

Interactive comment on “Recommendations for spectral fitting of SO₂ from MAX-DOAS measurements” by Zoë Y. W. Davis and Robert McLaren

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Review

Recommendations for spectral fitting of SO₂ from MAX-DOAS measurements

Zoë Davis and Robert McLaren

General Remarks

This article describes the results of some basic experiments aimed at determining an ideal wavelength window for the analysis of MAX-DOAS measurements of sulfur dioxide (SO₂). The authors placed gas cells containing known amounts of SO₂ in

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front of a MAX-DOAS instrument while recording spectra of an unpolluted atmosphere. When analyzed relative to spectra obtained without using the cells, these measurements should yield the known SO₂ column densities of the gas cells. Any deviation from these known values is attributable to errors induced during the fitting procedure.

In an effort to find an optimal setup for the DOAS fit, the authors varied the lower and upper boundaries of the fit wavelength window in an approach called ‘retrieval interval mapping’ (Vogel et al., 2013). They concluded that using the range 307.5 to 319 nm generally yielded the most accurate results in the considered cases. In addition, the effects of suppressing stray light either by use of a short-pass colored-glass filter in the spectrometer’s entrance optics or by accounting for it through inclusion of an offset polynomial in the DOAS fit was assessed. Both strategies appeared to generally improve the accuracy of the results.

This article is well-written and informative, and the results are useful for the atmospheric sciences and volcanic gas communities. My only concern is that the considered experiments may be too limited in scope to be able to support the relatively broad conclusions regarding the ideal fit window. In particular, the authors do not consider the impact of a rapidly varying ozone slant column density (SCD) as it occurs early or late in the day, instead only analyzing spectra recorded around solar noon. Also, the authors apply a relatively simple Ring correction in their retrievals, when a more sophisticated approach may improve the fit quality and/or allow the width of the fit window to be increased, thus improving the robustness of the fit results. Finally, the authors only tested a single spectrometer and it’s not entirely clear how these results apply to other, possibly more sophisticated MAX-DOAS instruments. Below, I have listed some recommendations on how the authors might improve their manuscript with regards to these points. Once these comments have been considered, I recommend the article be published in Atmospheric Measurement Techniques.

Specific Issues

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It is my experience that imperfect representation of the differential ozone absorption in the 300 to 340 nm region in the DOAS model can lead to errors in retrieved SO₂ column densities. These effects are not captured by the authors' experiments because they did not assess the effect of a varying solar zenith angle (SZA) and hence a change in the ozone SCD on their results. My worry is that these might affect the recommendations for wavelength fit window, possibly leading the authors to consider broadening the window to allow for better discrimination between SO₂ and O₃. To address this issue, the experiments could be repeated for a time early in the morning or late in the evening when the O₃ SCD is changing rapidly with time. This then leads to a mismatch in O₃ SCD between 2-degree and 90-degree MAX-DOAS observations, a mismatch that needs to be accounted for by the O₃ cross-section included in the DOAS fit. As the currently discussed experiments were all conducted around solar noon, the impact of O₃ in the spectra is likely negligible, but the results are not necessarily valid for measurements made throughout the day.

A more careful consideration of the Ring effect would also be worthwhile. The SO₂ and O₃ differential absorption features are of a similar bandwidth as the Fraunhofer lines in the solar spectrum. Hence, an imperfect removal of the filling-in of these lines by inelastic Raman-scattered radiation could potentially interfere with the SO₂ retrieval. I recommend the authors review the literature with regards to state-of-the-art Ring correction, in particular focusing on an additional dependency of the Ring effect on wavelength (Vountas et al., 1998 Langford et al., 2007), the potential impact of vibrational Raman scattering (Lampel et al., 2015), and the effect of the broad-band shape of the solar spectrum as it reaches the Earth's surface (Lampel et al., 2017). If each of these effects are properly accounted for, it may be possible to extend the width of the fit window beyond the authors' current recommendation which in turn could improve the fit accuracy. Or the authors may find that these effects are of second order importance and their consideration does not improve the SO₂ retrieval. But either way, I believe they should be tested in order to ensure that the authors recommendations reflect the state-of-the-art.

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Finally, it's a bit unclear to me how representative the results are for MAX-DOAS instruments in general. The authors use an Ocean Optics USB2000 spectrometer for their measurements. This instrument is very common and therefore represents a good choice for such a study. However, it is my experience that these relatively economical instruments suffer from a relatively poor stray-light rejection. Therefore, it is no surprise that suppression of stray light using an optical filter and/or accounting for it in the DOAS fit improves the results of the retrieval. At the same time, these results and recommendations may not apply to other, higher quality instruments. It would be of great value if the authors were able to compare their results with those obtained using a higher-grade spectrometer. If this is not possible, the authors should consider explicitly narrowing the scope of their manuscript to reflect the fact that the experiments were all made using this one type of instrument. For example, the authors might include the terms 'low-cost' or 'miniature' in the title and mention the make and model of the spectrometer in the abstract and prominently throughout the manuscript.

Minor issues and corrections:

P1L11 – I recommend rewording “the dSCDs also exhibited an inverse relationship with the DEPTH OF THE DIFFERENTIAL FEATURES IN THE SO₂ absorption cross-section. . .”

P1L15 – “... dependence on the SO₂ absorption features SUGGESTING THAT THE RADIANCE AT SHORTER WAVELENGTHS WAS increased by stray light. . .”

P1L18 and P7L25 – The uncertainty reported by the fit is not necessarily expected to be an accurate measure of the errors of the results. This is discussed by Stutz and Platt (1996). Please incorporate this information into your discussion.

P2L6 – I suggest adding “typically” before “uses the SO₂ B band. . .”

P2L15 – In my experience, it can be beneficial to include wavelengths with weak or negligible SO₂ absorption in the fit if the extended wavelength range allows for better

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discrimination between SO₂ and other aspects of the DOAS model (Ozone absorption, Ring effect).

P3L6 – "... may NOT BE IDEAL for smaller..."

P3L23 – please remove the superscript formatting on the "C".

P3L30 – Please clarify how the 87 ppb were arrived at. I think this is assuming that the 30 degree spectra were evaluated relative to a reference recorded looking towards the zenith through the same atmospheric boundary layer, correct?

P3L31 – Please include the time at which the measurements were made. This will allow the readers to deduce the solar zenith angle. How far apart in time where the 2-degree and 90-degree measurements made?

P4L2 – In the future, you might consider using a Hoya U330 filter. I believe this has better rejection of NIR radiation which can cause stray light in the spectrometer.

P5L23 – Wavelengths longer than 324 nm are commonly used in volcanic gas measurements. While they admittedly often encounter larger SO₂ SCDs, it's not clear to me that these wavelengths can be discounted across the board for MAX-DOAS measurements simply based on the increased DOF. See comment above on improved discrimination between SO₂, ozone and Ring features.

P5L29 – It's not clear to me how increased Rayleigh scattering due to higher air pressure would preferentially remove shorter UV wavelengths. Is there a citation that you could provide for this? Couldn't one just as easily argue that increased Rayleigh scattering of previously unscattered sunlight would increase the measured radiance at shorter wavelengths? I suspect that another effect or combination of effects is responsible, possibly having to do with radiation being removed from the atmospheric half-sphere by absorption on the ground. In this case, it might be the wavelength-dependence of the ground albedo that is responsible.

P7L3 – I suspect you meant to write " $\lambda > 307 \text{ nm}$ " here?

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P7L5 – Again, I suggest rewording to "an inverse relationship with the DEPTH OF DIFFERENTIAL SO₂ ABSORPTION FEATURES..."

P7L14 – "... absorption minimum and STRAY light..."

P7L20 – "due TO the increasing..."

P7L20 and P8L18 – You mention "absorption non-linearity effects" here. In my opinion, this is a bit misleading because the DOAS model does not actually require the absorption to be linearly related to the dSCD. Instead, the optical depth (= logarithm of I/I₀) is considered proportional to the SCD, as is described by the Beer-Lambert-Bouguer Law. The issue is actually more complex and has to do with the non-commutative nature of the convolution of absorption cross-sections and the application of the Beer-Lambert Law. Details can be found in Platt and Stutz (2008).

P7L34 – "fit error was $> 1.1 \times 10^{-6}$..." (remove two instances of "greater"/"greater than")

P8L11 – I did not understand this sentence. Can you clarify what you mean by "could be overestimated by the same windows for low concentration measurements"?

P8L13 – suggest adding "known" before "fit error for many windows".

P8L18 – Whether or not strong absorption effects related to the convolution contributed to the errors here might be assessed by comparing two synthetic spectra calculated for a known SCD: $\text{conv}(\exp(-\sigma_{\text{HiRes}} \cdot \text{SCD}))$ compared with $\exp(-\text{conv}(\sigma_{\text{HiRes}}) \cdot \text{SCD})$

P8L20 – "DEPTH OF features..."

P12L3 – "<10% less OR >10% more..."

P14Figure4 – Please provide units for the y axis.

P17Figure7 – It could be worth pointing out that using starting wavelengths of 304 vs 308.5 nm changes the results by an order of magnitude (!) for the base case.

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References:

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