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Measurements of O₃, SO₂, NO₂ and HCHO column amounts using a Brewer spectrometer

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ABSTRACT

O₃, SO₂ and NO₂ vertical column amounts and aerosol optical depths at 18 wavelengths from 303 to 363nm were measured daily for the past two years by using a Brewer MK3 double spectrometer in direct-sun mode. We describe the algorithms we use and compare them to the standard algorithms. For O₃ and SO₂ the standard algorithm was modified by using all 6 measured wavelengths instead of only 4 or 5 and by including a correction for the diffuse irradiance entering the instrument's field of view. This reduces the statistical error of the retrievals by 40% and 50%, respectively, for O₃ and SO₂. The NO₂ retrievals are based on a spectral fitting technique using wavelengths between 349 and 363nm. A 'Bootstrap method' has been developed to calibrate the Brewer for NO₂ measurements. This method selects data with lowest NO₂-amounts and uses them to derive the needed extraterrestrial solar spectrum. We discuss possible reasons why an intent to apply to same technique for deriving total HCHO columns failed. The main advantage of direct sun methods compared to scattered light methods is that the uncertainty in the air mass factor is significantly smaller. We think that a better correction for the diffuse irradiance entering the instrument's field of view will further improve the retrievals, especially in the low wavelength range (303 to 320nm) used for O₃ and SO₂.

Keywords: Brewer spectrophotometer, Trace gases, Aerosol optical depth, Direct Sun

1. INTRODUCTION

The Brewer spectrometer is a widely used instrument for measuring total column ozone (O₃) using a narrow field of view (FOV) optics¹ and spectral ultraviolet (UV) irradiance reaching the ground from a separate entrance port with a Teflon diffuser^{2,3}. Recently it has been used for aerosol optical depth (AOD) measurements⁴⁻¹⁰. Only little attention has been given to exploit its capability of deriving the atmospheric amount of optically thin trace gases (i.e. other than ozone), although there exist operational algorithms for sulfur dioxide (SO₂) and nitrogen dioxide (NO₂). *Kerr*⁶ presents a time series of SO₂ total columns amounts at Mauna Loa, Hawaii, USA. *Francesconi et al.*¹¹ analyze NO₂ total columns in Rome and Ispra, Italy. *Fioletov et al.*¹² derived SO₂ from volcanic origin using the instrument's global irradiance measurements.

In this paper we briefly describe the algorithms we are using to derive trace gases and aerosol optical depth with a MK3 Brewer spectrometer near Washington DC, USA, and show some results. We also discuss possible reasons for the currently limited use of optically thin trace gas measurements with the Brewer.

2. INSTRUMENT

The measurements are performed at Goddard Space Flight Center, Greenbelt, Maryland, USA (38.98°N, 76.83°W, 90m a.s.l.), using a MK3 Brewer spectrometer¹ in direct sun mode. Our instrument has a wavelength range from 282.6 to 363.6nm and a triangular slit function with full width half maximum from 0.47nm to 0.67nm that decreases with wavelength (see table 1). It is a double monochromator with very low internal stray light (<10⁻⁸). It can operate either in a 'scanning mode', where the gratings are moved and any wavelength can be selected, or in a 'slit mask mode', which allows nearly simultaneous measurements of 6 wavelengths that are about 3nm apart.

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To derive atmospheric trace gases we are operating the Brewer in the slit mask mode at 3 wavelength ranges (see table 1). The LOW range is the grating position with slit mask wavelengths from 303 to 320nm used in the standard software for O₃ and SO₂ measurements. The MEDIUM and HIGH wavelength ranges required modification of the software and placement of the gratings to measure between 327 to 343nm and 349 to 363nm respectively. Note that slit #5 measures 340nm in the MEDIUM range, a wavelength that is often used in sun photometers to measure AOD¹³. In the HIGH range the wavelength center at slit #5 is around 360nm, corresponding to the reflectivity channel of TOMS/Earth Probe¹⁴. The wavelength calibration of the Brewer was done as described in Gröbner *et al.*¹⁵ and the expanded wavelength uncertainty for field conditions was determined to 0.015nm. This is a two standard deviation uncertainty level (2σ or expanded uncertainty), which will be used for all uncertainties given in this paper.

The narrow FOV port of our Brewer was absolutely calibrated in the laboratory in the same way as described by Kazadzis *et al.*¹⁶ using 1000W FEL lamps in different distances from the instrument (150 to 350cm).

Table 1: Wavelengths in slit mask mode at different grating positions

| Wavelength range | Wavelength center and resolution [nm] | | | | | |
|------------------|---------------------------------------|---------------|---------------|---------------|---------------|---------------|
| | Slit #1 | Slit #2 | Slit #3 | Slit #4 | Slit #5 | Slit #6 |
| LOW | 303.21 (0.63) | 306.32 (0.62) | 310.06 (0.60) | 313.50 (0.62) | 316.79 (0.60) | 319.98 (0.58) |
| MEDIUM | 327.46 (0.58) | 330.32 (0.57) | 333.76 (0.55) | 336.91 (0.56) | 339.92 (0.54) | 342.82 (0.53) |
| HIGH | 348.82 (0.53) | 351.47 (0.52) | 354.61 (0.50) | 357.51 (0.51) | 360.24 (0.49) | 362.85 (0.47) |

3. ALGORITHM

Figure 1 shows optical depths of the main atmospheric trace gases that absorb in the Brewer's wavelength range. All optical depths are calculated from an altitude integral using temperature dependent cross sections and a yearly average temperature profile corresponding to the location's latitude and are convoluted with the instrument's slit function. The oxygen dimer (O₂-O₂) optical depth is for 1 atmosphere pressure. The absorption cross sections for NO₂, O₃, SO₂, formaldehyde (HCHO), bromine oxide (BrO) and O₂-O₂ are taken from Vandaele *et al.*¹⁷, Burrows *et al.*¹⁸, Vandaele *et al.*¹⁹, Meller and Moortgat²⁰, Wilmouth *et al.*²¹, and Greenblatt *et al.*²², respectively. The column amount is given in Dobson Units (DU). 1DU corresponds to 10⁻³atm-cm or a column density of approximately 2.7x10¹⁶cm⁻². A change of 0.01 in optical depth corresponds to a 1% change in intensity of the measured signal at 0° solar zenith angle (SZA), i.e. an air mass factor (AMF) of 1. For example, an increase in total ozone of 3DU decreases the intensity at 310nm for 0.7% at AMF=1.

The trace gas algorithms for direct sun measurements are based on equation (1). For each wavelength we can write:

$$(1) \quad F = F_0 \cdot e^{-m \cdot \tau} + \Delta F_{\text{SCATT}}$$

F is the measured irradiance, F₀ the extraterrestrial irradiance corrected for the Sun-Earth distance, m the AMF, τ the total vertical optical depth (see figure 1), and ΔF_{SCATT} the diffuse irradiance entering the FOV.

The Brewer's FOV in direct sun mode is about 2.7° full angle²³. An iris with variable size inside the optical path can increase it up to 8.4°. The influence of ΔF_{SCATT} was discussed on a theoretical base by Arola and Koskela²⁴. They point out the importance of ΔF_{SCATT} for retrievals in the LOW wavelength range. We took direct-sun measurements in all three wavelength ranges with variable iris sizes in order to make estimations of the magnitude of ΔF_{SCATT}. Although the analysis of the data is still in process we have indications that the influence of ΔF_{SCATT} is minor in the HIGH and MEDIUM ranges, but significant in the LOW range.

The product of AMF and optical depth in (1) is a sum of different terms, each standing for extinction by different species. Forming the natural logarithm and rearranging (1) yields (2).

$$(2) \quad \ln F_0 = \ln(F - \Delta F_{\text{SCATT}}) + m_{\text{MOL}} \cdot \tau_{\text{MOL}} + m_{\text{MOL}} \cdot \tau_{\text{O}_2\text{O}_2} + m_{\text{AER}} \cdot \tau_{\text{AER}} + m_{\text{O}_3} \cdot \tau_{\text{O}_3} + \\ m_{\text{SO}_2} \cdot \tau_{\text{SO}_2} + m_{\text{NO}_2} \cdot \tau_{\text{NO}_2} + m_{\text{HCHO}} \cdot \tau_{\text{HCHO}} + m_{\text{BrO}} \cdot \tau_{\text{BrO}}$$

In the subscripts MOL stands for molecular scattering, AER stands for aerosol extinction and the other subscripts stand for absorption by the specific trace gas. For molecular scattering we use the formula from *Bodhaine et al.*²⁵, adjusted for a CO₂-content of 370ppm and a total water vapor column of 1.4cm (=median at our station) as described in *Owens*²⁶, and the mean surface pressure at the station. The AMF m are calculated using (3):

$$(3) \quad m = \sec\{\arcsin[k \cdot \sin(SZA)]\}$$

where k is given by

$$(4) \quad k = \frac{R}{R+z}$$

R is the Earth's radius and z is the effective layer height of the species. We use $z=8.3\text{km}$ for air (i.e. molecular scattering and O₂-O₂ absorption), $z=23.2\text{km}$ for O₃ and BrO, and $z=2\text{km}$ for aerosols, NO₂, SO₂ and HCHO (i.e. we assume aerosols, NO₂, SO₂ and HCHO to accumulate in the lower troposphere).

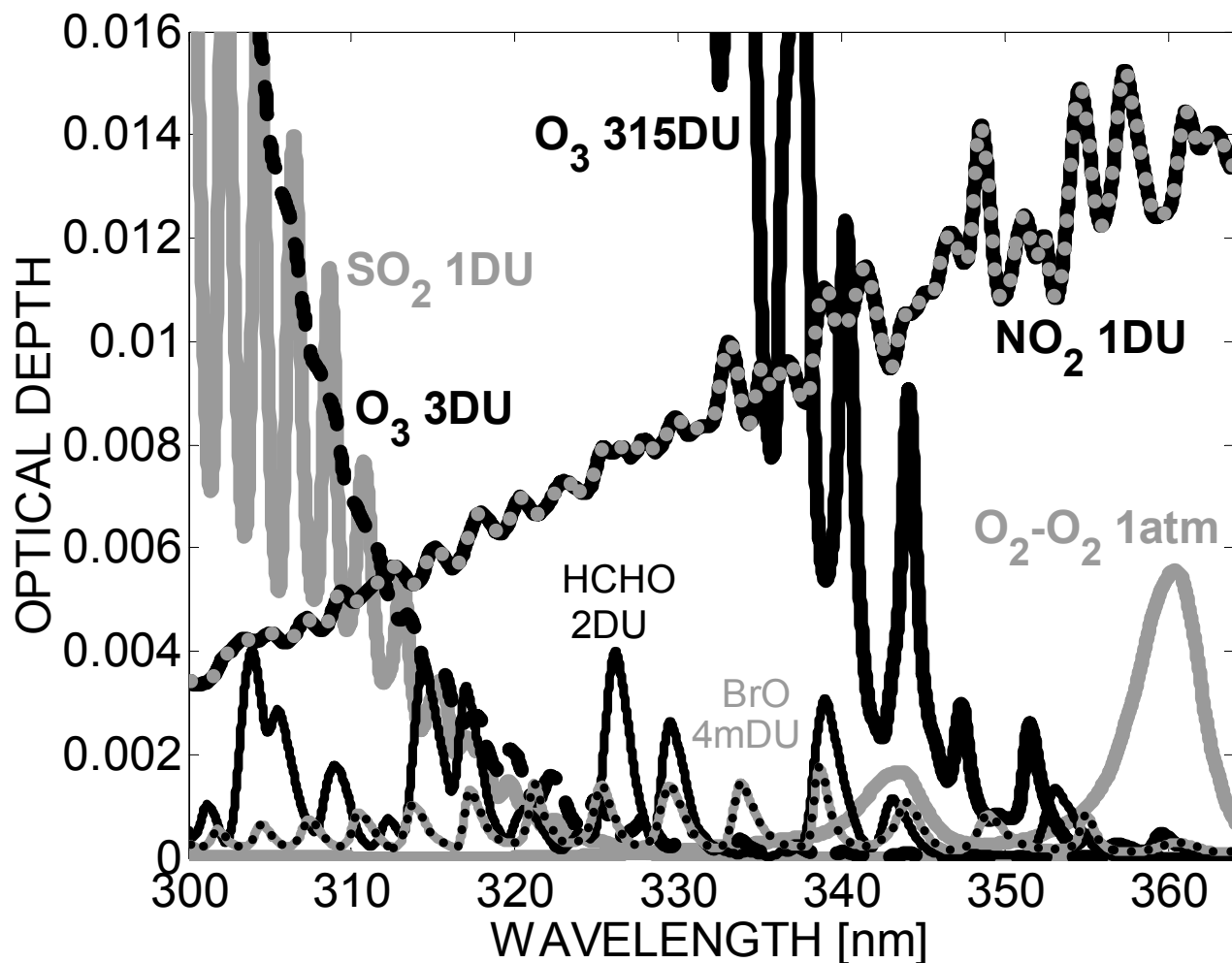


Figure 1: Typical optical depths of the main trace gases in the Brewer's wavelength range: O₃ 315DU thick solid black line, O₃ 3DU thick dashed black line, SO₂ 1DU thick solid gray line left side, NO₂ 1DU thick black-gray line, HCHO 2DU thin solid black line, BrO 0.004DU thin black-gray line, O₂-O₂ 1atm thick solid gray line right side

In the following paragraphs we explain the currently used algorithms for trace gases at our site and the modifications we want to apply in the future in order to improve the retrievals.

Currently used algorithms

O₃:

The upper left panel of figure 2 shows the optical depth of 315DU of O₃ (black line) and the 6 wavelength (6λ) centers of the slit mask wavelengths in the LOW range, which is used to derive ozone (vertical gray lines).

The standard Brewer algorithm for O₃²⁷ is based on equation (2) and uses directly the count rates at each slit for F. ΔF_{SCATT} , $\tau_{\text{O}_2\text{O}_2}$, τ_{SO_2} , τ_{NO_2} , τ_{HCHO} and τ_{BrO} are set to zero. m_{MOL} , m_{AER} and m_{O_3} are calculated as in equations (3) and (4) using effective layer heights z of 5km, 5km and 22km respectively. The wavelength dependence of τ_{AER} is assumed to be inversely proportional to the wavelength. This leaves only F_0 , the total ozone content, and the constant term of τ_{AER} as unknowns in (2). F_0 is determined by the original calibration of the instrument against the reference Brewer triad²⁸. The standard algorithm uses only slits #3 to #6 and gives different constant weights to each slit to stabilize the algorithm with respect to small wavelength calibration errors. This leaves 4 equations (one for each wavelength) and 2 unknowns (total ozone and one aerosol term), which allows determining total ozone. Slit #2 is not used because it is affected by SO₂ (see figure 2). Slit #1 is strongly affected by instrumental stray light in single monochromator Brewer instruments.

The algorithm we are currently using at Goddard Space Flight Center to derive total ozone ('6λ-algorithm') is based on the standard algorithm. However since the double Brewer has very little stray light we use all 6 wavelengths. In addition we include SZA-dependent estimations for ΔF_{SCATT} in equation (2), obtained from radiative transfer calculations for the given FOV. F_0 is determined from Langley calibrations. We use variable weights for each wavelength, which adjust for the different noise in the slits at each measurement (slit #1 has the lowest count rates and therefore the largest photon counting noise). The weights also take into account the influence of aerosols, SO₂, wavelength shifts etc. So e.g. slit #2 gets relatively little weight because of its strong sensitivity to SO₂. It turns out that at high SZA the weights of our 6λ-algorithm approach the weights of the standard algorithm, since the noise of slits #1 and #2 increases compared to the other slits, which reduces their weight. However, at low SZA the inclusion of slits #1 and #2 reduces the statistical noise in the ozone retrievals significantly. On an average the standard deviation of the total ozone over 5 subsequent sets of data is reduced by 40% at clear sky conditions when changing from the standard algorithm to the 6λ-algorithm.

The upper left panel of figure 3 shows the direct sun total ozone measurements and expanded standard error of 5 measurement sets for February 1st, 2005, at Goddard Space Flight Center using the 6λ-algorithm.

SO₂:

The upper right panel of figure 2 shows the optical depth of 1DU of SO₂ (black line) and the 6 wavelength centers of the slit mask wavelengths (vertical gray lines).

The standard Brewer algorithm for SO₂ is basically identical to the total ozone algorithm described in the previous paragraph. The derived total ozone is added and the SO₂-terms are not neglected in equation (2). Now slit #2 is also included and the weights for each slit are optimized with respect to SO₂.

In the new algorithm we are again using all 6 wavelengths and weights that adjust to the noise levels at each slit. It can be observed in figure 2 (upper right) that the optical depth for slits #2 to #6 at 3DU of ozone and 1DU of SO₂ are rather similar. Therefore, we believe that the inclusion of slit #1 is a large improvement for the SO₂ retrieval. On an average the standard deviation of the total SO₂ column over 5 sets of data was reduced by 50% at clear sky conditions when changing from the standard algorithm to the 6λ-algorithm.

The lower left panel of figure 3 shows the direct sun total SO₂ measurements for February 1st, 2005 using the 6λ-algorithm. This was one of the days with highest SO₂-concentration out of the whole database.

NO₂:

The standard Brewer algorithm for NO₂ was developed for single monochromator Brewer types measuring wavelengths from 430 to 450nm using the grating's 2nd order of scattering. No algorithm existed for double monochromator Brewers.

The algorithm we developed to derive total column of NO_2 is described in detail in *Cede et al.*²⁹ and will only briefly be summarized here. The method uses the slit mask measurements in the HIGH wavelength range (see table 1). In this wavelength region, the highest (gaseous) optical depths aside from NO_2 are from $\text{O}_2\text{-O}_2$ and ozone (see figure 1). HCHO and BrO show some minor influence, and SO_2 does not absorb at all.

The lower right panel of figure 2 shows the optical depth of 1DU of NO_2 (black line) and the 6 wavelength centers of the HIGH range (vertical gray lines). The algorithm is again based on equation (2). We know the measured intensities F at the 6 slits. We neglect ΔF_{SCATT} because we think the influence in the HIGH range is small. We estimate τ_{MOL} , $\tau_{\text{O}_2\text{O}_2}$ and all AMF as described above. We use the total ozone and SO_2 amounts obtained from our Brewer spectrometer measurements in the LOW wavelength range to estimate τ_{O_3} and τ_{SO_2} . HCHO and BrO amounts are less important at our site. However, we estimate a maximum amount of total HCHO of 2DU³⁰ and the total BrO amount not to exceed 0.004DU³¹, and include constant estimated ‘mean’ optical depths of 1DU for HCHO and 0.002DU for BrO in the algorithm for NO_2 retrieval. If we knew the extraterrestrial intensity F_0 , we could simultaneously fit a constant and linear aerosol term and the total NO_2 -column in equation (2) (see the linear fit in lower right panel of figure 2).

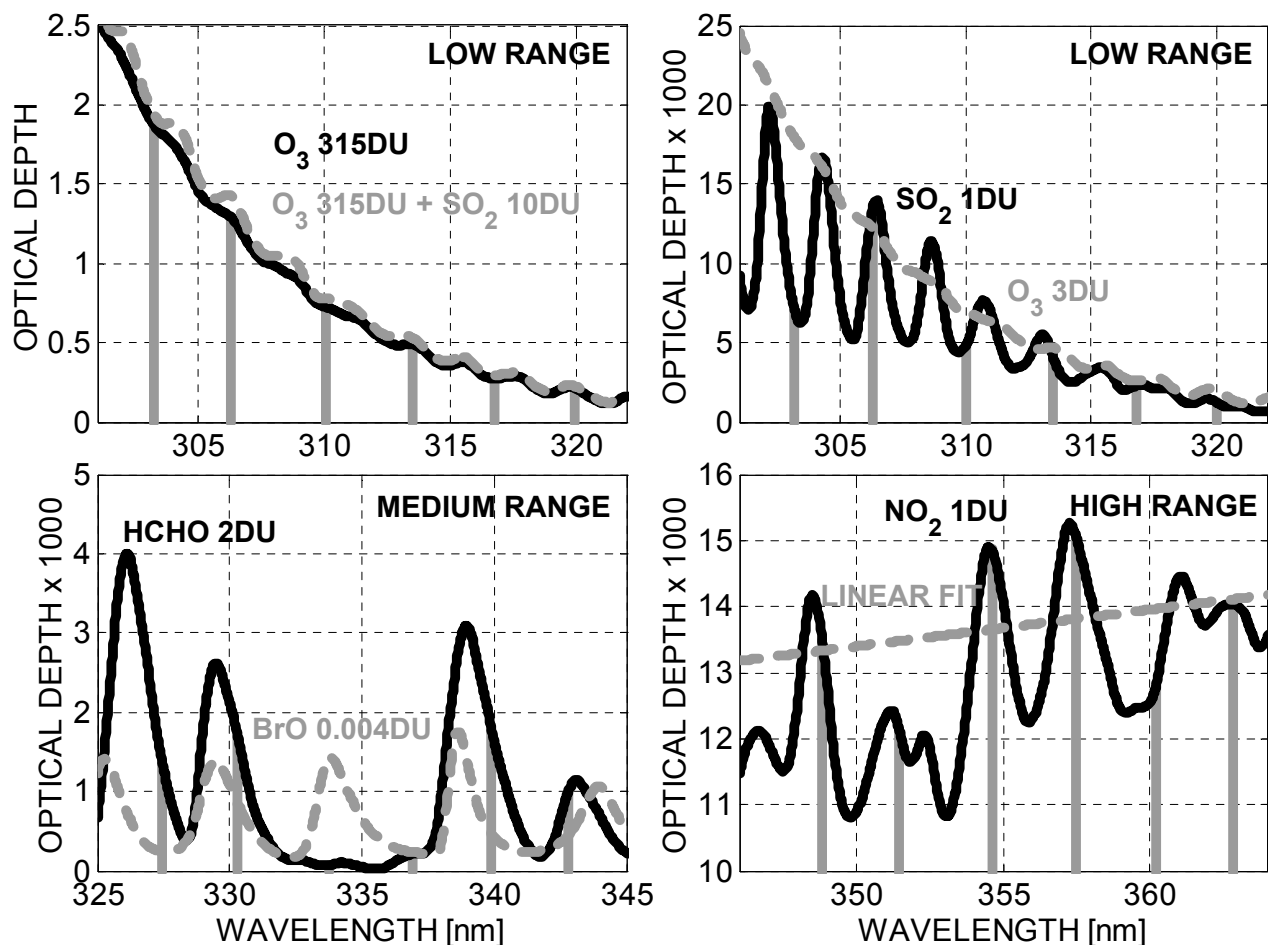


Figure 2: Typical optical depths of the retrieved trace gases in the three wavelength ranges (black lines) and wavelength centers of the slit mask wavelengths (vertical gray lines). Upper left: dashed gray line shows the effect of an additional amount of 10DU SO_2 on the optical depth; upper right: dashed gray line shows the optical depth of 3DU O_3 , for comparison; lower left: dashed gray line shows the optical depth of 0.004DU BrO , for comparison; lower right: dashed gray line is a linear fit in the optical depth at the 6 slits.

To obtain the F_0 we applied a so-called 'Bootstrap method'. This method uses a first guess of F_0 to determine the data with lowest NO_2 amounts ('reference group'). In the reference group the NO_2 amount is assumed to be zero and the final F_0 is obtained from the reference group. It turned out that we also had to include a wavelength shift parameter in the algorithm. Otherwise the effect of small wavelength shifts on F_0 would completely mask the NO_2 effect.

The upper right panel of figure 3 shows the direct sun total NO_2 measurements on February 1st, 2005. The gray dots also show data obtained from spectral scans using the same algorithm and calibration. However the classical scanning technique only worked for a very limited number of clear-sky days with excellent stable conditions since the time between the first and last measured wavelength is too long.

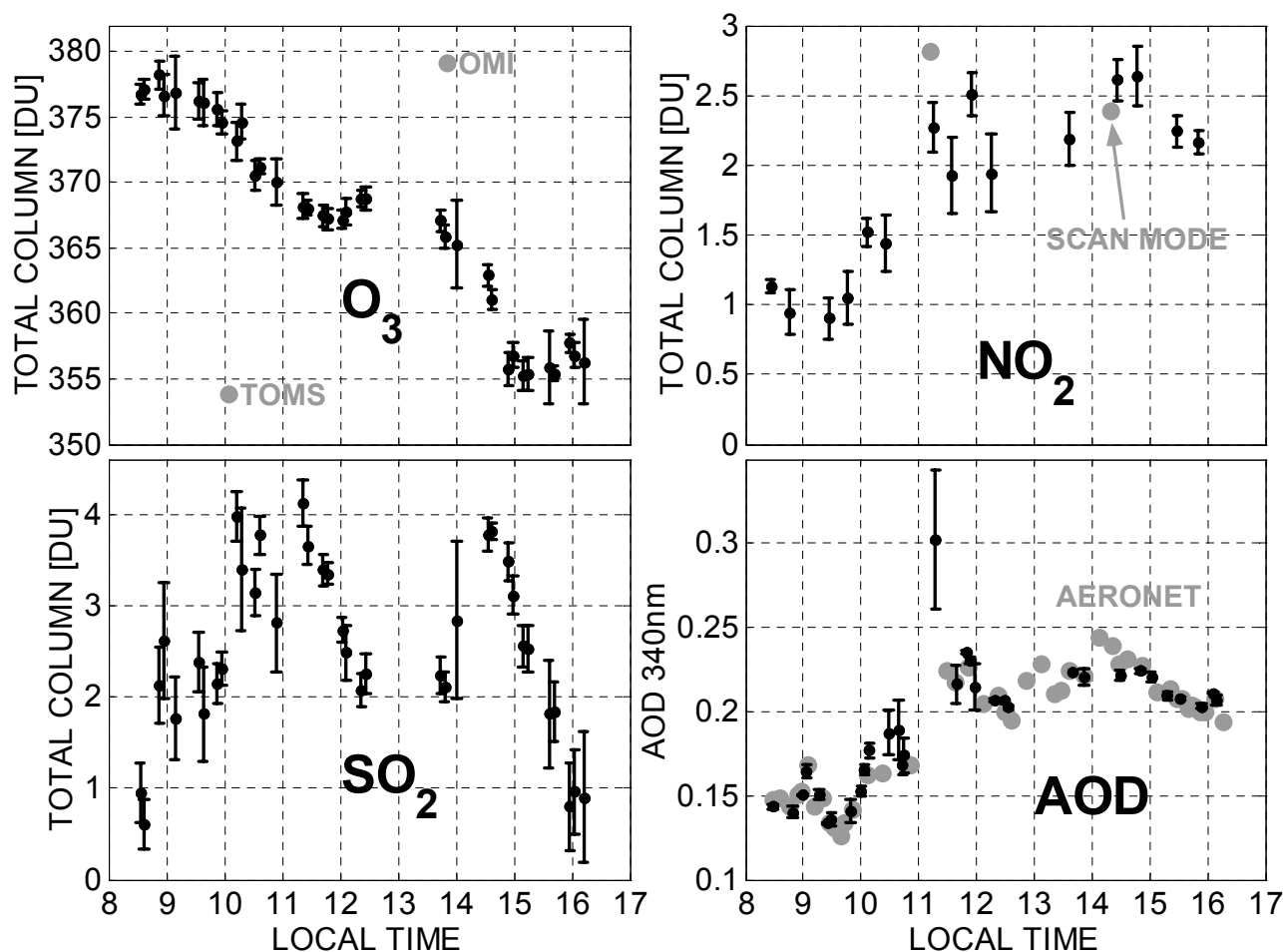


Figure 3: Trace gas and AOD measurements for February 1st, 2005, at Goddard Space Flight Center. Black dots and bars show the mean and expanded standard error of the direct sun retrievals in the slit mask mode. Upper left: gray dots show TOMS/Earth Probe and OMI overpass data; upper right: gray dots show retrievals from scan mode; lower right: gray dots show data from co-located AERONET-instrument.

HCHO:

The lower left panel of figure 2 shows the optical depth of 2DU of HCHO (black line) and the 6 wavelength centers of the MEDIUM range (vertical gray lines). To obtain HCHO we tried to apply the same technique than for NO_2 -retrievals. However the HCHO signal was not clearly visible in the data. There are possible reasons for that:

- The slit mask is not optimally placed on the HCHO-peaks.
- The amount and/or variation of HCHO are too little at our location.
- BrO is masking the HCHO-data (dashed gray line in figure 2).

- The influence of total ozone is still too large.

Hence we do not have HCHO-data at the moment.

AOD:

When the retrieved trace gas amounts are taken out in equation (2) and F_0 is known we can determine the AOD at the 18 wavelengths given in table 1. Currently we are using our laboratory-calibrated F and take the SUSIM/Atlas 3 spectrum [Van Hoosier, pers. comm.] convoluted with the Brewer slit functions for F_0 . We also include the SZA-dependent estimations for ΔF_{SCATT} in equation (2), obtained from radiative transfer calculations in the algorithm. Cede et al.³² describe the influence of the instrument's polarization sensitivity on AOD-retrievals. This effect is corrected in our Brewer.

The lower right panel of figure 3 shows the AOD at 340nm (=slit #5 in MEDIUM range) on February 1st, 2005. The gray dots also show data from a co-located AERONET instrument¹³ for comparison. Shortly after 11:00 local time a cloud was covering the direct sun path and causes a peak in the AOD and is eventually also responsible for the rather increased NO₂-amount from the scan data at about the same time (figure 2, upper right panel).

Future changes in the algorithms

- After completing the analysis of the 'scattered light measurements' with variable iris size we want to replace the radiative transfer estimations of ΔF_{SCATT} by empirical formulas resulting from the measurements. This should significantly improve the scattered light correction.
- We want to replace the current O₃ and SO₂ algorithms by a fitting technique similar to what we use for NO₂. Then we would derive both gases at the same time. We may also include an additional fitting parameter for the wavelength shift and the effective ozone temperature. To obtain the F_0 we think of a bootstrap technique for the SO₂-part.
- We may include weights for each slit in the NO₂ algorithm to adjust for the specific noise levels (currently all wavelengths have the same weight).
- We may include the actual surface pressure in the retrievals.

4. DISCUSSION

We think the main reason for the currently limited use of measurements of optically thin trace gases with the Brewer is the difficulty in calibration. In order to accurately measure trace gas amounts (other than O₃), the relative precision of the F_0 has to be much smaller than 0.1% (a systematic bias common to all wavelengths cancels out in the algorithms). This cannot be obtained by laboratory calibration and, in our opinion, not even with Langley calibrations at unpolluted sites considering all possible error sources^{24,32}. Wrong F_0 results in a SZA-dependent systematic error of the retrieved trace gas amounts. For example, we believe that we still have a +0.5DU bias in our SO₂ retrievals due to small errors in F_0 , which were obtained by Langley extrapolations.

We think that using the 'Bootstrap method' to obtain the F_0 improves the accuracy of the retrieved column amounts significantly. Currently we are using this technique only to derive NO₂, but we want to apply it also on SO₂ in the future.

Despite the difficulties in the calibration of direct sun trace gas measurement we believe that they are an important addition/alternative to scattered light Differential Optical Absorption Spectroscopy³³. In this technique spectral sky radiance is measured and the slant column density of the atmospheric species is derived. The slant column is then divided by the estimated AMF to obtain the vertical column. The large AMF in scattered light measurements decreases the influence of F_0 and gives high trace gas signal, which is definitely strength. However, the theoretical determination of the AMF depends on several atmospheric parameters such as the vertical trace gas profile, assumption of horizontal homogeneity, aerosols, clouds, etc. Therefore, even for clear-sky conditions, the uncertainty in the AMF for polluted regions is very high, typically around 100%^{34,35}.

In the direct sun method the uncertainty in the AMF is less than 1% for SZA < 80°. So in the case of NO₂ the accuracy of the direct sun measurements with the Brewer is better than from DOAS for vertical column amount larger than 0.5DU.

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