Journal of Volcanology and Geothermal Research 181 (2009) 141–153

Contents lists available at ScienceDirect

Journal of Volcanology and Geothermal Research

journal homepage: www.elsevier.com/locate/jvolgeores

# Novel retrieval of volcanic $SO_2$ abundance from ultraviolet spectra

G.G. Salerno [a,c,*], M.R. Burton [b], C. Oppenheimer [c], T. Caltabiano [a], V.I. Tsanev [c,d], N. Bruno [a]

[a] Istituto Nazionale di Geofisica e Vulcanologia, sezione di Catania, Piazza Roma 2, 95123, Catania, Italy
[b] Istituto Nazionale di Geofisica e Vulcanologia, sezione di Pisa, Via della Faggiola 32, 56126, Pisa, Italy
[c] University of Cambridge, Department of Geography, Downing Place, Cambridge, CB2 3EN, United Kingdom
[d] University of Cambridge, Department of Chemistry, Lensfield Road, Cambridge, CB2 1EW, United Kingdom

ARTICLE INFO

*Article history:*
Received 22 May 2008
Accepted 8 January 2009
Available online 23 January 2009

*Keywords:*
volcanic gas monitoring
scanning spectrometer network
DOAS
ultraviolet spectroscopy
Mt. Etna

ABSTRACT

The recent development of fixed networks of scanning ultraviolet spectrometers for automatic determination of volcanic $SO_2$ fluxes has created tremendous opportunities for monitoring volcanoes but has brought new challenges in processing (and interpreting) the copious data flow they produce. A particular difficulty in standard implantation of differential optical absorption (DOAS) methods is the requirement for a clear-sky (plume-free) background spectrum. Our experience after four years of measurements with two UV scanner networks on Etna and Stromboli shows that wide plumes are frequently observed, precluding simple selection of clear-sky spectra. We have therefore developed a retrieval approach based on simulation of the background spectrum. We describe the method here and tune it empirically by collecting clear, zenith sky spectra using calibration cells containing known amounts of $SO_2$. We then test the performance of this optimised retrieval using clear-sky spectra collected with the same calibration cells but for variable scan angles, time of day, and season (through the course of 1 year), finding acceptable results (~12% error) for $SO_2$ column amounts. We further illustrate the analytical approach using spectra recorded at Mt. Etna during its July 2006 eruption. We demonstrate the reliability of the method for tracking volcano dynamics on different time scales, and suggest it is widely suited to automated $SO_2$-plume monitoring.



## 1. Introduction

In recent years, methods and strategies for monitoring active volcanoes have undergone extensive and rapid technological development. Recent advances have improved these techniques in terms of the number of parameters investigated and their time resolution (Tilling, 1995; Scarpa and Tilling, 1996). Measurements of emitted gas fluxes from active volcanoes are important both for constraining environmental impacts and for understanding and predicting volcanic activity (e.g., Symonds et al., 1994; Kress, 1997; Robock, 2000; Halmer et al., 2002; Sparks, 2003; Oppenheimer, 2003; Oman et al., 2005). Sulphur dioxide ($SO_2$) is typically one of the most abundant volatile components in volcanic plumes (after $H_2O$ and $CO_2$) and its strong ultraviolet (UV) absorption band allows straightforward detection (Hamilton et al., 1978; Manatt and Lane, 1993). Volcanic $SO_2$ emission rate measurements have been carried out using ground-based UV remote sensing techniques for more than 30 years, becoming a standard practice in volcanic surveillance (e.g., Stoiber and Jepsen, 1973; Edner et al., 1994; Weibring et al., 1998; Sutton et al., 2001; Caltabiano et al., 2004). The development of cheap, lightweight UV spectrometers that utilise CCD detectors has greatly increased the number of volcanoes at which $SO_2$ flux is routinely monitored (Galle et al., 2003, 2005). This new technology has also opened up the opportunity of intensive measurements of $SO_2$ fluxes at high-temporal resolutions during daylight hours using static arrays of scanning spectrometers (Burton et al., 2003; Edmonds et al., 2003; McGonigle et al., 2003; Galle et al., 2006; Rivera et al., 2007).

Open-path UV spectra are usually analysed using the Differential Optical Absorption Spectroscopy (DOAS) method (e.g., Noxon, 1975, 1978; Perner and Platt, 1979; Platt and Perner, 1983; Plane and Nien, 1992; Platt, 1994; Plane and Saiz-Lopez, 2006). Since its first application in the 1970s, DOAS has been widely used for the investigation of tropospheric gases in passive mode using scattered sunlight as a radiation source. Following the Beer–Lambert law to describe the intensity of the incident light after passing through an absorbing medium, the principle of DOAS is based on the so-called "differential optical depth" separating the broadband modulation from the narrowband absorption structures in spectra marked by trace-gases (typically with wavelength of 10 nm or less). To perform DOAS analysis, two spectra are necessary. The first, with intensity $I(\lambda)$, is the spectrum resulting when the volcanic plume is present in the field-of-view (FOV) of the spectrometer, the second is (ideally) an identical spectrum but without volcanic gas with intensity $I_o(\lambda)$

* Corresponding author. Istituto Nazionale di Geofisica e Vulcanologia, sezione di Catania, Piazza Roma 2, 95123, Catania, Italy. Tel.: +39 095 7165829; fax: +39 095 435801.
*E-mail addresses:* salerno@ct.ingv.it, ggs25@cam.ac.uk (G.G. Salerno), burton@pi.ingv.it (M.R. Burton), co200@cam.ac.uk (C. Oppenheimer), caltabiano@ct.ingv.it (T. Caltabiano), vip20@cam.ac.uk (V.I. Tsanev), bruno@ct.ingv.it (N. Bruno).

0377-0273/$ – see front matter 
doi:10.1016/j.jvolgeores.2009.01.009

(Solomon et al., 1987). $I_o$ is referred to as the reference spectrum. In volcanological applications, the collection of reference spectra is complicated when carrying out real-time DOAS analysis of spectra acquired by automated UV scanners, due to the typical presence of wide plumes above the stations. In order to address this problem, we investigate here the performance of a modelled reference spectrum, obtained from a high-resolution solar spectrum in the DOAS retrieval (Kurucz et al., 1984; Salerno et al., 2006).

To test the model, we collected Clear Sky Spectra (CSS) using two $SO_2$ calibration cells. Spectra were collected at each of the five UV Scanners installed on Mt. Etna by the Catania section of the Istituto Nazionale di Geofisica e Vulcanologia (INGV) in late October 2004 (Fig. 1). This set of instruments constitutes the FLAME (FLux Automatic MEasurements) $SO_2$ monitoring network discussed by Burton et al. (2004).

Using these data, a sensitivity analysis on potential sources of uncertainty for the DOAS retrieval was undertaken (Balci, 1997; Rodgers, 2000; Ascough et al., 2005). Performing experimental tests on the resolution of the spectrometers, and detecting the spectral fitting region, we optimised the DOAS modelled reference spectrum [$I_o - m(\lambda)$] retrieval parameters (Margelli and Giovanelli, 2002). The derived $I_o - m(\lambda)$ was validated by evaluating cell-CSS, investigating the uncertainty affecting the retrieval due to the diurnal variation of sunlight and seasonal effects. A detailed error assessment was conducted through analysis of sets of 100 spectra collected for each scanning-angle.

The performance of this optimised retrieval and the modelled reference spectrum was tested on volcanic plume spectra collected at Mt. Etna by the FLAME network. Specifically, we selected data acquired during the 10-day eruptive event of July 2006 for a case-study.

## 2. Methodology

The basic setup for the collection of spectra with a calibration cell in the FOV of the UV scanner is shown in Fig. 2. We used two quartz $SO_2$ calibration cells (Low cell = Lo-cell and High cell = Hi-cell) of $3.2 \times 10^{17}$ and $8.5 \times 10^{17}$ molecules cm$^{-2}$ with 2.5 cm diameter and 1.1 cm length. The accuracy of both cells is ±5% as reported by the manufacturer (Resonance Ltd., Canada).

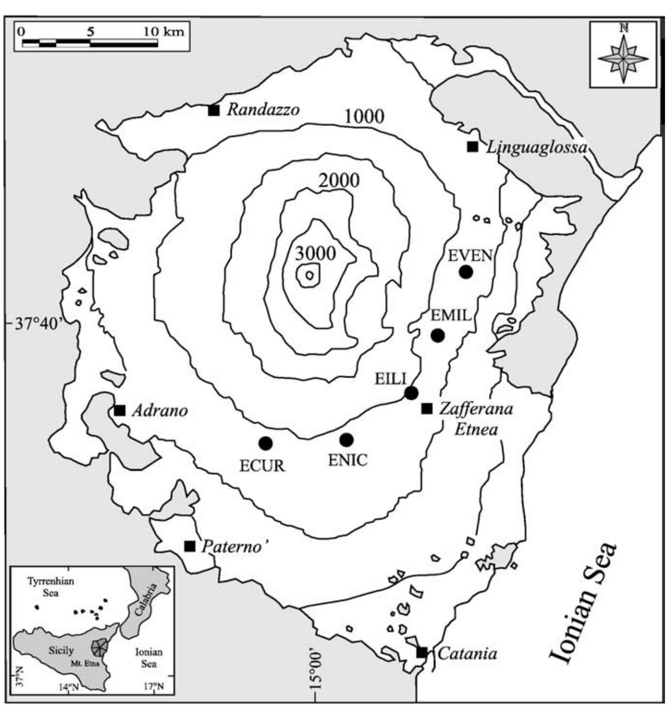


**Fig. 1.** Map of Mt. Etna volcano and its surroundings with the locations of the five FLAME UV Scanner station network (solid-black circles).

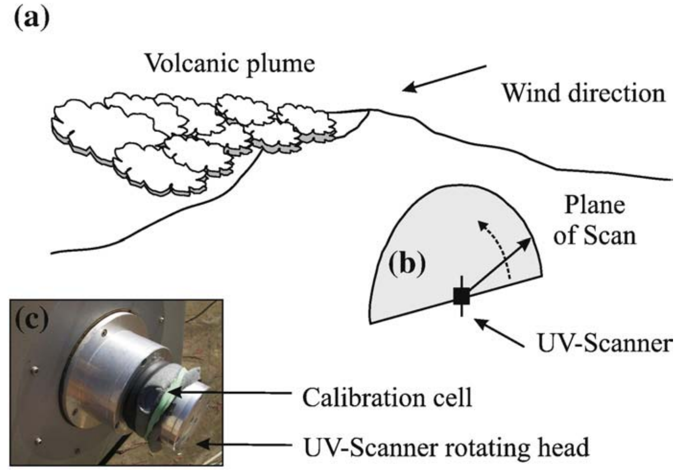


**Fig. 2.** (a) Cartoon showing the experimental configuration for the collection of the Cell Clear-Sky Spectra (cell-CSS). (b) Plane of scanning anticlockwise; (c) Calibration cell in the scanner's field-of-view.

Each UV scanner consists of an Ocean Optics S2000 spectrometer coupled with an ADC1000-USB A/D analogue-to-digital converter. The spectrometers comprise a 2048 pixel-detector array and 3600 grooves mm$^{-1}$ diffraction grating, which, combined with a 200 μm entrance slit, delivers a spectral resolution between ~0.6–0.9 nm (FWHM) over the wavelength range 295–375 nm. The spectrometer is connected via fibre optic cables (1000 μm) to a two quartz-lens telescope (8 mrad FOV) that views a 45°-angle aluminium-coated first-surface mirror, mounted in a rotating head. This is rotated using a 6000-step stepper-motor giving an angular resolution of ~1 mrad. We used a coated visible-light filter (HOYA U330) as a window in the rotating head to reduce stray light inside the spectrometer and for environmental protection. The device was controlled by a micro-controller mounted on a custom-made circuit board (Caltabiano et al., 2005). A dark-spectrum (background electronic noise) was recorded before the start of each scan by pointing the turning mirror downwards at a black surface (Stutz and Platt, 1996; Platt et al., 1997). The viewing geometry of the instrument permits scanning from ±12° above each horizon (12°–168°); typically 104 spectra were collected during the scan with angular spacing of 1.5°. Each complete scan through the sky consisted therefore of 105 spectra including a dark-spectrum, and took ~5 min to collect. Each recorded spectrum consisted of 10 co-added consecutive spectra, each of which was acquired with 200 ms exposure time. An automated version of the retrieval scheme presented was used to evaluate $SO_2$ column amounts in real-time.

Calibration cells were surrounded by 11.6 × 5.0 × 0.6 cm polyurethane foam to eliminate light that had not passed through the cell. Calibration cells were placed on the window of the scanner and fixed to the rotating-head with an elastic strap of 19 cm diameter and 0.6 cm thickness. With this setup, we collected four sets of CSS viewing through both Lo- and Hi-cell using the five UV Scanners of Mt. Etna. In addition two sets of clear-sky spectra were collected without calibration cells. Measurements were performed approximately monthly between August 2006 and August 2007 for 30 min to 7 h depending on test requirements and plume direction (see supplementary data).

## 3. Data analysis

Data analysis was performed using a retrieval based on the Rodgers (1976, 2000) optimal estimation algorithm. This approach minimises the function $y - F(x)$ using a Levenberg–Marquardt iteration, where $y$