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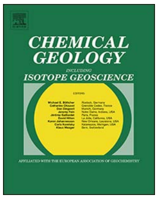

On the use of different spectral windows in DOAS evaluations: Effects on the estimation of SO_2 emission rate and mixing ratios during strong emission of Popocatépetl volcano

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ABSTRACT

Reported SO_2 emission values at strongly degassing volcanoes might be underestimated. Scanning spectroscopic instruments are widely used at volcanoes to quantify SO_2 emission rates and, occasionally, molar ratios between SO_2 and other gases such as BrO. Frequently, Differential Optical Absorption Spectroscopy is applied to evaluate spectra in the ultraviolet range. If radiative transfer effects are not considered in the evaluations, the retrieved column densities may vary depending on which spectral window is used. We compare the use of different windows for data collected at Popocatépetl volcano during strong degassing periods, when high column densities lead to especially high dependence on the applied evaluation window. We propose the use of three different windows (310–322 nm, 314.7–326.7 nm and 322–334 nm) and a simple algorithm to choose the most accurate column density from them. The SO_2 evaluation using proper spectral windows would allow a more realistic estimation of the SO_2 emission rates.

1. Introduction

Remote detection and quantification of volcanic gas emissions using molecular light absorption has become an important tool in volcanic research and monitoring during the last decades. Differential Optical Absorption Spectroscopy (DOAS, e.g. Platt and Stutz, 2008) is the main technique applied to measure sulfur dioxide (SO_2) emissions at many volcanoes around the world (e.g. Galle et al., 2003), be it in traversing or in fully automated scanning geometry (e.g. within the NOVAC network (Network for Observation of Volcanic and Atmospheric Change), Galle et al. (2010)). Using scattered sunlight as source, strong absorption lines above 300 nm can be utilized to easily detect the SO_2 column densities present in the emission plumes of volcanoes.

Uncertainties in the straight forward application of standard DOAS retrievals to quantify volcanic SO_2 column densities have been discussed elsewhere, e.g. in Mori et al. (2006), who find a wavelength dependent decrease of the apparent absorbance as the distance between instrument and volcanic plume increases and as the SO_2 column densities of the plume increase, and e.g. in Kern et al. (2010) and Kern et al. (2012), where improvement of DOAS measurements in volcanic environments based on radiative modeling is proposed. Based on modeling of radiative transfer, they identify situations, in which the light dilution between volcanic plume and instrument lead to a potential underestimation of the gas load by DOAS measurements, and situations when multiple scattering within the plume region leads to stronger apparent absorption, especially within condensed plumes. Vogel et al. (2013) have performed general studies on the selection of an adequate spectral retrieval range. Salerno et al. (2009) investigate the dependence of the DOAS retrieval for determination of volcanic SO_2 on various instrumental and environmental parameters using calibration cells of known SO_2 content. They also vary the spectral region of the evaluation, but focusing on the range between 300 and 320 nm where the strongest absorption features are observed.

Very high column densities lead to SO_2 optical densities too high to justify the weak absorber assumption made for standard DOAS evaluations, which are usually performed for differential optical densities up to about 0.05, while in volcanic plumes optical densities above one can be found (Bobrowski et al., 2010; Platt and Stutz, 2008). For this case, Bobrowski et al. (2010) discuss the possibility to apply an alternative evaluation range from 360 to 390 nm, a region where the SO_2 absorption features are much weaker thus the weak absorber assumption holds for much higher SO_2 column densities.

In this study, a series of evaluation ranges, spanning from the strong absorption patterns around 320 nm to the ranges described by

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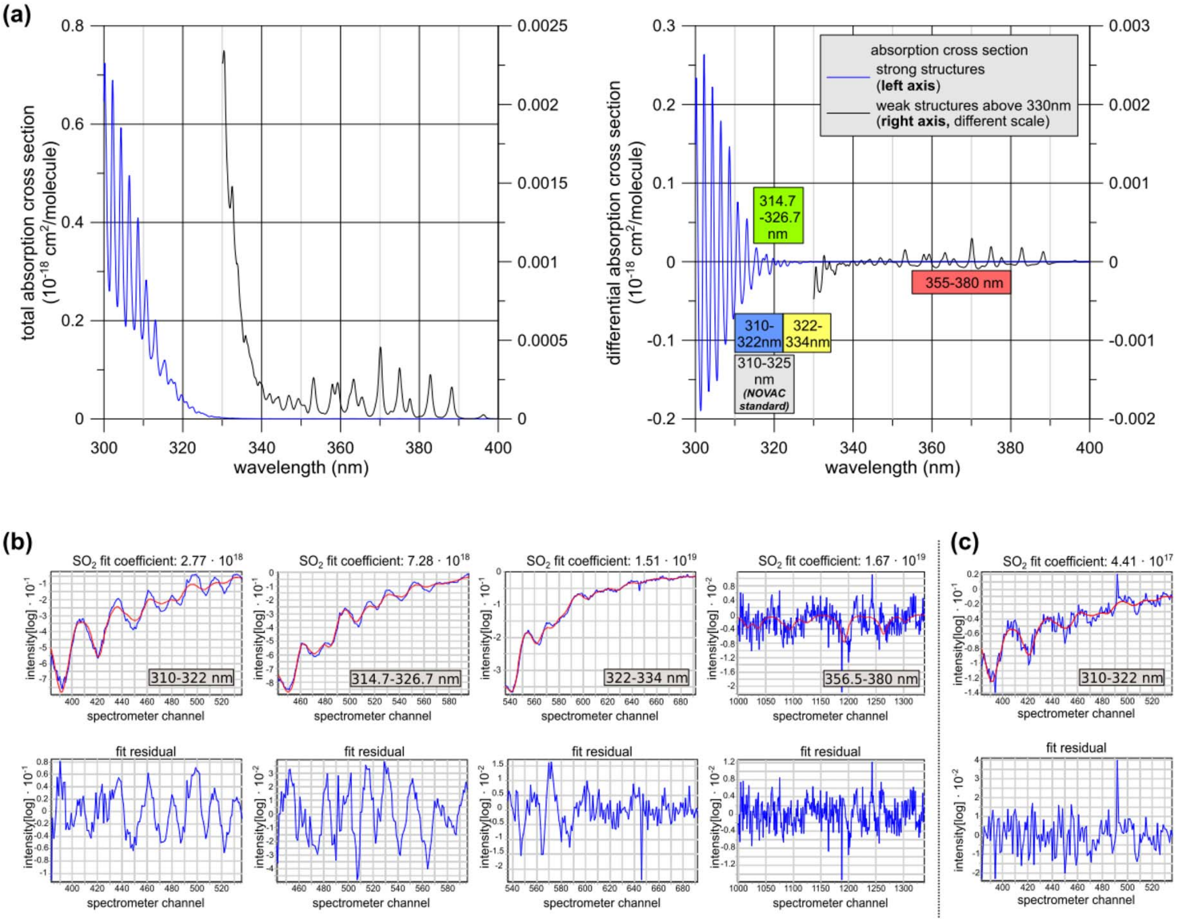

Fig. 1. (a) Total and differential absorption cross section spectra of SO_2 (Vandaele et al., 2009, and Hermans et al., 2009), convolved with the instrumental line-shape function. The boxes indicate the evaluation windows used.(b) Examples of four different evaluation windows for SO_2 retrieval together with the corresponding fit residual spectra (Cruz Blanca station instrument, based on spectra recorded from 61° scanning angle from a scan taken on 29th of July 2013, starting at 13:46 UTC). Red lines correspond to the fitted SO_2 absorption spectra, blue lines correspond to the measured spectrum.(c) SO_2 retrieval in the 310–322 nm range for the spectrum recorded at 32° scanning angle from the same scan, but towards the border of the plume. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Bobrowski et al. (2010), is applied to a set of data obtained by scanning DOAS instruments at Popocatépetl volcano during very high gas emission periods in 2013.

Based on results from this period, we discuss the implications on the obtained SO_2 emission rates for a larger period from 2007 to 2015, presently inferred from a standard evaluation in the 310 to 326 nm range for the NOVAC instruments at Popocatépetl; and briefly discuss the implications on the determination of molar gas ratios such as an ongoing investigation of the BrO/SO_2 molar ratios in the plume of Popocatépetl volcano.

Fig. 1(a) depicts the SO_2 absorption structures between 300 and 400 nm, based on Vandaele et al. (2009) and Hermans et al. (2009) and after convolution with the instrumental line-shape function used in this study. Both, the absolute cross section as well as the differential cross section (obtained by applying a polynomial high pass filter) are strong below 320 nm, then decline rapidly with some relatively small absorption features standing out between 360 and 390 nm. Boxes indicate the principal evaluation windows used in this work.

Two different aims of the optimization of the retrieved SO_2 column densities have to be distinguished: For the calculation of SO_2 emission rates, where typically a straight light path is assumed, the optimization of the retrieved SO_2 column densities has to focus on finding a column density close to that of the straight line. However, if the molar ratio with respect to another volcanic gas is to be determined from the same measurement, it is sufficient to find evaluation ranges which analyze light with similar paths for the different gases. An extension of the light path within the volcanic plume may even improve the possibility to detect trace gases and elevate the signal to noise ratio by probing an enhanced region of volcanic gas.

One possibility to avoid very high column densities is performing measurements further away from the crater where the plume is more diluted, although the plume width reduces the possibility to measure good plume-free reference spectra on the horizon. At volcanoes such as Popocatépetl, gas emissions with very high column densities do not occur every time, although they are frequent.

2. Instrument description and evaluation procedure

Data from NOVAC scanning DOAS instruments installed around Popocatépetl volcano was used for this study. Their distance from the volcano varies between 3.5 and 8 km (Fig. 2). The detailed study of the evaluation range is principally based on measurements performed by instrument D2J2143 located 4 km northwest of the crater at Cruz Blanca; effects on the overall SO_2 emission rate obtained are shown based on data from the three of the four instruments, which were working most continuously.

The instruments are equipped with a telescope which scans the sky from horizon to horizon in conical geometry with 60° aperture angle, so that their viewing angle always is inclined towards the volcano. To indicate the scan angle, we use the NOVAC convention that −90° corresponds to the left side horizon of the scanned cone, 0° to the frontal direction closest to zenith, and +90° to the right side horizon. Every scan takes typically 5–10 min, depending on the intensity of the measured light.