

Interactive comment on “High-precision atmospheric oxygen measurement comparisons between a newly built CRDS analyzer and existing measurement techniques” by Tesfaye A. Berhanu et al.

Anonymous Referee #2

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Review of manuscript “High-precision atmospheric oxygen measurement comparisons between a newly built CRDS analyzer (Picarro G-2207) and existing measurement techniques” by Tesfaye A. Berhanu et al. submitted to Atmospheric Measurement Techniques General comments: This paper from A. Tesfaye et al. presents the principle, the method and experimental tests conducted on a new CRDS analyzer dedicated to high precision oxygen measurements in the atmosphere and possibly additional measurement of isotopic content of O₂. The first in-situ monitoring results obtained with this instrument are also presented and compared to other current existing measurements

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technics running in parallel. In the introduction, the authors remind us about the scientific context and the scientific interest to measure O₂ mixing ratio in the atmosphere, in the framework of carbon cycle budget and natural/anthropogenic source/sinks attributions, due to the strong link between the oxygen variability and the carbon cycle (combustion and respiration reactions). Then they highlight the analytical challenge to obtain a high precision measurement of O₂ due to the very low level of atmospheric variability and they then shortly review the existing measuring technics currently available and the main experimental difficulties associated. In the second section, (Materials and methods), part 2.1, there is a description and discussion of the analyser design principles and characterizations (p4-14). The authors first describe the general instrument principle and design (including associated program modules), then explain the best conditions to be met for an ideal high precision measurement of molecular oxygen and finally constrains linked with an operational deployable field instrument. This provides them justification for the technical and methodological choices made such as spectroscopic model used, water vapour measurement and correction considerations, O₂ measurement method design as well as O₂ isotopic content measurement. On my opinion this section is a bit too long (about 1/3 of the full article) and also sometime a bit difficult to follow as a non-specialist of spectroscopy. I would suggest to shorten and simplify a bit this section if possible so that it can be more easy to follow. In the case it is not possible to shorten it I would recommend to modify the title of the article to better take into account this section which is anyway useful and interesting (but at the moment reading the title, I would expect the work to focus more on instrumental atmospheric data inter-comparison than technical and spectral analysis). The second subsection (part 2.2 and following) presents the instrumental tests and evaluation conducted in the laboratory at Picarro, at the University of Bern and in the field in Switzerland (two sites, Jungfrauoch and Beromünster). Experimental set up and conditions as well as methodologies adopted for the tests are presented in these subsections. The last section (section 3) presents and discuss the results of the different laboratory tests and in-situ monitoring. I would suggest to re-organize a bit this section with the previous

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one. I think this would be easier for the reader to follow if the test results (in section 3) were merged together with the description of the tests procedure (in section 2). So I would merge 2.2.1 with 3.1.1, 3.2.2 with 3.1.2 (actually labelled 3.2 but should be 3.2.2) and also 2.3.3 and 3.2.3 (water correction). I would then keep all the in-situ parts together in section 3. In the last subsection, the authors present some results for test conducted with the analyser on the isotopic mode. The paper ends with a last concluding section. 2 One general comment and concern of this paper is the reporting unit used for O₂ concentration all over the article. The authors used either the ppm unit (most of the time) or the per meg unit (also depending on the instrument used). As there are inter-comparison results used here to validate the new instrument but presented with a mix unit data, it is not easy to follow and to fully compare all data sets as well as precision of the different methods and instruments. Even though there is currently no official international unit to report O₂/N₂ mixing ratio, and also no Central Calibration Laboratory, there were recommendations given in the last WMO GAW report (report n°242) to report the O₂/N₂ mixing ratio in per meg units and also if possible to report it on the Scripps Institution of Oceanography (SIO). I would then suggest to make a choice of unit (preferentially per meg) all over the paper and present all the results in a uniform way. When necessary there is a relationship that might be used to express changes in O₂/N₂ ratio and equivalent changes in O₂ mole fraction (Keeling et al, 1998; WMO GAW report n° 142). Having all number on the same unit would greatly help in the data comparison sections and table 1 (for example) except if this is not applicable. My general feeling about the paper is good, it is generally well written and most of the time clear. I would recommend this article for publication in AMT after revision, as this is a quite interesting new method to measure O₂ with a great potential for atmospheric monitoring. Nevertheless, I would highly recommend to take into account the remarks and suggestions raised in the present review in order to straighten and improve the present manuscript. In particular, some additional calculation of mean values and standard deviations would help better evaluate the performances of the instrument compared to current ones. Specific comments: Abstract: Line 21: May need

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to precise that the given short term precision given here refers to the O₂ mixing ratio (not to the isotopic ratio). Line 21-23: In this sentence the authors state that the long term stability of the instrument is excellent and prevent high frequency calibration to assess an overall uncertainty of <5 ppm. The recommended calibration frequency is every 12h. With regards to my knowledge and own experience, paramagnetic technics only recall 24h calibration frequency to achieve similar precision. So I would suggest to moderate a bit this sentence, especially the beginning “In contrast to the currently existing techniques”. The section two of the paper “material and methods” which is the longest part of the paper is not really mentioned in the abstract. May be a few more words should be added in the abstract to remind the reader about the work described in this later section. Introduction: The introduction section is not labelled as for the other sections (it should be section 1). Line 34-36: I would suggest to update the CO₂ mixing ratio to the one of year 2017 (around 405 ppm). Line 47-51: There are also WMO/GAW precision recommendations and guidelines for O₂/N₂ ratio, as describe in the last GAW report (GAW report n°242, table 1 and p42-44). Line 55 and 56: Gas chromatography => gas chromatography Lien 57: As far as I know the techniques described in the previous sentence are not really commercially available. The sensors or detectors can be delivered by commercial companies but cannot be used directly to monitor O₂ concentration. There is a need to “customize” these 3 detectors to build a monitoring instrument reaching the precision goal needed for atmospheric monitoring. This is most of the time done by the laboratories themselves! Line 61: I would add the following words at the end of the sentence: “. . . of the analysis method especially for continuous monitoring”. Material and methods: iC_u Analyser design principles: Line 79: Please define DFB Line 99-100: What is the typical range of variation for noise between the different instruments? Line 102: This is the first time that the Per meg unit it used in the paper (i.e. ppm is used most of the time). As already stated, it would be better to choose and harmonized the unit all over the paper. Line 116: I’m not an expert in spectroscopy, and the formalism used here to describe the absorption band is a bit unclear for me and a non-specialist. I don’t know if there is a way of clarifying

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or simplifying this another way? Line 143-145: This sentence is not clear, I suppose there is a verb missing: “In addition, the optical power in the ringdown cavity IS set by the ring-down detector threshold, which . . .” Line 159-160: This sentence is not clear: I think it should be “It stands out that the residuals that are largely an odd. . .” Line 185: Can the authors argue why they consider the dependence of Z on O2 too small to be significant? Line 196: please correct “for in measurements”. Line 224: Can the author explicit what they mean by 161 isotopologue of water. This is absolutely not clear for a non-specialist in spectroscopy. Line 277: Please define “scm”. Line 300: I would suggest to change “. . . adds additional . . .” to “. . . adds more. . .” Line 308-309: I’m a bit surprised that the instrument is providing a dry mole fraction for O2 using the water dilution experiment as it is stated by the authors above in the manuscript (line 273-274) “more works need to be done to investigate the water vapour correction of the oxygen measurement”. My feeling is that the present day correction is still not fully satisfying and should be used with caution! There is also no direct explicit correction equation given in the text nor explanation on how this correction is implemented (or to they use the directly the linear function given on figure 7?). Line 327-330: Taking into account the low precision of the analyser for isotopic content as stated by the authors, is there still an interest to measure them within the context of environmental studies? Could the authors give us a few example and/or possible application of O2 isotope measurement in the environment that could be achieve with that instrument? ĩĈŭ Laboratory tests at Picarro, Santa Clara: This section and following subsections should be relabelled, 2.2; 2.2.1; 2.2.2 etc. . . Line 346: Please define sccm. ĩĈŭ Laboratory measurements at the University of Bern: Line 351-355: Could you please add a reference describing the Bern O2 analytic measurement systems (Both for The Fuel cell system and for the Mass Spectrometer) if available. Line 356: Could you please give us a bit more details about the “pressure controlling unit”: What is it, What kind of flow meter? (short description or reference). 4 Line 367-377: I’m a bit surprised that there was no direct measurement made to the IRMS without the tee junction. To my knowledge the IRMS is the only one instrument that can provide a very high precision O2/N2 mea-

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surement and should be seen as the reference instrument. So I would have made the test in three steps, first with the Tee measuring on both instruments, then directly on the IRMS without the tee which would have given a reference value and then directly to the Picarro. All this at the different splitting ratios. Is there a reason why the direct measurement to the IRMS was not done? Line 380: please replace “case b” by “case ii”. Line 378-389: The conclusion of this section are a bit disappointing as none of the results are shown and only one value is given (without uncertainty). Would it be possible to show the results of the tests? Previous studies by A. Manning have shown that the tee junction effect could be relevant at the level of precision that we are looking for atmospheric O₂ monitoring. The impact given here (0.5ppm) is already more than half of the global precision stated for the instrument (<1 ppm line 23). So, if the instrument is to be commercialized, I would deeply recommend to go deeper into that question and firmly establish the conditions of use of a Tee junction or not. Line 403: How was established this correction function? What is the link with the test from figure 7? See also comment for line 308-309. Line 424: Add a reference to JFJ measurements and set up. Line 465: Please remove “is avoided” at the end of the sentence. Can the authors give us more precision about what they call “preconditioned”? Line 463-469: I have one question regarding this evaluation. Why do the authors use glass flasks? Why not connecting directly the CO₂ free cylinder to the analytical device? This would avoid potential contamination during flask filling. Results and Discussions: See general comments for re-organisation proposition. Line 483-490: Looking at figure 9, it doesn't seem to me that there is a real drift. For me a drift would show a smooth continuous tendency to increase or decrease in the values. Here what I see is more something like a large variability on the measurement, I see an anti-correlation between O₂ values et Y parameter and to a lesser degree a correlation between peak height and O₂ as well. So I don't really understand what the authors mean by drift here. Could you please clarify. Are there also some ideas to eliminate or identify those small drift as stated on line 490? Line 511: What is a very good agreement? Can the authors give us an estimate of the mean difference (on a comparable unit for exam-

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ple?). This would help to evaluate the accuracy of the new instrument and see how well it meets the WMO recommendation or not. Same goes for table 1 which is difficult to use because of the different units for the different instruments! Line 517-519: This is absolutely needed if the final goal is to get high precision O₂ measurement. There is no need for high precision CO₂ measurement but this dilution effect is to be taken into account as already done with present day “homemade” monitoring systems, even for atmospheric monitoring purpose. Line 521: Please change “The measurement precision of the Picarro G-2207 measurement was calculated...” to “The measurement precision of the Picarro G-2207 measurement was calculated...” Line 521-526: What about the precision of the reference instrument that should be the IRMS? Line 527-536: I fully agree that it is difficult to compare the graph as there is this problem of unit already highlighted in this review. I’m not sure how significant is the small difference in the correlation coefficient calculated here. 5 Line 541-542: I agree that the drift at the beginning could be linked with unstable condition after unpacking but the drift remains all over the measuring period and usually Picarro are stable within 3-5 hours after starting measurements. Line 551-553: Did the manufacturer find the cause of this drift. Was there any significant change in the hardware or software configuration of the initial instrument? Line 558-562: Did the authors also made water measurement comparisons between Licor and Picarro on wet air conditions? Line 564-565: This sentence is very confusing. Please reword as follow: “... in O₂ measurements in both cases. (Figures 15c & 15d) shows in case...” Line 573-577: Can the authors provide some more precise numbers such as for example mean values and standard deviation calculated from data shown in figure 15c and 15d. This would greatly help quantify the variability and give a comparison element with regards to the given instrumental precision. Line 581-583: I disagree with this statement, there are several sections of the paper dealing with the water correction factor. There was a choice stated in the paper and made by the manufacturer to enable wet air measurement, so the water correction is a key issue if the instrument is going to be sold soon and to assess high precision measurement. I’m convinced the correction factor is not easy task to handle

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and the results presented here are not sufficient to close the problem and give a final solution but this has to be further investigated. Line 585-593: How are the Picarro data calibrated (based on the in-situ calibration cylinders that have been measured also I suppose)? Could the author quantify a bit more precisely the “very good agreement” like for example providing the mean and the standard deviation of the data for both analysers over the full period. For me, based on the figure 16, it seems that there is a little offset between both instrument (paramagnetic a bit lower) and that there is a slight higher variability for the Picarro instrument compared to the other one but it is difficult to assess with only the figure. Line 595-607: I understand that the isotopic mode is not well suited for ambient O₂ concentration measurement but what about the isotopic values? Any comment about those? Line 641: Can the authors provide a table with the individual values for each flasks and instrument so that we can really compare the results and evaluate the precision and repeatability of the measurements on each instrument? Can we add mean values and standard deviation for the three replicates? Line 644: I think the authors mean “. . .of water and CO₂ in addition. . .” Line 653-655: Would the authors then recommend using the isotopic mode of the instrument at the moment (at least for atmospheric monitoring on atmospheric range) or still need some work to improve it and be sure it is reliable? (at least for atmospheric monitoring on atmospheric range)? Conclusion: Line 672-677: I feel that the conclusion driven here are a bit optimistic. It is stated several time in the paper that there is still work to do on this question. I would suggest to reword a little bit that conclusion in that way. Line 680-681: Here also I would like to see the data with mean values and standard deviation before drawing such an optimistic conclusion (see comments in the previous sections). I think this conclusion also lack a more general statement about the future applications of this instrument and possible improvement (especially for the isotopic mode). 6 Figure 1: The parameter τ is not define neither in the legend of the figure nor in the text. I wonder why the measurements presented here are made at 333Hpa and not at 340 hPa which is the nominal working pressure of the instrument (see line 86) ? Figure 9: There are strange value above each of the three upper graphs (+2.1028e5

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on the upper one). What do they mean? Line 773: correct “shown to show”.

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