

Interactive comment on “A new aerosol collector for on-line analysis of particulate organic matter: the Aerosol Collection Module (ACM)” by T. Hohaus et al.

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Received and published: 23 July 2010

Reply to the comments of Anonymous Referee #4

The authors would like to thank the referee for her/his careful reading and positive feedback/helpful remarks that helped to improve the quality of the manuscript. In the following we respond to the individual comments and describe their realization. We have repeated the comments here in italics and added comment numbers for easy reference between points in the responses. Our replies follow each excerpt. Changes

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to the manuscript text are presented in bold.

Specific Comments:

1. The manuscript bills the technique in several places as ‘continuous’ and ‘on-line.’ The system is clearly limited to certain lower limit of collection period, however, and this time is long enough to make me hesitant to agree to the terms the authors apply. For example, the collection time for the beta-pinene experiment was 60-minutes, and 6-hours for the ambient study. I understand this reasoning has inherent flaws, since every instrument has dead time associated with detection. Having collection periods with timescales on the order of hours, however, strikes me as much beyond the appropriate (albeit arbitrary) threshold to be fully ‘online’. I agree with the term “quasi-online,” used only once (in the abstract) and suggest that this terminology be used through-out the text and in the title as well.

[Response]: We agree that the best description for the working principle of the ACM is “quasi on-line”. This has been changed through-out the manuscript.

2. The authors discuss the ACM as a new aerosol collector capable of being applied to a number of different types of detectors, but then exclusively apply it to the GC-MS/FID detector. I think it would be more straight-forward to discuss the technique from the beginning as the ACM-GC-MS, and then say as a part of future work that the front-end ACM part may be able to be combined with other detectors. As it is written, however, the manuscript seems to promise more universality than it tries to demonstrate.

[Response]: This manuscript should serve both purposes: presenting the Aerosol collection module as an new option to sample aerosol and also presenting its first application where it is coupled to an GC/MS-FID. Therefore to clarify that this manuscript presents a new collector but also that one application is shown for the ACM we changed the title of the manuscript to: **A new aerosol collector for quasi on-line analysis of**

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particulate organic matter: the Aerosol Collection Module (ACM) and first applications with a GC/MS-FID.

3. *Several places within the manuscript lack sufficient references and comparison to previous work. For example, there is no discussion of other particle collection and analysis systems that utilize a cooled plate that is later heated for aerosol desorption (e.g. TD-PB-MS, Tobias et al., 2000). While the obvious difference is that the ACM discussed here can theoretically be applied to a number of different detectors, it would still be generally useful to discuss the inherent advantages and disadvantages that it offers with respect to similar techniques that utilize cold aerosol collection for quasionline detection (with appropriate citations).*

[Response]: We extend the discussion on previous work conducted and added the appropriate references. This part in the introduction reads now: **In recent years instruments which utilize the concept of collecting particle samples on an impaction surface followed by desorbition and mass spectrometric analysis of the sample were developed by a number of groups (e.g. Tobias et al. 2000, Williams et al, 2006). The Thermal Desorption Particle Beam Mass Spectrometer (TDPBMS) (Tobias et al., 2000) focuses particles in an aerodynamic lens with subsequent sampling in a high vacuum chamber on a cooled impaction surface. In the TDPBMS the particles are temperature-programmed thermally desorbed and analyzed using a quadrupole mass spectrometer. In a recent study another type of aerosol collector (Thermal Desorption Aerosol GC/MS-FID (TAG)) with 1h time resolution has been presented by Williams et al., 2006. The TAG system collects aerosols, including both gas and particle phase of the aerosols, on an impaction surface which are subsequently thermally desorbed and analyzed by compound separation using a GC and subsequent analysis with a MS detector. While these approaches utilize higher sample flows than the ACM described herein, none of the instruments was developed to be compatible with a range of different detectors.**

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4. *The ACM relies on the fact that the collected aerosol is: (a) un-perturbed by the collection process, (b) collected efficiently, and (c) volatile enough to desorb at the temperatures supplied. These assumptions may be appropriate in many cases, but will not always be the case. I have associated questions with these assumptions that are not discussed in the manuscript. For example:*

4a. *How much will semi-volatile aerosol evaporate in the reduced pressure of the instrument before collection, and therefore bias the resultant measurements?*

[Response]: By choosing octadecane for test aerosols a relatively high volatile test aerosol was investigated. The result is that evaporation before collection does not perturb the measurements. See also answers to referees 1, item 3 and 5, item 1 for more details on this point.

4b. *Will the particle beam always be reliably focused such that all particle will hit the collection area (how does the set-up differ from the AMS geometry, for example)? How likely are particles to avoid collection due to their ability to bounce off the surface (this has been a topic of discussion with the AMS instrument)? What other factors significantly influence the fraction of particles that are collected?*

[Response]: The ACM inlet is of the same design as the AMS inlet. Therefore the particle beam is focus in the same way as as for the AMS and it is ensured that all particles hit the collection surface. We stress the fact, that it is the same inlet as for the AMS by changing the describing sentence in the manuscript to: **The sample introduction system and the vacuum system are of a same design as for the Aerodyne aerosol mass spectrometer (Jayne et al., 2000) and are only briefly summarized here.** Concerning the bounce issue it is referred to the authors response to the comments of Anonymous Referee #5 for item 1.

4c. *The particle material adsorbed to the collector will only adsorb if it has sufficient*

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volatility at the desorption temperature (e.g. 225° C). How much material will remain undetected in this case? It will clearly depend on the aerosol composition, but this will introduce a significant bias into the measured results. While this initial manuscript need not exhaustively answer all these questions, the fact that these (and clearly other) assumptions exist should at least be mentioned in passing, and reference to other groups that have looked into some of these issues should be given. This will aid the reader in understanding how to interpret data from the ACMGC-MS, and will also aid future development of the instrument.

[Response]: We agree that only material will be desorbed that is sufficiently volatile at the applied desorption temperature. With regard to the question what can be desorbed from the collection surface and the according changes to the manuscript it is referred to the authors response to the comments of Anonymous Referee #1 for item 2 and item 9.

5. The manuscript describes the instrument as discusses as “capable of linear, quantitative measurements of ambient aerosol mass loadings.” This seems to be an overstatement if at least some mass must be missing due to the fact that it will not desorb at the temperatures used, and because the GC-MS is able speciate far less than 100% of the compounds introduced. One proof given for this statement is the Figure 9 comparison with the AMS, but in this figure the integrated ACM-GC-MS peak area is given in arbitrary units. I do not doubt that in many circumstances the ACM-GC-MS will scale with the AMS linearly, but this does not mean that the instrument discussed here is able to quantitatively report mass loadings – and certainly not without being rigorously “calibrated” with another instrument such as the AMS (which would have a number of uncertainties that would need to be mention in a forthcoming manner). Furthermore, any chemical aerosol detector misses certain types of particles (AMS included: low volatility organics and other refractory material) and this always must be taken into account.

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[Response]: In order to make the point clear that the ACM-GC-MS measures a fraction of the organic aerosol the discussion of the ambient observations was changed and includes the following sentences now (see also answers to referee 1):

The correlation between the two sets of data is linear with a high correlation coefficient, indicating that the overall ACM-GC-MS measurements are representative of the ambient organic aerosol mass loading. and

The first ambient atmospheric aerosol measurement indicates that the ACM-GC-MS system is also capable of linear, quantitative measurements of individual organic compounds in ambient aerosol mass loadings.

6. The discussion of the use of FID and MS as detectors was somewhat confusing to me. I realize that the FID detector was also connected within the GC-MS system, but the authors should use more clarity in going back and forth between the two. This adds a bit to the confusion of the fact that the ACM is already de-coupled from the detector.

[Response]: We clarified through-out the manuscript the use of the GC-FID data versus GC-MS data. For the description of the changes in the manuscript it is referred to the authors response to the comments of Anonymous Referee #1 for item 4.

7. Minor points/questions

7a. Page 1365: The description of the ACM particle collection system describes what seems to be narrow cone where the particles are trapped. Is this the appropriate mental image of the collection surface? A small diagram inset in the instrument schematic, or in the supplementary online material, might help clarify this.

[Response]: Figure 1 shows a schematic of the ACM set up. The collector in this figure is an almost authentically representation of the tapering inside the collector. The dimensions of the collector are compared to the rest of the schematic (vacuum chamber,

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detectors etc.) enlarged but the relative proportion of the collector assembly in Figure 1 are close to reality.

7b. Page 1366, Line 18: What is 'helium 6.0'?

[Response]: With the term helium 6.0 it was referred to the purity of the helium gas used as a carrier gas. The term is used by the distributing company's. The purity of the helium gas has a minimum purity of 99.9999%. We change the expression in the manuscript accordingly. **In every experiment and set up presented here the carrier gas is helium with a minimum purity of 99.9999%**

7c. Page 1372, Line 24: What is Linde, 4.8? Does the 4.8 refer to the company part number? If nothing else the references to the Linde gas products should be consistent (with or without registered trademark sign; with or without comma between 'Linde' and number; etc.).

[Response]: As for the helium 4.8 referred to the purity of the oxygen used for the ozone production. The term is used by the distributing company's and means that the oxygen has a minimum purity of 99.998%. We change the expression in the manuscript accordingly to: **The ozone was generated from pure oxygen with a minimum purity of 99.998% through electrical discharges and introduced into the chamber with two inlets, one near a wall and the other at the center of the chamber.**

7d. Page 1372, Line 27: The authors state that the concentrations of aerosol precursor and ozone were "orders of magnitude above ambient levels." They justify why this is, but in the next paragraph. For clarity of reading I think it would be helpful to move part of the justification to immediately after this initial sentence.

[Response]: We changed the manuscript as suggested.

7e. Page 1373, Line 14: Define CPC

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[Response]: Done.

7f. Page 1373, Line 17: Define SMPS

[Response]: Done.

7g. Page 1373, Line 25: Add "to prevent re-condensation of gases onto valve and lines."

[Response]: Added.

7h. Page 1378: What types of air masses does Billerica typically see? The authors state that "Similar chromatograms from urban samplings were also observed . . .". Does this imply that the Billerica sampling location is a 'typical urban environment'?

[Response]: The geographical location of Aerodyne Research, Inc. is indeed an urban environment. An area which is located in an industrial park with a highway closeby. Therefore one would expect e.g. freshly emitted hydrocarbons. To clarify that the sampling location is an urban environment, we added this information to the manuscript: **The first ambient air measurements with the ACM GC-MS were conducted in an urban environment at the Aerodyne Research, Inc. laboratory in Billerica, USA.**

7i. Places within the manuscript lack consistent use of grammatical tense (present and past). Please be careful to refer to the instrument and experiments consistently.

[Response]: The manuscript was checked for the use of past and present tense and corrected where necessary.

8. Technical Corrections:

8a. Page 1368, Line 4: Line-break should be "cryo-focusing" not "cry-ofocusing".

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[Response]: Corrected.

8b. Page 1372, Line 21: Remove "which is"

[Response]: Removed.

8c. Page 1372, Line 23: "content" should be "contents"

[Response]: Corrected.

8d. Page 1372, Line 27: Change "are" to "were"

[Response]: Done.

8e. Page 1373, Line 17: No comma after TSI in parentheses

[Response]: Removed.

8f. Page 1374, Line 17: Move "filter" to after "(HEPA)"

[Response]: Done.

8g. Page 1377, Line 8: Change "taken" to "collected"

[Response]: Changed.

8h. Page 1378, Line 7: Change "is" to "was"

[Response]: Changed.

8i. Figure 2: Arrows in figure are too small, especially the directional arrows indicating direction of flow from blue/green box. I would suggest adding the caption of mode C1029

state (e.g. 'Standby/backflush') to the figure itself. This would make glancing at the figure much more meaningful. Also, 'particle' is misspelled in the last sentence of the caption.

[Response]: The figure was changed to enhance clearness. The spelling was corrected.

8j. Figure 4: Shift fit coefficients in last two lines of figure legend one tab to right so that the equal signs line up vertically. Remove "the different" from last sentence of caption.

[Response]: The figure and caption was changed accordingly.

8k. Figure 5: Remove '26.11.08 11:18' from legend unless it is crucial for the reader to know the time/date the experiment was performed. Also add "expected" to retention time of alkanes so that the reader knows that this was not measured by the authors.

[Response]: The time was removed from the legend. The retention times of the alkanes, as stated in the caption and in the manuscript, were actually measured by the authors during the calibration measurement of the GC/MS-FID system. These measurements were used to determine the linear retention indices for nopinone, myrtanal and myrtenol to further verify/strengthen the identification of these compound.

8l. Figures 6, 7: Time should start with zero and be in minutes. This would make reading the graph much more useful (again, it does not matter that the experiment took place on 28.11.2008).

[Response]: We changed Figure 6 as suggested. Figure 7 was exchanged in favour for a scatter plot. Please refer to the authors response to the comments of Anonymous Referee #1 for item 28.

8m. In general, please be consistent with font size and whether a box around legend

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is show. Figure 8, for example, has no box, while all the other figures do.

[Response]: Figures were change to be consistent.

References:

Tobias, H. J., Kooiman, P. M., Docherty, K. S. and Ziemann, P. J.: Real-time chemical analysis of organic aerosols using a thermal desorption particle beam mass spectrometer, *Aerosol Science and Technology*, 33, 170-190, 2000.

Williams, B., Goldstein, A., Kreisberg, N., and Hering, S.: An insitu instrument for speciated organic composition of atmospheric aerosols: Thermal desorption aerosol gc/ms-fid (TAG), *Aerosol Sci. Technol.*, 40(8), 627–638, 2006.

Interactive comment on *Atmos. Meas. Tech. Discuss.*, 3, 1361, 2010.