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Interactive comment on "Improved retrieval of nitrogen dioxide (NO₂) column densities by means of MKIV Brewer spectrophotometers" *by* H. Diémoz et al.

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The authors are very grateful to the anonymous referee for the insightful and thorough revision of their paper. A point-by-point list of responses is written further below. Additional or modified statements to the revised manuscript are reported in *italic* font. Furthermore, a supplementary document with updated tables, figures and additional references is available as a pdf file (attached to the answers to referee Alexander Cede).

Comment #1: The algorithm includes several changes compared to the standard algorithm. I believe the paper would benefit from addressing the effect of each change on the retrieved slant and vertical columns.

Answer #1: Section 3 was thoroughly revised by including an estimate of the effect for each one of the listed improvements (6 slits, spectroscopic datasets, grating position, oxygen dimer, filters and AMFs). The updated text is reported further below:

Algorithm: "Compared to the standard algorithm, the new method brings several improvements, *which are described and quantified further below:*

1. while the former makes use of [...] and minimise the measurement noise.

Although this first optimisation has little effect on measurement noise when the grating position is already optimally chosen (cf. step 3), the use of six slits instead of only five interestingly turns out to be beneficial in reducing the Brewer sensitivity to slight wavelength shifts (reduction of about 30%, for Brewer #066) and to the Ring effect (Grainger and Ring, 1962) (about -80%, calculated on unpolarised irradiances), which impacts diffuse light during zenith sky measurements. This occurs because the influence of the irradiance registered through the second slit, corresponding to a wavelength of about 431.6 nm, very close to a deep Fraunhofer line, is reduced. A different use of the additional degree of freedom is proposed in Sect.7.1;

2. the spectroscopic dataset [...] are filtered by the slit function.

The update of the cross section datasets represents a major improvement in the algorithm. Indeed, from previous modelling results (Diémoz et al., 2013) the retrieval using the weighting coefficients by Kerr (1989) leads to large overestimations, even more than 50%. On the other hand, the I0-effect is generally expected to be negligible for NO_2 retrievals, since nitrogen dioxide is a weak absorber, unless very large slant *column densities are to be measured*;

3. an optimal position of the grating [...] The resulting grating position depends on both the spectral dispersion and resolution of a specific instrument.

For Brewer #066, the selected position (microstep 1012) is close to the default position (1000, corresponding to a shift of about 0.13 nm). This optimisation minimises the interference by water vapour (0.009 DU VCD for a saturated atmosphere, compared to 0.02 DU at the standard position) while keeping almost unaltered the sensitivity to other variables. However, the advantages of a different grating position could be much more evident on other instruments with different dispersion properties. Several European MKIV Brewers were examined and some of them show a wavelength sensitivity as large as -0.20 DU/microstep at the standard grating position (more than double compared to Brewer #066). For those instruments, the choice of a different wavelength set is likely to substantially improve the Brewer stability;

4. the residual interference by the oxygen dimer [...] *The contribution of the O_2-O_2 correction is usually of the order of 0.02 DU on VCDs for Izaña*;

5. *since the spectral transmission of the "neutral" density filters is actually not constant and generally varies, as a function of wavelength, with a different pattern compared to any other factor taken into account in the algorithm, the linear combination is not able to remove this effect. Therefore, a correction factor which depends on the selected filter must be added to the linear combination to compensate the filter interference. As shown by Diémoz et al. (2013), systematic errors as large as 0.2 DU (for Brewer #066 when the thickest filters are used, and even larger for different Brewers) may be introduced in the retrieved VCDs if the filter correction is neglected*;

6. the air mass [...] were employed for the purpose. *The resulting polarised AMFs differ only by few percents at SZA=90° from the NDACC recommended AMFs for Izaña (Van Roozendael and Hendrick, 2012), i.e. 2% and -3% for the parallel and perpendicular observation geometries, respectively (Fig.1). Differences become larger (e.g., 30% at*

SZA=95°) when zenith angles beyond 90° are considered and are due to use of both different atmospheric profiles and radiative transfer models (the polarised AMFs were obtained by a full-spherical solver, the NDACC AMFs with a pseudo-spherical one). Interestingly, the AMFs calculated for the parallel polarisation are generally larger than those in the perpendicular polarisation, as a consequence of multiple scattering, which affects more the former than the latter. It must be highlighted, on the other hand, that the standard Brewer algorithm incorrectly uses direct sun AMFs for all geometries of observation, which results in overestimations of about 10% for SZA$< 80°$ and about 60% at twilight."

Comment #2: Could you apply your algorithm to the 5 standard wavelength positions?

Answer #2: The algorithm can be applied to any wavelength set. However, it should be noticed that the standard wavelength positions are 6, not 5, since irradiances through all six slits are normally recorded. This is specified in the revised manuscript in the following sections:

3 Algorithm: "while the former makes use of *a subset of all recorded data, i.e. the spectral irradiances at only 5 wavelengths* [...] the new algorithm includes the measurements that are routinely performed (and *saved by every Brewer in the data files*) through all six slits".

7.2 Reprocessing of historical datasets: *"Every Brewer stores all raw data in its files (B-files). Moreover, the standard routines already measure the solar irradiance through all six slits, although data at only five wavelengths are traditionally processed by the retrieval algorithm. This makes it possible, in principle, to apply the new algorithm to* *past time series. [...]"*

8 Conclusions: "Since every Brewer stores all raw data *(at all six slits)* in its files [...]".

Comment #3: Can your algorithm be modified so the research groups without any radiative transfer calculation experience can use it?

Answer #3: In principle, the new algorithm can be easily implemented in the standard Brewer operating software. A new section was written to explain the necessary steps in detail:

7.3 Updates to the Brewer operational software: *"Once the performances of the new algorithm have been extensively studied, the Brewer operational software may be updated with few efforts and shared with the Brewer users community. This will let all research groups benefit of the improvements, even those without any radiative calculation experience. The weighting coefficients, which are hard-coded into the software at present, should instead be read from an external file, which can differ among instruments and be provided by calibration facilities or other research groups. The same modification should be applied to take into account the spectral sensitivity of the attenuation filters, as the software already does when calculating the aerosol optical depth. As for the grating position and the differential cross section, the Brewer software already allows to adjust their values in the configuration files. Unpolarised zenith sky AMFs can be easily calculated using the software provided by NDACC (Van Roozendael and Hendrick, 2012) for the selected measuring site and stored in an external file, from which the Brewer software should be instructed to read from. The error on AMF resulting from neglecting the polarisation was found to be low at twilight (last point of Sect.3). Finally, the oxygen dimer interference was found to be*

unimportant and may be neglected to a first approximation".

Comment #4: How different are the retrieved columns if NDACC recommended AMF are used?

Answer #4: Differences are in the order of -3–2%, as reported in Sect. 3 of the revised manuscript (cf. answer #1 of the present document, point 6 of the list). The supplementary materials include a graph of several AMFs in different geometries (answer #31).

Comment #5: Accuracy of the retrieval can be better demonstrated using climatological data reported by Gil et al., 2008. In general, more consistent comparison should be shown. Since all three geometries are analyzed all three should be compared (if possible) to the NDACC retrievals. It is also interesting to note that the NDACC reference instrument chosen for the intercomparison did not operate at the optimal for the intercomparison schedule.

Answer #5: All available instruments operating in Izaña were used in the revised manuscript for comparison purposes. For this reason, Sects. 2 and 5 were remarkably updated as follows (and the PIs of the two NDACC instruments, M. Navarro-Comas and F. Hase, were added as co-authors of the final manuscript).

2 Measurement site and instruments: *"The measurements discussed in the present paper were performed at the Izaña Atmospheric Research Center, Tenerife, Canary Islands (28.31° N, 16.50° W, 2400 m a.s.l.) during an ad-hoc field measurement campaign in September and October 2012. The site, which is described in more details by Gil et al. (2008), was chosen to achieve the maximum atmospheric stability* *necessary for an accurate calibration. On that occasion, Brewer #066 was temporarily moved to the Izaña observatory from its original location, Aosta, Italy, where it has been regularly operating since 2007 (Diémoz et al., 2007). Co-located instruments, associated to the Network for the Detection of Atmospheric Composition Change (NDACC), were used as references for comparison purposes and are thus described further below along with the Brewer.*

2.1 MKIV Brewer spectrophotometer

The MKIV Brewer spectrophotometer [...]

2.2 Fourier Transform Infrared Spectrometer

Since January 2005, a Bruker IFS 125 HR Fourier Transform Infrared Spectrometer (FTIR) owned by the Institute for Meteorology and Climate Research (IMK) has been measuring at the Izaña observatory. The FTIR is operated in solar absorption geometry. The maximum optical path difference achievable is 250 cm corresponding to a spectral resolution of 0.0035 cm^{-1}*. Normally, a resolution of 0.005 cm*$^{-1}$ *is chosen. The spectrometer is equipped with two detectors, an InSb and a photovoltaic MCT. The spectral range covered is 650 to 5000 cm*$^{-1}$ *and the NDACC optical filter set is used. The precision is estimated to 2% for most species. More details are provided by Schneider et al. (2005).*

2.3 UV-visible spectrometer

A new MAX-DOAS spectrometer (RASAS-II) has been operating by the Instituto Nacional de Technica Aerospacial (INTA) since 2011. The instrument collects the scattered radiation from the sky in the 415–530 nm spectral range. It is based on a Shamrok SR-163i spectrograph and a 1024×255 pixels DU420A-BU Andor Idus CCD camera. Light enters the spectrograph through a fused silica round-to-line fibre bundle. The fibre end width is 100 μ*m. The diffraction grating is holographic with 1200 grooves mm*$^{-1}$ *and blazed at 300 nm. The linear dispersion is 0.11 nm pixel*$^{-1}$*. The FWHM of the spectrograph in the selected spectral window ranges between 0.52 and 0.58 nm. The spectrograph and detector are housed in a thermostated hermetic container keeping the spectrograph at a constant temperature, thus maintaining the alignment of the spectra with time.*

The RASAS II instrument uses the Differential Optical Absorption Spectrometry (DOAS) technique and air mass factors from radiative transfer code to retrieve the NO_2 *column. Whereas the instrument automatically takes spectra from 45° solar zenith angle (SZA) to twilight, measurements at low SZAs are considered of poor quality since the accuracy is strongly dependent on the signal to noise ratio and on the atmospheric conditions (aerosol optical depth). Only in extremely clear and stable conditions the data at low SZAs be used. On the contrary, under these favourable weather conditions, at twilight the technique is reliable and the errors are low. A detailed description of RASAS-II can be found in Puentedura et al. (2012)".*

5 Results: *"Estimates of* NO_2 *column densities using the new algorithm will be described in this section and compared to nearly-simultaneous (*$\Delta t = 10$ *min) data obtained with co-located reference instrumentation associated to NDACC. The comparisons are performed under the optimal conditions of each instrument: direct sun measurements from the Brewer will be examined with reference to those provided by the FTIR, while zenith sky estimates at twilight from the Brewer will be compared to the RASAS retrievals.*

5.1 Direct sun measurements

A subset of the data series recorded in the direct sun geometry during the Izaña campaign is displayed, as an example, in Fig. 3. The results with the new algorithm are representative of stratospheric values of 0.1 DU typically reported in the literature (e.g., Brühl and Crutzen, 1993; Gil et al., 2008; Herman et al., 2009), as expected from the clean site of Izaña. Furthermore, although the signal from the Brewer is very noisy, the estimates with the new algorithm also agree with the FTIR data on average. The mean bias between the two sets is -0.012 DU (the Brewer slightly underestimating), which is far below the Brewer uncertainty (Sect. 6), and the root mean square difference is 0.06 DU. Figure 4 displays an histogram of the differences between the two instruments together with an equivalent normal probability distribution function. Normality is verified through the Kolmogorov-Smirnov test (p-value = 0.92, calculated under the null hypothesis that the samples are drawn from a normal distribution). The Brewer exhibits some negative VCDs, mostly due to random measurement noise and, to a minor extent, to thin clouds which were not filtered by the cloudscreening algorithm. The good comparison with the FTIR on average proves that the negative retrievals are counterbalanced by high positive random errors and the overall bias remains low.

Measurements from the Brewer at the standard set of wavelengths have been processed as well with the standard algorithm (after calculating the corresponding extraterrestrial constant). The retrieval by the standard algorithm remarkably overestimates, with values about 100 % higher than the new algorithm. These differences are in good agreement with previous model studies (Diémoz et al., 2013).

5.2 Zenith sky measurements

Figure 5 shows the scatterplot between the estimates by the Brewer operating in the

perpendicular polarisation and the RASAS-II spectrometer. This zenith sky comparison is performed in term of slant column densities (SCDs) to overcome any issues related to different zenith sky AMF calculations between algorithms. Also, both instruments use the same spectroscopic datasets and effective temperatures to retrieve NO_2. *Although correlation between the two series is evident (Pearson's correlation coefficient* $\rho = 0.98$*;* $R^2 = 0.95$*; slope*$= 0.99$*), a nearly constant offset of -0.2 DU (distance between the regression line and the* $y = x$ *line) can be noticed between the series. This underestimation by the Brewer, corresponding to a mean bias in the vertical column of -0.015 DU over the measured range, is slighlty lower than the estimated uncertainty of the Brewer for zenith sky measurements (Sect. 6.3).*

The comparison between RASAS-II retrievals and zenith sky measurements in parallel polarisation by the Brewer is shown in Fig. 6. This time, both the correlation ($\rho = 0.87$*;* $R^2 = 0.76$*) and the fit parameters (slope*$= 0.85$*; intercept*$= 0.7$ *DU) are worse compared to the perpendicular polarisation. The corresponding mean bias in the vertical column is 0.013 DU over the measurement range.*

In principle, the discrepancies between the two instruments could be due to inaccuracies in determining the Brewer ETCs in both polarisations (notably, the constant offset in the perpendicular polarisation dataset). However, no better results throughout the full range of AMFs were found by perturbing the values of the calibration constants, which degrades the comparison at either low or high AMFs (not shown). The results of the comparison certainly require more investigations and further work, e.g. a longer intercomparison campaign. However, one of the likely reasons may be already found in the Ring effect, which would explain the slightly larger effect on parallel polarisation compared to the perpendicular one, as found by Barton (2007). More details are provided in Sect 6.3.

Finally, it must be noted that the root mean square (RMS) residual of the fit between the two datasets (0.96 DU for SCDs in perpendicular polarisation and 3.3 DU for parallel polarisation) can be further decreased by averaging a larger number of the *samples for each measurement"*.

Please, refer to the supplementary material for the figures mentioned in the text. The abstract and conclusions were also updated as follows:

Abstract: "*the results in the direct sun and zenith sky geometries were compared* to those obtained *by two reference instruments from* the Network for the Detection of Atmospheric Composition Change (NDACC): *a Fourier Transform Infrared Radiometer (FTIR) and an advanced visible spectrograph (RASAS-II) based on the Differential Optical Absorption Spectrometry (DOAS) technique*".

8 Conclusions: "*Comparisons of the Brewer measurements to two reference NDACC radiometers were performed, with generally good correlations and mean biases in the vertical column amounts of -0.012, -0.015 and 0.013 DU for direct sun and twilight zenith sky at perpendicular and parallel polarisations, respectively, over the corresponding measurement ranges"*.

Comment #6: Error analysis is done for the "best case" scenario: direct sun measurements over the unpolluted high altitude site assuming "constant" atmospheric conditions. It would be very beneficial to estimate the error for more polluted conditions and also for zenith sky measurements.

Answer #6: According to the referee's suggestion, Sect. 6 was thoroughly revised and extended. The updated text (reported further below) includes an uncertainty estimate for the polluted case and zenith sky measurements.

6 Uncertainty budget: *"The uncertainty estimate in Brewer measurements is a complex task owing to the large number of the involved parameters and their reciprocal correlations. Furthermore, an analytic assessment of the uncertainty is not feasible and the influence of the various factors on the retrieved NO$_2$ is expected to be non-linear. A Monte Carlo method (MCM) approach (BIPM et al., 2008) was therefore adopted.*

In this section, the Brewer uncertainty will be discussed for three different cases. In the first scenario, the relatively simple case of direct sun measurements in a pristine site with similar characteristics as the Izaña observatory will be discussed. In the second simulation, the Brewer is assumed to be initially calibrated at a pristine site, as in case 1, but then moved to a more polluted environment for operation. Finally, in the third part, the uncertainty of zenith sky measurements will be discussed for the same environmental conditions as in case 1. It must be noticed that case 1 and 3 must be analysed independently, since not only the uncertainty on the AMFs, but also the uncertainty on slant column densities may potentially differ between both geometries, e.g. due to the different light intensity and used filters.

6.1 Case 1: direct sun measurements at a pristine site

The first scenario assumes that the Brewer operates at the same high-altitude site (only stratospheric NO$_2$ is considered, with VCD=0.1 DU) where the Langley plot has been performed and that the atmospheric conditions remain constant compared to the calibration period. Several sources of uncertainties, both in the calibration and the measurement phase, are considered taking into account the instrumental characteristics of Brewer #066:

1. random noise was artificially added [...]

The latter can be further reduced by increasing the number of samples (which were decreased for the Langley plot, as described in Sect. 4).

Finally, the influence of the filters uncertainty on direct sun measurements is generally low, since Brewer #066 employs only few and weak density filters in this observation geometry at the Izaña conditions.

6.2 Case 2: direct sun measurements at a polluted site

The second case is representative of a Brewer spectrophotometer accurately calibrated at a high-altitude site without tropospheric NO_2 *(VCD=0.1 DU) and then operated at a polluted site. The calibration was simulated with the same criteria as in case 1. Conversely, the measurement phase presents some relevant differences:*

1. the standard atmosphere (Anderson et al., 1986) was modified by including a 5-km-thick polluted layer above ground NO_2 *concentration* $4 \cdot 10^{10}$ *mol* cm^{-2}*), thus increasing to 1 DU the total nitrogen dioxide VCD;*

2. the NO_2 *effective height used in the calculations was decreased to 10 km (the actual height is not influential for direct sun retrievals) with an uncertainty of 5 km;*

3. the NO_2 *effective temperature was increased to 260 K and the corresponding uncertainty was set to 20 K;*

4. the altitude and pressure of the measurement site were set to 570 m a.s.l. and 950 hPa, respectively, i.e. the conditions of the original location of Brewer #066 in Aosta, Italy. The O_2*-*O_2 *correction was updated correspondingly.*

Figure 8 shows the uncertainty estimated for case 2. Compared to case 1, the overall absolute uncertainty increases (0.14–0.27 DU, depending on the SZA), but the relative uncertainty, i.e. the ratio between total uncertainty and the NO_2 *VCD, remarkably decreases (to 14%–26%), revealing that the quality of Brewer estimates in direct sun geometry is higher for larger* NO_2 *columns. Moreover, it must be noticed that the contribution of the cross section uncertainty to the overall uncertainty increases for case 2 compared to case 1, as also expected from the propagation of uncertainty in Eq. 1 (the cross section uncertainty being proportional to the total* NO_2 *content in the atmosphere). Finally, it is important to mention that if the Brewer were calibrated at a polluted site, the main assumption of the constant atmospheric conditions needed by the Langley technique would not be met. This case is beyond the scope of the paper and will not be discussed here.*

6.3 Case 3: zenith sky measurements at a pristine site

In the last scenario, zenith sky measurements are simulated in the same conditions as in case 1 (VCD=0.1 DU). In this third case, however,

1. the measured irradiances are different from case 1, as also their dependence on the SZA, due to the different observation geometry and set of used filters. Indeed, in direct sun measurements, a thick filter is placed before the other neutral density filters, whereas a thinner polarising filter is used for the zenith sky geometry;

2. the zenith sky AMFs are much more impacted by the atmospheric profiles than the direct sun AMFs. A sensitivity study was performed using several atmospheric profiles and aerosol loads. The resulting AMF uncertainty ranges from about 2% at SZA=60° to 8% at SZA=20°. At twilight, the AMF uncertainty is 7%, in accordance with the results by Gil et al. (2008).

The zenith sky uncertainty is depicted in Figs. 9 and 10 for the parallel and perpendicular polarisations, respectively. A notable contribution is given by the filter uncertainty. Indeed, thicker filters, which are characterised by higher uncertainty, are used at low SZAs for zenith sky estimates. This impacts not only measurements, but also the calibration.

The analysis, however, does not take into account some likely major contributors to the zenith sky uncertainty, which are difficult to quantify. First, diffuse irradiance is impacted by the Ring effect, which even state-of-the-art radiative transfer models cannot accurately reproduce at present by taking polarisation into account at the same time. A previous study by Barton (2007) reported considerable overestimations by the Brewer (up to 800%) due to the Ring effect, especially using parallel polarisation, but the author himself admits that those results could have been compromised by unrealistic simulations by the used radiative transfer model. In the present work, simulations of unpolarised zenith sky irradiances with and without taking into account RRS gave rise to VCD differences of 0.02–0.06 DU, with a marked SZA dependence. However, the effect using polarised irradiances could be different.

A second contributing factor to the uncertainty of zenith sky estimates is the unknown efficiency of the polarising filter, likely lower than 100%. As a consequence, photons from the zenith polarisation could be detected by the Brewer even when the instrument is supposed to measure in the parallel plane (more light is expected from the perpendicular polarisation at twilight), thus representing a relevant source of straylight. Both issues should be investigated in more detail in future works.

Finally, it should be kept in mind that when zenith sky SCDs by the Brewer and RASAS are compared, one should not take into account the uncertainty contribution from the AMFs (only employed for SCD to VCD conversion), cross sections and NO_2 *effective temperature (since the same set of cross sections is used for both instruments). The resulting SCD uncertainty at twilight decreases then to 0.25 DU for both polarisations."*

Comment #7: p. 7370, line 8: 'but also to reprocess with higher accuracy the long-term raw datasets recorded at the existing measuring stations.' It is unclear how this can be done since the original algorithm uses five "standard" wavelengths versus proposed six wavelengths derived through an optimization process accounting for instrumental and atmospheric parameters (point 3, page

7372). Does the additional, 6th, wavelength really provide an additional degree of freedom compared to the standard algorithm?

Answer #7: Please, refer to answers #1 (point 1), #2 and #3. The new Sect. 7.2 also describes the necessary steps in order to reprocess historical datasets:

7.2 Reprocessing of historical datasets: *"Every Brewer stores all raw data in its files (B-files). Moreover, the standard routines already measure the solar irradiance through all six slits, although data at only five wavelengths are traditionally processed by the retrieval algorithm. This makes it possible, in principle, to apply the new algorithm to past time series. However, some fundamental steps are required prior to reprocessing historical datasets:*

1. in order to recalculate the specific set of weighting factors for each instrument, the dispersion function must be well characterised. To this purpose, the traditional Brewer dispersion test, based on the identification of several emission lines (e.g., from mercury, cadmium or zinc lamps), has been updated to reprocess the lines in the visible range and is now accessible to the whole Brewer users community as a software update. As an alternative, the diffraction grating law can be applied to calculate the dispersion function in the visible from the dispersion in the UV (normally measured during ozone calibration campaigns). Although the grating position at which the historical series has been measured may not be optimal for a specific instrument, the new algorithm can be applied anyway to the standard wavelengths used for the retrieval. Additionally, it provides an estimate of the uncertainty due to non-optimised settings. Furthermore, tests using a unique set of weightings for several Brewers are currently being performed to assess the sensitivity to different dispersion functions and wavelength settings;

2. the spectral attenuation of the filters must be well known, especially when using high attenuation filters. Based on a preliminary analysis, each single instrument manifests *different properties and must be independently characterised. A new routine has been developed to assess the spectral attenuation of each filter in the visible range using the internal lamp. However, since noise is considerable when using the thickest filters, a great number of tests should be scheduled. An alternative approach is to statistically analyse the long-term series and retrieve the effect of filters by forcing the continuity of the* NO_2 *retrievals between contiguous measurements with different filters;*

3. the ETC should be determined. If a Langley campaign at a high-altitude site or calibration transfer from a travelling standard are not feasible, statistical methods such as the Minimum-Amount Langley Extrapolation or the Bootstrap Method (e.g., Cede et al., 2006; Herman et al., 2009) are available to provide the necessary extraterrestrial calibration constant. Unfortunately, in all cases, calibration drifts can occur after some time. To investigate the Brewer stability, the following techniques are suggested: measurements obtained with the internal standard lamp as a source, instead of the sun, may be used to track the ETC (standard lamp test); statistical techniques to determine the ETC could be applied on several time portions of the series and the results could be compared; the analysis of the wavelength shifts, relative to the Fraunhofer solar structure (Slaper et al., 1995), in the UV spectra measured by a Brewer could provide very valuable information about any wavelength instabilities affecting the retrieval. Also, a detailed logbook of the instrument, constantly updated by the operator, is essential to keep track of any maintenance or replacements. In the event that some discontinuities are identified, a piecewise calibration may be applied to different portions of the series.”

Comment #8: p. 7372, point 2: Io-correction has a small effect on the NO2 column itself

Answer #8: The referee’s remark was included in the updated text. Please, refer to answer #1 (point 2).

Comment #9: p. 7372, point 3: How different is the optimized set of wavelengths for Brewer #066 compared to the standard wavelengths. Have you tried to apply your algorithm to the 5 standard wavelengths?

Answer #9: Table 2 (supplementary material) was updated to show both sets of wavelengths. Please, refer also to answer #2.

Comment #10: p. 7372, point 4: Do you ignore aerosol and cloud effect on scattering in your O2O2 RT modeling?

Answer #10: The O_2-O_2 correction was obtained in the case of clear sky, with a “standard” aerosol profile. Section 3, point 4, was updated as follows: “the residual interference by the oxygen dimer has been corrected through the use of *the SCIATRAN* radiative transfer model (Rozanov et al., 2014) taking into account the atmospheric pressure at the measurement site *in case of clear sky and using the standard aerosol profile by Anderson et al. (1986)*”.

Comment #11: p. 7373, point 5: please explain how it is different from the “spectrally-flat factors” used in the standard algorithm.

Answer #11: Point 5 was rewritten as follows to explain in more detail the effect of the filters: *“since the spectral transmission of the “neutral” density filters is actually not constant and generally varies, as a function of wavelength, with a different pattern compared to any other factor taken into account in the algorithm, the linear combination is not able to remove this effect. Therefore, a correction factor which depends on the selected filter must be added to the linear combination to compensate the filter interference. As shown by Diémoz et al. (2013), systematic errors as large as*

0.2 DU (for Brewer #066 when the thickest filters are used, and even larger for different Brewers) may be introduced in the retrieved VCDs if the filter correction is neglected".

Comment #12: p. 7373. Table 1 lists the new and standard cross sections used. Please specify temperature of the standard cross sections. What effect on the SCD do they have compared to the standard algorithm? I think you should add information on the updated cross sections as point 7 to "Compared to the standard algorithm, the new method brings several improvements:"

Answer #12: Table 1 was modified according to the referee's suggestion (cf. supplementary material). The effect of the new cross sections on column densities has been included in Sect. "Algorithm" (cf. answer #1, point 2).

Comment #13: p. 7374, line 4: What does the "the same set of data" mean? Did you rotate the grating to a standard position to measure light intensity at the 5 standard wavelengths and then to the optimized position to measure 6 different wavelengths?

Answer #13: Two sets of measurements were indeed obtained by turning the grating in both the standard and new positions, as the referee noticed. A sentence was added to Sect. 4, "Calibration campaign", to avoid misunderstanding: *"The Brewer was operated alternately with the grating at the standard (1000) and optimised (1012) position to allow comparison between the standard and improved algorithms. Since measurements must be performed in different observation geometries and grating positions,* the number of samples to average for each measurement were reduced [...]".

Also, the caption of Fig. 3 was modified accordingly: "A subset of the NO_2 vertical column densities (VCDs) retrieved in the direct sun geometry during the Izaña calibration

campaign. *The Brewer data obtained with the grating at the standard position were analysed with the standard algorithm, while the data at the optimised grating position were processed with the new method. FTIR measurements are represented as green squares.*".

Comment #14: p. 7374, line 26: Could you please explain how atmospheric turbulence impacts the accuracy of the NO2 slant column measurements at AMF $<$ 1.5 especially at the site located at 2400 m with mainly stratospheric NO2?

Answer #14: The sentence was modified as follows: "Lower AMFs are not considered because the rate of change of the airmass and the NO_2 absorption are small, *and changing atmospheric conditions could remarkably affect the regression (Harrison and Michalsky, 1994)*".

Comment #15: I suggest moving discussion of the accuracy of the proposed algorithm results from Section 5.1 into 5.3, and focus solely on the intercomparison between SCD derived from the two algorithms. I think it will be very valuable to understand which of the improvements has the largest impact on the SCD.

Answer #15: The "Results" section was mainly rewritten (cf. answer #5). The impact of the improvements has been described in the "Algorithm" section (cf. answer #1).

Comment #16: p. 7376. Which of the three instruments described by Gil et al., 2008 was used for intercomparison? Two of them operate at SZA between 45o and 94o. Is it possible to compare VCD from the Brewer perpendicular polarization zenith measurements with the NDACC VCD measurements at all SZA not just twilight?

Answer #16: All used instruments are described in Sect. 2 in more detail in the revised paper (cf. answer #5). As explained in Sect. 2.3, *"Whereas the instrument automatically takes spectra from 45° solar zenith angle (SZA) to twilight, measurements at low SZAs are considered of poor quality since the accuracy is strongly dependent on the signal to noise ratio and on the atmospheric conditions (aerosol optical depth). Only in extremely clear and stable conditions the data at low SZAs be used. On the contrary, under these favourable weather conditions, at twilight the technique is reliable and the errors are low"*. Therefore, only twilight data from RASAS-II are delivered by Instituto Nacional de Technica Aerospacial (INTA).

Comment #17: p. 7375, line 11: Based on Figure 1 a significant number of measurements are around 0 molecules/cm2 at small SZA. This might be an indication of calibration issues leading to underestimation of SCD.

Answer #17: Based on the uncertainty analysis, the main reason of measurements around 0 molecules cm^{-2} is random noise (and wavelength errors). The new Fig. 4 clearly shows that low values by the Brewer are counterbalanced by high values (Sect. 5.1, cf. answer #5). Systematic errors (e.g., calibration issues), if any, are much lower than random errors.

Comment #18: p. 7368, line 24: 'thus impacting on' remove 'on'

Answer #18: The sentence was modified according to the referee's suggestion.

Comment #19: p. 7369, line 7: Please provide a more direct reference than

http://www.woudc.org/ to the information about the number of Brewers operated in NO2 measurement mode.

Answer #19: The sentence was modified as follows: "Among them, according to the *metadata archive of the* World Ozone and Ultraviolet radiation Data Center (WOUDC, *http://woudc.org/data/MetaQuery/metaquery_e.cfm*), more than 60 MKIV Brewer spectrophotometers have been put in operation [...]".

Comment #20: p. 7369, line 24. Please explain what you mean by "no on-site service exists to track the NO2 calibration of the Brewer instruments operating worldwide". Do you mean radiometric/wavelength calibration at the measurement site or another instrument colocated with each Brewer?

Answer #20: The sentence was rewritten as follows: "Finally, no on-site service *with reference travelling standards (as available for ozone calibrations)* exists to track the NO_2 *radiometric and wavelength* calibration of the Brewer instruments operating worldwide".

Comment #21: p. 7377. The paper focuses on the NO2 algorithm from the Brewer. I think the only reason to include the discussion of the supplementary linear polarization and O2O2 products if you use them for cloud and aerosol screening in you NO2 algorithm. If this is not the case I would remove section 5.4 from the paper.

Answer #21: The section was removed in the updated manuscript as suggested by the referee.

Comment #22: p. 7379, lines 6-7: Replace "surrounding conditions do not relevantly changes compared" for "atmospheric conditions remain constant compared"

Answer #22: The sentence was modified according to the referee's suggestion.

Comment #23: p. 7380, line 13: "aerosol Angstrom exponent" is mentioned for the first time here. Please explain how it is used in your algorithm earlier in the paper.

Answer #23: The manuscript was updated as follows:

3 Algorithm: "[...] and minimises the influence by the Rayleigh scattering, ozone absorption, aerosol extinction *(assuming that the aerosol optical depth is approximately linear with wavelength in the measurement range)* and spectrally-flat factors [...]".

6.1 Case 1: direct sun measurements at a pristine site: "the effect of the aerosol Ångström exponent, *representative of the spectral curvature of the aerosol optical depth*, was assessed [...]".

Comment #24: p. 7381, line 7: Could you please explain why do you expect "the relative uncertainty of the NO2 retrievals to drop for higher VCDs of nitrogen dioxide (i.e., more polluted conditions)." Under more polluted conditions your main assumption of the constant atmospheric conditions compared to calibration period is not met. In addition, the Langley calibration itself is much harder to do correctly. NO2 effective temperature over the polluted sites can be between

260 and 280K (in summer) compared to 220 ± 20K assumed in the analysis. Effect of the NO2 effective height on AMF also will be more significant at SZA $>$ 80°.

Answer #24: The uncertainty estimation of direct sun measurements at a polluted site after calibration at a pristine site is discussed in Sect. 6.2 in the revised manuscript (cf. answer #6). Calibrations at polluted sites are beyond the scope of the paper and are not discussed. Finally, direct sun measurements at SZA $> 80°$ are not possible with Brewer spectrophotometers. This is stressed in Sect. 4: "Higher AMFs are avoided due to possible shadows by the quartz window border in the field of view *(direct sun)* and steep variations of NO_2 [...]" and Sect. 6.1: "The standard deviation of all NO_2 retrievals was then taken as the standard (combined) uncertainty of the measurement as a function of the solar zenith angle. *The latter was varied within the same range of measurement as in the campaign (78° being the maximum SZA due to shadows by the quartz window border in the direct sun field of view).*".

Comment #25: It is also important to mention that direct sun measurements are not impacted by Ring effect and the AMF calculation is very simple at SZA $<$ 80° and are not impacted much by the NO2 profile.

Answer #25: It is has been stressed several times throughout the revised paper that the Ring effect impacts only diffuse radiances:

3 Algorithm (point 1): *"and to the Ring effect (Grainger and Ring, 1962) (about -80%, calculated on unpolarised irradiances), which impacts diffuse light during zenith sky measurements [...]".*

3 Algorithm (point 3): "the Ring effect *(only affecting zenith sky measurements)* [...]".

6.3 Case 3: zenith sky measurements at a pristine site: *"diffuse irradiance is impacted by the Ring effect [...]"*.

As for the direct sun AMF calculations, the following sentence was added to Sect. 6.1: *"The* NO_2 *profile is expected not to remarkably impact the direct sun AMF, whose calculation is very simple for SZAs*$< 80^{\circ}$*, being the secant of the SZA at the mean height of the absorber layer [...]"*.

Comment #26: Zenith sky measurements will have a larger total error, please give an estimate of it.

Answer #26: The new Sect. 6.3 is dedicated to the uncertainty estimation of zenith sky measurements. Please, refer to answer #6 for more details.

Comment #27: Table 1. Please include (estimate) temperatures for the cross sections used in "stan- dard" algorithm

Answer #27: Table 1 was modified according to the referee's suggestion. The revised table is shown in the supplementary material.

Comment #28: Table 2. Please include "standard" wavelengths

Answer #28: Table 2 was modified according to the referee's suggestion. The revised table is shown in the supplementary material.

Comment #29: Table 3. I recommend to remove Table 3

Answer #29: Table 3 was removed according to the referee's suggestion.

Comment #30: Figure 1. Please add 2012 to the graph. This graph will be more informative if diurnal variability for selected days is shown (VCD as a function of SZA over the course of the day) where one can see retrieved changes for a single day as a function of SZA. The horizontal lines are also confusing. It is stated that they are climatological morning and afternoon results. What SZA are they representative of? You also should add spread of the climatological data.

Answer #30: Figure 1 (supplementary material) was redrawn according to the referee's suggestions, removing the climatological results and including FTIR data. A new figure (Fig. 2) was introduced in the paper, based on referee's suggestion, which shows the diurnal evolution of NO_2. The text in Sect. 4 was updated as follows: *"As an example, Fig. 2 shows the daily* NO_2 *evolution of direct sun measurements at Izaña on a selected day (269)"*.

Comment #31: Figure 2. I find this figure somewhat confusing [...] A figure with AMF for different geometries (zenith 2 polarizations, NDACC zenith recommended and direct sun) on the Y-axis and SZA on the X-axis will be very valuable.

Answer #31: Figure 2 was removed from the paper. Zenith sky measurements are compared to the reference instrument in detail in Figs. 5 and 6 (supplementary material) and Sect. 5.2. A new figure with AMFs for different geometries (Fig. 1 of supplementary materials) was included in the revised paper.

Comment #32: Figure 3. Please add the results of the linear regression fit: slope, intercept and R2.

Answer #32: The results of the fit were added to the main text (cf. answer #5) and to the captions of the figures (cf. supplementary material).

Comment #33: I would remove Figures 4 and 5 unless you are using them to show cloud screening algorithm for NO2.

Answer #33: The figures were removed according to the referee's suggestion.

Interactive comment on Atmos. Meas. Tech. Discuss., 7, 7367, 2014.