**Atmospheric
Measurement
Techniques**
Discussions

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

H. Diémoz et al.

h.diemoz@arpa.vda.it

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The authors are very grateful to Dr. Alexander Cede 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. A supplement with updated tables, figures and additional references is annexed as a pdf file.

Comment #1: How does the uncertainty change between using the optimized

wavelengths as in Brewer #66 and the standard wavelengths as in all the other MKIV Brewers?

Answer #1: This information was included in the manuscript (section "Algorithm"):

Algorithm: "3. ... 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".

Comment #2: On the other hand I suggest removing section 5.4 (O2O2 columns and degree of polarization from zenith sky data). These "supplementary products" are very interesting and deserve their own paper, but do not really fit into this manuscript.

Answer #2: The section has been removed as suggested, as well as all references to the "additional products" in the manuscript.

Comment #3: Is the algorithm suggested in the paper the best choice? [...] the weights chosen in this work do not minimize the effect of wavelength shift [...] Is it possible to include the wavelength shift in the weights, i.e. requiring the weighted sum over the dl0/dlambda to be zero? Is it possible that a spectral fitting algorithm, where several parameters (including the NO2 slant column and the wavelength shift) are retrieved simultaneously from the data be more suitable? I do not expect the authors to develop other algorithms for comparison, but these questions should be addressed.

Answer #3: The manuscript was expanded and a new section "Discussion" was added. Sensitivity to wavelength misalignments and possible solutions were described in the following subsection:

7.1 Sensitivity to wavelength: *"In a Brewer spectrophotometer, the wavelength scale is adjusted with reference to the line emission spectrum of a mercury lamp. The test gives the position of the line (usually, at about 296 or 302 nm) to the precision of about 0.1 steps. Some factors, however, may degrade the instrumental wavelength alignment. Temperature changes inside the monochromator, for example, can affect the positioning to an extent of about 0.3 steps K^{-1}. Also large relocations of the grating, e.g. due to scanning routines or switch of the diffraction order of the grating from ozone to nitrogen dioxide measurements, can slightly misplace the wavelength scale. Moreover, the accuracy – and thus, the uncertainty – is additionally determined by errors on the dispersion function and changes on the optical axes, including lamp reference alignments and intensity of the lamp (relative intensity of multiplet lines).*

The uncertainty analysis in the present paper clearly proves that an optimal choice of the grating position is not sufficient to remove the Brewer sensitivity to wavelength misalignments and to reach the required accuracy. Indeed, the wavelength uncertainty remains one major contributor to the overall measurement uncertainty and more

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efforts must be spent in the future to solve the issue. As a step forward, an alternative and possibly more effective approach consists in including the wavelength shift in the algorithm, such as in Kerr (2002) and Cede et al. (2006). One degree of freedom can be reserved to an additional vector, the wavelength derivative of the solar spectrum. The obtained vector would not only absorb any small wavelength misalignment, thus improving the stability of the retrieval, but it would also provide an indication of the wavelength accuracy of the instrument. This would be an essential quality parameter in the reprocessing of historical datasets".

Comment #4: Line 202 states that "Although the discrepancies are very low and far below the uncertainties of both instruments". This is not totally obvious to me. Section 6 is an excellent analysis of the uncertainty in the vertical NO2 columns from direct sun measurements, but the data in section 5.3 are zenith sky measurements during twilight. I suggest that the uncertainty analysis in the manuscript should be done separately for the uncertainty in the slant columns and the uncertainty in the air mass factors. In this way it is valid for both, direct sun and zenith sky observations. If the values at the left side of figure 6 are the uncertainty of the slant columns and we assume an air mass factor of 10 or more for the twilight measurements, then the 0.02 DU discrepancy for the data in section 5.3 is not 'far below the uncertainties of both instruments'.

Answer #4: Unfortunately, uncertainties in direct sun and zenith sky geometries must be assessed independently, since not only the uncertainty on the AMFs, but also the uncertainty on slant columns densities may potentially differ, e.g. due to the different light intensity and used filters in both geometries. Therefore, the "Uncertainty" section has been expanded and zenith sky measurements have been included in the Monte Carlo analysis. The updated text is reported further below ("RASAS-II" refers to the NDACC UV-visible zenith sky spectrometer, cf. answers to referee #1):

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6. Uncertainty budget: *"... 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."*

[...]

6.3 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).

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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."

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Comment #5: I also suggest that the comparison to the NDACC instrument (section 5.3) should be done at the basis of the slant columns. This would reduce the possible reasons for differences, since point 2 (line 207) and point 4 (line 217) would not apply in that case.

Answer #5: The manuscript was updated as follows and Figs. 5–6 were drawn on the basis of the SCDs.

5 Results ... 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*

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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."

The old text related to the VCDs comparison ("Two groups of data can be identified [...] the spanned range of VCDs is rather short to allow an accurate comparison between both data series") was removed.

Comment #6: Data reprocessing I suggest extending the last paragraph of the paper by addressing the following questions: What steps are needed to reprocess the historic data of a MKIV Brewer?

Answer #6: A new subsection was added to the "Discussion" section to address the issues raised by the referee:

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*

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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 #7: How does the 'non-optimized' grating position affect the data quality?

Answer #7: Please, refer to answer #1.

Comment #8: Are individual weights for each Brewer needed?

Answer #8: This test is currently being performed on some selected European Brewers. As already reported, Sect. 7.2 was updated as follows:

7.2 Reprocessing of historical datasets: *"... 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".*

Comment #9: How well do the dispersion and the ND filter attenuation have to be known?

Answer #9: Please, refer to answers #1 and #6. Additionally, the "Algorithm" section was updated as follows to include the information asked by the referee:

3 Algorithm: *"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".*

Comment #10: The authors use the term 'air mass enhancement factor'. Isn't the standard way in literature just to call it 'air mass factor'?

Answer #10: Any recurrence of the longer form was replaced by "air mass factor", as suggested.

Comment #11: Line 7: 'with deviations of less than 0.02 DU', Add: 'in the vertical column amount from zenith sky data during twilight.' But a better way would be to analyze the uncertainty separately for slant columns and air mass factors as mentioned above.

Answer #11: The uncertainty was calculated separately for each observation geometry and the corresponding text has relevantly changed. Please, refer to answers #4 and #5.

Comment #12: Line 7: 'easily implementable generalization...'. It should be noted that this technique is only 'easily implementable' at very clean sites with basically no tropospheric NO2.

Answer #12: The sentence was rewritten as follows:"... an easily implementable *extension* of the standard Langley technique *for very clean sites without tropospheric NO$_2$* was developed...".

Comment #13: Line 10: 'drift of nitrogen dioxide' -> 'drift of stratospheric nitrogen dioxide'.

Answer #13: The sentence was updated according to the referee's suggestion.

Comment #14: Line 52: or the zenith sky -> or the sky.

Answer #14: The sentence was updated according to the referee's suggestion.

Comment #15: Line 88: 'If the weighting coefficients are properly chosen, the last sum is cancelled out' -> 'is minimized'. Only for a given set of values for the other parameters (the ones used in the determination of the weights) it cancels out.

Answer #15: The sentence was updated according to the referee's suggestion.

Comment #16: Line 107: if W is the slit function, then equation 2 should have W(lambda'-lambda). If instead what is meant is the filter function (the 'flipped' slit function) than the integral can go over W(lambda-lambda').

Answer #16: The formula was modified as suggested, i.e. W(lambda' - lambda).

Comment #17: Line 107: What a-priori value for X (NO2) is being used?

Answer #17: The sentence was rewritten as follows: "where X is an a priori value *of the absorber VCD (a value of 0.1 DU, typical of stratospheric columns at the measurement site (Brühl and Crutzen, 1993; Gil et al., 2008; Herman et al., 2009) was used in this work)...".*

Comment #18: Table 2: I assume the old coefficients were calculated for the standard NO2 grating position and the new weights with the optimized grating position. So can the old and new weights really be compared?

Answer #18: As stated by the referee, the old and new weights cannot be compared. The table was not intended to provide a comparison between the coefficients, but only to list them. The caption was modified as follows for ease of comprehension:*"Wavelengths and NO_2 weighting coefficients used within the old (Kerr, 1989) and new method at the corresponding grating positions (microsteps 1000 and 1012, respectively)".*

Additionally, the following sentence was added to the text:

4 Calibration campaign: "... discarded due to rain or fog. *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.".*

Comment #19: Line 162: 'whilst atmospheric turbulence at midday is large'. Please explain in more detail. Do you have a reference?

Answer #19: 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 #20: Line 170: 'agree well with both the expected stratospheric VCD for the clean site of Izana and the climatological values reported by Gil et al.': what is the difference between 'expected VCD' and 'climatological values'?

Answer #20: The section underwent major changes following the suggestions by anonymous referee #1 and simultaneous measurements from a FTIR radiometer are now used for comparison with the Brewer measurements. Please, refer to the respective responses to referee #1.

Comment #21: Figure 3: the caption should say what the data are. I assume it is vertical NO2 column amounts.

Answer #21: The figures were updated according to comment #5 (slant column densities) and the caption was updated to explain what the data are. Please, refer to the new figures in the supplementary file.

Comment #22: Line 201: 'Deviations of 0.01–0.02 DU may be noticed between the series'. What does this refer to? The difference between the data and the linear fit?

Answer #22: The sentence was removed. Please, refer to answer #5 for the updated text.

Comment #23: Line 323: 'the accuracy of the measurements is expected to improve in more polluted conditions' I don't understand this. Do you refer to the relative uncertainty, which would decrease with higher column amounts?

Answer #23: The uncertainty estimate in the case of direct sun measurements in a polluted site was addressed in detail in a separate section. The updated text is reported further below:

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

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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".

Please also note the supplement to this comment:
http://www.atmos-meas-tech-discuss.net/7/C3042/2014/amtd-7-C3042-2014-supplement.pdf

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