Atmospheric Measurement Techniques Discussions

Atmos. Meas. Tech. Discuss., referee comment RC2
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Comment on amt-2021-45

Anonymous Referee #2

Referee comment on "Characterisation of gas reference materials for underpinning atmospheric measurements of stable isotopes of nitrous oxide" by Ruth E. Hill-Pearce et al., Atmos. Meas. Tech. Discuss., https://doi.org/10.5194/amt-2021-45-RC2, 2021

This paper describes the characterization of compressed gas reference materials containing nitrous oxide, and their application to measurement of atmospheric N2O and its stable isotopes. Of particular importance is the finding that dynamic dilution does not appear to be impacted by isotopic fractionization. This work confirms previous work and offers new insights into stability as a function of cylinder pressure. This work supports on-going efforts to better understand and implement measurements of N2O and stable isotopes of N2O.

General Comments

While you do describe the gravimetric process and compare N2O to the WM/GAW N2O scale, you do not offer an assessment of new isotopic reference materials (USGS51 and USGS52) or alternate sources of stable isotopes of nitrogen and oxygen and application to N2O. Therefore, I suggest the following title better described this work.

Characterization of Gas Reference Materials for Underpinning Atmospheric Measurements of Stable Isotopes of Nitrous Oxide

Some readers may be unfamiliar with the terms “validation” and “certification”. It might help to expand on what these terms. For example, for certification, equation (5) indicates that a single primary standard is used to "certify" (or value-assign) a mixture. Is that primary standard part of a suite of standards that define a “scale”, or is each PRM unique in its application to “certify” mixtures? Is the validation process simply comparing a new gravimetric standard to others to verify consistency, or is there more to it? Can a gravimetric standard have both a gravimetric value and a “certified value”? For example, in figure 3 you state that this shows the residuals of certified amount fractions vs gravimetric amount fractions. Is this the same as the residuals from a linear fit of

analyzer response vs gravimetric amount fraction, which provides a measure of consistency of gravimetric preparation? I guess I don't understand why one would "certify" mixtures against a single 325 ppb reference material when you appear to have a consistent set of gravimetric standards that could be used to define a "scale". If that is in fact what you have done, then perhaps this could be explained more clearly.

What are the terms in in equation 8 and where do they come from?

Figure 5: I'm not clear what the "parent" has to do with this. Why not show X(P) - X(Po) where X(P0) is the amount fraction at the initial pressure (as in Fig 6)? Importantly, it looks like one of the cylinders in "a" is changing (triangles). It shows a decrease of ~0.2% from start to finish, certainly the CRDS can detect that level of change.

Figure 6: It seems like the uncertainty plotted is not relevant here. Clearly the repeatability is very good, and so we can conclude that the amount fractions are stable to within +/- 0.05 ppm (maybe less) in these cylinders. Also, why are these data so much more precise than N2O amount fractions in Fig 5a? Here the scatter for all points is < 0.05 ppb, whereas in fig 5a it is ~0.1%, or about 0.3 ppb.

Figure 7: Is the linear regression fit based on just the dynamic standards or both dynamic and static standards? It is odd that the mean residual does not appear to be "zero".

Figure 8: Do the NPL PRMs represent a defined NPL scale that can expected to be maintained in a consistent manner over time?

Specific Comments

78: I suggest: "… this technique has demonstrated a precision (Allan deviation) of < 0.05 nmol/mol …"

96: replace ("Scott Marrin") with "(Scott Marrin, now Praxair)"

114: Is "electropolishing" correct? I am not familiar with electropolished Luxfer cylinders. If electropolishing is correct, please specify the company that performed the electropolishing.

122: How was gas from the transfer vessel introduced? By flushing or expansion to vacuum?

347: Venting a cylinder in 1.5 hours would also result in significant cooling and potential thermal fractionation, so it seems that your tests suggest that adsorption AND thermal fractionation of N2O are less than the level of detection, except for the one cylinder in fig. 5 that appears to show a change in N2O.

392: You say you used linear interpolation to account for drift. Is this at odds with experiments that suggest stability over time and with changing pressure?

395: delete "measured"

425: replace "averaged" with "average"

Figure 5: Figures are not labelled "a", "b", etc.

Figure 6: Were these tests also performed over a short period, similar to those in Fig. 5?

Missing reference to "WMO (2020)"

540: Is this a reference to a WMO Greenhouse Gas Bulletin?, e.g. https://Public.wmo.int/en/resources/library/wmo-greenhouse-gas-bulletin

541: The link appears to be out of da