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Comparison of COSPEC and two miniature ultraviolet spectrometer systems for SO₂ measurements using scattered sunlight

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Abstract The correlation spectrometer (COSPEC), the principal tool for remote measurements of volcanic SO₂, is rapidly being replaced by low-cost, miniature, ultraviolet (UV) spectrometers. We compared two of these new systems with a COSPEC by measuring SO₂ column amounts at Kīlauea Volcano, Hawaii. The two systems, one calibrated using in-situ SO₂ cells, and the other using a calibrated laboratory reference spectrum, employ similar spectrometer hardware, but different foreoptics and spectral retrieval algorithms. Accuracy, signal-to-noise, retrieval parameters, and precision were investigated for the two configurations of new miniature spectrometer. Measurements included traverses beneath the plumes from the summit and east rift zone of Kīlauea, and testing with calibration cells of known SO₂ concentration. The results obtained from the different methods were consistent with each other, with <8% difference in estimated SO₂ column amounts up to 800 ppm m. A further comparison between the COSPEC and one of the miniature spectrometer configurations, the 'FLYSPEC', spans an eight month period and showed agreement of measured emission rates to within 10% for SO₂ column amounts up to 1,600 ppm

m. The topic of measuring high SO₂ burdens accurately is addressed for the Kīlauea measurements. In comparing the foreoptics, retrieval methods, and resultant implications for data quality, we aim to consolidate the various experiences to date, and improve the application and development of miniature spectrometer systems.

Keywords Ultraviolet spectroscopy · Gas monitoring · SO₂ emissions · Kīlauea volcano · COSPEC · DOAS · FLYSPEC

Introduction

SO₂ emission rate measurements are one of the key geochemical indicators used in volcanic hazard assessment. Their prominence partly reflects the relative ease by which SO₂ can be measured in the atmosphere by ultraviolet (UV) spectroscopy as compared with other volcanic gas species, exploiting the coincidence of a widely available UV source (daylight) and the strong absorption spectrum of SO₂. Since the 1970s, the correlation spectrometer (COSPEC) has been used by many volcano observatories for remote sensing of SO₂ emissions (Stoiber and Jepsen 1973; Stoiber et al. 1983). However, since 2001, volcanologists have begun using recently available miniature UV spectrometers (Galle et al. 2002; McGonigle et al. 2002) as they are considerably cheaper, smaller and consume less power than the COSPEC (McGonigle and Oppenheimer 2003; Oppenheimer and McGonigle 2004; Horton et al. 2005; Williams-Jones et al. 2005; Galle et al. 2002; Edmonds et al. 2003). Because the new devices record UV spectra with <1-nm resolution, they offer flexibility in spectral retrieval methods, and target gas species (e.g., Bobrowski et al. 2003; O'Dwyer et al. 2003).

The miniature UV spectrometers are connected to fore-optic systems used to gather light energy passing through the plume, and are controlled using acquisition and processing software. A number of researchers have developed their own approach in addressing these features resulting in a wide range of permutations of spectrometer, optics, and

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software. This paper presents a comparison between two distinct configurations. Both are based on the Ocean Optics USB2000 UV spectrometer and use the differential optical absorption spectroscopy (DOAS) approach (Perner and Platt 1979; Platt 1994) for spectral retrieval. One configuration, referred to as the ‘FLYSPEC’ (Horton et al. 2005; Williams-Jones et al. 2005) is a collimating lens-coupled spectrometer, which uses a set of in-situ reference cells of known SO₂ concentration to generate calibration spectra for least squares fitting of observed data. The other is an optical fiber and telescope-coupled spectrometer, which uses a laboratory spectrum of known SO₂ concentration for least squares fitting. This latter configuration was originally referred to by Galle et al. (2002) as the ‘mini-DOAS’, a name that has been commonly adopted to refer to miniature spectrometer configurations that use a laboratory rather than in-situ reference spectrum, and high resolution (all pixel) fitting. Although the new generation of miniature spectrometer configurations all use the DOAS technique for data retrieval, ‘DOAS mini-spectrometer’ will be used here to refer to the configuration that uses a laboratory reference spectrum.

We report a comparison of the FLYSPEC and DOAS mini-spectrometer approaches with the COSPEC, for measurements of calibration cells and volcanic SO₂ column amounts. In addition, we present eight months of side-by-side COSPEC and FLYSPEC emission rate data from Kīlauea Volcano to provide confidence for observatories with established SO₂ monitoring programs considering the transition from COSPEC to a miniature UV spectrometer system.

Methods

COSPEC instrument and data retrieval description

The COSPEC is a mask correlation spectrometer in which incident UV light is spectrally dispersed onto the radius of a spinning correlation disk. This disk contains quad-

rants, which are etched to transmit light corresponding to peaks or troughs of the SO₂ absorption spectrum, enabling discrimination against solar Fraunhofer lines and stratospheric ozone absorption (Moffat and Millán 1971; Millán and Hoff 1978). By processing the chopped output signal from the detector located after the disk, overhead SO₂ column amounts are determined. The analogue COSPEC signal was digitized using a 16-bit A/D converter (DI-700, DATAQ Instruments) collected through the USB port of a sub-notebook computer each second, and merged with time-stamped GPS position data. The data were converted to concentration-pathlength units (ppm m) using calibrations recorded at the limits of each traverse for cells of known SO₂ concentration. In order to accurately quantify the high SO₂ emissions from the ongoing eruption of Kīlauea, the COSPEC is fitted with a high concentration calibration cell of 1,395 ppm m, whereas most COSPECs operate with a high concentration cell <500 ppm m.

Miniature spectrometer system and data retrieval descriptions

The miniature spectrometer systems exploit the same UV spectral region as the COSPEC for quantifying SO₂ but record complete spectra nominally every 50 ms to 5 s, depending upon the amount of light energy available. The spectral energies are quantified by a linear 2,048 pixel charge-coupled device (CCD) array with approximately 134 pixels representing the SO₂ spectral band.

The FLYSPEC was developed to emulate the COSPEC functionality. In addition to the similarities in the calibration cell concentrations (Table 1), the peak-to-trough combinations used for deriving SO₂ amounts for the FLYSPEC were selected to minimize instrumental noise and maximize the correlation with the COSPEC. Spectra are automatically summed over time to generate one-second data (the COSPEC data rate) and a three-point boxcar average is incorporated to approximate the COSPEC noise characteristics.

Table 1 Hardware, software, and experimental differences in the three spectrometer systems

Instrument configuration	FLYSPEC ^a	DOAS ^b	COSPEC
Slit width (μm)	25	50	
Resolution (nm)	~0.25	~0.6	2
Foreoptics	Collimating lens	4 fiber bundle + two lens telescope	Cassegrain telescope
Field of view (mrad)	44	7	30 × 10
Processing software	SOEST, University of Hawaii	DOASIS, version 2.7.1.9	
Fit window (nm)	305–315 (4–9 peak-trough combinations, or all pixels)	303–313 (all ~134 pixels)	300–315 (9 peak-trough combinations)
Reference spectra	In situ, using 409 and 1,570 ppm m calibration cells	laboratory reference ^c	In situ, using 400 and 1,395 ppm m calibration cells
Integration time (ms)	300–1000	125–350	1000

^aHorton et al. 2005

^bMcGonigle et al. 2002

^cVandaele et al. 1994

Compared to the COSPEC, the new generation of miniature spectrometers has a strong advantage in conditions where light is momentarily obstructed. A COSPEC uses a correlation disc that mechanically chops the incoming light signal. If the light is intermittently attenuated by trees or other overhead obstructions, the signal can become erratic, and the data unusable. For instance, in order to operate a COSPEC in a helicopter where the blades chop the line of sight for the zenith telescope, a long time constant (16 s) must be used, which can compromise the spatial resolution for the plume cross-section (Galle et al. 2002).

System configurations

The main difference in features for the new generation of miniature spectrometer systems are defined by:

1. Foreoptics configurations: (a) a fiber optic and telescope (b) a fiber optic and collimating lens or (c) a collimating lens.
2. Source and number of reference spectra: (a) from a single calibrated laboratory spectra or (b) in-situ, using multiple calibration cells.
3. SO₂ retrieval and processing software: (a) DOASIS, using all pixel fitting (b) user-authored software using only peaks and troughs, or all pixel fitting or (c) Ocean Optics (OOIbase32) software

The systems employed in this comparison use the USB2000 spectrometer powered via a USB connection to a laptop PC (Fig. 1). Technical specifications on the spectrometer can be accessed at Ocean Optics Inc. (<http://www.oceanoptics.com/products/usb2000visnir.asp>.) Differences between the hardware configurations, foreoptics and exper-

imental parameters for the three spectrometer systems are summarized in Table 1.

Both the DOAS mini-spectrometer and FLYSPEC computer interfaces provide real-time displays of the collected spectra and the corresponding SO₂ concentrations, to enable location of the plume boundaries. Integration times for both were optimized so that there was maximum radiance without pixel saturation by light.

Evaluation of SO₂ column amounts

Ultraviolet sunlight passing through volcanic plumes undergoes extinction primarily by molecular absorption (including by target gas species) and scattering (Rayleigh and Mie). The scattering introduces broadband losses that vary slowly in the spectral domain and can be differentiated from the spectral absorption signatures. The absorption features can be decomposed into high and low frequency components, and treated with numerical filtering methods to derive the concentrations of trace gases.

In using the DOAS methodology, both the DOAS mini-spectrometer and FLYSPEC approach require collection of a *dark* spectrum (where light is blocked from entering the spectrometer) and a *clear sky* spectrum (pointing at zenith sky outside the plume), before traversing underneath the plume and recording sample *gas* spectra. In order to determine the SO₂ concentration-pathlength in each sample *gas* spectrum, these two techniques execute several common steps:

1. The *dark* spectrum is subtracted from the *gas* and *clear sky* spectra to remove the dark current and electronic noise on the CCD array.

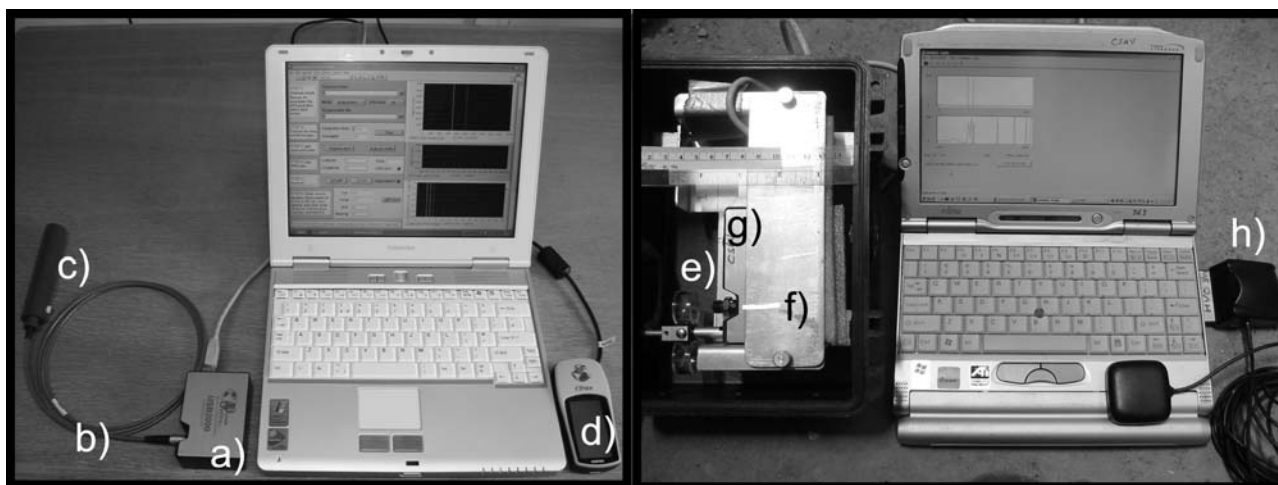


Fig. 1 Miniature spectrometer systems used for comparison with the COSPEC at Kilauea Volcano, Hawaii. *Left*: In the DOAS approach, a laboratory reference spectrum was used to calibrate data retrieved from the miniature spectrometer. The miniature spectrometer (a) is connected by fiber optic cable (b) to the telescope (c). GPS receiver (d) provides continuous tracking to locate all spectra saved to the laptop computer via USB cable. *Right*: The FLYSPEC uses inter-

nal calibration cells (e) to acquire reference spectra for data fitting. A “telescope” (f) consisting of a small collimating lens is directly attached to the spectrometer (g) input aperture, and views the sky through a bandpass UV filter window installed in the protective case. Continuous GPS location data from the receiver (h) are integrated into the data stream, which is saved to the laptop computer

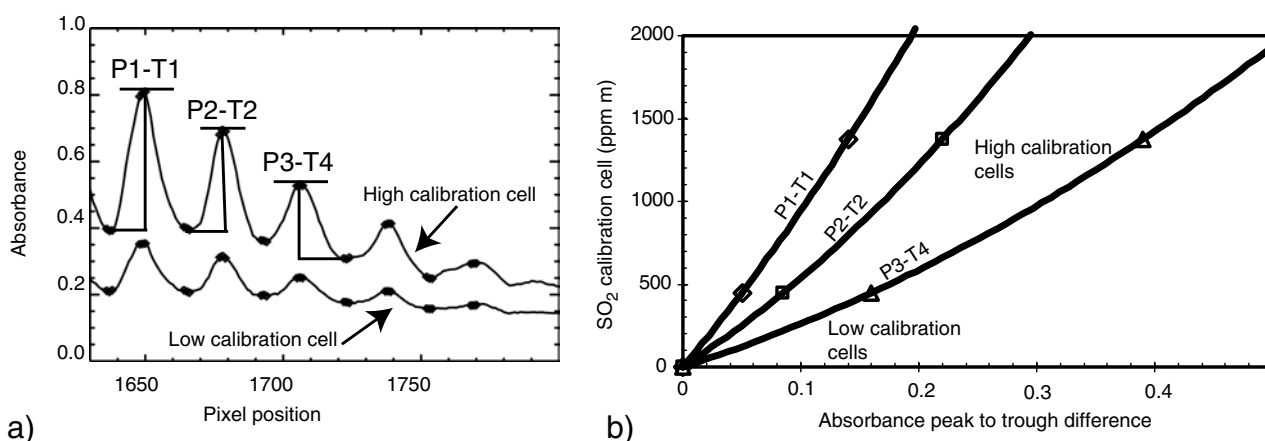


Fig. 2 **a** Absorbance peak-trough differences for the low and high calibration cells are used to derive calibration coefficients for the FLYSPEC real-time SO₂ retrieval. **b** A three-point quadratic is used to fit the cell concentrations versus the absorbance peak-to-trough differ-

ence. The derived coefficients are applied to the sample spectra peak to trough differences. The typical peak (P) to trough (T) differences used are: P1–T1, P2–T2, P3–T4, and P5–T4 (not shown)

2. Each *gas* spectrum is then divided by the *clear sky* spectrum to isolate the in-plume extinction, and partly compensate for the ring effect (Platt 1994).
3. The negative logarithm is then computed, to generate an absorption spectrum.
4. The absorption spectrum is subjected to a high pass filter or divided by a polynomial best-fit curve, in order to remove slowly varying scattering-induced extinction and the low frequency component of the SO₂ absorption, and to isolate the rapidly varying SO₂ absorption component.
5. The resulting absorption spectrum is smoothed to remove high frequency noise.
6. This spectrum is fit to a *reference* spectrum using a least-squares procedure, and the SO₂ column amount is retrieved.

The key difference between the FLYSPEC and DOAS mini-spectrometer approaches is the manner in which the spectra (*differential* spectra) are processed in step 6 to determine the SO₂ concentrations-pathlengths. In the case of the DOAS mini-spectrometer approach, a single *reference* SO₂ absorption spectrum of known concentration (obtained by convolving a 0.01-nm resolution laboratory spectrum (Vandaele et al. 1994) with the USB2000's line shape) is scaled to a measured sample spectrum using a nonlinear least squares algorithm. The SO₂ column amount is found from the fitting coefficients.

In the FLYSPEC approach, high and low concentration *reference* spectra are acquired while situated outside the plume by recording *dark*, *clear sky* and *gas* spectra (the latter using two quartz cells containing known amounts of SO₂), which are then processed with steps 1–5 (Horton et al. 2005). For situations where collecting new calibrations is difficult (i.e., unattended continuous or airborne operation, variable light conditions, or limited clear background sky availability), the FLYSPEC software can recall previously collected reference spectra. The peak minus trough absorption values for four to nine peak-and-trough combinations between 305 and 315 nm are plotted against the known cal-

ibration cell concentrations, and quadratic lines of best fit plotted through each peak-and-trough's data, and the origin (Fig. 2). For all processed *differential* spectra from sample measurements, peak minus trough absorption values are found for each of the same peak-and-trough combinations, and an SO₂ concentration pathlength is derived using the polynomial coefficients from the calibration cell spectra. The SO₂ results derived from each peak-and-trough combination are then averaged to determine the final SO₂ column amount.

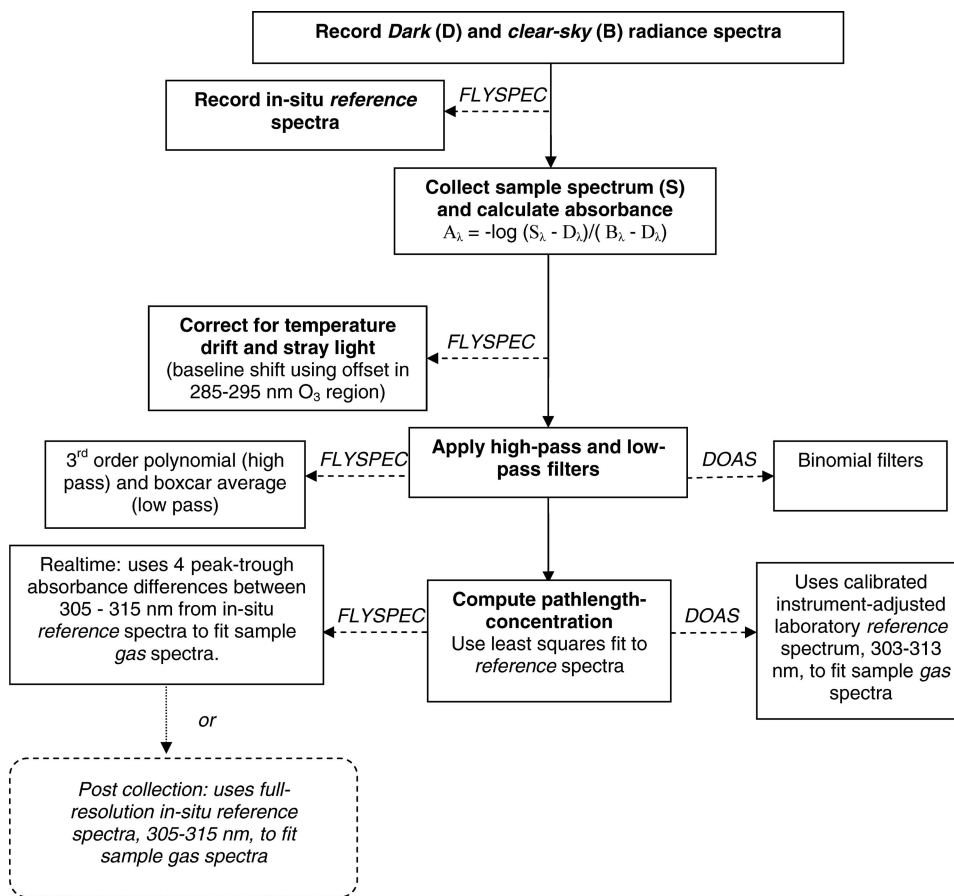
The *differential* spectra from the FLYSPEC approach can also use the full sample spectra as in the DOAS mini-spectrometer approach, but compared to the cell-derived reference spectra, rather than an adjusted laboratory reference spectrum. The SO₂ column abundance is derived by averaging the weighted results from the low- and high-calibration cell reference spectra. Although the peak to trough method of fitting is faster and simpler, both versions of the FLYSPEC retrieval provide similar spectral concentrations, with a difference of <5%. Figure 3 provides a summary of the characteristics of the two miniature spectrometer retrievals.

Measurements and results

Calibration cell measurements

Pathlength-concentrations of six quartz SO₂ calibration cells of known values between 89 ppm m and 1,570 ppm m were measured using the FLYSPEC and DOAS mini-spectrometer configurations by placing these cells in the fields of view of the corresponding instruments. These measurements were made outside the volcanic plume by collecting scattered light from the zenith sky; the data are presented in Table 2 and Fig. 4. Although both datasets yield a slope and r^2 close to 1 when fit with a line, the DOAS mini-spectrometer data are best fit with a 3rd-order polynomial (Fig. 4). The SO₂ column amounts from the DOAS mini-spectrometer were consistently lower than those from

Fig. 3 DOAS mini-spectrometer and FLYSPEC data evaluation. The flowcharted sequence shows that although there are differences in details of data smoothing and offset, the two methods diverge primarily in how the absorbance data are converted to column amounts. A_λ is the absorbance as a function of wavelength (λ) and S_λ , D_λ , and B_λ are the spectral intensities of each sample, dark, and clear sky



the FLYSPEC for the higher concentration cells, with a discrepancy of $\sim 4\%$ for the 1,570 ppm m calibration cell. The COSPEC response was not measured due to the complications associated with repeatedly changing the internal calibration cells. The correlation between the peak to trough and full spectrum fit retrievals for the FLYSPEC yields a slope = 0.9908, and $r^2 = 0.9999$.

COSPEC and miniature spectrometer plume measurements

The two miniature spectrometer configurations and the COSPEC were mounted on the side of a car with the fields of view pointing at the zenith sky. The summit and east rift zone (ERZ) plumes of Kīlauea were traversed by vehicle (Elias et al. 1998); these two emission sources provided distinctly different SO_2 column amounts. Four summit and six ERZ traverses were made, with the position of each UV spectrum or column abundance logged at 1 Hz by continuously recording GPS units. GPS data were used in tandem with the spectral concentrations to determine integrated column amounts, which were multiplied by wind speeds to derive fluxes (e.g., Stoiber and Jepsen 1973; Galle et al. 2002) (Table 3).

Figure 5 provides an example trace comparing the column amounts retrieved for the three spectrometers at the summit and ERZ. For the ERZ, the DOAS mini-

spectrometer generally tracked the COSPEC trace more faithfully than did the FLYSPEC, as shown by point-to-point correlations (Table 3); however, the DOAS traces are systematically lower for traverses with higher SO_2 column abundances, as reflected by the associated slopes (Table 3). This is consistent with the observed under-reporting by the DOAS mini-spectrometer for the high concentration calibration cells. Thus, the overall agreement of FLYSPEC and COSPEC is better for the SO_2 -rich ERZ traverses, while the DOAS mini-spectrometer and COSPEC were in better agreement for the lower SO_2 column abundances of the summit traverses. The DOAS mini-spectrometer yielded ERZ emission rates an average of 19% less than the COSPEC; by comparison, the FLYSPEC yielded results an average of 8% less than the COSPEC. Average differences for the summit traverses were +3% for the DOAS and -7% for the FLYSPEC with respect to the COSPEC.

Eight-month COSPEC-FLYSPEC emission rate comparison

From August, 2003 to May, 2004, side-by-side COSPEC and FLYSPEC were used by the U.S. Geological Survey-Hawaiian Volcano Observatory (HVO) to make the twice weekly SO_2 emission rate measurements at Kīlauea (Elias et al. 1998). The results confirm the consistency of the methods, with less than 10% difference in integrated

Table 2 DOAS mini-spectrometer and FLYSPEC response to standard calibration cells

Cal-cell (ppm m)	DOAS mean (ppm m)	Standard deviation	% error	n ^a	FLYSPEC mean ^b (ppm m)	Standard deviation	% error	n ^a	FLYSPEC mean ^c (ppm m)	Standard deviation	% error
89	93	3.5	4.5	9	85	1.9	-4.5	30	84	2.7	-5.6
90	91	4.6	1.1	7	93	2.7	3.3	33	89	3.4	-1.1
358	331	2.7	-7.5	9	340	3.2	-5.0	46	345	3.9	-3.6
367	346	1.8	-5.7	7	350	3.4	-4.6	50	360	3.4	-1.9
409	386	2.5	-5.6	12	405	4.8	-1.0	38	411	4.4	0.5
776	717	3.2	-7.6	8	747	9	-3.7	24	756	9.3	-2.6
1570	1355	3.9	-13.7	10	1592	6.5	1.4	35	1577	6.8	0.4

^aNumber of data points collected to generate mean

^bFits all pixels over the 305–315 nm window

^cUses peak-to-trough differences for fit

column abundance calculated between the two techniques, even at Kīlauea's summit, where column abundance and emission rates are low (<100 t/d). A correlation between the two data sets yields an $r^2 = 0.994$, and slope = 0.998. Since the uncertainty in the emission rate measurements is 20–30% (due largely to errors in wind speed) (Elias et al. 1998; Stoiber et al. 1983; Doukas 2002; Williams-Jones et al. 2005), the difference between the two spectrometer systems is well within the uncertainty of the measurements themselves.

Baseline noise comparison

The mean and standard deviation for a 100-s section of baseline outside of the plume were compared for the three spectrometer configurations for each of the summit and ERZ traverses. Ideally, the baselines should be steady and near zero outside of the volcanic plume so that the plume signal can be easily recognized and evaluated. Baseline noise is a result of sky conditions, spectrometer response (which is affected by temperature and humidity), and processing algorithm. In order to improve signal to noise, the DOAS mini-spectrometer co-added 4 to 16 individual

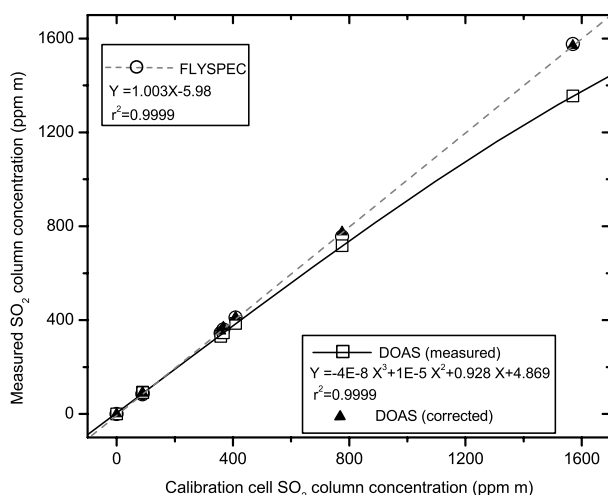


Fig. 4 The FLYSPEC (dotted line, open circles) and DOAS mini-spectrometer (solid line, open squares) response to clear sky (zero SO₂) and six individual calibration cells ranging in value from 89 to 1,570 ppm m show nearly identical retrievals at concentrations <400 ppm m. While the FLYSPEC response is linear, the DOAS data is best fit with a 3rd order polynomial. The DOAS data were corrected (closed triangles) using the polynomial calibration curve. FLYSPEC retrieval uses all-pixel fit method.

Table 3 A comparison of SO₂ emission rates and correlation statistics for the summit and ERZ traverses

Location	Traverse	COSPEC SO ₂ t/d	DOAS SO ₂ t/d	% difference ^a	FLYSPEC ^b SO ₂ t/d	% difference ²	DOAS-COSPEC correlation		FLYSPEC- COSPEC correlation	
							r ²	Slope	r ²	Slope
Summit	1	89	93	4.5	81	-9.0	0.891	0.895	0.970	0.992
	2	104	106	1.9	99	-4.8	0.938	0.967	0.985	1.036
	3	109	110	0.9	101	-7.3	0.963	0.781	0.968	0.876
	4	88	93	5.7	82	-6.8	0.853	0.975	0.967	0.993
East rift	1	1292	1066	-17.5	1191	-7.8	0.996	0.827	0.995	0.964
	2	839	696	-17.0	771	-8.1	0.983	0.843	0.981	0.952
	3	2422	1720	-29.0	2219	-8.4	0.990	0.765	0.980	0.860
	4	1181	1081	-8.5	1125	-4.7	0.991	0.822	0.977	0.942
	5	1634	1296	-20.7	1449	-11.3	0.990	0.833	0.982	0.907
	6	1284	1101	-14.3	1223	-4.8	0.991	0.855	0.976	0.840

^aBetween the indicated miniature spectrometer configuration and COSPEC

^bUses peak minus trough differences for fit

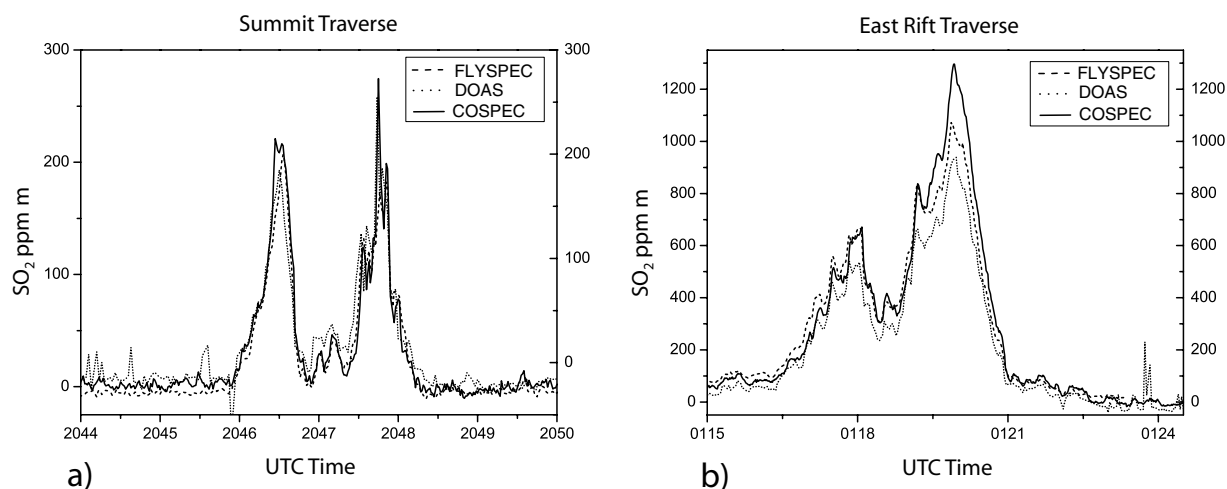


Fig. 5 Comparison of path concentration results between COSPEC (solid), FLYSPEC (dashed), and DOAS mini-spectrometer (dotted) for example traverses on July 23, 2003 (a) at the summit of Kīlauea

Volcano (b) for the east rift zone plume. Correlation data for the 10 traverses appear in Table 3

radiance spectra, which were collected every 125–350 ms, yielding data points every 500–4,800 ms. The FLYSPEC averaged 1–3 spectra to yield 1-Hz data to optimize comparisons with the COSPEC. The signal-to-noise ratio is proportional to the square root of the number of co-added spectra, therefore, the higher number of co-adds for the DOAS miniature spectrometer yields less noisy radiance spectra; however, this does not translate into less noise in the derived concentration pathlengths. There was no systematic change in standard deviation as a function of integration time or number of co-added spectra.

The minimum, maximum and mean standard deviations for the clear sky baseline for the ten traverses are presented in Table 4. Although a large amount of scatter was observed for all of the techniques, the DOAS mini-spectrometer yielded baseline sections with the highest noise, while the full spectrum fit FLYSPEC data generally had slightly less noise than data from the other configurations. This is partially due to the lower effect of jitter or electronic noise on the all pixel fitting, and three point boxcar smoothing of the derived concentration pathlength values for the FLYSPEC retrieval.

Sources of uncertainty for this comparison

Sources of error for the three instruments and techniques have been documented previously (Millán 1980; Platt 1994;

Edmonds et al. 2003; Galle et al. 2002; Horton et al. 2005; Williams-Jones et al. 2005). Of particular note in the Kīlauea experiments were errors contributed by sky conditions that provided insufficient or excessive radiance, causing poor signal-to-noise, or pixel saturation within the fitting window, respectively. These problems could only be partially corrected by adjusting the integration times.

Discrepancies between the FLYSPEC and DOAS mini-spectrometer methodologies such as differing instrumental fields of view or plume view from aiming of the spectrometers were assumed to be negligible due to the ground-level altitude of the plume. There were inconsistencies in time registration of the data that were corrected by manually aligning the column abundance traces when necessary.

Discussion

Data retrieval and hardware considerations

Reference spectra

As shown in the presented data, the SO₂ retrievals based on laboratory reference spectra and in-situ calibration cells are comparable for pathlength concentrations up to at least 400 ppm m. There is simplicity in using in-situ reference spectra, as the spectrometer and much of the atmospheric modeling required when using a laboratory spectrum is bypassed, and fitting challenges due to discrepancies between measured and library spectra are eliminated. On the other hand, the method of using library reference spectra and DOASIS is well established and provides accessible retrieval algorithms and flexibility. While the systems are very robust, using a miniature spectrometer vigorously in the traverse mode, or repeatedly shipping the instrument, may increase the likelihood of wavelength-pixel shifts. These shifts can be corrected by using known spectral features (e.g., Fraunhofer lines) to make software adjustments;

Table 4 Comparison of 100 s of SO₂-free baseline noise for the three configurations

Background noise (baseline σ in ppm m)	DOAS	FLYSPEC ^a	FLYSPEC ^b	COSPEC
Minimum	4.5	1.8	4	2.9
Maximum	14.2	7.0	11.9	10.4
Mean	9.8	4.3	6.7	5.6

^aFits all pixels over the 305–315 nm window

^bUses four peak to trough differences for fit

however, using calibration cells confirms the overall agreement of a fitting algorithm.

The laboratory spectra used for most DOAS fitting was measured using a very accurate, precise, and sensitive Fourier Transform Spectrometer (Vandaele et al. 1994). The reference spectrum, derived from the measured data, is expressed as SO₂ absorption cross section as a function of wavenumber. This quantity is a fundamental physical property of the SO₂ molecule, and is the proportionality constant between concentration and absorbance in Beer's law. The calculated absorbance spectrum is most commonly expressed in terms of a unit concentration pathlength (Edmonds et al. 2003; McGonigle et al. 2002), and is used as the basis for scaling sample spectra.

When using calibration cells to acquire reference spectra, the accuracy and reliability of the cells themselves are crucial. Those used in our comparison were supplied by the manufacturer of the COSPEC, and were calibrated against "standard cells" manufactured and calibrated by COSPEC co-developer M. Millán. The oldest cells continue to provide stable values more than 20 years after they were produced. The uncertainty in the absolute value of the standards was reported by M. Millán during the initial development of the COSPEC, and ranges between 30 and 51 ppm m for cells up to 1,296 ppm m, or about 4% (Bill Morrow, Resonance, Ltd., pers. comm.) Resonance Ltd., the current manufacturer of the COSPEC, reports that when measuring standard calibration cells singly and in various combinations up to 1,600 ppm m, the RMS residual is approximately 6 ppm m (using a COSPEC fitted with a high concentration disc assembly). This implies that the 3 σ confidence interval for the calibration of an unknown cell relative to the standards is ± 18 ppm m. Although uncertainty in the abundance of SO₂ in the quartz calibration cells can contribute to a systematic error in column abundance measurements, inaccurately labeled calibration cells are easily detected as outliers when tested with multiple cells. Calibration cells can be costly (up to US\$1,500/pair), and a system measuring moderate burdens may retrieve accurate SO₂ abundance based on a single, infrequently calibrated laboratory reference spectrum (Edmonds et al. 2003; McGonigle et al. 2002).

Considerations for high SO₂ burden measurements

The results from the comparisons at Kīlauea highlight the issue of measurement accuracy at high SO₂ burden. A number of sources can contribute to poor estimates including non-linearity in measurement systems (electronics, optics, and detector), and method (COSPEC, DOAS, etc.). The linearity between concentration pathlength and absorbance (Beer-Lambert law) also breaks down at high SO₂ burdens. Kazahaya et al. (2004) report a linear response with the COSPEC fitted with a high concentration correlation disc, up to 8,000 ppm m. FLYSPEC measurements using calibration cell combinations ranging from 500 ppm m to 3,000 ppm m show that the FLYSPEC response is linear

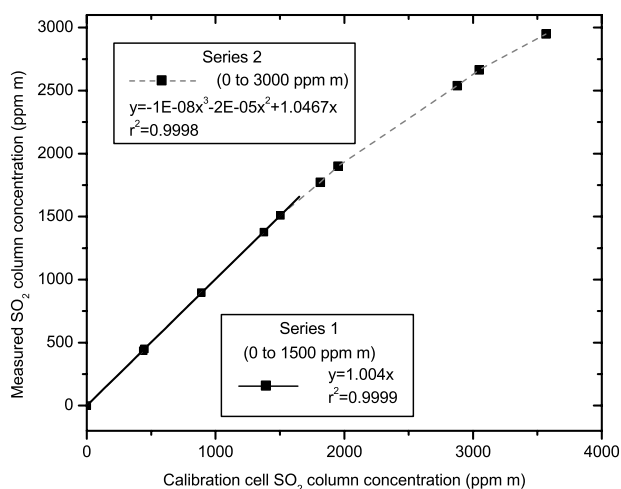


Fig. 6 Flyspec measurements using calibration cell combinations ranging from 500 ppm m to 3,000 ppm m suggest that the Flyspec response is linear up to around 1,500 ppm m (series 1, solid black line), but that the entire range is best fit with a third-order polynomial (series 2, dashed grey line)

up to around 1,500 ppm m, but that the entire range is best fit with a third order polynomial (Fig. 6), as were the DOAS measurements in this comparison (Fig. 4). Spectra with good signal in the entire fit window range, combined with a robust fitting algorithm, may yield accurate retrievals for high SO₂ burdens. However, developing an empirical calibration curve using in-situ cells over a wide range of concentration pathlengths allows accurate measurements by a spectrometer system in a variety of conditions. Using this approach, the DOAS miniature spectrometer data was corrected using the polynomial in Fig. 4 to yield results within 2% of the known calibration cell values (Fig. 4). A number of factors could have contributed to the underestimation of SO₂ by the DOAS miniature spectrometer, including linearity issues and fit window parameters (see following section). Further study of linearity and high SO₂ retrieval strategies for the miniature spectrometer systems is warranted.

Fitting windows and optical configuration

For the new miniature spectrometer systems, selecting an appropriate pixel-range for the spectral fitting window is critical for retrieving accurate SO₂ column amounts, and is specific for each individual spectrometer, depending on slit width, grating specification, and wavelength range. The wavelength calibration of a spectrometer determines the wavelength to pixel registration, so although the wavelengths for an appropriate fit window remain constant, the pixel range will vary from spectrometer to spectrometer.

The dynamic range of spectral radiance that can be measured at each detector pixel is limited. Strong absorption by SO₂ at the minimum wavelengths of the fit window can result in insufficient radiance reaching the detector, causing poor signal-to-noise and associated low sensitivity. The maximum pixels of the fit window are sensitive to

saturation by light, which results in signal clipping. Thus, the minimum and maximum pixels of the fit window must be carefully selected to optimize radiance and absorption. The difference in the selection of fit window for the FLYSPEC and DOAS miniature spectrometer (Table 1) highlights the trade-off of accepting noisier data at the shorter wavelengths, and encountering light saturation sooner at the high end of the window. Adjusting the edges of the fit window where low or excessive radiance yields poor data may increase data quality. For all the UV spectrometers, when measuring concentrations greater than several thousand ppm m, a narrower window shifted toward longer wavelengths improves retrieval accuracy due to the lack of radiant energy at shorter wavelengths.

Because of the distinctions in foreoptics and spectrometer configuration, the light available to the two miniature spectrometer systems in this study is significantly different. The larger slit width used for the DOAS mini-spectrometer provides more light to the spectrometer, allowing spectra to be collected within shorter integration times (Table 1). The longer integration times of the FLYSPEC did not compromise the spatial and temporal resolution of the plume measurements, or yield higher noise than the DOAS mini-spectrometer.

The spectrometer slit width for the FLYSPEC is small, thus the wide field of view collimating lens is used to provide enough light to the spectrometer. When operating under dark, heavy clouds, or other low light conditions, FLYSPEC integration times may need to be increased to many seconds, and instrument response may become erratic. At volcanoes with low plumes, i.e., Kīlauea or Masaya (Nicaragua), the wide field of view functions well, however, it may cause challenges when measuring higher volcanic plumes where a narrower FOV would define the plume edges more accurately. The light scattering from high cirrus clouds can be expected to have a greater effect on the FLYSPEC because of the wider field of view.

Benefits of incorporating an optical fiber, as in the DOAS miniature spectrometer tested here, include improved flexibility in configuring permanent installations or aircraft-, vehicle-, or person-based platforms. The 4-fiber bundle used in this comparison, increases the light throughput as compared to a single fiber, and enhances the ability to direct light onto the slit. Using a small collimating lens as in the FLYSPEC eliminates concerns regarding the delicacy of the optical fiber and telescope for transport and mobile uses. Each of the hardware configurations that we tested has its benefits, and an optimal combination of features can be selected depending on the proposed application. For example, in low light environments such as northern latitude winter, using the larger spectrometer slit width with front-end optics that maximize light throughput would be optimal.

Dynamic range

During periods of extreme variations in sky and light conditions, the COSPEC has a slight advantage for novice

operators, as no user interaction is required to assure that valid spectra are generated. In the miniature spectrometers, proper selection of integration time is required to retrieve useable spectra. For instance, at Kīlauea, under some conditions, FLYSPEC measurements over a 5-km traverse using a single integration time can yield some spectra with marginally sufficient radiance, and some with light saturation. The FLYSPEC data acquisition software flags spectra with a critical number of saturated pixels, so that suspect data are not incorporated into the data stream. A narrower field of view, such as that used in the DOAS mini-spectrometer compared here, could reduce the number of rejected spectra.

Like the COSPEC, the new generation of mini-spectrometers is sensitive to a high solar zenith angle, and frequent reductions in integration time as the sun approaches zenith are needed to generate unsaturated spectra. Also, measurements along an uneven roadway, with a high sun angle can cause intermittent saturation, and affect the data quality. The wide field of view of the FLYSPEC accentuates this effect, although a mechanically adjusted aperture or iris effectively attenuates the incoming light.

Considerations for the future

Improvements to the miniature spectrometer systems in the future might include:

- (1) Spectrometer temperature control. Although this could reduce baseline drift (Bobrowski et al., 2003), and eliminate one of the sources of error for fitting with a laboratory reference spectrum, it would increase the size, weight, cost, and power demands of a system. It may be unnecessary for short term or traverse measurements due to the strong absorption feature of SO₂.
- (2) Spectrometers with higher CCD resolution for better performance in variable sky conditions.
- (3) Modifications or additions to the SO₂ retrievals to (a) compensate for the non-linearity in SO₂ absorption at high concentrations by defining a calibration curve using multiple cells, or identifying robust high concentration peak-to-trough combinations or fit windows, or developing non-linear spectral amplitude scaling factors (b) further correct for atmospheric effects by identifying humidity and other air mass effects, (c) consider fitting a discontinuous window to eliminate features unrelated to SO₂, and (d) review possible improvements to radiative transfer models for laboratory reference based systems.

Conclusions

The new generation of miniature UV spectrometers based on the Ocean Optics USB 2000 is already being widely adopted, and evolution of the systems is occurring very rapidly. We have favorably compared two of these systems

whose main distinctions are (1) spectrometer slit width and optical accessories, (2) method of generating reference spectra, and (3) SO₂ retrieval algorithm. The differences in performance were primarily related to dissimilar fields of view and the accuracy of the algorithms at high SO₂ abundance. Under-reporting of high SO₂ burdens by the DOAS were addressed by applying a calibration curve to correct the data. An eight-month comparison between the COSPEC and one of the systems, the FLYSPEC, showed that a migration to the miniature spectrometers can proceed without loss in accuracy or precision.

The commercialization of miniature spectrometer systems for volcanic applications is in progress (www.nova-sol.com; www.resonance.on.ca); however, costs and convenience will likely continue to promote independently designed systems. As this new tool becomes widely used and expands volcanic gas research and monitoring capabilities, selection of configuration options, including reference spectrum generation, fitting algorithm, and optical configuration, may best be addressed by reviewing the proposed applications. A blending of features from various configurations may yield the most flexible, robust systems, accurate over a wide range of SO₂ burdens.

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