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Atmospheric Measurement Techniques
Discussions

Interactive comment on "Preparation of primary standard mixtures for atmospheric oxygen measurements with uncertainty less than 1 ppm for oxygen mole fractions" *by* Nobuyuki Aoki et al.

Anonymous Referee #1

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This paper presents an improved method for preparing gravitational mixtures of O2, N2, Ar, and CO2 in air, with potential importance for a range of atmospheric measurements, particularly for detection of long-term trends in O2/N2 ratio. I sense the basic gravitational work was done with great care. But the presentation itself is not polished, and I had difficulty following some of the methods and discussions, such as the comparisons with natural air. The presentation is sufficiently unclear that it will be of limited value in documenting the method and results. There is also at least one outstanding analytical issue that may need to be addressed with further lab work. I recommend resubmission after major revision, although with the large number of substantive issues, this would be equivalent to withdrawing and resubmitting.

General concerns:

I can't follow the method by which the absolute mole ratios in the reference (natural) air cylinder CR00045 were assessed based on comparison the standards. This is not well explained, and seems possibly problematic. I specifically missed clarification that the mass spectrometer used to measure d(O2/N2) and d(Ar/N2) in fact measures the dominant isotopologue ratio 16O2/14N2 and Ar/14N2. Thus it should be sufficient to know the absolute 16O2/14N2 and Ar/14N2 ratios in the gravimetric standards to assess the absolute 16O2/14N2 and Ar/14N2 of CR00045 through the delta measurements. From the absolute 16O2/14N2 and Ar/14N2 ratios in CR00045, one could determine the absolute O2/N2 and Ar/N2 ratios including all isotopologues in CR00045 simply by knowing the isotopic abundances in natural air. Eqs (3) and (4), which I assume are being used in this comparison, look incorrect because they include irrelevant information on the isotopic abundances of the standard mixture. Could the authors perhaps have made the incorrect assumption that the mass spectrometer actually measures the delta based on the sum of all isotopologues?

The paper overlooks the possibility that the concentrations delivered from the tanks for analysis might differ from gravimetric ratios by either homogeneous or inhomogeneous fractionation. Numerous previous studies (e.g. Leuenberger et al., AMT 2015; Langenfelds et al, 2005, JGR -Atmospheres 110(D13); Keeling et al, JGR 1998; Keeling et al Tellus B 2004) have drawn attention to these issues, which often dominate errors and therefore cannot be ignored. As shown by both the Keeling and Leuenberger studies, a pertinent measurement is to assess the change in composition of the tank as it is depleted. This effectively is a constraint on both types of fractionation. Surface adsorption/fractionation at lower pressure ranges could be assessed by filling an evacuated tank up to modest pressure (e.g. 3 atmospheres) and looking at composition anomalies in the residual gas caused by the filling. Tests of this sort could be done with similar tanks filled with natural air, sparing the gravimetric tanks. Perhaps the authors have other ideas. In any case, some additional lab work is needed to assess these effects, which cannot realistically be assessed theoretically.

Another omission is a discussion of the interferences from gases other than O2/N2, Ar, and CO2 on the mass spectrometer measurement. Ne, He, Kr, CH4, H2, and N2O all have abundances over 0.1 ppm in air, but presumably not in the gravimetric tanks. The effects may be small but need evaluation or discussion.

It's unclear what was learned from the paramagnetic measurements that compare gravimetric standards to a tank of synthetic air. Also, the discussion of the paramagnetic measurements lacks a discussion of interferences. I suggest that this content be cut, as it doesn't appear to address anything important.

The study lacks a direct comparison with the previous gravimetric work of Tohjima et al (2005). Section 6.1 is entitled "Comparison between O2/N2 ratios on the AIST and NIES scales", but instead of reporting such a comparison, e.g. by exchanging cylinders with NIES, this section does something else entirely: They use their measurements to report a trend in O2/N2 by combining the previous absolute estimate of O2 mole fraction at Hateruma station in Tohjima et al, with a new absolute determination at Hateruma done by the authors 15 years later. The inferred trend in O2/N2 at Hateruma is shown to be significantly smaller than the trend measured at La Jolla over the same period by the Scripps group. But before they make this very speculative comparison, they first need to carry out a direct comparison of standards. Also, I believe that the NIES group has made measurements over the full time frame at Hateruma. Surely, the NIES data should be examined before comparing with La Jolla.

Other points:

Page 2, line 21. The context of the 500 per meg figure is unclear. I assume it may reflect the decrease over some time period of measurement, but this isn't clear nor is the reason for this statement.

Page 2, lines 21-31. This paragraph is intended to provide motivation, but I found it

hard to follow. It also misses important content. I suggest this prose be replaced with a summary of current practice of calibrating O2/N2 measurements and explaining why the development of absolute standards would satisfy an important need by overcoming the reliance on the long-term stability of O2/N2 ratios in high pressure aluminum gas cylinders. Here might also be a good place to mention the relevance of homogenous and heterogeneous fractionation mechanisms and the relevance of good practice in withdrawing air from tanks. Page 3, line 30. Punctuation problem. "as such" is start of new sentence.

Page 3, line 31. Meaning of "calibration lines" is unclear to me.

Section 2.3.2. This section lacks adequate motivation. Why is it relevant to measure the O2/N2 and Ar/N2 ratios of the gravimetric mixtures when their ratios are known from the gravimetric preparation? I think the context here is a comparison with natural air. Another title for this section and few sentences of explanation are needed.

Page 5, line 11. I can't follow, as the distinction between sample and standard is unclear here. Is CRC0045 the sample or the standard? Note that the delta value for CRC00045 will be zero by definition. This is true whether the delta value is based on the dominant isotopes or not. This content therefore makes no sense to me.

Page 5, line 14 and Eq. (3) and (4). In the context of this section, it is unclear what is meant by δ(O2/N2) and δ(Ar/N2) without isotopic label. Does this refer to a ratio formed based on the sum of all isotopologues?

Page 5, Eq. (3) and (4). Why do 18O17O, 18O18O, 15N15N not appear in these equations?

Page 5, line 25. It would be good here to repeat that the label "standard" refers to CRC00045.

Section 2.3.3. Similar to the last section, the section title seems wrong and motivation is lacking. It's especially confusing that a comparison to synthetic air is being done.

How was the value of 20.650% determined? Since the uncertainty on 20.650% is much greater than the uncertainty on the gravimetric mixtures, it's hard to see the point of this comparison. As discussed above, I suggest cutting this section.

Page 6, lines 25 and 26. Meaning of "work" unclear. Is this meant in a thermodynamic sense? Work versus heat? Generally, this paragraph is hard to follow.

Page 6, lines 32, 33 and 36. Meaning of "equilibrium" is unclear, and is perhaps the wrong word choice. It seems it is defined operationally by the stability of the readings over time. I miss a statement about temperature measurements. How was temperature measured?

Page 7, line 16-17. "The mass difference decreases. . ." Unclear that this is a statement about the sign, as it reads more as a statement about magnitude, e.g. would the difference be smallest with a very large temperature difference? Would be clearer if stated as "warmer cylinders appear lighter (or heavier?)". Even on multiple readings I can't figure out which direction is implied.

Page 7, lines 21-28. The information in this paragraph should be condensed and merged with the previous paragraph. It would be easier to follow the earlier paragraph if the temperature measurements were discussed BEFORE discussing the impact on weighings.

Page 6-7, I urge that Sections 3.1 and 3.2 be merged into one section to improve readability. I note that there is no discussion of how the surface temperature of the cylinders was measured. Okay, reading further, I see it is eventually discussed. Maybe this should be mentioned above in Materials and Methods, where more detail could be given, e.g. how was thermocouple attached? Was it left in place during weighings?

Page 8, line 25. "humidity and temperature factors". If the point is that the effect is due to temperature alone, why does this sentence mention temperature factors.

Page 11. The leak-up rate of 0.013 mg/day is more than two orders of magnitude faster

than the upper bound reported in Keeling et al Tellus B, 59, 2007 for a presumably similar valve at cylinder pressure. The rate is admittedly small in the context of their application, but perhaps not in other applications, so their findings may raise concerns. They should at least cite Keeling et al and mention that the rate appears high compared to other work.

Page 8, line 28. Section 4. The header needs rewording. Suggest "Gravimetric Error Propagation"

Page 11, line 3 "Table 5 shows. . ." Aside from the major question I raised above about the overall logic of this calculation, I miss how the value of (16O2/14N2) standard and (40Ar/14N2) standard are assigned.

Page 12, line 37 "The d(O2/N2) values obtained were 0.16%..." I can't follow this sentence.

Page 13, lines 4-10. This looks like important information, but I can't follow. I guess this reflects my difficulty understanding the overall logic of their approach.

Page 13, line 17-18, "Using these samples. . .". I can't follow. The sentence appears to assume that the atmospheric O2/N2 ratio is constant. What time of year? Are these annual mean values?

Page 13, line 20. Same problem as my last comment.

Page 13, line 25. This paragraph is hard to follow. The need for Ar corrections is not explained. Wouldn't it be possible to work directly from O2/N2 measurements reported by the NIES group, who have taken care of this detail themselves? As mentioned previously, it's strange here not to directly compare gravimetric standards, so this section as a whole is problematic.

Page 14, line 1-5. As mentioned in Keeling et al (JGR, 1998), the Scripps scale factor has in fact been compared to gravimetric standards.

Section 6.2. I can't follow why this information is being presented and how it differs from material in the previous section. For example, between this and the previous section, two inconsistent values (0.2680761 and 0.2680701) for the O2/N2 ratio at Hateruma are reported for 2015. Confusing.

Page 14, line 25. "From 2000 to 2015, it was noted. . ." The basis for this estimate is not clear. Also, to report O2 changes in ppm risks causing confusion unless some context is given. Does this mole fraction basis include CO2? How does this estimate compare to one based on combining information on the change in O2/N2 with known changes in CO2 abundance?

Page 15, line 15. See early comment about this reported rate. Needs context to avoid misunderstanding.

Figure 1. It's unclear why these curves converge to zero. If the data shown is the change relative to the last point, this should be explained in the caption.

Figure 4. Unclear which curve goes with which axis.

Figure 5a. The x axis is labeled O2/N2, but could it actually be showing both O2/N2 and Ar/N2?

Table 2. This table is garbled. Some cells and some column headers appear to have inappropriate line breaks. The rows don't line up properly and the +/- symbols are often not located properly.

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