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Atmospheric Measurement Techniques Discussions

Interactive comment on "Airborne measurements of oxygen concentration from the surface to the lower stratosphere and pole to pole" *by* Britton B. Stephens et al.

Anonymous Referee #1

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In this paper, the authors describe in detail their techniques to improve airborne system for in-situ (AO2) and flask-based (Medusa) measurements of atmospheric O2. As cited in the Introduction of their paper, some previous studies have reported that the measurements of d(O2/N2) and d(Ar/N2) obtained onboard aircrafts were fractionated significantly from their natural values, and the cause(s) of the fractionation not completely understood. In the present study, the authors have examined some possible causes of the fractionation processes and have succeeded in reducing or correcting for the large fractionation of AO2 d(O2/N2) by using Medusa d(O2/N2)* (d(O2/N2) corrected for thermal fractionation) as reference points. This paper makes a valuable contribution to improving our analyses and interpretation of such datasets as the au-

thors' published HIPPO data, as well as airborne measurements of O2 in general. I have found the paper to be well written and should be published in AMT with a few additional minor revisions identified below.

1) P12, line30: "(Sect. 4.4)," should be changed to "(Sect. 4.4).".

2) P13, lines 20-25: The authors suggest that the thermal fractionation found in Medusa flask is due to the flask dip tube being cold in comparison to the surrounding flask air. However, if continuous flow with a high flow rate of 1,559 to 2,700 ml min-1 is established in the flask, then, I expect, no significant fractionation would occur during the air sampling. I think fractionation occurs during the time period after the rotary valve is isolated and then the flask stopcocks closed (several minutes to an hour). I would like to hear the authors' thoughts on this.

3) P14, lines 1-14: The Medusa d(O2/N2) measurements are corrected for thermal fractionation effects, however, the relationships between the d(Ar/N2) and APO shown in Fig. S5 are not those one would expect from thermal fractionation. Do authors agree? It seems to me that short-term variations in APO due to fossil fuel consumption and/or to air-sea O2 and CO2 fluxes, with the OR being different from 1.1, would constitute bigger contributing factors than the thermal fractionation.

4) P16, line 6: "140 hPa (Fig. S7" should be corrected to "140 hPa (Fig. S7)".

5) P16, line 22: "(Fig. 8" should be corrected to "(Fig. 8)".

6) P18, lines 5-28: I did not know that the preferential adsorption of H2O to stainless steel could prevent O2 adsorption, leading to fractionation of O2 and N2. I think this is a valuable insight, but it seems to be speculative. If the effect is the cause of the temporal decrease in AO2 d(O2/N2) seen in Fig. S9, then the decrease should be attenuated with time (in other words, negative biases for calibration gases decrease as the drying proceeds). Did the authors examine long-term AO2 measurements in the laboratory to confirm whether this H2O and O2 adsorption effects did in fact attenuate

with time? Some quantitative evaluation of the effect would be helpful.

7) Related to the comment 6) above, I think it may be better to consolidate the scales of vertical and horizontal axes of the figures in Fig. S9. Such changes will make the comparison of the slopes and variabilities easier.

8) P21, line 13: “exlude” should be corrected to “exclude”.

9) P22, lines 9-11: I think CH4 concentration decreases rapidly with increasing altitude in the stratosphere. Does this altitudinal decrease of CH4 affect the observed AO2 d(O2/N2) in the lower stratosphere, due to the hydrocarbon effect suggested by the authors? Also, considering the authors’ discussion, it seems to me that sufficient drying of sample air is vitally important for the VUV absorption detector for O2. How dry does the air have to be? It would be quite helpful if the authors could provide the reader with information like, “lower than xx ppm.” Such information will be helpful for the researcher who hopes to employ the authors’ VUV technique for high time resolution measurements of the atmospheric O2 concentration.

10) P25, lines 2-4 and summary: The authors repeatedly mention that the larger fractionation found in AO2 than in Medusa will be reduced by increasing the sample flow rate. I do agree with this. But I also assume that the authors are aware of the method used in Yamagishi et al. (2008, https://acp.copernicus.org/articles/8/3325/2008/) to increase flow rate at the air intake and split the air with no significant inlet fractionation. A similar method is being used in some continuous observations of d(O2/N2) by Japanese institutes. I remember that Stephens et al. (2007) also developed a special tee configuration for this purpose. I would be very much interested in hearing from the authors about this method.

11) Figure 8 and Table S3: The authors have made significant effort in correcting for various fractionation processes; I think this has inevitably made the correction methods appear somewhat complicated. Do the blue symbols in Fig. 8 show delta_d(O2/N2) with no correction for the AO2 data, or after the ascent-minus-descent adjustment?

Do the yellow symbols indicate delta_d(O2/N2) with all the corrections for the AO2 data (ascent-minus-descent adjustment, time-of-flight correction to match Medusa, and pressure correction to match Medusa)? Is it correct to assume that the “raw AO2 d(O2/N2) minus Medusa d(O2/N2)*” data and the “corrected AO2 d(O2/N2) minus Medusa d(O2/N2)*”data in Table S3 correspond to the blue and yellow symbols in Fig. 8, respectively? If that is the case, then the blue symbols are not “raw unadjusted” AO2 d(O2/N2) measurements… as stated in the Fig. 8 caption. Also, slight altitudinal decreases of delta_d(O2/N2) by about 5 to 7 per meg can be seen in the binned average vertical profiles (red lines) obtained from the Atom2, Atom3, and Atom4 campaigns. Can the authors explain the cause of these altitudinal decreases? Since it is my impression that the observation methods have improved very much from the early START08 campaign to the recent Atom4 campaign, it should be possible to discuss such slight altitudinal decreases.

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