

Author's response to AMT review - first stage (Response to reviewer Jochen Rudolph) Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2017-412, 2017

“Preparation and analysis of zero gases for the measurement of trace VOCs in air monitoring”

5 Jennifer Englert, Anja Claude, Alessia Demichelis, Stefan Persijn, Annarita Baldan, Jianrong Li, Christian Plass-Duelmer, Katja Michl, Erasmus Tensing, Rina Wortman, Yousra Ghorafi, Maricarmen Lecuna, Guido Sassi, Maria Paola Sassi, Dagmar Kubistin

The authors are grateful to Jochen Rudolph for his time and effort in evaluating this manuscript and for his constructive suggestions for improvements. Concerning the proposal to publish this work as a technical note, we do not oppose but would like to leave this decision to the editor. All points made by the reviewer are addressed on the following pages.

Referee #1: Jochen Rudolph

Comment 1:

Introduction: The part describing the principle of several methods for generation of hydrocarbon free air should be removed. The presented methods are not complete. For example, “pressure swing” methods and use of clean oxygen and nitrogen to prepare clean air are not mentioned, charcoal is by far not the only adsorbent used for air purification. Furthermore, the information provided is essentially textbook level and only vaguely connected to the methods tested here and no information about the performance of the different methods is provided, which greatly reduces the usefulness of this part for the reader. The explanations about the importance of clean gases in general should be removed, the paper contains no information about purifying gases other than removing non-methane VOC from air.

Response:

We followed the suggestion of referee #1 and removed the part describing several methods for generating hydrocarbon free air. Instead we just listed the different principles which are applicable for atmospheric monitoring with some references for the interested reader.

25 p.2 lines 8ff: “Commonly used purification technologies in atmospheric monitoring include but are not limited to gas purifiers based on inorganic media (e.g. Conte et al., 2008) or activated carbon (Van Osdell et al., 1996; Sircar et al., 1996), metal catalysts (Liotta, 2010; Heck et al., 2009) and photocatalytical techniques (Debono et al, 2013; Huang et al., 2016).”

We did not remove the explanations about the importance of clean gases in general, as we think this is important information for understanding the need of pure zero gases and the research content of this paper. The reviewer is right that no other gas matrix than VOC-free zero air was tested for this paper. But the method described for testing this gas could be applied for other gas matrices like pure nitrogen as well as for other target analytes.

Comment 2:

The description of steps [1] to [4] (beginning of 2.2) should be clarified. A clear description (and distinction) of “what was done” and “what was determined” at this point will allow to shorten the later (often indirect) explanations of how data were evaluated and what was found. For example, it is later explained that (as far as I understand) step one included measurements using different volumes of zero air. This needs to be explained right away (including the volumes used, after all this is the experiment chapter).

Response:

We agree and inserted a more detailed description of what was done in step 1 to 4. We moved the explanation of the method for determining internal blanks of the analysis system from chapter 3.1 into this chapter (2.2).

p.4, lines 3ff:

10 **“2.2 Experimental measurement setup and procedure**

For comparability a common procedure was applied by the three labs. Sample volumes used were dependent on the requirements of the different analysers. In general, sample volumes between 400 ml to 3000 ml were applied. For all following steps a repetition of five consecutive runs was recommended:

- 15 [1] In step 1, the in-house zero gas was measured directly by the analysis systems to quantify its VOC impurities. Additionally all analysis systems were checked for internal blanks. Identification of internal blanks, i.e. system artefacts, and discrimination of them from zero gas impurities was done by measuring different sample volumes of the in-house zero gas. A proportional relationship of the detector response with the sampled volume is expected for impurities in the in-house zero gas, whereas for GC system internal blanks the detector response is expected to be independent of the sample volume. The tested in-house zero gas was used for the following steps of the experiment
- 20 (2 to 4).
- [2] In the next step the in-house zero gas from step 1 was supplied to one specific purifier to quantify the VOC impurities originating from the purifier itself.
- [3] In the third step the efficiency of VOC removal of the tested purifier was checked by supplying a VOC mixture and measuring the outcome of residual VOCs.
- 25 [4] In the last step the incoming VOC concentration for step 3 was checked by supplying the same preparation of VOC mixture directly to the analysis system (no purifying).”

Comment 3:

30 *The procedures used to generate (and as to determine the quality, see comment 7) “in house zero air” has to be given in the experimental section.*

Response:

Information about in-house air is given in Section 2, p5, line 6:

“For the in-house zero gas DWD used compressed and dried (water content ~ 1000 µmol/mol) ambient air purified by a palladium catalyst. VSL and INRIM used synthetic air cylinders (grade 6.0, water content < 0.5 µmol/mol, total hydrocarbons content < 0.05 µmol/mol). “

The quality can be further derived from the separate in-house zero air measurements in Table 1. We added some words to the results section 3, p.6 line 6ff:

“Before assessing the purifier efficiency, in-house zero gas quality and internal blanks were determined by step one of the measurement procedure (Sect. 2.2.). The results for VSL and DWD are shown in the first two columns in Table1. In the DWD in-house zero air all substances were below the detection limit, with exception for benzene (4pmol/mol), acetaldehyde (124pmol/mol) and acetone (52pmol/mol). The observed peaks were independent of the sample volume (see supplemental Fig. S1and S2), and showed the characteristics of an internal blank and are not regarded as an impurity of the DWD in-house zero gas. For VSL, blank values were observed at a level of 20-50 pmol/mol for several alkanes (Table 1The results are consistent within the specification of the used synthetic air grade 6.0 allowing up to 50nmol/mol of hydrocarbons. This highlights the need for further purification of commercial cylinders to assure low impurities levels for high quality zero air. With the INRIM system, which focused on OVOCs only, no blanks were observed in their in-house zero gas.”

Further, we added a plot into the supplemental (Fig. S1, supplemental p.7):

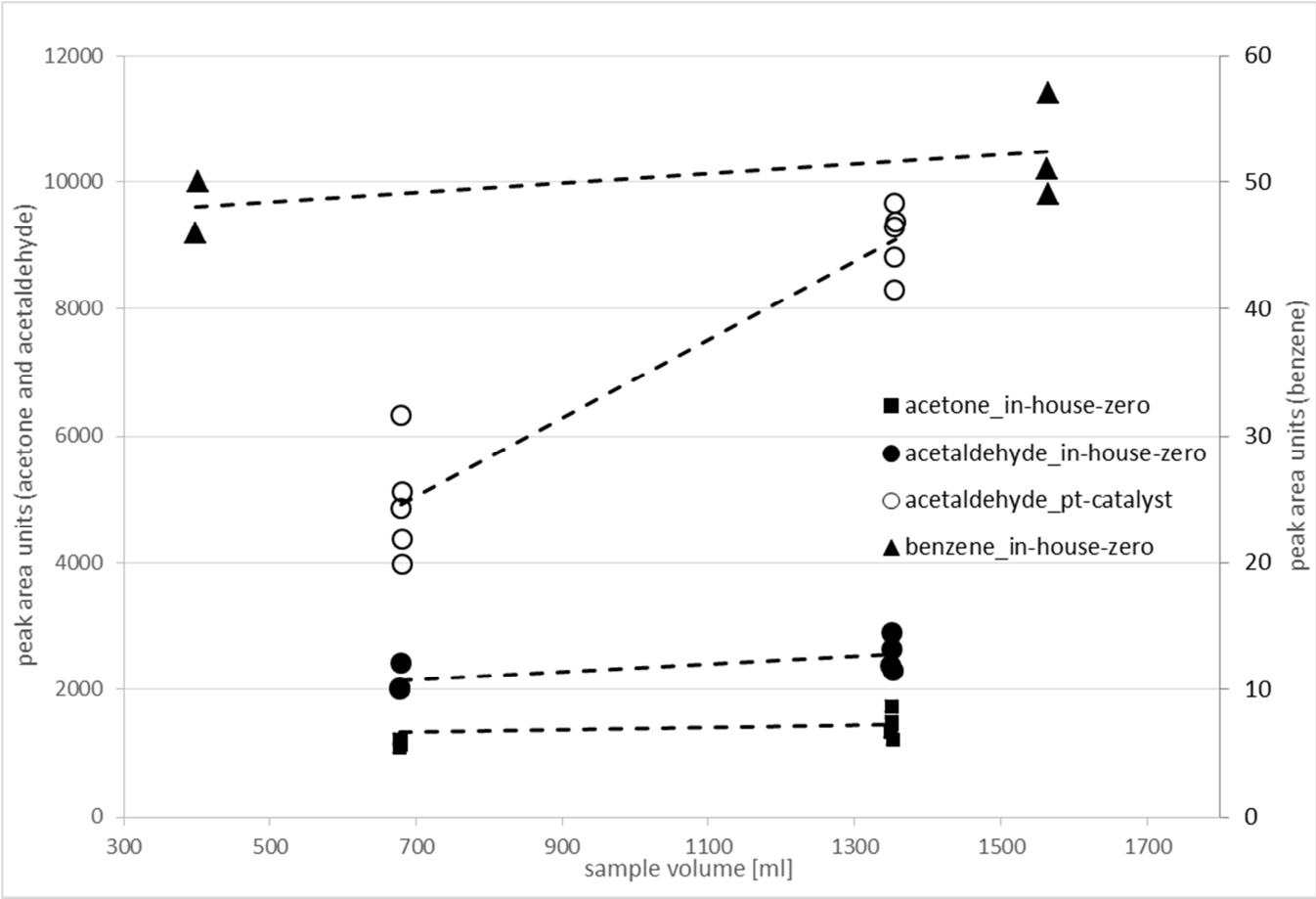


Figure S1. Peak areas for benzene, acetaldehyde and acetone observed at two different sample volumes: 1590ml and 390ml for benzene and 680ml and 1350ml for acetaldehyde and acetone. All peaks observed in the directly measured in-house zero air (filled symbols) are independent of the sample volume. For acetaldehyde however, peaks observed in samples of in-house zero gas which was flushed through the platinum catalyst at an early stage of usage (empty circles) are strongly affected by the sample volume.

Comment 4:

Subchapters 3.1 and 3.2 should be moved to a supplement. The typical reader of such a paper will not be interested in the details of peak evaluation and DL determination and knowledge of these details is not necessary to understand the results presented here.

Response:

We agree and moved chapter 3 to the supplement.

Comment 5:

Table 1 should be removed. Its content is only very indirectly connected to the subject of the paper and the information presented has already been discussed in numerous publications and textbooks.

Response:

We moved Table 1 into the supplement together with Section 3. Even though it sums up textbook information we think it valuable to keep it in the supplement with Section 3.

Comment 6:

Table 2 should be moved to a supplement. The detection limits (as far as they are relevant) are obvious from Table 3 (I assume the <... indicates a concentration below the lower detection limit, a footnote explaining this should be added). If concentrations are above the DL the DL has little relevance for the findings presented here.

Response:

We moved Table 2 to the supplement. In Table 3 (is now Table 1 after this revision) the "<..." indeed are concentrations below the detection limit. This is already explained in the header of the table.

Comment 7:

Table 3 should be separated into 3 tables (NMHC, Terpenes, OVOCS) which will avoid the many "empty" boxes. The "saved space" should be used to present the residual VOC concentrations for the use of "in-house zero gas" as feed for the

gas purifier as well as the VOC level in the “in-house” zero air without gas purifier. In my opinion, this information is of high interest for potential readers. What are the residual levels of VOC when using a “standard” combination of clean air supply and a given gas purifier. A detail for Table 3 (and some other places in the paper), the number of significant digits presented should be consistent with the accuracy of the given data.

5 Response:

We separated Table 3 like suggested and inserted the information about VOC concentrations in the in-house zero gas (step1 of the experiments) and VOC impurities released by the purifiers (step 2 of the experiments). We did not change the digits of the result data. As detection limits are in low pmol/mol range for the measured compounds these are the results we obtained from the raw data.

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Comment 8:

The finding that catalysts have to be “cleaned” by running for some time is not new, this part should be moved to a supplement. A useful information (if available) would be the time constant (if available) at which the different contaminants are removed from the catalysts, which would be relevant for justifying the two hour conditioning time used here.

15 Response:

We removed this information from the conclusion part but left it in the experimental section. With the low time resolution of the gas chromatography technique used for the experiments of this paper we are unfortunately not able to provide the requested time constant. Typically in two hours we gain two gas chromatography measurements taking into account the time needed for sample enrichment and analysis with separation of the different VOCs on capillary columns. So, we just can give the information that zero gas was sufficiently clean (below detection limit) after two hours of flushing and heating the catalysts in this case. To specify the time constant a high time resolution instrument like a PTR-MS would be of an advantage.

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Comment 9:

25 *Figure 6 and the detailed discussion of the results of Figure 6 should be moved to the supplement. Breakthrough as well as memory effects and dependence of the efficiency of adsorbents on humidity are nothing new. Moreover, it seems from Figure 7 that (even when averaging) giving a value for efficiency for the adsorbent is arbitrary since the result will (least for some of the < C5) depend on the duration of exposure to a feed with a given VOC level as well as the history of exposure to feeds with different VOC levels. The low efficiency for most <C5 HC and the high variability of efficiency for most C4 HC is*
30 *evident from Table 3.*

Response:

We agree and moved Figures 6 and 7, and parts of the discussion to the supplement.

Comment 10:

All chromatograms should be moved to a supplement. From the chromatograms I could not gain any important insight which is not already evident from Table 3.

We moved the chromatograms from Fig. 2-5 to the supplement.

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Comment 11:

In the supplement the authors should provide linear regression information for the results obtained for step [1] in chapter 2.2 (sampling of different volumes) for compounds where the peak areas are not below the DL. This will allow readers interested in details to distinguish between “system blanks” and signals depending on sampled volume.

10 Response:

We added a respective plot for benzene, acetaldehyde and acetone to the supplemental (p.7)

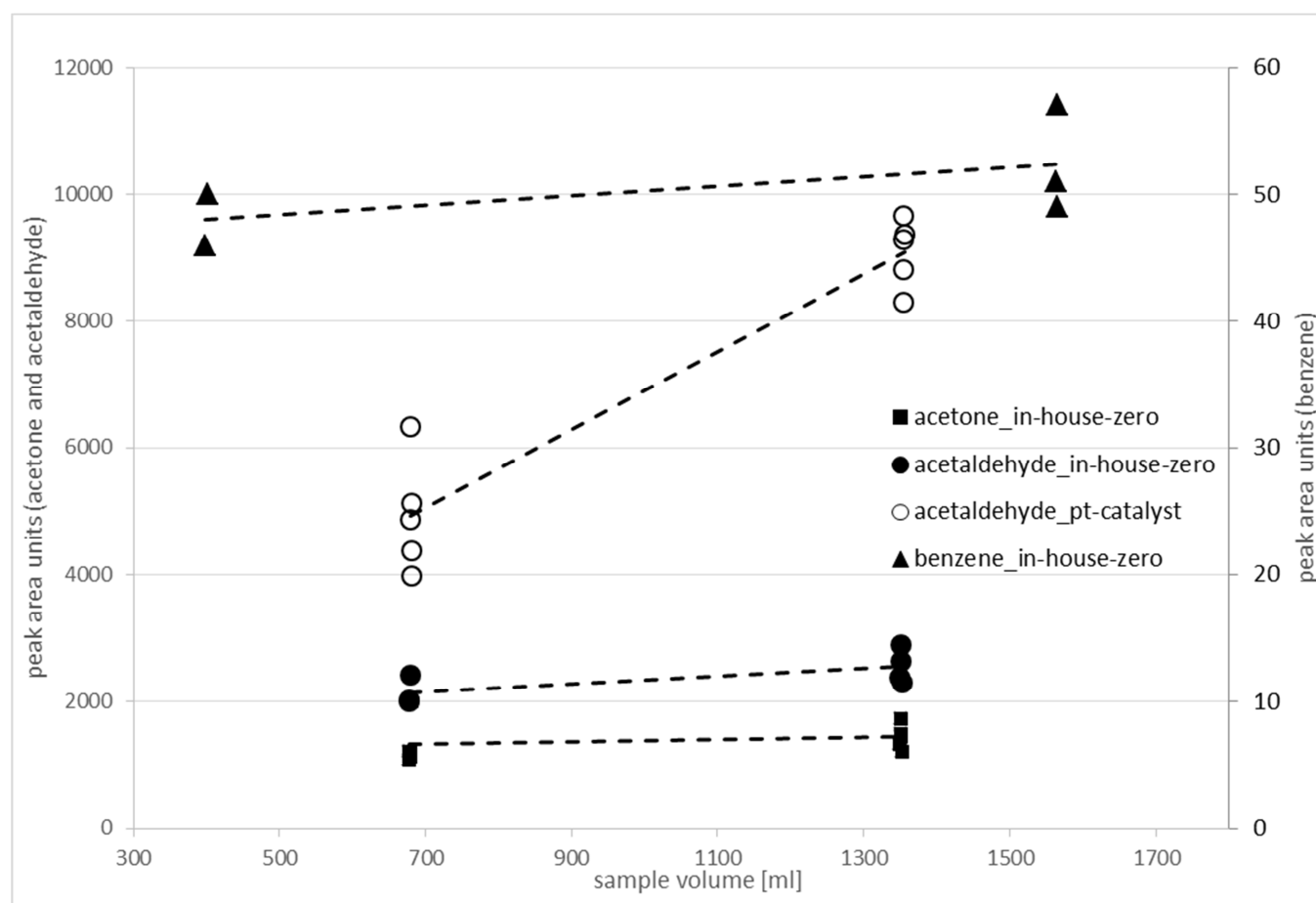


Figure S1. Peak areas for benzene, acetaldehyde and acetone observed at two different sample volumes: 1590ml and 390ml for benzene and 680ml and 1350ml for acetaldehyde and acetone. All peaks observed in the directly measured in-house zero air (filled symbols) are independent of the sample volume. For acetaldehyde however, peaks observed in samples of in-house zero gas which was flushed through the platinum catalyst at an early stage of usage (empty circles) are strongly affected by the sample volume.

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Comment 12:

Conclusions: The first paragraph is mostly a summary of the introduction. It also contains statements that cannot be derived from the results presented here (e.g. the importance of monitoring blanks). This paragraph should be removed.

Response:

5 We have modified the conclusion; parts of the first two paragraphs were removed or moved to the last paragraph (underlined below):

p.10, line 1ff:

“Two tested catalysts in this study were able to remove a large range of different VOCs. High mole fractions up to 50 nmol/mol were purified and residual concentrations were below the detection limits of the systems going down to less than 1 pmol/mol for NMHCs.

10 The tested adsorption cartridge was not suitable to remove light NMHCs (C₂ to C₄). There was a breakthrough behaviour of these compounds which was not constant. Also, VOC memory effects were observed. To characterise these effects repetition of measurements (> 5) would be of an advantage. However, it removed heavier VOCs, OVOCs and monoterpenes. An advantage of the adsorption cartridge is the lack of electricity. It could be a good alternative for applications where the breakthrough of light VOCs is of no relevance. A big disadvantage is the high influence of humidity on the lifetime of this
15 kind of purifier. The tested model in this study was only adequate for use with very dry air up to maximum 1 µmol/mol water content. With this awareness it is highly recommended to enquire the maximum applicable water content of the used gas from the manufacturer of a purifier.

Finally, zero gas is often produced by compression of ambient air which constitutes a complex matrix with residual humidity. The cleaning process to receive high purity zero gases is a challenge to any purifying system. It is highly important to explicitly examine a gas purifier for its intended application. Tests should be done at the given conditions, e.g. the same flow rates and the same gas matrix with special focus on given target component concentrations and humidity. For the tests, measurement systems with adequate detection limits are essential. Potential internal blanks have to be detected and well characterised. Their long-term behaviour has to be controlled, especially for the enduring use in air quality monitoring stations”.

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