

Interactive comment on “Atmospheric CO₂, CH₄, and CO with CRDS technique at the Izaña Global GAW station: instrumental tests, developments and first measurement results” by Angel J. Gomez-Pelaez et al.

Anonymous Referee #1

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This work describes the GHG measurement system at Izaña Observatory (IZO). Several novel measurement methods or improvements to standard methods are described, including a new correction to CO₂ in Picarro analyzers that is caused by inhomogeneous mixing in the measurement cell of the analyzer that is affected by flow rate. It should be published after corrections outlined below.

One major comment that should be addressed is the determination of the CO₂ correction for inlet pressure variation should be tested more. Details and recommendations are below. A second is that the authors use a few more complex fits and equations for

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corrections than reported previously in the literature for these same instruments, and there is little justification or evaluation of the improvement that these complex corrections make on the data, or reduction in error/uncertainty (e.g. quadratic fit to the CO₂, and water vapour corrections).

Major & Minor comments:

Acronyms: Some are introduced without definition in the abstract (CO₂, WMO); Others esp. in the introduction are defined backwards from the usual convention, i.e. the acronym comes first with the expansion in parentheses. But not consistently. And some are introduced (WMO) prior to definition. The authors should carefully go through the text and fix these.

L29: awkward (requirements are higher as higher the lifetime...). Requirements are more stringent for gases with a longer lifetime perhaps?

P2, L4: American billion?

P2, L4, ppm should be defined here as micromoles per mole of dry air, or dry mole fraction. (and similar for ppb).

P2 L8 awkward: "therefore, the required frequency... is much lower".

P2 L30 Tertiary should not be capitalized I don't think.

P2 L32 until now

P3 L12 "being" should be ", rejecting the first hour as stabilization time."

Table 1 caption should say "for two averaging times". Some note should be made explaining the negative water vapour values here.

Table 2 - wouldn't this be a more appropriate place to report the average H₂O? It would be good to know if the water vapour had completely left the stream by the time these SD's were taken. Some explanation of the higher SD's over these 10 minutes com-

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pared to the Table 1 results should be made - perhaps the cylinder is still "stabilizing", but then did the authors see a trend in the measurement over the 10 minutes? Was any such trend or noise caused by water vapour still drying out?

P4 L4: How was the ambient pressure test conducted? This paragraph should have more detail (pressure chamber?). I agree the effect of ambient pressure is small - you could note that this analyzer is not meant for use on aircraft where large pressure changes might occur. But I still wonder if this effect on the measurements is transient or dependent only on the absolute ambient pressure. Yver Kwok et al state that they find no ambient pressure dependence on CO₂ and CH₄.

P4 L10: these pressures should be given in millibar or SI units - presumably this is gauge pressure, psig. Absolute pressure would be better, perhaps stating the regulator gauge pressure in parentheses. Was the effect only noted for these two pressures, or was there more testing done at intermediate pressures? Was it repeatable, or are these numbers given only for the single test between two pressures? (this is a question I had later, on how the fit was made to the outlet valve - was the fit based only on two points, and was it evaluated for a repeated test?).

p4 L23: "during that first calibration" - what calibration? perhaps "During the calibration described above,"

P4 L27, awkward phrasing "to the computation". Perhaps just "Pre-processing refers to the computation of raw data 3-second means... as well as the computation of some derived variables". (what variables?). Also "no" should read "not".

P5 L3-10. It is not clear why certain variables are associated with certain species codes. I thought that the species code had to do with which laser was making the measurement (or the frequency range it was covering). One sentence explaining this perhaps would be useful to the reader. It might not be useful to mention the CO₂_dry and CH₄_dry variables, as they confuse things and they are not used in this work at all - they get updated after the h₂o_reported scan. I find the explanation of each variable

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useful however. I think CO₂_dry is erroneously mentioned twice: once with species=2 and once when species=3.

Why are both the MPV and SV fields used - should mention why these are monitored - presumably your gas handling uses both solenoid and MPV valves controlled by the Picarro software?

P5 L19, I believe the flow in the orifice itself is sonic, and is supersonic immediately downstream, depending on the ratio of upstream to cavity pressure. Also pressure units should be in mb or other SI, with torr in parentheses.

P5 L20 was this linear relationship between OV and inlet pressure confirmed in your tests? This should be investigated and shown, not just assumed, as the inlet pressure/flow correction is using the OV variable as a direct proxy for flow rate essentially.

P5 Eq 1 - it would be good to see some more information on this fit. Was it really based only on the two different pressures investigated in the test? Could a fit to more pressures be performed? how good or bad is the fit - what are the residuals from the test itself? This is one of the main findings of this work, and has not been reported before, as the authors point out, so more work is needed to show the reader how the correction was determined, how it performs, and its consistency over time and after a reboot. The fit should be tested by performing a test again and checking for consistency and for errors after the fit was applied, esp. its reliance on the OV variable.

I do believe that because the inlet orifice is not a physical orifice but rather a proportional valve fixed at a certain opening, after the analyzer has a power cycle (reboot), it may not come back to the same spot exactly (the valve is not so precise, so given the same voltage might open to a different diameter slightly), and following that, the OV may not be in the same spot, i.e. for the same inlet pressure as prior to the power cycle, the OV value may differ. I think that this would render equation 1 incorrect and would need to be re-calculated. This should be checked and determined. It may be necessary to install a pressure sensor upstream of the CRDS instrument and perform

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a linear fit on that rather than relying on the OV. This may not be true if there is a physical critical orifice upstream whose aperture never changes. The aircraft analyzers do have a physical critical orifice so that they can maintain a constant given flow rate, even after the instrument is rebooted.

p6 L22: perhaps rephrase to : "provided results that satisfied our accuracy requirements".

P6 L24: This helps avoid...

P6 L25: that might propagate to the interior of the cylinders...

P7 L6: What reason is given for going to a quadratic fit for CO₂ here? In other literature (including Yver Kwok et al) a linear fit is generally used. Perhaps the authors can justify the use of a more complex curve for this instrument. It is useful to note that the residuals of a calibration should be compared to the assigned 1-sigma uncertainty of the gas standard relative to the scale. For NOAA tanks, this is something close to 0.02-0.03 ppm (as cited in Andrews et al., but could be checked for specific cylinders perhaps?). You wouldn't expect the residuals to be better than that.

P7 L6, L9: I would suggest replacing "real dry mole fraction" by "the dry mole fraction assigned by the CCL on the WMO scale".

p7, L16 "high-accuracy"

p7, L17 should read: the calibration fits are generally performed using a limited range...

p7 Is the virtual tank concentration its assigned value (x-axis) or measured value (y-axis)? Presumably, following the convention of equations 4-6, it is the x-axis, assigned value that is constant at 400 ppm and the raw response for that value is what is calculated using the equations. Perhaps just state this in the text when you mention the tank values.

p8-9: explain that the drift you are referring to is drift in the P, T sensors that then

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causes the cavity to be controlled at a slightly drifting temperature. P9, L1: Was this supposed to read .152 degrees C / year rather than Torr?

Fig 2: is the slope of the red line here equal to the left hand side of equation 8?

Eqn 8 & 9: A little more information on this would be good. Does this analysis assume that Temperature drift is a linear function of pressure drift? I guess if they are both linearly drifting with time, this makes sense.

What is the slope? (Yver Kwok report a mean of 2.4). Perhaps a plot of the fractional change rather than the plot in Figure 2 would be more applicable to explain equations 8 & 9 (similar to figure 14 in Y-K).

p9: The singular of species is species, so I think it should be "for each species" (here and throughout the paper).

Fig 3: the Y-axis here is odd in terms of units. Not sure what to do about it.

p11: L14: explain "since CO standards use to drift upward"? When?

p11 L15: why at different rates? (or perhaps different rates from the target gas). If the 4 tertiary standards are drifting at different rates, one would expect residuals to be increasing in time on the fits as well? It seems that without further evidence, it might be more appropriate to just state that it is likely that the standards and/or target tanks are drifting.

Fig4: the labels should be on the Yaxis rather than as titles. Not sure if this was stated earlier, but each of these points represents an average of how long and every how often? This could be mentioned in the caption to remind the reader.

Figure 5: I don't find this figure particularly useful. If kept, labels should be put in the photo of the various components.

Figure 6: y-axis is unlabeled, should have the variable even though there are not units on this raw measurement.

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p14 L24: 39 minutes seems to be very long, when looking at figure 6, the water vapour could change significantly in that time, especially at the higher H₂O values at the beginning of the test. Is such a long average really required, when you are achieving 1-minute precision of 0.87 ppb?

Also, given the complex equations presented here for CO water correction, how different is the final result from the internal correction (i.e. the variable "CO" in the raw output)? It would be necessary for the reader to evaluate this and how it depends on the level of water vapour, to see if it's worth implementing.

P15-16, Regarding the -40C trap, can you relate this to a maximum H₂O value you see in the data after that point? What is the magnitude of the water correction at those values, and how different is it to CO₂_dry and CH₄_dry? Rella et al. indicate that at low water vapour values, the internal correction works well. Again, the water vapour tests are cumbersome, especially for field analyzers, in many cases - it would be useful to the readers to know what kind of improvement is gained from the tests as opposed to using the factory correction in cases where there already is partial drying like this.

P16, L7-8: Awkward phrasing "for not discarding". Perhaps "We retain a pre-processed 30-second mean if the following conditions are met: ". Then rephrase the conditions accordingly (i.e. "the mean values of the following variables are within...") etc.

L9: condition 2 awkward: was exit supposed to be "exist"?

P16 L17: clarify when 10 minutes are discarded (after a calibration or any sample path switch?).

P18 L14: remove the final "in space", as earlier this sentence stated in space and time.

Fig 11, caption should include the fact that these are 12-hour averages (if that is the case).

Table 4, first row, month says 2017? I wonder if the information in this table would be better expressed in a figure somehow, with dashed lines indicating the WMO compati-

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bility goals?

P21 L4: shown

In section 6.3, the reason for the CRDS-RGA differences for CO is ascribed as due to the CRDS standard drift, but here in Section 7, it is indicated that the drift did not improve the comparison. Can the authors give any explanation for this? Even if the RGA tanks are also drifting, the correction described in Section 7 would put both data sets relative to the same tanks after all.

Finally, overall, given the large effort involved in achieving very high accuracy for this data set, do the authors envision prescribing an uncertainty to their measurements? [perhaps this is outside the scope of this paper, but something to think about maybe for the future].

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