

Interactive comment on “Diode laser based gas analyzer for the simultaneous measurement of CO₂ and HF in volcanic plumes” by Antonio Chiarugi et al.

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Summary

This manuscript describes a new instrument for measuring CO₂ and HF abundances in volcanic gas. The instrument measures the absorption of light emitted by two tunable diode lasers (TDL) as it passes through an optical cell along a fixed path. The light path is extended beyond the physical length of the cell by multiple reflections on mirrors on either end of a multi-pass cell. A specific gas is measured by tuning the laser wavelengths across a characteristic near infrared absorption line of that gas and measuring the attenuation of the laser light after having passed through the measurement cell.

C1

Though the operating principle is similar to that of some existing instruments, the authors have succeeded in adapting the TDL absorption technique to a confined sample space. The multi-pass cell allows in-situ measurements to be made with relatively high sensitivity and high temporal resolution. Such an instrument is ideally suited for airborne measurements, where an aircraft flies the instrument through the plume downwind of a volcano. In this study, the authors present the results of first test measurements performed on the ground in proximity to degassing fumaroles on Vulcano Island, Italy. These show that the instrument appears to be functioning as expected and in particular allow derivation of the detection limits, sensitivity, accuracy and precision of the instrument.

The manuscript is well-organized and easy to follow. Aside from a number of minor corrections, it would benefit from a more thorough literature review as well as a more detailed description of the instrument and the test measurement study site. These points are elaborated on in more detail below. After these issues are considered, I recommend this manuscript be accepted for publication in Atmospheric Measurement Techniques, as the work presented here represents a significant step forward in our ability to accurately measure certain major components of volcanic gas.

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.

C2

As far as I am aware, there is at least one commercial TDL-based instrument for measuring CO₂ and HF. The BOREAL Gasfinder (<http://www.boreal-laser.com/products/>) can be ordered in CO₂ and HF versions, and has both an open-path and in-situ measurement modes. I believe that the sensitivity of the in-situ measurements is likely inferior to that of the new instrument described here, as the measurement cell does not appear to have a multi-pass configuration. Also, the two species cannot be measured by the same instrument – two separate instruments are needed. However, due to the similar or even identical measurement principle of this commercial instrument to the prototype described here, it should probably be mentioned in the manuscript and the differences explained.

In general, the introduction might be improved by mentioning from the very beginning that the design goal of this instrument was to implement an instrument for use in airborne measurements. This would make it clear why many of the other techniques that are available already would not work well.

Since one of the main aspects of the manuscript is the description of the new instrument, the addition of a few more details would be valuable. For one, the 'optical scheme' shown in Figure 1 describes the physical setup of the individual components but does not describe the operation principle of the instrument very well. A schematic of the light path could help here. In this schematic, the path of light from each of the two lasers to the detectors could be followed. This would also augment the description in the text better than the current Figure 1. In the end, it is less important if a component is mounted on the top or bottom of the breadboard than it is to know which optical elements are passed in which order.

As it stands, the functionality of the reference channel did not become entirely clear to me. I understand that the etalon adds interference fringes to the reference signal which can then be used to calibrate the frequency scale of the measurement. But the light also passes a gas cell containing HF and CO₂? Is the purpose of this just to ensure that the laser wavelength does indeed overlap with the absorption line of the

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respective gases? Can't this also be ascertained from the etalon fringes themselves? Perhaps a recording from the reference channel can also be plotted, and the evaluation of this channel explained in more detail? It would be interesting to see what the etalon interference fringes look like. It is my understanding that the reference channel is only used for spectral calibration and not otherwise used in the retrieval of the CO₂ or HF abundance. Is this correct?

It's interesting to see how the instrument's performance appears to improve slightly with decreasing pressure in the sample cell. Perhaps a bit more detail could be provided on how these underpressures were obtained? Was the pump pulling through a pinhole? Or was a more sophisticated flow controlled used?

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.

Minor corrections

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

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

P1, L22 – Consider adding Aiuppa et al 2005, 'Chemical mapping of a fumarolic field:

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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.

P1, L23, consider omitting 'to be performed'

P1, L24, 'quantify due to THE slow and differing...'

P2, L1, consider replacing 'chemical-based' with 'electrochemical'.

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.

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

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.

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

C5

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?

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

P2, L20, 'CO₂ is HIGHLY insoluble...'

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

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

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

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).

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

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

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?

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

P3, L27, Consider rewording to 'source of concern DUE TO THE DESIRE FOR AN OPEN PATH CONFIGURATION'.

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

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

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

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

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

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

P5, L5, Consider replacing 'exploit' with 'use'

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

P5, L15, '... multipass cell ARE sent...'

P5, L24, 'All electronics ARE placed...'

P5, L25, Please explain the acronym FPGA

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

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?

P6, L6, 'the 1 liter volume'

P6, L12, '4 cell LiPo batteries'

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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.'

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

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

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

P6, L21, '... HF absorption LINE...'

P7, L2, replace 'alternatively' with 'alternatingly'

P7, L5-6, Replace 'a region' with 'an interval'

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

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?

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.'

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

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.

P7, L16, Omit 'of' before 0.25 s.

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

C8

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

P7, L18, Are you sure you need to multiply by a second order polynomial? I would have expected the addition of a polynomial to describe 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.

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

P7, L25, 'multiplied BY a SECOND order...'

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?

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

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.

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

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

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'was' and 'were' unless referring to studies that were conducted previous to the work presented here.

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

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?

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

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.

Figure 3 caption, '... in the bottom plot.'

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.

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

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.

C10

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

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

P10, L6, Consider replacing 'emission peak' with 'gas cloud'

P10, L7, '... the only way to completely solve this problem...'

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

Figure 6 caption, 'bottom plots'

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.'

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?

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

P12, L13, '... a factor of 1.3'

C11

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

Figure 7 caption, '... a 3-minute interval.'

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.'

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.

P13, L15, 'emission peak could be used to correct'

Figure 8, again plots mixing ratios rather than concentrations

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.

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.

P14, L8, '... by detecting water absorption...'

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

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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.

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.

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