



Diode laser-based gas analyser for the simultaneous measurement of CO₂ and HF in volcanic plumes

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Abstract. A portable analyser is described for simultaneous detection of CO₂ and HF emitted by volcanoes and fumaroles. The system is based on two fibre-coupled distributed feedback lasers and only one multipass cell, and provides the absolute concentration values of the two gases, without requiring a calibration procedure, at a maximum rate of 4 Hz. The spectrometer can operate both in a closed-cell configuration and in an open-cell set-up, with the latter mitigating problems associated with chemisorption of the HF molecule. The concept, practical realization and laboratory performance of the device are presented, together with results from a first test campaign measuring volcanic gases emitted from the crater of Vulcano, Italy. We obtained an in-field sensitivity of 320 ppb for CO₂ and 20 ppb for HF at 2 s integration time.

1 Introduction

The dynamics of magma storage and ascent are reflected in the composition and flux of gases released by active volcanoes (Symonds et al., 1994; Giggenbach, 1996; Allard et al., 2005; La Spina et al., 2010). The major volatile species, H₂O, CO₂, SO₂, HCl and HF, all have pressure-dependent solubility profiles, producing significant variability in gas composition as a function of pressure in the magmatic system (Lesne et al., 2012) which is then further modulated by the degassing style and magma dynamics (La Spina et al., 2016). The viscosity of magma controls its flow dynamics, and this is in turn controlled by the dissolved water contents of the magma and vesicularity, producing complex non-linear re-

lationships between magma ascent and degassing (Gonnermann and Manga, 2003).

The thermodynamics of phase changes from dissolved to exsolved volatiles and crystal formation, together with adiabatic expansion, all contribute to the evolution of magmatic temperature (Blundy et al., 2006; La Spina et al., 2015), providing a further feedback mechanism as viscosity is also highly dependent on temperature. Unravelling this complex behaviour is a fundamental aim of volcanological science, and a key underpinning for this research is precise and accurate measurements of gas compositions at the surface. A further important scientific outcome from such measurements is new insight into atmospheric chemistry processes occurring within volcanic plumes. The aim of this work is to present results from a new instrument designed to be usable from airborne platforms.

A variety of methods have been developed to measure volcanic gas compositions, all with individual strengths and weaknesses. Hydrogen fluoride is measurable with filter packs (Pennisi and Le Cloarec, 1998; Mather et al., 2004; Allard et al., 2016), diffusion tubes (Rüdiger et al., 2017) and direct sampling by bubbling through alkali solutions (Giggenbach and Matsuo, 1991; Wittmer et al., 2014), all of which require post-collection analysis in a chemical laboratory. Open-path Fourier transform spectroscopy (Burton et al., 2000, 2007; Duffel et al., 2001, 2003; Horrocks et al., 2003) measures both CO₂ and HF directly in the field. In situ sensors such as MultiGas (Aiuppa et al., 2005, 2008; Shinohara et al., 2005, 2008; Roberts et al., 2017) have allowed automated measurements of plume gas compositions, primarily CO₂ and S species, but not HF to date, and very fast

changes in gas composition are challenging to quantify due to the slow and differing frequency response of commonly used optical CO₂ and electrochemical S sensors. Drifting calibrations make the traceability of long-term installations challenging. Remote sensing using infrared (Mori and Notsu, 1997; Francis et al., 1998) or ultraviolet spectroscopy (Galle et al., 2002, 2010; Edmonds et al., 2003; Butz et al., 2017) is effective for safe determination of plume gases and has the key capacity to measure gas compositions during explosive activity, but requires large path-integrated concentrations of gas. This is particularly critical for the rapid measurements of quickly changing gas concentrations which are envisaged in an airborne sampling context. Tunable diode laser-based in situ spectrometers may overcome the challenges of chemical sensors, allowing traceable, accurate, precise and high-frequency measurements, and many volcanic gases have accessible near- and mid-infrared absorption spectra. They can also work at a high frequency (> 1 Hz), which is a requirement for airborne surveys where rapid changes in gas concentration are common. However, tunable diode laser (TDL) instruments are usually bulky, delicate and ill-suited to the rigours of volcanological fieldwork. A final requirement for volcanic gas sensing is that multiple gases are measured in the same volume of gas at the same time, while avoiding chemisorption processes. This allows the direct determination of volcanic gas molar ratios, which are key to unravelling volcanic processes. Sulfur dioxide is relatively easy to quantify due to a strong UV absorption spectrum and low background concentration, allowing straightforward SO₂ flux quantification (Stoiber et al., 1983; Galle et al., 2003; Mori and Burton, 2006). So, the knowledge of SO₂ flux, when added to the in situ measurements of the ratios among SO₂ and other gases, extends the information about flux to these gases too.

In the context of the European Research Council project CO2Volc, which has the aim of improving our understanding of global emissions of CO₂ from volcanoes, we identified the need for a custom-built TDL platform for volcanological applications. Here, we report on the first measurements of CO₂ and HF conducted with the first analyser of the planned CO2Volc TDL platform, which was tested in the laboratory and on fumaroles on Vulcano island, Italy. The species CO₂ and HF are ideally suited for revealing magma dynamics, being two end-members for solubility in magmas: CO₂ is highly insoluble and begins to exsolve from magma at depths typically > 10 km, while the bulk of the HF degassing occurs at very low pressures.

2 State of the art for in situ volcanic gas measurements

The requirements for a successful and effective volcanic gas analyser are stringent. The instrument must be compact and light for field portability to allow easy field deployment with a variety of transport solutions, including backpacks, aero-

planes and drones. It must also be robust enough to allow operation in hostile and harsh environments, such as high humidity, fluctuating temperature and high concentrations of acid gases. Moreover, volcanic gas sensors would ideally have low power requirements to allow prolonged field measurements and the capability to work unattended through remote control or fully autonomously. Finally these constraints must not limit instrumental performance, maintaining high selectivity to multiple molecules (in order to identify specific volcanic gas species), high sensitivity (in order to quantify small changes in gas concentration), high precision and accuracy (in order to measure low concentrations in dilute plumes) and response times of the order of 1 s (to permit airborne measurements and resolve rapid changes in gas composition). In addition to these requirements, the detection of acid gases such as HF requires further precautions due to the rapid chemisorption of acid molecules on surfaces of the instrument, precluding pumps and filters. Typically, the limits on what makes an instrument field-portable on a volcano are the carrying capacity of a group of two or three people. Thus, up to 10 kg for an instrument and a few kilograms for batteries is typically ideal.

Several laser spectrometers have been developed to measure multi-species gas emissions (Richter et al., 2000, 2002) but these were poorly suited for the challenging volcanological field context, in particular for the key requirement of simultaneous measurements of multiple gas species and for the problems connected with chemisorption. Several analysers fulfil the requirements for CO₂ and H₂O measurements, from both academia (Gianfrani et al., 2000; Rocco et al., 2004) and industry (e.g. LICOR 7000 and LICOR 840A, www.licor.com). This device yields an accuracy of 1 % for both gases, with a RMS noise of 25 ppb for CO₂ and 2 ppm for H₂O at 1 s integration time. Its weight is less than 9 kg, and the power consumption is within 40 W. However, this device requires that gases are pumped through a narrow tube, which makes simultaneous measurements with acid gases impossible.

Hydrogen fluoride could be measured using cavity ring-down spectroscopy (CRDS) (Morville et al., 2004), but low pressure operation is needed, which is extremely challenging to achieve without experiencing strong chemisorption. Several other commercial devices offer HF detection, but none of them fulfils all the requirements for volcanological applications. The simplest ones are those used in human exposure monitoring (GfG Instrumentation, Model TN 2014 Micro IV, www.goodforgas.com), but the response time is too long (~ 90 s) and the cross sensitivity, in particular to hydrogen chloride (which is typically also present in volcanic plumes), is very strong. In commercial Fourier transform infrared (FTIR) spectrometers, as in Environnement S.A., Model MIR FT, (www.environnement-sa.com), the detection limit is rather high (about 180 ppb with a time response of 2 s), and typically a multipass cell is needed for in situ measurements, which can provide a chemisorption

surface. A higher sensitivity (2 ppb) can be reached with ion-mobility spectrometry (IMS) (Molecular Analytics, Particle Measuring Systems, Model ProSentry-IMS HF Analyser, www.pmeasuring.com), but again weight (23 kg) and power consumption (more than 500 W) are too high. Very high sensitivity can be obtained with off-axis integrated cavity output spectroscopy (ABB – Los Gatos Research, Hydrogen Fluoride Analyser, www.lgrinc.com) (detection limit of 0.2 ppb in 1 s, but with a power consumption of about 100 W and a weight of about 29 kg). Overall, we determined that none of these commercially available solutions were suitable for volcanological applications, as their weight, power and chemisorption characteristics do not fit our constraints. Furthermore, our specific requirements include measuring combinations of several volcanic gas species, such as CO₂ and HF, in the same volume of air, and devices like these do not exist on the commercial market.

As we show here, the new instrument was designed to balance the competing requirements of low weight and power consumption, physical robustness and the required selectivity, sensitivity and time-response performance. We adopted direct absorption in combination with a multipass cell as a detection technique which, though noisier and less sensitive than CRD or ICOS, allows a great simplification of the apparatus and does not need extremely high reflectivity of the cell mirrors. When measuring in the plume of a volcano, the cleanliness of the mirrors is a serious concern.

In principle, detection limits and accuracy could be increased by 1 order of magnitude when adopting a detection technique based on laser frequency modulation (Corsi et al., 1999; D'Amato and De Rosa, 2002). Yet, this kind of detection raises severe concerns about calibration, in particular in an environment where temperature, pressure and mixture composition can vary significantly. This is because in these techniques the calibration relies on the stability of the line-shape which, on the contrary, is affected by the physical conditions of the measurement. So, the next developments in this class of instruments will be to adopt direct absorption.

The practical realization and the laboratory performance of the device will be described. Finally, we will show the results obtained during a first test campaign at the crater of Vulcano volcano (Aeolian Islands, Italy).

3 Experimental set-up

The optical set-up of the analyser is based on two near-IR distributed feedback (DFB) fibre-coupled diode lasers and only one multipass cell (Fig. 1). In order to optimize the instrument size and to better exploit the available space, the laser sources and the entrance of the cell are on one side (top) of the optical breadboard, while the reference arm, the detectors and the exit of the cell are on the other side (bottom), as in Fig. 2.

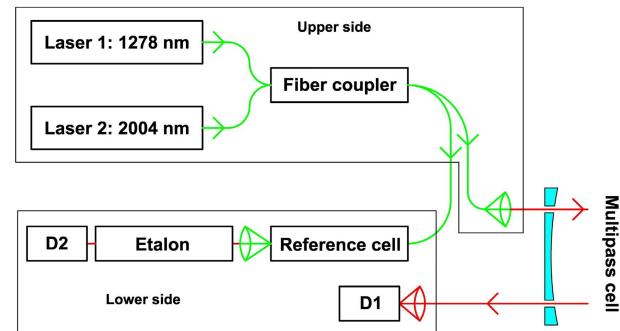


Figure 1. Optical scheme of the analyser. The outer line encompass the components according to their locations, as in Fig. 2.

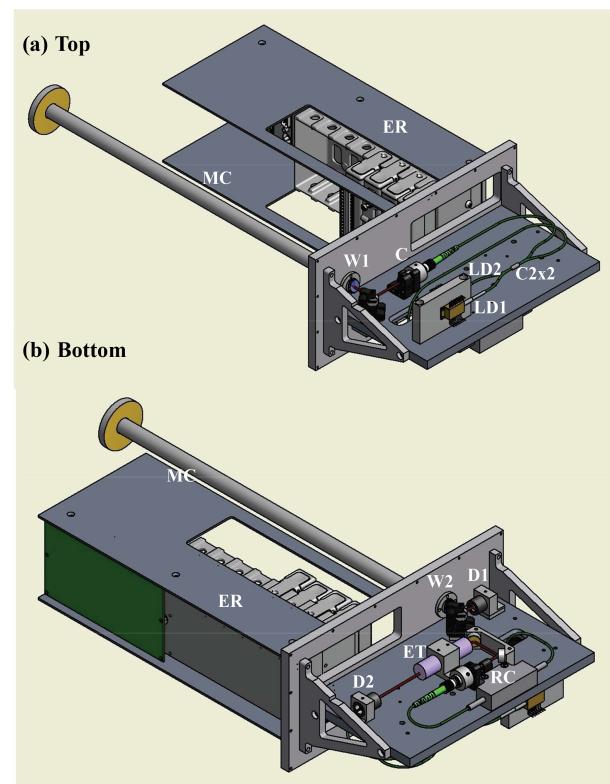


Figure 2. Set-up of the analyser. (a) Top view. LD1 and LD2 diode lasers, C2 × 2: fibre coupler 2 × 2 50/50 transmission; C: collimator, W1: CaF₂ window for the entrance of the multipass cell MC. (b) Bottom view. RC: reference cell, ET: BK7 etalon, W2: CaF₂ window for the output of the multipass cell MC, D1 and D2: detectors. ER: rack for electronics.

On the top of the breadboard, two fibre-coupled DFB lasers emitting respectively at 1.278 and 2.004 µm (Eblana Photonics EP1392-DM and EP2000-DM, output power 5 and 2 mW) are directly mixed in a 2 × 2 fibre coupler, 50/50 transmission, working around 1.3 and 1.5 µm (Thorlabs 10202A-50-APC) which, in principle, is not dichroic for the two laser wavelengths. Nevertheless we do not need

an exact splitting ratio, and the attenuation of the coupler at 2 μm is low enough to allow us to use it. So, about half of the power of both lasers is collimated and sent into the multipass cell, while the other half of the power of the two beams is sent towards the bottom of the breadboard.

The multipass cell (Fig. 3) is a home-made Herriott cell (Herriott and Schulte, 1965) with a total path length of 20.23 m in 52 passes. It has two quartz mirrors mounted on a carbon fibre pipe. The pipe is in a stainless steel holder, which can be fixed to the analyser body by means of three spines. This allows for fast and easy mounting and removal of the cell for cleaning or replacement. As several identical cells were aligned in the same optical set-up, in the case of a replacement no realignment of the analyser is necessary, and just the orientation of the final mirror may require optimization. The beam enters the multipass cell and gets back into the analyser across two CaF₂ windows, tilted by an angle of 23° in order to avoid interference fringes.

On the bottom of the breadboard, the beam exiting from the multipass cell is sent into a 20 mm plano-convex lens and focused onto a main detector (Hamamatsu G12183-010K, InGaAs PIN, 0.9–2.6 μm, φ1 mm, uncooled), which is suitable for both laser wavelengths.

The other beam exiting from the 2 × 2 coupler is sent through a reference cell (manufactured by Wavelength References) containing both HF and CO₂ to verify the right settings of the two lasers, in particular for HF, which is usually absent in the atmosphere. The reference beam is then collimated and sent through a custom-built etalon in order to obtain a relative frequency reference for the linearization and calibration of the frequency scale. The etalon is made from BK7, 6 cm long and with free spectral range (FSR) 0.0554/0.0558 cm⁻¹ (1662/1674 MHz) at 1278 and 2004 nm, respectively. Finally, the reference signal is measured with a detector identical to that used in the measurement channel.

The electronic part of the instrument is placed next to the cell (as shown in Fig. 2) and consists of a CompactRIO by National Instruments (cRIO 9074), which combines a dual-core processor, a reconfigurable FPGA (field programmable gate array), and five commercial plugins for fast acquisition (four independent channels, 1 MHz at 16 bits), slow acquisition (eight multiplexed channels, 500 kHz at 12 bits), digital I/O, thermocouple reading and data storage. Laser current drivers, laser temperature controllers and preamplifiers for detectors are home-made.

In order to protect the optics and electronics against the volcanic gases, they are enclosed within a plastic cover, which is sealed with a rubber O-ring on the aluminum breadboard of the instrument. This means that HF is measured only in the volume of the multipass cell, but CO₂ is inside the plastic cover too. However, due to the choice of optic fibre components, inside the box the main beam travels in the air only from the collimator to the first CaF₂ window and from the second window to the main detector. This path length is in

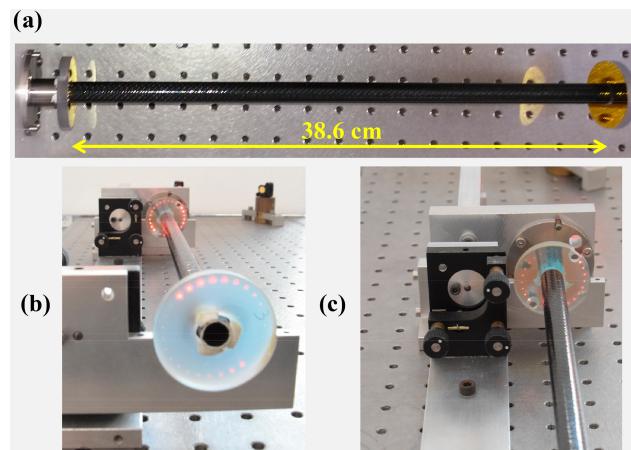


Figure 3. Home-made multipass cell in the open-cell configuration (a). Photo (b) shows the whole cell with the alignment laser beams on the mirrors; photo (c) is a detail of the entrance/exit mirror.

total 11.5 cm, to be compared to about 20 m. So, by neglecting this additional path, we overestimate the ambient concentration of CO₂ by 6×10^{-3} or about 2 ppm. The relative effect is smaller when measuring CO₂ concentrations above the ambient concentration.

The device can operate in an open-cell configuration or in a closed-cell configuration. In the first case, we do not need any sampling air mechanism and the acquisition time is not limited by the time necessary to completely refresh the air inside the cell volume. In the latter, the cell is closed with a Teflon tube and the air is sampled by a rotary pump, which provides an average flow of 20 L min⁻¹. So, the 1 L volume of the multipass cell is flushed in about ∼3 s.

The pressure and the temperature inside and outside the cell are measured respectively by a silicon piezoresistive pressure sensor (Motorola, MPX2100A, with accuracy of about 1 %) and by a PT100 sensor (National Instruments, NI 9217 RTD, with accuracy of about 0.8 %).

The total power requirement for the normal operation of the spectrometer is about 20–25 W (in the open-cell configuration without pump) and 50 W (in the closed-cell configuration with pump). The power is provided by a one (open-cell configuration) or two (closed-cell configuration) 4-cell LiPo battery with 6800 mAh at 14.8 V.

The instrument is robust and compact (with size of 60.5 × 27.6 × 13.2 cm), with a weight of about 8–9 kg (pump and batteries included), which makes it particularly suitable as a portable instrument for in situ operation in a hostile environment such as a volcanic area. The spectrometer can work for about 4–5 h completely unattended and be remotely controlled via WiFi from outside the area of toxic gas emission.

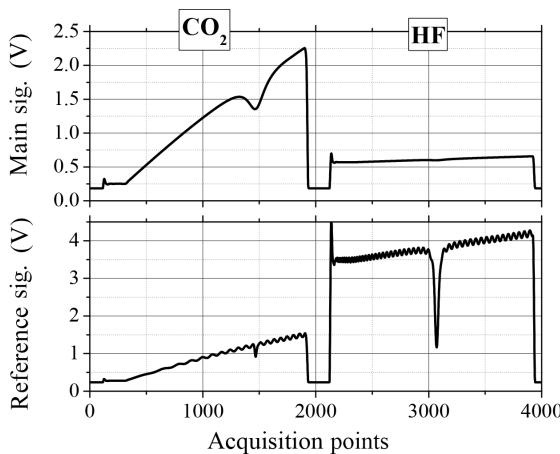


Figure 4. Typical signals recorded by the measurement detector D1 (top) and reference detector D2 (bottom) during a test campaign at Vulcano volcano.

4 Acquisition technique and data processing

In the acquisition procedure the two laser emission frequencies are scanned respectively across the selected absorption lines of the target molecules by modulating the laser current with a ramp signal. The 2 μm -laser scans over the CO₂ absorption line at 4989.97 cm^{-1} (2004.02 nm), while the 1.3 μm laser is scanned over the HF absorption line at 7823.82 cm^{-1} (1278.148 nm). The maximum tuning of the two lasers provides two frequency scans of 0.8 cm^{-1} (24 GHz) around the CO₂ line and 1.5 cm^{-1} (45 GHz) around the HF line.

The two signals measured by the main detector (D1) and by the reference detector (D2) are acquired synchronously on two acquisition channels of the CompactRIO at 1 Msample/s with a resolution of 16 bits. The main and reference signals, sampled each with 4000 points per scan, are averaged 25 times and saved for post-processing. Typical in-field main and reference signals are shown in Fig. 4.

The two laser sources work in sequence and are switched on alternately: when one laser is switched off, the current of the other laser is modulated and conversely. As shown in Fig. 4, the modulation signal of each laser consists of three parts: (i) an initial interval, with a duration of 100 μs , during which the laser is turned off to get the background signal of the detector when no laser power is incident on it (in the following we refer to this signal as a “zero-power signal”); (ii) an interval of 300 μs during which the laser current is maintained fixed at the starting value of the ramp, to allow the stabilization of the signal before starting the frequency scan; and (iii) the linear ramp with a duration of 1.6 ms. The repetition frequency for the complete sequence of modulations is about 250 Hz. If the time for averaging and saving data is also considered, the integration time for the absorption spectra of CO₂ and HF is 0.25 s. The time interval between the

two laser scans is 2 ms, so that the two measurements can be considered simultaneous.

The concentration values of the two gases are calculated by the absorption signal registered by the main detector (top of Fig. 4), which include the two absorption spectra of the target molecules, and by and measured pressure and temperature, according to the Beer–Lambert law. For each acquisition the zero-power signal can be subtracted, so that the absorbance can be derived independently from the absolute laser power. Consequently, we do not need to know the exact splitting ratio of the beam splitter or any kind of variability in the laser power. Moreover the changes in reflectivity of the mirrors in the multipass cell, related to the interaction with the external ambient, do not influence the measured absorbance value except for affecting the signal-to-noise ratio.

The reference spectrum (bottom of Fig. 4) consists of two kinds of signal: the interference fringes due to the etalon and the absorption lines of the two molecules. Knowing the etalon FSRs, the interference signal allows us to obtain a relative frequency reference for the calibration of the frequency scale. The presence of the absorption signals is only necessary to check that the laser emission frequencies do not change over time. This is particularly important for HF, which is usually absent in the atmosphere, since, without a reference cell, it is impossible to verify the stability of the laser emission frequency and its overlap with the selected absorption lines.

Here we present a quick description of the data processing, since a more detailed analysis has already been reported (Viciani et al., 2008). The absorption spectra, after subtracting the zero-power signal, are fitted with the exponential of a Voigt profile multiplied by a second-order polynomial, which simulates the sloping laser power due to the ramping of the driving current. When necessary, one or more sinusoidal curves are also included in the fitting function to take into account the presence of optical fringes. As the Voigt profile, we use the four generalized Lorentzians approximation (Puerta et al., 1981; Martin and Puerta, 1981), for which the only free fitted parameters are the line amplitude and centre frequency, while the Lorentzian and Gaussian half widths at half maximum (HWHM) are fixed. The values of the HWHM are calculated as a function of temperature and pressure, measured for each acquisition, and of the molecular parameters (air-broadening coefficient and line-width temperature coefficient) according to the HITRAN database (Rothman et al., 2013). Obviously, the frequency calibration of the x axis becomes essential for this approach so that, for each saved absorption spectrum, the corresponding reference signal is recorded and fitted according to the etalon transmission equation, which is multiplied by a second-order polynomial and for the absorption signal of the reference cell. According to the fit results and knowing the etalon FSRs, the frequency scale can be determined for each acquisition.

The integrated absorbance for the two molecules is calculated according to the fitting parameters of the Voigt function,

and the concentration N is calculated from the absorbance knowing the multipass path length and the gas line-strength of CO₂ and HF, according to the HITRAN database (Rothman et al., 2013). Finally, the mixing ratio (MR) is obtained according to the equation:

$$\text{MR} = \frac{N}{N_0} \frac{T}{T_0} \frac{P_0}{P}, \quad (1)$$

where N is the calculated molecule concentration in cm⁻³, P and T are the measured values of pressure (in atm) and temperature (in K), $P_0 = 1$ atm, $T_0 = 296$ K and $N_0 = 2.470 \times 10^{19}$ cm⁻³.

5 Laboratory performance of the instrument for the CO₂ channel

In order to test the laboratory performance of the instrument and to verify the reliability of the inferred concentration values, a mixture of known concentration was used in the closed-cell configuration. This kind of test, if done with a HF mixture, would be deeply influenced by the property of the acid HF to stick to the inside tube closing the cell or inside the pipes connecting the multipass cell to the tank of the mixture. We also verified (as shown in the next section) that, by using Teflon sampling pipes, the problem is reduced but not completely resolved, due to chemisorption of the HF to water vapour film or dust covering the inside of the tubes. Consequently, we decided to carry out this laboratory test only for the CO₂ channel and to evaluate the performance of the HF channel directly in-field by using the open-cell configuration.

The measurement was carried out by introducing a constant flow (about 0.3 L min⁻¹) into the multipass cell of calibrated mixture (591 ± 3 ppm CO₂ in synthetic air) at atmospheric pressure and also at 700 mbar to simulate a typical pressure at the top of a 3000 m volcano (e.g. Etna). For the measurements below room pressure we used a scroll pump and two needle valves at the entrance and exit of the multipass cell to set the pressure at the desired value.

In Fig. 5 we show a normalized absorption spectrum of the CO₂ mixture, detected by our instrument at the maximum rate of 4 Hz, at atmospheric pressure and at a temperature of about 295 K, together with a fitted absorption line which includes optical fringes.

In order to determine the accuracy of the measurement we followed the same formalism described in Viciani et al. (2008). The mixing ratio uncertainty is determined by combining the accuracy of the temperature and pressure measurements (respectively 1 and 0.8 %), the accuracy of the CO₂ line strength according to the HITRAN database (between 1 and 2 %) (Rothman et al., 2013) and the uncertainty in the fitting procedure (0.2 %). The resulting total accuracy is < 4 %.

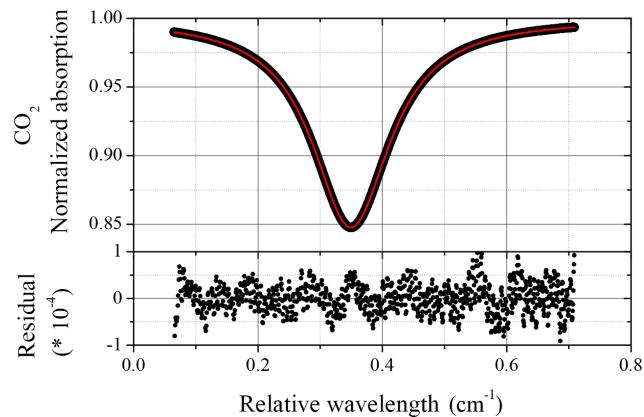


Figure 5. Normalized absorption spectra of a CO₂ calibrated mixture (of about 590 ppm in synthetic air) around 4989.97 cm⁻¹ (2004.02 nm) and Voigt fit results (red line). The residuals of the fitting procedure are shown in the bottom plot. The integration time is 0.25 s. The measurement was carried out at ambient pressure and at a temperature of 295 K.

From the spectra of Fig. 5 we retrieve a CO₂ mixing ratio of (592 ± 12) ppm. This value is in agreement with the concentration of the calibrated mixture.

In order to evaluate the long-term stability of the instrument, we repeated the same measurement at a rate of 4 Hz, for about 1 h in both conditions of atmospheric pressure and about 700 mbar. Assuming as precision two times the standard deviation σ of the obtained mixing ratio values, we infer a CO₂ precision for 1 h measurement of 0.1 % (600 ppb) at atmospheric pressure and of 0.03 % (200 ppb) at 700 mbar. The lower precision at ambient pressure is due to the fact that the absorption signal is as broad as the laser scan and it is not easy for the fitting procedure to clearly identify the parameters of both the second-order polynomial which describe the background and the optical fringes. When the pressure is reduced and the absorption signals are narrower, the fitting protocol becomes more precise.

In the present case, the sensitivity of the instrument, defined as the minimum variation in the mixing ratio detectable by the instrument, is entirely determined by the precision. In order to evaluate the ultimate sensitivity of the CO₂ channel, an Allan–Werle variance analysis of the obtained mixing ratios was carried out. An Allan–Werle variance plot of the CO₂ measurements is reported in Fig. 6 as a function of the integration time.

We can conclude that the CO₂ sensitivity at the fastest integration time of the instrument (250 ms) is about 500 ppb at atmospheric pressure and less than 100 ppb at lower pressure. For an integration time of 1 s, a sensitivity of about 300 ppb at atmospheric pressure and of about 60 ppb around 700 mbar is obtained. The best achievable sensitivity for the CO₂ channel can be reached for 110 s of integration time (about 80 ppb) at atmospheric pressure and for 30 s of integration time (about

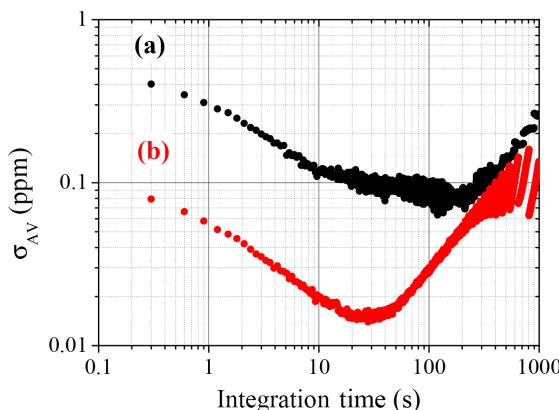


Figure 6. Allan–Werle variance plot of 1 h in-flow measurements of a CO₂ calibrated mixture of about 590 ppm in synthetic air, at a rate of 4 Hz in two different conditions: for a pressure of 985 mbar and a temperature of 295 K (curve a) and for a pressure of 687 mbar and a temperature of 294 K (curve b).

15 ppb) at 700 mbar. Again, we believe that this reduction of the best integration time at low pressures is due to the better capability of the fitting protocol to clearly identify the background signals and the optical fringes.

6 In-field performances of the instrument for CO₂ and HF channels

Two test campaigns were carried out in order to evaluate the performance of the instrument and in particular the HF measurement, as it is the most sensitive to chemisorption processes.

The first campaign was performed in April 2015 at the crater of Vulcano volcano (Aeolian Islands, Italy). During this campaign the instrument was deployed in the closed-cell configuration, with ambient pumped through a 1 m Teflon tube into the cell (as in Fig. 3b). The integration time for each measurement was 1.5 s. We placed the instrument downwind of degassing fumaroles, exposing it to a variety of gas concentrations.

The results obtained for about 10 min of concentration measurement of HF and CO₂ are reported in Fig. 7. A correlation between the concentration peaks of different gases is observed, but the peaks are not well aligned in general, and the HF peaks show a significant delay compared with CO₂. The analysis of concentrations clearly shows that a maximum correlation between the two gases is reached for a delay of about 16 s. Moreover, even if this delay is considered, the correlation is poor, with a coefficient of only 30 %. We attribute these observations to chemisorption of HF molecules, which stick inside the pipes or inside the tube covering the cell, in spite of the use of Teflon components. When a gas cloud arrives at the pipe inlet, part of the HF is lost as it reacts with the walls, producing a delayed HF peak. The only

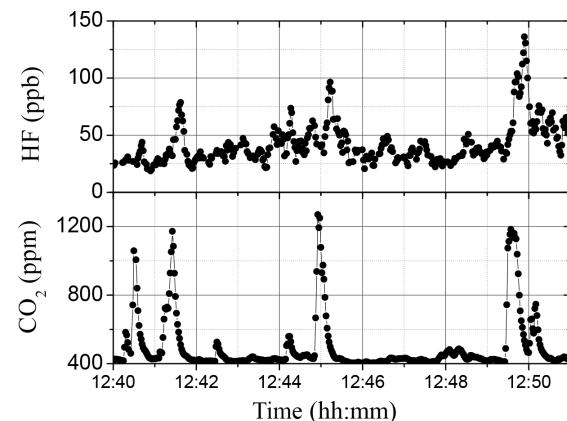


Figure 7. Time series of CO₂ and HF mixing ratios measured at the crater of Vulcano volcano on 22 April 2015, taken by the spectrometer in the closed-cell configuration. The measurements were carried out in an average condition of 990 mbar of pressure and 300 K of temperature. The integration time is 1.5 s. The delay in the integration times of the HF peaks with respect to the CO₂ peaks is due to chemisorption on instrument components in the closed cell configuration.

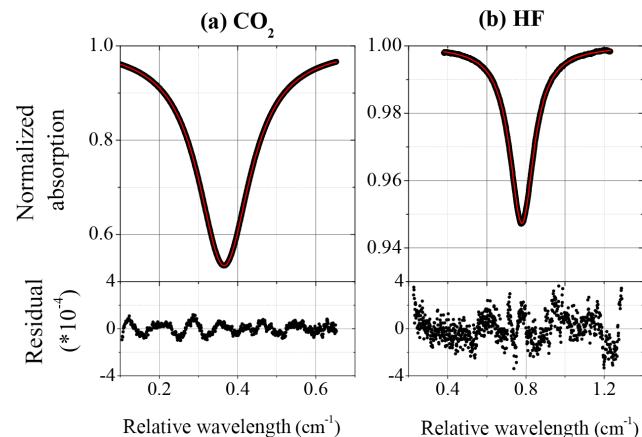


Figure 8. Typical normalized absorption spectra of CO₂ (a) and HF (b) detected in proximity to a fumarole of the Vulcano volcano on 20 May 2015 and Voigt fit results (red line). The residuals of the fitting procedure are shown in the bottom plots. The CO₂ mixing ratio is 2350 ppm and the HF mixing ratio is 4.5 ppm. The integration time is 2 s. The measurement was carried out at a pressure of 990 mbar and at a temperature of 312 K.

way to completely solve this problem is to remove all the pipes and the tube covering the cell.

The open-cell configuration was employed in a second campaign, also at the crater of Vulcano volcano, during May 2015.

A typical normalized absorption spectrum for both CO₂ and HF, with a 2 s integration time for each measurement, is shown in Fig. 8. The measurement was carried out close to a fumarole of the volcano, with a pressure of 990 mbar and

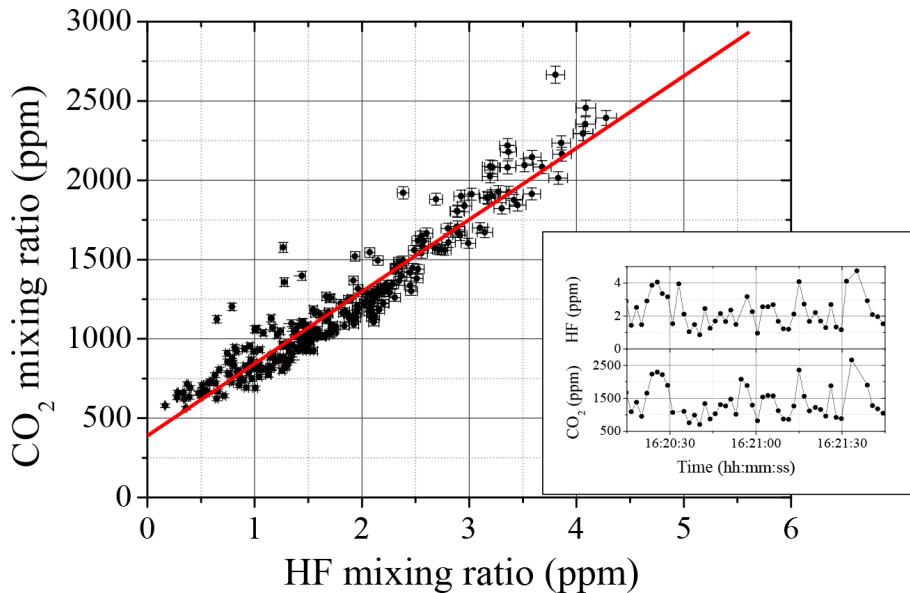


Figure 9. CO₂ mixing ratio as a function of the HF mixing ratio for 13 min of measurement in proximity to a fumarole of the Vulcano volcano on 20 May 2015. The red line is the result of a linear fit. The error bars are the accuracy of the mixing ratio values. The measurement was carried out in the open-cell configuration at a pressure of 990 mbar and at a temperature variable between 310 and 320 K. The inset shows a close-up of the time series of CO₂ and HF mixing ratios during a 90 s interval.

a temperature changing between 310 and 320 K. The results of the Voigt fitting procedure and the corresponding residuals are also shown in Fig. 8. Three optical fringe patterns for CO₂ and two ones for HF are also included in the fitting curve.

The accuracy of the mixing ratio values is determined by the same parameters described in the previous section: the uncertainties in temperature, pressure and CO₂ line strength are the same as in the laboratory test; the accuracy of the HF line strength according to the HITRAN database is between 1 and 2 % (Rothman et al., 2013); the uncertainty of the fitting procedure is 0.2 % for CO₂, exactly the same as in the laboratory test reported in Fig. 5, and 0.7 % for HF. The resulting total accuracy is < 4 % for CO₂ and < 4.5 % for HF. By assuming the worst uncertainty, the CO₂ mixing ratio for the spectrum of Fig. 8a is (2350 ± 50) ppm and the HF mixing ratio for the spectrum of Fig. 8b is (4.5 ± 0.1) ppm.

The advantage of the open-cell configuration with respect to the closed-cell employed in the previous campaign becomes obvious when a correlation analysis between the two gases is performed. The delay of the HF peaks with respect to the CO₂, observed in Fig. 7, is now absent and a maximum correlation between the two gases is obtained without introducing any delay. The CO₂ mixing ratio as a function of the HF mixing ratio during 13 min of measurements is reported in Fig. 9 and the linearity indicates a high correlation between the two gases, corresponding to a correlation coefficient of 95 %. This high correspondence is better shown in the inset of Fig. 9, where a close-up of the simultaneous time

series of CO₂ and HF mixing ratios during a 90 s interval is displayed.

A linear fit of the data of Fig. 9 allows us to infer both the CO₂ ambient mixing ratio not due to volcanic emissions (calculated as the CO₂ value when the measured HF is zero), and the ratio between the CO₂ and HF mixing ratios. The obtained results are (390 ± 20) ppm for the CO₂ ambient mixing ratio and (460 ± 50) for CO₂/HF ratio. These data fit well with the global trend for CO₂ concentration; see for instance the NOAA website (www.esrl.noaa.gov/gmd/ccgg/trends/global.html).

Our measurements of CO₂/HF with a molar ratio of 570 ± 30 were performed downwind of the F0 fumarole on Vulcano, so we expect most of the measured gases to be sourced from here. However, we cannot exclude mixing with other fumarolic sources. This allows a comparison with measurements collected with OP-FTIR on F0 fumarole in 2002 (Aiuppa et al., 2004), which revealed a CO₂/HF molar ratio of 175 ± 20. This difference may reflect either a change in gas composition from fumarole F0 or a potential contribution from different fumarolic sources in each measurement. In order to evaluate the in-field sensitivity of the instrument we assume as signal-to-noise ratio (S/N) the ratio between the normalized absorption signal and two times the standard deviation (2σ) of the residual corresponding to the Voigt fit.

In Fig. 10 the S/N as a function of CO₂ and HF mixing ratios is reported. As noise value for the data of Fig. 10 we use the mean value of the noise related to different fit results of the detected spectra. The mean noise value is 8.5×10^{-5} for CO₂ and 2.4×10^{-4} for HF.

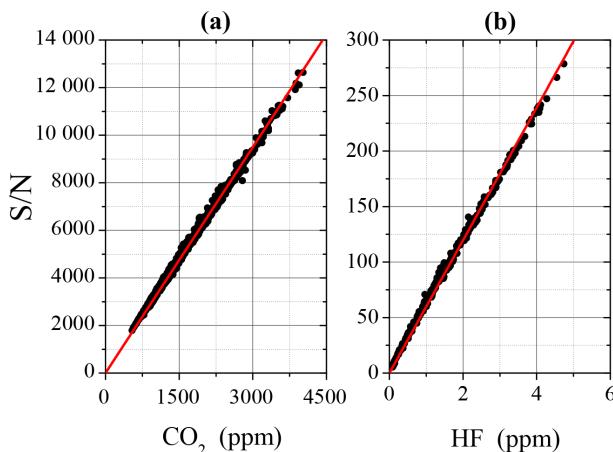


Figure 10. Signal-to-noise ratio (S/N) as a function of CO₂ mixing ratio (a) and HF mixing ratio (b) for 13 min of measurement in proximity to a fumarole of the Vulcano volcano on 20 May 2015. The measurement was carried out in the open-cell configuration at a pressure of 990 mbar and at a temperature variable between 310 and 320 K.

The sensitivity for the two channels of the spectrometer can be obtained as the variation in the mixing ratio corresponding to a variation of the signal equal to the noise, and it can be inferred from the slope of the linear fit of the data in Fig. 10. The obtained sensitivity for the CO₂ channel, with an integration time of 2 s, is 320 ppb, which is only slightly higher with respect to the value of 250 ppb obtained during the Allan–Werle variance laboratory test shown in Fig. 6. We can conclude that the sensitivity performance of the CO₂ analyser is not seriously degraded by the in-field operation and it reduced only by a factor of 1.3. Consequently, from the laboratory Allan–Werle variance analysis we can estimate an in-field sensitivity, at the fastest integration time of 250 ms, of about 650 ppb and an in-field ultimate sensitivity (at 110 s of integration time) of about 100 ppb, which can be further increased if we work at a lower pressure (about 20 ppb for an integration time of 30 s at a pressure of 700 mbar).

For the HF channel, a sensitivity of 20 ppb with an integration time of 2 s can be obtained from the linear fit of Fig. 10b.

This performance can degrade over time as the mirrors of the multipass cell become dirty due to water, dust and gas emissions from the volcanic plumes, and the detected power is consequently drastically reduced. When the instrument operates very close to the fumaroles, in about 30 min the sensitivity of the spectrometer (for an integration time of 2 s) degrades to 2 ppm for CO₂ and to 200 ppb for HF. On the contrary, if the instrument operates in lower acid gas and aerosol concentrations, for instance on board an aircraft, it could run for long periods of time without significant degradation of the signal-to-noise ratio.

In situ degradation of the mirrors could be partially solved by keeping the mirrors clean with an air blade, which in-

volves a light flux of air blown through the carbon fibre pipe holding the mirrors. The air can be taken far from the high concentrations at the emission points and blown onto the mirrors by using a pump with a dust filter at its inlet. Consequently, a small volume of air close to the mirrors will be filled with this purged air, for which HF concentration is negligible and CO₂ concentration is close to its ambient level. This means that the effective distance between the mirrors is reduced. This reduction (estimated as lower than 0.3 %) must be taken into account when concentration values are calculated. Moreover, for CO₂, the values of concentration before or after each emission peak could be used to correct the peak values.

7 Conclusions

We produced a new analyser for the simultaneous measurement of the mixing ratios of CO₂ and HF in volcanic gas emissions. This device features low weight and power, as well as resistance to the harsh environmental conditions. The in-field spectrometer sensitivity, obtained during a campaign at the crater of Vulcano, is 320 ppb for CO₂ and 20 ppb for HF, for an integration time of 2 s. According to laboratory tests, this sensitivity decreases by about a factor of 2 when the instrument is employed at its maximum rate of 4 Hz. However, the device performances improve when the measurements are carried out at a pressure lower than the atmospheric one. In particular the CO₂ sensitivity increases to about a factor of 5 when the pressure is reduced by 700 mbar, which is the typical pressure at the top of a 3000 m volcano (e.g. Etna).

We are planning to extend the measurement to H₂O, by detecting water absorption close to a CO₂ absorption line. This requires a higher tunability DFB laser at 2 μm, which is under procurement. Moreover we are designing a portable experimental platform for in situ simultaneous measurements of five volcanic gases (HCl, CO₂, HF, H₂O and SO₂). The platform will include a UV spectrometer and two mid-IR spectrometers, one of which will be the instrument described in this paper. The platform will be employed for measurement campaigns in-field and on board aircraft.

In order to allow deployment on board drones, we will reduce their size and weight by replacing the cRIO crate with a smaller electronics, namely Red Pitaya by StemLab. We will use only fibre-coupled lasers in the near infrared, so eliminating most mirrors and their holders, and we will use aluminum and carbon fibres only for those parts which strictly require mechanical hardness. All other parts will be realized by 3-D plastic printing. As drones can fly much closer to plumes than manned aircraft, the concentrations to be measured are expected to be at least 1 order of magnitude higher than in the present measurements, and so the multipass cells will be shorter and lighter too.

Data availability. Experimental data used in this paper are freely available upon request from the National Institute of Optics (CNR-INO).

Competing interests. The authors declare that they have no conflict of interest.

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