Atmos. Meas. Tech. Discuss., 7, C3813–C3818, 2014
www.atmos-meas-tech-discuss.net/7/C3813/2014/

Atmospheric Measurement Techniques Discussions

Interactive comment on "ACTRIS non-methane hydrocarbon intercomparison experiment in Europe to support WMO-GAW and EMEP observation networks" *by* C. C. Hoerger et al.

Anonymous Referee #1

Received and published: 20 November 2014

This is another comprehensive and interesting intercomparison of techniques to determine non-methane hydrocarbons. This has been a challenging and ongoing task for many years. It is good to see the establishment of ambitious Data Quality Objectives (DQOs). Unfortunately, it seems it is still hard to comply with these DQOs and there seems to remain various, sometimes poorly understood reasons for that. Nevertheless, it is very encouraging to see joint efforts to tackle all these challenges. Overall, the paper shows some valuable material and associated discussion. It also mentions various limitations. After addressing the issues lined out below, I would recommend the publication of this manuscript in AMT.

Major issues:

1) One limitation of this study is that only dry samples were used in the intercomparison. Also, I assume these samples did not contain O3. As a consequence the performance of important instrumental parts critical in removal of H2O and O3 and their potential impact on the samples could not be compared. This limitation should be mentioned explicitly in the abstract and the conclusion.

2) Page 10431, lines 18-22: If I understand it correctly, it seems HPB and Empa assigned values to NMHC_N2 and NMHC_air and at the same time participated in the intercomparison. This an unusual approach and contradicts the statement on page 10432, lines 10-11, that "The composition and the mole fraction in the cylinders were unknown to all participants". The authors should comment on this and justify why no external entity performed this task.

3) One interesting point the authors especially make is that the "Perkin Elmer Online Ozone Precursor Analyser" is the only commercially available all-in-one instrument tested in this study. Still, table 4 lists some different configurations among these instruments and the results vary to some extent. This provides some unique opportunity to discuss the different performance results and potentially find some recommendation for standard approaches, at least for these instruments. It would be valuable to include another separate chapter which would include this kind of discussion.

4) Page 10432, lines 25-27: It seems that the references to Solberg (2012; 2013) serve as a justification for introducing the ACTRIS DQOs. It would be valuable to briefly describe the measurement system used in the Solberg references, as this measurement system seems to be suitable to determine these annual trends.

4) Page 10436, line 10 - page 10437, line 11: The authors should also discuss that some laboratories show more accurate determination of selected NMHC in NMHC_air compared with NMHC_N2, e.g. SMR for isoprene and FZJ_B for acetylene (just to name two examples). This is something one would not expect in the first place.

Other comments:

Page 10425, line 1: According to table 3 I am counting 18 laboratories. Also, it seems some of the laboratories are not associated with either GAW or EMEP (SIR, FZJ, NILU). This should be clarified.

Page 10425, lines 10-14: It needs to be mentioned that both, NMHC_N2 and NMHC_air, were dry samples and most likely did not contain O3.

Page 10427, line 8: "Coverage factor" needs to be explained. Also it needs to be explained why the value k=2 was chosen.

Page 10427, line 13: The term "recently" needs to be removed as the PTR-MS technique has been around for some time.

Page 10429, lines 22-23: It looks like ambient air of Dubendorf had 1 % relative humidity, which I doubt which is what the authors wanted to say. The authors should mention the reason why they used a very dry NMHC_air sample and how they dried the sample.

Page 10431, lines 7-8: How much was the mole fraction drift for 1,3-butadiene and isoprene?

Page 10431, lines 7-14: This is a bit confusing. I assume that the values shown in table 5 refer to the cylinders prior to the intercomparison exercise. It is not clear why some mole fraction drift before and after the intercomparisons needs to be considered.

Page 10432, lines 17-18: Please add a justification why the trimethylbenzenes and monoterpenes were excluded from the intercomparison. Minor item: it should read "trimethylbenzene" instead of "trimethylbenene".

Section 2.6 Please clarify, if equations 7, 9, and 10 are also taken from JCGM (2008) or any other source. For equation 10 it would be good to include the derivation in the supplemental material.

Page 10433, lines 11-12: What is the justification to use k=2, since k may range be-

tween 2 and 3?

Page 10434, line 1: I think it should be $\Delta\chi$int instead of ΔAint.

Page 10435, line 6: This reference is not helpful, as it seems that login credentials are required.

Page 10436, line 4: Why were in particular C4-C6 alkanes chosen?

Page 10436, line 6: I assume the authors mean C7-C8 alkanes (not alkenes).

Page 10436, lines 10-11: The authors should justify why they use figures and tables to show the same information. Some of the redundancy could be removed.

Page 10436, line 10 - page 10437, line 11: I guess this section needs a separate individual header.

Page 10437, line 1: I think the authors mean table 7.

Page 10439, line 21: Replace "constrains" by "constraints".

Page 10441, lines 13-16: Unclear. The authors should explain why this would have a specific impact on C2-C3 hydrocarbons only.

Page 10442, lines 1-4: Section is unclear. Did the WCC-VOC measure ethane with PTR-MS?

Page 10442, lines 8-9: Unclear. I assume alkene mole fractions were low in the samples for all participants, not only for AUC, PAL, SMK, ZSF, and IPR. So why was it a specific challenge for these participants?

Page 10442, lines 23-24: Unclear. What are the specifics of a pressure regulator which is in particular inappropriate for ethyne?

Page 10444, lines 1-2: It should be elaborated what the authors exactly mean by the term "status of Nafion", in particular if this status depends on humidity. This may be of relevance, as this intercomparison exclusively refers to dry samples.

Page 10448, lines 7-17: These statements are a bit awkward, as only extremely dry samples were analysed. As a consequence it cannot be stated that cold trap systems exhibited a "very good performance" as they were actually not exposed to water. Also the sentence "overall however, this method appeared superior compared to Nafion dryers...." is awkward, since no "overall" statement can be made at all and the verb "appeared" is very weak.

Page 10448, lines 22-23: Unclear. How can pressure and flow rates only cause some of the deviations? What deviations in particular?

Page 10450, lines 1-2: Unclear. I thought all participants calibrated ethyne directly. Also, based on this paper no statement can be made about humid air samples as all samples analyzed in this study were extremely dry.

Page 10450, lines 12-13: Actually, not "many", but almost all participating instruments indicated losses of C7-C8 aromatics according to figure 4.

Page 10450, lines 19-20: "substantially underestimated" requires some quantification.

Page 10450, lines 20-21: "...some participants did not cover the major uncertainty contributions." does not really sound like a result, but rather a complaint. Would recommend to reword this a bit.

Table 4: Obviously, this table has two parts. I recommend to have Table 4a and 4b.

Table 5: Replace "cis-2-penten" by "cis-2-pentene".

Table 7: Some columns are not colored, although it seems the mixing ratios for these NMHCs are more than 100 pptv (2,2,4-trimethylpentane, 1-butene, and 2-methylpropene).

Table 9: Why do some columns contain extremely precise repeatabilities (around 0.001%)?

Figure 5, Figure caption: "Normalised mole fractions...", normalised to what? Men-

tion what the additional information provided by this figure is which is beyond what is already shown in tables 6 and 7.

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