Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2015-380, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 18 January 2016

Atmospheric Measurement Techniques Discussions

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

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Abstract

iFit is a new intensity-based retrieval algorithm for direct fitting of measured UV spectra, specifically developed for use in volcanology. It has been designed with a focus on minimising processing of the measured spectra prior to analysis. Here, we report a detailed presentation of the iFit algorithm, and test it in 4 case studies, examining clear sky spectra, SO_2 calibration cell experiments and volcanic SO_2 and BrO retrievals from traverse measurements performed on Mt. Etna volcano, Italy.

We show that the major source of fit error in the intensity fitting come from air mass factor independent solar spectrum errors, which are, however, easily characterised and removed by dividing the measured spectrum by a pre-calculated solar spectrum residual. Furthermore, we have quantified the magnitude of the flat spectrum in two spectrometers, and shown that this spectrum is strongly spectrometer dependent but temperature independent, opening the possibility for robust analysis and quantification of both SO_2 and BrO without the need for temperature stabilisation of the spectrometer.

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2015-380, 2016
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Published: 18 January 2016

We find that iFit can be robustly and easily applied to traverse measurements of volcanic plumes, producing bias-free profiles of SO_2, and high quality SO_2/BrO ratios without the need for clear sky background spectra. Fit residuals are typically pure instrumental noise when the residual solar spectrum is removed.

We believe that the iFit approach, which avoids the need for a clear sky spectrum and which achieves noise-limited fits, is ideally suited to the automated analysis of spectra produced by networks of scanning UV spectrometers around volcanoes.

Keywords: SO_2, volcanic gas, DOAS, UV spectroscopy, iFit

1. Introduction

The introduction of the USB2000 spectrometer (Galle et al., 2003) revolutionised the measurement of SO_2 fluxes in volcanology. The direct measurement of a spectrum allowed much more sophisticated analysis compared with the "black box" of the previously used COSPEC (Stoiber and Jepsen, 1973). Analysis of USB2000 spectra using differential optical absorption (DOAS) techniques (Platt and Stutz, 2008) rapidly became the standard approach for retrieval of SO_2. The detection and quantification of BrO in USB2000 spectra using the DOAS technique (Bobrowski et al., 2003) further cemented the association between the instrument and the retrieval approach, such that many groups began referring to the instrument by the analysis technique, e.g. mini-DOAS spectrometer. The flexibility of the USB2000 spectrometer and associated optics opened the possibility of arrays of scanning spectrometers arranged around volcanoes, permitting automatic, real-time monitoring of SO_2 fluxes. This led to the installation of such networks, first on Montserrat

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2015-380, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 18 January 2016

Atmospheric Measurement Techniques Discussions

(Edmonds et al., 2003), then on Etna and Stromboli (e.g., Burton et al., 2009; Salerno et al., 2009a, b), and later on over 20 volcanoes worldwide as part of the NOVAC project (Galle et al., 2010).

In this work we present a novel retrieval methodology for volcanic SO_2 and BrO from UV spectra, which we call "iFit" for intensity-fitting. We use an intensity-based approach in which we attempt to directly simulate and fit the measured spectrum as it is, with very limited manipulation of original data. The forward model is capable of calculating a UV spectrum from first principles, following the physical processes arising from radiative transfer and instrumental effects which produce the measured spectrum. The main initial motivation for the development of this approach was to avoid the requirement of the DOAS methodology of a measured 'clear-sky' reference spectrum, which can at times be impossible to measure from a fixed array because the plume is so wide that no clear sky spectra are available. Performing a DOAS analysis with a reference spectrum which includes an unknown amount of SO_2 results in an unknown bias in the measured SO_2 amounts; on the contrary, our approach does not require a measured reference spectrum, and therefore we can be confident systematic biases in SO_2 content are not present. In other words, using iFit we can be sure zero is actually zero on our SO_2 scale.

Apart from the advantages of a calculated clear-sky spectrum, there are also several inherent advantages of an intensity-based technique. These include automatic inclusion of the I_0 effect (Aliwell et al., 2002), thanks to a high resolution version of the solar spectrum. The intensity retrieval also allows quantification of the broad absorption produced by the presence of particulates. Furthermore, inclusion of light-

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2015-380, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 18 January 2016

Atmospheric Measurement Techniques Discussions

dilution effects is direct, and this will be investigated in more detail in a future paper. Finally, as we show in the case studies below, the SO_2 absorption itself has a large broadband component that is removed in the DOAS approach, but which contains useful information that aids in the intensity fitting procedure.

In the following sections we briefly review the DOAS approach, and describe a hybrid retrieval which is currently in use on Etna and Stromboli scanning networks. We then explain the iFit methodology in detail. We present case studies from clear sky spectra, calibration cell spectra and traverse measurements on Mt. Etna (Sicily, Italy). We then discuss the results from the case studies and conclude by examining new frontiers which are opened using the novel retrieval technique.

2. Volcanic Plume SO_2 and BrO Retrieval Methodologies

The most widely used volcanic plume SO_2 and BrO retrieval methodologies are based around the DOAS technique (Platt and Stutz, 2008). The DOAS technique consists of taking a measurement spectrum and a clear sky spectrum and dividing them to produce a transmittance spectrum. This is then converted to optical depth by taking the negative natural log of the transmittance. The optical depth spectrum is then normalised by dividing with a smooth polynomial fitted to the optical depth spectrum:

$$\text{DOAS spectrum} = (-\ln(I_m/I_{sky})) \,/\, poly[-\ln(I_m/I_{sky})] \qquad 1.$$

Where I_m is the measured intensity spectrum, I_{sky} is the measured clear sky spectrum and *poly*[] is a polynomial fit.

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2015-380, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 18 January 2016

Atmospheric Measurement Techniques Discussions

The resulting spectrum is therefore a differential optical depth spectrum, hence the DOAS name. By applying the same normalisation to calculated optical depth spectra the DOAS spectrum can be simply and, for weak lines, linearly fitted. Differential optical depths significantly greater than 0.1 demonstrate a non-linear relationship with increasing gas amount due to Beer's law:

$$t = I_m/I_{sky} = \exp(-\tau) = \exp(-\text{path\_amount} \,.\, \text{absorption coefficient}) \qquad 2.$$

where τ is the optical depth, and t the transmittance. The Taylor expansion of $\exp(-\tau)$ is

$$1 - \tau + (\tau^2/2) - (\tau^3/6)\ldots \qquad 3.$$

So it is clear that when τ is less than ~0.1, $(\tau^2/2)$ and higher orders are small and $\exp(-\tau)$ approximates to the linear relationship $1-\tau$. SO_2 abundances in volcanic plumes are often significantly greater than 0.1, and therefore more sophisticated techniques are required.

In order to accurately calculate optical depth spectra to fit to the measured DOAS spectrum we must first take account of the instrument lineshape (ILS) of our spectrometer, if the resolution of the spectrometer is too low to fully resolve the natural absorption lines, which is typically the case. Since raw spectra are measured in intensity, the convolution of the ILS with the measurement must also be performed in terms of intensity. Therefore, the correct procedure for the calculation of optical depth spectra to be fitted to the measured DOAS spectrum is to calculate a transmittance

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2015-380, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 18 January 2016

Atmospheric Measurement Techniques Discussions

spectrum by multiplying an absorption cross-section of the desired gas with the estimated gas amount in the spectrum, convolve this transmittance spectrum with the ILS, convert to optical depth by taking the negative natural log and then normalise with a fitted polynomial:

$$gas\_\tau = -\ln(ILS \otimes (\exp(-amt.xsec))) \,/\, poly[-\ln(ILS \otimes (\exp(-amt.xsec)))] \quad 4.$$

Where gas_τ is the calculated optical depth spectrum to be used in the DOAS fit, ⊗ represents a convolution, amt is the path amount of gas, and xsec is that gas's absorption cross-section.

It is important to note that:

$$-\ln(ILS \otimes (\exp(-amt.xsec.n)) \neq n.(-\ln(ILS \otimes (\exp(-amt.xsec))) \quad 5.$$

Where n is an arbitrary multiplication factor. In other words, when the gas amount changes a new transmittance spectrum must be calculated and reconvolved with the ILS; simply multiplying the optical depth spectrum by a factor will not produce the same, physically realistic, result.

It is therefore clear that the correct application of the DOAS approach requires that all calculations of fitted spectra are performed first in transmittance (intensity) and then converted to optical depth each iteration. The question we pose is: if we are performing the calculations of transmittance in terms of intensity, why not perform the fit in terms of intensity as well?

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2015-380, 2016
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Published: 18 January 2016

Atmospheric Measurement Techniques Discussions

Direct fitting of measured intensities is, in fact, frequently used for analysis of UV spectra. The Global Ozone Monitoring Experiment (GOME) is analysed with such a method (Van Roozendael et al., 2012). In their analysis they find significant advantages for the direct fitting approach over DOAS, which neglects the wavelength dependency of the photon path length, producing misfits in ozone retrievals.

We chose the direct fitting approach of iFit for three main reasons. Firstly, it avoids the requirement for a clear sky spectrum, thus greatly enhancing the flexibility and applicability of the retrieval. Secondly, in principle the fewer manipulations (i.e. converting to optical depth) of the raw spectrum the better, as with each manipulation there is the possibility to introduce errors. Finally, since the SO_2 fit is performed on the edge of a strong ozone absorption band there are low intensities at low solar zenith angles. In the DOAS approach this can lead to very large numbers in the DOAS spectrum, as clear sky spectra contain numbers close to zero. In the direct fitting approach there is no such division by small numbers, and the low intensity is manifested as an easy to manage increase in noise levels.

The DOAS retrieval is used both by NOVAC (Galle et al., 2010) and in the recently published SO_2 retrieval suite by Kantzas et al. (2012). In both cases clear sky spectra are required, limiting their applicability.

A hybrid direct-fitting DOAS approach was developed for the analysis of UV spectra collected with the FLAME (Flux Automatic MEasurement) network on Mt. Etna and Stromboli (Salerno et al. 2009a, b). This worked in differential optical depth, but

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2015-380, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 18 January 2016

included the Fraunhofer spectrum in order to avoid the need for a clear sky spectrum. The retrieval was investigated thoroughly and judged to be suitable for the automatic analysis of UV spectra produced by the FLAME networks (Salerno et al, 2009b).

Here we show that a fully direct intensity fit can produce robust results without the need for clear sky spectra. In the following sections we describe the iFit retrieval in detail, and apply it to several case studies, demonstrating its potential in the field of volcanology.

3. The Ocean Optics USB2000 and USB2000+ spectrometers

While the iFit retrieval can in principle be applied to any UV spectrum, it has been developed with a specific focus on analysing spectra produced by the Ocean Optics (www.oceanoptics.com) USB2000 family of spectrometers. These spectrometers are currently the default tool for volcanologists measuring SO_2 fluxes, thanks to their reasonable cost, robustness and ease of use. The spectrometers are illuminated with a fibre optic cable connected to a quartz collimator. Light enters the spectrometer through a vertical slit and illuminates a diffraction grating. The wavelength-sorted light then passes through focussing elements and optional filters before being detected with a 2048-element horizontal CCD. Three elements of this system are of particular relevance for the iFit retrieval. Firstly, the form of the instrument lineshape (ILS) is determined by the entrance slit, and can be modelled through a combination of a Gaussian-boxcar combination, with greater boxcar contribution with increasing slit width. The slit width is fixed when the spectrometer is manufactured, and there are a variety of different widths available, from 25 micron to 200 micron. Accurate

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2015-380, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 18 January 2016

Atmospheric Measurement Techniques Discussions

representation of the ILS is essential for producing good quality fits. This is achieved in iFit by directly fitting the width of the ILS during the retrieval, and manually adjusting the relative weight of Gaussian and boxcar forms until optimal fitting is achieved.

The second group of critical instrumental effects that must be addressed are dark current, bias and stray light. From the moment that charges are read out from the CCD, emptying the charge wells, electrons begin to accumulate at a rate which is both pixel-dependent and temperature dependent. This signal is called the dark current, and it is a ubiquitous process, continuing whether the CCD is illuminated or not. In typical well-illuminated situations the dark current is insignificant (less than 1 part per mil) compared with the measured signals, but in poorly illuminated cases it can become significant. The bias signal is the nominal 'zero' intensity level for the CCD, and is determined by the CCD electronic configuration and temperature. On the USB2000 spectrometers the bias level is inversely proportional to temperature, and at high temperatures the bias level may even fall below zero. For a thermo-stabilised instrument the dark current and bias can be removed from measured spectra by subtracting a dark spectrum, which is collected with the same exposure time and number of coadds as measured spectra, but with the CCD unilluminated.

Stray light can be produced by any photons which are scattered within the body of the spectrometer, producing a close-to-flat offset in addition to the bias. This effect can be greatly reduced through the use of a short-pass filter, which eliminates wavelengths greater than those required for SO_2 and BrO retrievals, typically those longer than 400 nm. USB2000's can be ordered with such an optional short-pass filter. In practice, the

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2015-380, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 18 January 2016

Atmospheric Measurement Techniques Discussions

effect of stray light is observed as a residual positive offset in parts of the spectrum in which no light should be present, below 300 nm. It is therefore essential to include ~20 nm of the spectrum below 300 nm when specifying the USB2000 spectrometer in order to correctly characterise the stray light signal. It can then be removed by taking the average of a section of the unilluminated spectrum below 300 nm and subtracting this value from the whole spectrum.

The third instrumental effect of note is the flat spectrum, produced by small pixel-to-pixel variations in the conversion rate of photons to electrons in the CCD array. We have characterised this effect by illuminating a spectrometer with broadband light from a deuterium lamp (Ocean Optics model DT1000) and dividing the resulting spectrum with a polynomial fit. The amplitude and structure of the flat spectrum varies significantly from one spectrometer to another but for a given spectrometer it appears to be temperature independent (Figure 1). Note that when a measured clear sky spectrum is used in the DOAS approach the flat spectrum is automatically removed. Instead, for iFit it must be accurately characterised, either via direct measurement or inclusion of the retrieval residual. Because it is pixel dependent it is not affected by wavelength shifts, and therefore may affect clear sky spectrum corrected DOAS retrievals if the spectrometer temperature changes after the clear sky spectrum is collected.

A final ubiquitous characteristic of CCD detectors is noise. There are two main sources of noise, read noise and shot noise. Read noise is produced upon read-out, amplification and analogue-to-digital conversion of the accumulated charge in each pixel of the CCD. Shot noise is an inherent characteristic of the particle nature of light,

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2015-380, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 18 January 2016

Atmospheric Measurement Techniques Discussions

with individual photons producing charge in each pixel. It follows Poisson statistics, and is therefore proportional to the square-root of the recorded digital counts. In well-illuminated situations shot noise dominates read noise in the USB2000. As we will demonstrate, the empirically derived measurement error is typically equivalent to the fit error, producing a fit residual which consists purely of instrumental noise.

4. The iFit algorithm

4.1 Pre-analysis procedures applied to the measured spectra

A specific objective of the iFit approach is to manipulate the measured spectra as little as possible, in order to avoid unintended side-effects in the retrieval. To this end the only procedures applied to the measured spectra prior to analysis were removal of the dark spectrum (if available), removal of the stray light effect, and division of the resulting spectrum by the previously measured flat spectrum (if available). Flat spectrum removal is performed in the pre-analysis stage because of the fixed pixel nature of the flat spectrum, which means it is unaffected by wavelength shifts, which are applied later in the forward model.

A final step in the pre-analysis procedure is to determine the measurement error (see section 4.5).

4.2 The iFit forward model

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2015-380, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 18 January 2016

Atmospheric Measurement Techniques Discussions

Armed with a thorough understanding of instrumental effects we may now consider the radiative transfer processes which control scattered sunlight spectra, and define the forward model which is used within iFit to simulate measured spectra.

Sunlight is the source of radiation in our ultraviolet spectra, and we must therefore take account of the absorption features in the Sun's emission spectrum, known as the Fraunhofer spectrum. In order to do this we use the 2005 FTIR-measured, atmosphere-corrected solar spectrum measured at Mauna Loa, Hawaii, USA reported by Kurucz et al. (http://kurucz.harvard.edu/sun/fluxatlas2005/). Some of absorption lines in the Fraunhofer spectrum are strong, practically black, and therefore we did not wish to smooth the spectrum before using it in our forward model, as this would eliminate important features in the final spectrum (this is in fact the source of the I_0 effect discussed by Aliwell et al., 2002). However, the Kurucz spectrum is two orders of magnitude high sampling frequency (grid spacing of 0.0013 nm) than our measurement spectrum (0.1 nm grid spacing), causing slow fitting if we perform forward model calculations on the Kurucz wavelength grid. We found by inspection that smoothing the original Kurucz 2005 solar spectrum with an 8 element boxcar and then interpolating onto a forward model grid with 0.01 nm spacing produced identical results as when we used the full Kurucz grid with no smoothing. With a 0.01 nm grid spacing the forward model ran at an acceptable speed on a modern desktop PC.

Closely related to the solar absorption spectrum is the Ring spectrum (Grainger and Ring, 1962), produced by inelastic molecular scattering. At low SZA's the Ring spectrum can be several percent of the spectrum, and must be accounted for. We use a

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2015-380, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 18 January 2016

Atmospheric Measurement Techniques Discussions

normalised inverse Kurucz 2005 solar spectrum to produce a Ring spectrum cross-section in the model.

Absorptions from gas species are accounted for using laboratory measured cross-sections. For all retrievals discussed here we include cross-sections for SO_2 (at 293 K: Bogumil et al., 2003), BrO (at 298 K: Fleischmann et al., 2003; 2004), O_3 (at 223 K: Voigt et al., 2001) and NO_2 (at 223 K: Voigt et al., 2002).

Wavelength shift and stretch were applied to the forward model, and therefore the forward model was calculated on a wider grid than the measured spectrum grid, with an additional 2 nm added to either end of the fit window limits.

The forward model calculation proceeds as follows. A model grid is created with 0.01 nm grid spacing and an additional 2 nm added at the start and end. The raw Kurucz 2005 solar absorption spectrum, smoothed with an 8 element boxcar, is interpolated onto this grid using cubic spline interpolation (this interpolation method is used throughout the forward model calculation). The Ring optical depth is then calculated as the normalised natural log of the interpolated solar spectrum. A Ring amount is multiplied with the Ring optical depth to produce a Ring transmittance. Absorption cross-sections for requested molecular species are also interpolated onto the model grid. The molecular cross-sections are multiplied with gas amounts to produce optical depth spectra for each species. The negative exponential of the optical depths produces transmittance spectra for each gas species. Finally a background polynomial of user-definable order is calculated.

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2015-380, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 18 January 2016

Atmospheric Measurement Techniques Discussions

The solar spectrum, Ring transmittance, gas transmittances and background polynomial are then all multiplied together to produce a raw spectrum, which in theory would be that observed if a perfect, infinitely high resolution spectrometer were used. However, because we are using an imperfect, relatively low resolution spectrometer we must now convolve the high resolution transmittance spectrum with a relatively broad ILS, which is calculated based on a variable resolution parameter and a fixed Gaussian to boxcar weighting (found by inspection). The convolved spectrum is then shifted and stretched onto the measurement spectrum grid. Thus, the measurement itself is never shifted, it is the forward model which adapts to the measurement.

4.3 Inclusion of a solar spectrum residual in the forward model

During analysis of scattered sunlight spectra we found that the form of the fit residual, (y-F)/y, where y is the measurement and F the forward model best fit, had extremely consistent structures, spectrum after spectrum. The cause of these structures was clearly not random noise, but rather the cumulative effect of systematic imperfections in the forward model, with the single greatest error source being the solar spectrum. Given the systematic nature of the residual features it was natural to attempt to average the residual for a few spectra to produce a low-noise residual spectrum and then divide subsequent measurements with the residual spectrum, together with the flat spectrum. This procedure worked well, and produced a quality of fit that was so close to the measurement spectrum that the final residual was pure random noise. We found that the quality of the fit did not degrade as a function of SZA, demonstrating that the main source of the residual features was independent of SZA, confirming the

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2015-380, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 18 January 2016

Atmospheric Measurement Techniques Discussions

hypothesis that the residual structures were produced by imperfections in the Kurucz solar spectrum.

The real challenge for iFit was therefore to be able to fit measured spectra with enough accuracy in the absence of a clear sky spectrum that we could obtain good solar spectrum residuals with a minimum of contamination from SO_2. As we show in the case studies this was achieved, with 1-2% fit residuals without using a solar spectrum residual. This limits the magnitude of SO_2 contamination to ~20 ppm.m.

4.4 Non-linear fitting of the forward model to the measurement

All retrieval procedures have two main elements, a forward model and an iterative algorithm which adjusts the parameters of the forward model in an efficient manner to achieve the best possible fit to the measured data. In the previous sections we have discussed the forward model, here we examine the second main element, the retrieval algorithm.

The approach taken was optimal estimation, which allows errors on both the forward model parameters and the measurement to be combined in a sensible fashion to achieve an optimal result (Rodgers et al., 1976, 2000). We used a version of optimal estimation which utilised a non-linear, variably damped, Levenberg-Marquardt (L-M) algorithm for rapid convergence to the best fit. In the optimal estimation standard terminology the group of forward model parameters fitted in the retrieval is called the state vector (x) and the forward model is a function of the state vector, F(x). The

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2015-380, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 18 January 2016

Atmospheric Measurement Techniques Discussions

objective of the retrieval is to adjust x until F(x)=y, where y is the measurement, in our case a UV intensity spectrum.

In order to calculate a new x at each iteration the retrieval requires knowledge of dF/dx, the gradient of F as a function of changes in elements of the state vector. This function is called a weighting function or Jacobian and has the symbol K. At each iteration new values for x are calculated using a Newton-Raphson method where $\Delta x=(y-F)/K$, with Δx being the change in the state vector in the next iteration. However, since several of the parameters in the state vector are non-linear with respect to the forward model it is clear that when the forward model is far from the measurement, particularly at the start of the fitting procedure, simply calculating the next x based on an implicitly linear assumption that K is constant will potentially send the state vector far from an improved fit. The L-M formulation of the retrieval includes a damping factor, lambda, which reduces how far a jump is made at each iteration. This factor is adjusted at each iteration to either be weaker if the fit is improving or stronger if the new iteration produced a worse result than the previous one, allowing efficient convergence even in highly non-linear systems.

A new K must be calculated at each iteration when using the L-M approach. We calculate K in a purely empirical fashion, running the forward model nx times, where nx is the number of elements of the state vector, and multiplying each individual state vector element by a factor of 1.1 to produce a partial derivative of F as a function of each element of the state vector. The weighting function is then the collected partial derivates of F as a function of each element of x.

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2015-380, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 18 January 2016

Atmospheric Measurement Techniques Discussions

4.5 Measurement error and fit errors

One of the most powerful and useful aspects of the optimal estimation approach is the accurate, quantitative treatment of errors in the resulting fitted elements of the state vector. The most critical input parameter to the final error attributed to each parameter is the error attributed to each element of the measured spectrum. This is calculated by taking the measured spectrum over the fit window, smoothing it with a 3-element boxcar and subtracting the smoothed spectrum from the original spectrum. The standard deviation of the result is used as an estimate of the noise level of each element of the measured spectrum. The validity of this approach is demonstrated by the similarity between the calculated standard deviation of the fit residual of the highest quality fits and the initial measurement noise determination (see section 5.2).

5. Test Cases

In the following sections we present a series of test cases, where the iFit retrieval is applied to spectra collected in a range of situations, from clear sky spectra, to SO_2 calibration cell spectra and finally volcanic plume traverse data. The purpose of these tests is to demonstrate the detection limit and error performance of the iFit system using the basic fit, flat spectrum removal and solar spectrum residual removal. By using the calibration cell spectra we determine the accuracy and precision of iFit. Finally, we use the traverse data test case to demonstrate the efficacy of the retrieval for volcanic plume SO_2 and BrO retrievals.

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2015-380, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 18 January 2016

Atmospheric Measurement Techniques Discussions

In the test cases several instrumental arrangements were used. For the clear sky and calibration cell tests we used two new USB2000+ spectrometers (model names HO7120 and HO7121) with 50 micron slit, grating #7 tuned to 280-400 nm, 2000 series detector with UV2 window, L2 detector lens, OF1-U325C bandpass filter, 1000 micron diameter solar resistant fibre, and an Ocean Optics 74-UV f/2 10 mm focal length quartz collimating lens, with 5.7° field of view. SO_2 calibration cells were originally within a COSPEC instrument and were placed directly in front of, and perpendicular to, the collimating lenses.

For the Etna traverse test case a USB2000 spectrometer was used (USB2G1338), with 200 micron slit, grating #7 tuned to 280-400 nm, 2000 series detector with UV2 window, L2 detector lens, 1000 micron diameter solar resistant fibre, and an Ocean Optics 84-UV f/4 100 mm focal length quartz collimating lens, with 0.57° field of view.

5.1 Flat spectra

The CCD sensor in the USB2000 spectrometers has a slightly different response for each individual pixel, which can be characterised by measuring a deuterium light source (Ocean Optics DT1000). This produces a spectrum called a flat spectrum, which can be removed from the measured intensity spectrum prior to fitting to improve fit quality. We measured the flat spectra for both our USB2000+ spectrometers and the USB2000 spectrometer, using a smoothed flat spectrum to normalise the result. Integration time was 1 ms and 10,000 spectra were coadded to produce each spectrum. We were curious to see if the flat spectrum was temperature

dependent, and conducted measurements after the USB2000+ spectrometers were left inside a 3-4°C fridge for 1 hour and in ambient 26°C to examine this question. The results are shown in Figure 1, and show a flat spectrum which is quite different for each spectrometer, with standard deviation of 2-3% and insignificant temperature variability.

There is an important point to make with regards to the flat spectrum. This spectrum is characteristic of the individual pixels of the CCD, and is therefore not affected by wavelength shifts in the spectrometer: it is absolutely fixed. USB2000 spectrometers exhibit temperature-dependent wavelength shifts, probably due to thermal expansion effects in the chassis. This helps to explain why in a classic DOAS analysis of traverse data collected using a clear sky spectrum the fit may degrade during the course of the traverse, if a non-temperature stabilised spectrometer is used. The radiation spectrum will be shifted relative to the flat spectrum, producing an increasingly significant misfit. This, together with better dark spectrum stability, is one of the main reasons why temperature stabilisation is a good idea, if the flat spectrum is not known. However, it is extremely simple to measure the flat spectrum, and once it is done can probably be used for extended periods of time before the CCD performance changes significantly. Therefore, by accurately characterising the flat spectrum, we avoid the necessity for temperature stabilisation, considerably simplifying the design, energy consumption and use of the spectrometers.

5.2 Test case 1: Clear sky

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2015-380, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 18 January 2016

Atmospheric Measurement Techniques Discussions

For our first test case we set up both USB2000+ spectrometers viewing the sky from the Pisa office of INGV on 14 June 2012. We started data collection at 12:20 and ended at 19:00 local time. Integration time was adjusted during the course of the day to maintain optimal intensity levels. Between 12:20 and 14:30 80 msec integration time spectra were co-added 600 times for each measured spectrum which were collected approximately every 42 seconds In this time period the sky was hazy with occasional cumulus clouds. Between 14:30 and 16:05 160 msec integration time spectra were co-added 200 times for each measured spectrum which were collected approximately every 32 seconds. In this time period there was clear blue sky with occasional cumulus clouds. Between 16:05 and the end of measurements 280 msec integration time spectra were co-added 50 times for each measured spectrum which were collected approximately every 14 seconds. In this time period there were white wispy clouds and blue sky, and from 16:30 onwards the sky was clear.

The FWHM of the ILS was fitted and a Gauss-Boxcar weighting of 0.95:0.05 was used. An order 5 polynomial was fitted together with shift, stretch, O_3, NO_2, SO_2 and Ring. A typical SO_2 fit window of 308-318 nm was used.

The result of the iFit retrieval applied without removal of the flat spectrum is shown in Figure 2, and demonstrates that even in its most basic form a residual with 2% standard deviation is achieved. Removal of the flat spectrum produces an improved fit, as shown in Figure 3, with a 1% standard deviation of the residual. Removing the solar spectrum residual produces the results shown in Figure 4, with a 0.2% standard deviation of the residual. This fit error is the same as the empirically determined

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2015-380, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 18 January 2016

measurement error, indicating that the fit has successfully included all the features of the measured spectrum.

The fit errors are plotted against empirically-determined measurement error for each of the three fit procedures in Figure 5. The steadily improving performance of the retrieval is clear as first flat and then solar spectrum residual are included. The final fit achieves close to 1:1 performance with the measurement error, confirming the fidelity of iFit.

Obtaining good zero baseline performance for SO_2 amounts when there is no SO_2 present is of critical importance for the iFit retrieval, and this performance is demonstrated in Figure 6. There we present the retrieved SO_2 amounts for each iFit procedure, when there is no SO_2 in the atmosphere. The impact of the flat spectrum is dramatic, significantly improving the performance of the SO_2 retrieved amounts. Removal of the solar spectrum residual produces very high precision results, with a systematic offset from zero which remains within $5e^{16}$ molecules.cm^{-2} or 20 ppm.m of zero until dusk. This is more than adequate performance for volcanic applications.

It is important to note that the performance of the solar spectrum residual does not degrade over the course of the day, other than that produced by the steadily increasing noise of the spectra. This is critically important, because it confirms that the solar spectrum residual is not air mass factor or solar zenith angle dependent, but is instead a product of inaccuracies in the measured solar spectrum.

5.3 **Test Case 2: Calibration Cell Tests**

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2015-380, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 18 January 2016

Atmospheric Measurement Techniques Discussions

On 15th June 2012 we conducted further measurements using the sky as a source of radiation, but this time using two calibration cells, one containing 126 ppm.m and the other 405 ppm.m SO_2. These cells were measured simultaneously with the two USB2000+ spectrometers during the course of the day from 12:50 until 19:44 local time. Spectrometer HO7120 was used with the 405 ppm.m cell, and measured spectra with 140 ms integration time and 150 co-adds, for a total measurement time of 21 seconds for each spectrum. Spectrometer HO7121 was used with the 126 ppm.m cell, and measured spectra with 100 ms integration time and 150 co-adds, for a total measurement time of 15 seconds for each spectrum. Fits using both flat removal and residual removal were performed, using a solar spectrum residual calculated by fitting the SO_2 calibration cell spectra with a flat spectrum. The typical fits for the HO7210 spectrometer using flat and solar spectrum residual fitting are shown in Figures 7 and 8 respectively. These indicate that the maximum value of SO_2 that could be left in the solar spectrum residual cannot exceed ~1% absorption, equivalent to an SO_2 amount of ~20 ppm.m.

The stable concentrations in this all-afternoon test allowed us to investigate the ideal SO_2 fit window. We did this by fitting the entire dataset with a range of fit windows, producing a mean and standard deviation for the entire set for each window. The results from this study are shown in Figure 9. We chose an optimal fit window of 308-318 nm, as this produces reasonably accurate results, within 10% of the gas cell amounts, and allows a stronger SO_2 line to be included to increase the sensitivity of the retrieval to small amounts of SO_2. We see that while the accuracy of the fit does change with the fit window, the empirical precision is impressively small, and

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2015-380, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 18 January 2016

consistent with retrieved SO_2 errors. This opens the possibility to correct the systematic differences between calibrated SO_2 amounts and retrieved SO_2 amounts.

We show the time series of SO_2 retrieved values using both solar spectrum residual and flat fits for the dataset up until light decreases to low levels in Figure 10. There is a fairly flat systematic underestimate of ~10% for the 405 ppm.m cell and 10% overestimate in the 126 ppm.m cell. These can be readily corrected. A modest 2-3% decline in SO_2 values is observed during the course of the day. The two retrievals produce near identical results, consistent with small residual of the flat fit.

5.4 Test 3: Etna traverse: SO_2

Our third test case uses data from an example dataset of spectra collected during a car-based traverse of Mt. Etna, Sicily, Italy on 7th January 2007. This dataset was chosen as the solar radiance in January is relatively low, and therefore represents a close to worst-case scenario. No flat spectrum was measured at the time of the traverse, but we produced one in July 2012 which improved the fit residual when it was removed from the measurement, demonstrating the stability of this feature. The abundant number of clear sky spectra between the plume measurements permitted an accurate determination of the residual solar spectrum with SO_2 fixed to zero. An example fit of an SO_2-rich spectrum is shown in Figure 11, and the retrieved SO_2 time series is shown in Figure 12. Good quality baseline fits and clean SO_2 profiles characterise the SO_2 traverses.

5.5 Test 4: Etna traverse: BrO

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2015-380, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 18 January 2016

We performed a BrO retrieval using a solar spectrum residual corrected fit, with a window of 337-352 nm, and simultaneously fitting BrO, SO_2, O_3, NO_2 and Ring spectra, as well as an order 4 polynomial, shift, stretch and FWHM of the instrument lineshape. Results from an example spectrum (the same used in Figure 11) are shown in Figure 13. Note the 0.3% residual, equivalent to the measurement error. The BrO time series is shown in Figure 14, showing greater variability than that in the SO_2 due to the relative weakness of the BrO absorption. Retrieved SO_2 values are plotted against BrO values in Figure 15, indicating a strong correlation between the two species and a BrO/SO_2 ratio of $2.4e^{-4}$. Note the consistency of the retrieved errors. We conclude that iFit performs well for both BrO and SO_2 retrievals.

6. Discussion

The main benefits of the iFit approach are that; it allows accurate determination of SO_2 amounts from spectra without the need for collection of a clear sky spectrum; the quality of fit is limited by measurement noise, not the forward model or retrieval procedure; inclusion of the flat spectrum greatly reduces the impact of temperature-dependent wavelength shifts; intensity-based retrievals include the full broadband absorption of SO_2, which can make up more than 50% of the total SO_2 absorption. Intensity-based retrievals also allow direct characterisation of aerosol/ash absorptions and accurate modelling of light dilution effects, and these two aspects will be addressed in future work.

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2015-380, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 18 January 2016

Atmospheric Measurement Techniques Discussions

iFit opens up the possibility for original new approaches to manual and automated SO_2 and BrO retrievals during both traverse and scanning measurements, and potentially removes the necessity for temperature stabilisation of spectrometers.

We have shown that the residual solar spectrum is not air mass factor dependent, indicating that it is the result of inaccuracies in the solar spectrum. Errors at the 1-2% level are not surprising for atmospheric corrected solar spectra, but the key capability of the iFit code to accurately fit the main gas absorptions until the 1-2% solar spectrum error limit is reached means that the residual spectrum is an essentially pure solar spectrum correction function. This can then, in theory, be re-applied independent of solar zenith angle, air mass factor, weather conditions, and so on. To date all of our tests have supported this capability.

The flat spectrum is pixel dependent, and will not shift with temperature induced wavelength shifts. By accurately characterising the flat spectrum we may elegantly remove its effects on the measured spectrum, making the resulting spectra robust to wavelength shifts, which may be accurately fitted in the iFit procedure. Using the flat spectrum removal procedure to produce a residual which is in turn removed allows iFit to produce noise-limited fits of SO_2 and BrO for traverse data.

Scanning data requires a slightly more complex approach. Here we may produce a stored residual solar spectrum for each spectrometer, which is then applied to all fits, taking account of any shifts between the measured residual and the current fit spectrum. Alternatively, and perhaps more robustly, we may use the capability of the flat-equipped fit to produce a 1-2% solar spectrum residual by fitting the vertical

viewing spectrum in a single scan. The elegance of this approach is that we account for nearly all SO_2 (down to at most 10-20 ppm.m) which may be present, as opposed to the classic DOAS clear-sky spectrum method, which introduces unknown magnitude biases into the scan retrieval. The iFit procedure may then perform a solar spectrum residual-corrected fit, achieving optimal quality results, scan by scan.

We may apply this approach to automated BrO fitting of scan data. BrO fitting is a challenge without a solar spectrum residual-corrected fit in iFit, because the 1-2% variability is much higher than the BrO absorption. It is therefore difficult to produce a BrO-free residual, because while BrO could be fixed to zero in the fit if there is volcanic gas present then there will be a systematic offset, the same problem DOAS has for SO_2. There are two solutions to this. Firstly, using the SO_2 amount retrieved from the vertical spectrum in a scan we may apply the mean SO_2/BrO ratio to fix the BrO content when fitting the vertical spectrum in the BrO window, producing a residual solar spectrum with little if any BrO. The residual solar spectrum may then be used throughout the scan to produce a BrO profile. Secondly, we may simply ignore the fact there is a potential bias in the BrO profile. The SO_2/BrO ratio will be determined by plotting SO_2 amounts against BrO and calculating the gradient of the plot using linear regression. In this case any bias in BrO has no effect on the SO_2/BrO ratio; indeed, the intercept of the regression will reveal the magnitude of the BrO bias.

The iFit approach is therefore ideally suited to the automatic analysis of spectra produced by automatic scanning networks. We will be shortly implementing iFit for the FLAME scanning UV networks on Etna and Stromboli, and propose that iFit be also applied to other networks of UV scanning systems.

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2015-380, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 18 January 2016

The background polynomial produced during the iFit procedure is the multiplication of the source intensity with the aerosol absorptions in the atmosphere and plume. By dividing the polynomial produced in an SO_2-rich spectrum with one in a clear sky spectrum we produce a pure plume aerosol/ash transmittance spectrum that may be used to accurately characterise interference in measurements made by the SO_2 camera. This information is challenging to produce from the classic DOAS fit, as the broadband absorptions of O_3 and SO_2 are lost. In theory they could be recalculated, but at that point the retrieval is effectively reproducing an intensity fit, which perhaps makes more sense to perform directly, as is the case for iFit.

7. Conclusions

iFit is a new intensity-based retrieval algorithm for direct fitting of measured UV spectra, specifically developed for use in volcanology. It has been designed with a focus on minimising processing of the measured spectra prior to analysis. Here, we report a detailed presentation of the iFit algorithm, and test it in 4 case studies, examining clear sky spectra, SO_2 calibration cell experiments and volcanic SO_2 and BrO retrievals from traverse measurements performed on Mt. Etna volcano, Italy. It can be robustly and easily applied to both scanning and traverse measurements of volcanic plumes, producing bias-free profiles of SO_2, and accurate SO_2/BrO ratios without the need for clear sky background spectra. Fit residuals are typically pure instrumental noise when the residual solar spectrum is removed.

We have shown that the major source of fit error in the intensity fitting come from the AMF-independent solar spectrum errors, which are however easily characterised and removed. Furthermore, we have quantified the magnitude of the flat spectrum in three spectrometers, and shown that this spectrum is strongly spectrometer dependent but temperature independent, opening the possibility for robust analysis and quantification of both SO_2 and BrO without the need for temperature stabilisation.

The iFit procedure calculates the full SO_2 and O_3 spectra, including their significant broadband components. We can therefore easily characterise the aerosol/ash transmittance spectrum allowing much improved corrections to SO_2 camera data. The intensity-based approach also opens the possibility to directly fit light dilution effects. Both of these subjects will be the focus of future work.

Acknowledgements

This work was produced with support from ERC grant CO_2Volc, StG 279802 (P.I. Mike Burton, INGV Pisa). GS was supported through a grant from Region d'Auvergne Chaire d'Excellence (P.I. Andrew Harris, LMV, Clermont Ferrand, France), and this paper represents CLERVOLC contribution 001. The work reported here was produced during a visit by GS to INGV Pisa, for which we acknowledge the support of A. Neri, R. Rapuzzi and L. Nannipieri. We gratefully acknowledge fruitful discussions with Christoph Kern and Vitchko Tsanev and instrumental support from Giuseppe Salerno.

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2015-380, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 18 January 2016

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Discussions

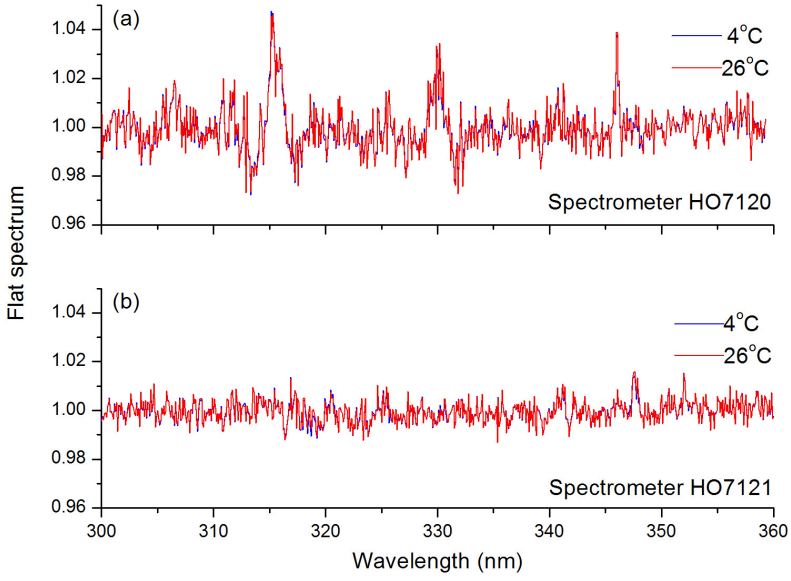

Figure 1. Flat spectra for USB2000+ spectrometers collected with a deuterium lamp and normalised with boxcar smoothed spectra, at 26°C and 4°C. Note that the behaviour of the two spectrometers is quite different, with HO7120 exhibiting significantly greater variability than HO7121. No significant difference in the flat spectra was observed with a 22°C temperature variation.

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2015-380, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 18 January 2016

Atmospheric Measurement Techniques
Discussions

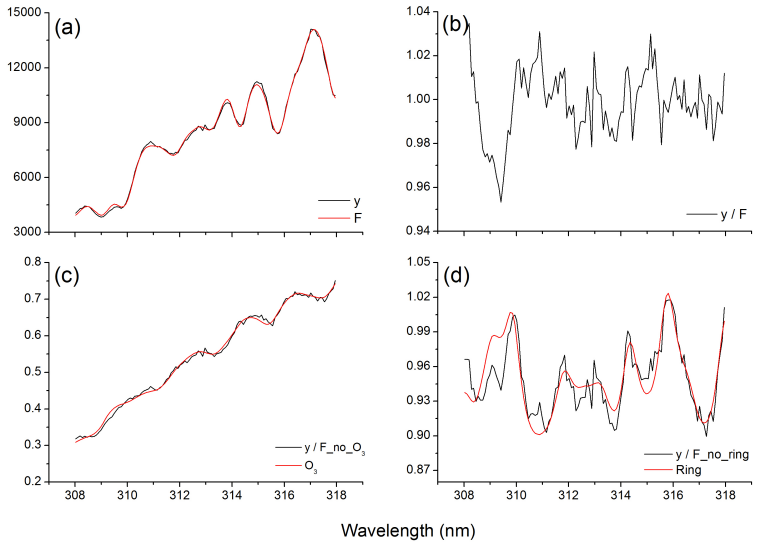

Figure 2. Examples of an iFit analysis of a clear sky spectrum with no flat spectrum removal. In (a) the measured spectrum and fit are shown in black and red respectively, note the intensity scale. In (b) the residual of the measurement (y) and the fit (F) is shown, calculated as y/F. In (c) the measured spectrum divided by a model calculated spectrum of the best fit without O_3 is shown, together with the fitted O_3 spectrum. In (d) the measured spectrum divided by a model calculated spectrum of the best fit without the Ring spectrum is shown, together with the fitted Ring spectrum.

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2015-380, 2016
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Published: 18 January 2016

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Discussions

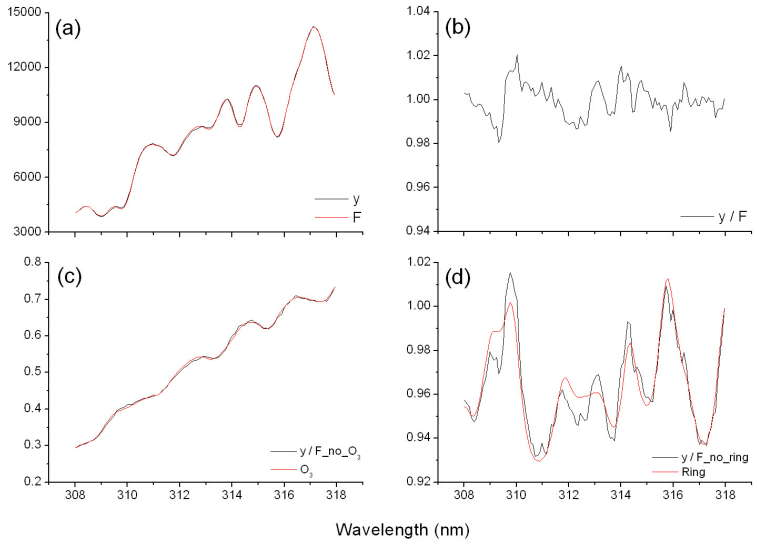

Figure 3. Examples of an iFit analysis of a clear sky spectrum with flat spectrum removed. In (a) the measured spectrum and fit are shown in black and red respectively, note the intensity scale. In (b) the residual of the measurement (y) and the fit (F) is shown, calculated as y/F. In (c) the measured spectrum divided by a model calculated spectrum of the best fit without O_3 is shown, together with the fitted O_3 spectrum. In (d) the measured spectrum divided by a model calculated spectrum of the best fit without the Ring spectrum is shown, together with the fitted Ring spectrum.

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2015-380, 2016
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Published: 18 January 2016

Atmospheric Measurement Techniques
Discussions

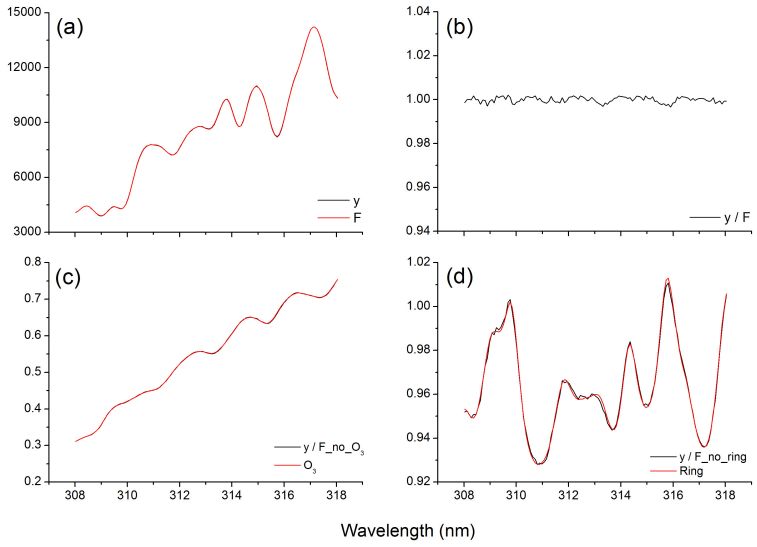

Figure 4. Examples of an iFit analysis of a clear sky spectrum with solar spectrum residual removed. In (a) the measured spectrum and fit are shown in black and red respectively, note the intensity scale. In (b) the residual of the measurement (y) and the fit (F) is shown, calculated as y/F. In (c) the measured spectrum divided by a model calculated spectrum of the best fit without O_3 is shown, together with the fitted O_3 spectrum. In (d) the measured spectrum divided by a model calculated spectrum of the best fit without the Ring spectrum is shown, together with the fitted Ring spectrum.

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2015-380, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 18 January 2016

Atmospheric Measurement Techniques Discussions

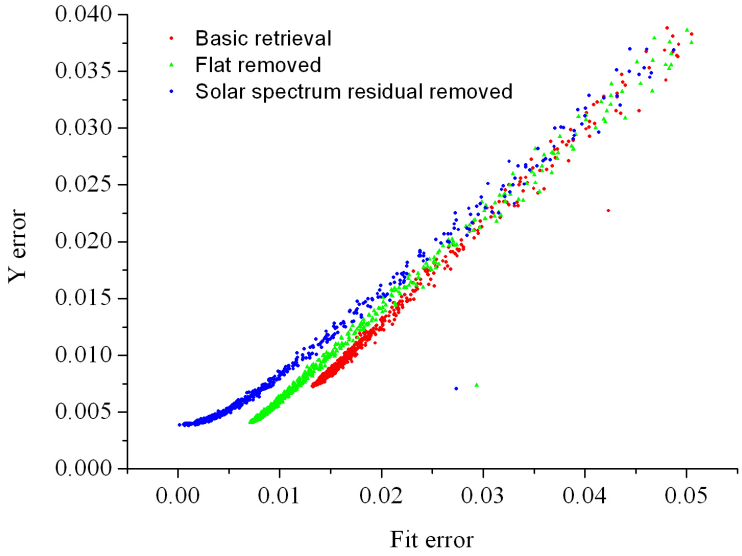

Figure 5. Errors produced by the iFit procedure for each spectrum during the 14th June clear sky test using the basic retrieval (red), retrieval with flat spectrum removed (green) and solar spectrum residual removed (blue). The fit error is calculated as the standard deviation of ((F-y)/y), where F is the fit and y is the measured spectrum. The y error is calculated by taking the standard deviation of the ratio of the measured spectrum with a 3-element boxcar smoothed version of the measured spectrum.

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2015-380, 2016
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Published: 18 January 2016

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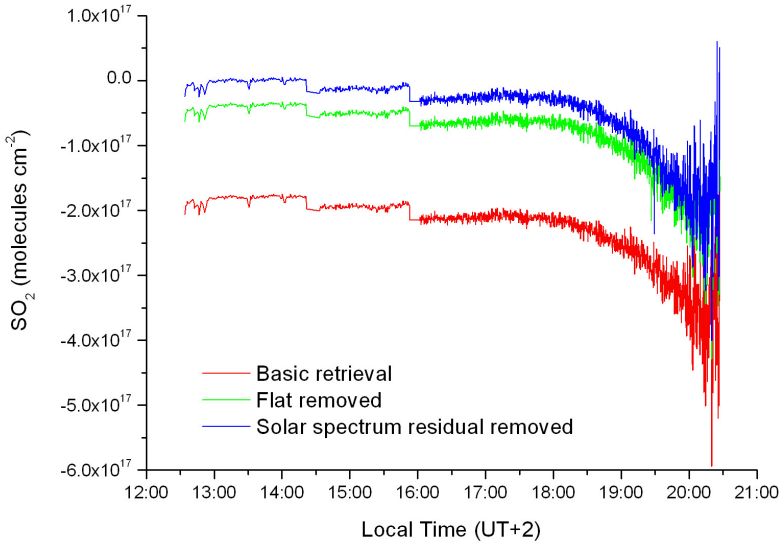

Figure 6. Retrieved SO_2 time series for three iFit retrievals during the 14th June clear sky test.

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2015-380, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 18 January 2016

Atmospheric Measurement Techniques
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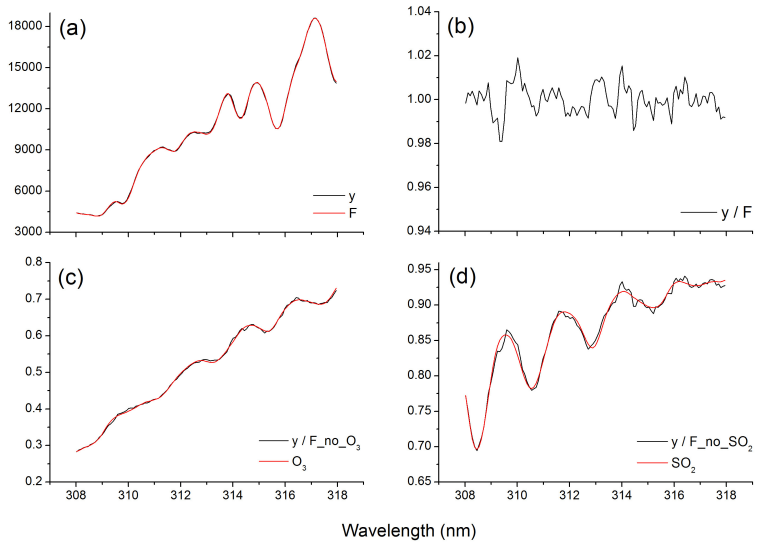

Figure 7. Example of a fit to a single spectrum with flat spectrum removed, collected with the HO7120 spectrometer on 15th June using the 405 ppm.m calibration cell and sky illumination. In (a) the measured spectrum and fit are shown in black and red respectively, note the intensity scale. In (b) the residual of the measurement (y) and the fit (F) is shown, calculated as y/F. In (c) the measured spectrum divided by a model calculated spectrum of the best fit without O_3 is shown, together with the fitted O_3 spectrum. In (d) the measured spectrum divided by a model calculated spectrum of the best fit without the SO_2 spectrum is shown, together with the fitted SO_2 spectrum. Note the ~1 % residual.

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2015-380, 2016
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Published: 18 January 2016

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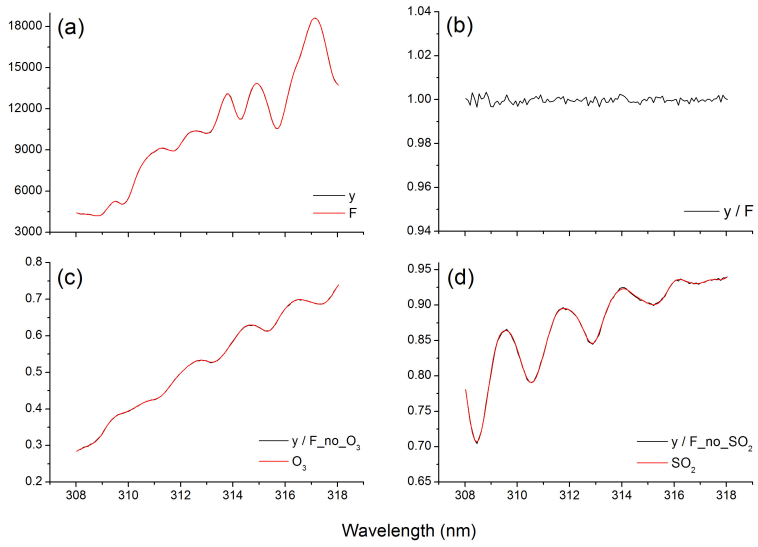

Figure 8. Example of a fit to a single spectrum with solar spectrum residual removed, collected with the HO7120 spectrometer on 15th June using the 405 ppm.m calibration cell and sky illumination. In (a) the measured spectrum and fit are shown in black and red respectively, note the intensity scale. In (b) the residual of the measurement (y) and the fit (F) is shown, calculated as y/F. In (c) the measured spectrum divided by a model calculated spectrum of the best fit without O_3 is shown, together with the fitted O_3 spectrum. In (d) the measured spectrum divided by a model calculated spectrum of the best fit without the SO_2 spectrum is shown, together with the fitted SO_2 spectrum. Note the 0.2 % residual.

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2015-380, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 18 January 2016

Atmospheric Measurement Techniques
Discussions

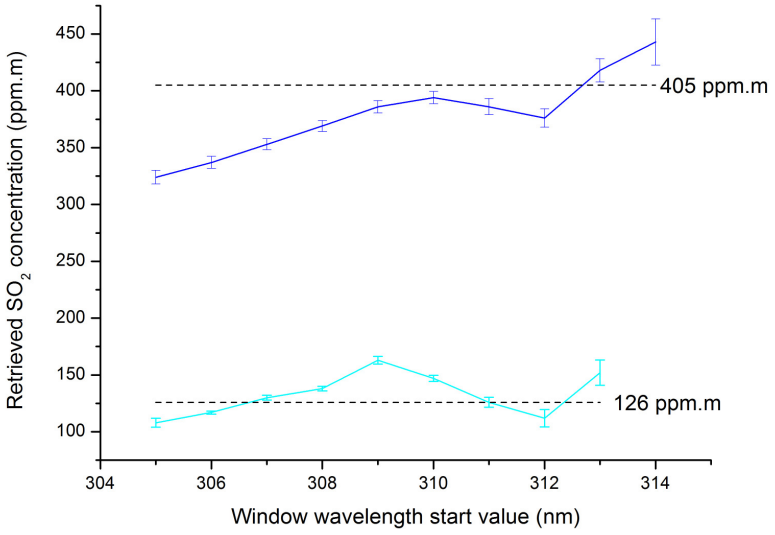

Figure 9. Results from an investigation into the effect of fit window on retrieved SO_2 amounts with flat removed for both the 405 and 126 ppm.m calibration cells. The window size was fixed at 10 nm. Each point represents the mean value of retrieved SO_2 for the entire dataset up until 6 pm, and the error bar is the ±1 standard deviation of the retrieved SO_2 values.

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2015-380, 2016
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Published: 18 January 2016

Atmospheric Measurement Techniques Discussions

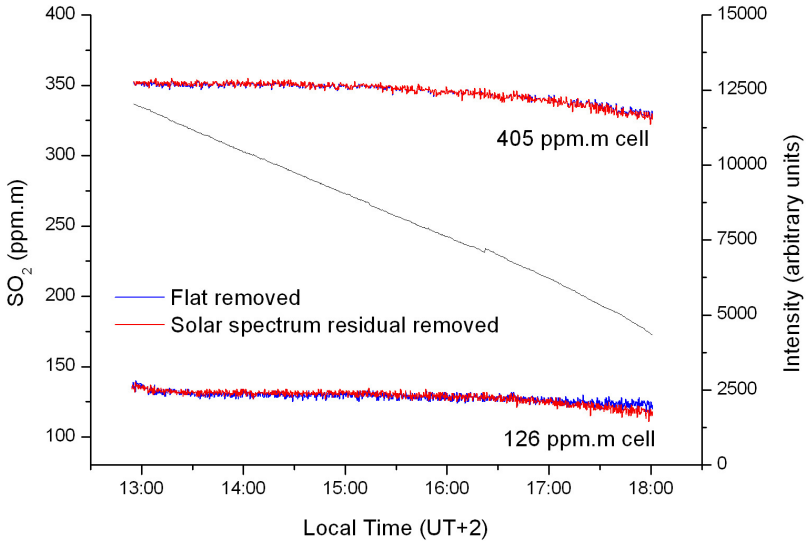

Figure 10. Retrieved SO_2 time series using the 308-318 nm fit window and both flat-removed and solar spectrum residual-removed fits, for both the 126 ppm.m 405 ppm.m cells. Note that systematic differences between stated and measured calibration cell SO_2 concentration-pathlengths arise from minor leakage from the 10 year old calibrations cells. Measured intensity is shown as a black line.

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2015-380, 2016
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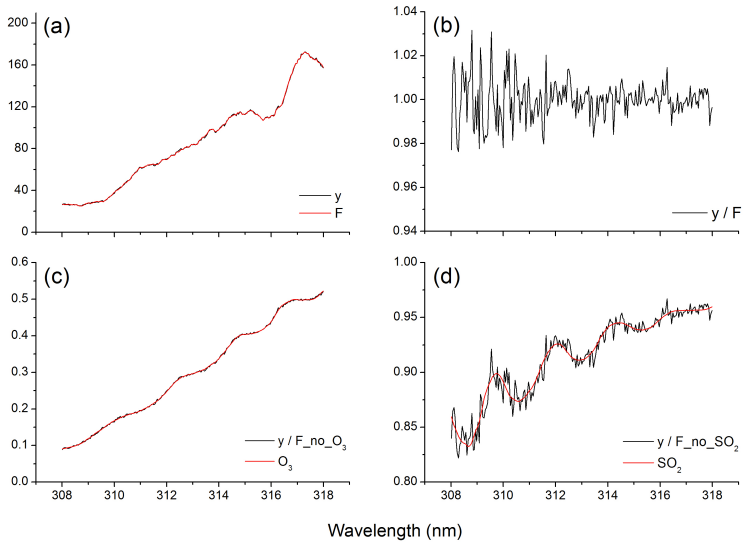

Figure 11. Example of a solar spectrum residual-removed fit to an SO_2-rich spectrum (215 ppm.m) collected during a car traverse under the volcanic plume produced by Mt. Etna on 7th January 2007. In (a) the measured spectrum and fit are shown in black and red respectively, note the intensity scale. In (b) the residual of the measurement (y) and the fit (F) is shown, calculated as y/F. In (c) the measured spectrum divided by a model calculated spectrum of the best fit without O_3 is shown, together with the fitted O_3 spectrum. In (d) the measured spectrum divided by a model calculated spectrum of the best fit without the SO_2 spectrum is shown, together with the fitted SO_2 spectrum. Measurement error and fit error were both 0.6 %, indicating that the fit residual is pure instrumental noise.

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2015-380, 2016
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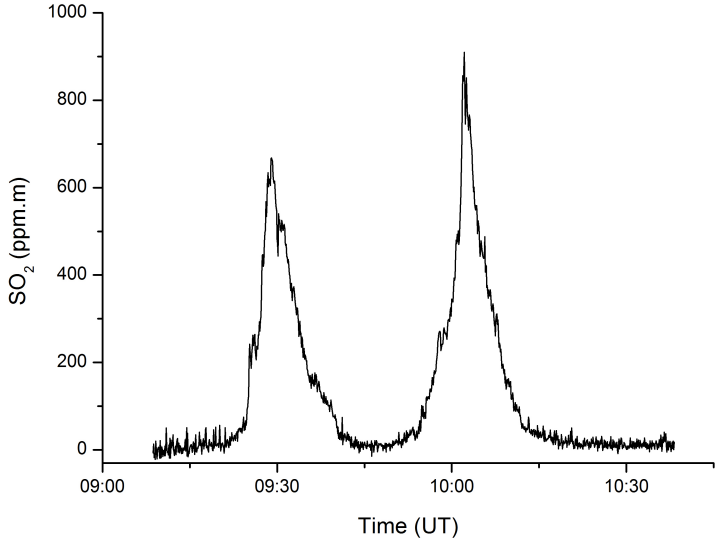

Figure 12. SO_2 time series from a car traverse under Mt. Etna plume on 7th January 2007, retrieved with a solar spectrum residual-removed fit.

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2015-380, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 18 January 2016

Atmospheric Measurement Techniques Discussions

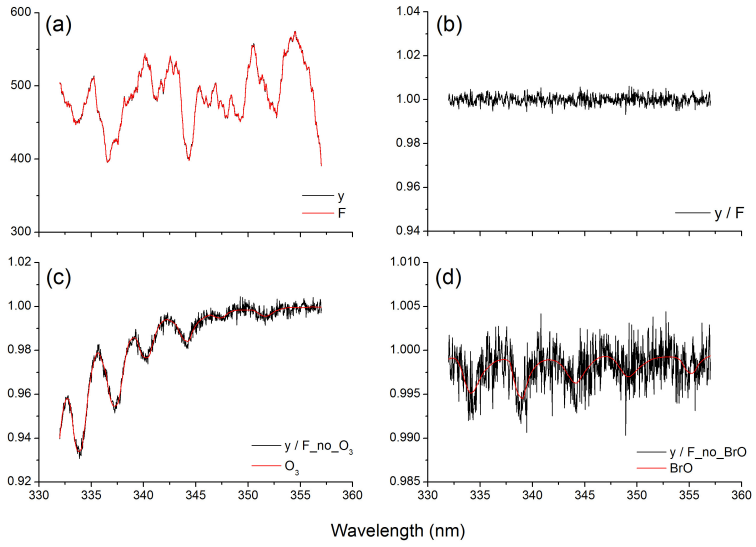

Figure 13. Example of a solar spectrum residual-removed fit to a BrO-rich spectrum collected during a car traverse under the volcanic plume produced by Mt. Etna on 7th January 2007. In (a) the measured spectrum and fit are shown in black and red respectively, note the intensity scale. In (b) the residual of the measurement (y) and the fit (F) is shown, calculated as y/F. In (c) the measured spectrum divided by a model calculated spectrum of the best fit without O_3 is shown, together with the fitted O_3 spectrum. In (d) the measured spectrum divided by a model calculated spectrum of the best fit without the BrO spectrum is shown, together with the fitted BrO spectrum. Measurement error and fit error were both 0.3 %, indicating that the fit residual is pure instrumental noise.

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2015-380, 2016
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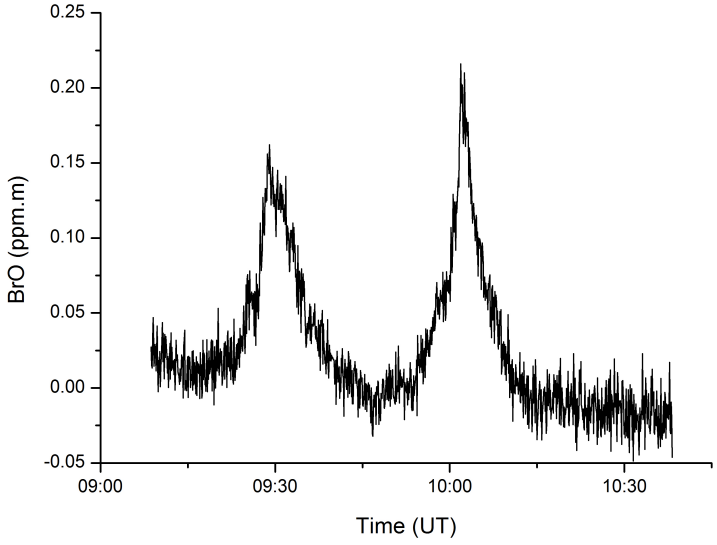

Figure 14. BrO time series from a car traverse under Mt. Etna plume on 7th January 2007, retrieved with a residual-removed fit.

Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2015-380, 2016
Manuscript under review for journal Atmos. Meas. Tech.
Published: 18 January 2016

Atmospheric Measurement Techniques Discussions

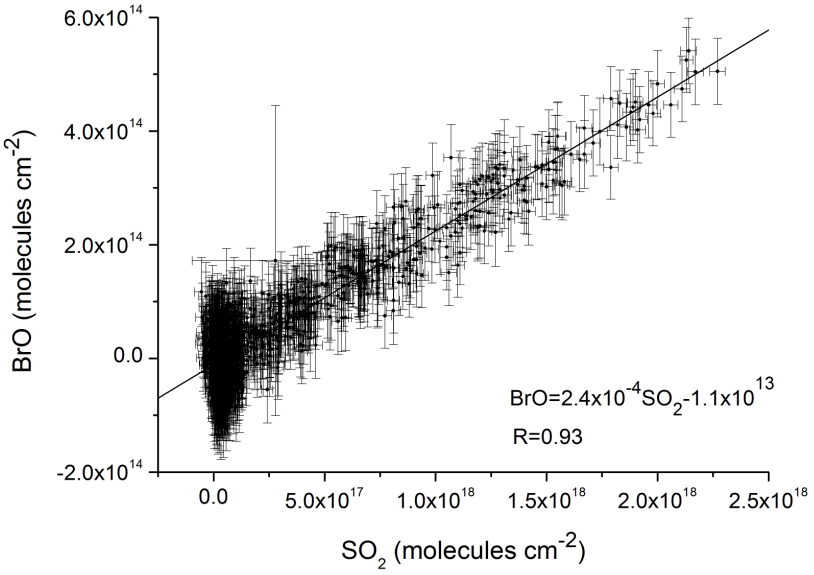

Figure 15. SO_2 plotted against BrO for each spectrum of the 7th January 2007 Etna traverse. Error bars are ±1 standard deviations from the retrieval.

References

Aliwell, S.R., M. Van Roozendael, P.V. Johnston, A. Richter, T. Wagner, D.W. Arlander, J.P. Burrows, D.J. Fish, R.L. Jones, K.K. Tornkvist, J.C. Lambert, K. Pfeilsticker, I. Pundt (2002), Analysis for BrO in zenith-sky spectra: An intercomparison exercise for analysis improvement. *J. Geophys. Res. Atm.*, Vol 107, D14, doi: 10.1029/2001JD000329

Andres R.J. and Kasgnoc A.D. (1998), A time-averaged inventory of subaerial volcanic sulphur emissions, J. Geophys. Res., 103, D19, 25251-25261.

Bobrowski, N., Hönninger, G., Galle, B. and U. Platt (2003), Detection of Bromine Monoxide in a Volcanic Plume, Nature, 423, 273-276.

Bogumil, K., J. Orphal, T. Homann, S. Voigt, P. Spietz, O.C. Fleischmann, A. Vogel, M. Hartmann, H. Kromminga, H. Bovensmann, J. Frerick and J.P. Burrows (2003), Measurements of molecular absorption spectra with the SCIAMACHY pre-flight model: instrument characterization and reference data for atmospheric remote-sensing in the 230–2380 nm region. *J. Photoch. Photobio. A*, 157 (2–3), 167–184.

Burton, M.R., T. Caltabiano, F. Mure, G. Salerno, D. Randazzo (2009) SO_2 flux from Stromboli during the 2007 eruption: Results from the FLAME network and traverse measurements. *J Volcanol. Geotherm. Res.,* 182 (3-4), 214-220, doi: 10.1016/j.jvolgeores.2008.11.025.

Edmonds, M., R.A. Herd, B. Galle, C.M. Oppenheimer (2003), Automated, high time-resolution measurements of SO_2 flux at Soufriere Hills Volcano, Montserrat. *Bull. Volc*., 65(8), 578-586, doi: 10.1007/s00445-003-0286-x.

Fleischmann, O.C., J.P. Burrows, and J. Orphal (2003). Time-windowing Fourier transform absorption spectroscopy for flash photolysis investigations. *J. Photochem. Photobiol. A.: Chem.,* 157, 127–136.

Fleischmann, O.C., M. Hartmann, J.P. Burrows, and J. Orphal (2004). New ultraviolet absorption cross-sections of BrO at atmospheric temperatures measured by a time-windowing Fourier transform spectroscopy. *J. Photochem. Photobiol. A.: Chem.,* 168, 117–132.

Galle, B., Oppenheimer, C. Geyer, A. McGonigle, A.J.S., Edmonds, M., Horrocks, L.A. A miniaturised UV spectrometer for remote sensing of SO2 fluxes: a new tool for volcano surveillance. J. Volcanol. Geotherm. Res. 2003, 119, 241-254.

Grainger, J.F., J. Ring (1962). Anomalous Fraunhofer line profiles. *Nature*, 193: pp 762.

Galle, B. M. Johansson, C. Rivera, Y. Zhang, M. Kihlman, C. Kern, T. Lehmann, U. Platt, S. Arellano, S. Hidalgo (2010), Network for Observation of Volcanic and Atmospheric Change (NOVAC)-A global network for volcanic gas monitoring: Network layout and instrument description. J. Geophys. Res. Atm., 115, D05304, doi: 10.1029/2009JD011823.

Kantzas, E.P., A.J.S. McGonigle, G. Tamburello, R.G. Bryant (2012) UVolc: A software platform for measuring volcanic SO_2 fluxes. *Computers and Geosciences*, 40, 194-199, doi: 10.1016/j.cageo.2011.07.011.

Platt, U. and Stutz, J. (2008), Differential Optical Absorption Spectroscopy – Principles and Applications. Springer, Berlin, pp 1–597.

Rodgers, C.D. (1976), Retrieval of atmospheric temperature and composition from remote measurement of thermal radiation. *Rev. Geophys. Space Phys*., 14, 609-624.

Rodgers, C.D. (2000), Inverse Methods For Atmospheric Sounding, Theory and Practice, Series on Atmospheric, Oceanic and Planetary Physics – Vol. 2, edited by F.W. Taylor, World Scientific.

Salerno, G.G. M.R. Burton, C. Oppenheimer, T. Caltabiano, V.I. Tsanev, N. Bruno (2009a), Novel retrieval of volcanic SO_2 abundance from ultraviolet spectra. *J. Volcanol. Geotherm. Res.*, 181(1-2), 141-153, doi: 10.1016/j.jvolgeores.2009.01.009.

Salerno G.G., M.R. Burton, C. Oppenheimer, T. Caltabiano, D. Randazzo, N. Bruno, V. Longo (2009b), Three-years of SO_2 flux measurements of Mt. Etna using an automated UV scanner array: Comparison with conventional traverses and uncertainties in flux retrieval. *J. Volcanol. Geotherm. Res.,* 183 (1-2), 76-83, doi: 10.1016/j.jvolgeores.2009.02.013.

Stoiber R.E. and Jepsen A. (1973), Sulfur dioxide contributions to the atmosphere by volcanoes, *Science*, 577-578, 182.

Van Roozendael, M., et al. (2012), Sixteen years of GOME/ERS-2 total ozone data: The new direct-fitting GOME Data Processor (GDP) version 5—Algorithm description, J. Geophys. Res., 117, D03305, doi:10.1029/2011JD016471.

Voigt, S., J. Orphal, K. Bogumil and J.P. Burrows (2001), The temperature dependence (203–293 K) of the absorption cross sections of O_3 in the 230–850 nm region measured by Fourier-transform spectroscopy. *J Photochem. Photobiol., A Chem. 143* (1), 1–9.

Voigt, S., J.Orphal and J.P. Burrows (2002), The temperature and pressure dependence of the absorption cross sections of NO_2 in the 250–800 nm region measured by Fourier-transform spectroscopy. *J Photochem. Photobiol., A Chem., 149* (1–3), 1–7.