

REPLY TO REVIEWER #1

SPECIFIC ISSUES

The manuscript would benefit from a more detailed literature review and inclusion of more relevant references to other, previously published work. In the introduction, it would be helpful to mention all the current methodologies that are typically used to measure HF in volcanic plumes: filter packs, diffusive tubes and chemical traps are missing, along with at least one reference for each. Direct sampling is also a means of measuring HF and CO₂, and is mentioned, but no references are given. Clearly, none of these techniques perform the analysis in the field, so they are in some ways inferior to the new instrument described here, but they are the current standard means of performing these measurements and worth describing and referencing.

We agree, this has been addressed through rewriting of the introduction and adding references.

- 1) In order to give a better description of the instrument, a schematic plot of the apparatus, where the path of light from each of the two lasers can be followed, has been added as Figure 1.
- 2) In order to clarify some aspects of the instrument (as the functionality of the reference signal, the meaning of the “zero-power signal”, the characteristics of the raw reference and main spectra, the importance of the fitting procedure), Section 4 has been expanded and re-arranged and Figure 4 (showing the acquired reference and main signals before processing) has been added.

In particular the role of the reference channel has been clarified with the following sentences:

“The reference spectrum (bottom side of Fig.4) consists of two kind of signal: the interference fringes due to the etalon and the absorption lines of the two molecules. Known the etalon FSR's, the interference signal allows to obtain a relative frequency reference for the calibration of the frequency scale. The presence of the absorption signals is necessary only to check that the laser emission frequencies don't change over time. This is particularly important for HF, which is usually absent in the atmosphere, since, without reference cell, it is impossible to verify the stability of the laser emission frequency and its overlapping with the selected absorption lines.”

The referee is right when saying that the reference channel is used only for the frequency calibration of the horizontal scale and it is not used directly for the retrieval of CO₂ or HF mixing ratio. However the frequency calibration becomes essential to have an absolute value of the concentration without need of calibration and to provide absolute measurements is one of the great advantage of the Direct Absorption technique. Moreover, also the use of the reference cell is important to check the stability of the laser emission frequency. For instances, the laser frequency could change for a failure in the driver of the pump current or for a change in the laser working point. In such cases the emission frequency can be shifted far from the absorption lines and, in particular for HF, which is usually absent in the atmosphere, it is impossible to understand if the laser emission is in the right position only checking the etalon fringes.

- 3) The mechanism we use to reduce the pressure inside the multipass cell during laboratory test is very trivial: we have only a scroll pump and two needle valves. During the flow of the gas mixture, we adjust the two valves to set the measured pressure at the desired value.

In order to explain better, we have added at the beginning of Section 5 the following sentence:

“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.”

- 4) Finally, it would be useful to include more details on the field experiments that were performed with the instrument at Vulcano Island. Where exactly was the instrument located (perhaps include a map?). More importantly, which fumaroles were being sampled? Vulcano is a well-studied field site. How do the results of the measurements compare with those obtained by others? See e.g. Aiuppa et al 2004, Intercomparison of volcanic gas monitoring methodologies performed on Vulcano Island, Italy and Inguaggiato et al 2012, Total CO₂ output from Vulcano island (Aeolian Islands, Italy), but there are many other reports too. While it is not the main thrust of this manuscript to provide new data for volcanology, comparing the obtained results with others would strengthen the case that the instrument is performing as expected.

We agree with the reviewer and we've included the following added paragraph.

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.

Minor corrections:

Please consider that in the following the number of pages, lines and figures refer to the old version of the manuscript.

Abstract, L4 – Consider changing ‘remove all problems to ‘mitigate problems associated with chemisorption’

Done

P1, L20 – Please give references for examples of direct sampling and sampling via alkali solutions.

We added several references for all types of sampling systems

P1, L22 – Consider adding Aiuppa et al 2005, ‘Chemical mapping of a fumarolic field: La Fossa crater, Vulcano island (Aeolian islands, Italy)’ and Shinohara (2005), A new technique to estimate volcanic gas composition: plume measurements with a portable multi-sensor system to the references for MultiGAS.

Done

P1, L23, consider omitting ‘to be performed’

Done

P1, L24, ‘quantify due to THE slow and differing: :’

Done

P2, L1, consider replacing ‘chemical-based’ with ‘electrochemical’.

Done

P2, L2, Please add references for remote sensing via ultraviolet spectroscopy, e.g Galle, B., C. Oppenheimer, A. Geyer, A. J. S. Mcgonigle, M. Edmonds, and L. Horrocks (2002), A miniaturised ultraviolet spectrometer for remote sensing of SO₂ fluxes: a new tool for volcano surveillance, *J. Volcanol. Geotherm. Res.*, 119, 241–254. and Edmonds, M., R. A. Herd, B. Galle, and C. M. Oppenheimer (2003), Automated, high time-resolution measurements of SO₂ flux at Soufriere Hills Volcano, Montserrat, *Bull. Volcanol.*, 65(8), 578–586, doi:10.1007/s00445-003-0286-x. and Galle, B., M. Johansson, C. Rivera, Y. Zhang, M. Kihlman, C. Kern, T. Lehmann, U. Platt, S. Arellano, and S. Hidalgo (2010), Network for Observation of Volcanic and Atmospheric Change (NOVAC)-A global network for volcanic gas monitoring: Network layout and instrument description, *J. Geophys. Res.*, 115, D05304, doi:10.1029/2009JD011823.

Also consider adding more references pertaining to IR spectroscopy.

Done, we added the references: Francis, P., Burton, M. R., Oppenheimer, C., Remote measurements of volcanic gas compositions by solar occultation spectroscopy, *Nature*, 396, 567-570, 1998, doi:10.1038/25115; Mori, T., Notsu, K., Remote CO, COS, CO₂, SO₂, HCl detection and temperature estimation of volcanic gas, *Geophys. Res. Lett.*, 24, 2047-2050, 1997

P2, L3, Please define ‘path amounts’. I assume you mean path-integrated concentrations.

We have replaced “path amount of gas” with “path-integrated concentrations of gas”.

P2, L4, I would argue that the technique described in this paper falls under the category of infrared spectroscopy and therefore is not ‘poorly suited’ for in-situ measurements.

We agree with the Referee and we have removed “is poorly suited for in-situ measurement”.

P2, L4, I’m not sure what an ‘in-situ spectrometer’ is.

In order to clarify the text, we replaced the sentence: "Tunable diode laser-based in-situ spectrometers may overcome the challenges of chemical sensors, allowing traceable, accurate and precise measurements," with "Tunable diode laser-based spectrometers may overcome the challenges of chemical sensors, allowing traceable, accurate and precise measurements directly on site,"

P2, L8, Ultraviolet spectroscopy mostly only measures sulfur dioxide. Therefore, it’s not clear why sensitivity to multiple gases is an ‘essential requirement for volcanic gas sensing’. Perhaps it’s essential to in-situ measurements?

The ratios among different concentrations provides information about the status of the magmatic chamber. But the concentrations of gases in the volcanic plumes is a partial information. In order to quantify the emissions, fluxes must be known instead. It is relatively simple to know the flux of SO₂ from a volcan, by using UV cameras. When coupled with this information, the knowledge of the

concentration ratios among SO₂ and other gases by in-situ measurements allows to retrieve the fluxes of these gases too.

We added the following sentence: "SO₂ is relatively easy to quantify due to a strong UV absorption spectrum and low background concentration, allowing straightforward SO₂ flux quantification {Stoiber1983,Galle2003,Mori2006}. So, the knowledge of SO₂ flux, when added to the in-situ measurement of the ratios among SO₂ and other gases, extends the information about flux to these gases too".

The added references are:

Galle, B., Oppenheimer, C., Geyer, A., McGonigle, A. J. S., Edmonds, M., Horrocks, L. A., A miniaturised UV spectrometer for remote sensing of SO₂ fluxes: A new tool for volcano surveillance, *J. Volcanol. Geotherm. Res.*, 119, 241–254, (2003), DOI={10.1016/S0377-0273(02)00356-6}.

Mori, T., Burton, M. R., The SO₂ camera: A simple, fast and cheap method for ground-based imaging of SO₂ in volcanic plumes, *Geophysical Research Letters*, 33, L24804, 2006.

Stoiber, R. E., Malinconico Jr., L. L., Williams, S. N., Use of the correlation spectrometer at volcanoes, in *Forecasting Volcanic Events*, edited by H. Tazieff, and J. C. Sabroux, pp. 425 – 444, (1983), Elsevier, New York.

P2, L9, Consider omitting ‘whilst avoiding chemisorption processes’ here and discuss it later.

We removed "whilst avoiding chemisorption processes", as it's already discussed later.

P2, L20, ‘CO₂ is HIGHLY insoluble...’

Done

P2, L20, Please clarify what becomes saturated with what at depths larger than 10 km.

We replaced "CO₂ is highly insoluble, and becomes saturated at depths typically > 10 km, while the bulk of HF degassing occurs at very low pressures" with "CO₂ is highly insoluble, and begins to exsolve from magma at depths typically > 10 km, while the bulk of HF degassing occurs at very low pressures"

P2, L28, I believe that quantifying small changes in gas concentration requires high ‘precision’, not high ‘sensitivity’, correct?

We prefer to use “sensitivity”. Please see note P9,L1 in the following.

P2, L29, Consider rewording to ‘(in order to RESOLVE RAPID CHANGES IN GAS COMPOSITION).

Done

P3, L3 – The LICOR LI-840A also measures CO₂ and H₂O. Consider rewording to ‘Several commercial instruments provide simultaneous detection of CO₂ and H₂O (e.g. LICOR 7000 and LICOR 840A).

We agree, done, and the reference has been modified too

P3, L13 (Environment) is not a valid reference. Please describe FTIR instruments in the text rather than in the reference list.

We didn't want to describe in general FTIR spectrometers, but only to mention another class of commercial devices. So we modified "In Fourier Transform Infrared (FTIR) spectrometers" in "In commercial Fourier Transform Infrared (FTIR) spectrometers"

P3, L21, ...on the COMMERCIAL market.

Done

P3, L22, The design requirements for volcanological applications in general vary quite a bit depending on access to the volcano, instrument deployment platform, volcanic hazards, monitoring vs basic research, and other factors. Perhaps it's best to focus on the design requirements for airborne measurements of volcanic plumes here?

We agree with the reviewer about the wide set of operating conditions related to volcanic applications. Yet, there are some constraint which apply to all kind of devices: capability of facing harsh environment, low power and weight, low detection limit and high accuracy. Shaking an instrument in a backpack when climbing on Etna or Vulcano, or vibrating it in a helicopter, is just a matter of frequency spectrum of vibrations, but the instrument must be anyway light, with low power consumption and so on. So we prefer to maintain our approach.

P3, L26, : : : less sensitive THAN CRD or ICOS, : : :

Done

P3, L27, Consider rewording to 'source

Done

P3, L29, '... multipass cell, optimizes the instrument size and reduces the weight'

Done

P3, L32, 'two GAS CONCENTRATIONS and THEIR RELATIVE ABUNDANCE'

Done

P3, L34, '...values of the two gases can be provided at a maximum rate of 4 Hz without the need for calibration.'

Done

P4, L3, '...laboratory PERFORMANCE of the device'.

Done

P4, L3, Consider omitting 'with an Allan-Werle Variance analysis' here and discuss this later.

We agree, done

P4, L5, Consider omitting the detection limits here, as these are results and should be reported on later.

Done, the sentence "Finally, the results obtained during a first test campaign at the crater of Vulcano volcano (Aeolian Islands, Italy) will show an in-field detection limit of 320 ppb for CO₂ and of 20 ppb for HF with an integration time of 2 s" has been changed to "Finally, we will show the results obtained during a first test campaign at the crater of Vulcano volcano (Aeolian Islands, Italy)".

P5, L5, Consider replacing ‘exploit’ with ‘use’

Done

P5, L12, ‘...orientation of the final mirror MAY require OPTIMIZATION.’

Done

P5, L15, ‘... multipass cell ARE sent...’

We have preferred to use “beam” instead than “beams”

P5, L24, ‘All electronics ARE placed...’

We have changed the sentence in “The electronic part of the instrument is placed aside the cell...”

P5, L25, Please explain the acronym FPGA

Done

P5, L30, ‘In order to protect THE optics and electronics from volcanic gases...’

Done

P5, L34, ‘So by neglecting this ADDITIONAL path, we overestimate the ambient concentration of CO₂ by 0.6% or about 2 ppm. The relative effect is smaller when measuring CO₂ concentrations above ambient.’

P5, L34, Do you overestimate the path by 0.6%? If you know about this issue, why not simply correct for it?

As said previously, in order to protect the optics against the volcanic gases, they are enclosed within a sealed plastic cover, so that the air inside this cover is not the same air measured between the mirrors of the multipass cell. Consequently we don’t know exactly how much we overestimate the CO₂ concentration, we can only affirm that our measurement can be overestimated of about 2 ppm when in the multipass cell there is ambient CO₂ and that the effect becomes lower when the air in the multipass cell contains a higher CO₂ concentration. To explain that, we have changed the sentence as suggested by the referee: “So by neglecting this additional path, we overestimate the ambient concentration of CO₂ by 0.6% or about 2 ppm. The relative effect is smaller when measuring CO₂ concentrations above ambient”.

Moreover it is impossible to measure definitely the CO₂ concentration inside the cover (for instance by flowing nitrogen into the multipass cell), because this value should be different each time we open and close the cover to adjust the optics.

P6, L6, ‘the 1 liter volume’

Done

P6, L12, ‘4 cell LiPo batteries’

Done

P6, L13, ‘... a weight of about 8 kg (pump and batteries included), WHICH makes it particularly suitable as a portable instrument for in-situ operation in a hostile environment such as in a volcanic area.’

Done

P6, L15, ‘unattended and be remotely controlled via WiFi from outside the area of toxic gas emission.’

Done

P6, L16, How far does the WiFi actually reach?

We do not consider the distance at which we can communicate via WIFI with a instrument a fundamental feature of our sensor, so we prefer not to give a precise number. In fact, this distance changes with the characteristics of the area in which the measurements are made and can be easily extended by choosing a different commercial component.

Usually we do not exceed 10-20 meters, a distance that gives us the opportunity to work in a more comfortable environment.

P6, L20, ‘... across a characteristic absorption LINE of the target molecules.’

We have changed the sentence in “...across the selected absorption line of the target molecules”

P6, L21, ‘... HF absorption LINE...’

Done

P7, L2, replace ‘alternatively’ with ‘alternatingly’

Done

P7, L5-6, Replace ‘a region’ with ‘an interval’

Done

P7, L8, ‘... around the CO₂ line and 1.5 cm⁻¹ around the HF line, respectively.’

Done

P7, L10, Please clarify what is meant by the ‘zero-power signal’. I assume you mean the intensity measured on either side of the absorption line?

No, we mean the signal acquired by the detector when the laser power is zero. This signal is acquired during the first interval of the ramp when the laser is switched off. In order to clarify this point we have added a sentence in the description of the ramp:

“As shown in Fig. 4, the modulation signal of each laser consists of 3 parts: (i) an initial interval, with a duration of 100 μ s, 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 “zero-power signal”); (ii)... ”

To describe the importance of the zero-power signal we have expanded a previous sentence in the following:

“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 don't need to know exactly the splitting ratio of the beam splitter or any kind of variability in the laser power. Moreover the changes of reflectivity of the mirrors in the multi-pass cell, related to the interaction with the external ambient, do not influence the measured absorbance value except for affecting the signal to noise ratio.”

P7, L10, ‘allows derivation of the absorbance independent of the absolute laser power. Consequently, the splitting ratio of the beam splitter and the reflectivity of the mirrors in the multi-pass cell do not influence the measured absorbance value except for affecting the signal to noise ratio.’

For the changed sentence, see the previous note

Differently from the changes in the reflectivity of the mirrors, the splitting ratio of the beam splitter don't affect the signal to noise ratio.

P7, L114, What is a ‘4000-points main signal’? Are you sampling the spectrum with 4,000 points per wavelength scan?

Yes. To better clarify, we have described the acquired scan at the beginning of the Section and in particular we have added the sentence:

“The two signals measured by the main detector (D1) and by the reference detector (D2) are acquired synchronously on 2 acquisition channels of the CompactRIO at 1 MSample/s with a resolution of 16 bits. The two main and reference signals, sampled each with 4000 points per scan, are averaged 25 times and saved for a post-processing. Typical in-field main and reference signals are shown in Fig. 4.”

P7, L16, I understand that the measurement of CO₂ and HF is nearly coincident for practical purposes of the measurement, but I would omit ‘simultaneous’ here because you just explained that the two gases are measured in alternating manner.

Done

P7, L16, Omit ‘of’ before 0.25 s.

Done

P7, L18, Again, please clarify what ‘zero-power signal’ means

Done (see previous note P7, L10).

P7, L18, ‘...ARE fit with... multiplied by a second order polynomial.’.

Done

P7, L18, Are you sure you need to multiply by a second order polynomial? I would have expected the addition of a polynomial to described the ramping intensity. As mentioned before, it would be nice to actually plot a raw spectrum that includes the interference fringes (in the reference channel) and the ramping up of the laser intensity.

In order to clarify the point, the absorption signal acquired by the main detector is shown in Fig. 4. The frequency scan is obtained by modulating the laser current, so also the output power of the laser results modulated according to the ramp and, without absorption, the signal should be described by a second-order polynomial. The absorption spectrum is the exponential of a Voigt profile multiplied for the polynomial describing the laser power. The polynomial is not a background signal but only the shape of the laser power.

To remove misunderstanding we have changed the sentence:

“...multiplied by a second-order polynomial, which simulates the sloping background due to the ramping of the driving current.”

with :

“...multiplied by a second-order polynomial, which simulates the sloping laser power due to the ramping of the driving current.”

P7, L22, which ‘molecular parameters’ from the HITRAN database are relevant? Can you please be more specific?

The HITRAN molecular parameters used in this calculation are specified:

“The values of the HWHM are calculated as a function of temperature and pressure, measured for each acquisition, and of the molecular parameters (airbroadening coefficient and linewidth temperature coefficient) according to the HITRAN database”

We would like to stress that all the details connected with the data processing (containing formula, parameters, error calculation etc.) were already described in a previous paper (Ref. Viciani et al. Appl. Phys. B, 90, 581-592, 2008), consequently we prefer not to give so many details in this paper. To emphasize this point we have added the following sentence:

“Here we present a quick description of the data processing, since a more detailed analysis has already been reported (Viciani et al. 2008).”

P7, L25, ‘multiplied BY a SECOND order...’

Done

P7, L20-27, The HITRAN database contains line strength information, not absorption cross-sections. The line strength is defined as the integral of absorbance of a given line. Since this TDL instrument resolves the individual absorption lines of CO₂ and HF, respectively, couldn't the line strength simply be measured as the integrated absorption over the measured wavelength interval? The advantage of deriving the line strength directly is that it should be independent of temperature and pressure, correct? Could you please explain why the four-Lorentz Puerta-Martin approximation is used rather than simply determining the line strength and calculating the column density and gas concentration from that?

According to the Beer–Lambert law, the intensity signal I measured after the multipass cell at a given optical frequency ν is a function of the laser intensity I_0 , of the gas cross-section σ , of the optical path length L associated with the multipass cell, and of the concentration N :

$$I = I_0 \exp[- N L \sigma(\nu)]$$

If we integrate the measured absorbance, we obtain:

$$\int [- \ln(I/I_0)] d\nu = N L S$$

where S is the line-strength. So, we can infer N from the integrated absorbance only if we know also S . In our fitting procedure (described in detail in Ref. Viciani et al. 2008), we fit the measured signal I with the function:

$$P(\nu) * \text{Exp}[- V(\nu, \text{fitting parameters})]$$

where $P(\nu)$ is a second-order polynomial and $V(\nu)$ is a Voigt profile approximated with the four-Lorentz Puerta-Martin function. With the parameters obtained by the fit, we calculate the integrated Voigt profile and:

$$N = \int V(\nu) d\nu / (L S)$$

This fitting procedure has 2 advantages with respect to the direct integration of the absorbance:

- (i) We don't need to know exactly I_0 (because it is one of the fitting parameter).
- (ii) The result of the integration of an experimental signal is very noisy because affected not only by the fluctuation of the signal but also by the fluctuation of the background outside the absorption. Differently the result of the integration of a Voigt function is less noisy and not at all affected by the background.

P8, L5, '...laboratory performance...'

Done

P8, L5-10, How do you know that chemisorption prohibits a laboratory test using a pre-mixed HF calibration gas? Did you attempt the experiment? Can you provide a reference from the literature as to why such an experiment would surely fail? I would think that dust and water vapor in the sampling apparatus could be avoided in a laboratory setting.

In order to do such a test with HF, we need a gas line including: a tank with a calibrated HF mixture, a pressure regulator, a Teflon pipe from the regulator to the multipass cell and the closed teflon cell. To have a reliable measurement, all the surfaces of these components should be completely free from dust and water vapor, otherwise they will be involved in chemisorption. We think this is a very difficult issue to obtain also in a laboratory! We think that it is more reliable to evaluate the performance of the HF channel in an open-cell configuration.

P8, L11, '... performance of the HF channel...'

Done

P8, L12 and throughout the manuscript: Consider running a global 'search and replace' on the entire manuscript and replace all instances of 'has been' and 'have been' with 'was' and 'were' unless referring to studies that were conducted previous to the work presented here.

We agree, all "has been" and most of "have been" were replaced

P8, L14, How was the under-pressure of 700 mBar achieved?

We have added in the text the following explanation sentence:

"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."

P8, L17, I don't understand why two optical fringes need to be included in the fit procedure when fitting the measurement channel. The reference channel passes the etalon, so it makes sense that fringes would appear there, but why are they included in the fit for the measurement channel? Also, they are not obvious in figure 3. Is that because they are very low-amplitude compared to the absorption line?

In all optical instruments there are unwanted reflections among optical surfaces which generate spurious interference fringes, usually known as "optical fringes". Often in Direct Absorption Technique with multipass cell the sensitivity of the instrument is limited by the optical fringes (see as an example

A. Fried et al., Applied Optics 29, 900-902, 1990; or V. V. Liger Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 55, 2021-2026, 1999).

A standard method to reduce the effect of the fringes is to include in the fitting function one or more sinusoidal curves to get rid of these fringes (see Ref Viciani et al. 2008). In Figure 5 there is no evidence of the fringes because their amplitudes are of the order of 10^{-3} , but without the two optical fringes in the fitting function the residual should show a sinusoidal behavior with amplitude 10^{-3} .

Obviously the effect of the optical fringes becomes relevant for low concentration values.

To explain better we have added in Section 4, in the description of the fitting function, the following sentence:

“When necessary, also one or more sinusoidal curves are included in the fitting function to take into account the presence of optical fringes.”

P8, L28, Please replace ‘lower pressure’ with the actual pressure that was used (700 mBar?)

Done

P8, L30, Please explain why a narrower line shape improves the identification of the background intensity, and why optical fringes are present in the measurement spectrum.

For the presence of optical fringes see note P8,117.

As already said, the function used to fit the signal in Figure 3 (top) is given by:

$$P(\nu) * \text{Exp}[-V(\nu, \text{fitting parameters})] * OF(\nu)$$

where $P(\nu)$ is a second-order polynomial which describes the background, $V(\nu)$ is the approximation of a Voigt profile and OF is a sinusoidal curve which describes the Optical Fringes.

For a broad lineshape, as wide as the laser scan (as that one of Figure 5), the exponential part is prevalent with respect to the other two terms, and it results very difficult to determine the fitting parameters for $P(\nu)$ and $OF(\nu)$. Consequently, repeated fitting procedure are affected by a variability in the determination of $P(\nu)$ and $OF(\nu)$. This variability is reduced when the lineshape becomes narrower because $P(\nu)$ and $OF(\nu)$ can be better identified by the fit.

In order to better clarify this point, we have added the following sentence:

“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.”

Figure 3 caption, ‘...in the bottom plot...’

Done

Figure 3 caption, and throughout the manuscript: When taking the average of multiple acquisitions to improve the signal to noise ratio, the term ‘integration time’ is typically used to describe the total time for all the individual acquisitions. The ‘acquisition time’ usually describes the time for just one acquisition. Consider using this verbiage throughout the manuscript.

Done in all the text of the paper.

P9, L1, 500 ppb appears to be the precision of the instrument, not the sensitivity of the instrument.

We apologize for the confusion between precision, sensitivity and detection limit.

We have corrected the text according to the following formalism:

The PRECISION is the stability of the instrument.

The DETECTION LIMIT is the minimum concentration which the instrument can measure and it is given by the acquired signal for which the signal-to-noise ratio $S/N = 1$.

The SENSITIVITY is the minimum variation in the concentration detectable by the instrument.

The sensitivity can not be better than the precision, but in principle it could be worst.

In our instrument the sensitivity is determined by the precision.

So the “500 ppb” is the precision and also the sensitivity.

We have maintain the term “sensitivity”, but to clarify this point we have added the following sentence:

"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."

P9, L2, Detection limit and precision are not quite the same thing. In this case, since you will always have at least 400 ppm CO₂ in the ambient air, the detection limit is not really relevant I guess. Instead, the precision is what will determine if a small volcanic plume can be detected or not.

We have replaced detection limit with sensitivity (see also note P9, L1).

P9, L6, please explain what is meant by ‘get rid of fringes’.

See notes P8,L17 and P8,L30.

In order to explain better we have changed the sentence:

“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.”

P9, L12, Please include more details on where the measurements were made, perhaps even a map?

See reply to point 4 above

P10, L6, Consider replacing ‘emission peak’ with ‘gas cloud’

Done

P10, L7, ‘...the only way to completely solve this problem...:’

Done

Figure 5 caption, ‘...is due to chemisorption on instrument components in the closed cell configuration.’

Done

Figure 6 caption, ‘bottom plots’

Done

Figure 6 caption and throughout the manuscript: Please be a little bit more precise when using the term ‘concentration’. Concentration is a measure of the number of trace gas molecules in the sample cell or in a known volume of air. A typical unit is molecules / cm³. A mixing ratio is the ratio of trace gas molecules to total air molecules in a given volume. Typical units are ppm or ppb. The TDL instrument measures absorbance, which can be converted into column density (units of molecules / cm²) using the Beer Lambert Bouguer Law. This can further be converted into an average concentration in the cell. However, converting to a mixing ratio requires knowledge of temperature and pressure, as described in your equation 1. Since you are measuring temperature and pressure and correcting for these effects, it’s fine to report mixing ratios, but please don’t call them ‘concentrations.’

We apologize for that. We have replaced “concentration” with the “mixing ratio” in the text of the manuscript, in the captions of Fig. 5, 6,7 and 8 and in the axes of Fig.7

P12, L6-8, Please clarify how you obtain the mean value of the noise from the residual. It appears that the residual contains some systematic structures as well as some statistical noise. How do you separate the two? Do you have any ideas where the systematic structures come from?

The structures in the residual are due to the presence of optical fringes (see note P8,L17), which have not been removed completely by the fitting protocol. The important point is that this structure is different for each spectrum, due to the random fluctuation of the phase of the optical fringes. So it can not be considered as a systematic structures. For different spectra the structure of the residual is different, but the standard deviation is very similar. So a typical noise value associated to the measurement can be inferred by the mean of the noise of different spectra.

To avoid misunderstanding we have removed the sentence: “most of which show a residual similar to that one displayed in Fig.6”.

P12, L10, Again, do you mean precision rather than detection limit?

We have changed “detection limit” with “sensitivity”. Please see note on Figure8 in the following and also note P9,L1.

P12, L13, ‘... a factor of 1.3’

Done

Figure 7 caption, Again, this figure plots mixing ratios, not concentrations.

Done

Figure 7 caption, ‘... a 3-minute interval.’

Done

P13, L6, Perhaps rephrase this sentence to ‘If the instrument is operated in lower acid gas and aerosol concentrations it could likely run for long periods of time without significant degradation of the signal to noise.’

We have replaced:

“On the contrary, when the instrument is far from the fumaroles, or on board an aircraft, it can work indefinitely without significant reduction in performance.”

with:

“On the contrary, if the instrument is operated in lower acid gas and aerosol concentrations, as for instance on board an aircraft, it could run for long periods of time without significant degradation of the signal to noise ratio.”

P13, L14, Do you mean 3 per mil or 3 percent? Since percent are used throughout the manuscript, consider replacing this with ‘0.3%’ if that is the appropriate value.

We mean 0.3% and we have replaced it.

P13, L15, ‘emission peak could be used to correct’

Done

Figure 8, again plots mixing ratios rather than concentrations

Done

Figure 8, If I understand correctly, then the estimated detection limit of the instrument for CO₂ was determined by extrapolating the measurements shown in Figure 8 a down to a S/N of 1. If this is true, this estimate would appear to have quite a large uncertainty given that no measurements were performed with S/N less than about 1800. If you want to peruse this methodology, please give the uncertainty of the detection limit obtained in this manner. In my opinion this is of somewhat limited use, however, as no measurements will ever be performed at less than about 400 ppm CO₂ which corresponds to a S/N of more than 1,000. For the CO₂ channel, the precision of the instrument is much more important than its detection limit.

Again we apologize for the confusion.

In Figure 8 we show the linear relationship between S/N and MR (mixing ratio), in order to find the slope through a linear fitting procedure.

According to the formalism in note P9,L1:

- the detection limit is the MR for which $S/N = 1$.
- the sensitivity is the variation in the mixing ratio corresponding to a variation of the signal equal to the noise. If S/N is a function F of the MR, the sensitivity (for a particular MR₀) is the inverse of the derivative of F with respect to MR, calculated in MR₀.

In the present case, where there is a linear relationship between S/N and MR, the detection limit and the sensitivity have the same value equal to the inverse of the slope.

Of course, we agree with the Referee that the detection limit for CO₂ is not an important parameter for our instrument. So we have replaced “detection limit” with “sensitivity”

P14, The manuscript lacks a ‘Conclusions’ section. The first paragraph on page 14 seems to belong to the conclusions so this might be an appropriate place for this heading.

Sorry for that, during the submission procedure we deleted accidentally the title of the “Conclusion” section. Now we have reinserted it.

P14, L8, ‘... by detecting water absorption...’

Done

P14, The manuscript only includes a single sentence about future work. Given that this document only describes the very first tests of a new instrument, I would expect much more future work planned for the system. For example, I’m sure the system is to be (or actually already was) run on an aircraft platform for determining plume composition downwind of various volcanoes. I

believe that detection of other gases (besides H₂O) will be or already have been added to the instrument's capabilities? What other instruments would be useful to run alongside this one? In particular, I'm thinking that it would be quite advantageous to measure SO₂ in parallel with the other gases so that emission rates for all species can be derived from remote sensing SO₂ measurements.

According to the suggestion, we have included the following sentence at the end of the Conclusion:

“Moreover we are designing a portable experimental platform for in-situ simultaneous measurements of 5 volcanic gases (HCl, CO₂, HF, H₂O and SO₂). The platform will include two mid-IR spectrometers, one of which will be the instrument described in this paper, and an UV spectrometer. The platform will be employed for measurement campaigns in-field and on board aircraft. In order allow deployment on board of drones, we will reduce size and weight by replacing the cRIO crate with a smaller electronics, namely Red Pitaya by StemLab, we will use only fiber-coupled lasers in the near infrared, so eliminating most mirrors and their holders, and we will use aluminum and carbon fibers only for those parts which strictly require mechanical hardness. All other parts will be realized by 3D plastic printing. As drones can fly much closer to plumes than manned aircraft, the concentrations to be measured are expected to be at least one order of magnitude higher than in the present measurements, and so the multipass cells will be shorter and lighter too.”

References: The reference list needs to be expanded to include more relevant publications. I have made a number of suggestions above and additional suggestions are also welcome. Some of the technical documents referenced are pretty much just URLs and might be better referenced in the text itself, depending on what the journal policy is for these.

The list of references has been expanded significantly, following the reviewer's suggestions. As for the citations of commercial devices, which refer to URLs, we moved the citations into the text.

REPLY TO REVIEWER #2

First and foremost, the 3D Figure 1 is useful, but would be much more useful if accompanied by a schematic diagram showing the optical configuration. That is, a box and line drawing showing the key elements (lasers, mirrors, detectors, fibres) and the light paths, particularly the multipass arrangement in the cell.

See point 3) of the reply to reviewer #1

Figure 2 would also be much more useful if they could provide line drawings showing what the cells are - to my untrained eye, I see a skinny black tube and a fat white tube, which provide little guidance if I wanted to build a similar instrument. Scale bars would be helpful for both figures.

Now Figure 2 is Figure 3. We have modified it, removing the closed cap version, and including two photos showing the spots of the laser onto the mirrors. Photo b) shows the whole cell in the alignment setup, and photo c) is a detail of the entrance/exit mirror. The caption has been changed from "Home made multipass cell in the open-cell configuration (a) and in the closed-cell configuration (b)." to "Home made multipass cell in the open-cell configuration (a). Photo b) shows the whole cell with the spots of the alignment laser onto the mirrors, photo c) is a detail of the entrance/exit mirror." We also added a reference to Herriott cells. The scale is given in the figure.

Second, there is frequent mention of key metrics such as precision, power consumption, size, weight, but the requirements are not quantified. The manuscript would be much more readable, and also easier to write, if the requirements were specified in the introduction. What precision is needed for their volcanic research? What power consumption is acceptable? How long must it operate on battery power, or what could be achieved if that was possible for 1 hour, 4 hours, 8 hours etc? Why is size important and what size thresholds are there? Once those parameters are defined, it becomes very clear to list alternatives that do not meet those requirements, and show how their instrument compares. The conclusion paragraph could also then be more concise and have greater impact.

We agree with the reviewer and we've added the text below to the introduction, to better explain the requirements for a field-based volcanic gas sensor.

This platform would allow multiple gases to be measured simultaneously at high frequency (at least 2-3 Hz) to permit airborne measurements, would have high precision and accuracy to allow dilute plumes to be measured, and would be compact, low-power and robust to allow easy field deployment with a variety of transport solutions, including backpacks, airplanes and drones.

We have also added this text to the section on state of the art in volcanic gas measurement

In addition to these requirements, the detection of acid gases, such as HF, require 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 kg for batteries is typically ideal.

In a related sense, the paper is quite long for the content. It would have greater value if more concise; for example removing frequent repetition (references to precision, power consumption, etc). In considering alternatives, they could be tabulated, with a row for each, and columns for the metrics mentioned above. A reader could then very quickly appraise the existing options and see why this new instrument is worth learning about.

We acknowledge this remark. Wherever possible, we removed redundancies. We don't report here the list of changes, as it would be too long. As for tables, this option could have been exploited when dealing with commercial devices. Nevertheless, we realized that the table should have featured too many columns, so being hard to read, and we left the descriptions in the text.

Line 120: I did not understand this sentence.

We replaced the sentence "The latter was a source of concern as we will have the option of using the optical cells in open air" with "When measuring in the plume of a volcano, cleanliness of the mirrors is a serious concern"

Line 150, 228: The manuscript uses mixed units for laser wavelength/frequency (e.g. laser wavelength in microns and spectroscopic features in wavenumbers). It would be helpful to provide both when using either, for example 1.27 μm (7875 cm^{-1}) and 7823.82 cm^{-1} ($1.27815\text{ }\mu\text{m}$).

We have added everywhere the missing information

Line 182: The data acquisition requirements do not seem very demanding (1 MHz/16-bit measurement), and thus the use of a system crate with dual-core processor and FPGA seems

extreme for an instrument which is nominally low power and compact. I am not particularly expert in what is available in such technology but I would first consider something like a BeagleBone single-board computer, raspberry Pi, and other devices which operate at just a few watts. Could they comment on why this approach was taken rather than something more specific to the task?

The crate cRIO by National Instrument is a good compromise for the task to be carried out, and features some important characteristics, namely it comes with all the drivers for LabVIEW environment, and it is possible to realize custom plug-ins, just like we did to supply and stabilize the temperatures of our lasers.

It is possible to add to a Raspberry a 4 input Analog to Digital Converter, with the same resolution (16 bit, see <https://learn.adafruit.com/adafruit-4-channel-adc-breakouts/overview>), but with at most 3300 samples per second. BeagleBone has a built in set of ADCs, but with 12 bit resolution. We are exploring the Red Pitaya board, whose ADCs feature 14 bits at 125 MS/second. It's a very interesting device, light and with low power consumption, but programming it is quite a complicate task, especially when compared to cRIO.

Line 235: Why did they not use two detectors and a dichroic splitter, so they could detect both wavelengths simultaneously, rather than switching them on and off? How were the scanning times determined, i.e. the ramp time of 1600 μ s, and the deadtimes of 100 μ s and 300 μ s? What is the time-constant of the detection system? Are these times excessive, or is the 1.6ms ramp time so fast that there is significant loss of fidelity due to scanning too fast over small features that are lost due to the analogue bandwidth?

As a matter of fact we should have used four detectors and two dichroic splitters, as we should have treated in the same way both the measurement arm and the reference arm. The suggestion is reasonable indeed, but it would complicate the instrument significantly. As for timing, there are several points to be taken into account. First of all, we need some hundreds ramps per second (250), in order to average out white noise. Then, we need a sufficient time (300 μ s) to stabilize the laser temperature after switching on. We also need some tens of point to retrieve a good zero value (100 μ s), and as many points as possible for fitting the waveform and the etalon fringes (1600 μ s). The set values are simply a good compromise among all these constraints. The bandwidths of the laser power supply and of the detectors are not an issue.

Line 250: It would be helpful if the authors could provide a calculation of the expected measurement time required to achieve their desired sensitivity, and compare that to the time they used in their experiments. In particular, to better understand the limits; for example, could we reasonably expect to achieve measurements of comparable precision and accuracy at 10/s or 100/s rather than 4/s? If not, what would we need to improve?

We would analyze this point from a different perspective. We want to save all the waveforms produced by the instrument for off-line analysis, though there is an on-board program providing a quick-look of the data. Our processing system takes about 150 ms to treat one waveform, which means that no more than 6 waveforms can be saved per second. Each waveform can be either a single shot, or the average of a variable number of ramps. With the numbers we set, we have a good compromise between time "wasted" and quality of data. For further information about quality of data please refer to the chapter about "Laboratory performances of the instrument for the CO₂ channel".

Line 257: They refer to simulation of a sloping background by *multiplying* a Voigt profile by a two-order polynomial (which I take to mean a quadratic). But fitting a background would

involve addition/subtraction of a polynomial; multiplication simulates a varying gain or optical power. Could the authors please clarify?

Please see the reply to point P7,L18 of Reviewer #1

Line 330: I did not understand this sentence: what do they mean by "get rid of fringes"? What fringes?

When interference fringes are due to thin optical elements, like windows, their period is comparable with the whole laser frequency scan. So, if the absorption line occupies a wide portion of the laser scan, it's difficult for the software to correctly identify the contribution of these fringes. The lower the pressure, the narrower the absorption line, the wider the portion of the scan free from absorptions, which can be used for a proper fit of the fringe. An alternative could be that of increasing the laser scan, provided that the overall tunability of the laser allows it. Please see the reply to point P9,L6 of Reviewer #1.

Line 388: The instrument measures ambient CO₂ concentration of (390 ± 20) ppm. How does that compare with standard data or independent measurement?

We inserted in the text a reference to the trend global data for CO₂ concentration issued by NOAA. We added the sentence: "These data fit well with the global trend for CO₂ concentration, see for instance the NOAA website (URL = <https://www.esrl.noaa.gov/gmd/ccgg/trends/global.html>)".

Line 434 (conclusion): Again, it would be helpful if the authors could compare their achievements against quantitative metrics. Some suggestions on how the instrument might be improved could be helpful (improved in terms of precision, accuracy, power, weight, size etc). I wondered if perhaps an AC measurement technique might be useful; their measurements are essentially DC, and thus sensitive to low-frequency (1/f) noise. Would fast modulation (of frequency or power) and demodulation (i.e. lock-in detection) be helpful?

We added in the text a further explanation of the reason for our choice of a DC technique: In principle, detection limits and accuracy could be increased of one order of magnitude when adopting a detection technique based of laser frequency modulation (two references have been inserted at this point). Yet, this kind of detection raises severe concerns about calibration, in particular in an environment where temperature, pressure and mixture composition can vary we always aim to versatility. This is because in these techniques the calibration relies on the stability of the lineshape which, on the contrary, is affected by the physical conditions of the measurement. So, also next development of this instrument will adopt direct absorption.

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

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

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Abstract. A portable analyzer, for simultaneous detection of CO₂ and HF emitted by volcanoes and fumaroles, is described. The system is based on two fiber coupled Distributed FeedBack 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 setup, to remove all the problems connected with the latter mitigating problems associated with chemisorption of the HF molecule. The concept, the practical realization and the laboratory performances laboratory performance of the device will be described. Moreover the results obtained during are presented, together with results from a first test campaign at measuring volcanic gases emitted by the crater of Vulcano volcano will be reported, to demonstrate the Italy. We obtained an in-field performances of the spectrometer sensitivity of 320 ppb for CO₂ and 20 ppb for HF at 2 s integration time.

10 1 Introduction

The dynamics of magma storage and ascent are reflected in the composition and flux of gases released by active volcanoes (?Giggenbach, 1996; Allard et al., 2005; La Spina et al., 2010). The major volatile species, H₂O, CO₂, SO₂, HCl, HF all have pressure-dependent solubility profiles, producing significant variability in gas composition as a function of depth 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 relationships between magma ascent and degassing (Gonnermann et al., 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 measurement 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 novel 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. ~~Direct sampling by dissolving hot fumarolic gases into alkali solutions followed by laboratory analysis allows a complete chemical description of sampled gases, but cannot be easily performed in dilute volcanic plumes, and sampling may be hazardous~~ HF is measurable with filter packs (Pennisi et al., 1998; Mather et al., 2004; Allard et al., 2016), diffusion tubes (Rüdiger et al., 2017), and direct sampling by bubbling through alkali solutions (Giggenbach et al., 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; ?, ?; ?; ?) measures both CO₂ and HF directly in the field. In-situ sensors such as MultiGas (Shinohara et al., 2008) (Aiuppa et al., 2005; Shinoara et al., 2010) have allowed automated measurements of plume gas compositions, primarily CO₂ and S species, ~~to be performed, but the range of gases which can be measured is currently limited, 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 ~~chemical-based~~ electrochemical S sensors. Drifting calibrations make traceability of long term installations challenging. Remote sensing using infrared (Mori et al., 1997; Francis et al., 1998) or ultraviolet spectroscopy (?)(Galle et al., 2002; ?, 2010; Butz et al., 2017) is effective for safe determination of plume gases, and has a key capacity to measure gas compositions during explosive activity, but requires large ~~path amounts of gas, and is poorly suited for in-situ measurements~~ 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 ~~and precise,~~ precise and high frequency measurements, and many volcanic gases have accessible near- and mid-infrared absorption spectra. They can also work at high frequency (> 1 Hz), which is a requirement for airborne surveys where rapid changes in gas concentration are common. However, TDL instruments are usually bulky, delicate and ill-suited to the rigours of volcanological fieldwork. A final essential requirement for volcanic gas sensing is that multiple gases are measured in the same volume of gas at the same time, whilst avoiding chemisorption processes. This allows the direct determination of volcanic gas molar ratios, which are the key to unravelling volcanic processes. SO₂ is relatively easy to quantify due to a strong UV absorption spectrum and low background concentration, allowing straightforward SO₂ flux quantification (???). So, the knowledge of SO₂ flux, when added to the in-situ measurement 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. ~~This platform would allow multiple gases to be measured simultaneously at high frequency (at least 2-3 Hz) to permit airborne measurements, would have high precision and accuracy to allow dilute plumes to be measured, and would be compact, low-power and robust to allow easy field deployment with a variety of transport solutions, including backpacks, airplanes and drones.~~ Here, we report on the first measurements of CO₂ and HF we conducted with the ~~new first analyzer of the planned~~ CO2Volc TDL platform, which was tested in the laboratory and on fumaroles on Vulcano island, Italy. ~~A key requirement for volcanological applications is the simultaneous measurement of multiple gas species, as it is the ratio of volcanic species which provides constraints on magma dynamics.~~ The species CO₂ and HF are ideally suited for revealing magma dynamics,

being two end-members for solubility in magmas; CO₂ is high-highly insoluble, and ~~becomes saturated~~ begins to exsolve from magma at depths typically > 10 km, while the bulk of HF degassing occurs at very low pressures.

2 State of the art for in-situ volcanic gas measurement

The requirements for a successful and effective volcanic gas analyser are stringent. The instrument must be compact and light for field portability, ~~but also to allow easy field deployment with a variety of transport solutions, including backpacks, airplanes 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) ~~and,~~ high precision and accuracy (in order to measure low concentrations in dilute plumes) and response times of the order of 1 s (~~in order to detect true~~ to permit airborne measurements and resolve rapid changes in gas composition ~~when concentrations are fluctuating rapidly~~). In addition to ~~all of~~ these requirements, the detection of acid gases, such as HF, require 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 kg 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 measurement of multiple gas species and for the problems connected with chemisorption. Several analyzers fulfill the requirements for CO₂ and H₂O measurements (Gianfrani et al., 2000; Rocco et al., 2004). ~~In the market there is at least one commercial device for the~~ Several commercial instruments provide simultaneous detection of ~~both gases (LI-COR-Li-7000?~~ CO₂ and H₂O (e.g. LICOR 7000 and LICOR 840A, URL = https://www.licor.com/env/products/gas_analysis/). 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 measurement together 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 fulfill all the requirements for volcanological applications. The simplest ones are those used in human exposure monitoring (GfG ~~?Instrumentation, Model TN 2014 Micro IV, URL = <http://goodforgas.com/shop/micro-iv-single-gas-detector>~~), 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 ?~~), Environnement S.A., Model MIR FT, URL =

<http://www.environnement-sa.com/products-page/en/emission-monitoring-en/multigas-stationary-monitoring-systems-en/mir-ft-2/?cat=12>

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 ~~measurement~~ measurement, 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 Analyzer, URL = 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~~ [ABB - Los Gatos Research, Hydrogen Fluoride Analyzer, URL = 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 don't 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.

~~In view of the design requirements for volcanological applications, we have designed, produced and tested a new portable diode laser spectrometer for the simultaneous in-situ measurement of CO₂ and HF.~~ As we show here, the new instrument ~~has been~~ 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 ~~have~~ adopted direct absorption in combination with a multi-pass cell as a detection technique which, though noisier and less sensitive ~~with respect to~~ than CRD or ICOS, allows a great simplification of the apparatus and doesn't need extremely high reflectivity of the cell mirrors. ~~The latter was a source of concern as we will have the option of using the optical cells in open air. The optical setup, based on two fiber coupled distributed feedback lasers (DFB) but only one home-made multipass cell, has been thought to optimize the instrument size and to reduce the weight to only 8-9 Kg. Moreover, such a setup insures that both laser beams run the same path and probe the same air in the same experimental conditions, so making this apparatus particularly suitable for simultaneous measurement of two gases concentration and for the estimation of their ratio. The analyzer can work completely unattended and, if necessary, remotely controlled via Wi-Fi, for several hours in battery mode, with a power consumption lower than 50 W. The simultaneous absolute concentration values of the 2 gases, without calibration procedure, can be provided at a maximum rate of 4 Hz. We have addressed the problem of chemisorption of HF with two possible configurations of the spectrometer: a closed-cell configuration, with a teflon tube enclosing the multipass cell and a pump system to inject air into the cell, and an open-cell configuration to reduce the contact between the gas and the surfaces of the instrument. When measuring in the plume of a volcan, cleanliness of the mirrors is a serious concern.~~

In principle, detection limits and accuracy could be increased of one order of magnitude when adopting a detection technique based of laser frequency modulation (Corsi et al., 1999; D'Amato et al., 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 lineshape which, on the contrary, is affected by the physical conditions of the measurement. So, also next developments of this class of instruments will adopt direct absorption.

The practical realization and the laboratory ~~performances~~ performance of the device ~~, with an Allan-Werle Variance analysis~~ will be described. Finally, we will show the results obtained during a first test campaign at the crater of Vulcano volcano (Aeolian Islands, Italy) ~~will show an in-field detection limit of 320 ppb for CO₂ and of 20 ppb for HF with an integration time of 2 s.~~

3 Experimental setup

- 5 The optical setup of the analyzer is based on two near-IR ~~DFB-Distributed FeedBack (DFB)~~ fiber coupled diode lasers and only one multipass cell (Fig. 2). 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.~~

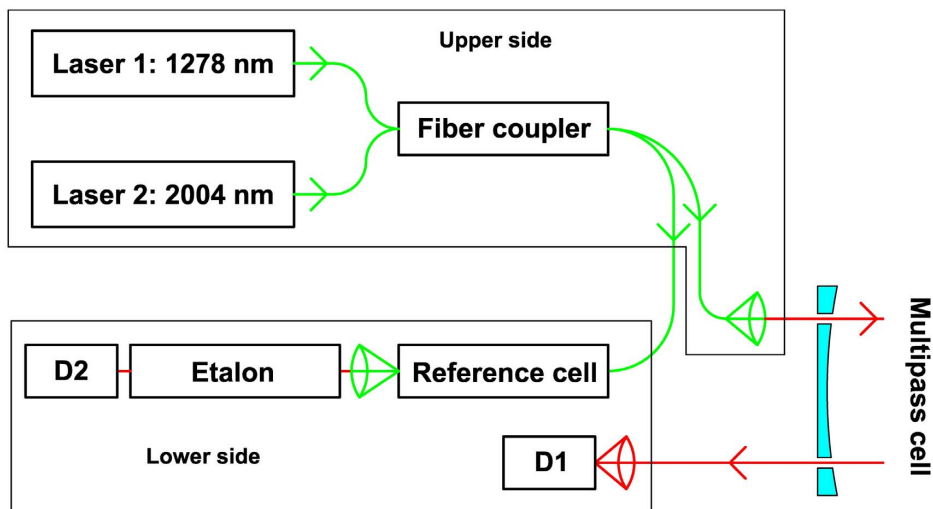


Figure 1. Optical scheme of the analyzer. a) Top view. LD1 and LD2 diode lasers; C2x2: fiber coupler 2x2 50/50 transmission; C: collimator; W1: CaF₂ window for Closed line encompass the entrance of the multipass cell MC components according to their locations, as per Fig. b) Bottom view. RC: reference cell; ET: BK7 etalon; W2: CaF₂ window for the output of the multipass cell MC; D1 and D2 detectors. ER: rack for electronics-2

On the top side of the breadboard, two fiber coupled DFB lasers emitting respectively at 1.278 μm and 2.004 μm (Eblana
 10 Photonics EP1392-DM and EP2000-DM, output power 5 mW and 2 mW) are directly mixed in a “2x2” fiber coupler, 50/50
 transmission, working around 1.3 μm and 1.5 μm (Thorlabs 10202A-50-APC). As a matter of fact, this component is a stan-
 dard one and in principle is not dichroic for the two laser wavelengths. Nevertheless we don’t need an exact splitting ratio, and
 the attenuation of the coupler at 2 μm is low enough to allow us to exploit-use it. So about half of the power of both lasers is
 collimated and sent into the multi-pass cell, while the other half of the power of the two beams is sent towards the bottom side

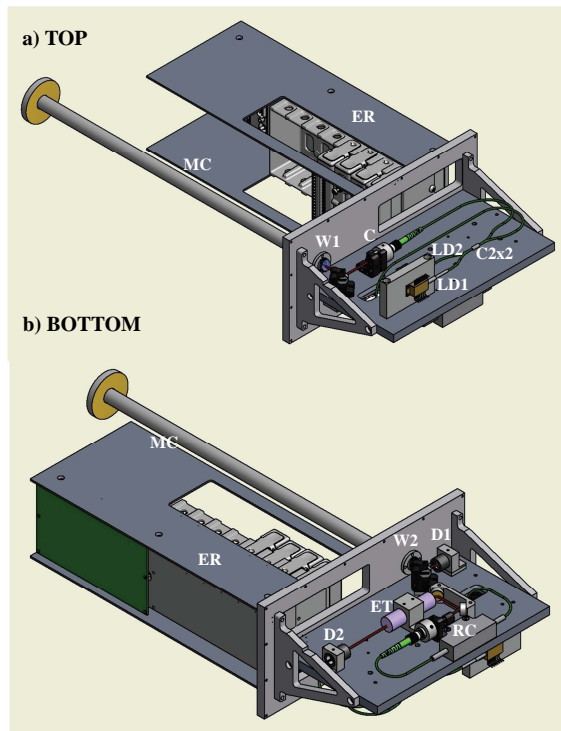


Figure 2. Setup of the analyzer. a) Top view. LD1 and LD2 diode lasers; C2x2: fiber coupler 2x2 50/50 transmission; C: collimator; W1: CaF₂ window for the entrance of the multipass cell MC. b) Bottom view. RC: reference cell; ET: BK7 etalon; W2: CaF₂ window for the output of the multipass cell MC; D1 and D2 detectors. ER: rack for electronics

15 of the breadboard.

The multipass cell (Fig. 3) is a home made ~~eeH~~-Herriott cell (Herriott et al., 1965) with a total pathlength of 20.23 m in 52 passes. It has two quartz mirrors mounted on a carbon fiber pipe. The pipe is kept by a stainless steel holder, which can be fixed to the analyzer body in a repeatable way by means of three spines. This allows a fast and easy mounting and removal of the cell in case of cleaning or replacement. As several identical cells ~~have been were~~ aligned in the same optical setup, in case of replacement no realignment of the analyzer is necessary, and just the orientation of the final mirror ~~could require to~~
 5 ~~be optimized~~may require optimization. The beam enters the multipass cell and gets back into the analyzer across two CaF₂ windows, tilted by an angle of ~~1923~~1923° in order to avoid interference fringes.

On the bottom side of the breadboard, the ~~beams~~beam exiting from the multipass cell is sent to a 20 mm plano convex lens and focused onto a main detector (Hamamatsu G12183-010K, InGaAs PIN, 0.9-2.6 μm, ϕ 1 mm, uncooled), which is suitable for both laser wavelengths.

10 The other ~~beams~~beam exiting from the 2x2 coupler ~~are is~~ sent across a reference cell (manufactured by Wavelength Refer-

ences), 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.

~~All the electronics is placed aside. The electronic part of the instrument is placed next to~~ the cell (as shown in Fig. 2). ~~The core of the instrument is a CompactRIO crate, 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 plug-ins for fast acquisition (four independent channels, 1 MHz at 16 bits), slow acquisition (8 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.

10

In order to protect the optics and electronics against the volcanic gases, they are enclosed within a plastic cover, 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 optics fibers 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 pathlength is in total 11.5 cm, to be compared to about 20 m. So by neglecting this additional path, we ~~would~~ overestimate the ambient concentration of CO₂ ~~of only about by~~ $6 \cdot 10^{-3}$ ~~; or about 2 ppm. The relative effect is smaller when measuring CO₂ concentrations above ambient.~~

15

The device can operate in an open-cell configuration (~~as in Fig. 3a~~) or in a closed-cell configuration (~~as in Fig. 3b~~). In the first case, we don't 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. So the ~~1+1 liter~~ volume of the multipass cell is flushed in about ~ 3 s.

5

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 one (open-cell configuration) or two (closed-cell configuration) ~~4 cells LiPo batteries~~ 4 cell LiPo battery, 6800 mAh at 14.8 V.

10

The instrument is robust and compact (with size of 60.5x27.6x13.2 cm), with a weight of about 8-9 Kg (pump and batteries included), ~~that which~~ makes it particularly suitable as a portable instrument for in-situ operation in a hostile ~~ambient as the environment such as a~~ volcanic area. The spectrometer can work for about 4-5 hours completely unattended and ~~, if the ease, be~~

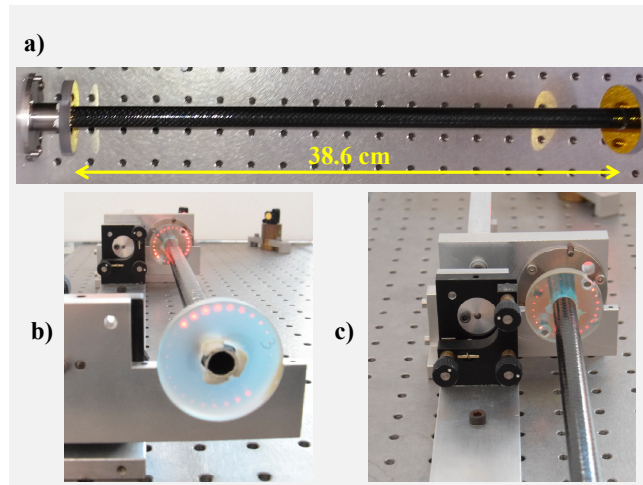


Figure 3. Home made multipass cell in the open-cell configuration (a) and in the closed-cell configuration (c). Photo b) shows the whole cell with the spots of the alignment laser onto the mirrors, photo c) is a detail of the entrance/exit mirror.

remotely controlled via Wi-Fi, far from the dangerous area of the toxic gases WiFi from outside the area of toxic gas emission.

15

4 Acquisition technique and data processing

The concentration values of the two gases are inferred by the absorption signals registered by the main detector, according to the Beer-Lambert law. The absorption signals are obtained by scanning the two lasers emission frequencies across the absorptions-

In the acquisition procedure the two laser emission frequencies are scanned respectively across the selected absorption
 20 lines of the target molecules, by modulating the laser current with a ramp signal. The 1.32 μm -laser is scanned over the HF absorption at 7823.82 scans over the CO_2 absorption line at 4989.97 cm^{-1} (2004.02 nm), while the 21.3 μm -laser scans over the CO_2 absorption at 4989.97 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 CO_2 line and 1.5 cm^{-1} (45 GHz) around the HF line, respectively.

25 The two signals measured by the main detector (D1) and by the reference detector (D2) are acquired synchronously on 2 acquisition channels of the CompactRIO at 1 MSample/s with a resolution of 16 bits. The two main and reference signals, sampled each with 4000 points per scan, are averaged 25 times and saved for a 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 alternatively/alternatingly: when one laser is switched off, the
 30 current of the other laser is modulated, and conversely. The time interval between the two laser scans is 2 ms, so that the two

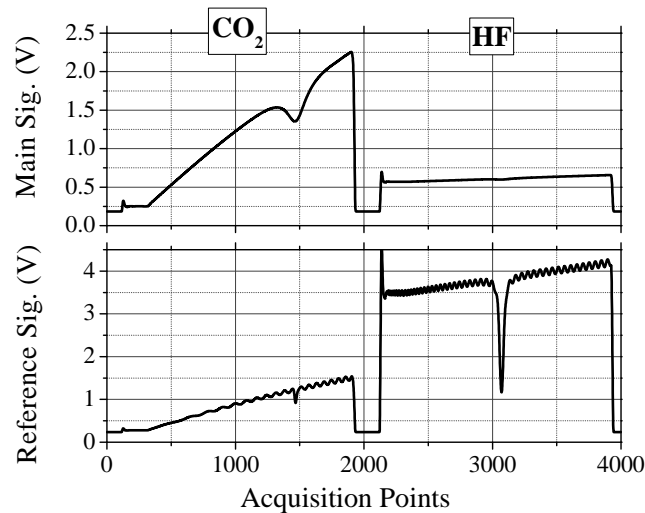


Figure 4. Typical signals recorded by the measurement detector D1 (top) and reference detector D2 (bottom) during a test campaign at Vulcano volcano.

measurements can be considered simultaneous for the purposes of our applications. As shown in Fig. 4, the modulation signal of each laser consists of 3 parts: a linear ramp (i) an initial interval, with a duration of 1.6 ms; a region of 100 μ s, during which the laser is turned off to get the detector background signal of the detector when no laser power is incident on it (in the following we refer to this signal as “zero-power signal; and a region”); (ii) an interval of 300 μ s 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; (iii) the linear ramp with a duration of 1.6 ms. The repetition frequency for the complete sequence of ramps modulations is about 250 Hz. The maximum tuning of the two lasers provides two frequency scans of 0.8 cm^{-1} around 1.5 cm^{-1} around CO_2 and 1.5 cm^{-1} around HF , respectively. 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 for the purposes of our applications.

The zero-power signal allows to know the absorption concentration values of the two gases are calculated by the absorption signal registered by the main detector (upper side 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 value of the laser power, consequently laser power. Consequently we don't need to know exactly the splitting ratio of the beam splitter and we can face or any kind of variability in the laser power. Moreover the changes of reflectivity of the mirrors in the multi-pass 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 and main signals are acquired synchronously on 2 channels at 1 MSample/s with a resolution of 16 bits. Each 4000-points main signal, which consists of the two absorption spectra and each 4000-points reference signal, are averaged 25 times and saved for a post-processing. Also pressure and temperature are saved together with each acquisition. If the time

for saving data is also considered, the acquisition time for the simultaneous absorption spectra of CO₂ and HF is of 0.25 s spectrum (bottom side of Fig. 4) consists of two kind of signal: the interference fringes due to the etalon and the absorption lines of the two molecules. Known the etalon FSR's, the interference signal allows to obtain a relative frequency reference for the calibration of the frequency scale. The presence of the absorption signals is necessary only to check that the laser emission frequencies don't change over time. This is particularly important for HF which is usually absent in the atmosphere, since, without reference cell, it is impossible to verify the stability of the laser emission frequency and its overlapping with the selected absorption lines.

5 ~~A detailed~~ Here we present a quick description of the data processing ~~can be found in~~, since a more detailed analysis has already been reported (Viciani et al., 2008). The absorption spectra, after subtracting the zero-power signal, ~~is~~ are fitted with the exponential of a Voigt profile multiplied by a ~~two-order~~ second-order polynomial, which simulates the sloping ~~background laser power~~ due to the ramping of the driving current. ~~When necessary, also one or more sinusoidal curves are included in the fitting function to take into account the presence of optical fringes.~~ We use as Voigt profile the four-Lorentz ~~Puerta~~ "Martin Puerta-Martin approximation (Puerta et al., 1981; Martin et al., 1981), where the only free fitted parameters are the line amplitude and center frequency, while the Lorentzian and Gaussian half widths at half maximum (HWHM) are maintained fixed. The values of the HWHM are calculated as a function of temperature and pressure, measured for each acquisition, and of the molecular parameters (~~airbroadening coefficient and linewidth temperature coefficient~~) according to the HITRAN database (~~(Rothman et al., 2013))~~(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, multiplied ~~for a two-order~~ by a second order polynomial and for the absorption signal of the reference cell. According to the fit results, and knowing the etalon FSR's, 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:

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

where N is the calculated molecules 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 ~~performances~~ performance of the instrument for the CO₂ channel

In order to test the laboratory ~~performances~~ performance of the instrument and to verify the reliability of the inferred concentration values, a mixture of known concentration ~~has been~~ was used in the closed-cell configuration. Such kind of test, if done

- 30 with an HF mixture, would be deeply influenced by the property of the acid HF to stick, inside the tube closing the cell or inside the pipes connecting the multipass cell to the tank of the mixture. We ~~have~~ also verified (as shown in the next ~~session~~section) that, by using teflon sampling pipes, the problem is reduced but not completely resolved, due to chemisorption of HF to water vapor film or dust covering the inside of the tubes. Consequently, we ~~have~~ decided to carry out this laboratory test only for the CO₂ channel and to evaluate the ~~performances~~performance of the HF ~~part~~channel directly in-field by using the open-cell configuration.
- 5 ~~A calibrated mixture of CO₂ at 591 ppm (± 3 ppm) in synthetic air has been used. The measurement has been~~ The measurement was carried out by introducing into the multipass cell a constant flow ~~of mixture~~ (about 0.3 l/min) of calibrated mixture (591 \pm 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.
- 10 We show in Fig. 5 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. ~~The results of the Voigt fitting procedure and the corresponding residuals are also shown in Fig. 5. Two optical fringes are also included in the fitting curve, together with a fitted absorption line which includes optical fringes.~~

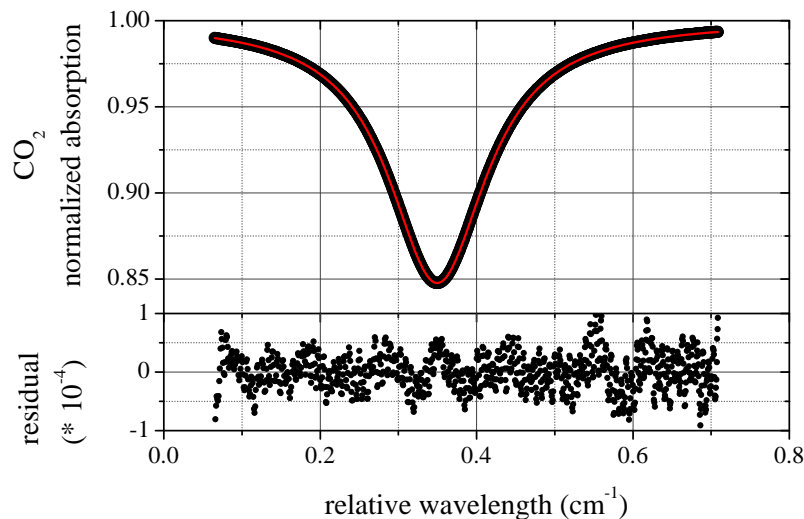


Figure 5. Normalized absorption spectra of a CO₂ calibrated mixture (of about 590 ppm in synthetic air) around 4989.97 cm⁻¹ (2004.02 nm) and Voigt fit results (red line). The residuals of the fitting procedure are shown in the bottom ~~part~~plot. The ~~acquisition~~integration time is 0.25 s. The measurement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

In order to determine the accuracy of the measurement we followed the same formalism described in (Viciani et al., 2008).
15 The mixing ratio uncertainty is ~~essentially determined by the following contributions: the is determined by combining the~~ accuracy of the temperature and pressure measurement (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) (Rothman et al., 2013)~~ and the uncertainty in the fitting procedure (0.2%). The resulting total accuracy is < 4%.

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.

5 In order to evaluate the long-term stability of the instrument, we ~~have~~ repeated the same measurement, at a rate of 4 Hz, for about 1 hour, in both conditions of atmospheric pressure and about 700 mBar. Assuming as precision the standard deviation (2σ) of the obtained ~~concentration-mixing ratio~~ values, we infer a CO₂ precision for 1-hour measurement of 0.1% (600 ppb) at atmospheric pressure and of 0.03% (200 ppb) at ~~lower pressure. This higher precision can be explained because at lower pressure the absorption signals are narrower~~ 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 easier not easy for the fitting protocol procedure to clearly identify the background signal 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. Moreover, 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 ~~the~~ CO₂ channel, an Allan-Werle Variance analysis of the obtained ~~concentration values has been~~ ~~mixing ratios was~~ carried out. An Allan-Werle Variance plot of the CO₂ ~~concentration~~ measurements is reported in Fig. 6 as a function of the integration time.

We can conclude that the CO₂ sensitivity at the fastest ~~acquisition-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 ~~detection-limit~~ ~~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 ~~atmospheres~~ atmospheric pressure and for 30 s of integration time (about 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 ~~system to get rid of fitting protocol to clearly identify the background signals and the optical~~ fringes.

10 6 In-field performances of the instrument for CO₂ and HF channels

Two test campaigns ~~have been were~~ carried out in order to evaluate the ~~performane~~ performance of the instrument and in particular of HF measurement, as this 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, producing exposure to a variety of gas concentrations.

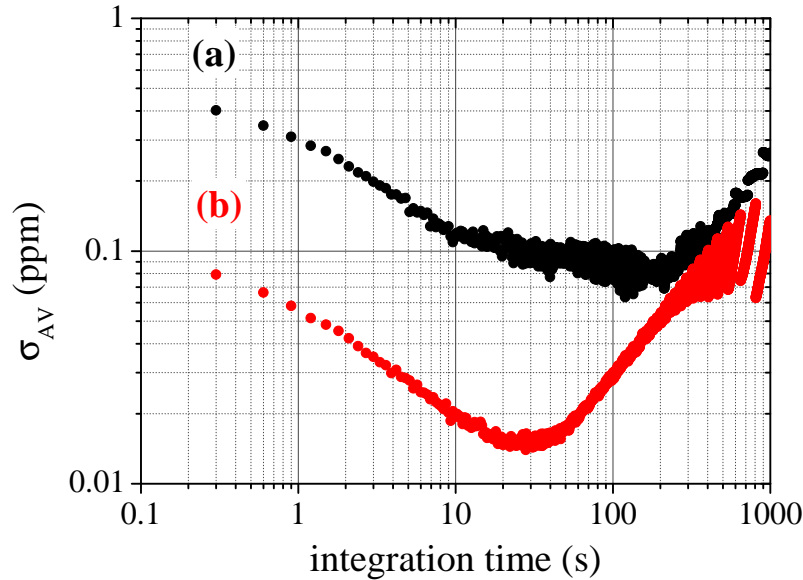


Figure 6. Allan-Werle Variance plot of 1 hour in-flow measurements of a CO₂ calibrated mixture of about 590 ppm in synthetic air, at a rate of 4 Hz in two different conditions: for a pressure of 985 mbar and a temperature of 295 K (curve a) and for a pressure of 687 mbar and a temperature 294 K (curve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

5 The results obtained for about 10 minutes 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. Correlation analysis of the two concentrations clearly shows that a maximum correlation between the two gases is reached for a delay of about 16 s. Moreover, the correlation is poor with a maximum correlation 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 ~~an emission peak a gas cloud~~ arrives to the pipe inlet, part of the HF is lost as it reacts with the walls, producing a delayed HF peak. The only way to ~~solve completely completely solve~~ this problem is to remove all the pipes and the tube covering the cell.

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

15 A typical normalized absorption spectrum for both CO₂ and HF, with 2 s integration time for each measurement, is shown in Fig. 8. The measurement ~~has been was~~ carried out close to a fumarole of the volcano, with a pressure of 990 mbar and a temperature changing between 310 K and 320 K. The results of the Voigt fitting procedure and the corresponding residuals are also shown in Fig. 8. Three optical fringes for CO₂ and two optical fringes for HF are also included in the fitting curve.

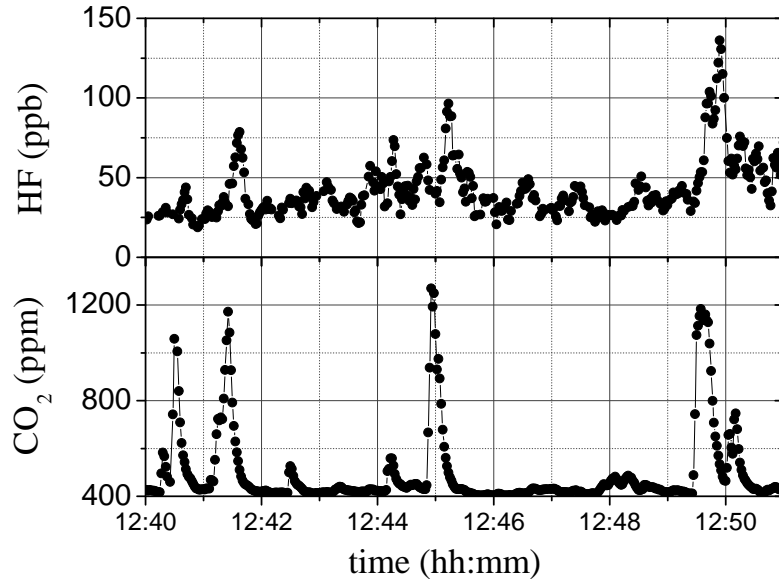


Figure 7. Time series of CO₂ and HF ~~concentrations-mixing ratios~~ measured at the crater of Vulcano volcano on the 22nd April 2015, performed by the spectrometer in the closed-cell configuration. The measurements ~~have-been-were~~ carried out in an average condition of 990 mbar of pressure and 300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

The accuracy of the ~~concentration-mixing ratio~~ values is determined by the same parameters described in the previous section: the uncertainties on 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 the ~~10%-and-20% Rothman et al. (2013)~~ 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 ~~<22.54.5%~~ <2.5% for HF. ~~The low-accuracy for HF is mainly due to the large uncertainty of the line strength reported in the HITRAN database.~~ By assuming the worst uncertainty, the CO₂ ~~concentration-value-mixing ratio~~ for the spectrum of Fig. 8a is (2350 ± 50) ppm and the HF ~~concentration value-mixing ratio~~ for the spectrum of Fig. 8b is ~~$(4.5 \pm 0.5)(4.5 \pm 0.1)$~~ (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 ~~concentration-mixing ratio~~ as a function of the HF ~~concentration-mixing ratio~~ during 13 minutes of measurement 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 zoom of the simultaneous time series of CO₂

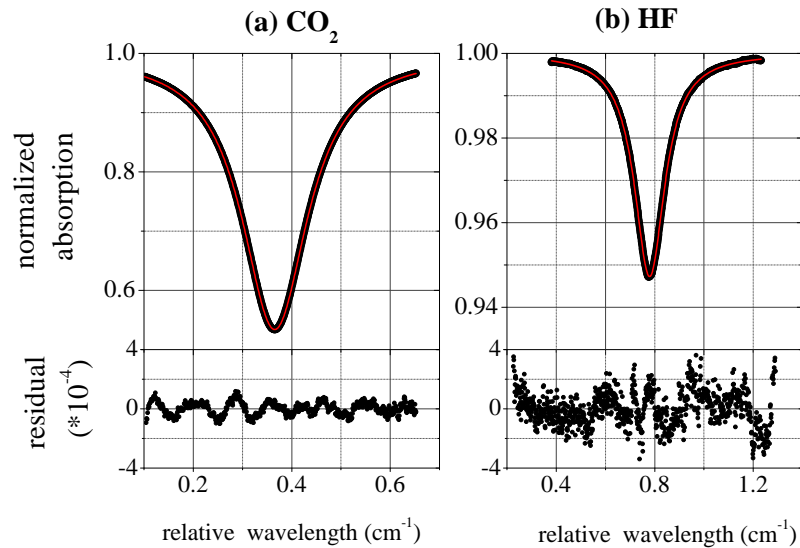


Figure 8. Typical normalized absorption spectra of CO₂ (a) and HF (b) detected in proximity of a fumarole of the Vulcano volcano on the 20th May 2015 and Voigt fit results (red line). The residuals of the fitting procedure are shown in the bottom parts plots. The concentration value of CO₂ mixing ratio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

and HF mixing ratios during a 3-minutes interval is displayed.

- 5 A linear fit of the data of Fig. 9 allows to infer both the CO₂ ambient concentration-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 concentrations mixing ratios. The obtained results are (390 ± 20) ppm for the CO₂ ambient concentration-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 (URL = <https://www.esrl.noaa.gov/g>). 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.
- 10

In Fig. 10 the S/N as a function of CO₂ and HF concentration-mixing ratios is reported. We use as noise value for the data of Fig. 10 the mean value of the noise related to different fit results of the detected spectra, most of which show a residual similar to that one displayed in Fig. 8. The mean noise value is $8.5 \cdot 10^{-5}$ for CO₂ and $2.4 \cdot 10^{-4}$ for HF.

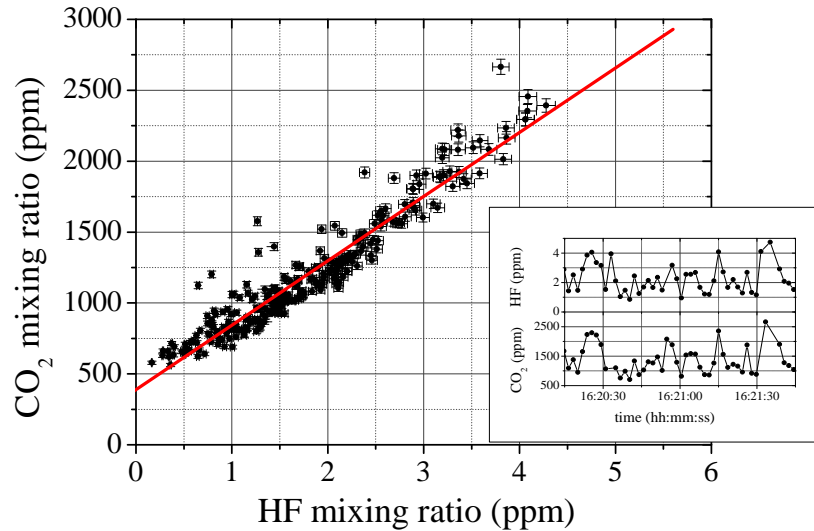


Figure 9. CO_2 concentration-mixing ratio as a function of the HF concentration-mixing ratio for 13 minutes of measurement in proximity of a fumarole of the Vulcano volcano on the 22nd April 2015. The red line is the result of a linear fit. The error bars are the accuracy of the concentration-mixing ratio values. The measurement has-been-was carried out in the open-cell configuration at a pressure of 990 mbar and at a temperature variable between 310 K and 320 K. The inset shows a zoom of the time series of CO_2 and HF mixing ratios during a 3-minutes 3-minute interval.

- 5 The sensitivity for the two channels of the spectrometer can be obtained as the concentration for which $S/N = 1$. It 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 detection limit sensitivity for the CO_2 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 performances of the CO_2 analyzer are not seriously degraded by the
- 10 in-field operation and they are reduced only by a factor eg-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 lower pressure (about 20 ppb for an integration time of 30 s at a pressure of 700 mbar).

For the HF channel, a detection limit sensitivity of 20 ppb, with an integration time of 2 s, can be obtained from the linear fit

15 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 minutes the sensitivity of the spectrometer (for an integration time of 2 s) degrades to 2 ppm

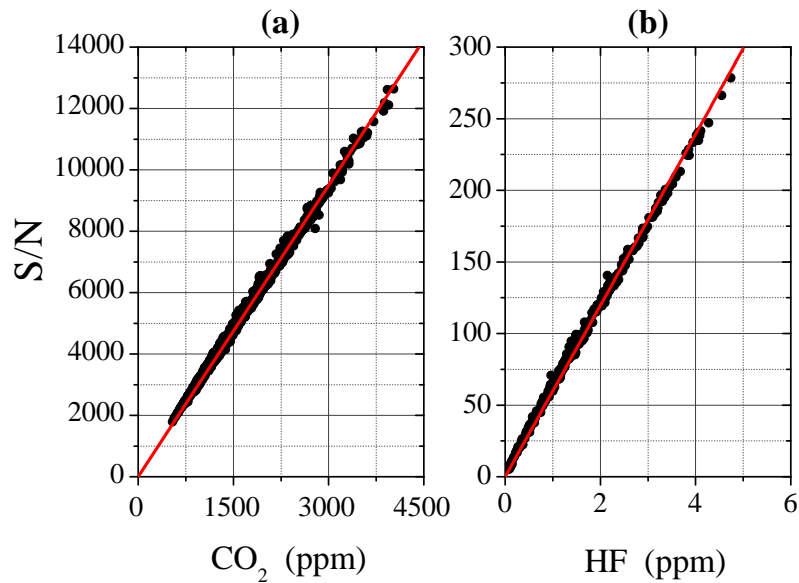


Figure 10. Signal-to-noise ratio S/N as a function of CO₂ ~~concentration-mixing ratio~~ (a) and HF ~~concentration-mixing ratio~~ (b) for 13 minutes of measurement in proximity of a fumarole of the Vulcano volcano on the 22nd April 2015. The red line is the result of a linear fit. The measurement ~~has-been-was~~ carried out in the open-cell configuration at a pressure of 990 mbar and at a temperature variable between 310 K and 320 K.

for CO₂ and to 200 ppb for HF. On the contrary, ~~when-if~~ the instrument is ~~far from the fumaroles, or operated in lower acid~~ gas and aerosol concentrations, as for instance on board an aircraft, it ~~can-work indefinitely without significant reduction in performance~~ 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, where a light flux of air is blown through the carbon fiber pipe holding the mirrors. The air can be taken a few meters apart, far from the high concentrations at the emission points, and blown on 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 purge air, where 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 ~~3%~~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 ~~must~~could be used to correct the peak values.

30 ~~We have-~~

7 Conclusions

We produced a new analyzer for the simultaneous measurement of the concentrations-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 2 when the instrument is employed at its maximum rate of 4 Hz. However, the device performances improve when the measurements are carried out
5 at a pressure lower than the atmospheric one. In particular the CO₂ sensitivity increases of about a factor 5 when the pressure is reduced to 700 mbar, a typical pressure at the top of a 3000 m volcano (e.g. Etna).

We are planning to extend the measurement to H₂O, by detecting a water absorption close to a CO₂ one. 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 5 volcanic gases (HCl, CO₂, HF, H₂O and SO₂). The platform will include two mid-IR spectrometers, one of which will be the instrument described in this paper, and an UV spectrometer. The platform will be employed for measurement campaigns in-field and on board aircraft.
10

In order allow deployment on board of drones, we will reduce size and weight by replacing the cRIO crate with a smaller electronics, namely Red Pitaya by StemLab, we will use only fiber-coupled lasers in the near infrared, so eliminating most mirrors and their holders, and we will use aluminum and carbon fibers only for those parts which strictly require mechanical hardness. All other parts will be realized by 3D plastic printing. As drones can fly much closer to plumes than manned aircraft, the concentrations to be measured are expected to be at least one order of magnitude higher than in the present measurements, and so the multipass cells will be shorter and lighter too.
5

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