Retrieval interval mapping, a tool to optimize the spectral retrieval range in differential optical absorption spectroscopy

L. Vogel[1] , H. Sihler[1,2] , J. Lampel[1] , T. Wagner[2] , and U. Platt[1]
[1]Institute of Environmental Physics, University of Heidelberg, Im Neuenheimer Feld 229, 69120 Heidelberg, Germany
[2] Max Planck Institute for Chemistry, Hahn-Mertner-Weg 1, 55128 Mainz, Germany

Remote sensing via differential optical absorption spectroscopy (DOAS) has become a standard technique to identify and quantify trace gases in the atmosphere. Due to the wide range of measurement conditions, atmospheric compositions and instruments used, a specific challenge of a DOAS retrieval is to optimize the parameters for each specific case and particular trace gas of interest. For example, a well chosen evaluation wavelength range is crucial to the DOAS technique. Although for many trace gases the overall dependence of common DOAS retrieval on the evaluation wavelength interval is known, a systematic approach to find the optimal retrieval wavelength range and qualitative assessment is missing. Here the authors present a novel tool to determine the optimal evaluation wavelength range. It is based on mapping retrieved values in the retrieval wavelength space and thus visualizing the consequences of different choices of retrieval spectral ranges. This visualization allows one to readily identify retrieval wavelength intervals which are likely to lead to erroneous results, or might lead to greater variability of retrieved values due to a large gradient of the retrieval interval dependency. The technique is demonstrated using the examples of a theoretical study of BrO retrievals for zenith-sky stratospheric BrO measurements and for BrO measurements in volcanic plumes. For both examples, the effects of: (1) the I_0-effect, (2) cross correlations between RCSs (reference absorption cross sections) and (3) added noise are examined using synthetic spectra. For zenith-sky DOAS, the tests confirmed the evaluation wavelength range 346-359 nm as suggested by Aliwell et al. (2002). This retrieval wavelength interval of BrO offers the least dependency on the I_0-effect although an I_0 correction of RCSs is still mandatory. BrO retrievals including lower wavelengths are not advised since strong O_3 absorption and slightly insufficient I_0 correction of RCSs may yield highly erroneous values even in this "best-case" scenario. BrO retrievals for measurement of volcanic plumes show a much lower I_0 dependency of the BrO SCDs on the retrieval wavelength interval, mostly due to an about 100-times weaker total O_3 SCDs. Whereas the fit applying I_0 corrected RCSs shows a good agreement with the true BrO SCD at most wavelengths, misleading SCDs are retrieved for uncorrected RCSs. An evaluation wavelength interval with a lower wavelength limit between 320-335 nm is found to be optimal because here the differences are smallest between retrievals applying uncorrected and I_0 corrected RCSs. In practice, the absorber strength at short wavelengths is most variable because of the great variability of volcanic SO_2 emissions and O_3 absorptions in early and late hours of the day. To ensure a comparable evaluation of data, measurements should be performed at the upper range of suggested interval. However, a specific retrieval wavelength interval can not be recommended for the evaluation of BrO in volcanic plumes here. Advanced modelling of synthetic spectra (including realistic

simulations of the atmospheric radiative transfer and the Ring effect) in comparison with measured spectra are needed in order to advise the specific retrieval wavelength interval to be chosen. At the example of synthetic spectra of passive DOAS measurements, the novel tool of retrieval wavelength mapping was introduced. However, the method is not limited to these types of instruments but can be applied to any DOAS measurement. Thus it enables a systematic study of important retrieval parameters, can highlight pitfalls in any DOAS retrieval and allows for an encompassing motivation of applied parameters.

Referee's recommendation

As outlined above, this paper describes and tests a new method of analyzing the quality of BrO DOAS spectral fits and may be applied to any type of DOAS measurement. It may be implemented using a PC with moderate specifications and shows great promise in helping one to determine the best fit range for a given trace gas, among other parameters. I recommend this discussion paper for full publication, once the following comments have been addressed satisfactorily and minor grammatical changes to both the text and figures/tables have been made.

Scientific Questions/Comments

Page 4200

line 8: In the DOAS community the meaning of χ^2 is known, but maybe you should define it here briefly anyway?

GENERAL POINT The authors chose 2 case studies: 1-stratospheric BrO and 2-volcanic BrO. Why not an additional tropospheric case utilizing MAX-DOAS (ie. MAX-DOAS BrO Arctic measurement such as seen in Wagner 2007 or Hoenninger 2004b)?

Page 4203

line 5: The Ring Effect is not considered. As you have stated, this may greatly affect results so why not create a synthetic Ring spectrum (as commonly done in MAX-DOAS retrievals) and include that when fitting your synthetic spectra, then compare these results with those without the Ring Effect correction? How were the Fraunhofer reference spectra determined and used in the fitting of the spectra?

Page 4204

line2: What is your rationale for the slit function chosen (ie. why was the resolution chosen to be 0.65 nm)? Why was the detector chosen to have 1024 pixels, don't most DOAS setups employ at least 2048 pixels nowadays? Are these choices important?

line 11: You say that the optical density is greater than 0.1. Strictly speaking I believe that optical density is $\ln(I_0/I)$, so I would re-word this sentence, unless I have missed something.

Page 4207

line 8: You chose a second order polynomial. Is this typical for these types of BrO fits in the field? In the field there are more broad band extinctions to worry about right? Would this be something that you would have to worry about when applying this technique to measurements performed in the field?

Page 4208

line 15: How do you chose the assumed SCD value when calculating your I_0 corrected absorption cross sections? Will this make the I_0 correction less accurate at times. Is there anything you can do to limit this source of error in the field? It seems a difficult task when you don't have any idea of the true SCD value. Secondly, in your Equation 2 for the I_0 correction you mention that the term $I_{k,0}$ in the denominator should consider all gases except the gas of interest. In the field you can not correct this but you could for this study. Why not do so for a sensitivity study to examine the potential source of error due to this effect? Is it really a major source of error?

line 20 Why were the 1% and 10% limits set? You refer to Table 2, but what is your rationale behind these choices (maybe a certain reference(s))?

Page 4212
lines 9-11: Why does a mistake in the I_0 correction of O_3 make a difference when NO_2 is varied in Figure 5???

Page 4215
lines 24-25: BrO shows the least dependence on changes in HCHO absorber strength. In the field you say this is different, and much higher anti-correlations are expected. Could you create a scenario that more closely models what is experienced in the field to determine a better BrO wavelength retrieval range for future studies? What is the suggested reason for this difference between your synthetic data and those in the field (perhaps comparing your results to the work done in (Vogel, 2011))?

General Questions

(1)Why was the synthetic BrO SCD set to $1.5\times\ 10^{-14}$ molec cm^{-2}? Is this near or at the detection limit or simply a common (average) retrieved value?

(2)Throughout the paper you often refer to (Aliwell, 2002) as your bench mark BrO study? What is your reasoning? Is it simply because this is known as the most comprehensive study to date and is confirmed by Theys, 2007?

(3)In this paper you use synthetic spectra but you know that spectra in the field behave differently and other effects need to be considered (ie. Ring effect). How can/will you modify your technique to make your determinations close to the "real-world" conditions in the future? Are you planning on including "advanced modelling of synthetic spectra including radiative transfer effects and the Ring effect" in the future?

Technical Corrections

The following lists grammatical suggestions and technical corrections to the text, listed by page and line number:

Page 4196
line 5: remove comma (, respectively.)
line 6: change ground based to ground-based (be consistent throughout the text)
line 6: change trace-gases to trace gases
lines 14-17: cut ALSO and add later. start sentence with Instrumental limitations.....ALSO need to be taken into account.
line 15: change wavelength depending to wavelength dependent
line 15: change sources of errors to sources of error
line 20: replace find with finding
line 21: here do you mean qualitatively or QUANTITATIVELY??
line 23: change visualize to visualizing
lines 23-24: change consequence to consequences
line 24: cut e.g. GENERAL POINT: the authors tend to use e.g. frequently throughout the text, try to limit it when not entirely necessary since it helps the text flow better
line 24: change text....of different choices of spectral retrieval ranges...
line 26: cut the ... demonstrated using examples of a .....
line 27: cut FOR ... stratospheric BrO and BrO measurements in volcanic....
line 27: optional in brackets ...stratospheric BrO (measurements) and ... I would cut it since it not necessary to state it twice in the same sentence

Page 4197
line 2: revise as ....of DOAS retrieval (active or passive), or alternatively as ... of (active or passive) DOAS retrieval.
line 6: change VIS to Vis
lines 7-8: change -law to -Law $\times 2$
line 13: change a trace gases to various gases
line 15: change e.g. to such as
line 18: change amount to amounts
line 25: add the ...lead to small errors in THE determination of the strong...

Page 4198
line 1: repetition of word DOAS not required, I would cut it in the following passage...active and passive (DOAS) instruments
line 2: ...artificial OR natural light sources...
line 3: remove comma (,respectively)
line 3: change star light to starlight
line 3: GENERAL POINT: throughout the text the authors often omit a word (e.g. one or

us) when phrasing a sentence like this: Active DOAS instruments allow to compare spectra.... it should be something like: Active DOAS instruments allow ONE to compare spectra....
line 4: replace passes with passed
line 6: ...due to the necessity of THE stable deployment of A light source (or A...THE)
line 7: ...as well AS
line 11: ...without THE necessities OF an additional emitter and reflectors.
line 13: change ground based to ground-based
line 14: Are car traverses using MAX-DOAS? If so, include it in the brackets ...balloon, ships and car traverses)??
line 15: Why is this a separate paragraph? I would include it at the end of the last paragraph??
line 15: ...overview OF different DOAS...
line 22: change interference to interferences
line 23: I suggest replacing involves with introduces
line 23: ...incorporating THE strong absorption...
line 25: cut e.g.
line 27: ...IN the presence of higher aerosol...
line 27: You did not state in implicitly in your text, but I assume that you did not consider cloud effects in this paper??

Page 4199
line 1: change RCS to RCSs. Moreover, the retrieval....
line 4: ...the problem only A few attempts...
line 4: Can you provide some references for these attempts here or maybe just refer to Table 1?
line 6: ..the retrieval wavelength ranges APPLIED are only motivated by a SINGLE comparison TO ONE other retrieval wavelength range.
line 9: This is illustrated IN..
line 10: change which to THAT... (BrO) that have been used in the past. (just so you are not repeating which in the same sentence)
line 13: ...one wonders whether A total of ....
line 16: ...systematic studies ON the retrieval...
line 18: replace ground based with ground-based
line 22: ... only two, relatively weak, ...
lines 24-25: The results of this study (Do you mean Theys et al. 2007 or Aliwell et al. 2002? I think you mean Aliwell et al., right?)
line 25: replace different with ANY
lines 26-27: ...time difference between THE measurement of THE...
line 28: Again, do you have any references or maybe refer to Table 1??

Page 4200
line 3: ... we introduce a novel tool THAT is suitable FOR systematically and quantitatively

studyING the ....
lines 10-11: I would re-word this sentence as follows: ....of THE results for a large set of evaluation wavelength ranges and offerS an intuitive tool FOR showING how certain....
line 22: cut (the subsequent)
line 23: ..concluding remarks in Sect. 6.
GENERAL POINT: At times there is a overload of bracketed material. It often makes the text harder to read. I have made suggestions such as in line 23 to limit the use of brackets in your text for this reason.

Page 4201
line 7: ...and allows US to study...
line 8: replace E.g., with For example, or For instance, ... interval dependency of:
line 13: THE influence of instrumental...
line 14: THE dependency of ...
line 15: I_0-effect and Ring effect (keep spelling constant)...passive DOAS...
line 23: The PLOTTED results are ...
line 23-24: either use colour-coded or colour coded (keep spelling constant)
line 25: The resulting maps allow ONE to ...

Page 4202
line 1: ..to A greater variability of THE retrieved values...
line 11: no comma needed (, respectively)
line 13: ... is apparent. In a first ....
line 14: ... they yield results THAT DEVIATE quite strongly from the true value, WHILE others....
line 19: THE computational...
line 20: All individual maps SHOWN ...
line 21: ... within 30 minS for THE given wavelength evaluation ranges....
line 22: ... this novel tool allows ONE to give a ...
line 24: IN THE TITLE -recommend changing at to FOR line 25: ...of the method described above...
line 26: ...stratospheric BrO...

Page 4203
line 3: ...allowing ONE to study...
line 4: ...neglected. The most important of these is the Ring Effect...
line 10: ...This IMPOSES certain limits on extending (applying) the results from the synthetic measurements studied to spectra measured in the field. (Is this what you mean??) I would re-word the sentence as above or something to that effect.
line 11: The prime focus OF this study..
line 17: replace RCS with RCSs
line 18: sunlight

line 23: ...multiplied BY the respective
line 25: ..according to THE Lambert-Beer Law:

Page 4204
line 4: ...This allows ONE to ...
line 6... cut out THUS
line 12: ..Lambert-Beer Law...
line 22: I_0-effect
line 26: ...effort IF applied to ...

Page 4205
line 3: ground-based
line 6: possibly cut e.g. Is it needed?
line 8: ...are the strong O_3 absorption structures ENCOUNTERED at ...
lines 10-11: change to balloon and satellite (no capitals required) ... in THE limb-viewing direction...
line 11: RCSs
line 15: ... AT higher resolution...
line 20: Since BrO's optical density...
line 23: ..seen in results presented later ...

Page 4206
line 2: The Fraunhofer REFERENCE spectrum...
lines 3-4: I understand what you mean but I would re-phrase this sentence to make it more clear, something like this: ...and it is assumed to be taken in close proximity in time with measurements at the lower elevation angles, and thus...
line 7: cut comma (, both)
line 10: cut e.g.
line 12: cut e.g.
line 19: Possible....HCHO must ALSO be taken into account due to THE similar..
line 20: ...and optical density ENCOUNTERED.
line 22: ..to allow FOR...
lines 24-25: A set of .....ARE APPLIED.

Page 4207
line 1: replace fitted with FIT
line 2: add a comma: ... , instead...
line 3: wavelength-pixel mapping
line 4: between THE Fraunhofer reference
line 5: cut e.g.,
line 7: THE stability of...
line 8: RCSs ...spectra

line 14: WITH which..
lines 15-16: This test ALSO..
line 19: Beyond (STUDYING)..
line 21: ... to small variations IN the amount of ...
line 24: replace ...are depending... with DEPEND

Page 4208
line 1: ...cross correlations. The original sets of...
line 2: replace fitted with FIT
line 3: ..of THE retrieved...
line 4: ...expressed as:
line 9: ...range (RELATIVE) to changes...
line 10: ...estimated by:
line 15: ...are resulting from: (1)....

Page 4209
line 5: ...to an optical density of 3×10^{-4}
line 7: you should not start a sentence with a number... Reword (for example)...Iterations of 10 and 50 correspond...
line 9: For one BrO absorption band with an average FWHM of 1.5 nm....
line 12: remove comma (, respectively)
line 15: RCSs
line 20: ..scenarios OF zenith..

Page 4210
line 4: ...In THE case...
line 9: replace an with A (...A lower limit of ...)
line 10: ...can be MAINLY attributed TO A slightly ERRONEOUS...
line 19: ...the results DEPEND mostly on...
line 19: This AGAIN is ...
line 20: ... OF the influence ...
line 21: replace (are decreasing) with DECREASE
line 22: ...CHANGE WITH THE retrieval wavelength interval INCLUDING THE BrO..
line 24: (cut the example of) and replace with: ...and residuals at three different wavelength ranges...
line 25: cut (both)

Page 4211
line 1: ...and THE use of ...
line 4: replace than with ASIDE FROM
line 6: replace test with TESTS ... Aliwell et al. (2002), ...
line 7: ...both in the retrieved BrO SCDS and shapeS of THE residual.

line 12: .. ,otherwise the retrieval...
line 20: ...WITH a lower limit...
line 28: The differences SHOWN ...

Page 4212
line 1: replace are resulting with RESULT
line 3: ..cross correlation of absorption cross sectionS..
line 4: ...varying THE NO_2 SCD ...
line 11: ...Indications OF THIS...
line 28: ...regardless OF WHETHER the RCSs are corrected for the I_0-effect OR NOT.

Page 4213
line 4: ...spectra exhibit wavelength DEPENDENT structures...
line 5: .. systematic wavelength DEPENDENT...
line 6: (more the word also) ... are ALSO more apparent ...

Page 4214
line 17: cut whereas
line 26: ... to THE different absorbers THAT interfere the most with the BrO....

Page 4215
line 1: cut ,e.g., It shows that the observed....
line 2: ..between THE RCSs ...
line 15: deviationS
line 19: I think you are referring to Fig.10. here not Fig. 11.?

Page 4216
line 7: THE area...
line 8: ..between THE lower limits of...

Page 4217
line 1: ...THE amplitude..
line 25: .. the zenith-sky DOAS SCENARIO).

Page 4218
line 19: ... wavelength DEPENDENT..
line 23: ..the RCSs...
line 24: change depending to DEPENDENT
line 25: cut , e.g.,
line 26: DEPENDENT
line 27: Ring Effect (be consistent)
line 27: .. in THE case of passive measurements. ONE SUCH example IS THE cross corre-

lations...

Page 4219
line 7: ... these findings ALSO remained true...
line 13: change ..are present to WERE present
line 16: ... appear to DEPEND on ... (or to be dependent on)
line 16: replace by the with DUE TO THE

Page 4220
line 7: ... THE least dependency..
line 13: I would replace about with $\sim$ OR rephase as: due to a total O_3 SCD that is about 100 times weaker.
line 25: ...order to advise ONE ON choosing a specific retrieval...

Page 4221
lines 4-6: (e.g. instrumental features...radiative transfer.) or replace e.g. with SUCH AS,
line 6: Previous publications WERE motivated by the COMPARISON of the applied retrieval wavelength interval WITH typically one ....
line 15: THE best values of THE resulting SCDs.
line 16: replace e.g. with SUCH AS, ...THE effect...
line 17: ...errors in THE I_0 correction, ...
line 22: replace where as with WHEREAS
line 25: ..I_0-effect...

Page 4222
line 6: cut E.g. and use For example, for certain measurement...
line 8: reference spectra
line 9: nighttime
line 11: FOR the example...
line 19-20: ....corrected and uncorrected RCSs ARE DISCUSSED.

Page 4223
line 2: why do you say white colour code? I would cut out white since other colours are present in deviations up to $\pm 1\%$? line 13: ...errors due TO NO_2 BECOME more pronounced...
line 14 ..increasES AND an overestimation of SCD occurs (see Fig. 13).
line 17: cut thus
line 25: replace at with UNDER

Comments for the Figures

Fig. 1. CAPTION...Deviations from the true BrO SCD are displayed on A logarithmic colour-coded scale.

Fig. 2. CAPTION: remove comma (, respectively).....WITH AN amplitude of 3×10^{-4}.

Fig. 3. CAPTION: ...for THE measurement scenario.....with THE uncorrected RCSs.....

Fig. 4. FIGURE: On the left hand side of the figure for case 9 you have the range listed as 345-359 nm, I believe this should read 346-359 nm, according to your text??

Fig. 4. CAPTION: Shown ABOVE ... The fit of THE BrO RCS and the residuum ....Regardless OF which...

Fig.5. CAPTION: ...zenith-sky DOAS scenario. Changes in .....the strong O_3 absorptions are CLEARLY dominating...

Fig. 6. CAPTION: ...on THE zenith-sky DOAS measurement scenario....on THE noise applied...THE second till fourth column depict..and calculated correction factorS USED to retrieve..

Not sure about your wording for the correction factor here? Do you mean: ....and calculated correction factor (defined as the standard deviation divided by the fit error)....

Fig. 9. CAPTION: Fit examples FOR selected...

Fig. 9. FIGURE: On the left hand side of the figure for case 9 you again have the range of 345-359 nm, I believe this should read 346-359 nm??

Fig. 13. CAPTION: ...from the true SCDs of trace gases OTHER than BrO in test I of THE measurement scenario OF volcanic plumes...

Comments for the Tables

Table 2. CAPTION:replace Zenith with zenith.

Table 3. CAPTION: ...absorption CROSS SECTION multiplied BY the respective SCD...