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Comment on amt-2022-243

Anonymous Referee #2

Referee comment on "Development of an International System of Units (SI)-traceable transmission curve reference material to improve the quantitation and comparability of proton-transfer-reaction mass-spectrometry measurements" by David R. Worton et al., Atmos. Meas. Tech. Discuss., <https://doi.org/10.5194/amt-2022-243-RC2>, 2022

Worton et al. present a neat development of a state-of-the-art multicomponent gas standard and evaluates its accuracy and stability. The major application of the standard will find in constraining the transmission of PTR-MS instruments which in turn will help in more accurate quantification of uncalibrated compounds based on the proton transfer reaction theory. The standard looks extraordinary in its meticulousness of preparation, is SI-traceable and well characterized in terms of stability of the included compounds. An impressive achievement was to embrace complex chemical compositions varying many orders of magnitude in vapor pressures providing unprecedented mass range of 32 to 671 Da. While the manuscript is generally well written and will be useful probably beyond the PTR-MS community, it has a potential for further enhancements of its clarity. I made just a few relatively minor comments which hopefully can be addressed in the revised version.

General

- It is somewhat surprising that the paper assumes preexisting knowledge from a general AMT reader about concepts such as mass spectrometer's transmission. I think it would be helpful for the novice PTR-MS audience as well as general community a paragraph or a section that explains the basics of transmission and then refer the reader for more details to Holzinger et al. (2019). Additionally, concepts used inconsistently (e.g. transmission curve and transfer curve) may unnecessarily increase readers' mental processing time.
- The inclusion of volatile cyclic siloxanes to gas standards is phenomenal but is not new and was already neatly conducted by other vendors with high reputation in the VOC community such as Apel-Riemer Environmental, Inc. who have been at the forefront of preparing those mixtures at a 5% accuracy confirmed by the GC measurement in about hundreds of PTR-MS papers (e.g. Tang et al., 2014; Werner et al., 2021). It is unclear how the NPL standard stands out because it does not compare other standards used by the community which seems like a lost opportunity for this otherwise excellent paper.

- Although the paper shows exemplary progress for future transmission measurements, I think it could be made clear that the NPL standard is not trying to monopolize the gas standard transmission market. As the fair comparison with other standards has not been provided, a note mentioning that other standards can also be potentially appropriate and useful for transmission measurements would be reassuring.
- The reference list seems somewhat modest and generally not acknowledging the progress in overcoming challenges in transmission measurements and calibrations which have been widely used by the PTR-MS community for almost 3 decades. I encourage making a stronger connection to the PTR-MS classic (e.g. Taipale et al., 2008) and recent literature (not only Holzinger et al., 2019) and further emphasizing the novelty and advancements that the new standard might offer.

Specific:

- I agree that n-hexane was a relatively good choice for the D3 solvent, but the statement in the SI is misleading about n-hexane undetectability by PTR-MS: "because the proton affinity of n-hexane is less than water and therefore does not undergo proton transfer and is not detectable by PTR-MS when operating in the H₃O⁺ mode.". What I want to remind is that there is no 100% pure H₃O⁺ mode so all PTR-MS instruments operate in a more or less mixed ionization mode with the O₂⁺ and NO⁺ being major impurities with relative proportions to H₃O⁺ typically ranging from 1 to several percent (Amador-Munoz et al., 2016). For instance, for a 1% of the O₂⁺ impurity, the detection limit for hexane would be expected only about 2 orders of magnitude higher than that for a VOC undergoing proton transfer. Therefore, if the n-hexane solvent is used in excess, there is no doubt that high signal will be observed on the charge transfer and hydride abstraction n-hexane ions. I therefore suggest it is clarified how the solvent may have affected the transmission measurements, interferences, and if the n-hexane signal on M86 and M85 and lower alkyl fragments (e.g. M71, M57, M43) may have been saturated.
- L221 It seems greatly overemphasized that D3 is challenging because of its low vapor pressure. It may be counterintuitive but despite D3 being solid at the room temperature, its vapor pressure is actually high (11.6 mmHg at 25 C) and has a low boiling point of 131 C +/- 8C at atmospheric pressure. It means that the D3 solid is unique and readily sublimates. I suggest changing "because of low vapor pressures" to "because of its unique phase transition properties" or something along those lines. I would also suggest to include some relevant properties such as boiling points and vapor pressures to the table.
- TMB has a lower vapor pressure than D3 and D4. I do not think it is critical but it fits better the 3rd category. A table with vapor pressures and boiling points could be useful.
- Figure 3 top right panel looks exactly as I would expect an outstanding standard to behave. However, I wonder about the reason for an unexpected slight instability of other compounds presented in the other panels. For instance, why is D3 (and acetone in SI Fig. S2) being generated over time and why are other compounds depleted if there are no oxidants in this relatively high concentration standard (1 ppm) and given the unique proprietary passivation of the cylinder that was promising a longer stability compared to a regular standard.
- What was the regulator and type of surfaces used and could metal surfaces be an explanation for a less excellent stability of the compounds? Methanol stabilization on metal surfaces is a known issue that should not be confused with the excellent preparation of the standard. Only two years of stability is decent but maybe slightly less than absolutely outstanding and it would be nice to improve that aspect if not for

this mixture maybe in the future.

- PFTBA should be spelled out on its first use. It is a very interesting compound that would make sense to describe a little further to the curious audience.
- Why were D6 and D7 siloxanes unincluded? This is surprising because their vapor pressure is still sufficiently high that can be seen even in the highly diluted atmosphere (e.g. Karl et al., 2018). At least adding D6 should have been feasible.
- It would be appropriate to discuss the effect of compound purity. For example, for a 98% purity, if the vapor pressure of compounds making up that 2% is orders of magnitude higher than the compound making up the 98%, the 2% might completely dominate the PTR-MS signal and potentially interfere with other compounds' protonated ions or fragments. I think it would be useful to show some PTR-MS data if you have analyzed the spectrum of the individual 98% pure compound – or if there is a different way to find out what exactly the impurities were?
- For the validation experiments how was the standard diluted for the GC and PTRMS measurements? I am missing the RH, the MFCs (and their materials of the seat and the seal, presumably Viton-free?). Were temperature and RH consistent in all measurements? I wonder if that could shed more light on the mechanism for the annual drifts for methanol, acetonitrile, acetone, and PFTBA.
- I am not a huge fan of the long and overly specific titles. I wonder if it might be possible to simplify the title just a little bit. Specifically, it might be considered shifting the emphasis in the title from "comparability" to more generally on "improved quantification" which in my opinion could resonate even more broadly.
- It would be valuable to add info on how processing of D3-D5 siloxane signals was done in your PTR-MS work. In the provided reference to Holzinger et al., 2019 it was not mentioned how the Si isotopes and the CH₄-loss fragments were dealt with to reconstruct the transmission curve as the approach requires to sum up all the ions specific to the analyte. In addition, it is unclear what the proton transfer reaction constants were used for those siloxanes.
- Overall, it was extremely enjoyable to read through this seminal work, but I think the conclusions and take-home messages could be even further expanded. For example, as a community should we invest more in the gas standards that can last for at least 2 years or would a properly designed and SI-traced liquid stock solution for dynamic calibration in the proper cal. box could allow even more thorough calibrations including compounds which are challenging or impossible to prepare in gas standards such as organic acids, and with the formulations that can span monoisotopic masses at least until 1000 Da.

Technical

- Introduction: "with high sensitivity (pmol mol⁻¹). ". Should be changed to something like "ultralow detection limits" (sensitivity is not the same as detection limit).
- L136 remove space before percent.
- Entire ms: Ensure consistency with spelling of sulfide/sulphide (either sulfide or sulphide).
- L95 Provide VICI valve model (and if it contained Viton seals that can potentially obfuscate methanol stability).
- 319-321 the use of transmission and transfer curves in one sentence can be rather confusing for some readers.

References:

Amador-Muñoz, O., Misztal, P. K., Weber, R., Worton, D. R., Zhang, H., Drozd, G., and Goldstein, A. H.: Sensitive detection of n-alkanes using a mixed ionization mode proton-transfer-reaction mass spectrometer, *Atmos. Meas. Tech.*, 9, 5315–5329, <https://doi.org/10.5194/amt-9-5315-2016>, 2016.

Holzinger, R., Acton, W.J.F., Bloss, W.J., Breitenlechner, M., Crilley, L.R., Dusanter, S., Gonin, M., Gros, V., Keutsch, F.N., Kiendler-Scharr, A. and Kramer, L.J., 2019. Validity and limitations of simple reaction kinetics to calculate concentrations of organic compounds from ion counts in PTR-MS. *Atmospheric measurement techniques*, 12(11), pp.6193-6208.

Karl, T., Striednig, M., Graus, M., Hammerle, A. and Wohlfahrt, G., 2018. Urban flux measurements reveal a large pool of oxygenated volatile organic compound emissions. *Proceedings of the National Academy of Sciences*, 115(6), pp.1186-1191.

Taipale, R., Ruuskanen, T.M., Rinne, J., Kajos, M.K., Hakola, H., Pohja, T. and Kulmala, M., 2008. Quantitative long-term measurements of VOC concentrations by PTR-MS—measurement, calibration, and volume mixing ratio calculation methods. *Atmospheric Chemistry and Physics*, 8(22), pp.6681-6698.

Tang, X., Misztal, P.K., Nazaroff, W.W. and Goldstein, A.H., 2015. Siloxanes are the most abundant volatile organic compound emitted from engineering students in a classroom. *Environmental Science & Technology Letters*, 2(11), pp.303-307.

Werner, C., Meredith, L.K., Ladd, S.N., Ingrisich, J., Kübert, A., van Haren, J., Bahn, M., Bamberger, I., Beyer, M., Blomdahl, D., Byron, J., et al. 2021. Ecosystem fluxes during drought and recovery in an experimental forest. *Science*, 374(6574), pp.1514-1518.