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Atmospheric Measurement Techniques Discussions

Interactive comment on "Analysis of non-methane hydrocarbons in air samples collected aboard the CARIBIC passenger aircraft" *by* A. K. Baker et al.

Anonymous Referee #2

Received and published: 26 November 2009

General comments:

The paper describes the technical details of a method to analyze non-methane hydrocarbons (NMHC) in air samples collected by an automatic air sampler onboard a civil aircraft used in the CARIBIC project.

Although the paper does not per se represent a novel approaches to measure non-methane hydrocarbons, it presents a well thought-out analytical method which warrants publication. The paper is a valuable contribution to those scientist who want to develop a new gas chromatographic trace gas method, improve or evaluate the quality of an existing method. The paper describes most necessary details on sample collection, water and bulk gas removal techniques, pre-concentration, cryo-focusing, separation, detection, calibration including the verification of long-term stability from one primary

calibration mixture to the next without exhausting any mixture, the use of working standards to prolong the lifetime of primary calibration mixtures, the results of participation in international inter-calibration efforts, and the assessment of critical parameters of the analytical system such as blank values and linearity.

However, a few important questions remain which should be answered by the authors before acceptance of the excellent manuscript. Most importantly:

A) Why were glass cylinders chosen which are not stable for alkenes, sacrificing ∼50% of the potential NMHC data? Is it possible to deactivate those cylinders? Have tests been performed to evaluate if ozone is stored in the cylinders, possibly reacting with alkenes?

B) Test results whether the drying agent Mg(ClO4)2 influences C5 and higher NMHC need to be more clearly presented to assess the possibility that Mg(ClO4)2 contributes to the depressed carbon response factors shown in Figure 3 for i-octane to o-xylene.

C) Similarly, tests should be performed to assess whether the strong absorbent Carbopack BHT (which was chosen despite the relatively low temperatures) possibly contributes to the depressed carbon response factors shown in Figure 3 for i-octane to o-xylene.

In addition to the general discussion of the CARIBIC NMHC dataset in chapter 3 and 4 the authors could improve the impact of their article by evaluating the quality of their dataset similar e.g. to Parrish et al., J. Geophys. Res., 103(D17), 22339-22359, 1998.

Specific comments:

Page 2380, line 14: Why were glass cylinders chosen over stainless steel cylinders? Stainless steel cylinder are typically used for non-methane hydrocarbons and previous work have shown that it is possible to condition them so that alkenes remain stable.

Page 2380, line 21: Which filter is used (type, materials, manufacturer)? Could it contaminate or alter the sample?

Page 2380, line 24: Are the glass flasks pre-evacuated? This could improve flushing.

Page 2380, line 25: What is the exact flush volume? 30 times?

Page 2381, line 5: How is the sample pressure measured? Which pressure sensor is used (type, material, manufacture)? Could it contaminate or alter the sample?

Page 2381, line 12/13: Are the samples send to Australia for further analysis?

Page 2381, lines 21-25: Are all glass cylinders problematic or only certain ones? Is it possible to deactivate them with water vapor? See also comment for page 2380, line 14.

Page 2382, lines 7-8 and Figure 1: It would be beneficial if the diagram of the analytical system were described more thoroughly, e.g. by showing more than one operating condition. Why are all valve ports in Figure 1 connected both by straight and bend connections? Only one is active. Which rotor materials are used?

Page 2382, lines 17-28 and page 2383, lines 1-5: Is the approach to regenerate the Mg(ClO4)2 new? Would this also work for wet tropospheric samples? Other groups have reported loss of isoprene and C7–C9 hydrocarbons on Mg(ClO4)2. Could this contribute to the depressed carbon response factors shown in Figure 3 for i-octane to o-xylene? The authors only show good agreement for C2–C4 hydrocarbons with and without Mg(ClO4)2, but do not detail the results for C5 and higher hydrocarbons in samples without interference. Are carbon responses also depressed or are they as for C2–C4 NMHC in samples without interference when Mg(ClO4)2 is not used?

Page 2383, lines 6-9: At -130°C is it necessary to use the relatively strong adsorbent Carbopack BHT? During NOMHICE (Apel et al., JGR, 108, D9, 4300, doi:10.1029/2002JD002936, 2003) it was observed that solid adsorbents often lead to poor agreement with the reference laboratory. Have tests been performed to exclude artifacts from the adsorbent, e.g. the depressed carbon response factors shown in Figure 3?

Page 2384, lines 25-28: Which flow controllers are used (type, materials, manufacturer)? Could they contaminate or alter the standard gas stream? Are the flow controllers NIST traceable? Do they need temperature stabilization? Have other linearity tests been performed, such as sampling of increasingly larger volumes of ppt range ambient air?

Page 2385, lines 9-20: It is excellent that the carbon response factors up to C6 are similar (with the known exception of acetylene). However, e.g. Plass-Düllmer et al., J. Chromat. A, 953, 175-197, 2002 have observed only marginally depressed carbon response factors up to C8 hydrocarbons. Did the authors perform tests to exclude that the reduced carbon response from i-octane to o-xylene are an artifact of the analytical system, e.g. from the used relatively strong adsorbent or the used drying agent?

Page 2385, lines 24-26: What types of tanks are used and how were they filled?

Page 2388, line 9: How were the back-trajectories calculated? Why 8-days?

Page 2388, line 14: How were the PV values calculated?

Page 2388, line 15: Citations for O3 and CO measurements?

Page 2389, line 18: insert “and reactivity towards the OH radical and ozone”.

Technical corrections:

Page 2381, lines 26-27: Pollman et al., 2008 (not 2007)

Page 2389, line 9: Strike out easily.

Manuscript Evaluation Criteria

In the full review and interactive discussion the referees and other interested members of the scientific community are asked to take into account all of the following aspects:

1. Does the paper address relevant scientific questions within the scope of AMT? Yes.

2. Does the paper present novel concepts, ideas, tools, or data? Not per-se, but as

detailed in the review, the paper presents a well thought-out analytical method which warrants publication.

3. Are substantial conclusions reached? As detailed in the review, substantial conclusions are reached in the sense that the paper is a valuable contribution to those scientist who want to develop a new gas chromatographic trace gas method, improve or evaluate the quality of an existing method.

4. Are the scientific methods and assumptions valid and clearly outlined? Yes. Most technical details are well described.

5. Are the results sufficient to support the interpretations and conclusions? Mostly, but for example an evaluation of the data quality of the whole dataset similar to Parish et al., 1998 would be a valuable addition to the paper.

6. Is the description of experiments and calculations sufficiently complete and precise to allow their reproduction by fellow scientists (traceability of results)? Mostly yes, except for questions detailed in the review.

7. Do the authors give proper credit to related work and clearly indicate their own new/original contribution? Yes.

8. Does the title clearly reflect the contents of the paper? Yes.

9. Does the abstract provide a concise and complete summary? Yes.

10. Is the overall presentation well structured and clear? Yes.

11. Is the language fluent and precise? Yes.

12. Are mathematical formulae, symbols, abbreviations, and units correctly defined and used? Yes.

13. Should any parts of the paper (text, formulae, figures, tables) be clarified, reduced, combined, or eliminated? See questions detailed in the review.

14. Are the number and quality of references appropriate? Mostly, except for the points raised in the review.

15. Is the amount and quality of supplementary material appropriate? It would be helpful to know if and how the data are available.

Interactive comment on Atmos. Meas. Tech. Discuss., 2, 2377, 2009.