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A diode-laser-based spectrometer for in-situ measurements of volcanic gases

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ABSTRACT We report the first results of the field operation of a novel, portable diode-laser spectrometer for gas-concentration measurements in volcanic areas. Remote detection of direct absorption line shapes was possible thanks to a telecom single-mode optical fiber that delivered radiation from a room-temperature distributed-feedback diode laser, emitting at 1.997 μm, to an open-path multiple-reflection cell, placed on gas effluxes. The system was deployed on two different active volcanoes in Italy, where simultaneous and continuous monitoring of CO_2 and H_2O concentrations has been demonstrated.

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Introduction

Fumarolic gases, released in volcanic areas, may provide significant information on the status of a volcano. Indeed, time variations of their chemical composition can be regarded as indicators of volcanoes' dynamics [1, 2]. These changes can be due to chemical reactions of magma with rocks or fluids, which take place during magma movements towards the surface. CO_2 and H_2O are among the most important volcanic gases. For instance, an increase of water vapor content in volcanic emissions may be related to the heat flow caused by magma movement while, in general, volcanic CO_2 is very abundant but has almost no interaction with acquifers and rocks, being much less reactive than other gases contained in magmas [3, 4]. In particular, the ratio between CO_2 and H_2O concentrations represents a very important parameter in studying volcanic activity [5]. Some volcanic gases are relevant to atmospheric physics and chemistry and may have significant impacts on the local climate as well as on human life conditions [6–8]. For these reasons, volcanic gases are occasionally or periodically monitored using physical and chemical analysis methods, such as mass spectrometry and gas chromatography, usually run in a laboratory environment. These methods require in-situ sampling that is often impractical and hazardous. An ideal volcanic gas sensor would allow for on-site, continuous monitoring, with unattended operation over long time periods. Additional requirements for in-situ devices include a compact and robust design, which enables operation in hostile conditions with wide temperature fluctuations and high humidity. A convenient approach is given by remote-sensing schemes. These are some of the reasons why optical remote-sensing techniques, such as those based on differential optical absorption spectroscopy (DOAS) [9], LIDAR [10] or Fourier-transform infrared (FTIR) spectrometry [11], have experienced a tremendous development in recent years.

Meanwhile, the great advances of optoelectronic technologies, in the last decades, have increased the use of laser methods for gas-monitoring applications [11–13]. In particular, telecommunication near-infrared semiconductor lasers, such as room-temperature distributed-feedback (DFB) diode lasers, have been widely recognized as ideal sources to develop highly sensitive, fast gas analyzers, based on absorption spectroscopy techniques [14, 15]. For most molecular species, these laser sources are not able to probe absorption due to fundamental vibration bands, usually occurring in the mid infrared. Nonetheless, relatively strong overtone and combination bands of some atmospheric gases occur at wavelengths between 1 and 2 microns, a spectral region presently covered by commercial high-quality diode lasers. Near-infrared diode-laser spectrometers are generally very compact and cheap, compared to traditional laser systems. Moreover, their high selectivity, easy tunability and low-amplitude noise ensure high accuracy and reproducibility levels in concentration measurements [16]. Their possible use in conjunction with optical fibers is particularly advantageous for environmental and industrial monitoring applications [17].

Recently, we applied this technology to monitor CO_2 and H_2O in volcanic fumaroles, using a dual-wavelength approach [18]. In that case, remote operation was ensured by use of optical fibers, delivering a two-color beam (1.57- and 1.39-μm diode-laser radiation) to a 20-cm-long cell, placed on the fumarole. The dual-wavelength spectrometer enabled us to measure water vapor concentration with a 3% accuracy, whereas it was revealed to be quite inaccurate for carbon dioxide measurements [19]. Subsequently, we implemented a new absorption spectrometer using a single room-temperature 2-μm DFB diode laser for real-time measurement of both CO_2 and H_2O concentrations. At this wavelength, a considerably larger fractional absorption can be de-

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tected, due to the occurrence of stronger ro-vibrational transitions. The measurement technique was based on recording of direct absorption profiles of a gas sample contained in a multiple-reflection cell with a path length of 50 m. Remote detection was still feasible thanks to telecom-type optical fibers [20]. Laboratory tests showed that it was possible to achieve a short-term reproducibility and an overall accuracy well below 1% for measurements on ambient CO_2. Simultaneous measurements of the CO_2 and H_2O concentrations with similar precision levels were also demonstrated, since two lines, one for each species, could be found within a single laser frequency scan [21].

In this paper, we present the first field test of a novel, portable configuration of the 2-μm diode-laser spectrometer, suitable for gas monitoring in volcanic effluxes. Two field campaigns were carried out, in 2002, on the Solfatara volcano, near Naples, and on Vulcano Island, an island belonging to the Eolian archipelago (north of Sicily), in Italy. These campaigns are part of an international research project supported by the Italian Institute for Geophysics and Volcanology (INGV). A large amount of experimental data was collected under different operational conditions and the possibility of performing in-situ, simultaneous measurements of CO_2 and H_2O concentrations was demonstrated.

Experimental arrangement

The set-up of the portable diode-laser spectrometer (PDLS) is shown in Fig. 1. Its basic design was already described in [20, 21]. The spectrometer is composed of two independent parts, one including the laser source and the other for the absorption cell. The laser system consists of a temperature-stabilized DFB diode laser (Sensors Unlimited, SU2000DFB-TE), emitting a single mode at 1.997 μm, and a low-noise current supply, both mounted on a breadboard of dimensions $60 \times 60\ \mathrm{cm}^2$ (BB1). Laser radiation passes through an optical isolator (OI) and is then injected into a telecommunication, single-mode, 30-m-long optical fiber through a fiber port, and carried to a second bench, 70-cm long and 40-cm wide (BB2). Here, a pre-amplified room-temperature InGaAs photodiode is used to detect the infrared radiation transmitted by a Herriott multiple-reflection cell (MRC), where gas absorption takes place. For this purpose, the laser is frequency scanned by adding a triangular wave to the injection current. The cell mainly consists of two protected gold-coated spherical mirrors and a metal plate, on which the mirror holders are fixed without any glass tube, in a so-called 'open-path' configuration. The MRC, especially built for field measurements in hazardous environments (S.I.T., Florence, Italy), provided a total absorption path length of 20 m. All mechanical parts were made of stainless steel (316) and designed to enable on-site substitution of damaged mirrors without any need for realignment. The BB2 is equipped with four independent telescopic legs in order to change its height with respect to the ground. The center of the bench has a large rectangular hole ($0.3 \times 0.4\ \mathrm{m}^2$) that allows the fumarole gas to flow between the MRC mirrors. Thanks to the open-path configuration, the detection bench could be used for in-situ analysis in different sites of a volcanic area, without any gas sampling.

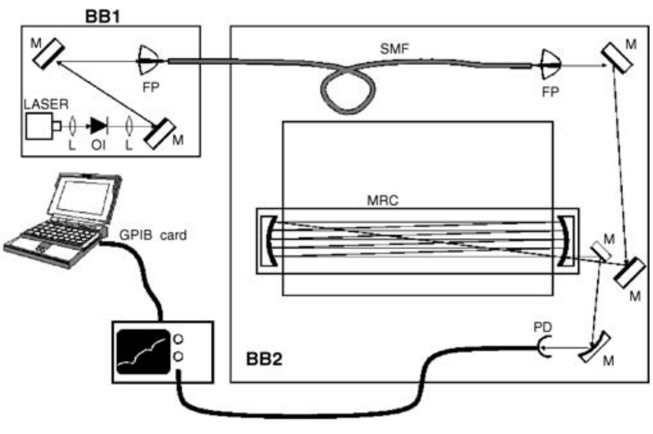

FIGURE 1 PDLS set-up. L: lens, M: mirror, OI: optical isolator, SMF: single-mode fiber, FP: fiber port, MRC: multiple-reflection cell, PD: photodiode, BB1: breadboard 1, BB2: breadboard 2

The spectrometer was also equipped with a digital thermometer in order to measure the temperature of the volcanic gas, with an accuracy of 0.1 K. Indeed, the sample temperature turned out to be crucial for an accurate determination of the concentration value, as this is calculated from the absorption spectra, via a calibration factor which is temperature dependent through the Boltzmann distribution [20]. For this purpose, a Chromel–Alumel thermocouple was directly placed in the gas cell.

The absorption spectra were acquired using a digital oscilloscope (Tektronix, TDS3034) and stored on a laptop computer which controls the oscilloscope via a GPIB interface. Continuous acquisition of the spectra and instrument setting were performed using a LabView program. The maximum acquisition rate was 0.6 Hz. This value is determined by the laser-scan frequency of about 2 Hz, when signal averaging over four spectra is performed, thus increasing the signal-to-noise ratio of the acquired spectra as well as the vertical resolution of the oscilloscope. Taking into account the photodiode bandwidth as well as signal averaging, the effective detection bandwidth ranged between 100 and 200 Hz. Data analysis was carried out by a MATLAB program (see the following section). The whole set-up was powered by a gasoline-engined generator, while a UPS (uninterruptable power supply) unit was adopted for the laser driver and for the photodiode voltage supply. The total electrical power consumption amounted to about 200 W.

Spectrometer operation

The PDLS operation is based on recording of direct absorption profiles, as described in [20]. The measurement principle can be briefly reviewed as follows. According to the Lambert–Beer law, the power $P(\nu)$, transmitted by an absorbing gas, is related to the integrated absorbance A by:

$$P(\nu) = P_0 \exp\left[A g(\nu - \nu_0)\right] , \tag{1}$$

where P_0 is the incident power, ν the laser frequency, ν_0 the line center frequency and $g(\nu - \nu_0)$ the normalized line-shape function. A represents our observable and can be expressed in terms of the gas concentration N by the relation

$$A = -S(T)LN\,, \tag{2}$$

where L is the absorption path length (in cm) and $S(T)$ the line strength (in cm/molecule), which is a function of the sample temperature via a well-known expression for the CO_2 and H_2O partition functions [21]. Linear sweeps as wide as 20 GHz enabled us to simultaneously recover the absorption profiles corresponding to the $R(34)$ line of the CO_2 $\nu_1 + 2\nu_2^0 + \nu_3$ combination band and to the $15_{0,15} \rightarrow 14_{0,14}$ line of the H_2O $\nu_2 + \nu_3$ band [22]. The integrated absorbances, A_1 and A_2, for the two lines are obtained as free parameters in a non-linear least-squares fit of the transmitted power to the function

$$f(\nu) = \eta_0(\nu)\exp\left[\frac{2A_1}{\pi}\frac{\gamma_1}{4(x-x_{c1})^2+\gamma_1^2} + \frac{2A_2}{\pi}\frac{\gamma_2}{4(x-x_{c2})^2+\gamma_2^2}\right], \tag{3}$$

using a MATLAB code based on a linearized method with Levenberg–Marquardt damping. In our case, indeed, the absorption spectrum is very well reproduced by one pair of Lorentzian functions, with centers x_{c1}, x_{c2} and widths γ_1, γ_2, the concentration measurements being performed at atmospheric pressure. The first term, $\eta_0(\nu)$, has a fourth-degree-polynomial dependence on the frequency, which accounts for the laser amplitude modulation caused by the current scan. Hence, if the product SL is known for each line, the concentrations of the two gases can be measured. The value of this product was previously determined through a laboratory calibration procedure using mixtures of synthetic air with CO_2 and H_2O, at different concentration levels. The analytical performances of the spectrometer, in terms of precision and accuracy, were tested through a large number of laboratory experiments, using certified-gas mixtures as well as ambient air [20, 21]. The PDLS thus enables retrieval of absolute gas concentrations in a wide range of values with high precision, without complex calibration procedures, such as those needed, for instance, when frequency-modulation spectroscopic techniques are used [14].

Tests on simulated data

The performance of the whole system was further investigated by appropriate tests on simulated data. These tests were necessary for two reasons. Firstly, the retrieval of the gas concentration from the absorption spectrum needs a non-linear fit procedure, as our model non-linearly depends on the unknown parameters. As a consequence, statistical errors and instabilities of the solutions might be significantly underestimated by a linearized least-squares method, as in the case of the Levenberg–Marquardt damping used here [23]. Furthermore, the analytical expression of the baseline signal is unknown, but it can be fairly approximated by a polynomial of arbitrary order. The higher the polynomial order, the better the fit agreement with the experimental data. However, that also increases the probability of perturbing the estimate of the Lorentzian curve parameters, A_1 and A_2, thus affecting concentration values. This is especially true for field measurements, for which a higher noise level, with respect to laboratory experiments, is expected.

A simulation of the absorption spectrum was generated, assuming a linear baseline and a concentration of 400 ppm for CO_2 and 35 000 ppm for H_2O at a temperature of 25 °C. A Gaussian-distributed noise, with a mean value equal to zero, was superimposed on the spectrum. Three values of the noise amplitude, equal to 5%, 10% and 30% of the maximum height of the Lorentzian curve, were chosen. The last value is used to simulate the worst possible condition; the first is rather close to the real case. We first tested the robustness of the linearized inversion procedure, by inverting the simulated data for several initial guesses of the free parameters as well as different Levenberg–Marquardt damping factors [23]. The retrieved concentrations, using as a fit function that is given in (3), were not seriously biased either by the initial parameter values or by the damping factor values, once convergence in the fitting process was achieved. On the other hand, the value of the damping factor, necessary to achieve convergence, turned out to be dependent on the choice of the initial guesses. Also, the number of iterations required for fit convergence is proportional, as expected, to the amplitude of the damping factor, as well as to the difference between the initial guesses for the parameters and their actual values (chosen for the simulation).

A second test was aimed at identifying the polynomial function best suited to reproduce the background baseline. The three simulated spectra were analyzed using both a second- and a fourth-order polynomial and the parameter values, as well as the agreement between the fit curve and the experimental data, were compared. An example of such a spectrum with the corresponding fit curve is shown in Fig. 2. The concentration values obtained from the simulation are shown in Table 1. We may note that for any choice of background, when the noise level is below 10%, the concentration values are in good agreement with those considered to produce the simulated spectrum. Also, the statistical errors on the parameters are obviously dependent on the noise super-

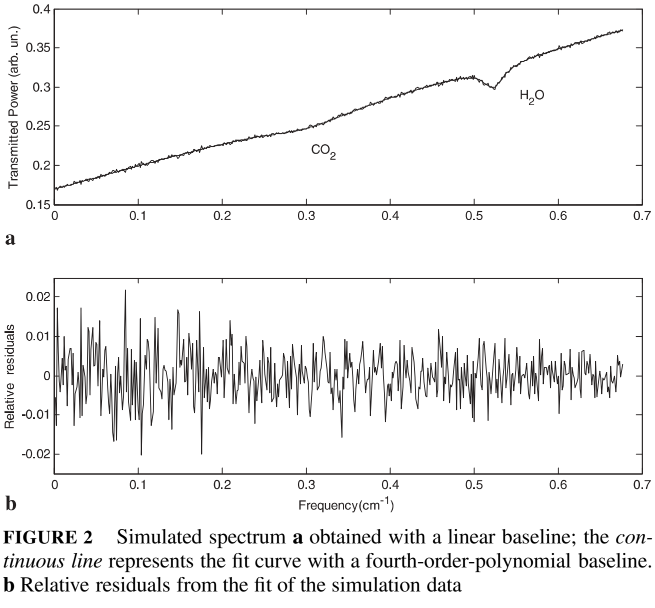

FIGURE 2 Simulated spectrum **a** obtained with a linear baseline; the *continuous line* represents the fit curve with a fourth-order-polynomial baseline. **b** Relative residuals from the fit of the simulation data

Polynomial degree	Noise level (%)	CO_2 (ppm)	H_2O (ppm)	χ^2 ($\times 10^{-6}$)
2	5%	450 (30)	34 700 (900)	1.76
4	5%	460 (50)	34 000 (1000)	1.76
2	10%	480 (80)	38 000 (2000)	7.76
4	10%	400 (100)	39 000 (3000)	7.74
2	30%	320 (170)	27 000 (5000)	71.3
4	30%	660 (590)	30 000 (6000)	70.7

TABLE 1 Fit performed on simulated spectra: results for different polynomial baselines with different noise levels

imposed on the spectrum. Nevertheless, noise levels as high as 10% are reflected in errors within 25% on the estimated concentration.

Results and discussion

Two field campaigns were performed in July and November 2002 on Vulcano Island (Eolian archipelago) and in the fumarole area of the Solfatara crater (Pozzuoli, Naples), in Italy. The former site is one of the most active Italian stratovolcanoes, with intense fumarolic emissions [24], while the latter is part of the 'Campi Flegrei' caldera, one of the volcanic areas with the highest risk in the world, recently undergoing very strong episodes of uplift and further subsidence [25]. All data were taken moving the detection unit of the PDLS among different sites within a selected volcanic area.

A first field campaign was carried out from the 22nd to the 26th of July on Vulcano Island, where many gaseous emissions are present even far from the main crater 'Fossa Grande'. A convenient place for the first measurements was 'Porto Levante' beach, near to thermal springs. Several absorption spectra were acquired in different locations of this area. An example of simultaneous detection of CO_2 and H_2O is shown in Fig. 3. The signal-to-noise ratio of the spectra is mainly limited by electrical noise due to the UPS unit, used to stabilize the laser power supply, and by small interference fringes. Gas concentrations were retrieved from the area under the absorption spectra, as described in previous sections. In this site several measurement series, each made of 200 acquisitions with four-spectra averaging, were performed. In a first configuration, the detection bench was positioned at a height of 0.2 m and, subsequently, it was directly placed on the ground, removing the telescopic legs. The measured temperature remained approximately constant at 32 °C during data recording. The time evolution of the CO_2 and H_2O concentrations and of their ratio, at ground level, is shown in Fig. 4. The statistical uncertainties, obtained from the fit, are reported as vertical bars in the figure, and are in the order of 5% for CO_2 and H_2O. Since Fig. 4 shows a nearly constant behavior of concentrations with time, it is possible to calculate their mean values, which are 420 (2) ppm and 11 340 (40) ppm, for CO_2 and H_2O, respectively. The standard errors are reported in parentheses. In the same area, a further measurement series was performed far from the beach fumaroles, in order to record the ambient concentration background. However, the main purpose of this field test was to monitor changes of gas concentrations with respect to a starting value, providing information on volcano dynamics in a certain time interval.

All concentration values were retrieved assuming a gas temperature of 32 °C. In principle, concentrations might be affected by small systematic errors due to possible temperature differences in subsequent acquisitions. The influence of these fluctuations on molecular line strengths, and thus on concentration values, was evaluated. Using (2), the relative concentration variation was calculated to be 3%/°C, for water vapor, and less than 1‰/°C, for carbon dioxide. Hence, since the maximum observed temperature change, in the measurement process, was equal to about 2 °C, we concluded that systematic errors fell within experimental uncertainties.

The open-path configuration was very suitable for measurements on Vulcano Island, characterized by an intense and diffuse degassing over large areas. In the whole campaign, no serious damage was caused by the volcanic environment to the

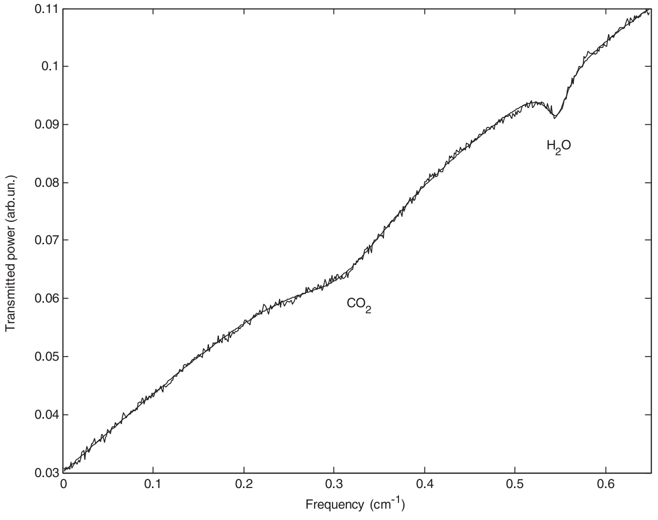

FIGURE 3 Example of simultaneous recording of CO_2 and H_2O absorption spectra, with the corresponding fit curve (*continuous line*), on Vulcano Island

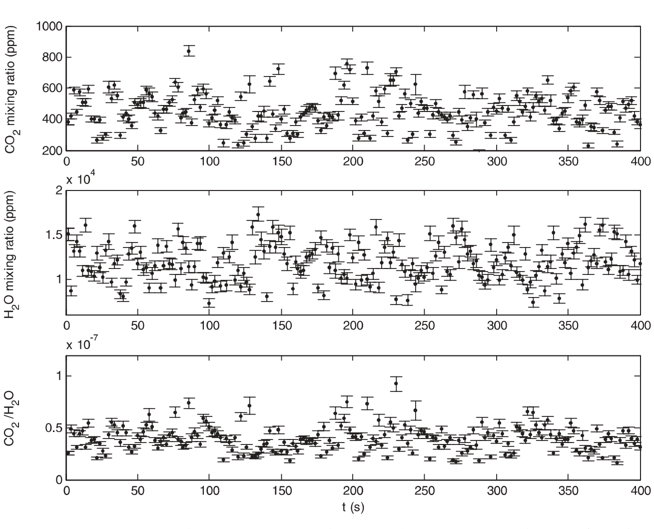

FIGURE 4 CO_2 and H_2O concentrations, and CO_2/H_2O ratio as a function of time (fit errors are represented by *vertical bars*). Each point results from an average over four spectra. These measurements were taken on Vulcano Island, 'Porto Levante', on 23rd July 2002

mechanical and optical components of our set-up. In fact, over a total measurement time of about 5 days, realignment or replacement of the MRC mirrors was never necessary. This is quite relevant if one considers that the PDLS was still a prototype. The spectrometer was also transported to the 'Fossa grande' crater by a helicopter, provided by the Italian Civil Protection. There, we found that even the strong emissions of acid gases from local vents were only slightly corrosive for the spectrometer mechanics and equipment. Anyway, data recording on this crater was not possible because an unpredictable fast swirl of small stones, at the helicopter takeoff, completely destroyed one of the mirrors of the detection bench.

Prior to a new measurement campaign, the spectrometer was slightly modified. In order to avoid problems related to external disturbances, such as wind and dust, the detection bench was covered, on all sides, with a protective box, leaving a small opening above the absorption cell. Also, since we recognized the external power generator as the major source of noise, a battery-operated power supply was used for the photodiode.

With these improvements, the spectrometer was transferred to Solfatara, on November 16th. The Solfatara crater was originally formed by an explosive eruption in the Campi Flegrei caldera, in 2600 B.C., but its fumaroles still exhibit very intense and spectacular emissions. The whole area presents several fumaroles, with different intensities and characteristics, mostly composed of H_2O (80%–90%) and CO_2 (10%–20%). The ambient air temperature was, on average, 30 °C, while values up to 110 °C were measured at the output of the vents. The gas temperature was continuously measured by the thermocouple and acquired by the oscilloscope. These values were used, in the data analysis, to account for line-strength variation in the calibration factors. The detection bench was placed just above a selected fumarole, with the height of the bench corresponding to the minimum elongation of the telescopic legs (i.e. 15 cm). In this way, direct measurements on the gas efflux were possible, with a good signal-to-noise ratio, as shown in Fig. 5. The CO_2 and H_2O concentrations, measured over a time interval of about 500 s (100 spectra), are shown in Fig. 6. In this case, concentrations were found to be typically one order of magnitude larger than those measured on Vulcano Island. Values ranging from 2340 (70) ppm to 9980 (120) ppm and from 74 100 (2600) ppm to 217 400 (4600) ppm were observed, for CO_2 and H_2O, respectively. The statistical errors from the fit are reported in parentheses. The mean ratio between CO_2 and H_2O concentrations, with 1-σ standard deviation, was 0.0427 (0.0013). Short-term variations of the H_2O and CO_2 contents, in the order of a few % and even more, may naturally occur during normal volcanic activity. That could partially explain the observed fluctuations of the measured concentration values, over time intervals of a few seconds. A significant variation in subsurface activity, instead, is expected to change concentrations by at least a factor two or three [5, 26].

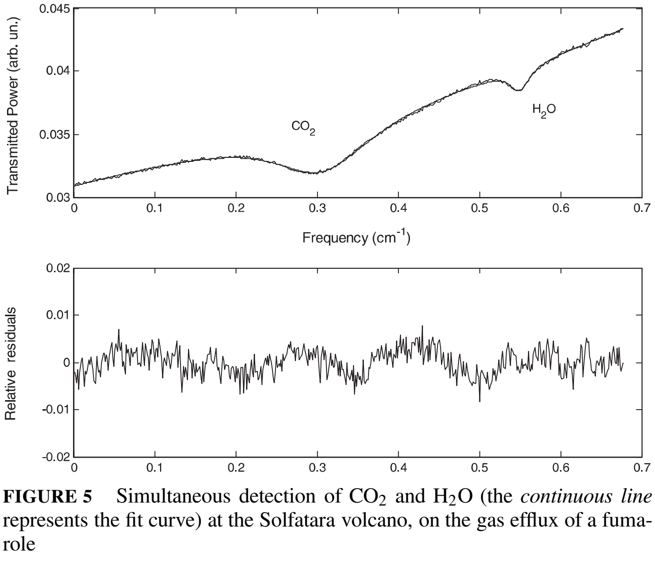

FIGURE 5 Simultaneous detection of CO_2 and H_2O (the *continuous line* represents the fit curve) at the Solfatara volcano, on the gas efflux of a fumarole

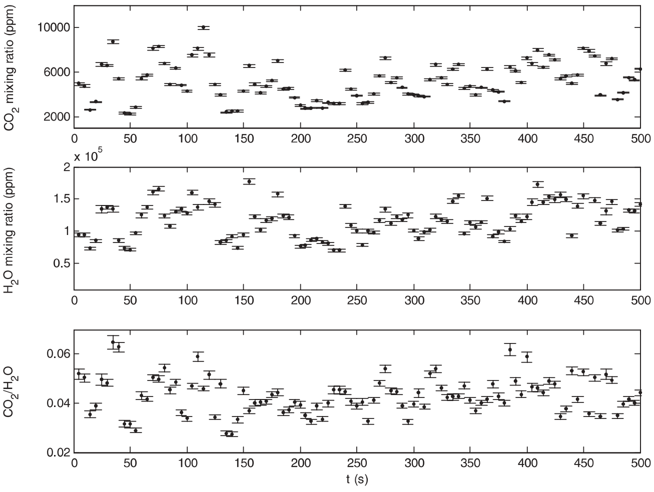

FIGURE 6 Concentration values and their ratio vs. time (*vertical bars* represent the errors from the fit). Each point is obtained by averaging eight acquired spectra. These data were taken at the Solfatara volcano in November 2002

Conclusions

We have demonstrated continuous operation of a portable diode-laser fiber spectrometer for gas monitoring in volcanic areas with intense and diffuse degassing. The selected sites were the Solfatara volcano, near Naples, and Vulcano Island, Sicily, in Italy. A custom-built multiple-reflection cell enabled us to make recordings of direct absorption profiles, for CO_2 and H_2O, thus measuring their concentrations very close to fumarolic emissions. Continuous time monitoring of these concentrations has been demonstrated for the two volcanoes. In particular, the best measurements were performed on vent flows of the Solfatara crater, providing values of CO_2 and H_2O concentrations with relative uncertainties ranging from 1 to 3%.

Our system proved to be a valid alternative to methods based on gas sampling, especially in view of the future development of an integrated network for volcanic surveillance. Indeed, the use of near-infrared diode lasers with telecom optical fibers allows for remote gas detection in different locations over a wide volcanic area. In addition, the possibility of performing field measurements is based on the relatively small and light equipment, with a total power consumption limited to 200 W. The compact and robust design of the spectrometer allowed it to survive a first test in chemically aggressive volcanic environments. However, on the basis of these first results, work is currently in progress to further improve the experimental apparatus, special care being devoted to even lighter and more compact mechanical components. Furthermore, an engineered version of the spectrometer would rely on an analog-to-digital converter for data transfer to a compact memory card, improving the time response and further reducing power consumption. At the same time, the gasoline engine can be replaced with rechargeable batteries.

At present, we are actively working at the integration of our spectrometer in a fiber-based network able to make multiple-point and multiple-parameter monitoring in a wide volcanic area, using also fiber Bragg gratings [27] for strain and temperature measurements.

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