Review of

iFit: An intensity-based retrieval for SO_2 and BrO from scattered sunlight ultraviolet volcanic plume absorption spectra

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General Remarks

This manuscript describes a new method for retrieving column densities of certain atmospheric trace gases from the spectral intensity of scattered ultraviolet radiation falling through them. It is very similar to the well-established technique of Differential Optical Absorption Spectroscopy (DOAS), but differs slightly in that the spectral measurements are described by a forward model in intensity space rather than optical depth space. As is the case for DOAS fits, the model parameters are iteratively adjusted in a fit routine until the best match between forward model and measurement is obtained. The parameters for which this best fit is obtained are considered the best estimate of the atmospheric state, which includes the trace gas column densities.

There are several novel and very innovative ideas presented in this paper. For one, the authors show that, for spectrometers typically used in volcanic gas measurements, the sensitivity of the individual CCD pixels to incident radiation varies by several percent. This is not unexpected but has not been studied in great detail because it was thought that this effect cancels out in conventional DOAS fits because the spectra are always compared to a reference measured with the same instrument. While this is true in first order approximation, the authors correctly note that most DOAS retrievals do allow for a small shift and/or squeeze of the spectrum when compared to the reference to account for temperature-induced changes of the spectrometer calibration, thus foiling the ‘canceling out’ of the variable sensitivity.

The authors go on to show that it is actually possible to model the collected moderate resolution UV spectra using a high-resolution solar reference spectrum collected with a different instrument of much higher resolution. The concept here is quite similar to the standard practice of convolving and down-sampling reference absorption cross-sections of trace gases measured with high-resolution spectrometers in the laboratory. From a practical standpoint, this is a very useful application as it eliminates the need for recording ‘clear sky’ reference spectra, at least when an intensity precision of a couple of percent is sufficient, for example when measuring volcanic plumes with more than 20 ppm.m of SO_2 in the measured column.

On the other hand, a few of the concepts discussed in the manuscript appear flawed or at least unclear. For one, the authors put a lot of emphasis on the fact that the iFit procedure performs the spectral fit in the intensity space as opposed to the optical depth space. To me, this seems to be a more or less arbitrary choice and it remains unclear why one is advantageous over the other. Performing the fit as is conventionally done in optical depth space requires converting the measured intensity spectra to optical depth by taking the logarithm. But performing the fit in intensity space first requires converting the column densities of the retrieved trace gases to intensity space by taking the exponent. I do not see a computational advantage here, except in the case of strong absorption (see specific comments below) and though the ability to take non-linear radiative transfer effects into account is hinted at, there's no way to assess the merits of this claim without a better description of the actual process.

It appears to me that the fit itself is not as different from the conventional DOAS method as the manuscript makes it sound. The paper lacks a mathematical formulation of the fit procedure. Given that the manuscript is focused on the iFit methodology, this is clearly needed. Once explicitly formulated, it will become clearer what the exact differences are between iFit and the conventional DOAS method. In fact, it would be good to do a side-by-side comparison of the two, both in theory and in application. Also, a significant number of additional references are required throughout, most of which are given by Reviewer 1.

The discussion of errors remained unclear to me. The measurement errors refer to the uncertainty of the retrieved trace gas column densities. If the fit is performed in intensity space, then the fit errors would refer to errors in measured intensity, not SO_2 column density. In this point the iFit approach seems like it might be at a disadvantage when compared to the conventional DOAS fit, where errors in optical depth are linearly related to errors in the retrieved column density. Also, the actual measurement error seems not to be defined by the noise, but rather dominated by the inaccuracy of the procedure, as evidenced by the dependency of the results on the lower limit of the fit window.

In conclusion, there are a number of interesting concepts introduced in this manuscript. However, the main focus of the manuscript is the fitting in intensity space (iFit) which is not described well enough to ascertain where its strengths truly lie. Is it really so much different than conventional DOAS? In which cases is it different? When is one method better than the other? All of these questions remain unanswered.

Specific Comments

L83 – The authors state that the broadband component of scattering and absorption is removed in the DOAS approach. This is not necessarily true. Many modern DOAS retrievals do not high-pass filter the absorption cross-sections, and instead include a polynomial (typically order 3 – 5, see Eq 4 below) in the optical depth fit to account for broadband changes in light transmittance. It is true that the information captured by this polynomial is usually not used for future analysis, and in that sense it is simply used to 'remove' the broadband component. However, the polynomial parameters essentially contain the exact same information as those of the iFit polynomial. I don't see a fundamental difference in the retrievals here, unless the authors can show how the iFit polynomial can be used in a way that the DOAS polynomial cannot be.

L99 ff – The DOAS approach described here is one very specific implementation of a DOAS fit that does indeed remove the broadband component from the spectra before applying the fit. However, this is not a common methodology. It's probably best to refer to Platt and Stutz (2008) for the common DOAS fit. Their section 8.3 is titled "DOAS Analysis Procedure". Here they describe the following method:

Starting from the Beer-Lambert-Law

$$I = I_0 \cdot e^{-\tau} \qquad \text{Eq 1}$$

where I is the measured intensity ('plume spectrum'), I_0 is the initial intensity ('clear sky' or Fraunhofer spectrum), and τ is the optical depth:

$$\tau = -\sum_i \sigma_i \cdot S_i + \varepsilon_R + \varepsilon_M \qquad \text{Eq 2}$$

Here, σ are the absorption cross sections, S are the column densities, and ε are the extinction coefficients for Rayleigh and Mie extinction.

The Beer's law can be conveniently rewritten as

$$lnI = lnI_0 - \tau \qquad \text{Eq 3}$$

A common forward model used in DOAS actually uses this equation and attempts to reproduce the logarithm of the measured 'plume spectrum' with a linear model:

$$lnI \approx lnI_0 - \sum_i \sigma_i \cdot a_i + R + P_\lambda \qquad \text{Eq 4}$$

Here, R is a Ring correction spectrum, a_i are forward model parameters that are varied to find a best match between model and measurement (these later give the respective column densities), and P_λ is a polynomial used to describe broadband structures. In this simple form, the polynomial will capture the same broadband structures that the proposed iFit polynomial would capture.

L119 ff – There are two main reasons why the simple DOAS method becomes inaccurate for strong absorption, but this is not one of them. DOAS does not assume a linear relationship between the optical depth τ and I_m/I_{sky}. Instead, DOAS assumes a linear relationship between τ and $\ln(I_m)$, or between τ and $\ln(I_m/I_{sky})$, as shown in Eq 3 above. This relationship holds true even for very high optical depths. No, the problem lies in two second-order effects:

1) The measurement is performed at insufficient resolution to fully resolve the absorption lines. In effect, the instrument convolves the absorption bands with the instrument line shape, and this occurs in intensity space. In cases of strong absorption, the absorption cross-sections used for the retrieval cannot simply be convolved in optical depth space (as shown in your Equation 5). More information can be found in Platt and Stutz (2008), section 6.7.2 Application of the DOAS Approach in Practical Situations, Case 3: Strong Absorbers at Low Resolution and a Smooth Light Source. Dealing with this issue does appear to be a little easier in intensity space, though the

model is still non-linear as the parameters we are interested in (the column densities) are still exponentially related to the measured intensity. The iFit might have a slight advantage in computational complexity here, since the computationally expensive convolution operation only needs to be performed once in each fit iteration, rather than separately for each individual absorption cross-section. But it is unclear how much this really improves processing speed. And this is only relevant for strong absorption.

2) In scattered light spectroscopy, the effective path that the radiation has taken on its way to the instrument becomes dependent on wavelength when strong absorption bands are encountered. At wavelengths of strong absorption, the effective path length is typically reduced as the probability for long paths is decreased. Neither the conventional DOAS nor the iFit approach can easily take this into account – at least it hasn't been shown in this manuscript.

L151 – 'Correct application of the DOAS approach requires all calculations of fitted spectra are first performed in transmittance…'. This is only true for strong absorbers. For weak absorbers, Eq 4 (above) provides a very simple model that is linear and thus much easier to solve.

L160 – iFit cannot take into account the wavelength dependency of the photon path length any more than conventional DOAS. At least you haven't shown how.

L163 ff– These three motivations are unclear to me. I agree that fitting the literature solar reference spectrum is advantageous, but this could easily be implemented in optical depth space too, or not? Fewer manipulations are better, but taking the logarithm is pretty straight-forward, and the iFit instead has to take the exponential of the absorption cross-sections, so which is better? The final point (regarding low spectral intensities at low solar zenith angles) is not clear to me. I think it can be avoided by implementing the conventional DOAS fit as described in Equation 4 above, right?

L 194 – What aspect of iFit is specific to Ocean Optics USB2000 spectrometers?

L204 – Can you give a reference for the combination of Gaussian and boxcar to describe the instrument line shape? How does the manual adjustment work?

L307-310 – It appears to me that the spectral resolution of the literature reference cross-sections could be important in the iFit approach. Are all these cross-sections measured at 0.01nm resolution or better?

L413 – 'The validity of the approach is demonstrated…' It is not clear to me that this is a valid statement. Since an average residual is being included in the fit, wouldn't one expect the result to be pure noise? What else could it be? Any processes not properly accounted for by the forward model are being removed by fitting the residual. Incidentally, the authors attribute the systematic structures in the residual to an imperfect solar reference spectrum, but there may also be other explanations. What about the presence of unknown trace gases in the boundary layer? Their absorption should also be approximately independent of solar zenith angle.

L503 – '…successfully included all features…'. Yes, this will always be the case if the residual is included in the fit, right?

L509 and figure 5 – It appears that the y-error (plotted on the vertical axis in figure 5) was calculated by dividing by a boxcar smoothing rather than a polynomial fit as was previously mentioned in the manuscript. Either way, I don't understand why the y-error would change. Shouldn't it be the same, regardless of which fit method was used? But the figure indicates lower y-errors for the 'flat removed' and 'residual removed' fit methods when compared to the basic iFit. Please explain.

L552 and figure 9 – What do you mean by 'the empirical precision'? Is that the precision derived from the measurement noise? Somewhat alarmingly, there appears to be a 25% difference in retrieved SO_2 columns when moving the lower fit limit from 305 to 314 nm. Where does this come from? I wonder if it might be caused by inadequate correction of stray light in the spectrometer. I can think of no other explanation why this would occur. What does this look like for a conventional DOAS fit?

L595 – 'the quality of the fit is limited by measurement noise…'. What does this actually mean? The fit precision? The measurement accuracy seems to depend quite severely on the lower wavelength of the fit window. This statement seems to imply that the quality of conventional DOAS fits is in some way compromised, but this has not been shown in the manuscript, except perhaps in the case of strong absorbers (but there are known solutions to this problem too, see reference above to Platt and Stutz 2008).

L599 – 'Intensity-based retrievals also allow direct characterization of aerosol/ash absorptions and accurate modeling of light dilution effects…' This was not shown in the manuscript, so the statement is impossible to asses. However, I cannot see any clear advantage of the iFit in these respects, other than perhaps a slightly easier implementation, but this is probably a marginal benefit at best, and was also not shown in the manuscript.

L603 – I would argue that the 'flat correction' and use of a literature solar spectrum open up new possibilities, not the fitting in intensity space. Flat correction and ensuing use of the Kurucz spectrum are very good ideas indeed!

L655 – The polynomial actually takes into account more than just aerosol absorption – it accounts for Rayleigh scattering, aerosol scattering, aerosol absorption, broadband absorption of unknown trace gases and broadband changes in the spectral sensitivity of the instrument.

L657 – Given the previous comment, it is really unclear how this polynomial will be used to characterize interference in SO_2 camera measurements. Please explain or omit this point. Also give a reference for the SO_2 camera technique. Also apply your changes to L687.

Minor issues

L 16 – The iFit fitting procedure could be useful in a wide range of applications. Perhaps it's better to say that volcano monitoring is just one of many potential applications.

L28 – Again, this could probably be applied to trace gases other than SO_2 and BrO too.

L43 –The USB2000 spectrometer is a specific model made by Ocean Optics. While it may have been the first such miniature spectrometer, there are now many others on the market, so it is probably best to avoid using a single make and model throughout the manuscript.

L81 – Include a reference for 'light dilution', e.g. Kern et al 2009

L 197 – I think the FLYSPEC doesn't use a fiber. This is not a requirement in any case.

L216 – The dark current also may contain 'hot pixels' that may not be insignificant.

L221 – What happens if the bias level falls below zero?

L235 – This assumes that the stray light is constant across the detector. Is it? I think some people use a first order polynomial, but I'm not sure which approach is better.

L301 – Please rephrase this sentence. I know what you mean, but it's misleading because the Ring effect is not related to the absorption processes responsible for the structured solar spectrum.

L304 – Please give a reference for your method of deriving the Ring correction spectrum.

L324 – 'Gas amount'. I think you mean column density?

L327 – This description of the fit method is still a bit unclear. How is the polynomial actually calculated? I assume the polynomial parameters are included as variable parameters in the fit? Please add an explicit, mathematical description of how the forward model as well as the procedure for each fit iteration.

L446 – 'The CCD sensor…' This paragraph repeats information given earlier on in the manuscript. Consider removing.

Figure 1 – The figure caption indicates that boxcar smoothing was used to normalize the spectra, not polynomial fitting as mentioned in the text.

Concluding remarks

Three important things are really missing from this manuscript:

1) an explicit mathematical description of the forward model and the iFit iterative method
2) a comparison to conventional DOAS methods such as the one given in Eq 1-4 above
3) a discussion of the advantages and disadvantages of the two methods, and a description of the situations in which one may be better than the other.

In its current state, the manuscript has not convinced me that the iFit approach is superior to conventional DOAS. It appears that there might be some advantages in cases where strong absorption is encountered, where the convolution of absorption cross-sections cannot be performed in optical depth space. In cases of weak absorption, however, the conventional DOAS fit seems advantageous because the model for describing ln(I) is linear, so the fit is linear (except when adding a spectral shift and squeeze, but Beirle et al (2013) describe a way to linearize even this problem).

Also, it should be noted that neither iFit nor conventional DOAS take into account the effect of variable light path length due to radiative transfer issues. For this, one would still need a fit coupled to a radiative transfer model such as described by Yang et al (2010) or Kern et al (2012). Several sections of the manuscript are misleading in this point.

The concept I found most interesting in this manuscript is the correction of the variable sensitivity across the detector with a 'flat spectrum', and the resulting ability to fit a reference solar spectrum from literature rather than a measured Fraunhofer spectrum. This concept would be widely applicable to absorption spectroscopy of the atmosphere. However, couldn't one argue that this technique can just as easily be applied to a conventional DOAS fit as it can to iFit if one simply puts the logarithm of the literature Fraunhofer reference into Eq 5 as $\ln(I_0)$? In any case, these concepts are novel and actually quite useful, so I recommend that the manuscript be reconsidered for publication in Atmospheric Measurement Techniques once the aforementioned concerns are addressed.

References

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Kern C, Deutschmann T, Vogel L, Wöhrbach M, Wagner T, Platt U (2009) Radiative transfer corrections for accurate spectroscopic measurements of volcanic gas emissions. Bull Volcanol 72:233–247. doi: 10.1007/s00445-009-0313-7

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