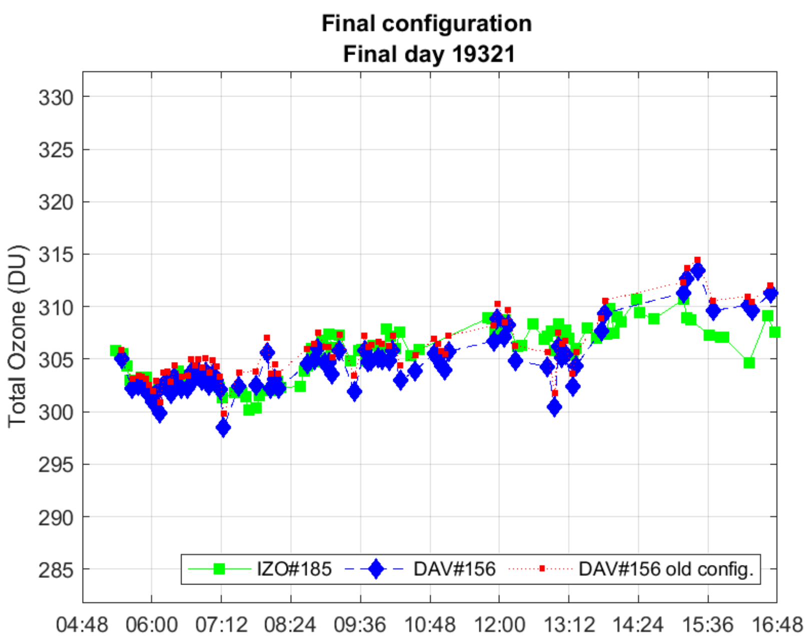

Final configuration
Final day 18821
Total Ozone (DU)
325
320
315
310
305
300
295
290
07:12
08:24
09:36
10:48
12:00
13:12
14:24
15:36
16:48
IZO#185
DAV#156
DAV#156 old config.

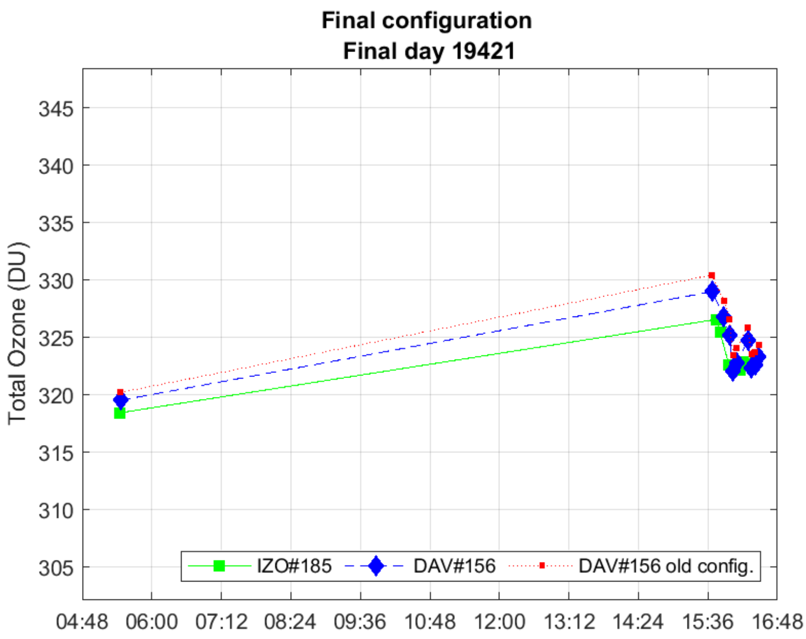

Final configuration
Final day 18921
Total Ozone (DU)
360
355
350
345
340
335
330
325
320
12:40
12:43
12:46
12:48
12:51
12:54
12:57
13:00
IZO#185
DAV#156
DAV#156 old config.

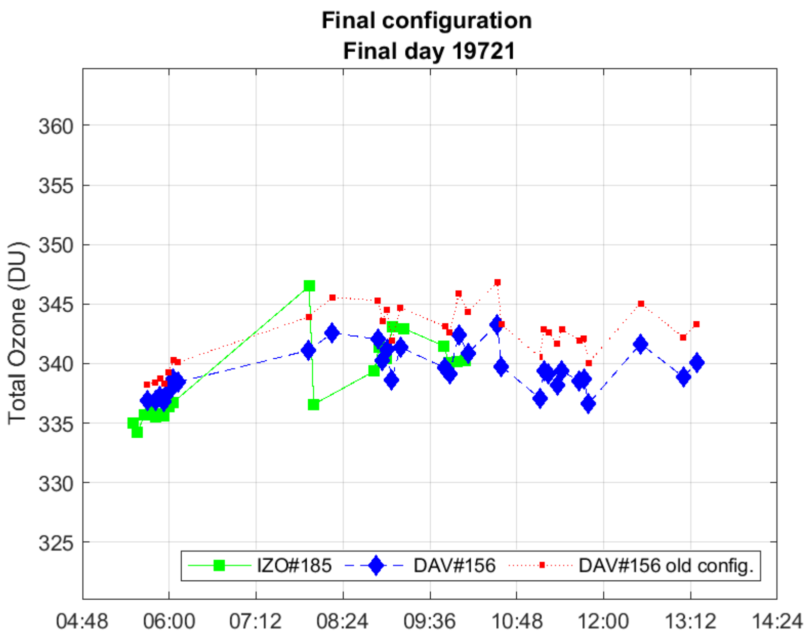

Final configuration
Final day 19021
Total Ozone (DU)
350
345
340
335
330
325
320
315
310
305
10:48
12:00
13:12
14:24
15:36
16:48
18:00
IZO#185
DAV#156
DAV#156 old config.


Final configuration
Final day 19121
Total Ozone (DU)
340
335
330
325
320
315
310
305
300
295
04:48
07:12
09:36
12:00
14:24
16:48
19:12
IZO#185
DAV#156
DAV#156 old config.


Final configuration
Final day 19221
340
335
330
325
320
315
310
305
300
295
290
Total Ozone (DU)
IZO#185
DAV#156
DAV#156 old config.
06:00 07:12 08:24 09:36 10:48 12:00 13:12 14:24 15:36 16:48 18:00


Final configuration
Final day 19321
330
325
320
315
310
305
300
295
290
285
Total Ozone (DU)
IZO#185
DAV#156
DAV#156 old config.
04:48 06:00 07:12 08:24 09:36 10:48 12:00 13:12 14:24 15:36 16:48


Final configuration
Final day 19421
Total Ozone (DU)
345
340
335
330
325
320
315
310
305
IZO#185
DAV#156
DAV#156 old config.
04:48
06:00
07:12
08:24
09:36
10:48
12:00
13:12
14:24
15:36
16:48


Final configuration
Final day 19721
Total Ozone (DU)
360
355
350
345
340
335
330
325
IZO#185
DAV#156
DAV#156 old config.
04:48
06:00
07:12
08:24
09:36
10:48
12:00
13:12
14:24

7 Brewer K&Z#158

7.1 Calibration Summary

The Fifteenth Intercomparison Campaign of the Regional Brewer Calibration Center Europe (RBCC-E) was held from July 6th to the 16th, 2021, at the Physikalisch-Meteorologisches Observatorium PMOD (Davos, Switzerland).

Brewer K&Z#158 participated in the campaign in the period from July 8th to 13th. The campaign days of Brewer K&Z#158 correspond to Julian days 189 – 194.

For the evaluation of the initial status, we used **74** simultaneous direct sun (DS) ozone measurements from days **190** to **191**. For final calibration purposes, we used **109** simultaneous DS ozone measurements taken from day **193** to **194**.

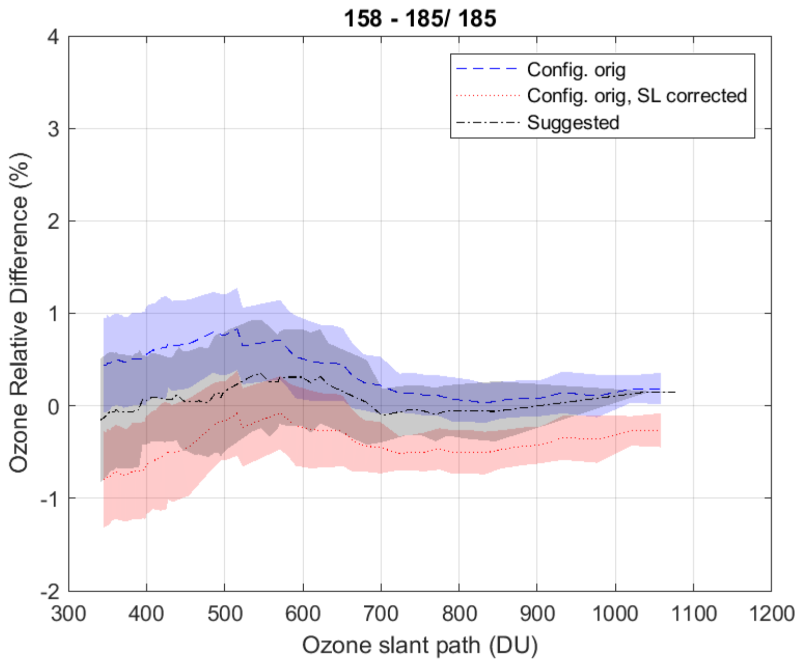


Figure 7-1 – Mean DS ozone column percentage difference between Brewer K&Z#158 and Brewer IZO#185, plotted as a function of the ozone slant path. Results for the current (issued in the previous calibration campaign) configuration are show in blue; the red dotted line corresponds to the same configuration, but with the standard lamp correction applied; the black line corresponds to results obtained with the updated configuration proposed in the current campaign. The shadow areas represent the standard deviation of the mean. The comparison with the original configuration (with and without SL correction) is done during the blind days, while the comparison with the suggested configuration corresponds to the final days of the campaign.

As shown in Fig. 7-1, the current ICF (ICF17519.158, blue dashed line) produces ozone values with an average difference of around 0.5% with respect to the reference instrument. SL correction (Fig. 7-1, red dotted line) improves the comparison with Brewer IZO#185. Furthermore, R6, Dead time, HS and

HL show that the instrument has undergone various changes during the last two years. Therefore, we recommend applying the SL correction since the last calibration.

Regarding the performance of the filters, the analysis of the FI measurements does not show any non-linearity, but the comparison with the reference Brewer clearly shows the need to correct the filter #3.

No sun-scan (SC) tests were performed on the instrument's site before the intercomparison. However, The tests done during the campaign confirm the current cal step value (1015, within a step error of ± 1).

The ozone absorption coefficient in use (0.3431) is quite different to the value derived from dispersion tests carried out after the maintenance done during the campaign. A new value 0.34 was adopted in final configuration, calculated from the dispersion test performed after the campaign.

Taking into account all this, we suggest some changes to the configuration of Brewer K&Z#158.

7.1.1 Recommendations and Remarks

1. The R6 standard lamp test results from Brewer K&Z#158 have not been stable during the last 2 years. We update its value to **559**.
2. We also suggest a new R5 reference value of **848**.
3. Dead time (DT) remains the same, $\mathbf{3{\cdot}10}^{-8}$, despite the changes observed since the last calibration.
4. We suggest to correct the filter #3, with a coefficient value of **-15**.
5. We update the absorption coefficient in the configuration file to **0.34**.
6. Finally, we suggest updating the ETC value from **1792** to **1835**, although only one day of simultaneous measures with the reference was available for the ETC calculation.

7.1.2 External links

Configuration File

http://rbcce.aemet.es/svn/campaigns/dav2021/bfiles/158/ICF18821.158

Calibration Report

https://docs.google.com/spreadsheets/d/12-4EoZzJkJDv5Pgpdt3PNZlZLXahvdlubhqOyijRack/edit#gid=1694024224

Calibration Reports Detailed

Historic and instrumental

http://rbcce.aemet.es/svn/campaigns/dav2021/latex/158/html/cal_report_158a1.html

Temperature & Filter

http://rbcce.aemet.es/svn/campaigns/dav2021/latex/158/html/cal_report_158a2.html

Wavelength

http://rbcce.aemet.es/svn/campaigns/dav2021/latex/158/html/cal_report_158b.html

ETC transfer

http://rbcce.aemet.es/svn/campaigns/dav2021/latex/158/html/cal_report_158c.html

Izaña Atmospheric Research Center, La Marina 20, 38071 S/C de Tenerife, Spain
Tf: +34922151718/Fax: +3492274475

7.2 Instrument History: Analysis of Average files

7.2.1 Standard Lamp Test

As shown in Figure 7-2 and 7-3, the standard lamp test performance has not remained stable since the last calibration in June 2019. The current R6 value is 18 units less that the reference value given in the previous intercomparison campaign.

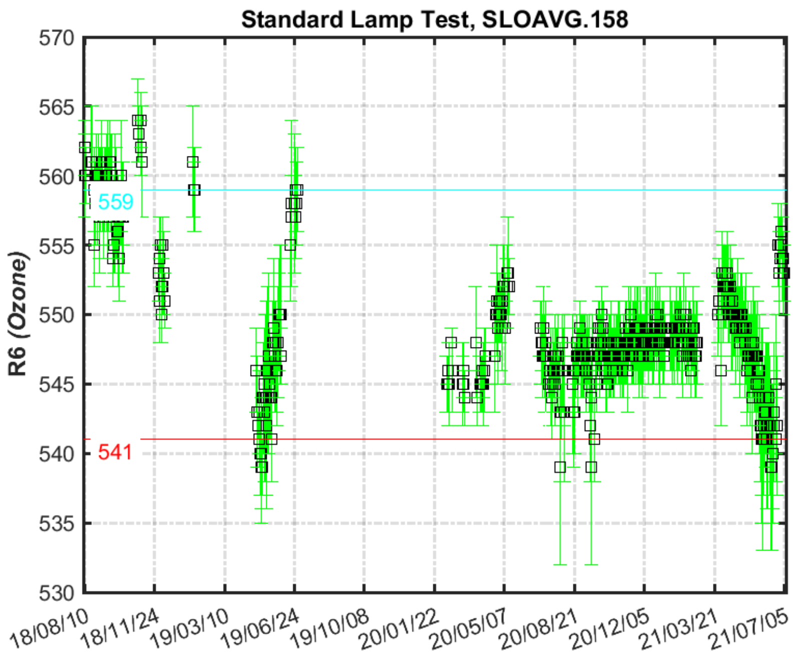


Figure 7-2 – **Standard Lamp test R6 (Ozone) ratios. Horizontal lines are labeled with the original and final reference values (red and blue lines, respectively)**

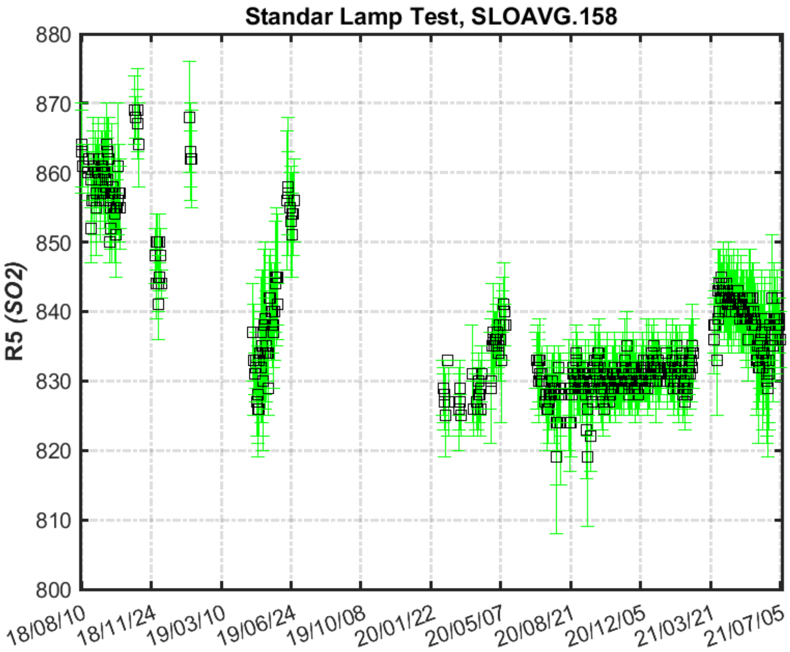


Figure 7-3 – **Standard Lamp test R5 (SO_2) ratios**

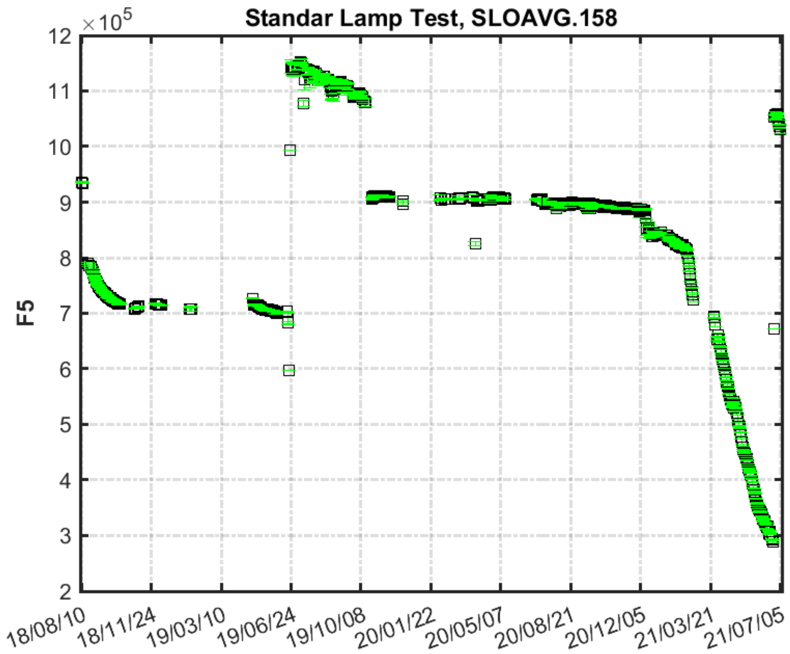


Figure 7-4 – **SL intensity for slit five.**

7.2.2 Run Stop and Dead Time

Run stop test values are within test tolerance limits most of the time for all slits. But there are two periods when the values are out of the limits, in July 2019 and in March 2020.

Despite the instability of the dead time over the last two years (Fig. 7-6), after the maintenance carried out in the campaign, the dead time value is the same as in the previous setting,**3**·**10**$^{-8}$, so it will remain unchanged in the ICF.

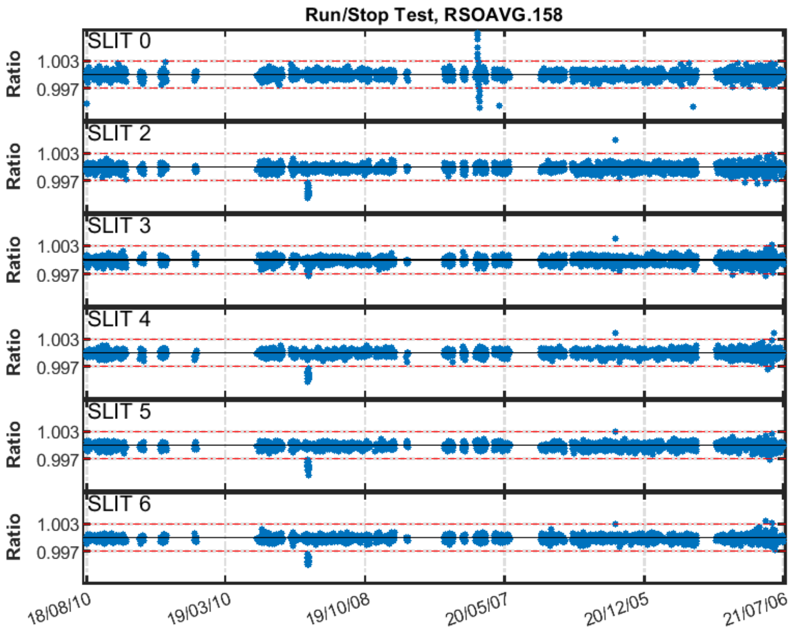


Figure 7-5 – **Run/stop test**

7.2.3 Analog Test

Fig. 7-7 shows that the high voltage has remained almost constant around at **1333** over the last two years, but analog test shows two different periods for the standard lamp current.

7.2.4 Mercury Lamp Test

No noticeable internal mercury lamp intensity events have been observed during the campaign, see Fig. 7-8.

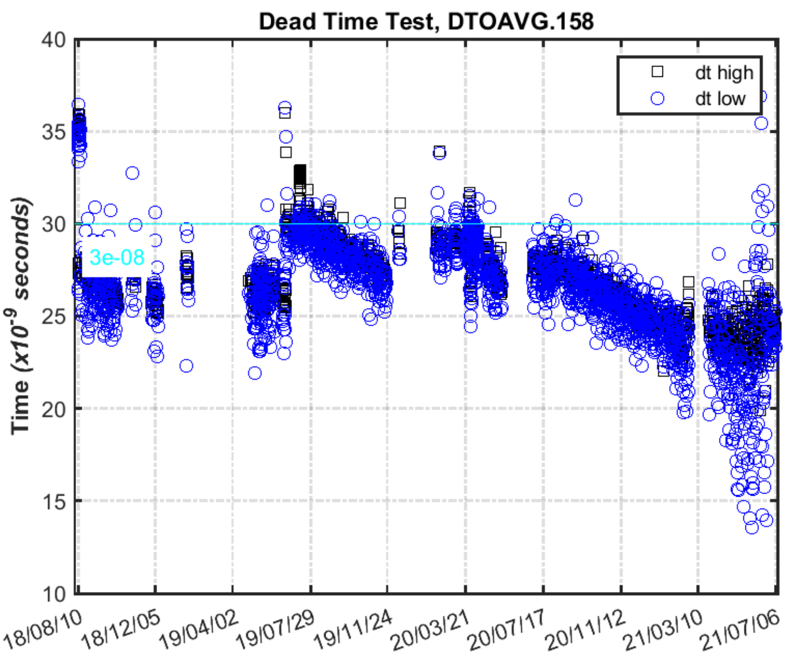


Figure 7-6 – **Dead Time test. Horizontal lines are labelled with the current (red) and final (blue) values.**

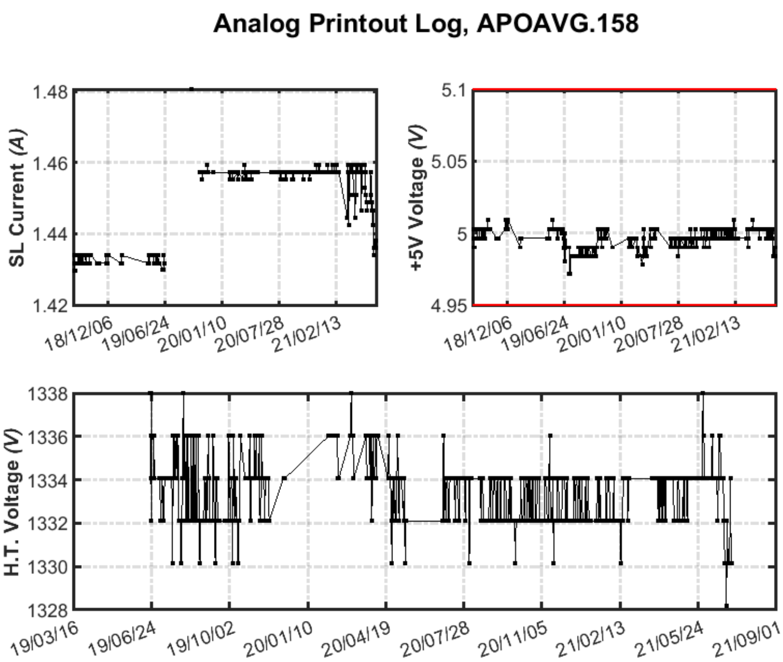


Figure 7-7 – **Analog voltages and intensity.**

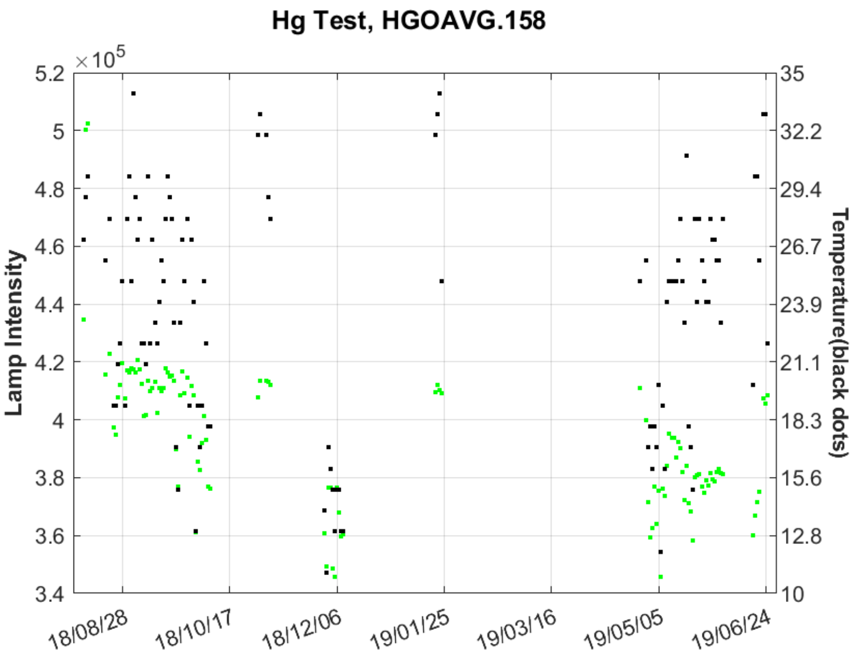
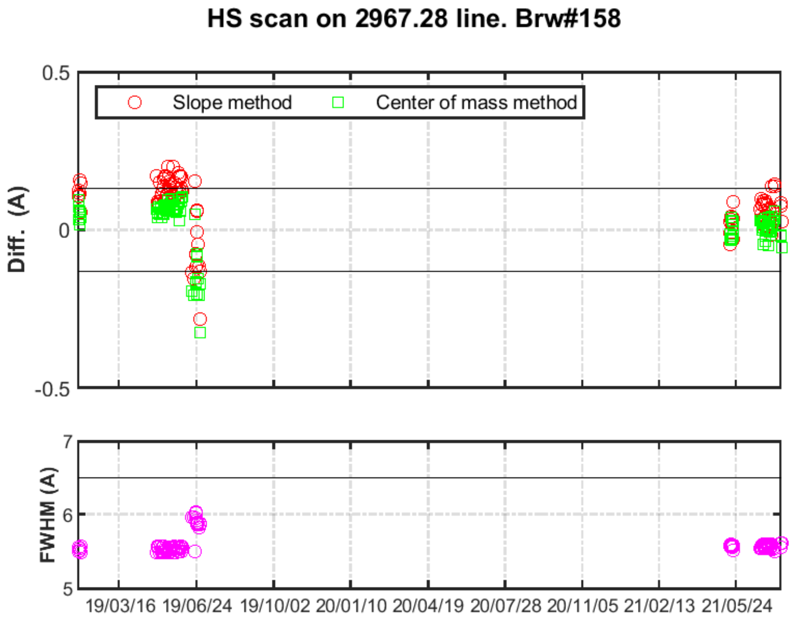


Figure 7-8 – Mercury lamp intensity (green squares) and Brewer temperature registered (black dots). Both parameters refer to maximum values for each day.

7.2.5 CZ scan on mercury lamp

In order to check both the wavelength settings and the slit function width, we analyzed the scans performed on the 296.728 nm, and 334.148 nm mercury lines, see Fig. 7-9. As a reference, the calculated scan peak, in wavelength units, should be within 0.013 nm from the nominal value, whereas the calculated slit function width should be no more than 0.65 nm. Analysis of the CZ scans performed on Brewer K&Z#158 during the campaign show good results, with the peak of the calculated scans within the accepted tolerance range. Regarding the slit function width, results are good, with a FWHM lower than 6.5 Å.



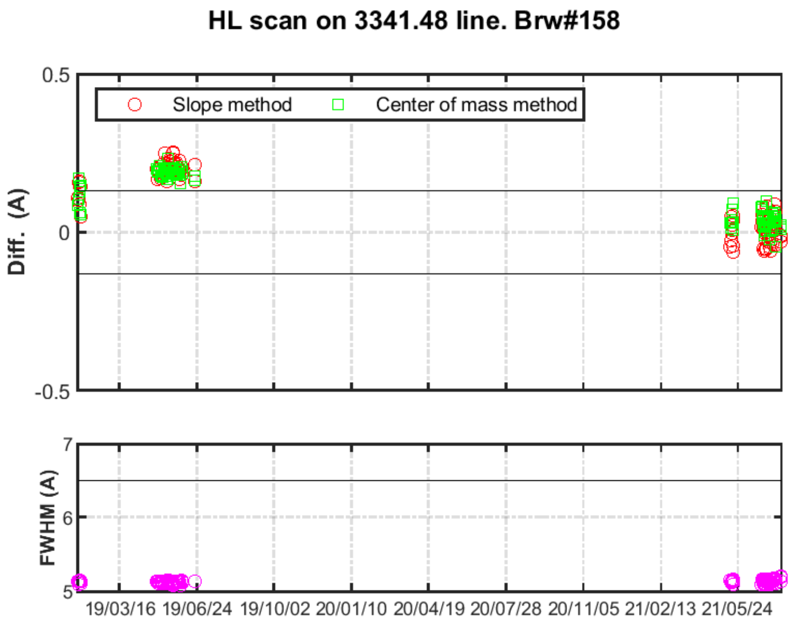


Figure 7-9 – CZ scan on Hg lines. The upper panels show differences with respect to the reference line (solid lines represent the limit ± 0.013 nm) as computed by the slopes (red circles) and center of mass (green squares) methods. Lower panels show the Full Width at Half Maximum value for each scan performed (solid lines represent the 0.65 nm limit).

7.2.6 CI scan on internal *SL*

CI scans of the standard lamp recorded at different times can be compared to investigate whether the instrument has changed its spectral sensitivity. We shown in Fig. 7-10 percentage ratios of the Brewer **K&Z#158** CI scans performed during the campaign relative to the scan CI19021.158. Unfortunately, the change in the lamp intensity is framed due to maintenance operations. Therefore, the results of this test are inconclusive.

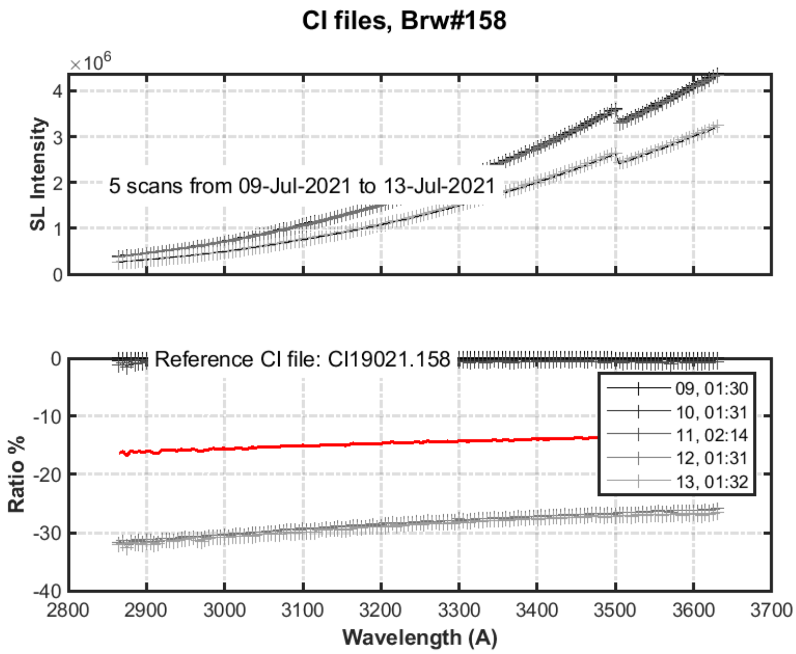


Figure 7-10 – CI scan of Standard Lamp performed during the campaign days. Scans processed (upper panel) and relative differences with respect to a selected reference scan (lower panel). Red line represents the mean of all relative differences

7.3 Absolute Temperature Coefficients

Temperature coefficients are determined using the standard lamp test. For every slit, the raw counts corrected for zero temperature coefficients are used in a linear regression against temperature with the slopes representing the instrument's temperature coefficients. From this we obtain the corrected *R6* and *R5* ratios to analyze the new temperature coefficients' performance.

The current coefficients present a bad agreement to reduce the temperature dependence. Therefore, a new set of coefficient were calculated as the Figure 7-11 shown (temperature range from **13**$^\circ$ **C** to **32**$^\circ$ **C**. The results obtained are summarized in Table 7-1.

We have also extended our analysis using two months of data measured before the campaign (Fig. 7-12). Finally, these two sets of coefficients are compared using two months of data after the campaign. Fig. 7-13 shows how the temperature coefficients obtained during the campaign perform better.

Table 7-1 – Temperature Coefficients. Calculated coefficients are normalized to slit#2

	slit#2	slit#3	slit#4	slit#5	slit#6
Current	0.0000	-0.4100	-1.0500	-1.9500	-2.4600
Calculated	0.0000	-0.5000	-0.8000	-1.3000	-2.0000
Final	0.0000	-0.4790	-0.8240	-1.3380	-1.9550

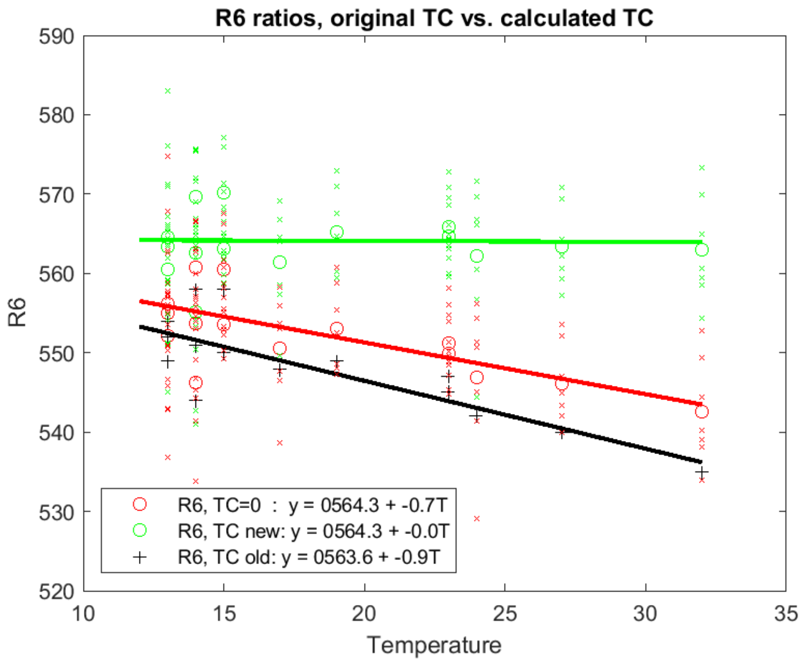


Figure 7-11 – Temperature coefficients' performance. Red circles represent standard lamp R6 ratios calculated from raw counts without temperature correction (temperature coefficients set to 0). Black crosses and green circles represent standard lamp R6 ratios corrected with original and calculated temperature coefficients, respectively. Data corresponds to the present campaign.

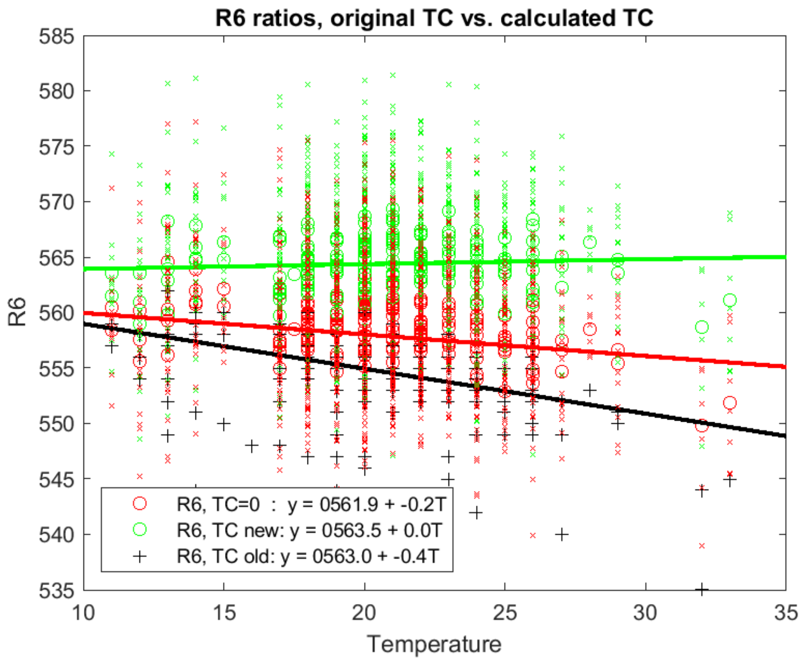


Figure 7-12 – **Same as Fig. 7-11 but for the whole period between calibration campaigns.**

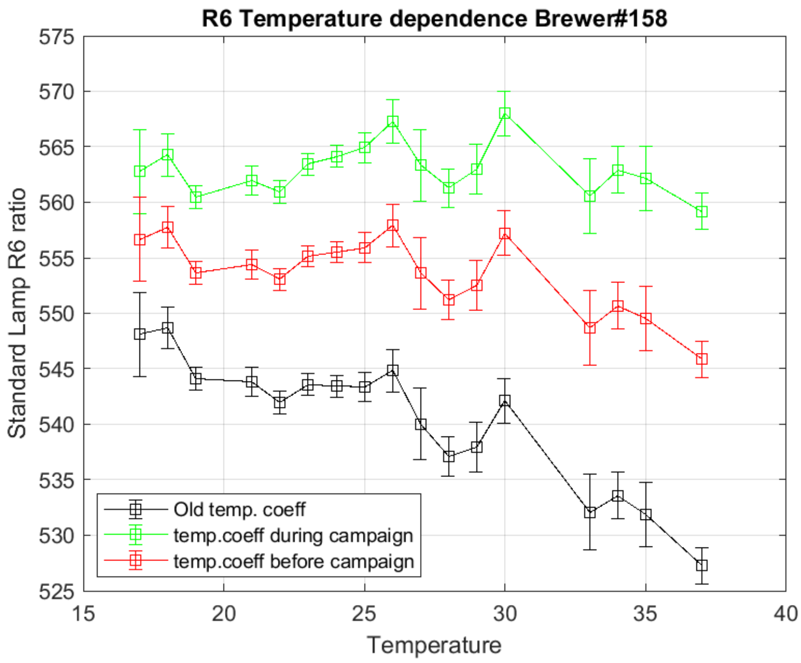


Figure 7-13 – Standard lamp R6 (MS9) ratio as a function of temperature. We plotted R6 ratio recalculated with the original (black), the obtained before (red) and during the camping (green) temperature coefficients

7.4 Attenuation Filter Characterization

7.4.1 Attenuation Filter Correction

The filter's spectral dependence affects the ozone calculation because the Brewer software assumes that their attenuation is wavelength-neutral. We can estimate the correction factor needed for this non-linearity by multiplying the attenuation of every filter and every wavelength by the ozone weighting coefficients.

During the calibration period, a total of **80** FI tests were analyzed to calculate the attenuation for every filter and slit. Fig. 7-14 shows the results of these tests, and Table 7-2 shows the calculated ETC corrections for each filter.

The analysis of the FI tests does not show any non-linearity, however the comparison with the reference Brewer clearly shows the need to correct the filter #3 with a correction of -15 ETCs.

Table 7-2 – **ETC correction due to Filter non-linearity. Median value, mean values and, 95% confidence intervals are calculated using bootstrap technique**

	filter#1	filter#2	filter#3	filter#4	filter#5
ETC Filt. Corr. (median)	1	-4	-3	3	3
ETC Filt. Corr. (mean)	-1.6	-3.4	-4.4	2.5	1.7
ETC Filt. Corr. (mean 95% CI)	[-5.2 1.8]	[-7.6 0.6]	[-7.6 -1.2]	[-1.3 6.3]	[-2.2 5.5]

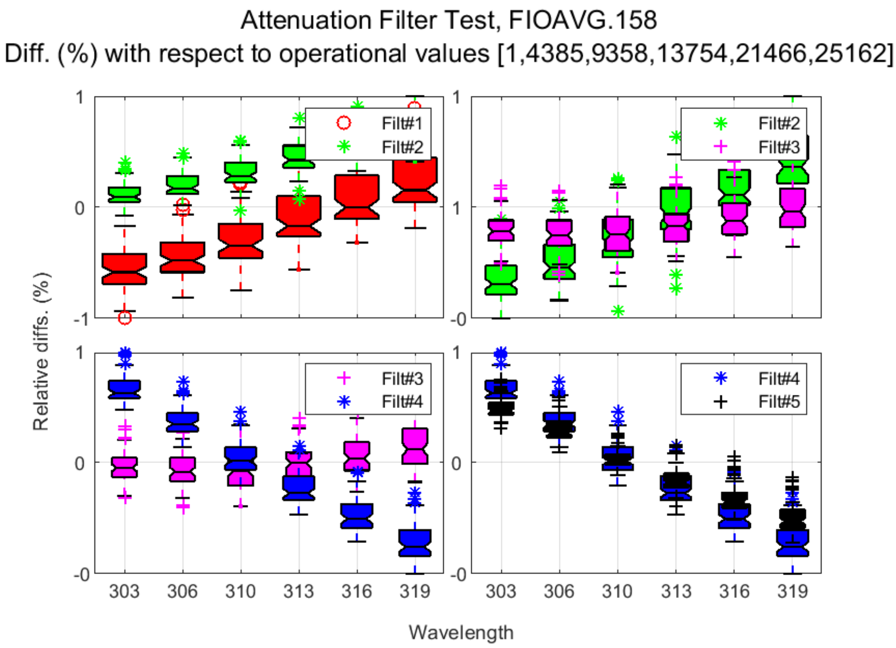


Figure 7-14 – Notched box-plot for the calculated attenuation relative differences of neutral density filters with respect to operational values. We show for each subplot relative differences corresponding to correlative filters (color box-plots). Solid lines and boxes mark the median, upper and lower quartiles. The point whose distance from the upper or lower quartile is 1 times larger than the interquartile range is defined as outlier.

7.5 Wavelength Calibration

7.5.1 Cal-Step determination

The sun scan routine takes DS ozone measurements by moving the micrometer about 15 steps below and above the ozone reference position (wavelength *Calibration step-number*). A Hg test is required before and after the measurement to assure the correct wavelength setting during the *sun scan* test. Ozone *versus* step number ideally shows a parabolic shape with a maximum at the ozone reference position. With this choice, small wavelength shifts ($\approx \pm 2$ steps) do not affect the ozone value. This optimal micrometer position is a near-linear function of the ozone slant path at the time of the scan, see Fig. 7-15

During the campaign, 10 sun-scan (SC) tests covering a ozone slant path range from 400 to 1200 DU were collected (see Fig. 7-16). These sun-scan tests confirm the current cal step value (**1015**, within ±1 step error).

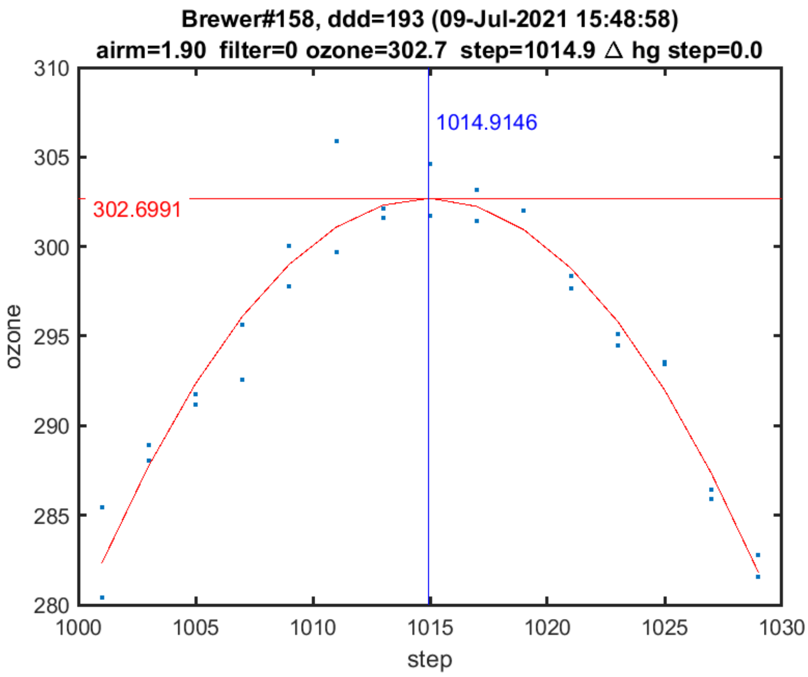


Figure 7-15 – **Ozone measurements moving the micrometer 15 step around the operational CSN defined in the initial configuration**

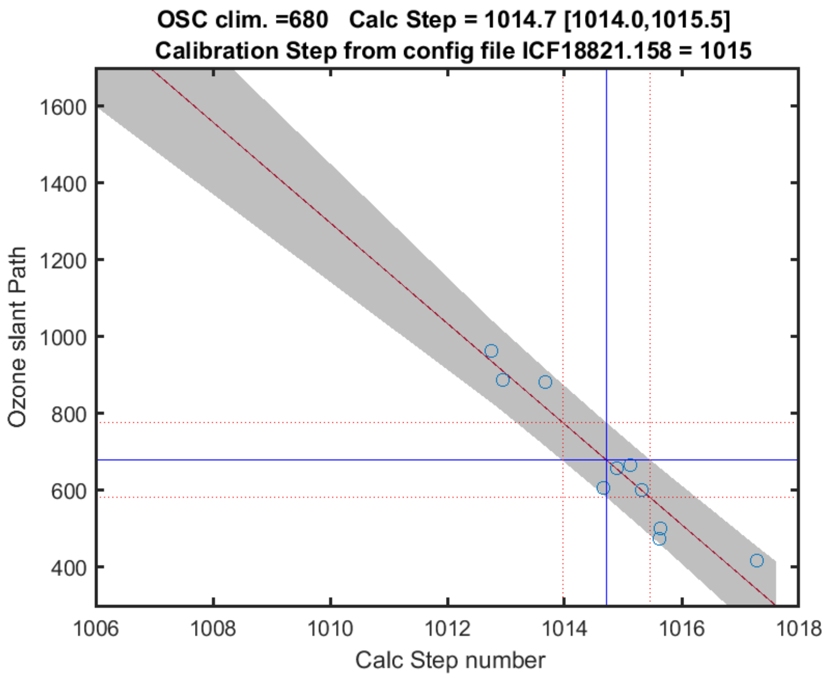


Figure 7-16 – Ozone Slant Path *vs* Calc – Step number. Vertical solid line marks the calculated *Cal Step Number* for a climatological OSC equal to 680 (horizontal solid line). Grey area represents a 95% confidence interval

7.5.2 Dispersion Test

We analyzed the dispersion tests carried out in the previous and present calibration campaigns. For all of them, we processed data from Mercury and Cadmium spectral lamps, using quadratic functions to adjust the micrometer step number to wavelength positions. The results of this historical analysis are summarized in Table 7-3.

The dispersion test carried out during the campaign was done only before maintenance, so these tests were repeated after the campaign. According to these last tests, an absorption coefficient equal to **0.34** is suggested in the final configuration. In particular, Fig. 7-17 shows that the quadratic fitting was good for the last dispersion test, with residuals being lower than 0.1 Å in almost all slits. For this dispersion tests, Table 7-4 provides individual wavelength resolution, ozone absorption coefficient, sulfur dioxide absorption coefficient, and Rayleigh absorption for the operational CSN and those at ± 1 step.

Table 7-3 – **Dispersion derived constants**

	Calc-step	O3abs coeff.	SO2abs coeff.	O3/SO2
Current	1015	0.3431	2.3500	1.1636
02-Aug-2018	1015	0.3414	3.1983	1.1452
23-Jun-2019	1015	0.3409	3.1866	1.1445
09-Jul-2021	1015	0.3419	3.1946	1.1462
15-Jul-2021	1015	0.3401	3.1968	1.1418
02-Aug-2021	1015	0.3397	3.1903	1.1398
Final	1015	0.3400	2.3500	1.1636

Table 7-4 – 2021 dispersion derived constants

step= 1014	slit#0	slit#1	slit#2	slit#3	slit#4	slit#5
WL(A)	3032.02	3063.08	3100.54	3135.09	3168.05	3200.12
Res(A)	5.4599	5.5154	5.4114	5.4871	5.4009	5.2515
O3abs(1/cm)	2.5945	1.7787	1.0048	0.6764	0.37492	0.29352
Ray abs(1/cm)	5049.8807	4831.7655	4584.4625	4370.5959	4178.2655	4001.4206
SO2abs(1/cm)	3.3987	5.6701	2.4115	1.8874	1.056	0.60843
step= 1015	slit#0	slit#1	slit#2	slit#3	slit#4	slit#5
WL(A)	3032.09	3063.15	3100.61	3135.16	3168.12	3200.19
Res(A)	5.4599	5.5153	5.4113	5.487	5.4009	5.2514
O3abs(1/cm)	2.592	1.7771	1.0045	0.67599	0.37499	0.29302
Ray abs(1/cm)	5049.3484	4831.2672	4584.0021	4370.1678	4177.8661	4001.0473
SO2abs(1/cm)	3.3836	5.6911	2.4197	1.8758	1.0572	0.6061
step= 1016	slit#0	slit#1	slit#2	slit#3	slit#4	slit#5
WL(A)	3032.16	3063.22	3100.69	3135.23	3168.19	3200.26
Res(A)	5.4598	5.5152	5.4112	5.4869	5.4008	5.2514
O3abs(1/cm)	2.5895	1.7755	1.0042	0.67557	0.37506	0.29248
Ray abs(1/cm)	5048.8162	4830.7689	4583.5418	4369.7398	4177.4668	4000.674
SO2abs(1/cm)	3.3687	5.7102	2.4281	1.8641	1.0584	0.60369
step	O3abs	Rayabs	SO2abs	O3SO2Abs	Daumont	Bremen
1014	0.34074	93955.1652	3.1819	1.1433	0.35188	0.34312
1015	0.33966	93931.7109	3.1903	1.1398	0.3508	0.34202
1016	0.33847	93908.2633	3.1965	1.1361	0.34969	0.34087

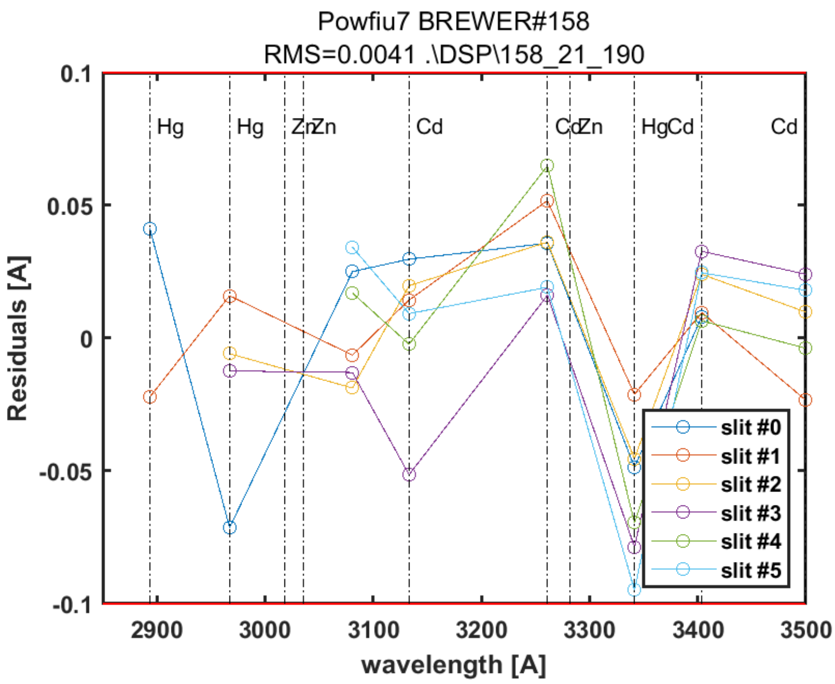


Figure 7-17 – 2021 residuals of quadratic fit

7.5.3 Umkehr

For the Umkehr calibration, only the lines shorter than 3400 Å were used. The Umkehr offset is calculated by forcing the wavelength of slit #4 at the ozone position to be the same as on slit #1 at the Umkehr setting. The Umkehr offset calculated is **2417**. Table 7-5 summarizes the dispersion test for umkehr: wavelength, resolution and ozone absorption coefficient.

Table 7-5 – 2021 Umkehr dispersion constants

step= 1015	slit#0	slit#1	slit#2	slit#3	slit#4	slit#5
WL(A)	3032	3063	3101	3135	3168	3200
Res(A)	5.4599	5.5153	5.4113	5.487	5.4009	5.2514
O3abs(1/cm)	2.592	1.7771	1.0045	0.67599	0.37499	0.29302
Ray abs(1/cm)	0.50493	0.48313	0.4584	0.43702	0.41779	0.4001
step= 2417	slit#0	slit#1	slit#2	slit#3	slit#4	slit#5
WL(A)	3134	3164	3200	3234	3265	3296
Res(A)	5.3687	5.3847	5.2622	5.3684	5.2721	5.1373
O3abs(1/cm)	0.67962	0.39315	0.2929	0.12039	0.060468	0.033371
Ray abs(1/cm)	0.43779	0.42015	0.4001	0.38271	0.36703	0.35258

7.6 ETC Transfer

Based on the Lambert-Beer law, the total ozone column in the Brewer algorithm can be expressed as:

$$X = \frac{F - ETC}{\alpha\mu} \tag{1}$$

where F are the measured double ratios corrected for Rayleigh effects, α is the ozone absorption coefficient, μ is the ozone air mass factor, and ETC is the extra-terrestrial constant. The F, α and ETC parameters are weighted functions at the operational wavelengths with weighting coefficients $w = [0, 1, -0.5, -2.2, 1.7]$ for slits 1 to 5, with nominal wavelengths equal to $[306.3, 310.1, 313.5, 316.8, 320.1]$ nm.

The transfer of the calibration scale (namely ETC) is done side by side with the reference instrument. Once we have collected enough near-simultaneous direct sun ozone measurements, we calculate the new extraterrestrial constant after imposing the condition that the measured ozone will be the same for simultaneous measurements. In terms of the previous equation for ozone, this leads to the following condition:

$$ETC_i = F_i - X_i^{reference}\alpha\mu \tag{2}$$

For a good characterized instrument, the ETC determined values show a Gaussian distribution and the mean value is used as the instrument constant. One exception to this rule is the single monochromator Brewer models (MK-II and MK-IV) which are affected by stray light.

Brewers are calibrated with the one parameter (1P) ETC transfer method: only the ozone ETC constant is transferred from the reference instrument. The so-called “two parameters calibration method” (2P), where both the ozone absorption coefficient and the ETC are calculated from the reference, is also obtained and serves as a quality indicator of the calibration. We consider a calibration optimal when both ETC values agree within 10 units, and the ozone absorption coefficient calculated from the dispersion tests and obtained with the 2P method agree within ± 2 micrometer steps, or approx. ± 0.002 atm.cm^{-1}. This range represents a total ozone difference of about 0.5% at airmass equal to 2, and total ozone of 300 DU.

The ETC is obtained by comparison with the reference brewer **IZO#185** using near-simultaneous measurements during **2** days (two measurements are considered near-simultaneous if they are taken less than **3.5** minutes apart). Measurements with airmass difference greater than 3% were removed from the analysis.

7.6.1 Initial Calibration

For the evaluation of initial status of Brewer K&Z#158, we used the period from days **190** to **191** which correspond with **74** near-simultaneous direct sun ozone measurements. As shown in Fig. 7-18, the current calibration constants produce an ozone values slightly higher than the reference instrument (0.5%). When the ETC is corrected taking into account the difference between the SL and R6 reference (SL correction), the results clearly improve.

Table 7-6 shows the results of the 1P and 2P calibration methods. Mean daily total ozone values for the original and the final configurations are shown in Table 7-7, as well as relative differences with respect to IZO#185.

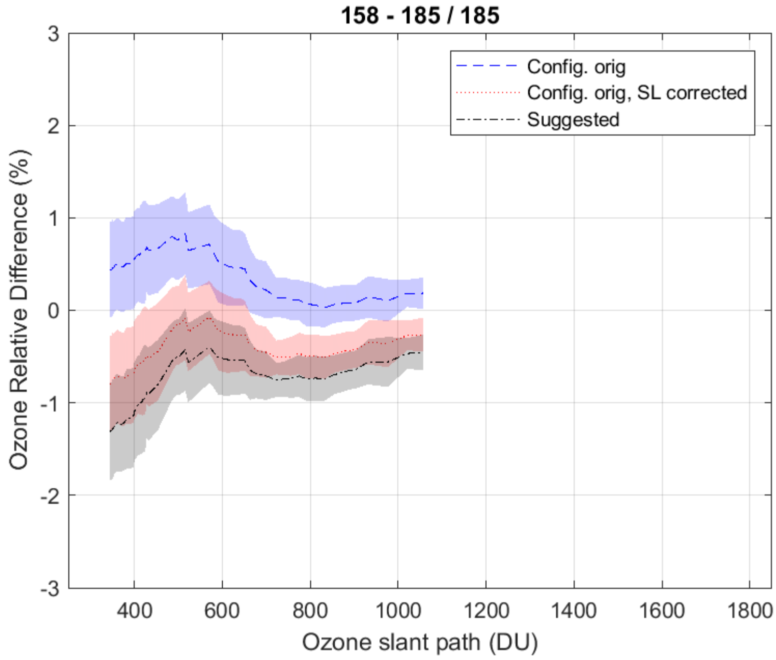


Figure 7-18 – Mean direct-sun ozone column percentage difference between Brewer K&Z#158 and Brewer IZO#185 as a function of ozone slant path.

Table 7-6 – Comparison between the results of the 1P and 2P ETC transfer methods for the blind days.

Table 7-7 – Daily mean ozone with original calibration, without and with (the latter, in the columns marked with a star) the standard lamp correction and the reference. Initial calibration. The 'rd' columns contain the porcentual relative difference, $\mathrm{rd} = \{O_3(\textbf{K\&Z\#158}) - O_3(\textbf{IZO\#185})\}/O_3(\textbf{IZO\#185}) * 100$

	Day	O3#185	std	N	O3#158	std	rd	O3(*)#158	std(*)	rd(*)
08-Jul-2021	189	340.6	0	2	338.9	1.1	-0.5	333.6	1.2	-2.1
09-Jul-2021	190	324.9	2	20	329.2	3.4	1.3	324.6	2.6	-0.1
10-Jul-2021	191	312.2	2.1	52	316.9	4.3	1.5	312.5	3.1	0.1

7.6.2 Final Calibration

After the maintenance on day 192, a new ETC value was calculated (see Fig. 7-19). For the final calibration, we use **109** simultaneous direct sun measurements from days **193** to **194**. The new value is 43 units higher than the current ETC value (**1792**). Therefore, we recommend using this new ETC, together with the new proposed standard lamp reference ratios, **559** for R6. We updated the new calibration constants in the ICF provided.

The ETC value in the final ICF corresponds to the 1P transfer. As shown in Table 7-8, the agreement between the 1P and 2P ETCs is above the maximum tolerance limit of 10 units. Also the difference between the absorption coefficients retrieved from the dispersion tests and form the 2P calibration is greater than 0.002 atm.cm^{-1}. Nevertheless, the ETC does not present OSC dependence as can be seen in Fig. 7-19.

Mean daily total ozone values and relative differences with respect to IZO#185 for the original and the final configurations are shown in Table 7-9.

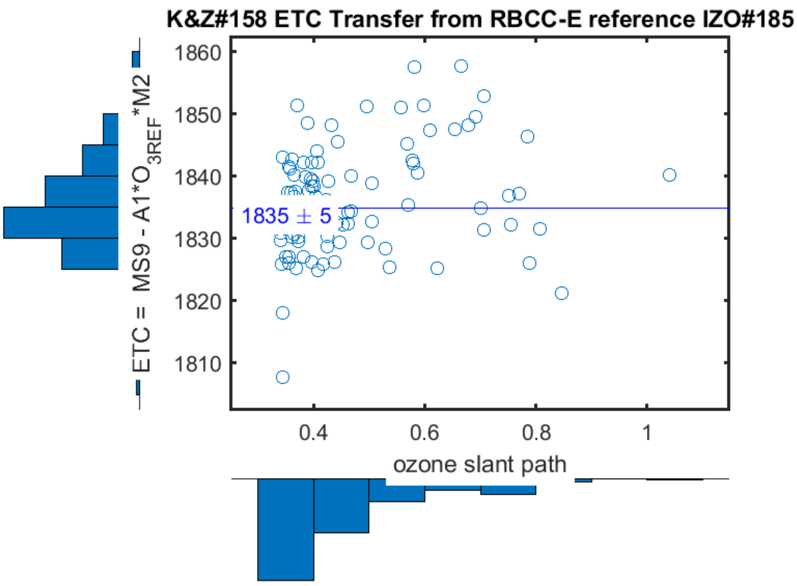


Figure 7-19 – Mean direct-sun ozone column percentage difference between Brewer K&Z#158 and Brewer IZO#185 as a function of ozone slant path, with OSC up to 2.

Table 7-8 – Comparison between the results of the 1P and 2P ETC transfer methods for the final days.

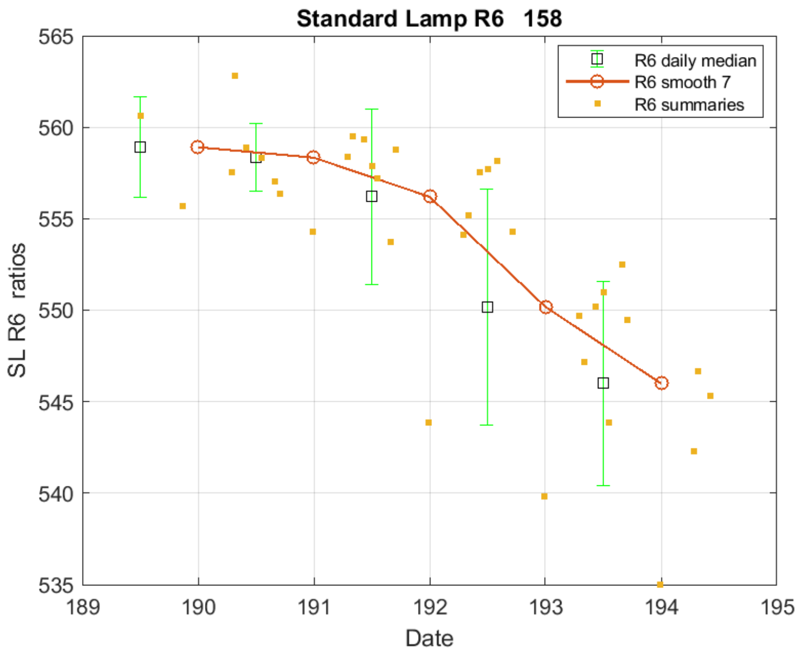
	ETC 1P	ETC 2P	O3Abs final	O3Abs 2P
full OSC range	1835	1818	3400	3444

Table 7-9 – **Daily mean ozone and relative differences with respect to the reference, with the original and final (the latter, in the columns marked with a star) calibrations. Data from the final days.**

	Day	O3#185	std	N	O3#158	std	rd	O3(*)#158	std(*)	rd(*)
11-Jul-2021	192	318	1.2	23	318.7	1.5	0.2	319	2	0.3
12-Jul-2021	193	305.8	2.6	86	305.3	1.8	-0.2	305.7	2.7	0

7.6.3 Standard Lamp Reference Values

The reference values of standard lamp ratios during the calibration period were **559** for R6 (Figure 7-20) and **848** for R5 (Figure 7-21).



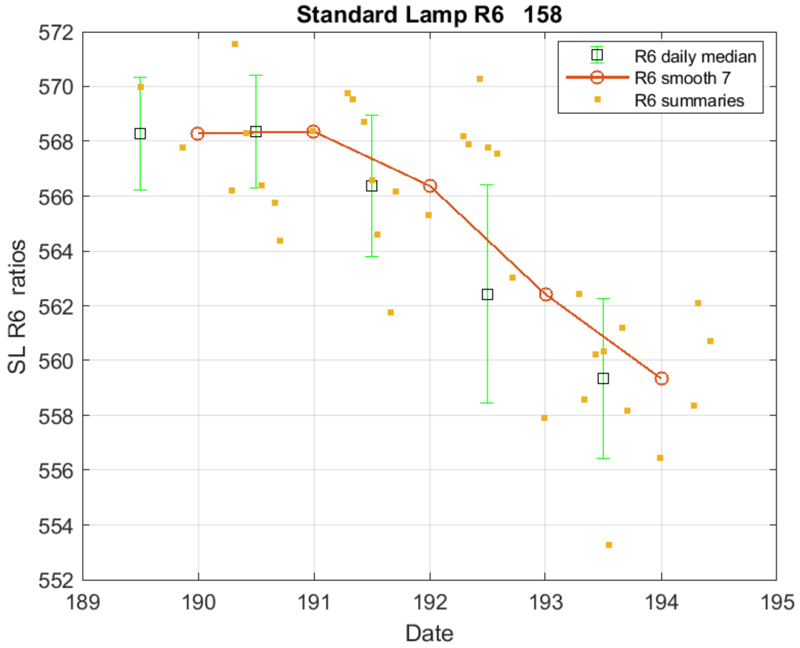
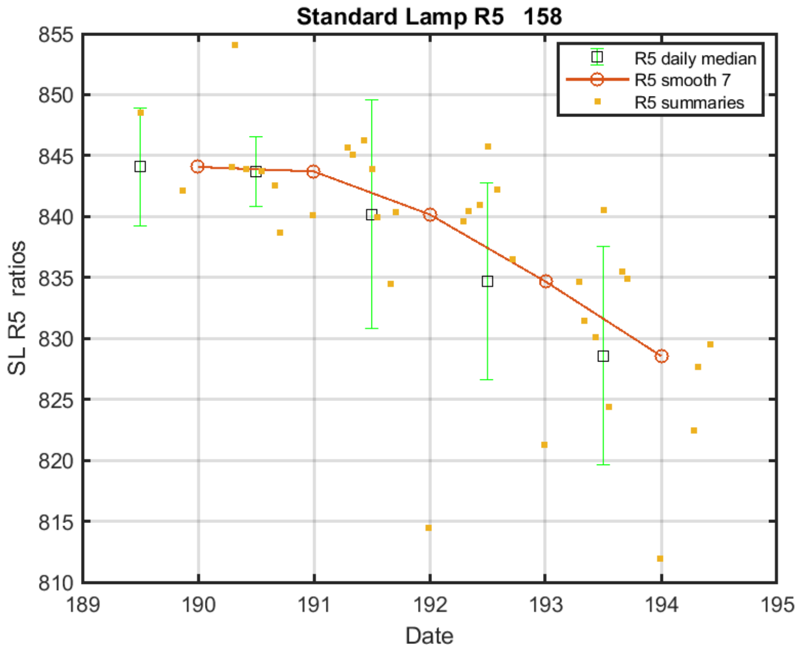


Figure 7-20 – Standard Lamp O_3 R6 ratios: daily mean and standard deviation (squares), seven day running mean (circle) and individual tests (black dots). Reprocessed using old (top) and new (bottom) instrumental constants



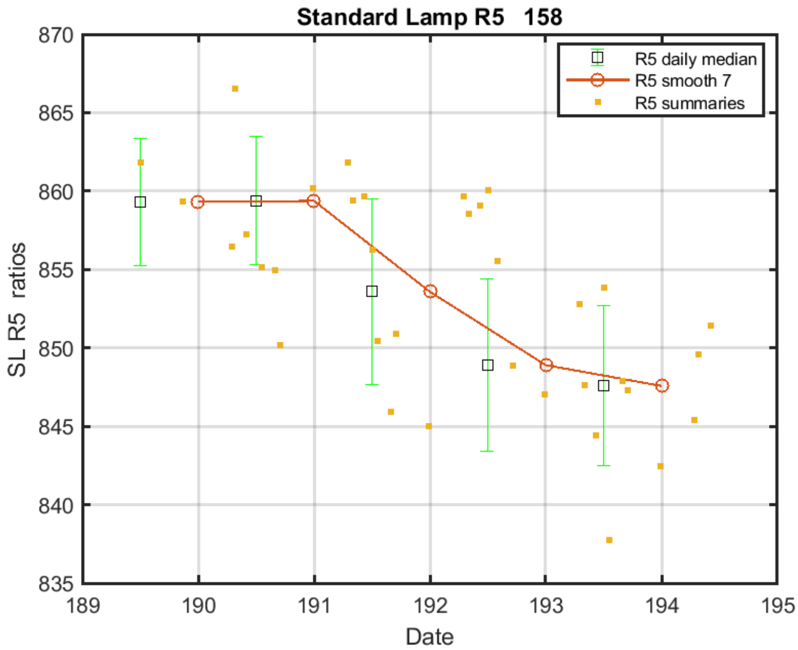


Figure 7-21 – Standard Lamp SO_2 R5 ratios: daily mean and standard deviation (squares), seven day running mean (circle) and individual tests (black dots). Reprocessed using old (top) and new (bottom) instrumental constants

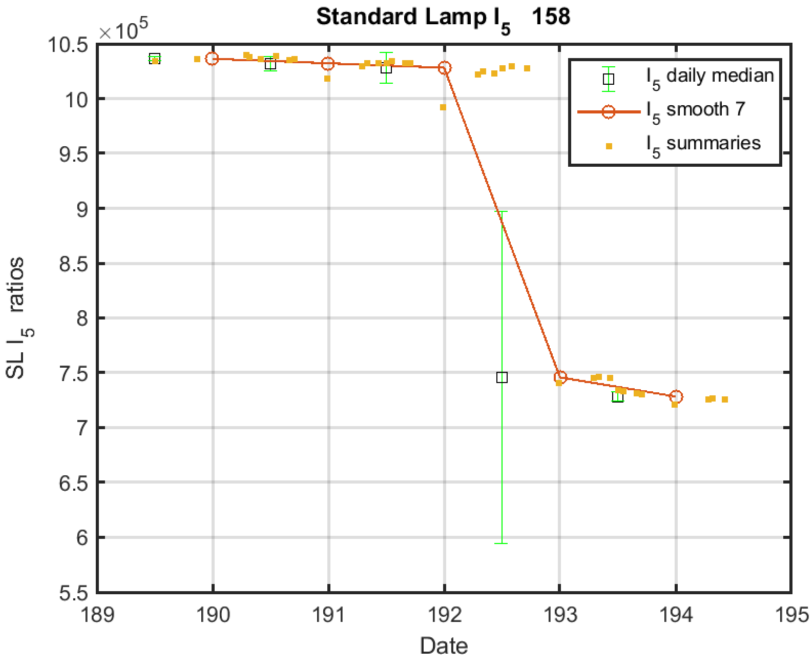


Figure 7-22 – **Standard Lamp intensity: daily mean and standard deviation (squares), seven day running mean (circle) and individual tests (black dots)**

7.7 Configuration

7.7.1 Instrument constant file

	Initial (ICF17519.158)	Final (ICF18821.158)
o3 Temp coef 1	0	0
o3 Temp coef 2	-0.41	-0.479
o3 Temp coef 3	-1.05	-0.824
o3 Temp coef 4	-1.95	-1.338
o3 Temp coef 5	-2.46	-1.955
Micrometer steps/deg	0	0
O3 on O3 Ratio	0.3431	0.34
SO2 on SO2 Ratio	2.35	2.35
O3 on SO2 Ratio	1.1636	1.1636
ETC on O3 Ratio	1792	1835
ETC on SO2 Ratio	332	332
Dead time (sec)	3e-08	3e-08
WL cal step number	1015	1015
Slitmask motor delay	14	14
Umkehr Offset	2463	2463
ND filter 0	0	0
ND filter 1	4385	4385
ND filter 2	9358	9358
ND filter 3	13754	13754
ND filter 4	21466	21466
ND filter 5	25162	25162
Zenith steps/rev	2972	2972
Brewer Type	3	3
COM Port #	1	1
o3 Temp coef hg	0	0
n2 Temp coef hg	0	0
n2 Temp coef 1	0	0
n2 Temp coef 2	0	0
n2 Temp coef 3	0	0
n2 Temp coef 4	0	0
n2 Temp coef 5	0	0
O3 Mic #1 Offset	0	0
Mic #2 Offset	0	0
O3 FW #3 Offset	178	178
NO2 absn Coeff	-3	-3
NO2 ds etc	770	770
NO2 zs etc	740	740
NO2 Mic #1 Offset	8028	8028
NO2 FW #3 Offset	178	178
NO2/O3 Mode Change	2497	2497
Grating Slope	0.9989	0.9989
Grating Intercept	-13.86	-13.86
Micrometer Zero	1738	1738
Iris Open Steps	250	250
Buffer Delay (s)	0	0
NO2 FW#1 Pos	0	0
O3 FW#1 Pos	256	256
FW#2 Pos	0	0
uv FW#2 Pos	0	0
Zenith Offset	0	0
Zenith UVB Position	0	0

7.8 Daily Summary report

Day	osc range	O3#185	std	N	O3#158	std	rd	O3(*)#158	std(*)	rd(*)
190	700>osc>400	324.4	2	16	322.5	1.2	-0.6	324	2.4	-0.1
190	osc<400	326.5	0.6	4	324.6	1.1	-0.6	327.3	1.1	0.2
191	1500>osc>1000	309.9	0.8	2	309.5	0.3	-0.1	308.9	0.3	-0.3
191	1000>osc>700	309.7	0.6	7	308.3	0.5	-0.4	307.6	0.6	-0.7
191	700>osc>400	311	1.8	15	310.8	1.8	-0.1	311.2	2.6	0.1
191	osc<400	314.4	1	40	311.9	1.5	-0.8	314	1.5	-0.1
193	1500>osc>1000	305.5	0	1	305.7	0	0.1	306	0	0.1
193	1000>osc>700	303	2.1	7	303.2	2.4	0	302.9	2.7	-0.1
193	700>osc>400	304.5	3.2	29	304.5	2.4	0	304.8	3.3	0.1
193	osc<400	306.7	1.2	46	304.3	1.2	-0.8	306.6	1.5	0

7.9 Summary Plots

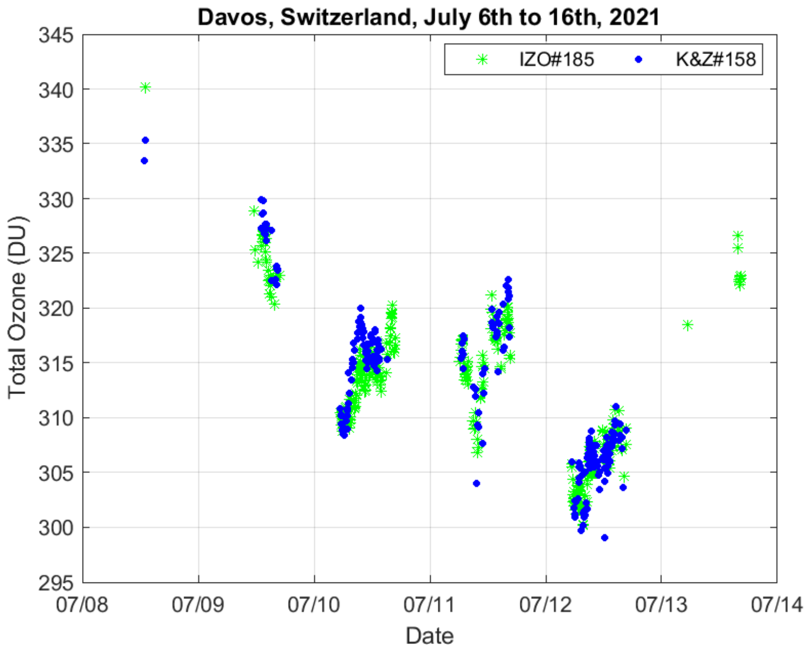
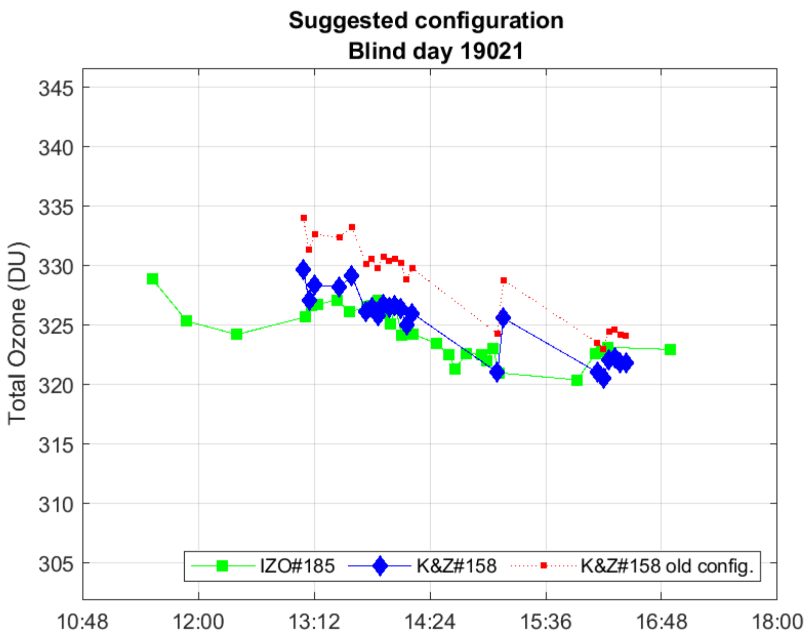
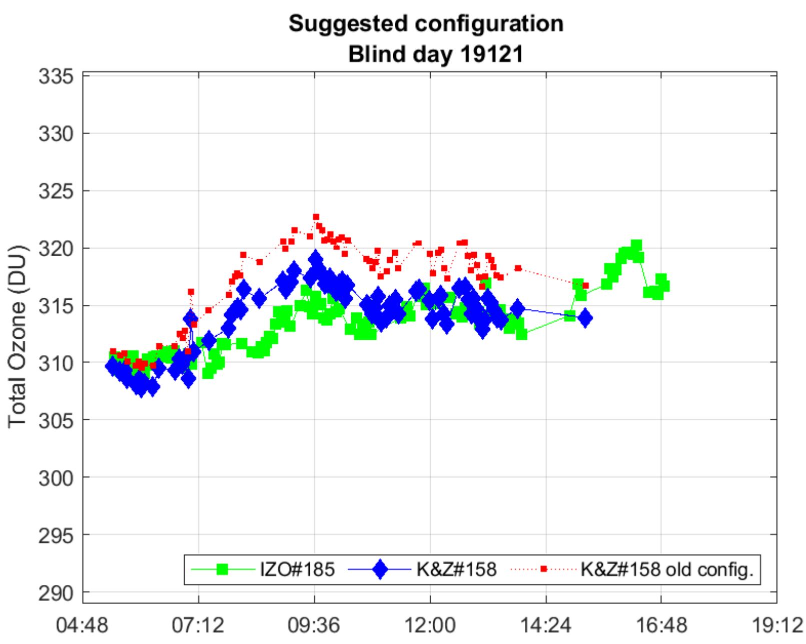
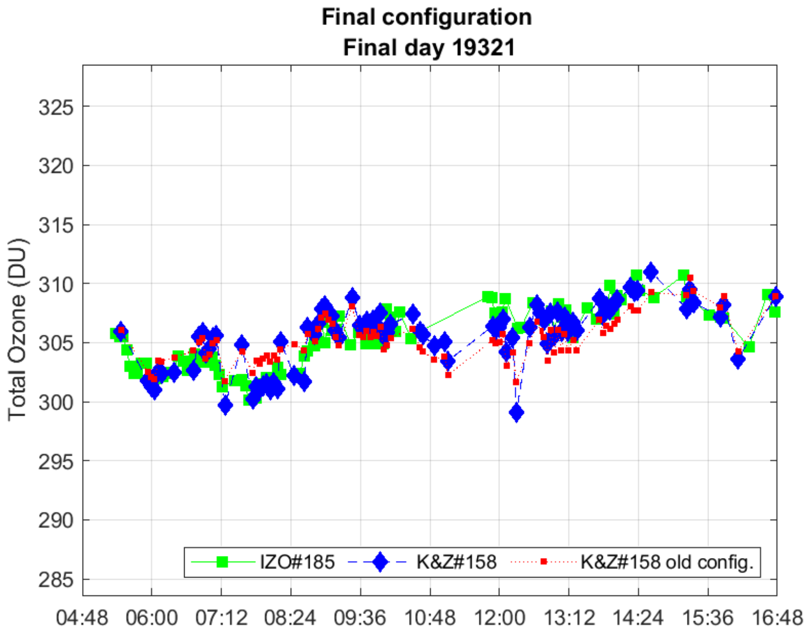


Figure 7-23 – Overview of the intercomparison. Brewer K&Z#158 data are evaluated using final constants (blue circles)


Suggested configuration
Blind day 19021
Total Ozone (DU)
345
340
335
330
325
320
315
310
305
10:48
12:00
13:12
14:24
15:36
16:48
18:00
IZO#185
K&Z#158
K&Z#158 old config.


Suggested configuration
Blind day 19121
Total Ozone (DU)
335
330
325
320
315
310
305
300
295
290
04:48
07:12
09:36
12:00
14:24
16:48
19:12
IZO#185
K&Z#158
K&Z#158 old config.


Final configuration
Final day 19321
Total Ozone (DU)
325
320
315
310
305
300
295
290
285
04:48
06:00
07:12
08:24
09:36
10:48
12:00
13:12
14:24
15:36
16:48
IZO#185
K&Z#158
K&Z#158 old config.

8 Brewer WRC#163

8.1 Calibration Summary

The Fifteenth Intercomparison Campaign of the Regional Brewer Calibration Center Europe (RBCC-E) was held from July 6th to the 16th, 2021, at the Physikalisch-Meteorologisches Observatorium PMOD (Davos, Switzerland).

Brewer WRC#163 participated in the campaign in the period from July 6th to 16th. The campaign days of Brewer WRC#163 correspond to Julian days 187 – 197.

For final calibration purposes, we used **328** simultaneous DS ozone measurements taken from day **190** to **194**. As no maintenance was required for Brewer WRC#163, we used the same data set for the evaluation of the initial status as for the final calibration.

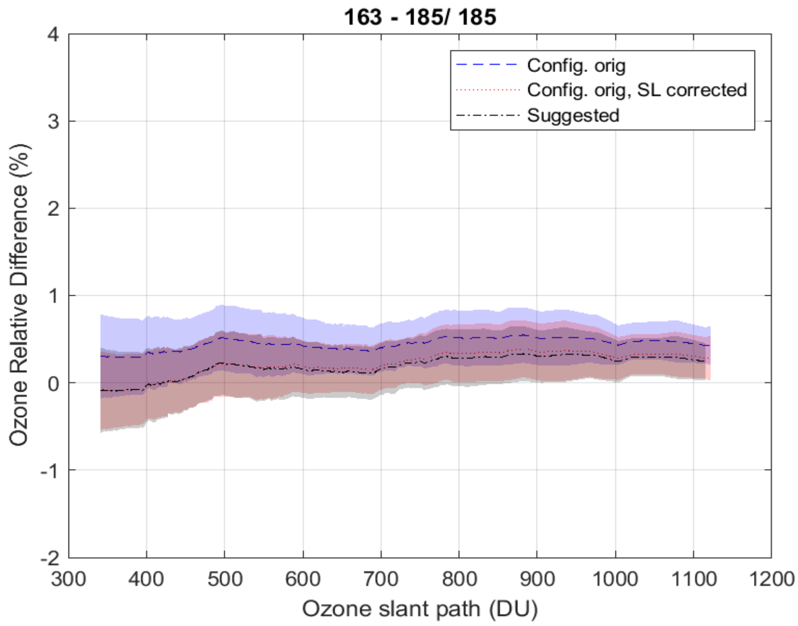


Figure 8-1 – Mean DS ozone column percentage difference between Brewer WRC#163 and Brewer IZO#185, plotted as a function of the ozone slant path. Results for the current (issued in the previous calibration campaign) configuration are show in blue; the red dotted line corresponds to the same configuration, but with the standard lamp correction applied; the black line corresponds to results obtained with the updated configuration proposed in the current campaign. The shadow areas represent the standard deviation of the mean. The plot corresponds to the final days of the campaign.

The Brewer WRC#163 was last calibrated in the El Arenosillo campaign in 2019 (ICF17519.163). However, the Calibration Step Number was adjusted on site in January 2021 (ICF01921.163), from 1021 to 1018. This is the only parameter that changes in the last calibration file compared to that of 2019. R5 and R6 show a change in the behaviour of the Brewer on June 30, 2020. This change is not due to the replacement of the standard lamp, which was done on January 21, 2021. Despite these changes, ozone calculated using the current ICF (ICF01921.163, blue dashed line in Fig. 8-1) produces ozone values with an average difference of around 0.4% with respect to the reference instrument, which is a rather small difference. As expected, the SL correction (Fig. 8-1, red dotted line) improves the comparison with Brewer IZO#185. We recommend applying the SL correction from the 2019 calibration to the current one.

Dead time (DT) shows a difference of 2 ns between the current and the last campaign value, changing from $3{\cdot}10^{-8}$ to $2.8{\cdot}10^{-8}$. This is a significant change for double Brewers, and we have adopted it in the final configuration.

The sun-scan tests (SC) at Davos station before the campaign confirm the cal step value set in January (**1018**, within a step error of ± 1).

We changed the ozone absorption coefficient from 0.341 to the new value **0.3418**.

All the other parameters analyzed (run/stop tests, Hg lamp intensity, CZ & CI files, ...) show reasonable results.

Taking into account all this, we suggest the following changes to the configuration of Brewer WRC#163.

8.1.1 Recommendations and Remarks

1. The R6 standard lamp test could be updated to **283**.
2. We suggest a new R5 reference value of **522**.
3. We suggest updating the DT to **2.8**$\cdot$**10**$^{-8}$ seconds, which is two nanoseconds less than the value proposed in the last intercomparison.
4. Given the noise in HV, in the intensity and in the voltage of the SL, it is recommended to check the digital analog converter.
5. We recommend updating the Ozone Absorption Coefficient to **0.3418**.
6. Finally, we suggest maintaining the ETC value of **1490**.

8.1.2 External links

Configuration File

http://rbcce.aemet.es/svn/campaigns/dav2021/bfiles/163/ICF18821.163

Calibration Report

https://docs.google.com/spreadsheets/d/12-4EoZzJkJDv5Pgpdt3PNZlZLXahvdlubhqOyijRack/edit#gid=680218151

Calibration Reports Detailed

Historic and instrumental

http://rbcce.aemet.es/svn/campaigns/dav2021/latex/163/html/cal_report_163a1.html

Temperature & Filter

http://rbcce.aemet.es/svn/campaigns/dav2021/latex/163/html/cal_report_163a2.html

Wavelength

http://rbcce.aemet.es/svn/campaigns/dav2021/latex/163/html/cal_report_163b.html

ETC transfer

http://rbcce.aemet.es/svn/campaigns/dav2021/latex/163/html/cal_report_163c.html

8.2 Instrument History: Analysis of Average files

8.2.1 Standard Lamp Test

The standard lamp tests, Figure 8-2 and 8-3, show a change in the instrument behaviour in June 2020, which is not associated with any known event. The R6 and R5 parameters changed respectively around 5 and 55 units. A change in R5 in January 2021 can be associated with a standard lamp replacement, Fig. 8-4.

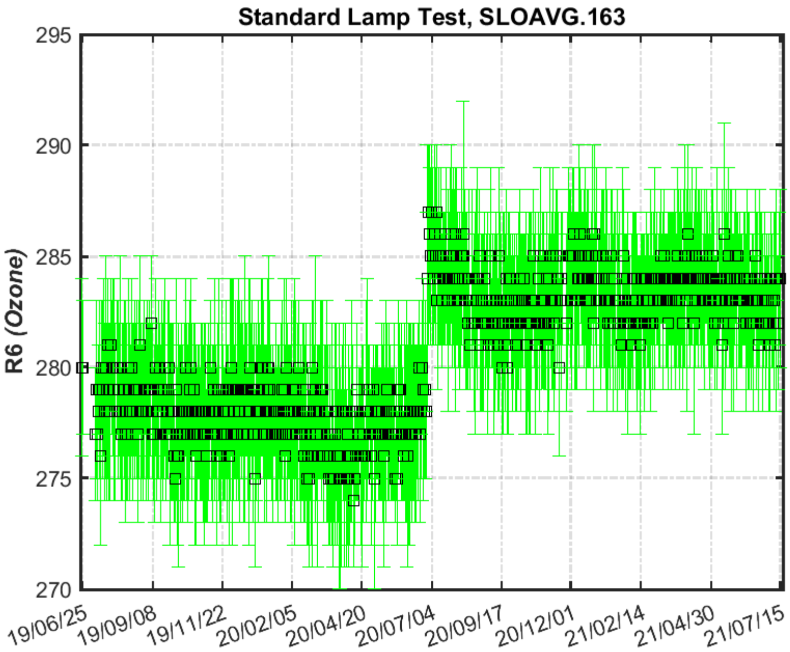


Figure 8-2 – **Standard Lamp test R6 (Ozone) ratios. Horizontal lines are labeled with the original and final reference values (red and blue lines, respectively)**

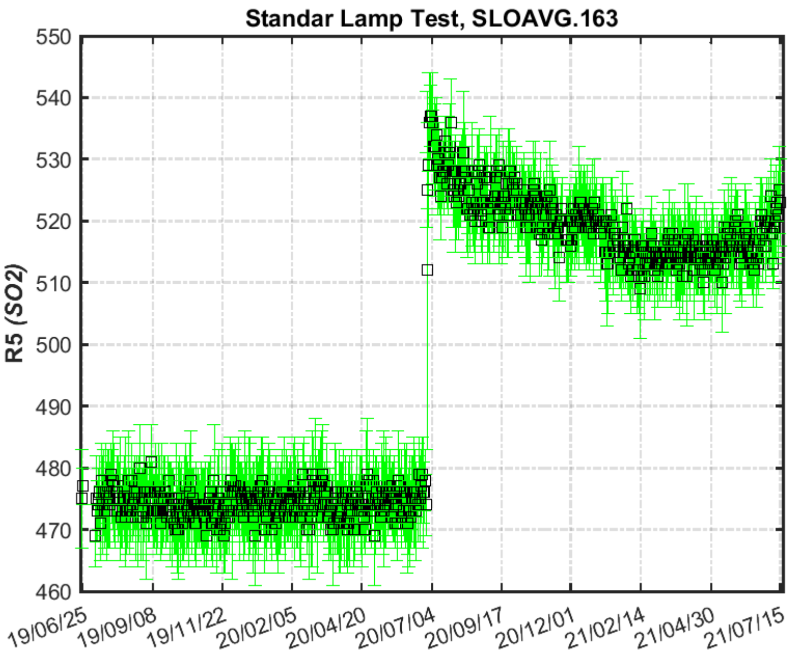


Figure 8-3 – **Standard Lamp test R5 (SO_2) ratios**

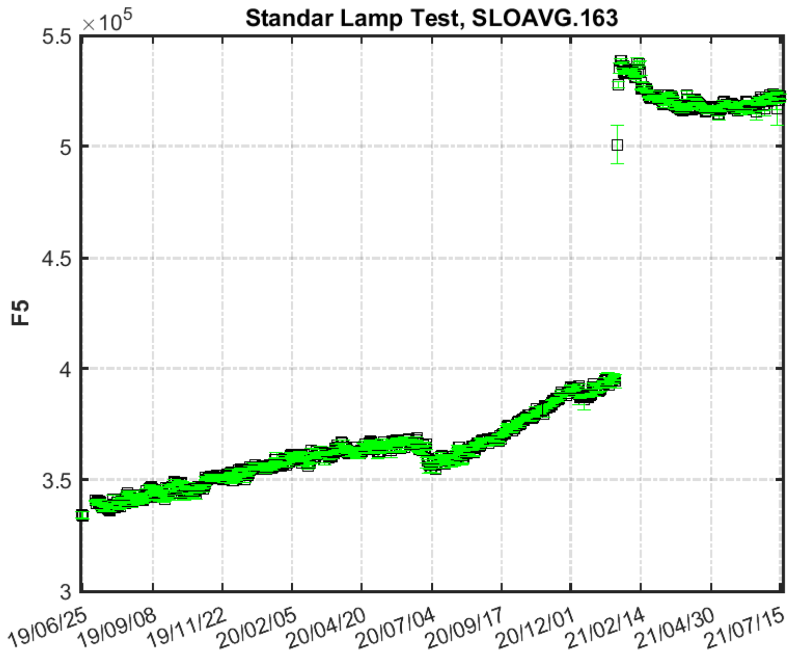


Figure 8-4 – **SL intensity for slit five.**

8.2.2 Run Stop and Dead Time

Run stops test values are within the test tolerance limits for all the slits with only a small number of outliers in slit 0, as can be seen in figure Fig. 8-5.

As shown in Fig. 8-6, the current DT reference value of **3**$\cdot$**10**$^{-8}$ seconds is slightly larger than the value recorded during the calibration period, **2.8**$\cdot$**10**$^{-8}$s. Therefore, this new value has been used in the new ICF.

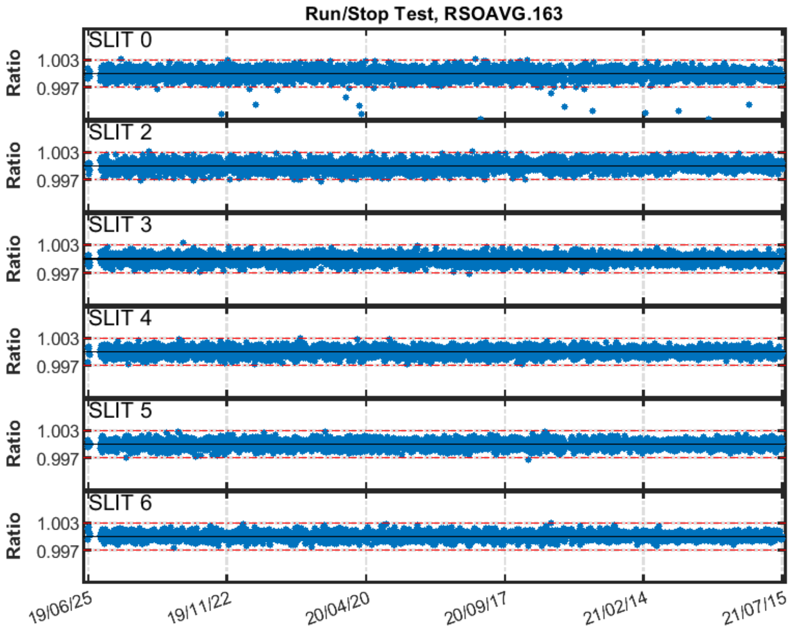


Figure 8-5 – **Run/stop test**

8.2.3 Analog Test

Fig. 8-7 shows that the high voltage has been very noisy over the last two years, with a mean value of **1058**. The intensity and voltage of the SL have also been quite noisy. This behavior has not been observed in the ozone measurements, so we suggest to review the digital analog converter.

8.2.4 Mercury Lamp Test

No noticeable internal mercury lamp intensity events have been observed during the campaign (see Fig. 8-8). However, in December 2020 there is a small change associated with a maintenance.

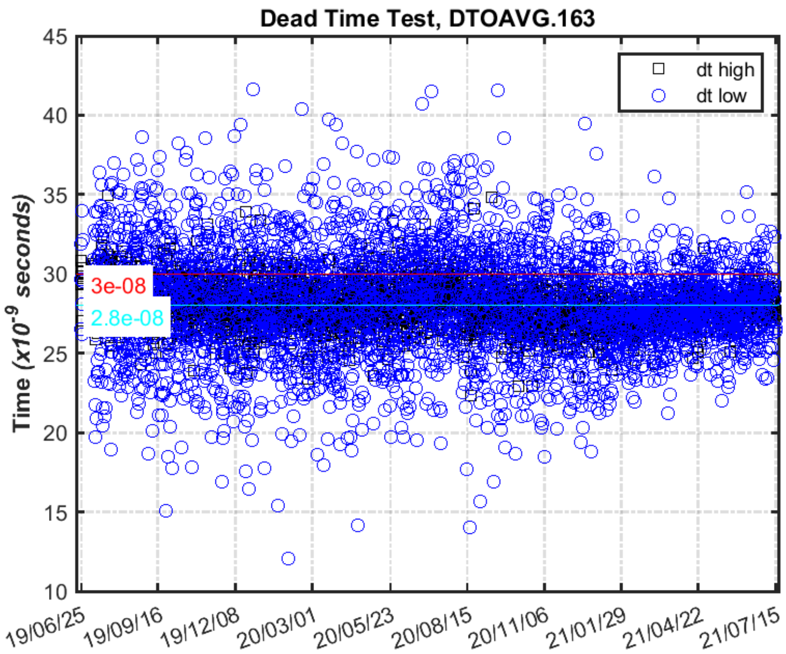


Figure 8-6 – Dead Time test. Horizontal lines are labelled with the current (red) and final (blue) values.

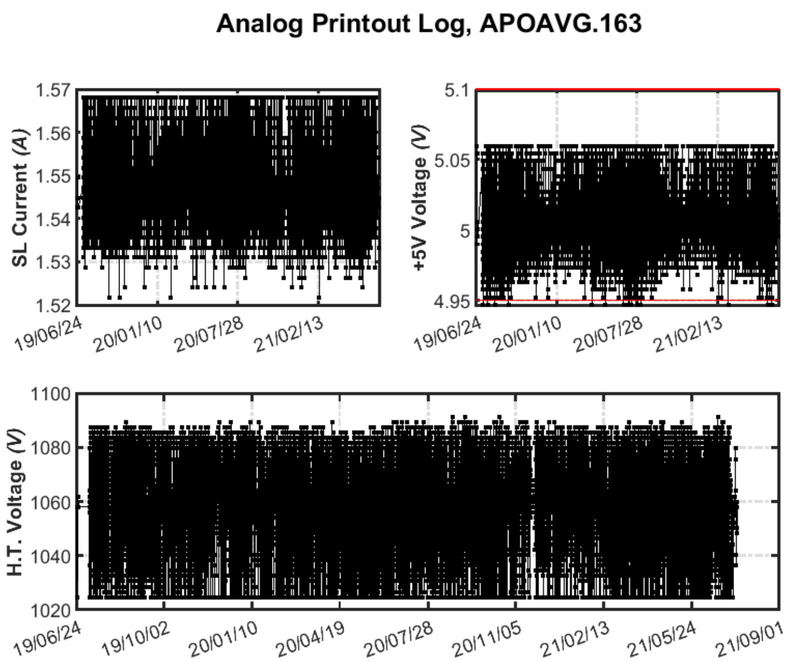


Figure 8-7 – Analog voltages and intensity.

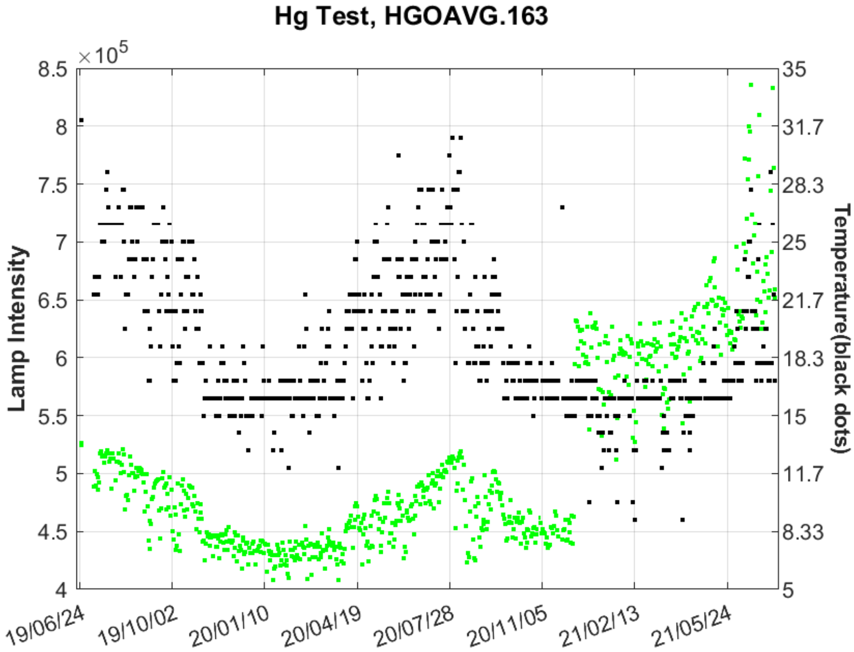
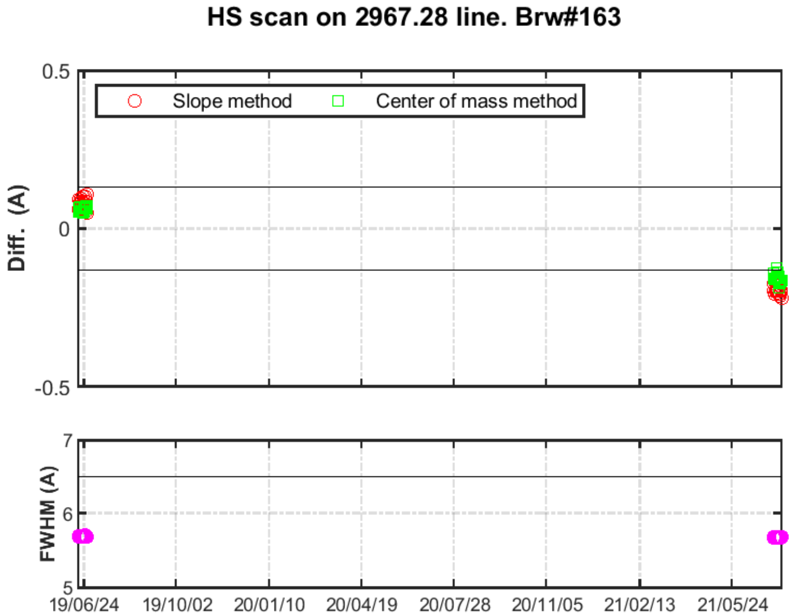


Figure 8-8 – Mercury lamp intensity (green squares) and Brewer temperature registered (black dots). Both parameters refer to maximum values for each day.

8.2.5 CZ scan on mercury lamp

In order to check both the wavelength settings and the slit function width, we analyzed the scans performed on the 296.728 nm, and 334.148 nm mercury lines, see Fig. 8-9. As a reference, the calculated scan peak, in wavelength units, should be within 0.013 nm from the nominal value, whereas the calculated slit function width should be no more than 0.65 nm. There are no measurements for the last two years, but the analysis of the CZ scans performed on Brewer WRC#163 during the campaign show reasonable results. The peak of the calculated scans is close to the accepted tolerance range, although slightly below. Regarding the slit function width, results are good, with a FWHM lower than 6.5 Å.



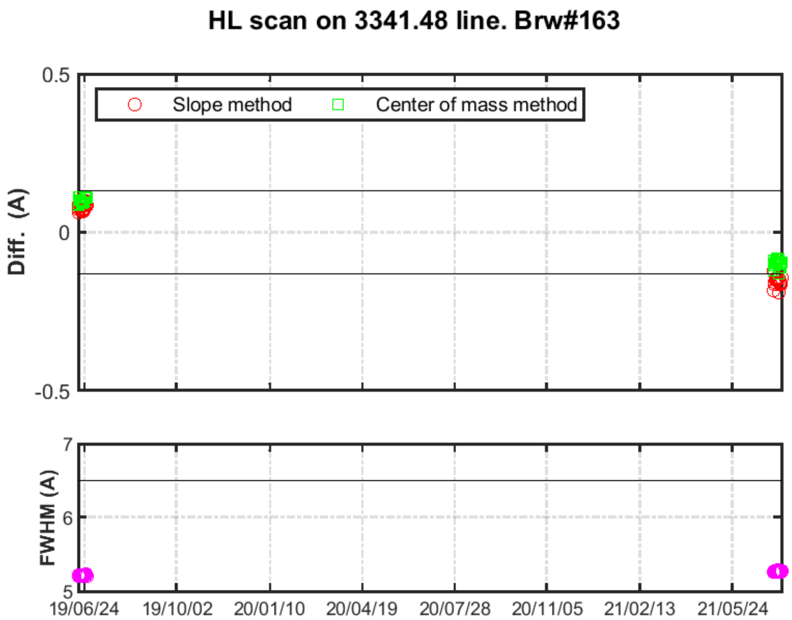


Figure 8-9 – CZ scan on Hg lines. The upper panels show differences with respect to the reference line (solid lines represent the limit ± 0.013 nm) as computed by the slopes (red circles) and center of mass (green squares) methods. Lower panels show the Full Width at Half Maximum value for each scan performed (solid lines represent the 0.65 nm limit).

8.2.6 CI scan on internal *SL*

CI scans of the standard lamp recorded at different times can be compared to investigate whether the instrument has changed its spectral sensitivity. We shown in Fig. 8-10 percentage ratios of the Brewer **WRC#163** CI scans performed during the campaign relative to the scan CI18921.163. As it can be observed, the lamp intensity has varied respect to the reference spectrum around 5%. Similar variation have been observed in the daily R6 and R5 values. This behavior is normal for a SL lamp.

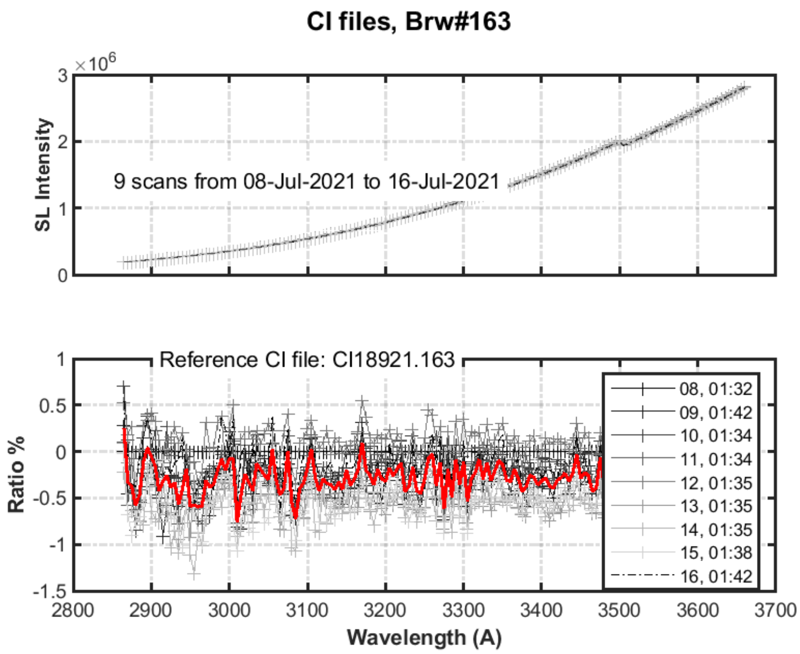


Figure 8-10 – **CI scan of Standard Lamp performed during the campaign days. Scans processed (upper panel) and relative differences with respect to a selected reference scan (lower panel). Red line represents the mean of all relative differences**

8.3 Absolute Temperature Coefficients

Temperature coefficients are determined using the standard lamp test. For every slit, the raw counts corrected for zero temperature coefficients are used in a linear regression against temperature with the slopes representing the instrument's temperature coefficients. From this we obtain the corrected *R6* and *R5* ratios to analyze the new temperature coefficients' performance.

As shown in Fig. 8-11 (temperature range from **16**° **C** to **33**° **C**, the current coefficients do an excellent job at reducing the temperature dependence, performing even better that the coefficients calculated using the data from the present campaign. The values of the coefficients are summarized in Table 8-1.

We have also extended our analysis using the data recorded since the previous campaign. As shown in Figs. 8-12 and 8-13, the current and new coefficients have a similar performance, the current coefficients being slightly better. For this reason, in the final ICF we have used the current coefficients.

Table 8-1 – **Temperature Coefficients. Calculated coefficients are normalized to slit#2**

	slit#2	slit#3	slit#4	slit#5	slit#6
Current	0.0000	0.1845	0.1625	0.4778	-0.4826
Calculated	0.0000	0.2300	0.2100	0.5200	-0.4800
Final	0.0000	0.1845	0.1625	0.4778	-0.4826

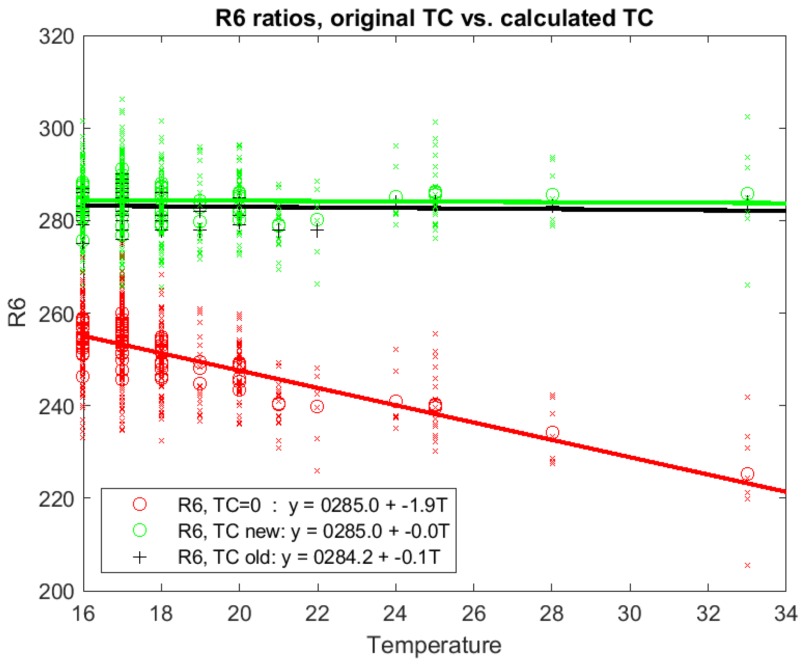


Figure 8-11 – Temperature coefficients' performance. Red circles represent standard lamp R6 ratios calculated from raw counts without temperature correction (temperature coefficients set to 0). Black crosses and green circles represent standard lamp R6 ratios corrected with original and calculated temperature coefficients, respectively. Data corresponds to the present campaign.

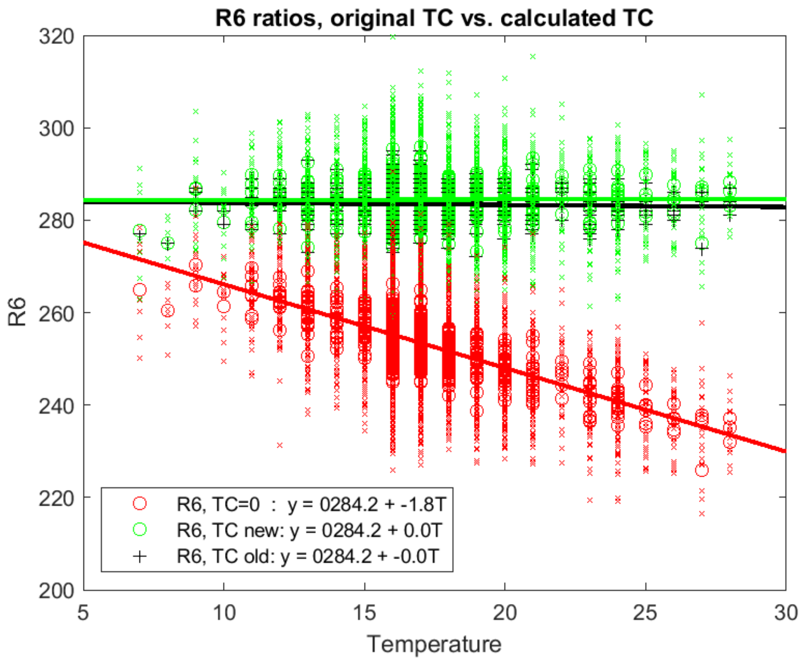


Figure 8-12 – **Same as Fig. 8-11 but for the whole period between calibration campaigns.**

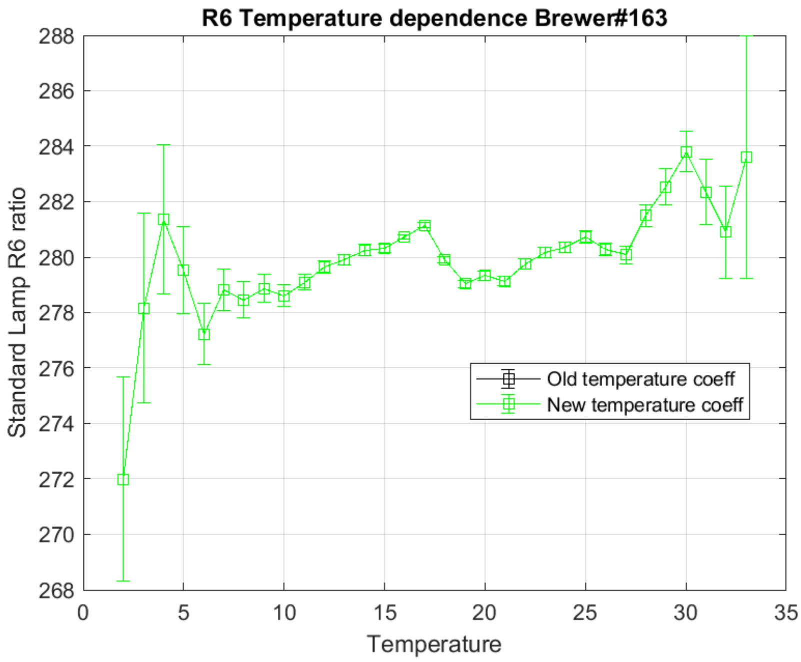


Figure 8-13 – **Standard lamp R6 (MS9) ratio as a function of temperature. We plotted R6 ratio recalculated with the original (black) and the new (green) temperature coefficients**

8.4 Attenuation Filter Characterization

8.4.1 Attenuation Filter Correction

The filter's spectral dependence affects the ozone calculation because the Brewer software assumes that their attenuation is wavelength-neutral. We can estimate the correction factor needed for this non-linearity by multiplying the attenuation of every filter and every wavelength by the ozone weighting coefficients.

During the calibration period, a total of **18** FI tests were analyzed to calculate the attenuation for every filter and slit. Fig. 8-14 shows the results of these tests, and Table 8-2 shows the calculated ETC corrections for each filter.

Table 8-2 – ETC correction due to Filter non-linearity. Median value, mean values and, 95% confidence intervals are calculated using bootstrap technique

	filter#1	filter#2	filter#3	filter#4	filter#5
ETC Filt. Corr. (median)	5	-14	-6	-5	-25
ETC Filt. Corr. (mean)	0.4	-6.4	-14.9	-19	-25.9
ETC Filt. Corr. (mean 95% CI)	[-8.2 12.2]	[-20 8.5]	[-27.6 -2.1]	[-47.4 8.3]	[-66.4 9.1]

Calculated mean attenuation values for every filter are compared with operational values (see Table 8-2 and Figure 8-14), updating them (`ICF` file) when necessary. Individual values for every wavelength and every filter should be used for aerosol optical depth calculations. In the case of Brewer WRC#163 the observed transitions between successive filters are quite smooth in terms of attenuation (relative percentage differences lower than 10% when changing filter). Table 8-2 shows how most of the filters are affected similarly, except filters #1 and #5, that are either minimally affected or not used. Taking into account the relative ozone difference with respect to the reference Brewer IZO#185, we do not suggest the application of any ETC filter correction.

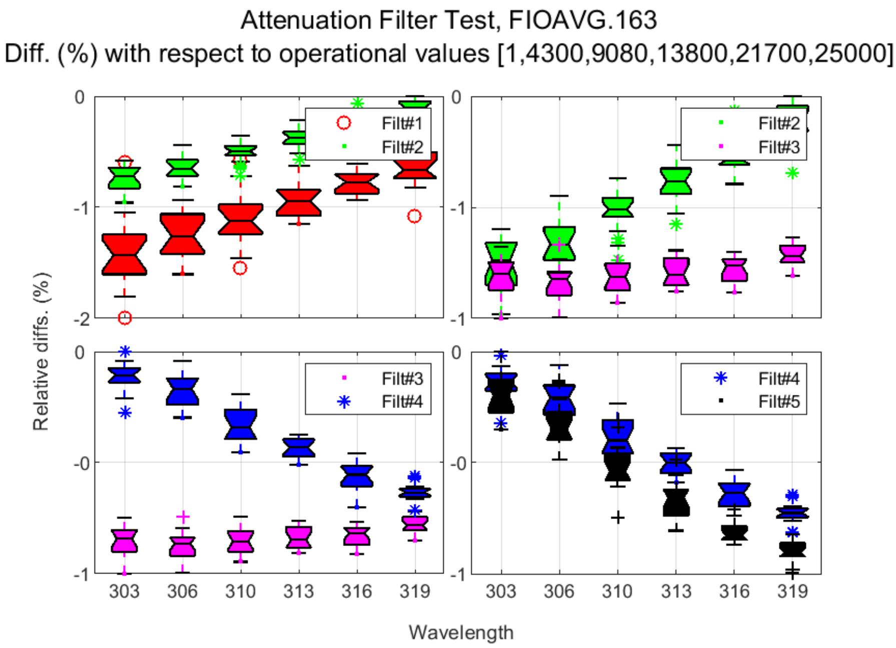


Figure 8-14 – **Notched box-plot for the calculated attenuation relative differences of neutral density filters with respect to operational values. We show for each subplot relative differences corresponding to correlative filters (color box-plots). Solid lines and boxes mark the median, upper and lower quartiles. The point whose distance from the upper or lower quartile is 1 times larger than the interquartile range is defined as outlier.**

8.5 Wavelength Calibration

8.5.1 Cal-Step determination

The sun scan routine takes DS ozone measurements by moving the micrometer about 15 steps below and above the ozone reference position (wavelength *Calibration step-number*). A Hg test is required before and after the measurement to assure the correct wavelength setting during the *sun scan* test. Ozone *versus* step number ideally shows a parabolic shape with a maximum at the ozone reference position. With this choice, small wavelength shifts ($\approx \pm 2$ steps) do not affect the ozone value. This optimal micrometer position is a near-linear function of the ozone slant path at the time of the scan, see Fig. 8-15

Previous to the campaign, 8 sun-scan (SC) tests covering a ozone slant path range from 400 to 1200 DU were collected, see Fig. 8-16)). No additional SC measures are required during the campaign as Brewer WRC#163 routinely operates from Davos station. The calculated Cal-Step Number (CSN) was 1 step higher than the value in the current configuration: **1019** *vs.* **1018**.Taking all this into account, we suggest keeping the current CSN, **1018**.

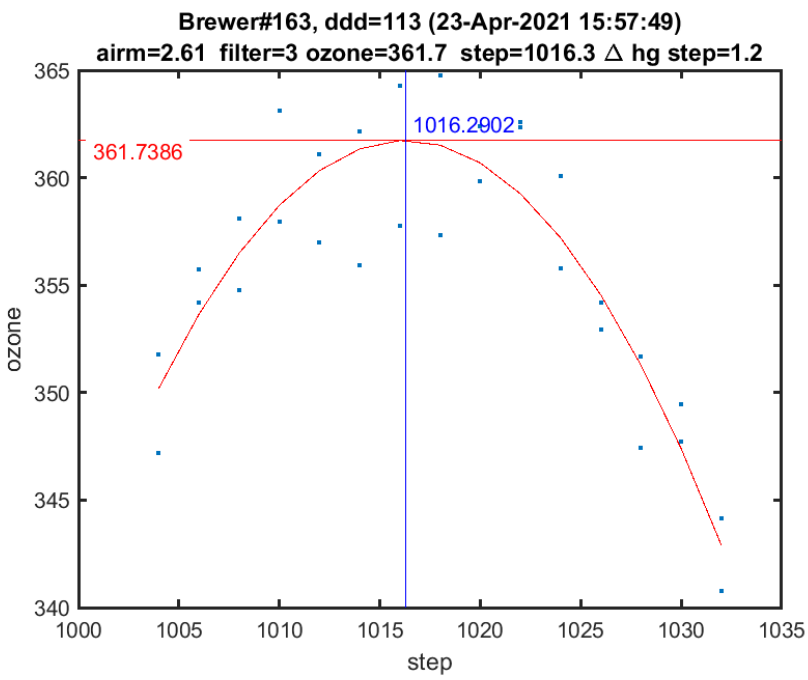


Figure 8-15 – **Ozone measurements moving the micrometer 15 step around the operational CSN defined in the initial configuration**

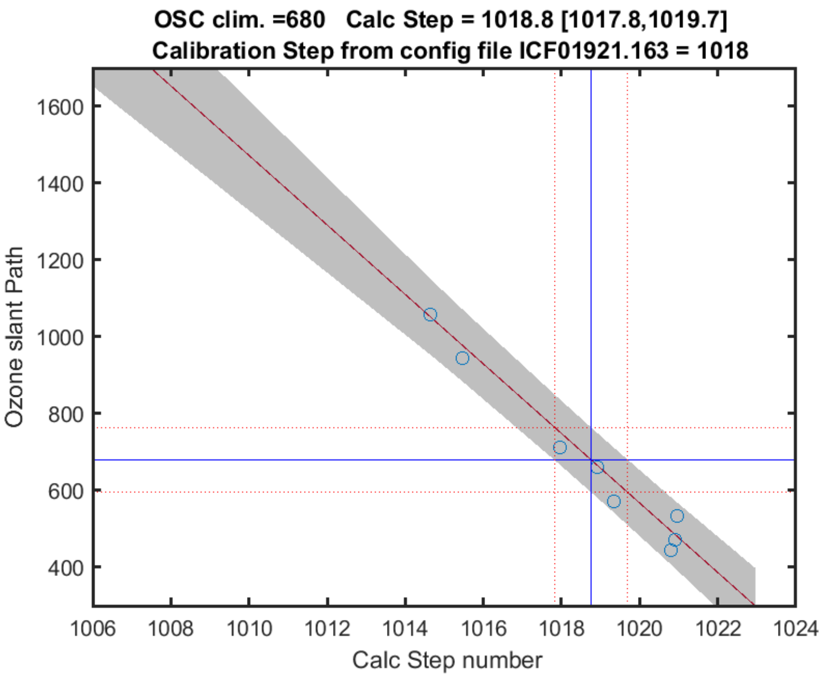


Figure 8-16 – Ozone Slant Path *vs* Calc – Step number. Vertical solid line marks the calculated *Cal Step Number* for a climatological OSC equal to 680 (horizontal solid line). Grey area represents a 95% confidence interval

8.5.2 Dispersion Test

We analyzed the dispersion tests carried out in the previous and present calibration campaigns. For all of them, we processed data from Mercury and Cadmium spectral lamps, using cubic functions to adjust the micrometer step number to wavelength positions. The results of this historical analysis are summarized in Table 8-3.

In particular, for the current campaign, Fig. 8-17 shows that the cubic fitting was good for all the dispersion tests, with residuals being lower than 0.1 Å in almost all slits. For the dispersion tests performed, Table 8-4 provides individual wavelength resolution, ozone absorption coefficient, sulfur dioxide absorption coefficient, and Rayleigh absorption for the operational CSN and those at ± 1 step.

We discard the dispersion test carried out during the campaign due to its abnormally low value. An absorption coefficient equal to **0.3418** is suggested in the final configuration.

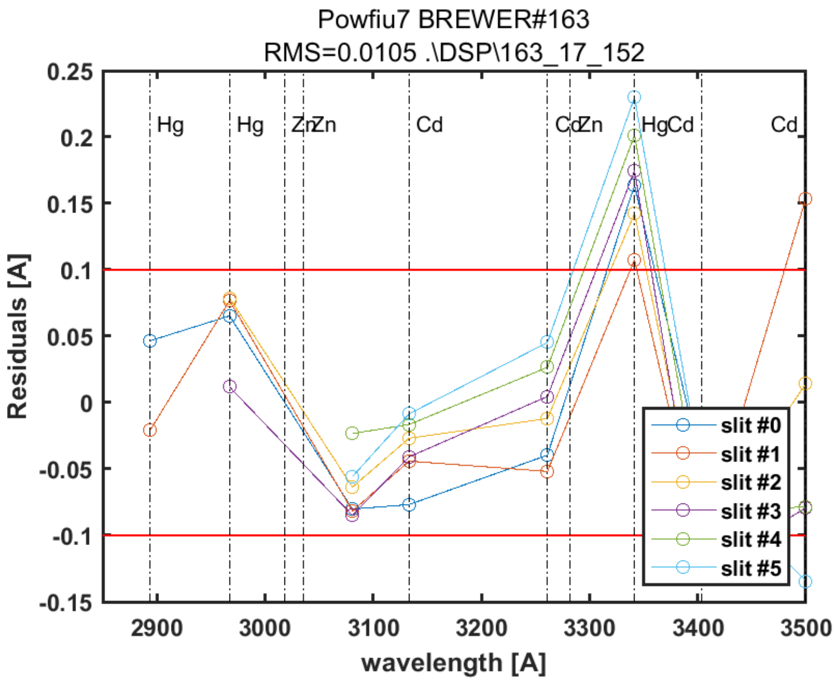


Figure 8-17 – 2021 residuals of cubic fit

Table 8-3 – **Dispersion derived constants**

	Calc-step	O3abs coeff.	SO2abs coeff.	O3/SO2
Current	1018	0.3410	2.3500	1.1342
01-Jun-2017	1018	0.3399	3.1892	1.1399
02-Aug-2018	1018	0.3404	3.1815	1.1417
23-Jun-2019	1018	0.3407	3.1879	1.1424
20-Jan-2021	1018	0.3409	3.1850	1.1418
23-Jun-2021	1018	0.3418	3.1679	1.1452
14-Jul-2021	1018	0.3390	3.1826	1.1374
Final	1018	0.3418	2.3500	1.1342

Table 8-4 – **2021 dispersion derived constants**

step= 1017	slit#0	slit#1	slit#2	slit#3	slit#4	slit#5
WL(A)	3031.94	3062.95	3100.38	3134.91	3167.85	3199.87
Res(A)	5.7046	5.6515	5.5738	5.6158	5.5036	5.421
O3abs(1/cm)	2.5984	1.7809	1.0053	0.67647	0.37496	0.2945
Ray abs(1/cm)	5050.4152	4832.6674	4585.4908	4371.6444	4179.3853	4002.7483
SO2abs(1/cm)	3.4403	5.6095	2.3998	1.9158	1.0522	0.61521
step= 1018	slit#0	slit#1	slit#2	slit#3	slit#4	slit#5
WL(A)	3032.02	3063.02	3100.45	3134.98	3167.92	3199.94
Res(A)	5.7045	5.6514	5.5737	5.6157	5.5035	5.4209
O3abs(1/cm)	2.5958	1.7793	1.0049	0.67611	0.37499	0.29403
Ray abs(1/cm)	5049.8846	4832.1706	4585.0318	4371.2175	4178.9871	4002.3761
SO2abs(1/cm)	3.4248	5.6307	2.4077	1.9044	1.0535	0.61304
step= 1019	slit#0	slit#1	slit#2	slit#3	slit#4	slit#5
WL(A)	3032.09	3063.09	3100.53	3135.05	3167.99	3200.01
Res(A)	5.7044	5.6513	5.5736	5.6156	5.5034	5.4208
O3abs(1/cm)	2.5932	1.7777	1.0046	0.67575	0.37502	0.29357
Ray abs(1/cm)	5049.354	4831.6738	4584.5728	4370.7908	4178.5889	4002.0038
SO2abs(1/cm)	3.4094	5.6512	2.4156	1.893	1.0547	0.61083
step	O3abs	Rayabs	SO2abs	O3SO2Abs	Daumont	Bremen
1017	0.34277	96930.434	3.1588	1.1485	0.35339	0.34478
1018	0.34176	96906.6241	3.1679	1.1452	0.35245	0.34381
1019	0.34075	96882.8209	3.1762	1.142	0.35148	0.34281

8.5.3 Umkehr

For the Umkehr calibration, only the lines shorter than 3400 Å were used. The Umkehr offset is calculated by forcing the wavelength of slit #4 at the ozone position to be the same as on slit #1 at the Umkehr setting. The Umkehr offset calculated is **2423**. Table 8-5 summarizes the dispersion test for umkehr: wavelength, resolution and ozone absorption coefficient.

Table 8-5 – **2021 Umkehr dispersion constants**

step= 1018	slit#0	slit#1	slit#2	slit#3	slit#4	slit#5
WL(A)	3032	3063	3100	3135	3168	3200
Res(A)	5.7045	5.6514	5.5737	5.6157	5.5035	5.4209
O3abs(1/cm)	2.5958	1.7793	1.0049	0.67611	0.37499	0.29403
Ray abs(1/cm)	0.50499	0.48322	0.4585	0.43712	0.4179	0.40024
step= 2423	slit#0	slit#1	slit#2	slit#3	slit#4	slit#5
WL(A)	3134	3164	3200	3233	3265	3296
Res(A)	5.5794	5.5078	5.4352	5.4714	5.3727	5.2997
O3abs(1/cm)	0.67852	0.39567	0.29392	0.12354	0.061188	0.033385
Ray abs(1/cm)	0.43789	0.42028	0.40023	0.38284	0.36716	0.35273

8.6 ETC Transfer

Based on the Lambert-Beer law, the total ozone column in the Brewer algorithm can be expressed as:

$$X = \frac{F - ETC}{\alpha\mu} \tag{1}$$

where F are the measured double ratios corrected for Rayleigh effects, α is the ozone absorption coefficient, μ is the ozone air mass factor, and ETC is the extra-terrestrial constant. The F, α and ETC parameters are weighted functions at the operational wavelengths with weighting coefficients $w = [0, 1, -0.5, -2.2, 1.7]$ for slits 1 to 5, with nominal wavelengths equal to $[306.3, 310.1, 313.5, 316.8, 320.1]$ nm.

The transfer of the calibration scale (namely ETC) is done side by side with the reference instrument. Once we have collected enough near-simultaneous direct sun ozone measurements, we calculate the new extraterrestrial constant after imposing the condition that the measured ozone will be the same for simultaneous measurements. In terms of the previous equation for ozone, this leads to the following condition:

$$ETC_i = F_i - X_i^{reference}\alpha\mu \tag{2}$$

For a good characterized instrument, the ETC determined values show a Gaussian distribution and the mean value is used as the instrument constant. One exception to this rule is the single monochromator Brewer models (MK-II and MK-IV) which are affected by stray light.

Brewers are calibrated with the one parameter (1P) ETC transfer method: only the ozone ETC constant is transferred from the reference instrument. The so-called “two parameters calibration method” (2P), where both the ozone absorption coefficient and the ETC are calculated from the reference, is also obtained and serves as a quality indicator of the calibration. We consider a calibration optimal when both ETC values agree within 10 units, and the ozone absorption coefficient calculated from the dispersion tests and obtained with the 2P method agree within ± 2 micrometer steps, or approx. ± 0.002 atm.cm^{-1}. This range represents a total ozone difference of about 0.5% at airmass equal to 2, and total ozone of 300 DU.

The ETC is obtained by comparison with the reference brewer **IZO#185** using near-simultaneous measurements during **5** days (two measurements are considered near-simultaneous if they are taken less than **3.5** minutes apart). Measurements with airmass difference greater than 3% were removed from the analysis.

8.6.1 Initial Calibration

For the evaluation of initial status of Brewer WRC#163, we used the period from days **190** to **194** which correspond with **328** near-simultaneous direct sun ozone measurements. As shown in Fig. 8-18, the current calibration constants produce ozone values slightly higher than the reference instrument (0.4%). When the ETC is corrected taking into account the difference between the SL and R6 reference (SL correction), the results slightly improve.

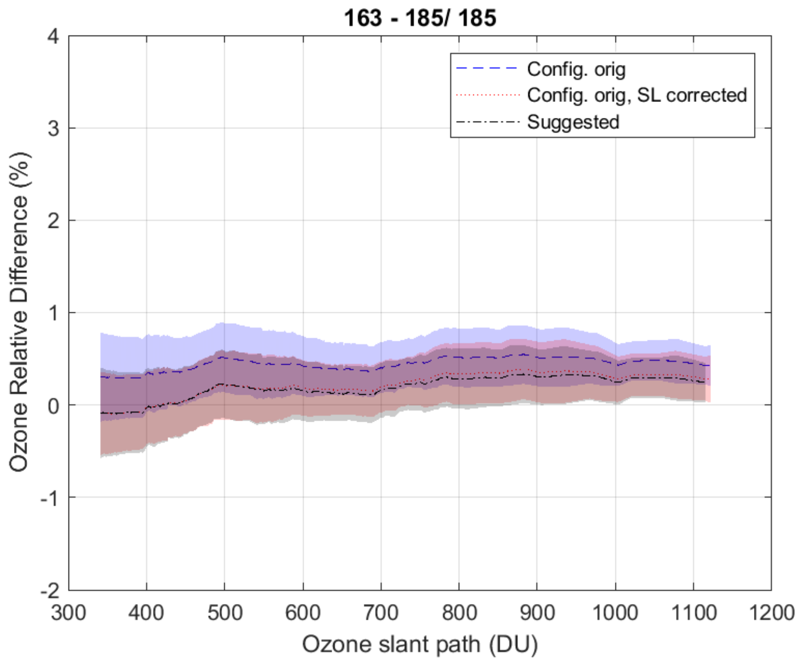


Figure 8-18 – Mean direct-sun ozone column percentage difference between Brewer WRC#163 and Brewer IZO#185 as a function of ozone slant path.

8.6.2 Final Calibration

A new ETC value was calculated (see Fig. 8-19) also using the **328** simultaneous direct sun measurements from days **190** to **194**. The calculated value using the full OSC range with the 1P transfer is only one unit higher than the current ETC value (**1490**). Therefore, we recommend maintaining this ETC. As shown in Table 8-6, the agreement between the 1P and 2P ETCs is on the maximum tolerance limit of 10 units.

Mean daily total ozone values and relative differences with respect to IZO#185 for the original and the final configurations are shown in Table 8-7.

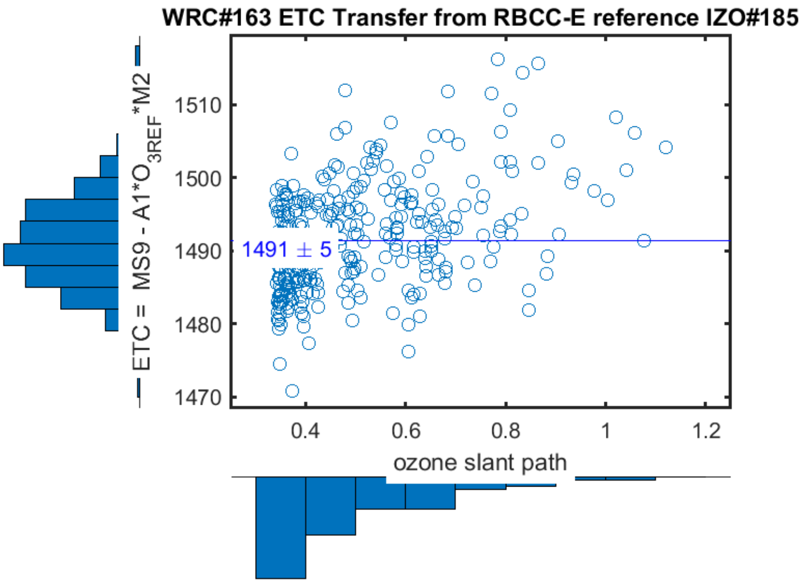


Figure 8-19 – **Mean direct-sun ozone column percentage difference between Brewer WRC#163 and Brewer IZO#185 as a function of ozone slant path.**

Table 8-6 – **Comparison between the results of the 1P and 2P ETC transfer methods for the final days.**

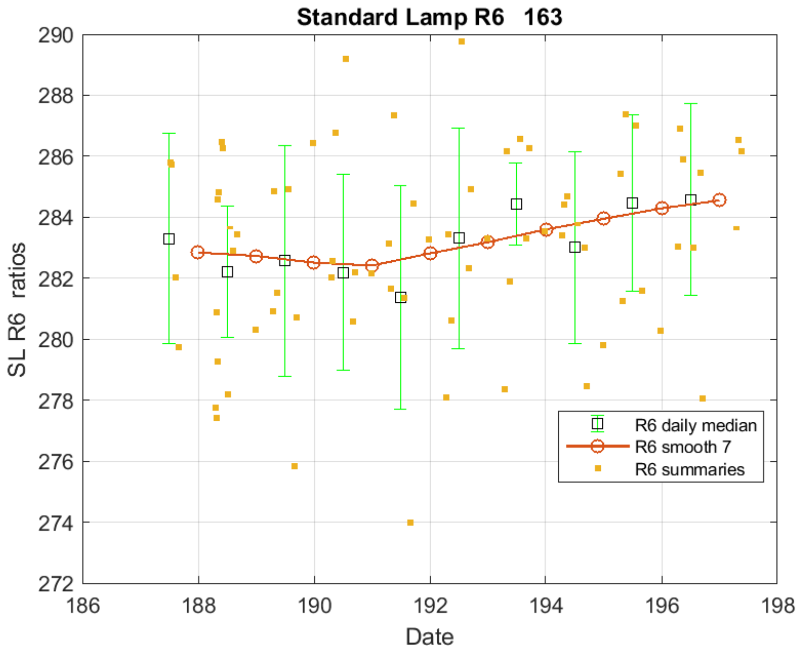
	ETC 1P	ETC 2P	O3Abs final	O3Abs 2P
full OSC range	1491	1483	3418	3437

Table 8-7 – Daily mean ozone and relative differences with respect to the reference, with the original and final (the latter, in the columns marked with a star) calibrations. Data from the final days.

	Day	O3#185	std	N	O3#163	std	rd	O3(*)#163	std(*)	rd(*)
09-Jul-2021	190	324	2.1	31	325.1	2	0.3	324	1.8	0
10-Jul-2021	191	313.4	2.7	123	314.3	2.7	0.3	313.3	2.6	0
11-Jul-2021	192	314.9	3.3	71	316.7	3.3	0.6	315.7	3.4	0.3
12-Jul-2021	193	305.5	2.6	102	307	2.5	0.5	306	2.4	0.2
13-Jul-2021	194	318.4	0	1	320.2	0	0.6	319.6	0	0.4

8.6.3 Standard Lamp Reference Values

The reference values of standard lamp ratios during the calibration period were **283** for R6 (Figure 8-20) and **522** for R5 (Figure 8-21).



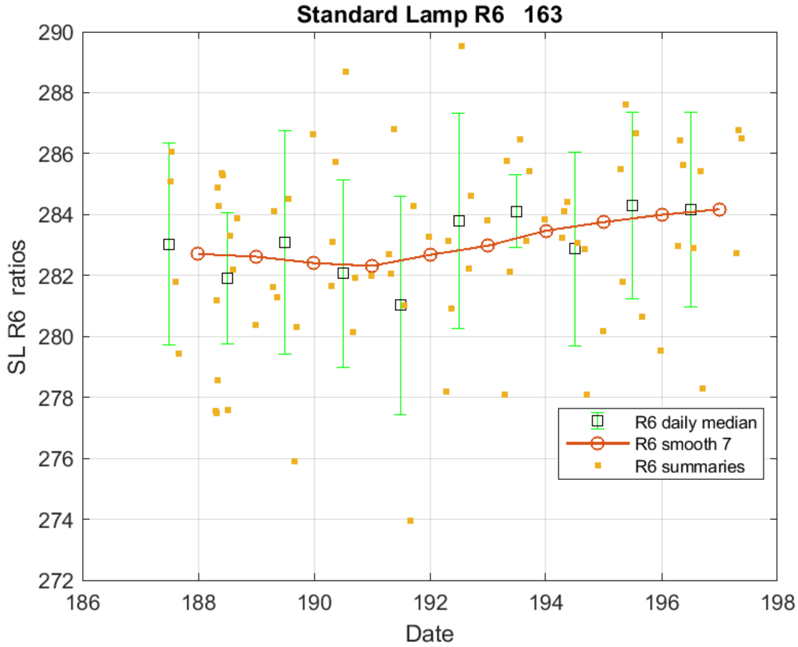
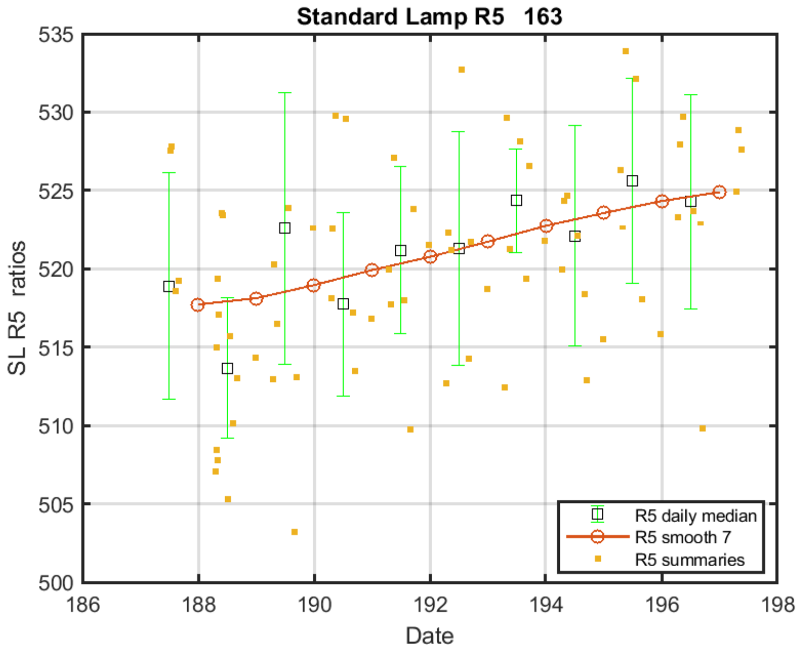


Figure 8-20 – Standard Lamp O_3 R6 ratios: daily mean and standard deviation (squares), seven day running mean (circle) and individual tests (black dots). Reprocessed using old (top) and new (bottom) instrumental constants



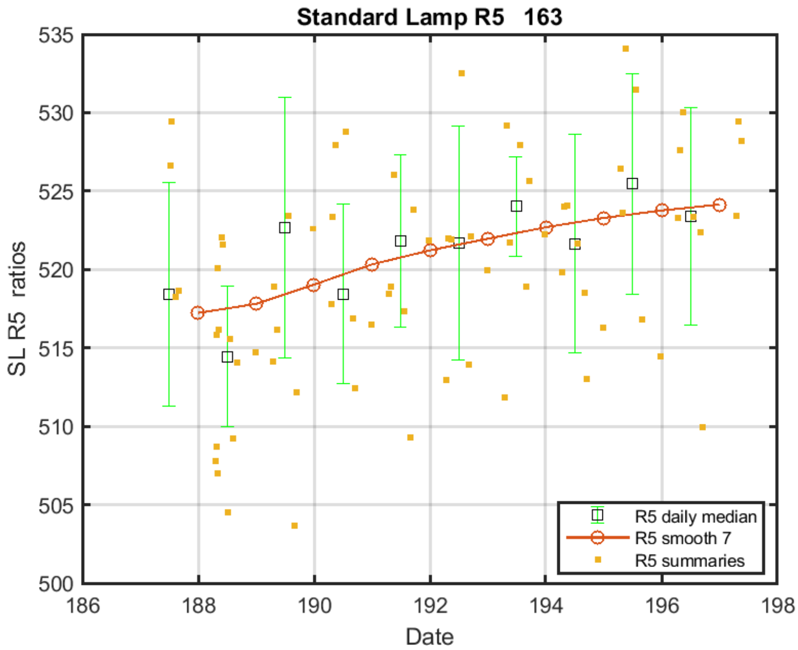


Figure 8-21 – Standard Lamp SO_2 R5 ratios: daily mean and standard deviation (squares), seven day running mean (circle) and individual tests (black dots). Reprocessed using old (top) and new (bottom) instrumental constants

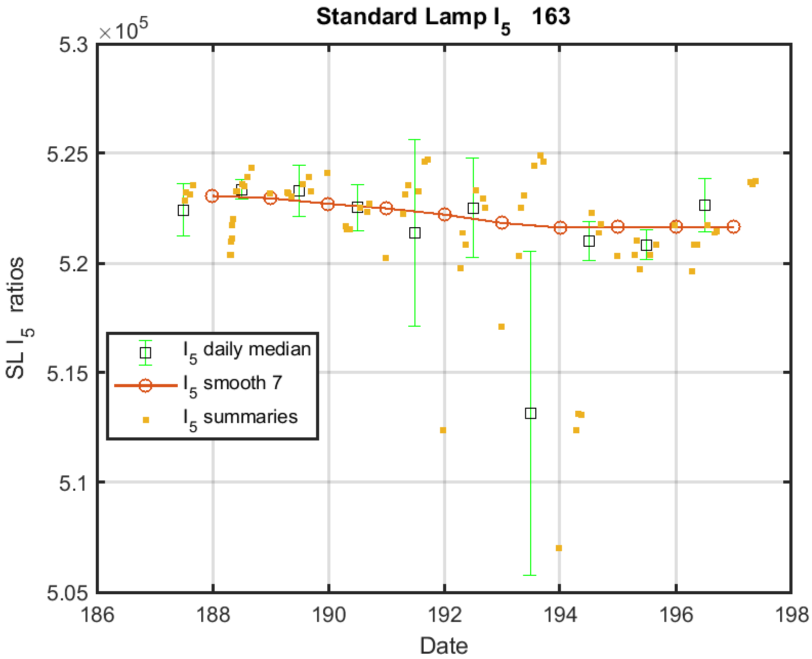


Figure 8-22 – Standard Lamp intensity: daily mean and standard deviation (squares), seven day running mean (circle) and individual tests (black dots)

8.7 Configuration

8.7.1 Instrument constant file

	Initial (ICF01921.163)	Final (ICF18821.163)
o3 Temp coef 1	0	0
o3 Temp coef 2	0.1845	0.1845
o3 Temp coef 3	0.16251	0.16251
o3 Temp coef 4	0.47783	0.47783
o3 Temp coef 5	-0.48255	-0.48255
Micrometer steps/deg	0	0
O3 on O3 Ratio	0.341	0.3418
SO2 on SO2 Ratio	2.35	2.35
O3 on SO2 Ratio	1.1342	1.1342
ETC on O3 Ratio	1490	1490
ETC on SO2 Ratio	105	105
Dead time (sec)	3e-08	2.8e-08
WL cal step number	1018	1018
Slitmask motor delay	14	14
Umkehr Offset	1693	1693
ND filter 0	0	0
ND filter 1	4300	4300
ND filter 2	9080	9080
ND filter 3	13800	13800
ND filter 4	21700	21700
ND filter 5	25000	25000
Zenith steps/rev	2972	2972
Brewer Type	3	3
COM Port #	1	1
o3 Temp coef hg	0	0
n2 Temp coef hg	0	0
n2 Temp coef 1	0	0
n2 Temp coef 2	0	0
n2 Temp coef 3	0	0
n2 Temp coef 4	0	0
n2 Temp coef 5	0	0
O3 Mic #1 Offset	-1	-1
Mic #2 Offset	-4	-4
O3 FW #3 Offset	242	242
NO2 absn Coeff	-3	-3
NO2 ds etc	770	770
NO2 zs etc	740	740
NO2 Mic #1 Offset	8028	8028
NO2 FW #3 Offset	178	178
NO2/O3 Mode Change	2503	2503
Grating Slope	0.9965	0.9965
Grating Intercept	10	10
Micrometer Zero	1741	1741
Iris Open Steps	250	250
Buffer Delay (s)	0.6	0.6
NO2 FW#1 Pos	64	64
O3 FW#1 Pos	256	256
FW#2 Pos	0	0
uv FW#2 Pos	0	0
Zenith Offset	0	0
Zenith UVB Position	2242	2242

8.8 Daily Summary report

Day	osc range	O3#185	std	N	O3#163	std	rd	O3(*)#163	std(*)	rd(*)
190	1000>osc>700	323	0	2	325.3	1.1	0.7	325	1.1	0.6
190	700>osc>400	323.7	2.1	25	323.9	1.9	0.1	323.7	1.9	0
190	osc<400	326.3	0.7	4	325.9	0.5	-0.1	325.5	0.6	-0.2
191	1500>osc>1000	310.1	0.6	3	311.6	0.5	0.5	311.4	0.4	0.4
191	1000>osc>700	311.7	3	15	312.9	3.8	0.4	312.6	3.8	0.3
191	700>osc>400	313.4	3.6	45	314	3.4	0.2	313.6	3.3	0.1
191	osc<400	314.3	1.1	56	313.7	1.5	-0.2	313.4	1.4	-0.3
192	1000>osc>700	316.6	1.5	5	318.1	1.5	0.5	318	1.5	0.5
192	700>osc>400	316.5	2.2	41	316.8	2.1	0.1	316.8	2.1	0.1
192	osc<400	313.2	4	22	312.8	4	-0.1	312.9	4	-0.1
193	1500>osc>1000	305.1	0.6	3	305.6	0.5	0.2	305.7	0.7	0.2
193	1000>osc>700	303.2	1.9	14	303.8	2.9	0.2	303.9	2.8	0.2
193	700>osc>400	304.2	3	36	304.9	2.4	0.2	305.2	2.5	0.3
193	osc<400	306.8	1.3	43	306.9	1.3	0	307.3	1.3	0.2
194	1500>osc>1000	318.5	0	1	319.8	0	0.4	319.6	0	0.4
194	1000>osc>700	322.8	0.2	2	324	0.4	0.4	323.8	0.4	0.3
194	700>osc>400	323.8	1.7	8	324.6	2.3	0.2	324.5	2.4	0.2

8.9 Summary Plots

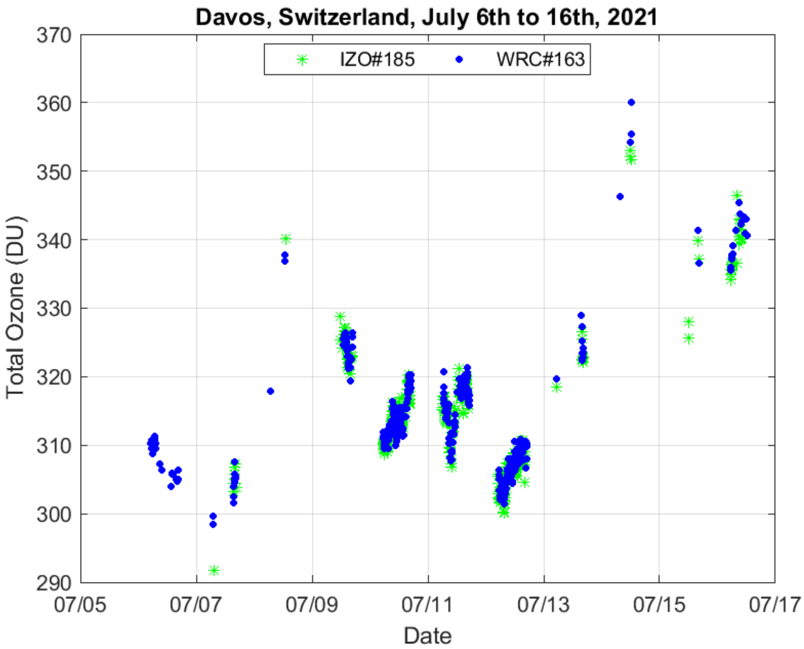
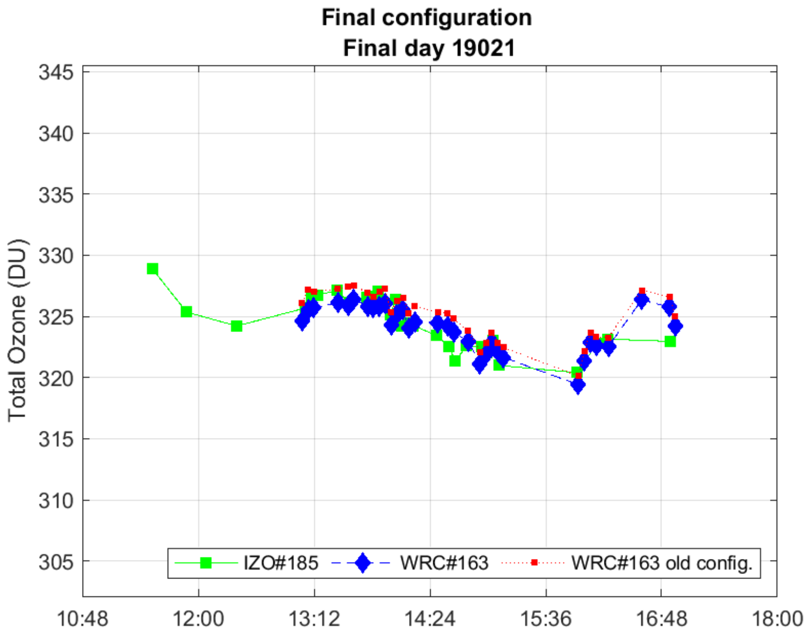
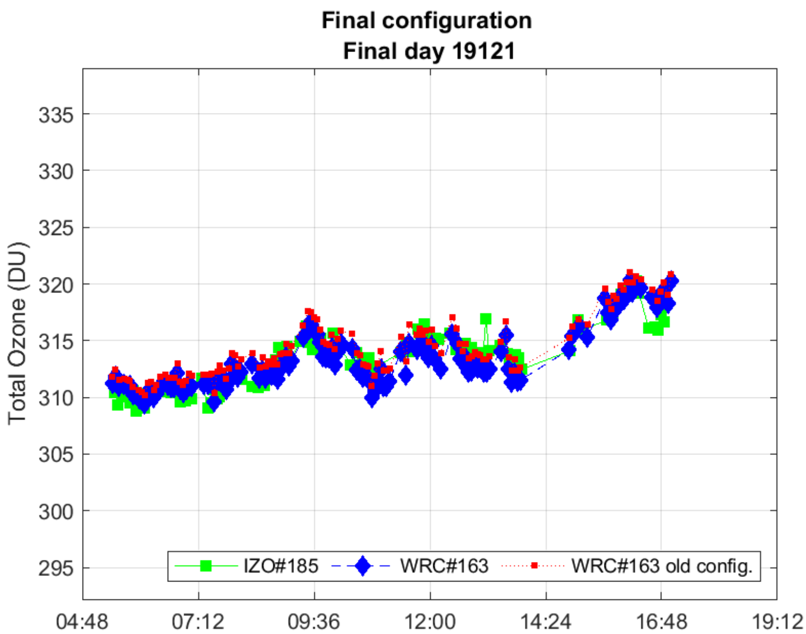
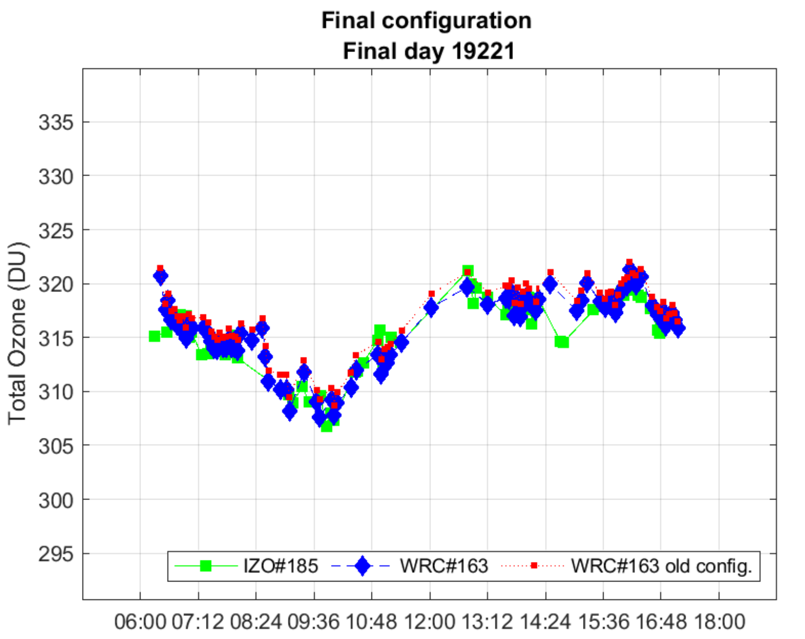
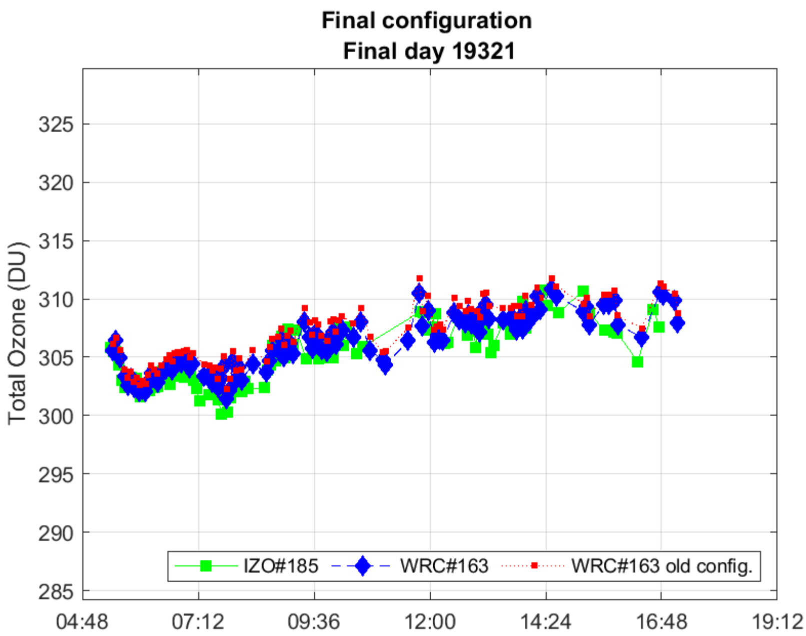


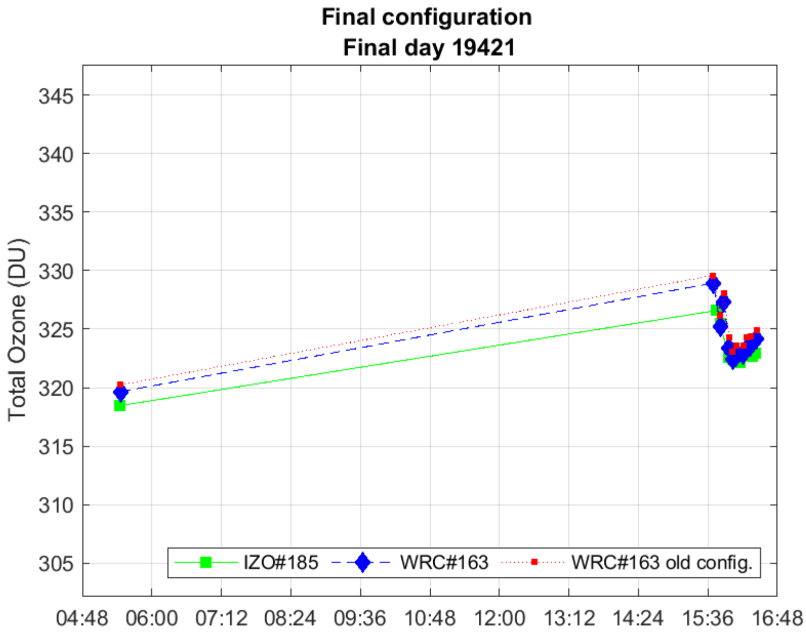
Figure 8-23 – Overview of the intercomparison. Brewer WRC#163 data are evaluated using final constants (blue circles)


Final configuration
Final day 19021
Total Ozone (DU)
345
340
335
330
325
320
315
310
305
10:48
12:00
13:12
14:24
15:36
16:48
18:00
IZO#185
WRC#163
WRC#163 old config.


Final configuration
Final day 19121
Total Ozone (DU)
335
330
325
320
315
310
305
300
295
04:48
07:12
09:36
12:00
14:24
16:48
19:12
IZO#185
WRC#163
WRC#163 old config.


Final configuration
Final day 19221
Total Ozone (DU)
335
330
325
320
315
310
305
300
295
IZO#185
WRC#163
WRC#163 old config.
06:00 07:12 08:24 09:36 10:48 12:00 13:12 14:24 15:36 16:48 18:00


Final configuration
Final day 19321
Total Ozone (DU)
325
320
315
310
305
300
295
290
285
IZO#185
WRC#163
WRC#163 old config.
04:48 07:12 09:36 12:00 14:24 16:48 19:12


Final configuration
Final day 19421
Total Ozone (DU)
345
340
335
330
325
320
315
310
305
04:48
06:00
07:12
08:24
09:36
10:48
12:00
13:12
14:24
15:36
16:48
IZO#185
WRC#163
WRC#163 old config.

9 Brewer K&Z#245

9.1 Calibration Summary

The Fifteenth Intercomparison Campaign of the Regional Brewer Calibration Center Europe (RBCC-E) was held from July 6th to the 16th, 2021, at the Physikalisch-Meteorologisches Observatorium PMOD (Davos, Switzerland).

Brewer K&Z#245 participated in the campaign in the period from July 8th to 13th. The campaign days of Brewer K&Z#245 correspond to Julian days 189 – 194.

For the evaluation of the initial status, we used **67** simultaneous direct sun (DS) ozone measurements from days **190** to **191**. For final calibration purposes, we used **93** simultaneous DS ozone measurements taken from day **192** to **194**.

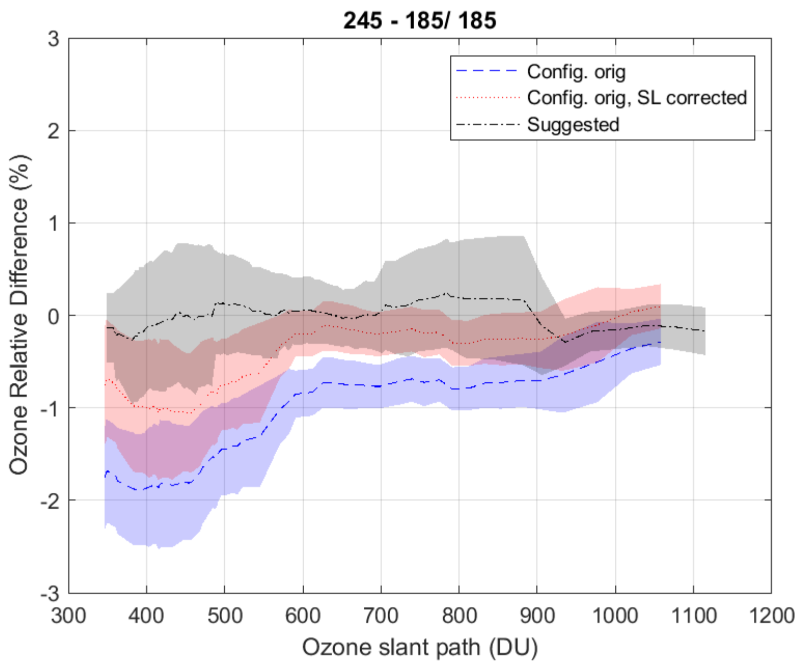


Figure 9-1 – **Mean DS ozone column percentage difference between Brewer K&Z#245 and Brewer IZO#185, plotted as a function of the ozone slant path. Results for the current (issued in the previous calibration campaign) configuration are show in blue; the red dotted line corresponds to the same configuration, but with the standard lamp correction applied; the black line corresponds to results obtained with the updated configuration proposed in the current campaign. The shadow areas represent the standard deviation of the mean. The comparison with the original configuration (with and without SL correction) is done during the blind days, while the comparison with the suggested configuration corresponds to the final days of the campaign.**

As shown in Fig. 9-1, the current ICF (ICF15921.245, blue dashed line) produces ozone values with an average difference of around −1.4% with respect to the reference instrument. SL correction (Fig. 9-1, red dotted line) improves the comparison with Brewer IZO#185. Therefore, we recommend applying the

SL correction since the last calibration.

Dead time (DT) shows a difference of around 5 ns between the value in the current ICF and the registered in the campaign, with its value changing from 2.5·10^{-8} to 2·10^{-8} ns. This is a significant change for double Brewers.

We appreciate a clear temperature dependence in the standard lamp observations, which indicates the temperature coefficients can be improved.

The neutral density filters didn't show nonlinearity in the attenuation's spectral characteristics. We have not applied any correction to filters.

The sun-scan tests (SC) at the instrument's station before the campaign, confirm the current cal step value (1029, within a step error of ± 1).

We do not suggest changing the Ozone Absorption Coefficient, retaining its current value of 0.3466.

All the other parameters analyzed (run/stop tests, Hg lamp intensity, CZ & CI files,...) show reasonable results.

Taking into account all this, we suggest some changes to the configuration of Brewer K&Z#245.

9.1.1 Recommendations and Remarks

1. The R5 and R6 reference values can be updated respectively to **509** and **422**.
2. We suggest updating the DT to **2·10**$^{-8}$ seconds.
3. We have found that new temperature coefficients improve the behaviour of the instrument, and we include them in the final ICF for the campaign.
4. The neutral density filters show the same behaviour as in the previous campaign, and we suggest retaining the same correction factors.
5. Finally, we suggest updating the ETC value from **1620** to **1605**.

9.1.2 External links

Configuration File

`http://rbcce.aemet.es/svn/campaigns/dav2021/bfiles/245/ICF19321.245`

Calibration Report

`https://docs.google.com/spreadsheets/d/12-4EoZzJkJDv5Pgpdt3PNZlZLXahvdlubhqOyijRack/edit#gid=2139295989`

Calibration Reports Detailed

Historic and instrumental

`http://rbcce.aemet.es/svn/campaigns/dav2021/latex/245/html/cal_report_245a1.html`

Temperature & Filter

`http://rbcce.aemet.es/svn/campaigns/dav2021/latex/245/html/cal_report_245a2.html`

Wavelength

`http://rbcce.aemet.es/svn/campaigns/dav2021/latex/245/html/cal_report_245b.html`

ETC transfer

http://rbcce.aemet.es/svn/campaigns/dav2021/latex/245/html/cal_report_245c.html

9.2 Instrument History: Analysis of Average files

9.2.1 Standard Lamp Test

As shown in Figure 9-2 and 9-3, the standard lamp test performance have changed since the last calibration, primarily in August 2020. This change is not due to a standard lamp replacement, so a change in the instrument should be considered.

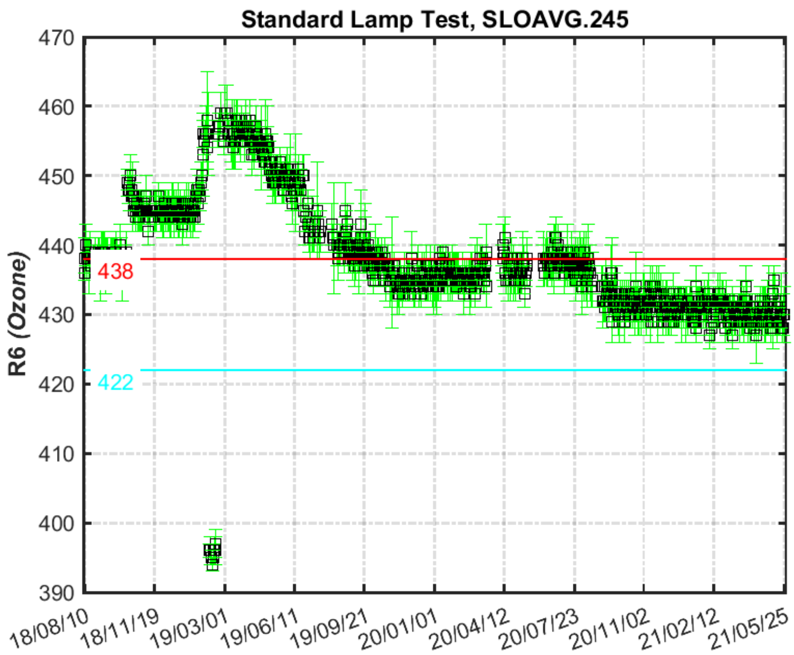


Figure 9-2 – **Standard Lamp test R6 (Ozone) ratios. Horizontal lines are labeled with the original and final reference values (red and blue lines, respectively)**

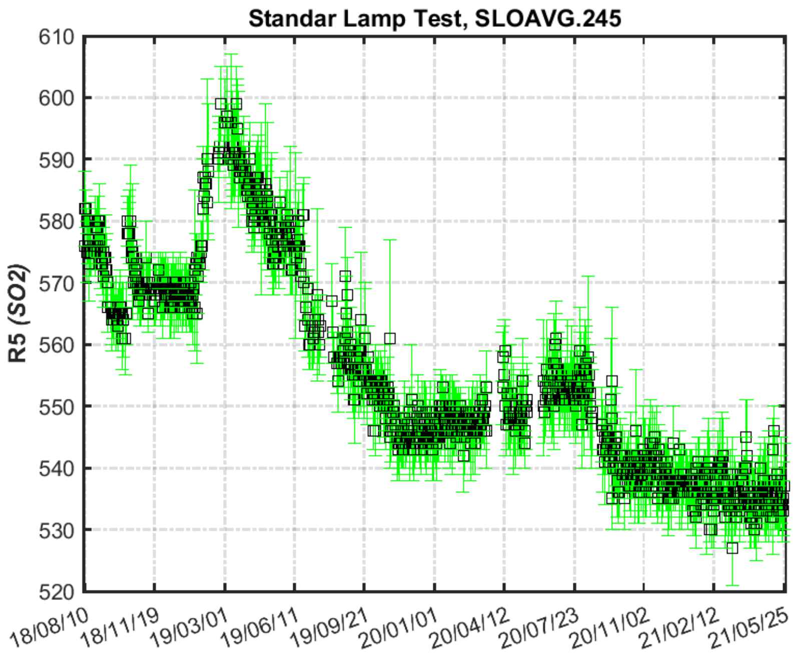


Figure 9-3 – **Standard Lamp test R5 (SO_2) ratios**

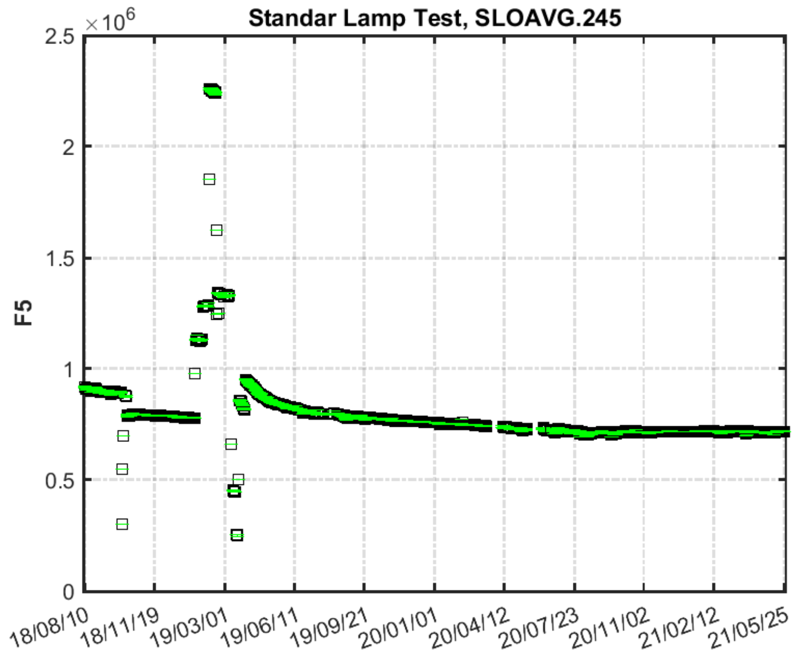


Figure 9-4 – **SL intensity for slit five.**

9.2.2 Run Stop and Dead Time

Run stops test values are within the test tolerance limits for all the slits with only a small number of outliers, as can be seen in figure Fig. 9-5.

As shown in Fig. 9-6, the current DT reference value of $\mathbf{2.5{\cdot}10}^{-8}$ seconds is larger than the value recorded during the calibration period, $\mathbf{2{\cdot}10}^{-8}$s. Therefore, this new value has been updated in the new ICF.

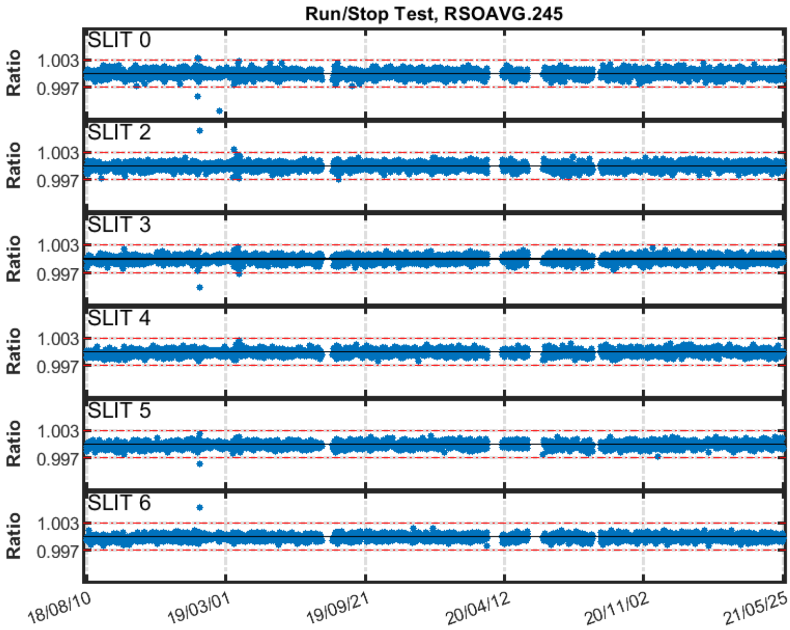


Figure 9-5 – **Run/stop test**

9.2.3 Analog Test

Fig. 9-7 shows that the high voltage has remained almost constant around 1406 since the last calibration. Furthermore, analog test values are within the test tolerance range.

9.2.4 Mercury Lamp Test

No noticeable internal mercury lamp intensity events have been observed during the campaign, see Fig. 9-8.

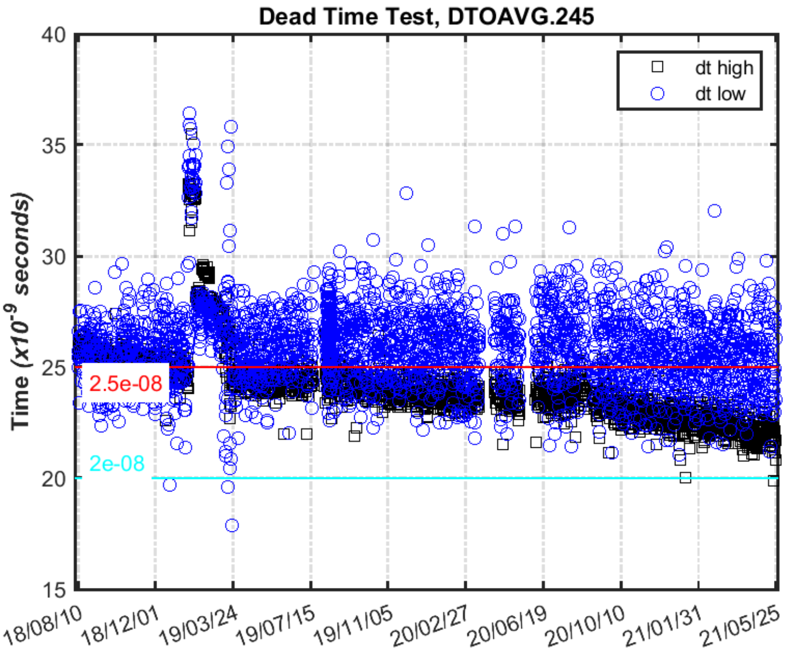


Figure 9-6 – Dead Time test. Horizontal lines are labelled with the current (red) and final (blue) values.

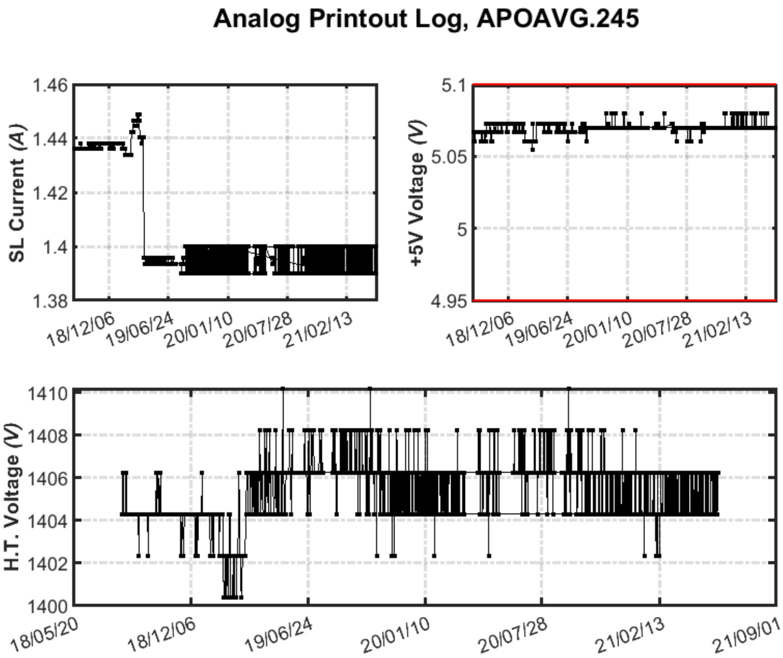


Figure 9-7 – Analog voltages and intensity.

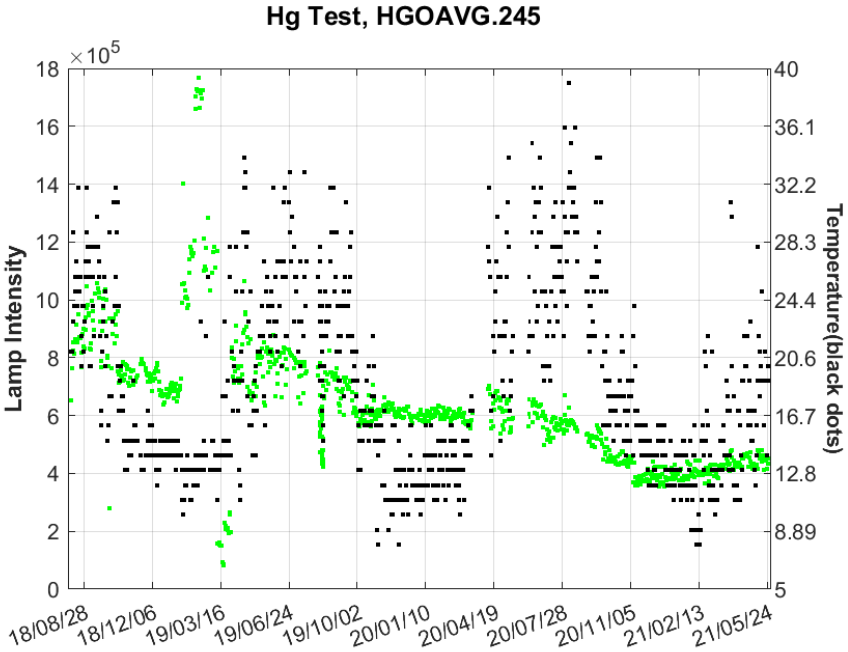
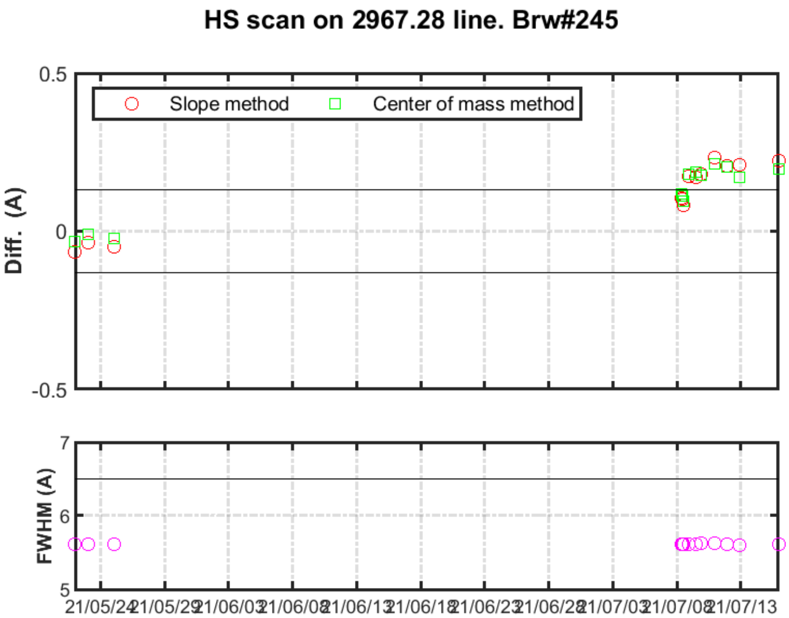


Figure 9-8 – Mercury lamp intensity (green squares) and Brewer temperature registered (black dots). Both parameters refer to maximum values for each day.

9.2.5 CZ scan on mercury lamp

In order to check both the wavelength settings and the slit function width, we analyzed the scans performed on the 296.728 nm, and 334.148 nm mercury lines, see Fig. 9-9. As a reference, the calculated scan peak, in wavelength units, should be within 0.013 nm from the nominal value, whereas the calculated slit function width should be no more than 0.65 nm. Analysis of the CZ scans performed on Brewer K&Z#245 during the campaign show reasonable results, with the peak of the calculated scans close, although slightly above the accepted tolerance range. Regarding the slit function width, results are good, with a FWHM lower than 6.5 Å. As can be seen in Fig. 9-9, there are only a few scans available since the last calibration. We recommend including the HS and HL scans in the operating program.



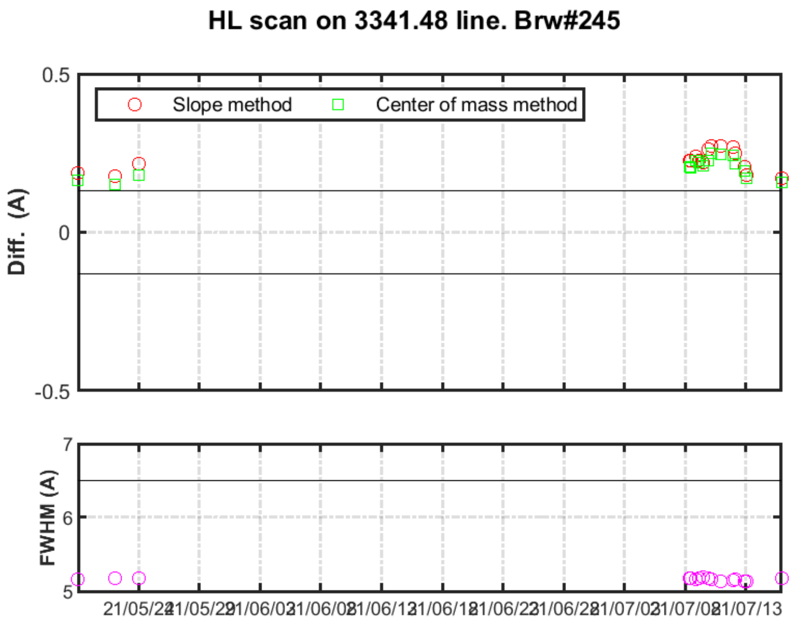


Figure 9-9 – CZ scan on Hg lines. The upper panels show differences with respect to the reference line (solid lines represent the limit ± 0.013 nm) as computed by the slopes (red circles) and center of mass (green squares) methods. Lower panels show the Full Width at Half Maximum value for each scan performed (solid lines represent the 0.65 nm limit).

9.2.6 CI scan on internal *SL*

CI scans of the standard lamp recorded at different times can be compared to investigate whether the instrument has changed its spectral sensitivity. We shown in Fig. 9-10 percentage ratios of the Brewer **K&Z#245** CI scans performed during the campaign relative to the scan CI19021.245. Unfortunately, the possible changes in the lamp intensity are framed due to maintenance operations. Therefore, the results of this test are inconclusive.

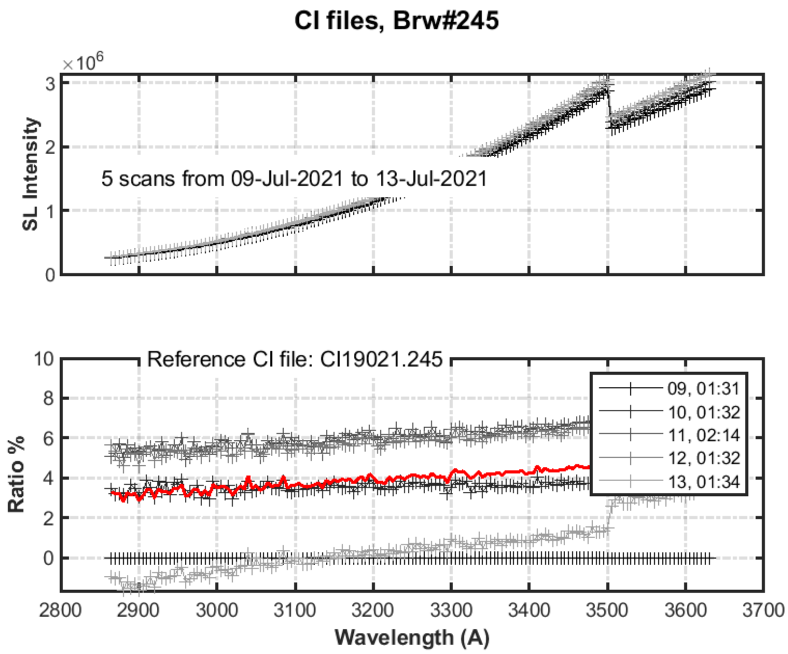


Figure 9-10 – CI scan of Standard Lamp performed during the campaign days. Scans processed (upper panel) and relative differences with respect to a selected reference scan (lower panel). Red line represents the mean of all relative differences

9.3 Absolute Temperature Coefficients

Temperature coefficients are determined using the standard lamp test. For every slit, the raw counts corrected for zero temperature coefficients are used in a linear regression against temperature with the slopes representing the instrument's temperature coefficients. From this we obtain the corrected *R6* and *R5* ratios to analyze the new temperature coefficients' performance.

Figure 9-11 shows the temperature coefficients' performance applied to the camping data, with a temperature range from **13**$^\circ$ **C** to **31**$^\circ$ **C**. As can be seen, the current coefficients do not perform well and do not reduce the temperature dependence. Therefore, a new set of coefficient were calculated. The results obtained are summarized in Table 9-1.

We have also extended our analysis using the data recorded since the previous campaign. As shown in Figs. 9-12 and 9-13, the new coefficients have a better performance. For this reason, in the final ICF we have used the current coefficients.

Table 9-1 – Temperature Coefficients. Calculated coefficients are normalized to slit#2

	slit#2	slit#3	slit#4	slit#5	slit#6
Current	0.0000	-0.0654	-0.2799	-0.5480	-1.0115
Calculated	0.0000	-0.5000	-1.5000	-2.0000	-2.6000
Final	0.0000	-0.1800	-0.1700	-0.2200	-0.2900

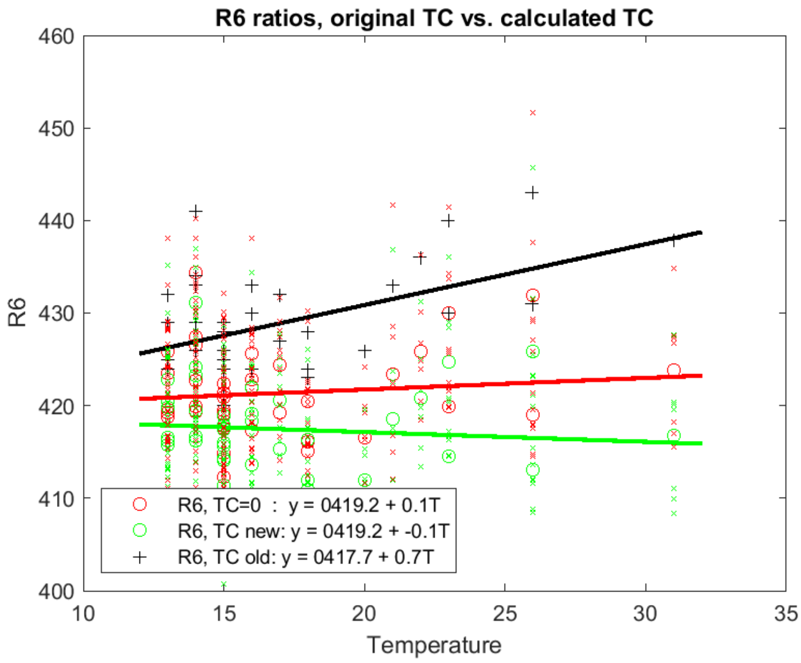


Figure 9-11 – Temperature coefficients' performance. Red circles represent standard lamp R6 ratios calculated from raw counts without temperature correction (temperature coefficients set to 0). Black crosses and green circles represent standard lamp R6 ratios corrected with original and calculated temperature coefficients, respectively. Data corresponds to the present campaign.

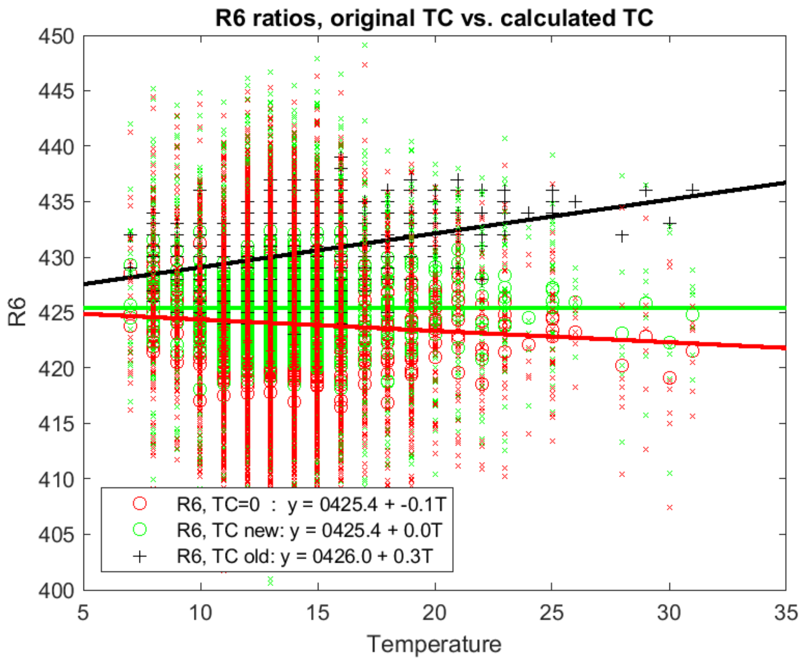


Figure 9-12 – **Same as Fig. 9-11 but for the whole period between calibration campaigns.**

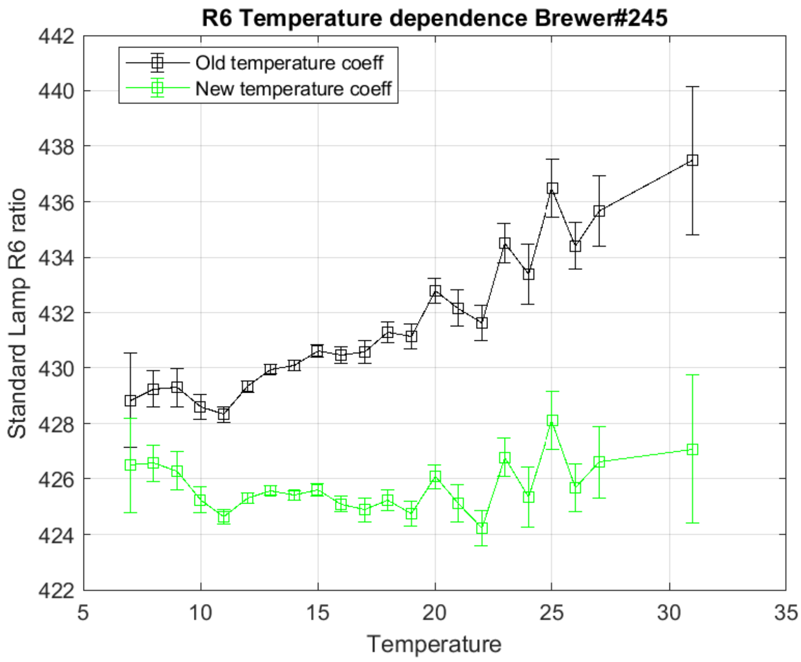


Figure 9-13 – **Standard lamp R6 (MS9) ratio as a function of temperature. We plotted R6 ratio recalculated with the original (black) and the new (green) temperature coefficients**

9.4 Attenuation Filter Characterization

9.4.1 Attenuation Filter Correction

The filter's spectral dependence affects the ozone calculation because the Brewer software assumes that their attenuation is wavelength-neutral. We can estimate the correction factor needed for this non-linearity by multiplying the attenuation of every filter and every wavelength by the ozone weighting coefficients.

During the calibration period, a total of **12** FI tests were analyzed to calculate the attenuation for every filter and slit. Fig. 9-14 shows the results of these tests, and Table 9-2 shows the calculated ETC corrections for each filter.

No correction factor is needed to account for non-linearity of ND filters. So, ND#1, ND#2, ND#3 and ND#5 present a correction factor lower than 5 units. For ND#4, the correction factor calculated is higher that 5 units. However, the wide range of the mean 95%CI suggest a great uncertainty for the calculated correction for Filter ND#4 (see Table 9-2), and therefore, no change is suggested.

Table 9-2 – **ETC correction due to Filter non-linearity. Median value, mean values and, 95% confidence intervals are calculated using bootstrap technique**

	filter#1	filter#2	filter#3	filter#4	filter#5
ETC Filt. Corr. (median)	1	5	19	-16	4
ETC Filt. Corr. (mean)	4.8	-0.3	5.5	-14.2	5.1
ETC Filt. Corr. (mean 95% CI)	[-3.9 14.4]	[-11.2 7.4]	[-1.3 12.1]	[-53.6 -1.8]	[-6.5 13.2]

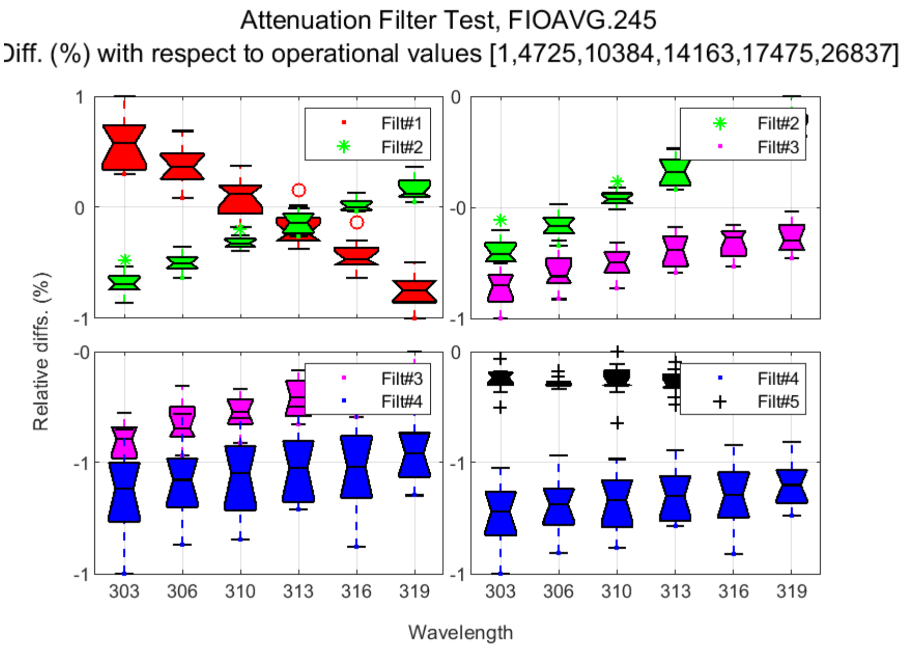


Figure 9-14 – Notched box-plot for the calculated attenuation relative differences of neutral density filters with respect to operational values. We show for each subplot relative differences corresponding to correlative filters (color box-plots). Solid lines and boxes mark the median, upper and lower quartiles. The point whose distance from the upper or lower quartile is 1 times larger than the interquartile range is defined as outlier.

9.5 Wavelength Calibration

9.5.1 Cal-Step determination

The sun scan routine takes DS ozone measurements by moving the micrometer about 15 steps below and above the ozone reference position (wavelength *Calibration step-number*). A Hg test is required before and after the measurement to assure the correct wavelength setting during the *sun scan* test. Ozone *versus* step number ideally shows a parabolic shape with a maximum at the ozone reference position. With this choice, small wavelength shifts ($\approx \pm 2$ steps) do not affect the ozone value. This optimal micrometer position is a near-linear function of the ozone slant path at the time of the scan, see Fig. 9-15

Before the campaign, 823 sun-scan (SC) tests covering a ozone slant path range from 400 to 1200 DU were collected, see Fig. 9-16)). The calculated Cal-Step Number (CSN) confirms the value in the current configuration: **1029**.

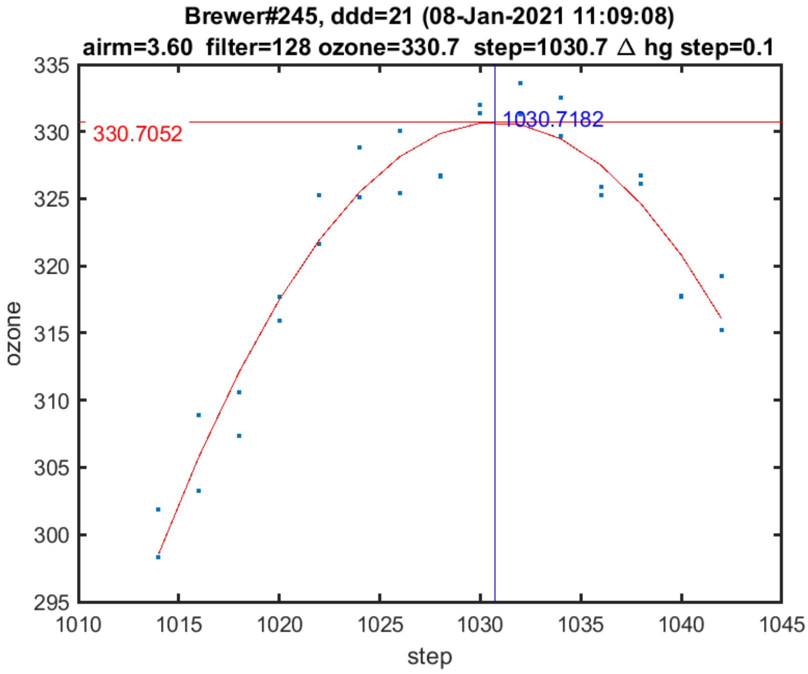


Figure 9-15 – Ozone measurements moving the micrometer 15 step around the operational CSN defined in the initial configuration

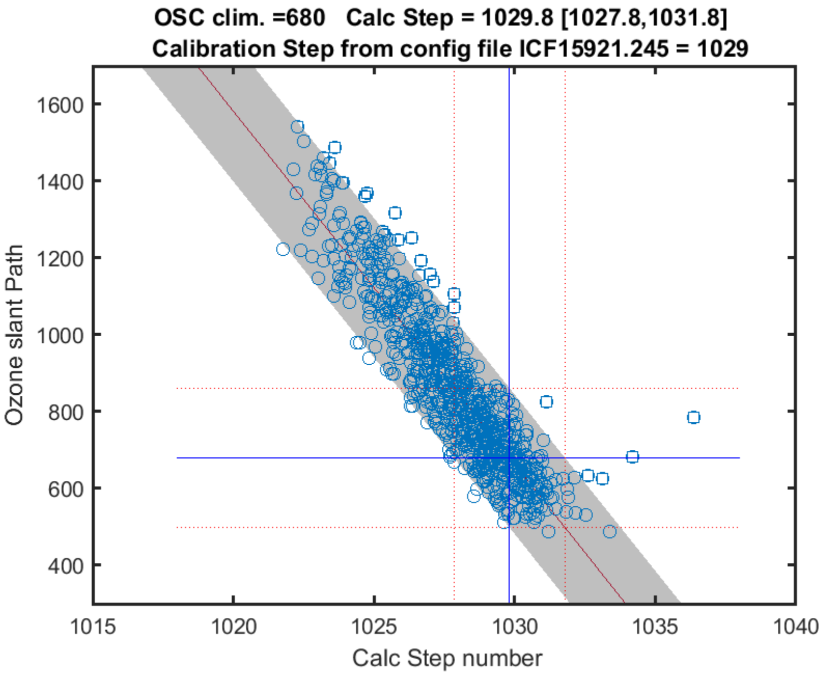


Figure 9-16 – Ozone Slant Path *vs* Calc – Step number. Vertical solid line marks the calculated *Cal Step Number* for a climatological OSC equal to 680 (horizontal solid line). Grey area represents a 95% confidence interval

9.5.2 Dispersion Test

We analyzed the dispersion tests carried out in the previous and present calibration campaigns. For all of them, we processed data from Mercury and Cadmium spectral lamps, using cubic functions to adjust the micrometer step number to wavelength positions. The results of this historical analysis are summarized in Table 9-3.

In particular, for the current campaign, Fig. 9-17 shows that the cubic fitting was good for all the dispersion tests, with residuals being lower than 0.1 Å in all slits. For the dispersion tests performed using the UV dome and the internal Hg lamp, Table 9-4 provides individual wavelength resolution, ozone absorption coefficient, sulfur dioxide absorption coefficient, and Rayleigh absorption for the operational CSN and those at ± 1 step.

We suggest keeping the current absorption coefficient, equal to **0.3466**, in the final configuration.

Table 9-3 – **Dispersion derived constants**

	Calc-step	O3abs coeff.	SO2abs coeff.	O3/SO2
Current	1029	0.3466	2.3500	1.1525
13-Jul-2018	1029	0.3389	3.2091	1.1368
21-Jul-2018	1029	0.3427	3.2053	1.1469
02-Aug-2018	1029	0.3401	3.2022	1.1347
09-Jul-2021	1029	0.3439	3.2269	1.1492
Final	1029	0.3466	2.3500	1.1525

Table 9-4 – 2021 dispersion derived constants

step= 1028	slit#0	slit#1	slit#2	slit#3	slit#4	slit#5
WL(A)	3032.06	3063.01	3100.46	3134.9	3167.81	3199.71
Res(A)	5.634	5.5226	5.4416	5.5487	5.4194	5.3849
O3abs(1/cm)	2.5938	1.7801	1.005	0.67696	0.37476	0.29574
Ray abs(1/cm)	5049.5577	4832.2067	4584.9656	4371.7423	4179.6003	4003.5933
SO2abs(1/cm)	3.4076	5.6494	2.4036	1.9189	1.0517	0.62032
step= 1029	slit#0	slit#1	slit#2	slit#3	slit#4	slit#5
WL(A)	3032.13	3063.09	3100.53	3134.97	3167.88	3199.78
Res(A)	5.6339	5.5225	5.4415	5.5486	5.4193	5.3848
O3abs(1/cm)	2.5911	1.7785	1.0048	0.67665	0.37479	0.29527
Ray abs(1/cm)	5049.0314	4831.7138	4584.5103	4371.3188	4179.2052	4003.2238
SO2abs(1/cm)	3.3937	5.6712	2.4118	1.9073	1.053	0.61823
step= 1030	slit#0	slit#1	slit#2	slit#3	slit#4	slit#5
WL(A)	3032.21	3063.16	3100.61	3135.04	3167.95	3199.85
Res(A)	5.6338	5.5224	5.4414	5.5485	5.4192	5.3847
O3abs(1/cm)	2.5888	1.7769	1.0045	0.67629	0.37485	0.29479
Ray abs(1/cm)	5048.5051	4831.2211	4584.055	4370.8954	4178.8101	4002.8544
SO2abs(1/cm)	3.3801	5.6918	2.4199	1.8958	1.0542	0.61612
step	O3abs	Rayabs	SO2abs	O3SO2Abs	Daumont	Bremen
1028	0.3448	100824.6908	3.2171	1.1524	0.35491	0.34637
1029	0.34386	100800.5422	3.2269	1.1492	0.35406	0.34547
1030	0.34281	100776.4003	3.2356	1.1458	0.35317	0.34455

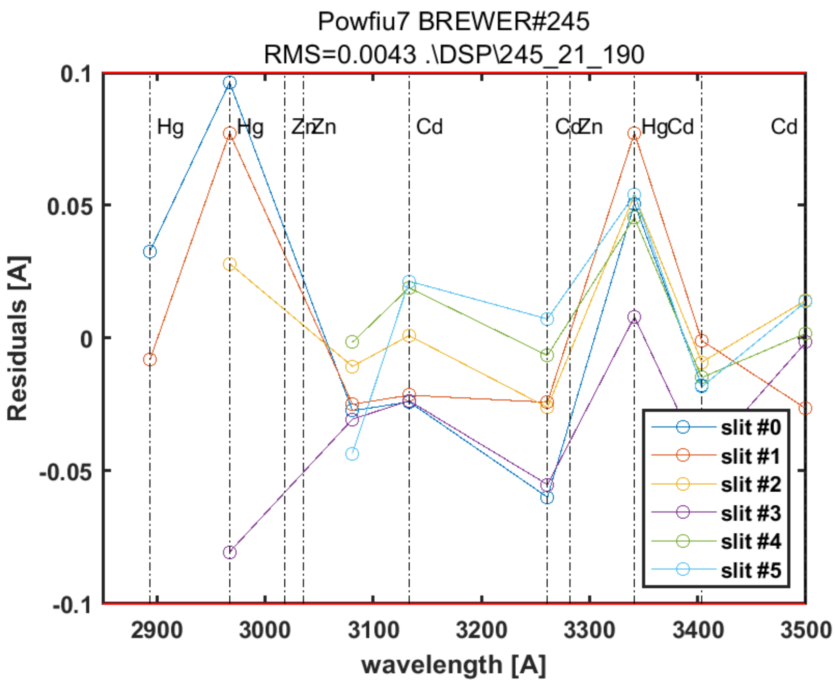


Figure 9-17 – 2021 residuals of cubic fit

9.5.3 Umkehr

For the Umkehr calibration, only the lines shorter than 3400 Å were used. The Umkehr offset is calculated by forcing the wavelength of slit #4 at the ozone position to be the same as on slit #1 at the Umkehr setting. The Umkehr offset calculated is **2443**. Table 9-5 summarizes the dispersion test for umkehr: wavelength, resolution and ozone absorption coefficient.

Table 9-5 – **2021 Umkehr dispersion constants**

step= 1029	slit#0	slit#1	slit#2	slit#3	slit#4	slit#5
WL(A)	3032	3063	3101	3135	3168	3200
Res(A)	5.6339	5.5225	5.4415	5.5486	5.4193	5.3848
O3abs(1/cm)	2.5911	1.7785	1.0048	0.67665	0.37479	0.29527
Ray abs(1/cm)	0.5049	0.48317	0.45845	0.43713	0.41792	0.40032
step= 2443	slit#0	slit#1	slit#2	slit#3	slit#4	slit#5
WL(A)	3134	3164	3200	3233	3265	3295
Res(A)	5.4966	5.4081	5.3236	5.4212	5.2894	5.2572
O3abs(1/cm)	0.67872	0.39741	0.29548	0.12649	0.06177	0.033388
Ray abs(1/cm)	0.43797	0.42038	0.40032	0.38297	0.36729	0.3529

9.6 ETC Transfer

Based on the Lambert-Beer law, the total ozone column in the Brewer algorithm can be expressed as:

$$X = \frac{F - ETC}{\alpha\mu} \quad (1)$$

where F are the measured double ratios corrected for Rayleigh effects, α is the ozone absorption coefficient, μ is the ozone air mass factor, and ETC is the extra-terrestrial constant. The F, α and ETC parameters are weighted functions at the operational wavelengths with weighting coefficients $w = [0, 1, -0.5, -2.2, 1.7]$ for slits 1 to 5, with nominal wavelengths equal to $[306.3, 310.1, 313.5, 316.8, 320.1]$ nm.

The transfer of the calibration scale (namely ETC) is done side by side with the reference instrument. Once we have collected enough near-simultaneous direct sun ozone measurements, we calculate the new extraterrestrial constant after imposing the condition that the measured ozone will be the same for simultaneous measurements. In terms of the previous equation for ozone, this leads to the following condition:

$$ETC_i = F_i - X_i^{reference}\alpha\mu \quad (2)$$

For a good characterized instrument, the ETC determined values show a Gaussian distribution and the mean value is used as the instrument constant. One exception to this rule is the single monochromator Brewer models (MK-II and MK-IV) which are affected by stray light.

Brewers are calibrated with the one parameter (1P) ETC transfer method: only the ozone ETC constant is transferred from the reference instrument. The so-called “two parameters calibration method” (2P), where both the ozone absorption coefficient and the ETC are calculated from the reference, is also obtained and serves as a quality indicator of the calibration. We consider a calibration optimal when both ETC values agree within 10 units, and the ozone absorption coefficient calculated from the dispersion tests and obtained with the 2P method agree within ± 2 micrometer steps, or approx. ± 0.002 atm.cm^{-1}. This range represents a total ozone difference of about 0.5ozone of 300 DU.

The ETC is obtained by comparison with the reference brewer **IZO#185** using near-simultaneous measurements during **3** days (two measurements are considered near-simultaneous if they are taken less than **3.5** minutes apart). Measurements with airmass difference greater than 3% were removed from the analysis.

9.6.1 Initial Calibration

For the evaluation of initial status of Brewer K&Z#245, we used the period from days **190** to **191** which correspond with **67** near-simultaneous direct sun ozone measurements. As shown in Fig. 9-18, the current calibration constants produce an ozone values slightly lower than the reference instrument (-1.4%). When the ETC is corrected taking into account the difference between the SL and R6 reference (SL correction), the results do not improve.

Table 9-6 shows the results of the 1P and 2P calibration methods. Mean daily total ozone values for the original and the final configurations are shown in Table 9-7, as well as relative differences with respect to IZO#185.

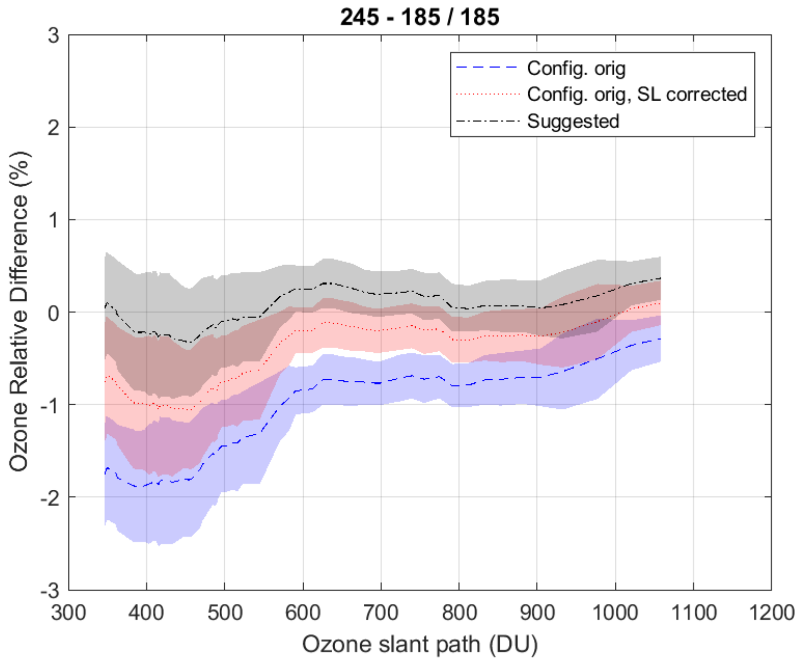


Figure 9-18 – Mean direct-sun ozone column percentage difference between Brewer K&Z#245 and Brewer IZO#185 as a function of ozone slant path.

Table 9-6 – Comparison between the results of the 1P and 2P ETC transfer methods for the blind days.

Table 9-7 – Daily mean ozone with original calibration, without and with (the latter, in the columns marked with a star) the standard lamp correction and the reference. Initial calibration. The 'rd' columns contain the porcentual relative difference, $\mathrm{rd} = \{O_3(\textbf{K\&Z\#245}) - O_3(\textbf{IZO\#185})\}/O_3(\textbf{IZO\#185}) * 100$

	Day	O3#185	std	N	O3#245	std	rd	O3(*)#245	std(*)	rd(*)
09-Jul-2021	190	324.2	2	21	317.9	1.1	-1.9	322.7	1.4	-0.5
10-Jul-2021	191	310.7	1.3	46	307.3	1.2	-1.1	310.9	1.2	0.1

9.6.2 Final Calibration

After the maintenance on day 191, a new ETC value was calculated (see Fig. 9-19). For the final calibration, we use **93** simultaneous direct sun measurements from days **192** to **194**. The new value is 14 units lower than the current ETC value (**1620**). Therefore, we recommend using this new ETC, together with the new proposed standard lamp reference ratios, **422** for R6. We updated the new calibration constants in the ICF provided. Of course, the new ETC has been calculated taking into account the new suggested dead time, $\mathbf{2{\cdot}10^{-8}}$.

The ETC value in the final ICF corresponds to the 1P transfer. As shown in Table 9-8, the agreement between the 1P and 2P ETCs is right on the tolerance limit of 10 units.

Mean daily total ozone values and relative differences with respect to IZO#185 for the original and the final configurations are shown in Table 9-9.

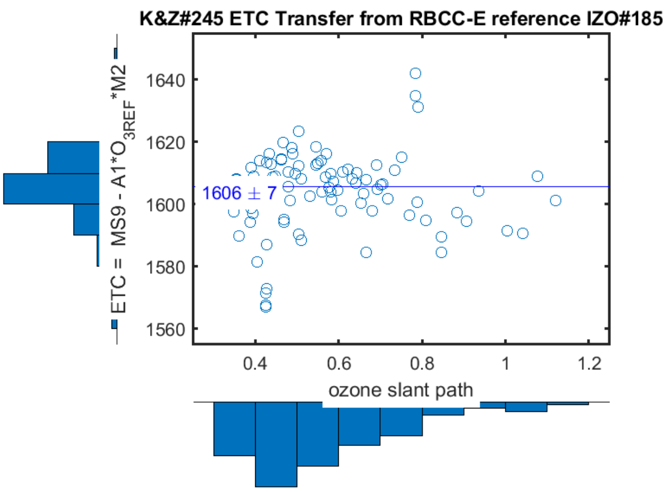


Figure 9-19 – **Mean direct-sun ozone column percentage difference between Brewer K&Z#245 and Brewer IZO#185 as a function of ozone slant path.**

Table 9-8 – **Comparison between the results of the 1P and 2P ETC transfer methods for the final days.**

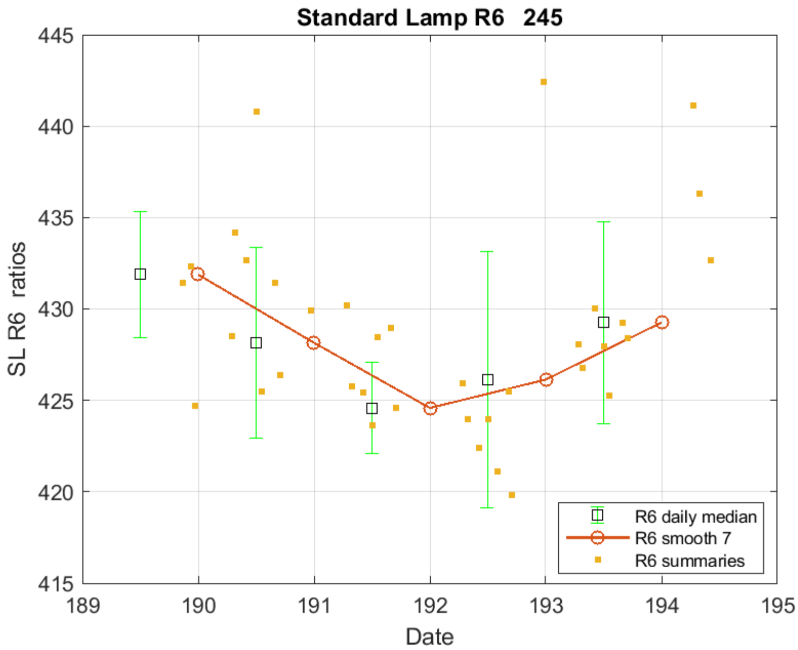
	ETC 1P	ETC 2P	O3Abs final	O3Abs 2P
full OSC range	1606	1598	3466	3485

Table 9-9 – Daily mean ozone and relative differences with respect to the reference, with the original and final (the latter, in the columns marked with a star) calibrations. Data from the final days.

	Day	O3#185	std	N	O3#245	std	rd	O3(*)#245	std(*)	rd(*)
10-Jul-2021	191	314.8	2.5	5	312.7	3.4	-0.7	312.9	3.6	-0.6
11-Jul-2021	192	315.2	3.7	22	314.8	3.8	-0.1	315.6	3.8	0.1
12-Jul-2021	193	304.6	2.8	65	303.5	2.6	-0.4	304.3	2.5	-0.1
13-Jul-2021	194	NaN	NaN	0	317.2	0	NaN	318.1	0	NaN

9.6.3 Standard Lamp Reference Values

The reference values of standard lamp ratios during the calibration period were **422** for R6 (Figure 9-20) and **509** for R5 (Figure 9-21).



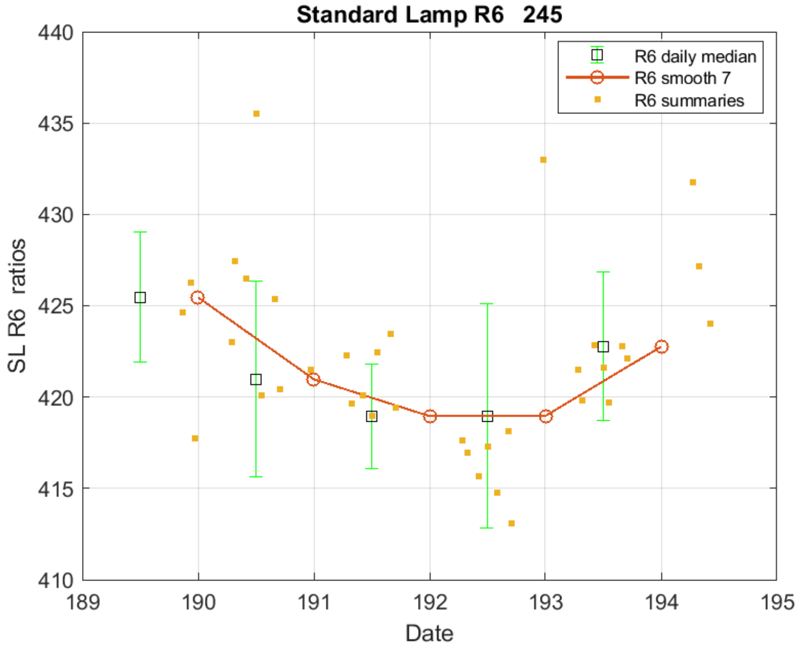
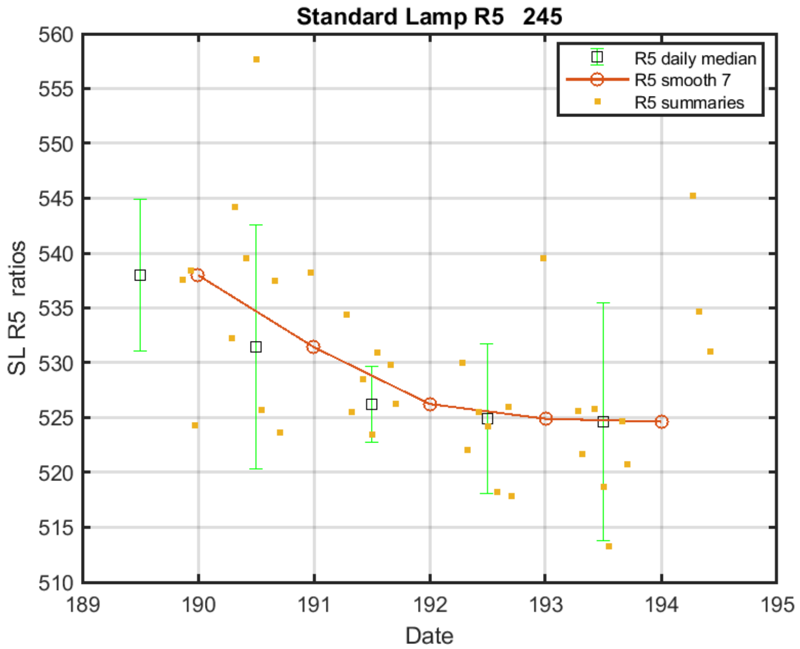


Figure 9-20 – Standard Lamp O_3 R6 ratios: daily mean and standard deviation (squares), seven day running mean (circle) and individual tests (black dots). Reprocessed using old (top) and new (bottom) instrumental constants



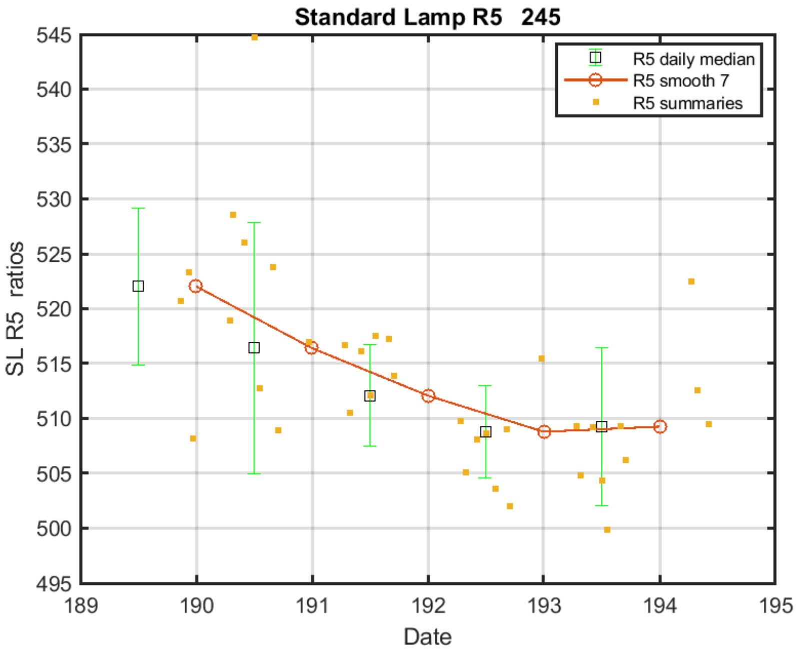


Figure 9-21 – Standard Lamp SO_2 R5 ratios: daily mean and standard deviation (squares), seven day running mean (circle) and individual tests (black dots). Reprocessed using old (top) and new (bottom) instrumental constants

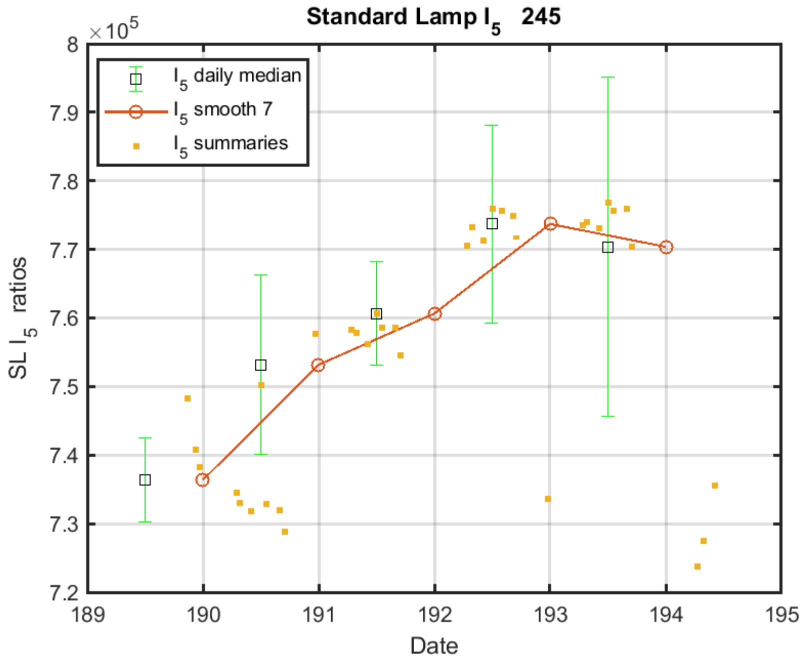


Figure 9-22 – Standard Lamp intensity: daily mean and standard deviation (squares), seven day running mean (circle) and individual tests (black dots)

9.7 Configuration

9.7.1 Instrument constant file

	Initial (ICF15921.245)	Final (ICF19321.245)
o3 Temp coef 1	0	0
o3 Temp coef 2	-0.0654	-0.18
o3 Temp coef 3	-0.2799	-0.17
o3 Temp coef 4	-0.548	-0.22
o3 Temp coef 5	-1.0115	-0.29
Micrometer steps/deg	0	0
O3 on O3 Ratio	0.3466	0.3466
SO2 on SO2 Ratio	2.35	2.35
O3 on SO2 Ratio	1.1525	1.1525
ETC on O3 Ratio	1620	1605
ETC on SO2 Ratio	46	46
Dead time (sec)	2.5e-08	2e-08
WL cal step number	1029	1029
Slitmask motor delay	14	14
Umkehr Offset	2441	2441
ND filter 0	0	0
ND filter 1	4725	4725
ND filter 2	10384	10384
ND filter 3	14163	14163
ND filter 4	17475	17475
ND filter 5	26837	26837
Zenith steps/rev	2972	2972
Brewer Type	3	3
COM Port #	1	1
o3 Temp coef hg	0	0
n2 Temp coef hg	0	0
n2 Temp coef 1	0	0
n2 Temp coef 2	0	0
n2 Temp coef 3	0	0
n2 Temp coef 4	0	0
n2 Temp coef 5	0	0
O3 Mic #1 Offset	0	0
Mic #2 Offset	0	0
O3 FW #3 Offset	242	242
NO2 absn Coeff	1	1
NO2 ds etc	770	770
NO2 zs etc	740	740
NO2 Mic #1 Offset	8028	8028
NO2 FW #3 Offset	178	178
NO2/O3 Mode Change	2515	2515
Grating Slope	1.0014	1.0014
Grating Intercept	-11.12	-11.12
Micrometer Zero	1723	1723
Iris Open Steps	250	250
Buffer Delay (s)	0	0
NO2 FW#1 Pos	64	64
O3 FW#1 Pos	256	256
FW#2 Pos	0	0
uv FW#2 Pos	0	0
Zenith Offset	0	0
Zenith UVB Position	2216	2216

9.8 Daily Summary report

Day	osc range	O3#185	std	N	O3#245	std	rd	O3(*)#245	std(*)	rd(*)
190	700>osc>400	323.9	2	18	319.7	1.1	-1.3	322.4	1.2	-0.5
190	osc<400	326	0.6	3	321.4	0.8	-1.4	324.6	0.8	-0.4
191	1500>osc>1000	309.9	0.8	2	310.7	0.1	0.3	311.5	0.1	0.5
191	1000>osc>700	309.9	0.6	13	309.1	0.8	-0.2	310.1	0.7	0.1
191	700>osc>400	311.4	2	28	310	2.5	-0.5	311.6	2.5	0.1
191	osc<400	313.3	0.5	6	311.5	1.7	-0.6	313.8	1.6	0.2
192	1000>osc>700	317.2	2.1	2	319.5	0.3	0.7	318.8	0.1	0.5
192	700>osc>400	316.6	2.6	17	317.4	3.1	0.3	316.3	3.1	-0.1
192	osc<400	311	5.2	2	312.9	3	0.6	310.4	3.4	-0.2
193	1500>osc>1000	305.1	0.6	3	304.1	1.2	-0.3	304.4	1.3	-0.2
193	1000>osc>700	303.2	1.9	14	303.3	3.7	0	303.3	3.5	0
193	700>osc>400	304	3	34	304.7	1.9	0.2	304	1.8	0
193	osc<400	306.4	1.1	11	307.5	1.2	0.4	306.1	0.9	-0.1
194	1500>osc>1000	318.5	0	1	NaN	NaN	NaN	318.1	0	-0.1

9.9 Summary Plots

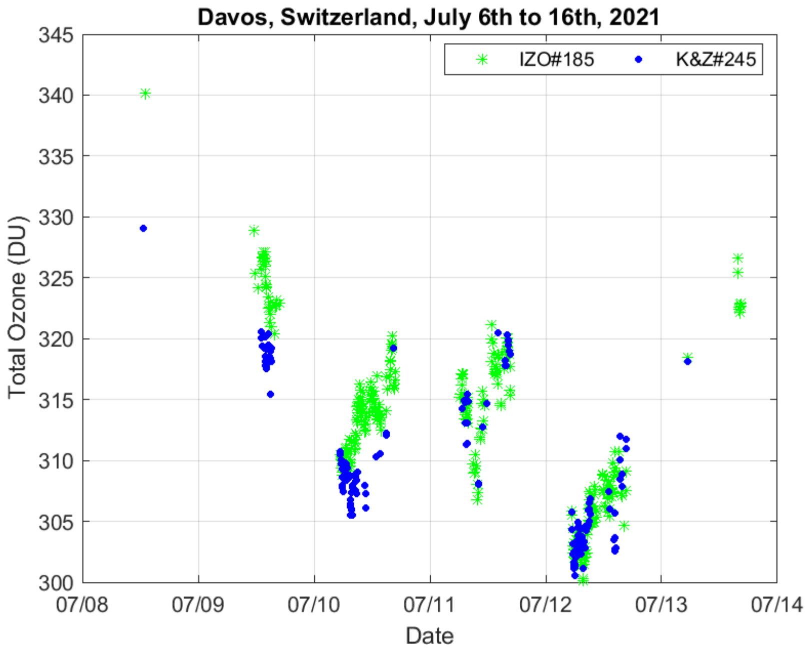
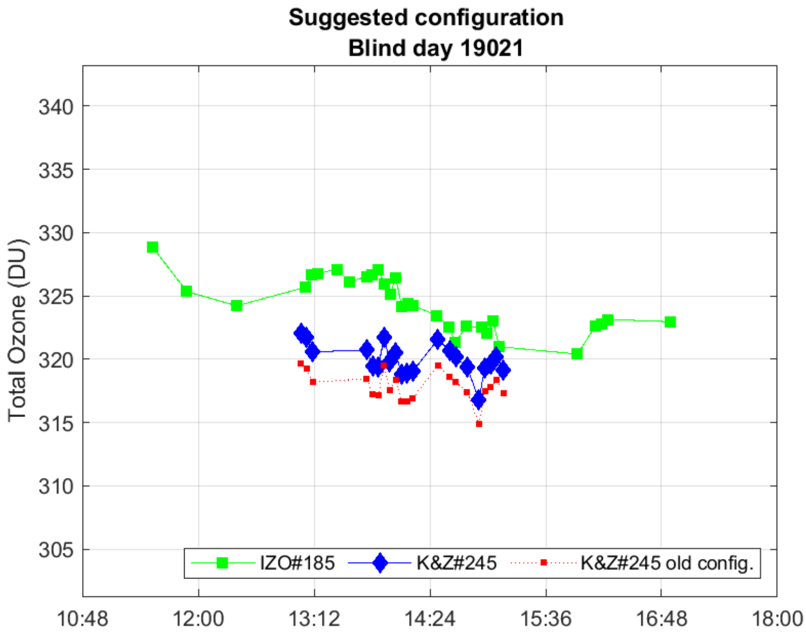
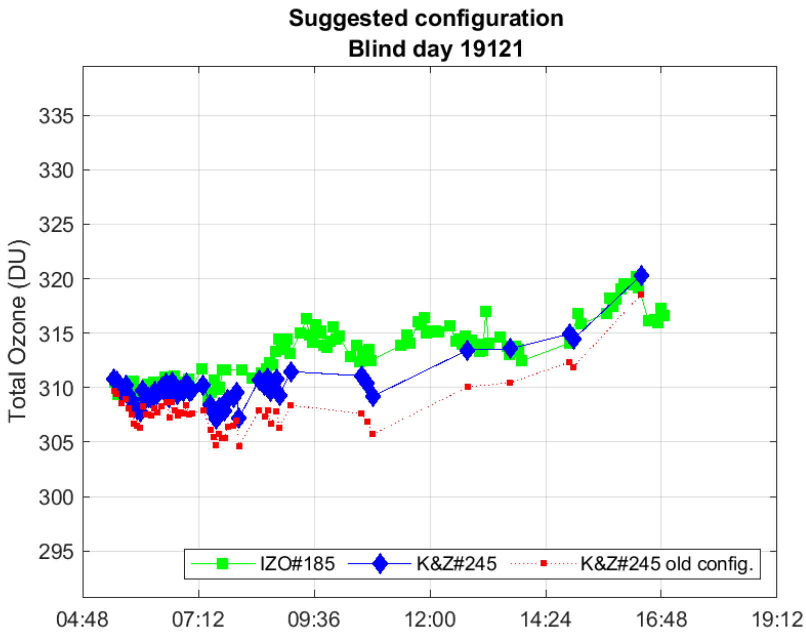
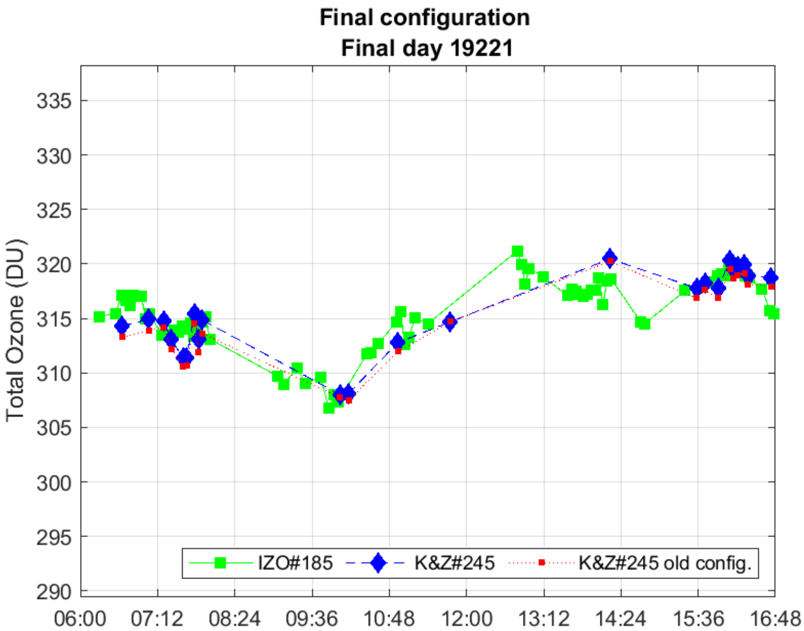
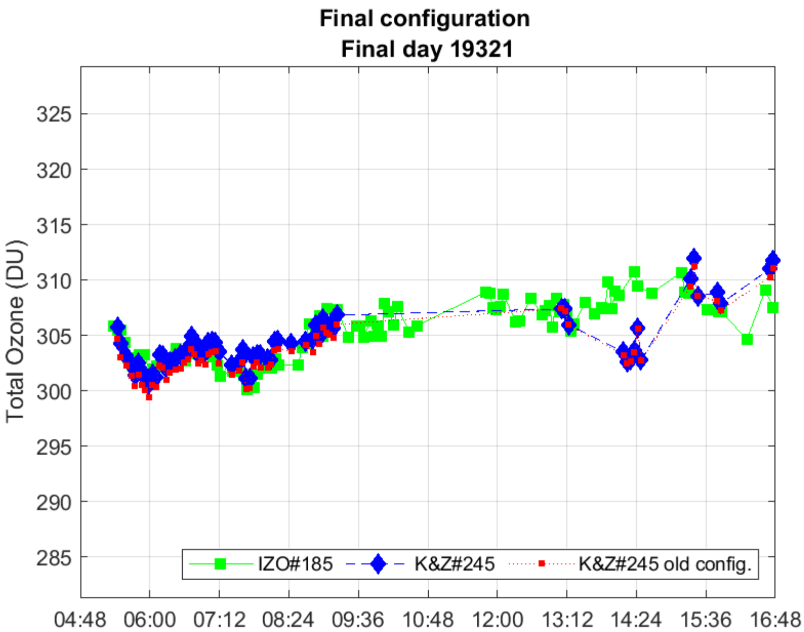


Figure 9-23 – Overview of the intercomparison. Brewer K&Z#245 data are evaluated using final constants (blue circles)


Suggested configuration
Blind day 19021
Total Ozone (DU)
340
335
330
325
320
315
310
305
10:48
12:00
13:12
14:24
15:36
16:48
18:00
IZO#185
K&Z#245
K&Z#245 old config.


Suggested configuration
Blind day 19121
Total Ozone (DU)
335
330
325
320
315
310
305
300
295
04:48
07:12
09:36
12:00
14:24
16:48
19:12
IZO#185
K&Z#245
K&Z#245 old config.


Final configuration
Final day 19221
Total Ozone (DU)
335
330
325
320
315
310
305
300
295
290
06:00
07:12
08:24
09:36
10:48
12:00
13:12
14:24
15:36
16:48
IZO#185
K&Z#245
K&Z#245 old config.


Final configuration
Final day 19321
Total Ozone (DU)
325
320
315
310
305
300
295
290
285
04:48
06:00
07:12
08:24
09:36
10:48
12:00
13:12
14:24
15:36
16:48
IZO#185
K&Z#245
K&Z#245 old config.

10 Maintenance Table

The table in the following page shows the most important maintenance work carried out on each participant instrument each day of the campaign.

n		Martes, 6/7	Miercoles, 7/7	Jueves, 8/7	Viernes, 9/7	Sabado, 10/7	Domingo, 11/7	Lunes, 12/7	Martes, 13/7	Miercoles, 14/7	Jueves, 15/7	Viernes, 16/7
	Previous Events	187	188	189	190	191	192	193	194	195	196	197
40	Local Brewer	o318721b	o318821b	o318921b. In Time	o319021b. In Time. windows cleaned.	Schedule reloaded. o319121b. In Time. DI test.	Schedule o319221b. In Time. power outage 08:15. New O3 Schedule.	Schedule o319321b. In Time.	Schedule o319421b. In Time.	Schedule o319521b. In Time. Cd DSP (dir)	Schedule o319621b. In Time. Hg DSP (int with dp). Zn DSP (dir).	Schedule o319721b. In Time. Changed to new ICF
72	Local Brewer	o318721b	o318821b	o318921b. In Time	o319021b. In Time. windows cleaned.	Infinite FR from 2: 00. Schedule reloaded. o319121b. In Time. Not wel alligned between10:30 and 12:15. In Time. DI test.	Schedule o319221b. In Time. Maintenace: Power supply replaced. power outage 08:15. New O3 Schedule.	Schedule o319321b. In Time.	Schedule o319421b. In Time.	Schedule o319521b. In Time. Cd DSP (dir)	Schedule o319621b. In Time. Hg DSP (int with dp). Zn DSP (dir).	Schedule o319721b. In Time Changed to new ICF
156	Local Brewer	o318721a	o318821a	o318921a. In Time	o319021a. In Time. windows cleaned.	Affected by a shadow in the early morning. Schedule reloaded. o319121a. In Time. In Time. DI test.	Schedule o319221a. In Time. power outage 08:15. New O3 Schedule.	Schedule o319321a. In Time.	Schedule o319421a. In Time.	Schedule o319521a. In Time. Cd DSP (dir)	Schedule o319621a. In Time. Hg DSP (int with dp). Zn DSP (dir).	Schedule o319721a. In Time. Changed to new ICF
158	Kipp			INSTALLED . o318921a. In Time	o319021a. In Time. DSP test. Doing Sun Scan: sc19021a.	Schedule changed to o319121a and then sc19121a. In Time. Some jumps in the measurements are detected.	Schedule sc19321a. In Time Maintenance: HV adjustment and SL replaced. power outage 08:15. After maintenace O3 schedule is load. We load again SC schedule at 14:20. New O3 Schedule.	Schedule sc19421a. In Time. Change to o319321a.	Schedule o319521a. In Time. UNINSTALLED 8: 00			
163	Local Brewer	o318721a	o318821a	o318921a. In Time	o319021a. In Time	Schedule reloaded. o319121a. In Time	Schedule o319221a. In Time. New O3 Schedule.	Schedule o319421a. In Time.	Schedule o319521a. In Time.	Schedule o319721a. Changed to o319521a. In Time. Cd DSP (dir)	Schedule o319621a. In Time. Hg DSP (int with dp). TI scan (glob). Hg DSP (glob).	Schedule pmoduvop. In Time.
185	reference	INSTALLED 14:45 with Sighting. Schedule to o318721a	o318821a	o318921a. In Time. 14:30 siting. Changed "Skip DS if too dim" in icf.	o319021a. In Time. windows cleaned. Leveling checked and siting.	Schedule reloaded. o319121a. In Time. Siting updated. leveling slightly changed (siting rest the same)	Schedule o319221a. In Time. power outage 08:15.	Schedule o319321a. In Time.	Schedule o319421a. In Time.	Schedule o319521a. In Time. Cd DSP (dir). Changed to sc19521a at the evening	Schedule sc19521a. In Time. Zn DSP (dir). Hg DSP (int with dp).	Schedule o319721a. In Time. HPHGSLDTRSAP POB1w1Clb2w1CZ NI
245	Kipp			INSTALLED . o318921a. In Time	DSP test. Schedule jawohl.	Affected by a shadow in the early morning. Schedule reloaded. o319121a. In Time. Maintenance at 11h.	Schedule o319221a. In Time. power outage 08:15. Maintenance: Filter oscillation switch on. New O3 Schedule.	Schedule o319421a. In Time. UV measurements removed from schedule.	Schedule o319421a. In Time. UNINSTALLED 8: 00			
WEATHER		After 185 instalation some moments with sun, just to make siting.	Completely overcast with some drizzle	Completely overcast with rain and storms	Completely overcast and raining in the morning. Some sun in the afternoon.	Sunny morning with high clouds. At noon gets more cloudy	Cloudy in the morning and at the end of day	Sunny with some high clouds.	Foggy and cloudy. Some sun at the end of the day.	Foggy, cloudy and Raining	Cloudy and raining. Same sun afternoon.	Mostly cloudy with some sun
NOTES												

11 Glossary

CI	Scan to the internal Standard Lamp
CSN	Cal step number
CZ	Custom Scan generally to the internal lamps
DSP	Dispersion File
DT	Dead Time
Hg	Internal Mercury Line
HL	Scan to the Internal Mercury Line of 295.nm
HS	Scan to the Internal Mercury Line of 345.nm
ICF	Instrument Constant File
OSC	Ozone Slant Column
R6	Ratio 6, Standard Lamp Ozone Ratio
R5	Ratio 5, Standard Lamp SO2 Ratio
SL	Standard Lamp
RS	Run Stop test
TC	Temperature Coefficients

12 Participants

Participant	Country	Instituion
Julian Gröbner	Switzerland	PMOD/WRC
Luca Egli	Switzerland	PMOD/WRC
Franz Zeilinger	Switzerland	MeteoSwis
Herbert Schill	Switzerland	PMOD/WRC
Rene Stubi	Switzerland	MeteoSwis
Pavel Babal	The Netherlands	Kipp & Zonen
Erik Noort	The Netherlands	Kipp & Zonen
Alberto Redondas	Spain	RBCC-E/State Meteorological Agency from Spain
Francisco Parra	Spain	RBCC-E/State Meteorological Agency from Spain
Alberto Berjón	Spain	RBCC-E/TRAGSA
Javier Lopez	Spain	RBCC-E/TRAGSA