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Atmospheric Measurement Techniques Discussions

Interactive comment on "Development and characterization of the CU ground MAX-DOAS instrument: lowering RMS noise and first measurements of BrO, IO, and CHOCHO near Pensacola, FL" *by* S. Coburn et al.

Anonymous Referee #1

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General Comments:

The authors present a new developed MAX-DOAS instrument for the detection of trace gases in the boundary layer with very high sensitivity due to very low achievable RMS values in the residual spectrum. The manuscript is well structured and clearly written. Appropriate figures are shown.

The authors present an analysis of arising unwanted spectral structures for MAX(or passive)-DOAS measurements if an insufficient temperature stabilisation is realised.

This theoretic investigation is so far the first one I know performed in such detail. The temperature instability would increase the RMS in the residual spectrum and thus the measurement error and detection limit. The authors conclude that the main reason for remaining structures in the RMS arise from temperature fluctuations. These structures are minimised in the presented instrument by a two stage temperature stabilisation of the spectrometer. Other existing MAX-DOAS instruments use only a one stage temperature stabilisation. A mayor part of the manuscript is to describe and demonstrate the good performance of the instrument. The application to field measurements is shortly shown for observations near Pensacola, FL.

However the instrument characterisation is incomplete to convince the reader of the better performance in comparison to existing ones.

- Throughout the manuscript typically the best achieved values which are shown in the figures are written in the text and not the typical or average values. This misleads the reader. If comparing the average achieved RMS values plotted in the figures, they are in the same range as other very good MAX-DOAS instruments (Table 1). Additionally the noise test is only based on elevation angles of 25° (vs. 80°), but typical MAX-DOAS observations use mainly lower elevation angles. Typically RMS values are higher for lower elevation angles due to stronger absorptions and a stronger ring effect. Thus the given RMS does not represent the value which would be achieved at low elevation angles e.g. 0°-5°.

- The manuscript focuses on spectral structures in the residual spectrum given by the RMS and also discusses noise tests. However a standard noise test, as typically performed for any spectroscopic instrument, to demonstrate the best achievable RMS value is completely missing. Such tests are performed with a light source without spectrally structured (e.g. halogen lamp) that spectral shifts of the spectrometer (e.g. due to the mentioned temperature fluctuation), can not lead to an increase of the RMS. Thus the real achievable limit in RMS can be determined which is typically higher than the theoretic value (from shot noise) due to other noise sources (e.g. electronic noise,

optical noise).

- Any discussion about temporal resolution is missing. As MAX-DOAS measurements rely on a series of measurement at different elevation angles which should be performed at almost same atmospheric conditions this would be essential. Also if the measurement quality could be improved with increasing photons due to longer integration, this will typically lead to unacceptable long measurement time for a sequence and are thus not applicable. Even longer integration times as described are in practise not possible. For a comparison to existing MAX-DOAS instruments it would be necessary to compare the performance at similar integration times.

- If MAX-DOAS evaluations are performed in that way that for each measurement spectrum the reference spectrum close in time is used (as also done in section 4) the temperature fluctuation between these measurements is relevant, which could be very small even in comparison to the presented temperature stabilisation over 8 hours. Thus the improvement with enhanced temperature stabilisation can become irrelevant for MAX-DOAS observations.

- The measurement results from the field observations at Pensacola, FL are not discussed or interpreted in terms of the chemistry. The given discussion is not put in context with the measurements. Thus either this discussion is removed or the discussion is extended to put the measurements in context.

Therefore mayor corrections and revisions are necessary prior publication in AMT. The authors have also to show what RMS is achieved under realistic MAX-DOAS conditions (small elevation angles, short integration times) and compare these to RMS values of state-of-the-art instruments.

Specific Comments:

P 247 Title: the word “first” is misleading, as these are not the first measurements of these trace gases.

P 248 Line 6: The detection sensitivity is proportional to the RMS of the residual spectrum, but not necessary directly. There is no direct mathematical link between RMS and detection limit. This has to be defined by statistical analysis like done in Stutz and Platt 1996.

P 248 Line 9: The RMS value $\sim$6x10ˆ-6 is not proven in the manuscript, as it is not achieved. The values from figure 1 are $\sim$ 9x10ˆ-5for 64 added spectra and decrease to $\sim$ 1x10ˆ-5 if 100 ratios are added. It is not proven that other noise sources (electronical, optical) except from photo statistic limit the RMS of the instrument. Therefore this statement is misleading.

P 248 Line 20: Please specify once FL.

P 249 Line 3: Please give reference if you state that halogens are relevant for air quality. I don’t thing so that this is the case for urban air quality.

P 249 Line 14: Please give references for the stated chemical reactions of BrO and bromine atoms.

P 250 Line 1: The first measurements of halogen oxides with DOAS are presented in Hausmann and Platt 1994. Please include this reference or state that you only mean passive DOAS observations.

P 250 Line 9: The influence of stratospheric absorbers is not always removed if you use a fixed zenith reference at low SZA. If the SZA is changing, the stratospheric absorber signal is changing. That means the stratospheric absorber is only removed for a spectrum recorded close in time to the reference spectrum for any other spectrum it is not completely removed. Thus the statement is wrong. But what you remove are the Frauenhofer lines.

P 250 Line 20: It is not proven that the RMS is not further improved for state-of–the-art instruments with further photo-count statistic. Possibly only a longer integration time was unpractical due to the required temporal resolution for MAX-DOAS measurements.

P 251 Line 17: To which mixing ratio a dSCD of 1x10ˆ13molec cmˆ-2 relates? Is this relevant for atmospheric processes (give references)?

P 252 Line 4: To which dSCD 2ppt relate?

P 252 Line 9: Define once abbreviation PSN for photo shot noise.

P 255 Line 22: Specify the temperature sensors (accuracy and temperature drift). What is the accuracy of the read out electronic?

P 255 Line 25: Are the fibre adjustment mounting and the detector mounting within the temperature stabilised housing?

P 256 Line 9 – 19: Please shorten this section as this information was already given before or is irrelevant.

P 257 Line 10: Please be consistent in the given values and write 0.8 pixels for 10°C, or 0.08 pixel °Cˆ-1.

P 257 Line 13: Remove information about offset as it is irrelevant here.

P 257 Line 24: How are the values of <5x10ˆ-5 to 1.5x10ˆ-4 read from the table for the presented instrument? What would be the RMS values for typical temperature stability of $\sim$0.1°C.

P 258 Line 5: "identical spectra" – Which spectra? (measured, Frauenhofer Spectrum, Literature cross sections). If you mean the zenith sky spectrum, this statement has to be clarified. Also a shift of this reference can be allowed in the DOAS analysis so that this error of the shift can be reduced. If you do not mean the zenith sky spectrum, this section 3.3 is unclear. Please clarify. It seems that you are talking until Line 12 from something different that after that (Notably,. . .). Please separate the two statements of a wavelength calibration of the reference measurement and spectrum and those of calibration accuracy of literature cross-sections.

P 258 Line 12 – 14: In the DOAS analysis a shift of the literature cross-sections can

be realised, so that this error can be reduced. Also different wavelength mappings of literature cross-sections have always to be corrected in DOAS analysis, but should be relative fixed between the cross-sections. Differences arise as different wavelength calibrations are used, e.g. the determination of the centre of an absorption line. Thus it is not clear why RMS structures should arise from wavelength uncertainties of the cross-sections especially if concentrations are very low.

P259 Line 1: Detector non-linearity investigations do not contain a detector non-linearity measurement which could clarify which saturation levels are applicable for the DOAS measurement with the given detector and if you work in the linear range. It is obvious that if you work in the range where the detector is non-linear (this seems to be the case for your 90% saturation), problems for the DOAS measurements arise. If this is not guaranteed the section becomes irrelevant. Also no information is given of the readout of the detector (binning, full imaging).

P 259 Line 6 and Fig3: Which saturation is given in %? From maximum counts or full well capacity? For a pixel or the read out register? In which relation are the max. counts to the full well capacity in the applied detector read out mode?

P 259 Line 21: If the saturation of one spectrum is reduced, the shot noise will increase what can partly cause the increase in RMS. How large is this contribution?

P 260 Line 3: Is 90% saturation still in the linear range of the detector?

P 260 Line 19: A same saturation level over a whole spectrum can not be achieved in practise as the spectral shape is changing for different elevation angles.

P 260 Line 25 – 27: This sentence is unimportant.

P 261 Line 10: This section does not contain a signal-to-noise test with a spectral unstructured emitter like a halogen lamp. The content of the section is difficult to follow due to different kind of modes of operation, applied methods and evaluation. Please clarify.

P 261 Line 11- 13: Remove sentence as it is irrelevant. What is intelligent for an averaging module?

P 261 Line 16/17: In the second operation mode measurements are taken for 80° and 25°. The further presented RMS values in Fig. 5 are based on these angles. Why do you show noise values only for these high (25°) elevation angle? For MAX-DOAS the measurements at very low elevation angles (0-5°) are most important as they are much more sensitive to trace gases near the ground and thus contain most information. In the analysis the RMS is typically higher for such low elevation angles as than the trace gas absorption and the ring effect is stronger. Small errors in both spectral structures increase the RMS. Thus the presented RMS does not represent the values achieved for low elevation angles which are most important for MAX-DOAS.

P 261 from Line 261: Please move the description of the analysis for the different fit ranges (BrO, IO, CHOCHO) to point 4, as it is also relevant for 4.2.

P 261 Line 26: Why do you use the reference from Hönninger and not one published in the literature (e.g. Spietz et al., 2005).

P 262 Line 4: You write here that you use a reference close in time to the measurement. But on P 250 Line 9 you write that the reference spectrum is recorded at low SZA. Please correct the statement on P 250.

P 262 Line 8 and following: How does the two methods relate to the two modes of operation?

P 262 Line 14: The wavelength region 415-440nm for the CHOCHO fit is not consistent with the fit shown in Figure 8. Please state why the IO reference is omitted for the CHOCHO fit and why CHOCHO is omitted for the IO fit.

P 262 Line 17 – 18: remove sentence as it is redundant.

P 262 Line 19: replace “IAM” by “software”

P 263 Line 3: The values of 1x10ˆ-5 and 6x10ˆ-6 are the absolute best achieved values in Fig. 5, but they are not the average values for a specific amount of counts. These are in the order of $\sim$ 4x10ˆ-5 and 1x10ˆ-5. The given values are misleading. The values for the added spectra are even much higher. What is the according temporal resolution for all these measurements?

P 263 Line 4: What is the integration time to record >10ˆ10 photons?

P 263 Line 10: The finding that the RMS increases if delta t increases is not new. That is why several groups already evaluate DOAS spectra to a reference close in time and not to one reference a day taken at small SZA, like first described in this work (P 250 Line 9). Also than small temperature fluctuation over longer periods become unimportant as the spectral characteristic has only to be absolute stable between measurement and reference spectrum.

P 263 Line 17: Your conclusion is not proven by your given values. With your achieved temperature stability of 0.005° and the values given in Table 2 the increased RMS can not be explained! Thus I conclude that other reasons are responsible and thus such a good temperature stabilisation is not necessary. How would the RMS values vary for different delta t for a light source without spectral structures (halogen lamp)?

P 264 Line 5-11: Why the numbers of spectra for the different trace gases are given? These values are irrelevant as they are not put in any context. Please shorten this section. Why O4 is not always detected?

P 264 Line 15-19: Where is the proof for using these scaling factors? Please compare e.g. to Stutz and Platt, 1996.

P 264 Line 22: Geometric AMF are a very strong simplification which is e.g. only valid at small SZA and at clear sky conditions. Please clarify this, as thus also the following values can contain large errors.

P 264 Line 25: How can you calculate average BrO dSCDs if it is most of the time

below the detection limit?

P 264 Line 28 to P 265 Line 17: This section is not put in context to the measurement values and thus these statements are not proven here. In the form they are written in the manuscript this section is redundant. If you can, calculate the BrO mixing ratio from your observation and put them in context to the mercury oxidation from Holmes et al., 2009. What MAX-DOAS sensitivity is required to observe 2 ppt of BrO?

P 265 Line 25: not “measure RMS” but “achieve RMS”. RMS values smaller than 10ˆ-5 are not proven in the manuscript (see statements above).

P 266 Line 2: The RMS values from the field campaign are very good, but much higher than the proposed RMS values. They are thus not much better than other research grade MAX-DOAS instruments (Table 1).

P 266 Line 12: “BrO located above 6km” – MAX-DOAS is not sensitive to even lower elevations. How do you determine these 6km? Please give reference. Also in Line 17 “within a few km” – please give reference.

Table 1: Please include the temporal resolution as this significantly influence the achieved RMS. What is the wavelength range for the evaluation for the achieved RMS? A larger range typically leads to higher RMS values.

Table 2: To which temperature stability of the presented instrument these values are related?

Table 4: Information is redundant as it is already given in Fig 6.

Fig. 1: Please improve the figure to clarify the setup in the instrument rack (e.g. principle sketch). From the picture the setup is not clear.

Fig. 4.: The different plots are difficult to relate to the different analysis. Please clarify and state where you use the two fit scenarios a) and b).

Fig. 5.: Include integration time to the accumulated photons, as this is essential for

MAX-DOAS. Are the averaged ratios are relevant for MAX-DOAS measurements due to their low temporal resolution? Why do you show these RMS values for 25° which is not a main MAX-DOAS elevation angle? RMS values are typically higher for lower elevation angles. The achieved average RMS values are in the range of the research grade MAX-DOAS RMS.

Fig. 7. and 8.: The achieved RMS values here are very good, but much higher than those proposed from Fig. 5. and written in the manuscript.

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