

Referee comments to

„Development of an SI-traceable transmission curve reference material to improve comparability of proton transfer reaction mass spectrometry measurements“ by David Robert Worton, Sergi Moreno, Kieran O’Daly and Rupert Holzinger

by Wiebke Scholz

The manuscript by Worton et al. describes the production and evaluation of several multi-component gaseous primary reference materials (PRM) with the aim to allow PTR-MS users to better constrain the transmission curves of their respective instruments. The manuscript discusses the challenges of including low-volatility compounds, but manages well to reproduce their concentrations in the different PRMs with uncertainties typically below 10%.

The quantitative addition of such high-mass low-volatility molecules to gas-standards will be of great use for the PTR-MS user community in general and is also important for atmospheric measurements. Challenges in the quantification of several compounds were overcome by using a combination of GC-MS and GC-FID and in some cases Cryo-GC-FID.

The PRMs described were prepared following standardized procedures and evaluation results are presented in great detail and with particular dedication to precision and uncertainty analysis in a well-structured manner. However, the manuscript was in parts difficult to understand on the first read, because abbreviations were used excessively and partly confusing.

The paper gives insight into the reproducibility and stability of gas standards that will be very valuable to end users. Transmission-curve constraints with one single reference material can simplify the lives of many PTR-MS users around the world and enhance data comparability and quantification.

I therefore suggest that the manuscript is published in AMT after some minor comments have been addressed:

1. The GC-MS method used is not fully described. Please specify especially the type of ionization (electron impact, chemical ionization ...) (lines 94 ff.)
2. How was the separation of the 3-carene and 1,2,4-TMB peak treated? Was a multipeakfit performed and the data corrected accordingly or do the two compounds influence the other's signal? (lines 96 ff.)
In line 144, the baseline separation issue is mentioned for Acetone and DMS as well, but it is missing in lines 96 ff.
3. For the Cryo-GC-FID, the volume of the loop, and the trapping / heating cycle are not described (l. 105 ff.)
4. Why are the FID data on acetonitrile so much more noisy than the acetonitrile GC-MS data and also so much more noisy than the methanol FID data, although the latter should give a smaller FID signal? Consider adding a sentence or two on this matter.

5. Please make sure, the abbreviations are used consistently, as these were confusing in parts:

- Line 57: NPL is not defined

(don't let the reader search for the hint in Dave Worton's email address...)

- Line 154: Is PTRMS NPL PRMs a subgroup of NPL PRMs?

If yes, please define, if no, please remove the „PTRMS“

- Line 152: Mentioning of the certified primary reference material without the short-form „CRM“ used in the supplement.

- Also, the supplement about the certified reference material with fig. S3 is not mentioned in the main text and so the difference between certified reference material and PRM remains unclear in the main text. It appears, as if the uncertainty for CRMs is larger than for PRMs due to the simpler preparation method. What does that mean for the PFTBA validation?

- In this context, there is also missing information on the BTEX NPL PRM in the main text (especially its age, and if it is produced also gravimetrically)

- Text and Fig. S3 in the supplement:

Decide on CRM, PTRMS CRM or NPL CRM to support the reader, except you want to address differences, that then should be clearly defined.

- The names of the different reference materials are not clearly motivated and therefore reduce the readability.

I suggest changing them so they e.g. contain the month and year of production. To guide the reader for a faster understanding of Table 2 consider coloring the Cylinder IDs in table 2 as you do in the figures.

6. line 158 ff:

- did you really measure „A“ always twice directly after each other or were the repeats performed on different dates / which longer breaks in between? If so, add this. Otherwise, consider correcting to $(AB)_nA$

- What is meant by „bracketing“ between the nearest neighbors? Consider using a more common word that is clear also for non-english natives.

- Add to Eq. 1 that it is calculating the relative difference in %

7. l. 198 „A638“ is mentioned twice

8. The footnotes in table 3 (a,b,c,...) do not correspond to the markers within table 3 (1,2,3,...)

9. it is not clear to me, why the reference would be a PRM that is produced from many old parent mixtures. Thus I wonder, what is the advantage of 2819 compared to using D961492? (line 149)
In general, only little information has been given on the stability of the parent mixtures.

10. In fig S2, D4-siloxane and D5-siloxane, biased data do not appear corrected again (as they do e.g. in the plot for 1,2,4-TMB). Please add a short comment regarding this to the figure caption.

11. The PTR-MS transmission curve constraints would be performed with the CRMs appearing only in the supplement fig. S3 in the future, as I understood. The preparation repeatability is reduced to 20-30%. Is this still sufficient to determine a transmission curve, which usually varies within a factor 1.5-2 or will the CRMs be cross-evaluated against the PRMs? Please clarify.

12. Another technique to determine the transmission curve is the addition of single species to the sample air in step-wise increasing concentrations and observe the change in primary ion signal and the ion signal of the sample molecule and repeating this for multiple compounds with different masses. This technique is time-consuming for the end-user but gives generally good results. By having one gas standard that combines many compounds spanning the whole mass range, the technique of comparing with the primary ion signal is certainly not possible anymore, which requires the CRM to really be precise and contain species that are detected at the kinetic limit. I am looking forward to your discussion of this point.

A short „how-to“ for the usage of your CRMs for transmission curve correction, potential error sources and prerequisites would add great value to your manuscript, especially for new users.