Bull Volcanol (2006) 68: 323–327
DOI 10.1007/s00445-005-0014-9

SHORT SCIENTIFIC COMMUNICATION

**Keith A. Horton · Glyn Williams-Jones ·
Harold Garbeil · Tamar Elias · A. Jeff Sutton ·
Peter Mouginis-Mark · John N. Porter · Steven Clegg**

Real-time measurement of volcanic SO_2 emissions: validation of a new UV correlation spectrometer (FLYSPEC)

Received: 11 June 2003 / Accepted: 18 May 2005 / Published online: 9 December 2005

Abstract A miniaturized, lightweight and low-cost UV correlation spectrometer, the FLYSPEC, has been developed as an alternative for the COSPEC, which has long been the mainstay for monitoring volcanic sulfur dioxide fluxes. Field experiments have been conducted with the FLYSPEC at diverse volcanic systems, including Masaya (Nicaragua), Poás (Costa Rica), Stromboli, Etna and Vulcano (Italy), Villarica (Chile) and Kilauea (USA). We present here those validation measurements that were made simultaneously with COSPEC at Kilauea between March 2002 and February 2003. These experiments, with source emission rates that ranged from 95 to 1,560 t d^{-1}, showed statistically identical results from both instruments. SO_2 path-concentrations ranged from 0 to >1,000 ppm-m with average correlation coefficients greater than $r^2=0.946$. The small size and low cost create the opportunity for FLYSPEC to be used in novel deployment modes that have the potential to revolutionize the manner in which volcanic and industrial monitoring is performed.

Keywords FLYSPEC · Volcanic emissions · Ultraviolet correlation spectrometer

Editorial responsibility: A. Woods

K. A. Horton (✉) · H. Garbeil · P. Mouginis-Mark · J. N. Porter
Hawaii Institute of Geophysics and Planetology, University of Hawaii at Manoa,
1680 East-West Rd., Post 504, Honolulu, Hawaii 96822, USA
e-mail: keith@higp.hawaii.edu
Tel.: +808-956-4139
Fax: +808-956-6322

G. Williams-Jones
Department of Earth Sciences, Simon Fraser University,
8888 University Drive, Burnaby, British Columbia, V5A 1S6, Canada

T. Elias · A. J. Sutton
U. S. Geological Survey, Hawaiian Volcano Observatory,
Hawaii National Park,
P.O. Box 51, 51 Crater Rim Drive, Hawaii 96718-0051, USA

S. Clegg
Department of Geology, University of Hawai'i at Hilo,
200 W. Kawili St., Hilo, Hawaii 96720, USA

Introduction

The ultraviolet correlation spectrometer (COSPEC) was initially developed by Barringer Research (Canada) in the 1960s for pollution monitoring of NO_x and SO_2 from industrial stacks, and was first applied to the study of volcanoes by Moffat and Millan (1971), Stoiber and Jepsen (1973) and Stoiber et al. (1983). Since then, it has been used extensively in conjunction with other geophysical and geochemical techniques for the study and routine monitoring of vigorously and quiescently degassing volcanoes (e.g., Caltabiano et al. 1992; Casadevall et al. 1987; Elias et al. 1998; Stoiber et al. 1986; Williams et al. 1990; Zapata et al. 1997). A limited number of COSPECs are still produced by Resonance Ltd. (Canada), however, the instrumental approach has remained essentially unchanged since its initial development. Nevertheless, until very recently, this has been one of the few reliable methods for SO_2 flux measurements at volcanoes. New spectroscopic techniques such as differential optical absorption spectroscopy (DOAS) and differential absorption lidar (DIAL) are now making the transition from atmospheric sciences to volcanology (Weibring et al. 1998; Weibring et al. 2002). In fact, with the advent of a new miniature UV spectrometer, Montserrat Volcano Observatory is now routinely using these miniature spectrometers, configured as automated scanning units (ScanSpec network), with spectral concentrations of SO_2 evaluated using the DOAS method (Edmonds et al. 2003; Galle et al. 2002; Platt 1994). Here we present work on a similar instrument, called the FLYSPEC for its small size, which uses a variation of the DOAS evaluation method, with the additional feature of incorporating an in situ correlation spectroscopy calibration system.

Instrument

The FLYSPEC consists of an Ocean Optics USB2000 ultraviolet spectrometer that uses an asymmetric crossed Czerny-Turner configuration. The detector is a 2,048-element charge coupled device (CCD) linear silicon array.

The spectrometer has a 2,400 lines mm^{-1} plane grating, which, combined with a 25 μm slit, results in an optical resolution of 0.25 nm over a wavelength range of 177–330 nm with a sampling resolution of 0.1 nm across the array. The entire spectrum in this range is sampled and stored. For the purposes of measuring SO_2 in real-time, a total of 8–9 absorption peaks and troughs between 304 and 320 nm are analyzed. Two known concentration SO_2 calibration cells, similar to those used in COSPEC, are mounted such that they may be easily inserted into the optical path of the instrument. With the addition of other UV absorbing gas calibration cells and selection of appropriate spectral peaks or curve fitting, it is possible to simultaneously measure multiple gases (COSPECs were developed to measure either SO_2 or NO_2). All of the spectrometer's components (i.e., optics, detector and electronics) are built into an extremely compact and lightweight unit (89 mm × 64 mm × 34 mm, 200 g; Fig. 1). Although the spectrometer is designed to accept an optical fiber input, we reduce light losses by mounting the "telescope", which consists of a small fiber-optic collimating lens, directly to the spectrometer input aperture. This lens, in combination with a UV band-pass filter window located in the FLYSPEC's durable case (Fig. 1), results in a field of view of ∼2.5° (44 mrad). The filter and case also reduce the amount of stray light reaching the spectrometer, while the case protects the spectrometer from harsh environments and vibration. All power to the system is provided by a sub-notebook computer (or any laptop) through the USB port for the spectrometer and through the PCMCIA slot for the GPS. An external GPS antenna provides flexibility in mounting for best satellite constellation viewing. The total mass of the FLYSPEC, including computer, protective case, cabling, and GPS is <2 kg and it can typically be operated continuously for 4–6 h with a standard high-capacity battery. This can be easily adapted to run for more extended periods off a 12 V vehicle battery or other power source.

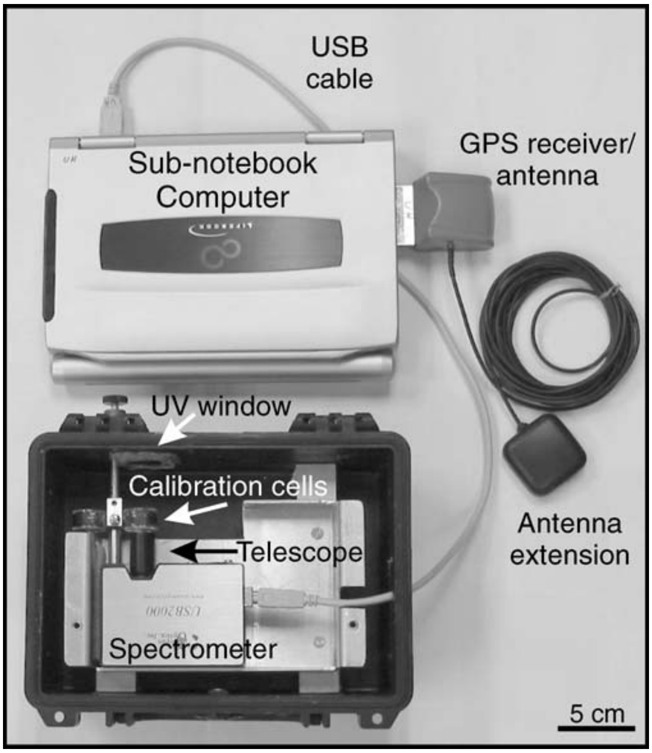

Fig. 1 FLYSPEC components consisting of a miniature spectrometer, sub-notebook computer, and GPS. High and low calibration SO_2 gas cells are shown mounted above the spectrometer and telescope. The "telescope" is a fiber-optic collimating lens mounted directly to the spectrometer input aperture. The lens, in combination with the UV band-pass filter window mounted on the case, provides a field of view of approximately 2.5°. Power for the spectrometer and GPS is supplied by the computer

Analysis

The FLYSPEC provides real-time display of the UV spectrum, calculation of the spectral absorbance, and a scrolling plot of the gas path-concentration in ppm-m, and corresponding GPS position and time. As with a COSPEC, the FLYSPEC has an adjustable data acquisition rate, with generally sufficient signal to noise at a full-spectrum acquisition rate of between 300–1000 ms.

Acquisition and subtraction of a dark frame is required to correct for dark current and electronic noise on the CCD array. To calibrate for SO_2 (or any given UV-absorbing gas species) path-concentration, a clear sky reference spectrum is collected outside of the gas plume. In addition, spectra are collected for the two (or more) calibration cells (Fig. 2A). The absorption

$$A_\lambda = -\log\left(\frac{S_\lambda - D_\lambda}{R_\lambda - D_\lambda}\right) \tag{1}$$

spectrum is thus calculated using the DOAS method (Platt 1994):where A_λ is the absorbance as a function of wavelength (λ) and S_λ, D_λ and R_λ are the spectral intensities of each sample, dark and references (clear sky and gas calibration), respectively (Fig. 2B). Absorbance peak-trough differences at each wavelength, as a function of the path-concentrations of the reference gas cells, are fit by a least-squares three-point quadratic to derive calibration coefficients. These coefficients are then applied to each profile spectrum deriving SO_2 column abundance in real-time.

This real-time comparison of reference background spectrum to measured spectra also has the benefit, which unlike COSPEC measurements, the FLYSPEC path-concentration results are relatively insensitive to changes in the background cloud cover or in elevation while collecting data due to increased number of wavelengths examined and fitting of the differences between SO_2 absorbance peaks and troughs. This retrieval method is in contrast to the laboratory spectrum DOAS method (Galle et al. 2002; Platt 1994), which uses a stored laboratory reference absorption spectrum that requires assumptions as to the atmosphere composition, and pressure and temperature of the plume. Many of the complications which must be addressed in fitting to model

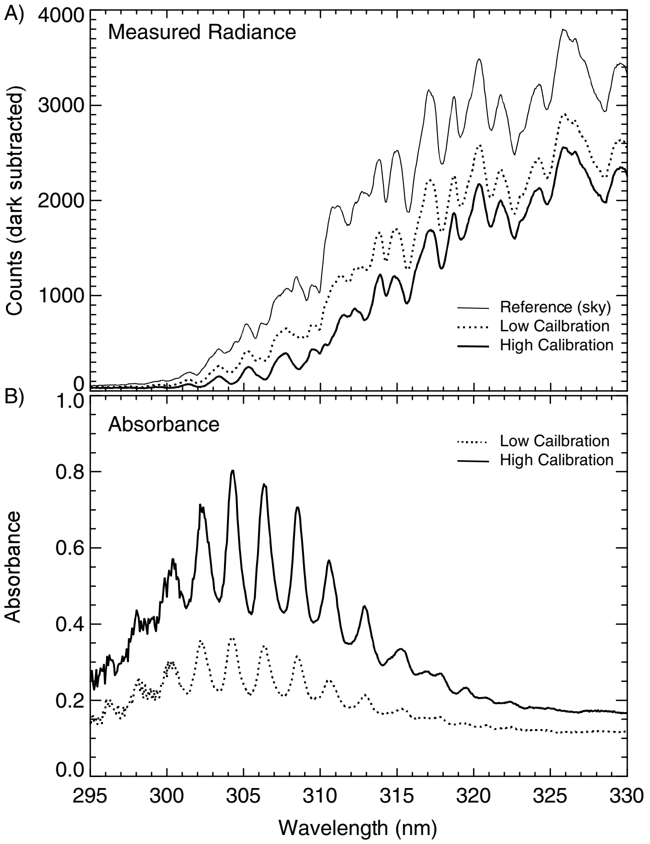

Fig. 2 (**A**) Raw spectral radiance measured by FLYSPEC showing the calibration spectra consisting of clear sky reference and low and high calibration cells. These spectra have all been dark-subtracted to reduce electronic and dark-current noise and correct for array non-uniformity. (**B**) Absorbance spectra of the low and high calibration cells

or laboratory spectra (e.g., inclusion of the Ring-effect Raman spectra and solar Fraunhofer lines) do not occur with FLYSPEC or COSPEC by nature of the correlation technique in which the radiance source (the solar illuminated sky) is the same for reference, calibration, and sample spectra. The ScanSpec network in Montserrat actually include a less frequent (3–4 timers per year) field calibration using known concentration gas cells in order to investigate possible instrumental drift (Edmonds et al. 2003).

However, where field conditions preclude the acquisition of fresh calibration spectra, e.g., when operating in stationary mode in the presence of SO_2, the FLYSPEC may employ stored calibration references in a similar fashion as the laboratory spectra DOAS method, with the advantage that the reference spectra are acquired with the FLYSPEC itself. This also eliminates the necessity of determining the slit function that must be convolved with laboratory reference spectra.

In typical FLYSPEC data collection mode, the derived path-concentration results (ppm-m) and corresponding GPS coordinates and time are saved in ASCII text format on the portable computer and can be examined with any spreadsheet software. Currently, all raw spectra are also stored in a binary file to allow reprocessing of the data should that be desired. In road-based data collection, an important part of gas flux calculations is the cosine correction for perpendicularity between the traverse segment and gas plume direction. The use of an integrated GPS allows for automation of this correction, greatly reducing post-processing time, and increasing the quality of the data, by eliminating the requirements for strictly consistent vehicle speed and operator input. Furthermore, by assuming a normalized plume speed of 1 m s^{-1} (used to facilitate comparison between different instruments and methodologies; Zapata et al. 1997), a velocity-normalized gas flux can be calculated upon completion of each traverse, further reducing post-processing time.

Deployment

Due to the significant reduction in required power, size, weight, and cost of the FLYSPEC, a number of different operational modes can potentially be used to provide ground-truth measurements as well as base-line information on volcanic activity.

Whereas COSPEC measurements have been infrequently made on foot, the small size and weight of the FLYSPEC now make it substantially easier to deploy in areas of difficult access. The real-time integration of GPS position/time with pathlength-concentration now make temporal and spatial mapping of dispersed SO_2 sources feasible. An ongoing research and mapping project at Kilauea caldera which demonstrates this capability, involves acquiring FLYSPEC data with walking traverses in and around the actively degassing fumarole field. Similar experiments have been conducted by us at Vulcano (Italy) and Poás (Costa Rica). FLYSPEC has been deployed in stationary, tripod-mounted mode at Kilauea (Hawai`i), Stromboli (Italy), Villarica (Chile), and Masaya (Nicaragua). In the more common COSPEC method, the FLYSPEC has been mounted on ground-based vehicles and transported beneath gas plumes from several different sources, e.g., Masaya, Kilauea, Etna (Italy).

Multiple instruments can also be deployed as a ground-based array near the gas source to measure the instantaneous spatial distribution of the column abundance of a plume. These data can potentially be used for analyzing vent degassing and plume dispersion behavior. The incorporation of solid-state microprocessors and data-loggers along with wireless telemetry to remote continuous monitoring systems greatly facilitates this. For example, the Montserrat Volcano Observatory has deployed up to 2–3 scanning UV spectrometers (ScanSpec) to simultaneously measure both the plume height and instantaneous gas flux; these data are then telemetered back to the observatory (Edmonds et al. 2003). Expanding the FLYSPEC field of view may allow for the "capture" of complete sections of plume and thus reduce the uncertainty of scanning measurements caused by corrections for changing incidence angles of UV radiation.

As with COSPEC measurements, the largest source of uncertainty is caused by difficulties in accurately