Exploiting ground-based optical sensing technologies for volcanic gas surveillance

Clive Oppenheimer and Andrew J.S. McGonigle

Cambridge Volcanology Group, Department of Geography, University of Cambridge, U.K.

Abstract

Measurements of volcanic gas composition and flux are crucial to probing and understanding a range of magmatic, hydrothermal and atmospheric interactions. The value of optical remote sensing methods has been recognised in this field for more than thirty years but several recent developments promise a new era of volcanic gas surveillance. This could see much higher time- and space-resolved data-sets, sustained at individual volcanoes even during eruptive episodes. We provide here an overview of these optical methods and their application to ground-based volcano monitoring, covering passive and active measurements in the ultraviolet and infrared spectral regions. We hope thereby to promote the use of such devices, and to stimulate development of new optical techniques for volcanological research and monitoring.

Key words *volcano monitoring – volcano plumes – IR and UV spectoscopy*

1. Introduction

Volcanoes emit gases (principally H_2O, CO_2, SO_2, HCl, HF and H_2S) and aerosols to the atmosphere, both during and between eruptions. Measurements of the chemistry, isotopic composition, and flux of these emissions, and their temporal variations are crucial in several applications (Oppenheimer *et al.*, 2003).

1.1. *«Imaging» volcanic plumbing systems and predicting volcanic activity*

Volcanic gas composition and flux relate to subsurface magmatic conditions and higher-level fluid-rock interactions, providing information

Mailing address: Dr. Clive Oppenheimer, Cambridge Volcanology Group, Department of Geography, University of Cambridge, Downing Place, Cambridge, CB2 3EN, U.K.; e-mail: co200@cam.ac.uk

on magma composition, volume, storage, and transport. For instance, temporal variations in the ratios of emitted CO_2/SO_2 and HCl/SO_2 have been used to infer changes in magmatic systems feeding volcanoes (*e.g.*, Noguchi and Kamiya, 1963; Gerlach and Casadevall, 1986), whilst gas flux measurements have been used to constrain the masses of degassing magmas (Symonds *et al.*, 1996). Such data are valuable for hazard assessment because volcanic activity is strongly controlled by the dynamics of degassing (Sparks, 2003). In the broader context of volcano monitoring efforts, the links between seismic, geodetic and gas geochemical signals can be strong. The degassing process may be closely associated with, even responsible for, observed seismicity and ground deformation.

1.2. *Understanding atmospheric and radiative effects*

Quantification of volcanic volatile emissions is also important in order to evaluate their hemispheric to global scale atmospheric and climatic impacts. The sulfur emissions from major explo-

sive eruptions can perturb the chemistry, dynamics and radiative transfer in both the troposphere and stratosphere, influencing surface climate (*e.g.*, McCormick *et al.*, 1995). Passively degassing volcano emissions must also influence tropospheric dynamics and chemistry, as recent investigations suggest that between 15 and 40% of the global tropospheric sulphate burden is volcanogenic (Chin and Jacob, 1996; Graf *et al.*, 1998; Stevenson *et al.*, 2003). These figures exceed the percentage source strength of volcanic sulphur by a factor of 2-4, reflecting the generally higher altitudes of atmospheric entrainment from volcanoes compared with biogenic or anthropogenic sources, and highlighting the importance of better understanding the tropospheric chemistry of volcanic emissions.

1.3. *Evaluation of environmental and health impacts*

From local to regional scales, volcanic emissions can result in serious environmental and environmental health consequences, including destruction of agricultural crops, contamination of pasture, and human respiratory morbidity and cardiovascular mortality. Large lava eruptions, such as that of Laki (Iceland) in 1783/1784, which released ≈ 120 Tg of SO_2, 7.0 Tg of HCl and 15 Tg of HF, have resulted in major pollution episodes responsible for regional-scale extreme weather, agricultural losses, and elevated human morbidity and mortality (Thordarson *et al.*, 1996; Witham and Oppenheimer, 2004). Individual passively degassing volcanoes can also represent major pollution sources. For example, Mt. Etna continuously emits of order 2 kg s^{-1} of HF, and > 8 kg s^{-1} of HCl (Francis *et al.*, 1998). Its SO_2 flux (≈ 70 kg s^{-1}) is comparable to the total industrial S emission from France, and substantially elevates tropospheric sulphate in southern Italy (Graf *et al.*, 1998). Adverse environmental and health impacts are observed downwind of many degassing volcanoes, including Masaya (Nicaragua), Kīlauea (Hawai`i), Poás (Costa Rica), Miyakejima (Japan) and Popocatépetl (Mexico) (*e.g.*, Baxter *et al.*, 1982; Mannino *et al.*, 1996; Delmelle, 2003; Fujita *et al.*, 2003).

At Masaya volcano, which has been degassing strongly for over a decade without significant eruption, boundary layer SO_2 concentrations are elevated over a downwind area > 1000 km^2, resulting in substantial economic impact from the loss of coffee crops, and exposing $\approx 50\,000$ people to levels exceeding WHO air quality standards (125 ppb over 24 h; 50 ppb over 1 yr). Downwind of Popocatépetl volcano, SO_2 quadrupled, and sulphate concentrations doubled in Mexico City when fumigated by the volcanic plume (Raga *et al.*, 1999).

The aims of this paper are to review briefly some of the latest developments in ground based optical sensing of volcanic gas and aerosol emissions. We focus particularly on those instruments that have come to the fore over the last ten years that are capable of augmenting or superseding the Correlation Spectrometer (COSPEC) device, which has seen widespread use over the last thirty years for volcanic SO_2 flux measurements. We also discuss the challenges that remain in implementing gas-monitoring networks, and in interpreting their data streams. It is hoped that this article will stimulate development of further optical sensing technologies, characterised by low cost, low maintenance, low weight and bulk, high temporal resolution, and multi-component sensitivity, that will meet key volcanological requirements.

2. General methodological background and challenges

The conventional way to measure volcanic emissions is by direct sampling, either by close-range collection of samples from fumarole vents and active lava bodies using «Giggenbach bottles», filter packs and condensing systems, or within atmospheric plumes from aircraft using various kinds of sampling apparatus and onboard analysers. A range of spectroscopic, gravimetric, isotopic and chromatographic techniques is available to determine chemical concentrations in real time or subsequently in the laboratory (Symonds *et al.*, 1994). Whilst direct sampling is capable of delivering very detailed and accurate analyses, it is difficult to sustain routine surveillance in this way, or to

provide data of sufficient temporal resolution to compare meaningfully with seismic and geodetic data streams. Arguably, the primary reason for this is the risk involved in the field, which generally restricts investigations to low temperature, subordinate vents (that probably do not characterize the bulk emission or represent the parts of the magmatic-hydrothermal system most sensitive to change in the event of renewed magmatic activity). Additionally, chemical reactions between the container material or reagents and the collected gas sample may mask the original chemical composition. Whilst the use of telemetered electrochemical sensors for continuous gas monitoring avoids many of the above complications (McGee and Sutton, 1994), this approach is not yet widespread and it suffers the problem that sensors may be destroyed in the event of an eruption.

In this section, we look at the general background to volcanic gas sensing using optical methods, highlighting some of the key issues in adapting and developing remote sensing instruments for volcanological purposes, and interpreting the data they yield. Much of the discussion applies to volcano monitoring devices in general.

2.1. *Spectroscopy background*

The sensing methods described in section 3 are based on the spectroscopic observation of molecular species of interest from their fingerprint rotational, vibrational and electronic transitions, usually seen in absorption (*i.e.*, the attenuation of a source of radiation behind the gas cloud; fig. 1) but sometimes in emission. Specific gases can be identified by their characteristic absorption spectra, and their abundances derived from the strength of the absorption, following the Beer-Lambert formula:

$$I(\lambda) = I_0 (\lambda)\exp(-\sigma(\lambda)NL) \qquad (2.1)$$

where $I(\lambda)$ is the observed intensity of radiation at wavelength λ, $I_0(\lambda)$ is the original intensity of radiation, before interaction with the sample, $\sigma(\lambda)$ is the absorption cross section, of the absorbing molecule at wavelength λ, and N is the mean concentration of the species over the pathlength L of the sample. Measurements of more than one species provide gas ratios, in an analogous manner to direct sampling; traverses or scans of volcanic clouds combined with plume
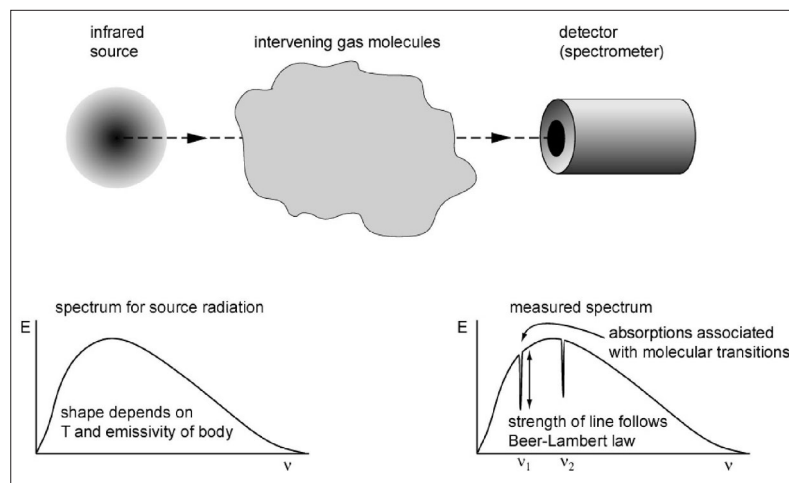

Fig. 1. Diagram of radiative transfer problem in absorption spectroscopy. From Horrocks (2001).

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transport speeds can be used to derive fluxes of gases.

The remote sensing measurements may be considered «passive» if the source of radiation is natural, and «active» if it is artificial. Examples of passive measurements include use of natural terrestrial radiation (*e.g.*, from active lava surfaces), diffuse sky radiation, or direct solar radiation (*i.e.*, occultation measurements). Active sources include lamps (usually used for broad spectral band observations), and lasers (sometimes multi-wavelength or «tuneable» for differential spectral measurements). The spectrometers may be dispersive, if the incoming light is separated spatially into its component wavelengths, or non-dispersive if the wavelength discrimination is achieved by other means (*e.g.*, by interferometry). Passive measurements are invariably «open-path» observations through the free atmosphere. Active measurements may be open-path, or «closed-path» wherein the gas sample is admitted to a cell, of given path-length, through which the beam is passed. An advantage of closed-path observations is that the cell's internal pressure may be lowered to reduce pressure-broadening effects on the spectral lines, permitting high-spectral-resolution measurements of trace species even in noisy regions of the spectrum. Multi-path cells of modest dimensions (*e.g.*, < 1 m) can simulate substantial atmospheric paths (*e.g.*, > 100 m) via multiple internal reflection.

For quantitative applications, it is usually necessary to separate out the spectral features of the volcanic gas species of interest from those of the background atmosphere (which are dominated by spectral lines originating from H_2O and CO_2, and molecular scattering at shorter wavelengths). This can be achieved by modelling the total atmospheric path (*e.g.*, using a radiative transfer code, atmospheric and meteorological data, and known absorption coefficients for all relevant species), or ratio-ing spectral observations acquired for the same path with and without the volcanic plume present (I_λ and $I_{0,\lambda}$, respectively). From inspection of (2.1), it can then be seen that the column amount of a given species (*i.e.*, the product of concentration and path length) can be obtained if $\sigma(\lambda)$ is known.

2.2. *Instrumental specifications: data acquisition*

Initial considerations in the design or exploitation of a gas sensor include the species to be targeted, and the dynamic range and sensitivity of the measurements. This requires, firstly, an appreciation of the molecules and/or isotopes worth observing from the perspective of what volcanologically-useful information they can provide, and the purpose of the investigation (volcano monitoring for activity prediction, quantification of concentrations of harmful gases, etc). The mixing of volcanic gases with the atmosphere and subsequent plume transport and dispersion act to dilute concentrations of species, making it particularly difficult to detect and measure the two principal volcanic gas components, H_2O and CO_2. The significant and rapid changes in humidity of the background atmosphere add to complications of sensing volcanic H_2O. H_2O and CO_2 also hamper spectroscopic observations of other gas species because of their abundant absorptions across the fingerprint region of the infrared spectrum, which can mask more subtle features of other trace gases.

Because of the budgetary constraints on volcano observatories and institutes, it is certainly true that it helps if instrumentation is comparatively cheap. Decisions always have to be reached in respect of costs of personnel, field vehicles and running costs, as well as equipment. However, given the potential cost benefits to society of effective volcano monitoring and accurate activity forecasts, volcanologists should be prepared to defend even expensive equipment purchases where a case can be made that the instrumentation will significantly enhance capabilities.

Observatories are often stretched not only in financial terms but also because of the many demands on the time of their personnel. This is especially the case during volcanic crises when operations are increased, and other parties (local officials, the public, the media, etc.) demand access to information. Field equipment should therefore be, generally speaking, easy to operate and maintain; data should be available in real time or near-real time, preferably with high

time-resolution, and ideally with minimal post-processing required. (Recording data from the COSPEC instrument – see Section 3.1.1 – has traditionally been achieved using chart recorders, demanding time-consuming, and potentially inaccurate, visual processing of the rolls of paper. This can often result in data not being processed for several days, despite their potential importance for hazards assessment). Internet-ready, digital data-streams have obvious advantages for remote access, and multi-parameter data interpretation.

Equipment should be robust enough for sustained operation, even in hostile conditions (acid gases, ash deposition, etc.), and generally low in weight in bulk, especially if its use relies on being moved around regularly and transported in vehicles (clearly, autonomous operation is the ideal since it frees up personnel for other activities). Power requirements should be modest as grid supplies are seldom an option on remote volcano locations.

2.3. *Error budgets and error reduction*

In order to interpret measurements, and the significance of any observed changes, it is crucial to understand sources and magnitudes of errors in the data. A number of data fidelity issues can be addressed in an automated fashion through various error checking regimes. Instrument response functions should be monitored regularly where necessary, with calibration and intercalibration issues addressed as appropriate. This may include careful examination of radiative transfer models, assumptions concerning atmospheric profiles, plume distribution (especially in the vertical), and Mie scattering processes.

While budgeting and reducing errors are essential exercises, they should be approached in the context of the necessary accuracy and precision for the volcanological task in hand, and the non-volcanological influences that can modify observations. For example, imagine a volcano where instantaneous SO_2 gas fluxes at source may change by an order of magnitude on timescales of days. It may be sufficient to discriminate changes in flux of a factor of 5 in order to identify reliably the source signal, and

therefore be unnecessary to go to great lengths to reduce errors. In respect of gas flux measurements, considerable attention has to be given to the estimation of plume transport speeds. It is widely acknowledged that uncertainty in plume speed (typically 20-40%) represents the major contribution to errors in measurements of SO_2 and other gas fluxes. A consistent approach to constraining plume speed is therefore essential. If plume speeds are poorly constrained there is little point in engineering spectrometer sensitivity to improve retrievals by only a few per cent. Absorption-correlation methods using spatially distributed instruments provide one means to track plume velocity accurately (Williams-Jones *et al.*, 2003).

2.4. *Data interpretation*

Having secured a geochemical data-stream, the next job is to interpret it. The basic tasks are to identify volatile sources, magma-hydrother-
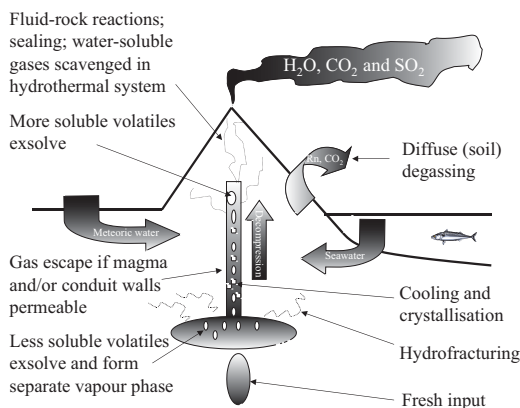

Fig. 2. Potential physical and chemical processes occurring in a magmatic-hydrothermal system, including the influence of magma dynamics in the chamber-conduit plumbing system, and interactions between magmatic fluids and the crust. These can strongly modulate the speciation and flux of various magmatic components emitted into the atmosphere, complicating the interpretation of geochemical measurements of surface emissions (from Oppenheimer *et al.*, 2003).

mal system interactions, the dynamics of degassing, and changes in these through time. Unfortunately, interpretation of the observations is far from straightforward because of the many factors that control magmatic volatile content (mantle melting, slab contributions, wall-rock assimilation, etc.), exsolution and gas separation of different volatile species from magma, and the subsequent chemical and physical interactions of the exsolved fluids, for example, with crustal rocks and hydrothermal fluids, as they ascend to the surface (fig. 2). Although thermodynamical codes enable «restoration» of observed gas analyses to equilibrium compositions (*e.g.*, Gerlach, 1993; Symonds *et al.*, 1994), identifying precise magmatic and hydrothermal conditions remain real challenges. Indeed, a casual perusal of the literature will reveal conflicting interpretations of similar observations - for instance, decreasing SO_2 fluxes could be due to i) depletion of volatiles in a magma body, or ii) a decrease in the permeability of the plumbing system. Process i) might indicate decreased eruption likelihood, while ii), perhaps induced by sealing of bubble networks, which would act to increase overpressure (*e.g.*, Edmonds *et al.*, 2003c), could increase the chance of an explosive eruption. Thus the same observation can be interpreted in different ways with contradictory hazard implications.

Advances in this area will benefit from development and validation of comprehensive physico-chemical models for volcanic degassing based on the integration of results from experiments on the controls on distribution of volatiles in synthetic and natural melts, analysis of dissolved volatiles preserved in melt inclusions, and observed volcanic gas geochemistry. Ultimately, such models can be applied to integrated geophysical, geodetic and geochemical monitoring data to support eruption forecasting.

3. Instrumentation

Over the last thirty years, ground-based optical remote-sensing techniques have been increasingly used for volcanic gas (and aerosol) monitoring (table I). Such techniques possess many of the advantages of seismic and deformation monitoring over direct sampling, such as the ability to obtain measurements in reasonable safety, allowing semi-continuous mon-

Table I. Overview of spectroscopic methods for ground-based optical sensing of volcanic gases.

Instrument	Transport methods	Volcanic gas species detectable	Flux measurements (Yes/No)
COSPEC	car, aircraft, boat	SO_2	Yes
UV grating spectrometers (*e.g.*, Ocean Optics USB 2000)	on foot, car, aircraft, boat	SO_2, H_2S, BrO	Yes
FTIR (*e.g.*, Brucker OPAG 22, MIDAC AM series)	car	CO_2, CO, OCS, CH_4, SO_2, H_2O, HCl, HF, SiF_4	Yes (with sun-tracker)
Other NDIR (*e.g.*, LI-COR CO_2 analysers)	on foot, aircraft	CO_2, H_2O	Yes (by plume profiling or ground flux surveys)
DIAL (*i.e.*, using atmospheric backscatter to return signal)	truck, ship	SO_2, other species feasible	Yes
Laser spectroscopy (short path, extractive)	car	as FTIR plus isotopes	No

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itoring even through violent eruptive periods. Additionally, gas concentrations may be retrieved non-invasively in near real-time, obviating the need for subsequent laboratory analysis, and eliminating the possibility of sample contamination. Because remote sensing techniques measure integrated gas concentrations through cross sections of the plume, in contrast to *in situ* sampling, they can potentially yield a more representative picture of bulk plume composition and flux.

In the following subsections, we briefly review some recent developments in optical sensing applications to volcanic gas surveillance. With the exception perhaps of the ASTER sensor on NASA'S Terra platform, spaceborne remote sensing is unlikely, in the near future, to provide a capability for frequent measurements of weaker tropospheric volcanic plumes, e.g., sustained by quiescent degassing. We focus, therefore, on ground-based approaches that are suitable for routine monitoring applications. For a fuller review of the field, including spectroscopic determination of volcanic aerosol concentrations and properties, see McGonigle and Oppenheimer (2003).

3.1. *UV spectroscopy*

3.1.1. Correlation mask instruments: COSPEC

Arguably, the most widely applied instrument for ground-based remote-sensing of volcanic plumes is the Barringer Research COSPEC, which was originally developed to measure industrial SO_2 and NO_x emissions (Moffat and Millán, 1971). Over the last thirty years, open-path ultraviolet (OPUV) COSPEC SO_2 measurements have been performed at numerous volcanoes worldwide (*e.g.*, Casadevall *et al.,* 1984; Stoiber *et al.,* 1986; Caltabiano *et al.,* 1994; Gerlach *et al.,* 1998, and references therein). The COSPEC is typically operated by measuring the absorption of ultraviolet (UV) zenith skylight, by overhead SO_2 (Millán and Hoff, 1978). This is achieved by dispersing the collected skylight with a grating and then imaging this spectrum on to the radial length of a spinning disk, behind which is a detector. The

disk has segments with etchings at radii that block light «correlating» either to wavelengths of low or high absorption (in the spectral region 300-315 nm), such that the output signal from the detector is modulated according the absorption of overhead SO_2. (A development of this form of correlation spectroscopy is to mount cells containing the gases of interest on a rotating chopper disk, in an analogous fashion to the COSPEC's etched masks. This gas correlation filter spectrometry method has been implemented to sense volcanic CO and OCS concentrations but operating in the infrared spectral region (Stix *et al.,* 1996).

Internal electronic processing yields SO_2 concentrations (in parts per million meters - ppm m; see Gerlach, 2003, for discussion of the problems inherent in use of these units), and calibration is achieved by placing quartz cells containing known amounts of SO_2 in the internal optical path of the spectrometer. Fluxes are obtained by traversing underneath the plume, approximately perpendicular to its axis, in a road vehicle, boat or aircraft, and recording SO_2 concentration as a function of position (from a GPS receiver). By integrating the concentrations across the plume and multiplying by plume speed, SO_2 fluxes are derived (typically expressed in tonnes per day, t d^{-1}, or kg s^{-1}).

The COSPEC possesses many advantages as a tool for volcanic surveillance. As this device operates using scattered skylight, alignment is trivial and measurements are possible in overcast conditions. However the accuracy of the derived fluxes is very dependent on the adequacy of the plume speed data (Stoiber *et al.*, 1983). Typically, the wind speed is obtained from distant radiosonde data, visual observations of the moving plume, or ground based anemometry. More accurate wind data can be obtained by videography, or from aircraft navigational equipment in the case of airborne traverses. A further source of error is that the diffuse skylight can be scattered into the COSPEC's field of view from above, below or within the plume (Millán, 1980; Moffat and Millán, 1971), in contrast to the flux calculation's assumption that light passes vertically through the entire plume. Scattering effects in ash-laden

plumes can introduce further scattering related errors (Andres and Schmid, 2001).

The COSPEC was originally applied in a volcanological context to assess whether changes in SO$_2$ gas fluxes could be associated with changes in eruptive activity of open conduit volcanoes (*i.e.* rising or falling of magmas, and sealing or opening of magma chambers). Positive correlations of increasing SO$_2$ flux with activity were observed during measurements at Mt. Etna (Malinconico *et al.*, 1979). In 1991, the SO$_2$ flux of Mt. Pinatubo was observed to increase by an order of magnitude over two weeks, in parallel with seismic unrest, providing evidence for a shallow intrusion of magma, and prompting a civil evacuation (Hoff, 1992; Daag *et al.*, 1996). Decreasing COSPEC SO$_2$ fluxes in parallel with decreasing post-eruptive activity have also been observed on many volcanoes, notably at Mt. St. Helens from 1980 to 1988 (McGee, 1992), following the 1980 eruption. Through COSPEC a catalogue of fluxes from actively and passively degassing volcanoes worldwide has been obtained, from which the total volcanic SO$_2$ flux to the atmosphere has been estimated at ~ 20 Tg yr^{-1} (Stoiber and Jepsen, 1973; Berresheim and Jaeschke, 1983; Stoiber *et al.*, 1987; Andres and Kasgnoc, 1998). COSPEC measurements have also revealed that many volcanoes emit SO$_2$ in excess of levels that could be sustained by degassing of their erupted magmas, highlighting the so-called «excess sulfur» issue (Wallace, 2001).

However, interpreting COSPEC data can be complicated. For instance, in the past both increasing and decreasing flux signatures have been found to pre-empt changes in volcanic activity (Symonds *et al.*, 2001). Furthermore, SO$_2$ fluxes are modulated by the action of hydrothermal systems (Doukas and Gerlach, 1995; Oppenheimer, 1996; Symonds *et al.*, 2001) and during transport in the atmosphere through deposition and chemical transformations (Malinconico, 1979; Oppenheimer *et al.,* 1998a). This is partly why monitoring gas ratios can be so informative. A final, more practical problem is that the COSPEC is no longer in routine production, and servicing and sourcing replacement parts is becoming increasingly costly and difficult.

3.1.2. Broad band measurement and spectral analysis

A potential drawback of the COSPEC is its «black box» nature. The original design of the COSPEC was very much engineering-oriented, with the goal to build a system capable of minimizing all «noise» (*i.e.*, other atmospheric absorptions, etc.) to deliver information on just one species (*e.g.*, SO$_2$). The result is an instrument that yields an estimate of the column amount of SO$_2$ in the field of view. While this greatly simplifies data retrieval and processing, it makes it difficult to assess potential errors that arise from wavelength shifts, scattering and solar elevation effects, thermal and mechanical distortions, etc. Also, the COSPEC response depends on the mask used and the concentration of gases present. An alternative approach is to measure broad band spectra with sufficient spectral resolution to be able to model trace gas concentrations. This ap-
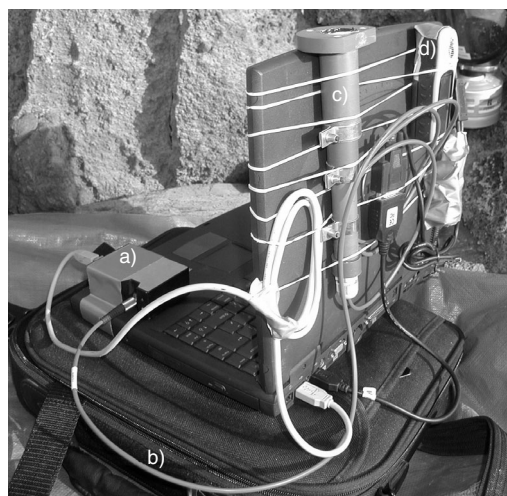

Fig. 3. Simple configuration of instrumentation for OPUV measurements using mimniature spectrometer (a) connected by fibre optic cable (b) to telescope (c). GPS receiver (d) provides continuous tracking to locate all spectra saved to laptop computer via USB cable. The ensemble could be further reduced in size and weight by replacing the laptop computer with a palm top unit. A reflective screen is desirable for visibility and enhanced battery life.
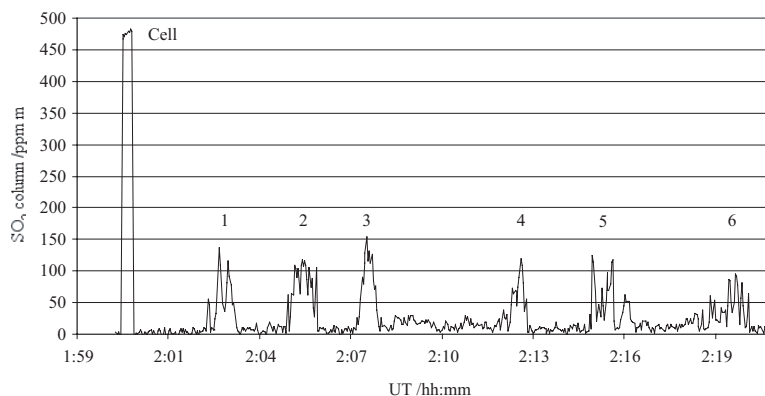
Fig. 4. Example of raw data collected in real-time by walking traverse at Meakan-dake volcano, Japan, using equipment shown in fig. 3. The first excursion shows a SO_2-filled quartz cell placed in front of the telescope. Six back-and-forth traverses beneath the plume, a few tens of metres from the source, follow. The timescale is subsequently corrected using the GPS log to a distance scale perpendicular to the plume transport direction. This provides the column cross section of SO_2, which is then multiplied by plume speed to yield flux. In this case the SO_2 emission amounts to around 40 g s^{-1}, highlighting the capability to measure very low fluxes from individual fumaroles.

proach is often termed differential optical absorption spectroscopy (DOAS; Platt, 1994).

The first volcanological DOAS observations were performed at sea from 1992 to 1997 (Edner *et al.*, 1994; Weibring *et al.*, 1998), to measure the SO_2 emitted by Etna, Stromboli and Vulcano. In general, the scattered skylight is collected using a vertically pointing telescope, and coupled into the spectrometer with an optical fibre, *i.e.*, the same OPUV approach used for COSPEC. Direct solar UV (*i.e.*, Sun occultation) is also used in DOAS observations, which has the advantage of simplifying the radiative transfer problem. Light is generally spectrally dispersed using a grating, and spectra are collected using a CCD array (or photomultiplier tube and scanning mechanism) outside the plume, through the plume, and with light blocked from entering the spectrometer (to read the «dark current»). In the retrieval process the latter spectra are subtracted from the former two types in order to reduce instrumental noise effects. All the «plume spectra» are then divided by an out-of-plume «background» spectrum, in order to reduce interferences caused by background atmospheric absorption and the solar spectral structure (Fraunhofer lines). The logarithm of the result is taken (along with high-

and low-pass filter stages), following Beer's law (2.1), and then SO_2 concentrations are derived by scaling a reference spectrum of known column amount over the ~ 303-315 nm fitting region to match the observed spectrum.

The instrument used on the Italian volcanoes was comparatively bulky. More recently, in 2001, volcanological field tests were carried out with a commercially available, miniature ultraviolet spectrometer (fig. 3; Galle *et al.*, 2003). This instrument is considerably smaller, lighter, cheaper, and lower in power consumption, than the COSPEC (Galle *et al.*, 2003) but the performance is comparable. Side-by-side intercomparisons with a COSPEC at Soufrière Hills Volcano (Montserrat) and Mt. Etna revealed good correspondence between the two instruments (Galle *et al.*, 2003; McGonigle *et al.*, 2003). Given the favourable characteristics of the smaller device, it is already attracting interest in the volcanological research community as a replacement technology for COSPEC. Because of its genuine portability (rather than «transportability», which better describes many other devices sold on the market with claims to be «portable»), SO_2 flux measurements can even be obtained by traversing beneath the plume on foot (fig. 4). This opens up the possibility of measurements at vol-

canoes that lack suitable roads or other forms of vehicular access, with a minimum of logistical support, and avoiding the high costs of airborne operation (McGonigle *et al.*, 2002).

The miniature UV spectrometer can be readily adapted for scanning measurements, whereby the field of view is manually turned through the plume (*e.g.*, from horizon to horizon; McGonigle *et al.*, 2002. It has also been configured for automated fixed position flux measurements, by way of a 45° turning mirror rotated by a stepper motor (Galle *et al.*, 2002; McGonigle *et al.*, 2003; Edmonds *et al.*, 2003a). A particularly promising development is the installation of a number of automated and telemetered plume scanners by the Montserrat Volcano Observatory (MVO) for Soufrière Hills Volcano. The use of multiple instruments in different locations helps in observing the plume under varying wind directions, and to permit crude, tomography-style retrieval of range-resolved SO_2 concentrations. This system is now delivering high temporal resolution (every few minutes) sustained SO_2 flux data during daylight hours (Edmonds *et al.*, 2003a). Such data will provide unprecedented opportunities for the cross-correlation of time-stamped geodetic, seismic and geochemical data streams, promising new volcanological insights into degassing and magma dynamics.

By virtue of recording spectra, broadband UV spectroscopy has the capability of detecting multiple gas species. Measurements of H_2S/SO_2 ratios have recently been accomplished at Vulcano, Italy using the miniature UV spectrometer in a closed-path configuration (*i.e.*, with a fixed path-length cell and artificial UV source; O'Dwyer *et al.*, 2003). The same instrument, applied to sky OPUV measurements at Montserrat, yielded SO_2/BrO ratios in the volcanic plume (the BrO being the oxidation product of volcanic HBr; Bobrowski *et al.*, 2003).

3.2. *Non-dispersive infrared (NDIR) spectroscopy*

As discussed, it is desirable, in many cases, to measure not only SO_2 but other volcanic gas species. This has been one of the great benefits of the conventional direct sampling approach to gas geochemistry, since many species can be measured down to ppt levels using laboratory analytical techniques. Of particular relevance, the availability over the last ten years or so of field portable, robust Fourier transform infrared (FTIR) spectrometers has extended the capabilities of remote sensing of volcanic gases in this direction. These devices operate across the so-called fundamental region of the infrared spectrum, providing access to the rotation-vibration absorption features of, among other species, HCl, H_2O, SO_2, HF, CO_2, SiF_4, OCS and CO.

FTIR spectrometers are based on Michelson interferometers, in which incoming light is split into two beams using an optical beam-splitter, which also recombines these beams after they are reflected at mirrors. One of the mirrors in scanned back and forth along the axis of its beam, introducing a variable path difference between the two beams, resulting in a time-variable signal from the single broad-band detector due to interference of recombined beams. Application of an inverse Fourier transform to the temporal signal yields spectra, which are analysed (using radiative transfer models or by ratio-ing in-plume and out-of-plume spectra) in order to determine the concentrations of volcanic gases absorbing in the optical path. A range of IR light sources: direct sunlight, fire fountains, artificial IR lamps, and hot rocks have been used in volcano FTIR surveillance highlighting the flexibility of the approach to adapt to the circumstances of activity, access and terrain. Love *et al.* (1998, 2000) have shown it is also possible to measure volcanic gases in emission (*i.e.*, their emission lines rather than their absorption lines) against a cold sky background. At Popocatépetl volcano, Mexico, Love *et al.* (1998) observed a steady increase in SiF_4/SO_2 ratio prior to an eruption in February 1997, followed by a tenfold decrease within a few hours. These results suggested a cooling of the gas prior to the eruption, attributed to adiabatic gas expansion on release of a conduit plug.

The first FTIR volcanic gas spectroscopy was carried out in 1991 at Asama volcano, Japan, (Notsu *et al.,* 1993), by Japanese researchers who have subsequently reported measurements at Unzen, Japan (SO_2 and HCl; Mori *et al.*, 1993), Aso, Japan (CO, OCS, CO_2, SO_2 and

HCl; Mori and Notsu 1997), and Vulcano, Italy (SO_2 and HCl; Mori *et al.*, 1995). The CO/CO_2 ratio obtained at Aso was used to constrain fumarole temperatures. Further developments have been undertaken by a UK-based group (Francis *et al.*, 1995; Francis *et al.*, 1996; Oppenheimer *et al.*, 1998c, 2002; Francis *et al.*, 2000). The last of these works permitted plume temperature estimates based on HF/SiF_4 ratio obtained at Vulcano. Later work on Mt. Etna resulted in the first FTIR spectroscopy of volcanic plumes by solar occultation (Francis *et al.*, 1998).

Since 1998, this group has carried out annual campaigns at Masaya volcano, Nicaragua, where high volcanic gas concentrations permitted measurements of volcanic CO_2 and H_2O, in spite of these species' high ambient concentrations (Burton *et al.*, 2000). Measurements at Masaya indicated consistent SO_2/HCl and HCl/HF molar ratios of 1.6 and 5, respectively, during 1998-2000, indicating steady-state, open system degassing (Horrocks *et al.*, 1999). In contrast, in 2001 a SO_2/HCl ratio of 4.5 was found, coinciding with reduced SO_2 fluxes, descent of the magma column in the vent on the crater floor, and preceding a small explosive eruption on the 23rd April (Duffell *et al*., 2003). Traverse flux measurements of HCl have also been obtained by operating the FTIR spectrometer with a solar tracker, in contrast to the usual method of combining OPUV-derived SO_2 fluxes with SO_2/HCl ratios from FTIR spectroscopy or direct sampling (Duffell *et al*., 2001).

FTIR measurements at Soufrière Hills Volcano, Montserrat have indicated that HCl/SO_2 molar ratios of 1-5 typify dome building episodes, and that lower ratios (down to 0.1) characterise non-eruptive periods (Oppenheimer *et al.*, 1998d, 2002; Edmonds *et al.*, 2001, 2002, 2003b). This behaviour has been explained in terms of an andesitic HCl source that exsolves on ascent from the magma chamber, and a deeper SO_2 reservoir (probably derived from intruded mafic magma) that degasses to the atmosphere discontinuously, depending on the plumbing system's permeability. Based on this interpretation, Edmonds *et al*. (2002) have identified the potential degassing signals that might herald the end of this eruption. Oppenheimer *et al*. (1998b) demonstrated the ap-

plication of FTIR spectroscopy from a helicopter at distances of ≈ 100 m from the lava dome.

The first routine FTIR spectroscopic volcano surveillance programme has been running since April 2000, at Mt. Etna, under the auspices of the Istituto Internazionale per Geofisica e Vulcanolgia (INGV; Burton *et al.*, 2003). The results obtained to date serve as an excellent advertisement for the value of FTIR spectroscopy in complementing other surveillance efforts (*e.g.*, geodesy, seismology and petrology), and in supporting monitoring efforts during volcanic crises (Calvari, 2001). In particular, a doubling of the SO_2/HCl ratio was observed prior to the 2001 Mt. Etna eruption and clear geochemical trends in SO_2/HCl, CO_2/SO_2, and HCl/HF for different active vents at different elevations through the course of the eruption. These kinds of data would have been impossible to collect in real time by any conventional technique. While the operation of FTIR spectrometers is relatively straightforward, processing the spectra and retrieving gas column amounts requires some expertise.

Representing another class of NDIR spectrometer in volcanological use are the instruments manufactured by LI-COR. These are generally dual-wavelength closed-path analysers, and have been used to measure both diffuse CO_2 emissions from the ground (McGee *et al*., 2000), and CO_2 fluxes by in-plume sampling (Gerlach *et al*., 1998). A third application of LI-COR is based on eddy correlation or covariance, which involves measurements of vertical windspeed and CO_2 concentration (*e.g.*, Anderson and Farrar, 2001).

3.3. *Laser techniques*

To date, the most commonly applied laser technique for volcano measurements is lidar, in which a pulsed laser beam is directed towards the plume. Recording the temporally varying intensity of backscattered light provides information about the atmospheric composition as a function of propagation distance along the beam's path. lidar has been used to measure concentrations and fluxes (via traverses) of sulfate aerosol (Casadevall *et al.*, 1984; Edner

et al., 1994; Porter *et al.*, 2002), and ash (Hobbs *et al.*, 1991). Parallel gas sampling and aerosol measurements can enable estimation of gas to particle conversion rates (*e.g.*, for SO_2 to SO_4^{2-} Stith *et al.*, 1978; Radke, 1982; Rose *et al.*, 1986). Although studies of anthropogenic plumes indicate SO_2 to SO_4^{2-} conversion rates of a few $\% \ h^{-1}$ in the lower troposphere (Eatough *et al.*, 1994), very few comparable investigations of volcanic plumes (which can have widely varied gas, ash and liquid water contents) have been undertaken (*e.g.*, Oppenheimer *et al.*, 1998a; Rose *et al.*, 2001; Horrocks *et al.*, 2003).

A variation on lidar, known as differential absorption lidar (DIAL) involves rapid switching the frequency of laser pulses on- and off-resonance of an absorption feature of the gas of interest. By dividing the lidar curves (returned signal *versus* height) obtained at the two wavelengths and applying the Beer-Lambert law, range-resolved gas concentrations (ppm) may be derived providing 2D or 3D plume structure, in contrast to the pathlength integrated concentrations (ppm m) obtained from FTIR, COSPEC and DOAS. The technique has been applied to the Southern Italian volcanoes using UV lasers (Edner *et al.*, 1994), in parallel with COSPEC and UV-DOAS instruments, revealing SO_2 concentrations up to 50% higher in the former case as a consequence of scattering-induced errors in the passive techniques. However, this DIAL apparatus was costly, heavy and bulky. Whilst DIAL offers unique capabilities for volcanology, it requires further innovation in order to become a suitable tool for routine observatory use.

Alternative sensing strategies using near and mid-infrared diode based lasers (Gianfrani *et al.*, 2000; De Natale *et al.*, 2001; Richter *et al.*, 2002) have been evaluated by monitoring the laser's absorption following numerous transits of a multipass cell, into which the volcanic gas sample is pumped. Due to the very narrow linewidths lasers can provide, the most promising application of these techniques is in spectrally resolving between isotopes to provide infield isotope ratios. Whilst only gas ratio measurements have been realised to date in the field, Richter *et al.* (2002) and Weidmann *et al.* (2003) have described a mid-IR laser system

capable of measuring all isotopes of CO_2, while Gianfrani *et al.* (2003) have presented a diode laser spectrometer able to measure water isotopes in the near-IR. An additional laser based technique that shows potential for field isotope measurements is photoacoustic spectroscopy, in which the sound waves, generated by resonant laser light exciting the target species, are measured (Meyer and Sigrist, 1990).

4. Concluding remarks

Surveillance of gas composition and flux are essential for interpretation of volcanic activity, since the nature of degassing exerts a strong control on eruption style, and is closely associated with volcano seismicity and ground deformation. New optical remote sensing techniques are emerging for the monitoring of volcanic emissions such as the miniature ultraviolet spectrometers described by Galle *et al.* (2003). These tools and their data-streams have the potential for full automation and telemetry, fast processing and evaluation, closer integration with other monitoring data-streams (*i.e.*, seismic, geodetic, etc.), and more sophisticated modelling and interpretation.

While instrument developments are always to be encouraged, we believe that the state of the art is already adequate to justify the proliferation of both IR and UV spectroscopic tools amongst the volcano observing community. This is beginning to happen, with FTIR spectroscopy routinely applied to monitoring of the Southern Italian volcanoes by INGV, and UV methods used on Montserrat by MVO. In addition to the immediate monitoring and hazard evaluation goals of such institutes, sustained surveillance programmes promise the most significant science gains in the future, as geochemical, geodetic and seismic data-streams are further integrated, cross-correlated, and modelled.

As we introduce tools that will replace or supplement other methods, it is crucial that we maintain continuity between old and new datasets. This demands the direct comparison and intercalibration of the various gas geochemical tools via laboratory and field experimentation,

as carried out periodically by the IAVCEI Commission on Volcanic Gases. Additionally, it helps to conform to internationally recognized data standards. One attractive development in this respect is the «WOVOdat» concept of the World Organisation of Volcano Observatories, which aims to establish standardised units and formats for surveillance data so that they may be brought together in a unified, digital database, accessible via the Web and linked with the Smithsonian Institution's unique database of historical eruptions. A further important benefit of proliferating optical sensing techniques capable of gas flux measurements is that this will lead to more accurate, and time-resolved estimates of the global emission of volcanic volatiles to the atmosphere.

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