Atmos. Meas. Tech. Discuss.,
doi:10.5194/amt-2018-165-RC2, 2018

Atmospheric Measurement Techniques Discussions

Interactive comment on "The importance of cylinder passivation chemistry for preparation and long-term stability of multicomponent monoterpene primary reference materials" *by* Nicholas D. C. Allen et al.

Anonymous Referee #2

Received and published: 23 September 2018

The manuscript "The importance of cylinder passivation chemistry for preparation and long-term stability of multicomponent monoterpene primary reference materials" by Allen and co-workers focuses on quantifying the long-term stability of gaseous monoterpene standards in a variety of commercially available cylinders. The authors find that a type of cylinder is suitable for storing these components, while others exhibit degradation after as little as 24 hours. The stability of the same species in sampling cylinders routinely used in the field is also investigated.

The method described in the manuscript is rigorous and the results are very important

for the broader atmospheric chemistry community. Monoterpene measurements are crucial to answer a number of open questions in tropospheric chemistry (missing OH reactivity, secondary aerosol formation, etc.), therefore establishing a solid metrological basis for these measurements is a very important and necessary step. However parts of the manuscript are unclear and would benefit from a few edits. I would therefore recommend publication on AMT once the points below are addressed.

Main points:

Lines 210-212: I find this paragraph confusing and after reading it many times I do not think it actually describes what you are doing with the normalised ratio. The crux of it all is the term 'gravimetric difference'. What you really are looking at here is the difference between the amount fraction you would expect in the absence of losses post-decant (in which case it would be equal to the gravimetric amount fraction of cylinder 1 as calculated from the dilution data) and the certified amount fraction obtained from a comparison with mixture BB as you described in lines 194-196. Please re-phrase.

Line 382 and Figure 5: One of the major outcomes of this study is the stability of the monoterpenes studied in one type of cylinder. This is shown in Figure 5 but this finding is backed up by surprisingly little statistical analysis. "appears [. . .] fairly constant" is the only description accompanying the plots in Figure 5. I feel that the conclusions of this study would be stronger if backed up by a more solid analysis. I would like the authors to add a weighted least-squares fit to the plots in Figure 5 and comment on the magnitude of the gradients in the light of its associated uncertainties from the fit. I would be surprised if this analysis did not support the authors' conclusions, but it needs to be shown. Also crop the x-axis at 80 days.

Minor points:

Lines 64-68: As you went through the effort of referencing work on terpene sampling, I feel it would be worth mentioning what these techniques actually are. I appreciate that a full account on terpene detection is beyond the scope of this manuscript, but it would

be nice to at least mention the techniques used by the papers cited.

Line 97: this is not the first occurrence of the word 'passivation' in the text. Please move the explanation of its meaning to line 90.

Line 106: "based on permeation" sounds too vague. Consider changing to something along the lines of "based on the dynamic dilution of limonene from a permeation tube".

Lines 114-115: you need to stress the difference between the 4 PRMs containing monoterpenes and the one containing n-octane. I recommend this edit: "PRMs containing the four monoterpenes, α-pinene (both the minus and plus optical isomers), 3-carene, R-limonene and 1,8-cineole, as well as one containing n-octane (used as an internal reference standard), were prepared independently (no comma!) in a balance of high purity. . .".

Line 116: "high purity dry nitrogen". I feel like the inclusion of "dry" here (as well as in lines 120 and 140) is redundant, especially as the water content is specified further down (line 123).

Line 141: No point in repeating the specs of the purifier here (they already appeared in lines 121-122). Just replace with "purifier".

Line 162: connected to what?

Line 180 and following: I do not understand the use of the quote marks for the cylinder number here and in the rest of the manuscript. 1, 2 and 3 are the effective labels of the mixtures, just like AA and BB. I would recommend removing these as they are confusing and redundant.

Line 202: how many runs were averaged in each set? Give a typical value in the text

Lines 324-327: this is very interesting and perhaps deserves a short explanation of why such effects arise at low pressures?

Lines 362-363: The sentence starting with "A sample of the reference. . ." is a repetition

of the sentence in lines 349-350.

Line 396: where does the figure "2.5%" come from? The largest difference in Table 2 is 1.96 %. Perhaps change to "no greater than 2%"?

Lines 466-473: revise the grammar of this entire paragraph.

Table 2: explain in the table caption why there are two columns for BB v CC.

Figures 2, 3, 4, 5: These all seem to be at a lower resolution than Figures 1 and 6. Would the authors provide higher resolution figures? The better resolution helps a lot, especially when zooming in on the electronic version of the paper.

Figure 4: the caption needs to actually introduce what the figure represents. Start off with "Typical chromatogram of. . ."

Tables S2-S7: in the captions, state what the percentage difference refers to. The response factors? The normalised ratios?

Tables S2 and S3: data in S3 is the repeat of S2, but the cylinder types are labelled differently. I understand that Experis and Quantum refer to the same thing, but it would make things easier to just stick to one name (and it would also be consistent with the following tables).

Tables S4-S7: in the captions, state why there are missing entries in these tables.

Typographical, grammar and language corrections:

The citation style is not in the AMT recommended format. Revise throughout.

Shouldn't all equations be numbered?

Line 43: avoid double parentheses when possible e.g., a hemiterpene of formula C5H8

Lines 78-79: This sentence sounds like a fragment of a larger sentence. I suspect it should be part of the previous sentence. Please rephrase. Also, change 'prevent the reference material dominating' to 'prevent the reference material from dominating'.

Line 163: replace ‘ml’ with ‘mL’ (occurs twice in this line)

Line 175: no need for the comma after Quantum.

Line 194: Replace ‘was’ with ‘were’

Line 195: Replace ‘valve’ with ‘value’

Line 204: add a comma after BB.

Lines 207-208: remove the comma after “where” and add a comma after BB.

Line 228: replace ‘run’ with ‘analysed’ or similar.

Line 234: response factors (plural)

Line 256: replace with “can produce traceable reference gas mixtures of a number of species, including terpenes”

Lines 258-263: the verb tenses are all mixed up (past, present). It makes following the text harder than it should be. Please pick one tense and stick to it.

Lines 267-268: remove “as was”

Lines 353: replace semicolon with colon

Line 488: change to “systems in the field”.

Line 496: I am not a huge fan of the word ‘dependency’. ‘Dependence’ is more commonly used when describing the relationship of a variable to another (temperature-dependence, pressure-dependence, and so on).

Tables S2-S7: In one of the headers, change “difference to” with “difference with respect to”

Figure S1: in the caption, change spectrum to spectra and remove the comma after terpinolene.

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