Author´s response to AMT review - first stage (Response to reviewer and short comments) 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"

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 both reviewers for their time and effort in evaluating this manuscript and for their suggestions for improvements. All points made by the reviewers are addressed on the following pages. We also thank the short comment author for his useful note. We have combined the specific responses to all comments in the following. Concerning the proposal to publish this work as a technical note, we do no oppose but would like to leave this decision to the editor.

Referee #1

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.

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:

"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:

[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 (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.

[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:

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):

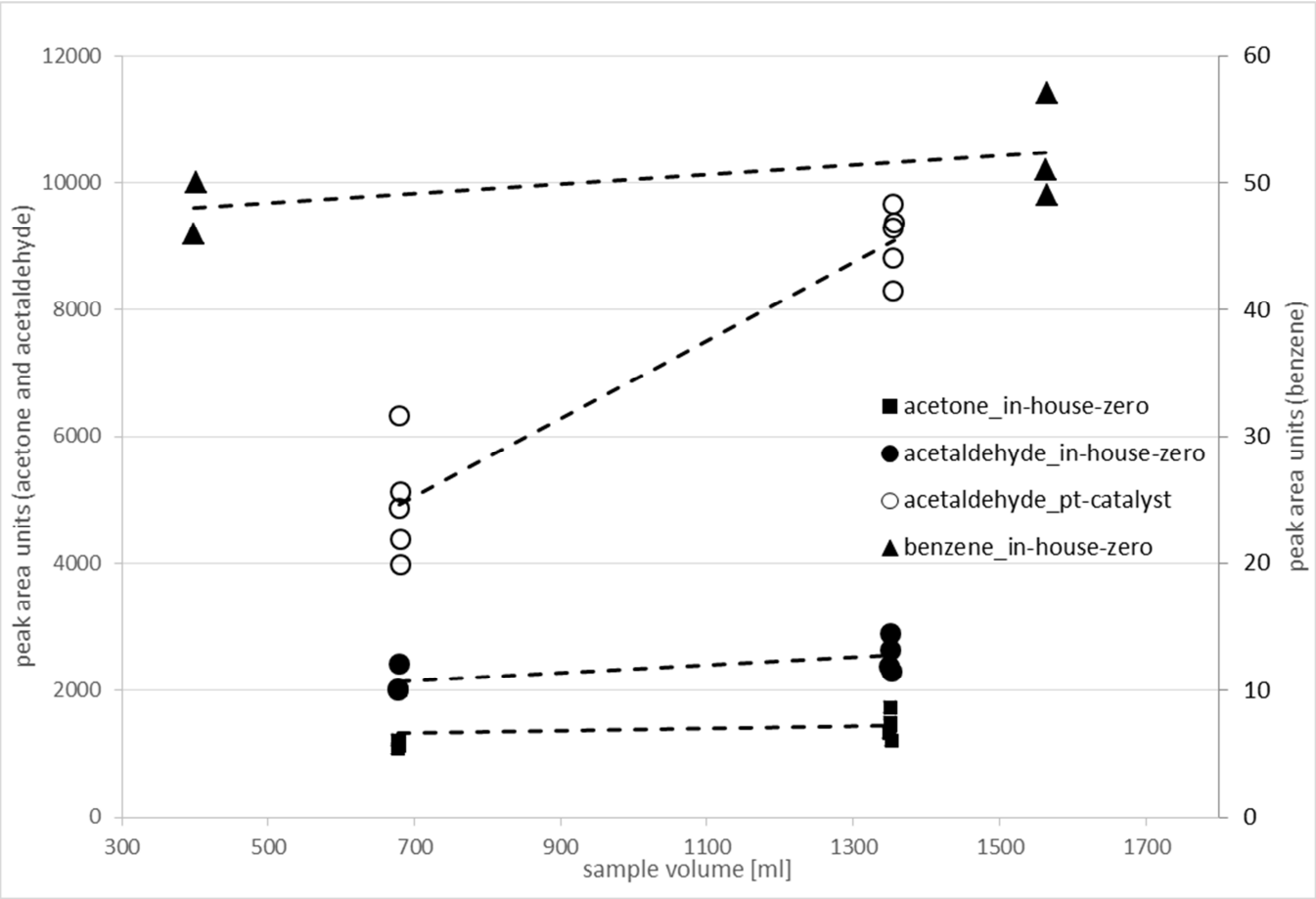

Figure S1. Peak areas for benzene, acetaldehyde and acetone observed at two different sample volumes: 1590ml and 390ml for benzene and 680ml and 1350ml for acetaldehyde and acetone. All peaks observed in the directly measured in-house zero air (filled symbols) are independent of the sample volume. For 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 3.1and 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.

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.

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.

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.

Comment 9:

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 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.

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.

Response:

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

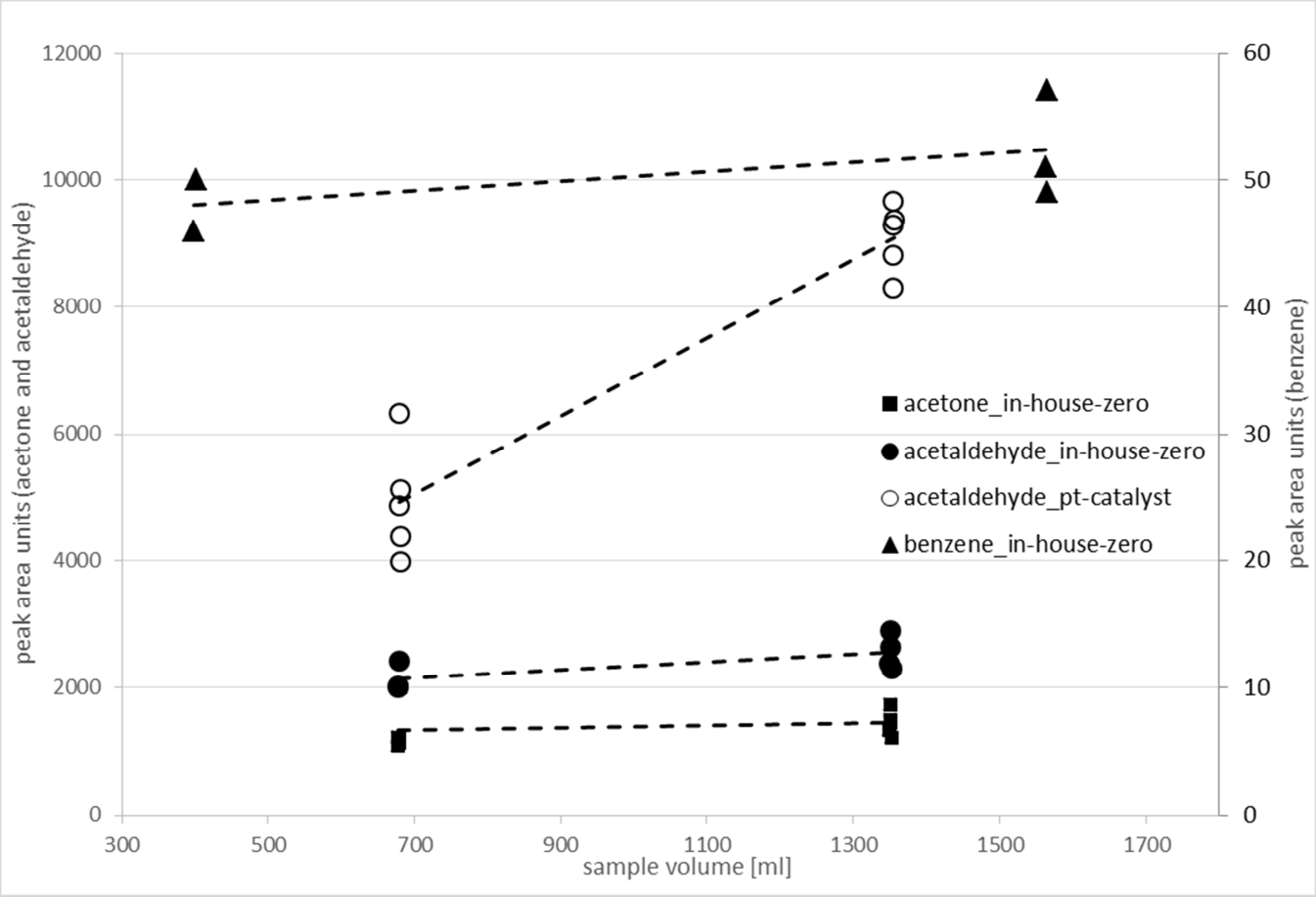

Figure S1. Peak areas for benzene, acetaldehyde and acetone observed at two different sample volumes: 1590ml and 390ml for benzene and 680ml and 1350ml for acetaldehyde and acetone. All peaks observed in the directly measured in-house zero air (filled symbols) are independent of the sample volume. For 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.

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 her (e.g. the importance of monitoring blanks). This paragraph should be removed.

Response:

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.

The tested adsorption cartridge was not suitable to remove light NMHCs (C_2 to C_4). 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 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. <u>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.</u> Their long-term behaviour has to be controlled, especially for the enduring use in air quality monitoring stations".

Referee #2

Comment 1:

In summary, the results presented are suitable to be published in AMT but as a Technical Note after streamlining the results presented together with an Electronic Supplement. The experiments conducted are tests with already available techniques for purifying air and thus no clear innovative approach is presented which may merit a publication as a full paper. The "introduction" should be condensed with finally leading to the research questions. The author team should justify their selection of the used purifying techniques.

Response:

We now provide a supplement and the introduction was condensed. We removed the part describing several methods for generating hydrocarbon free air. Instead we just listed the different principles with some references for the interested reader.

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) andphotocatalytical techniques (Debono et al, 2013; Huang et al., 2016) ."

The research question we address is the application of suitable gas purifiers for ambient VOCs monitoring stations – a respective line was added into the last paragraph of the introduction, where the selection of purifying techniques was justified:

p.3 lines 1-3:

" In this study, three purifiers were selected to test their removal efficiency of a defined amount of VOCs to be applicable for ambient air monitoring stations. An adsorption cartridge with an inorganic media was selected for low-cost zero gas production without the need of electricity. In addition, the commonly used catalytic technique with an infinite lifespan has been tested for two types of catalyst."

Comment 2:

In the "experimental" part all commercial suppliers of materials should be listed.

Response:

The supplier of the adsorption cartridge did not agree to have the trademark published. We added a remark referring to this in p.3 line 6-7:

"…specified by the manufacturer (it was agreed not to publish the name and trademark)."

Comment 3:

Details of the analytical systems used in the experiments should be reported in the supplement, likely in a Table.

Response:

We provided the requested table with information on the used gas chromatography instruments in the supplement (Table S1).

Comment 4:

The "data analytical details" chapter should be moved to the supplement as well as Table 1 and Table 2. A summary of the applied techniques is sufficient as part of the experimental/method section.

Response:

We moved chapter 3 together with Table1 1and 2 to the supplement. In section 2, p.4, lines 1-2 we added the applied method how detection limits were derived:

"Detection limits for all systems were determined using IUPACs method based on the Neyman–Pearson theory of hypothesis testing (IUPAC, 1995, Section S2 in the supplement)."

Comment 5:

The "results and discussion" part should focus on the performance of the purifying systems only. Additional information should be moved to the supplement. Figures 2 and 3 can be skipped. Figures 4, 5 and 6 may also be skipped or moved to the supplement, Figure 7 should be moved to the supplement.

Response:

We condensed the chapter and moved Figures 2 to 7 to the supplement.

Comment 6:

In the "conclusion" part of the paper please avoid duplication of the abstract and focus on aspects users of air purification systems should consider.

Response:

We shortened the conclusion and focused on the main points of the paper:

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.

The tested adsorption cartridge was not suitable to remove light NMHCs (C_2 to C_4). 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 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".

Short comment by Marta Doval Miñarro

This paper presents the performance of several gas purifiers to produce zero gas for measuring VOCs. The availability of high purity and certified zero gases for atmospheric measurements is one of the issues that has to be tackled in order to achieve further reductions in measurement uncertainty. The information presented in this paper is interesting and it moves towards this direction; however, I miss in the Introduction section a reference to previous work in this field. There are not many papers dealing with this topic so I find it necessary to cite the few of them in order to properly contextualise the manuscript of the authors. Some of the references I miss:

Miñarro et al. (2014) Zero gas reference standards. Analytical Methods 8, 15, 3014-3022.

Haerri H.P (2009) Trace gas analysis for the evaluation of zero air generators. Accreditation and Quality Assurance 14, 12, 647-654.

Response:

We inserted the references suggested. Thanks for this important suggestion.

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

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Abstract. Air quality observations are performed globally to monitor the status of the atmosphere, its level of pollution and to assess mitigation strategies. Regulations of air quality monitoring programmes in various countries demand high precision measurements for harmful substances often at low trace concentrations. These requirements can only be achieved by using high quality calibration gases including high purity zero gas. For volatile organic compound (VOC) observations, zero gas is defined being hydrocarbon free like purified air, nitrogen or helium and is essential for the characterisation of the measurement devices and procedures, for instrument operation as well as for calibrations. Two commercial and one self-built gas purifiers were tested for their removal efficiency of VOCs following a standardised procedure. The tested gas purifiers included one adsorption cartridge with an inorganic media and two types of metal catalysts. A large range of VOCs was investigated including the most abundant species typically measured at air monitoring stations. Both catalysts were able to remove a large range of VOCs whilst the tested adsorption cartridge was not suitable to remove light compounds up to C_4. Memory effects occurred for the adsorption cartridge when exposed to higher concentration. This study emphasises the importance to explicitly examine a gas purifier for its intended application before applying in the field.

1 Introduction

Volatile organic compounds (VOCs) play an important role in atmospheric chemistry. They are key substances in the tropospheric ozone and secondary organic aerosol formation, affecting human health and climate. Main sources of VOCs are biogenic processes (e.g. plant metabolism) and anthropogenic activities (e.g. fossil fuel or industrial solvents emissions). The variety of VOCs is enhanced by subsequent oxidation processes. Main sink process is the oxidation by the daytime cleaning agent, the hydroxyl radical (OH). Thus, the abundance of VOCs alters the self-cleaning capacity of the atmosphere and the removal of less reactive pollutants like carbon monoxide and the greenhouse gas methane.

VOC concentrations in the background atmosphere are typically at low levels of few pmol/mol up to some nmol/mol demanding for measurement techniques with very high sensitivities e.g. gas chromatography systems (GC) or state-of-the-art proton-transfer-reaction mass spectrometers (PTR-MS). High quality zero gases are needed for determining their background signals and for performing system checks e.g. blank, memory effect and leak detections. Additionally, zero gases are essential for dynamic calibration methods since VOC calibration standards are often generated either by permeation or diffusion into a controlled zero gas stream (ISO6145-10, 2002 and ISO6145-8, 2005, Demichelis, 2016). An alternative is the dynamic dilution of a highly concentrated static standard gas mixture with a zero gas stream using mass flow controllers (ISO6145-7, 2009). Besides, zero gases are applied for the operation of GC systems as carrier gas of GC columns and for fuel gas of flame ionisation detectors. The need for high purity zero gases is further driven by more stringent quality objectives from the WMO GAW programme (WMO GAW Report No. 171, 2007) or the ACTRIS network (Hoerger et al., 2015; ACTRIS, 2014). These networks aim to observe the long-term trends of VOC concentrations in the background atmosphere. Though, few studies with a detailed characterisation of the performance of gas purifiers have been conducted so far (e.g. Miñarro et al., 2016; Haerri, 2009).

A high quality zero gas is defined by containing insignificant concentrations of the target components to be measured. In particular for VOC measurements, the hydrocarbon compounds of the zero gas have to be below the detection limit of the instruments. The highest quality commercial zero gases in gas cylinders (air, nitrogen or helium grade 5.5. or higher) are specified to contain below 10 to 100 nmol/mol total hydrocarbons. These levels far exceed the needed purity for a zero gas in atmospheric background monitoring with concentrations down to some pmol/mol. To reduce the amount fraction of VOCs, different gas purification technologies are available. Preparation has to be simple, fast and low-cost and applicable at remote unattended stations. Furthermore, the preferred method is dependent on the VOCs present in the gas to be purified, the gas matrix and maintenance interval. 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) ~~and "pressure swing" methods~~.

In this study, three purifiers were selected to test their removal efficiency of a defined amount of VOCs to be applicable for ambient air monitoring stations. An adsorption cartridge with an inorganic media was selected for low-cost zero gas production without the need of electricity. In addition, the commonly used catalytic technique with an infinite lifespan has been tested for two types of catalyst.

2 Experimental

2.1 Tested purifiers and analytical methods

The tested commercial adsorption cartridge was based on inorganic media not being further specified by the manufacturer (it was agreed not to publish the name and trademark). Clean dry air (CDA) was stated to be used as the input gas with a maximum flow rate of 50 slpm. No additional heating of the purifier was required. The manufacturer claimed the removal of condensable organics below 1 pmol/mol without any further specifications of those compounds. Maximal incoming contaminant concentrations were indicated with 10 µmol/mol. The lifetime was stated with one year at nominal flow rate with 1 µmol/mol inlet challenge of moisture. The second purifier was a commercial catalyst with 3 - 5 % palladium oxide (manufacturer SAES Pure Gas, Model PS15-GC50-CDA-2). It was specified for CDA with a maximum flow rate of 3 slpm. Its operation temperature was 350 °C. Elimination of methane and NMHCs below 1000 pmol/mol was stated by the manufacturer. Maximum inlet impurities were 2 µmol/mol total hydrocarbons. At the rated flow of 3 slpm and at rated working temperature the manufacturer stated an infinite lifespan of the catalyst without the need of regeneration. The third purifier was a home-made metal catalyst built by the German Meteorological Service (Deutscher Wetterdienst, DWD). It consisted of a stainless steel tubing (1 inch diameter) with a length of 1 m filled with aluminium oxide pellets with 0.5 % platinum (Heraeus, Germany). The tubing was heated to 400 °C and was built in an aluminium profile box filled with perlite for thermal insulation. A stainless steel mesh (25 µm) at the end of the tubing was used for particle protection of the subsequent instruments.

The performance of the purifiers was tested by detecting residual VOC concentrations in the zero gas with gas chromatography (GC) systems (Table S1, supplemental information). Prior to GC analysis VOC fractions were pre-concentrated either by adsorbent materials or cryogenically cooled glass beads. Subsequently, the VOCs were thermally desorbed from these traps and separated in one or more capillary columns of the GC. For detection, flame ionisation detectors or mass spectrometers were deployed. Five different GC systems were used: two for non-methane hydrocarbons (NMHCs) operated by DWD (Hoerger et al., 2015, Plass-Duelmer et al., 2002) and the Dutch Metrology Institute (VSL), one for monoterpenes by DWD (Hoerger et al., 2015) and three for oxygenated VOCs (OVOCs) by DWD, VSL and the Istituto Nazionale di Ricerca Metrologica (INRIM) (Demichelis et al.,2016). A large range of VOCs was investigated including the most abundant species typically measured at air monitoring stations as well as acetonitrile (see Table ~~2~~1).

Detection limits for all systems were determined using IUPACs method based on the Neyman–Pearson theory of hypothesis testing (IUPAC, 1995, Section S2 in the supplement).

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 ~~in~~ between 400 ml to 3000 ml were applied. ~~-~~For all following steps a ~~R~~repetition of five consecutive ~~measurements~~runs was ~~5 runs~~recommended:

[1] In step 1, t~~T~~he in-house zero gas was measured directly by the analysis systems. ~~With this test, the labs~~ to quantify its VOC impurities. Additionally all analysis systems were checked for internal blanks. ~~cChecked for internal blanks of their analysers system. Furthermore, with the same~~and ~~testschecked the in-house zero gas used for the following steps of the experiment (2 to 4) could bewas checked for~~ and in-house VOC impurities~~ and. for internal blanks of their analysers (VOC amounts) by measuring the in-house zero gas (5 runs). The in-house zero gas was measured directly by the analysis systems.~~ 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 sample volumes used were dependent on the requirements of the different analysers. In general, sample volumes in between 400 ml to 3000 ml were applied~~ The tested in-house zero gas was used for the following steps of the experiment (2 to 4).

[2] In the next step the in-house zero gas from step 1 was supplied to ~~the~~one specific purifier ~~under test~~. ~~By this way it was~~to ~~c~~~~Check ed for~~quantify the VOC impurities originating from the ~~examined tested~~ purifier itself. ~~by measuring the in-house zero gas flowing through the tested gas purifier (5 runs).~~

[3] In the third step the ~~Determine the~~ efficiency of VOC removal of the tested purifier was checked by supplying a ~~measuring a~~ VOC mixture ~~flowing through the tested gas purifier (5 runs).~~ and measuring the outcome of residual VOCs.

[4] In the last step the~~Verify the~~ incoming VOC concentration for step 3 was checked by supplying ~~measuring~~ the same preparation of VOC mixture directly~~without gas purifier (5 runs).~~ to the analysis system (no purifying).

After step four a repetition of steps one and two was optional for the labs but is advisable to monitor the status of the set-up.

A unified flow rate of 1 slpm was applied being within the specification of each purifier model. The two catalysts were heated and flushed with zero gas for at least two hours before starting the experiments. This was needed to reduce VOC impurities originating from the catalysts being freshly installed. The experimental set-up is shown in Figure 1.

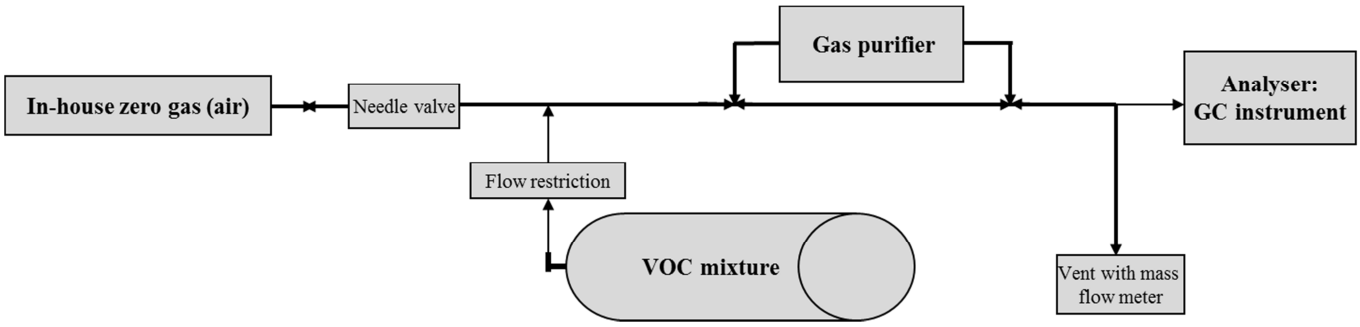

Figure 1. Experimental set-up for testing the purifier performance.

Test mixtures with different VOC mole fractions were produced by dynamic generation methods, e.g. dilution of high concentrated static VOC mixtures in cylinders (Figure 1) or diffusion methods (Demichelis, 2016). Following test mixtures were supplied: NMHCs at 1.2, 5 and 50 nmol/mol, monoterpenes at 1.2 nmol/mol, OVOCs from 10 to 70 nmol/mol and acetonitrile at 10 nmol/mol. 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).

3 Results and discussion

To ensure comparability between the participating groups the same measurement procedure described in Sect. 2.2 has been applied. All GC chromatograms were analysed visually. Peaks of VOCs in the chromatograms were integrated by GC software and mole fraction were subsequently determined for each single measurement and average mole fractions and standard deviations, respectively, were derived for each measurements series (Table 1~~3~~).

Before assessing the purifier efficiency, in-house zero gas quality and internal blanks were determined by step~~s~~ 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 1~~). This is~~ The results are consistent within the specification of the used synthetic air grade 6.0~~, which~~ allowing~~s~~ up to 50 nmol/mol of hydrocarbons. This ~~but also~~ highl~~e~~ig~~hgt~~ts the need for further purification of commercial cylinders ~~in order to yield a hig quality zero air~~to assure low impurities levels for high quality zero air ~~.~~. With the INRIM system, which focus~~s~~ed on OVOCs only, -no blanks were observed in their in-house zero gas. ~~-~~

Subsequently, VOC release of the purifier itself was checked (step 2 in Sect 2.2). E.g. the platinum catalyst showed acetaldehyde impurities scaled with the sample volume (Fig. S1 and S3~~1~~). By flushing the catalysts for two hours with zero air (1l/min), the relevant impurities were below the detection limits.

After characterisation of the blank values and purifier impurities, the purifier efficiencies were determined (step 3 in Sect. 2.2). In Table 1, the results of all labs are summarised. Both tested catalysts (palladium as well as platinum) removed NMHCs and monoterpenes to concentrations below the detection limits which were generally below 10 pmol/mol.

All tested OVOCs were removed to mole fractions below 100 pmol/mol by the tested purifiers. Only the lab of INRIM detected residuals of methanol and acetone above the detection limits of their system. These OVOCs are generally prone to adsorption and desorption effects on surfaces in the instruments and therefore subject to high measurement uncertainties and blank values. Consequently, detection limits are usually elevated as seen for the DWD and VSL systems (Table 1). For the INRIM system, however, rather low detection limits were indicated and no blank values were reported. Nevertheless, the fact that for both types of purifiers and for varying input concentrations (20-70 nmol/mol) similar mole fractions for methanol and acetone (Table 1) were detected by INRIM implies the possibility that here system blanks or artefacts were observed. Unfortunately, a repetition of the blank measurements was not performed at INRIM with this set-up after this experiment and no further conclusions can be drawn.

For the adsorption cartridge a breakthrough of light NMHCs (from C_2 to C_4) was observed by all testing labs (Table 1). At a sample flow of 1 slpm ethane, ethene, propane, propene, isobutane, ethyne, n-butane, trans-2-butene, 1-butene and 1,3-butadiene were not efficiently removed.

Except for ethane, the removal efficiency is not consistent for different input concentrations. For ethene, propane, propene, ethyne, trans-2-butene and 1-butene the 1.2 nmol/mol input was less efficiently purified compared to the higher inputs. Several reasons are possible: First, these results were produced by two different labs which tested the same model of cartridge but not the identical cartridge. The two cartridges may show different behaviours. Furthermore, DWD responsible for the 1.2 nmol/mol experiment used a zero gas for the tests which had a much higher humidity (water content ~ 1000 µmol/mol) than the test gas from VSL which came from a commercial synthetic air cylinder (water content < 0.5 µmol/mol). The humidity level has an impact on the purifier lifetime. The manufacturer of the adsorption cartridge stated that the

humidity of the DWD zero gas would saturate this kind of cartridge almost immediately (personal communication). It should only be used with very dry air with at maximum 1 µmol/mol water content. A closer look into the individual results of the measurements series of the VOC mixture running through the adsorption cartridge reveals another effect: The breakthrough behaviour is affected by the repetition of measurements and changes with each iteration (Fig. S6 in the supplement). This is reflected in high standard deviations for some substances in Table 1.

All C_5 and heavier NMHCs, monoterpenes and acetonitrile were removed to values below the detection limits of the systems. For OVOCs, see the discussion of the catalyst results above.

Table 1. Summarized results for the in-house zero gas (step 1 of the experiments) and for the purifier tests supplying zero air (step 2) and supplying a VOC mixture (step 3). Mean values of 5 subsequent measurements and absolute standard deviations (± pmol/mol). The different amounts of VOCs the purifiers were supplied with are indicated in nmol/mol. Testing labs are specified. The detection limits of the measurement systems are indicated in the case of zero measurements (< detection limit). Residual amounts above the detection limits of the systems are marked in light grey. Values above 100 pmol/mol are marked in dark grey. N.a. = not analysed.

Residual NMHCs [pmol/mol]:

Purifier:	**In-house zero gas (air)**		**Adsorption cartridge**					**Palladium catalyst**					**Platinum catalyst**	
Testing lab:	**DWD**	**VSL**	**DWD**		**VSL**			**DWD**		**VSL**			**DWD**	
Supplied amount of NMHCs [nmol/mol]:	**0**	**0**	**0**	**1.2**	**0**	**5**	**50**	**0**	**1.2**	**0**	**5**	**50**	**0**	**1.2**
ethane	< 3	< 20	< 3	1063 ± 7	< 20	4855 ± 70	42715 ± 419	< 3	< 3	< 20	< 20	< 20	< 3	< 3
ethene	< 7	< 21	< 7	967 ± 7	< 21	997 ± 231	7535 ± 505	< 7	< 7	< 21	< 21	< 21	< 7	< 7
propane	< 2	26 ± 11	< 2	992 ± 17	< 10	2764 ± 108	24513 ± 1674	< 2	< 2	< 10	< 10	< 10	< 2	< 2
propene	< 3	< 11	< 3	703 ± 93	< 11	< 11	26 ± 4	< 3	< 3	< 11	< 11	< 11	< 3	< 3
isobutane	< 1	< 10	< 1	769 ± 392	< 10	3483 ± 1264	2258 ± 1979	< 1	< 1	< 10	< 10	< 10	< 1	< 1
ethyne	< 10	< 15	< 10	928 ± 17	< 15	278 ± 73	2708 ± 538	< 10	< 10	< 15	< 15	< 15	< 10	< 10
n-butane	< 1	35 ± 12	< 1	675 ± 411	< 11	3475 ± 649	1232 ± 951	< 1	< 1	< 11	< 11	< 11	< 1	< 1
trans-2-butene	< 1	< 4	< 1	51 ± 39	< 4	< 4	< 4	< 1	< 1	11 ± 1	< 4	< 4	< 1	< 1
1-butene	< 2	< 4	< 2	195 ± 125	< 4	< 4	< 4	< 2	< 2	10 ± 1	< 4	< 4	< 2	< 2
isobutene	n.a.	< 6	n.a.	n.a.	< 6	< 6	< 6	n.a.	n.a.	< 6	< 6	< 6	n.a.	n.a.
cis-2-butene	< 1	< 3	< 1	5 ± 4	< 3	< 3	< 3	< 1	< 1	< 3	< 3	< 3	< 1	< 1
isopentane	< 1	24 ± 6	< 1	6 ± 9	< 3	< 3	< 3	< 1	< 1	< 3	< 3	< 3	< 1	< 1
n-pentane	< 1	29 ± 7	< 1	< 1	< 8	< 8	< 8	< 1	< 1	< 8	< 8	< 8	< 1	< 1
1,3-butadiene	< 1	< 1	< 1	< 1	432 ± 43	535 ± 183	619 ± 61	< 1	< 1	< 5	< 5	< 5	< 1	< 1
trans-2-pentene	< 1	< 1	< 1	< 1	< 13	< 13	< 13	< 1	< 1	< 13	< 13	< 13	< 1	< 1
1-pentene	< 1	< 1	< 1	< 1	< 3	< 3	< 3	< 1	< 1	< 3	< 3	< 3	< 1	< 1
2-methylpentane	< 1	21 ± 4	< 1	< 1	< 6	< 6	< 6	< 1	< 1	< 6	< 6	< 6	< 1	< 1
n-hexane	< 1	< 1	2 ± 0.5	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1	< 1
isoprene	< 2	< 4	< 2	< 2	< 4	< 4	< 4	< 2	< 2	< 4	< 4	< 4	< 2	< 2
n-heptane	< 1	49 ± 22	< 1	< 1	< 4	< 4	< 4	< 1	< 1	< 4	< 4	< 4	< 1	< 1
benzene	4 ± 2	< 3	< 2	< 2	< 3	< 3	< 3	< 2	< 2	< 3	< 3	< 3	< 2	< 2
2-2-4-trimethylpentane	< 1	< 4	< 1	< 1	< 4	< 4	< 4	< 1	< 1	< 4	< 4	< 4	< 1	< 1
n-octane	< 1	< 5	< 1	< 1	< 5	< 5	< 5	< 1	< 1	< 5	< 5	< 5	< 1	< 1
toluene	< 6	< 4	< 6	< 6	< 4	< 4	< 4	< 6	< 6	< 4	< 4	< 4	< 6	< 6
ethylbenzene	< 5	< 7	< 5	< 5	< 7	< 7	< 7	< 5	< 5	< 7	< 7	< 7	< 5	< 5
m-, p-, o-xylene	< 5	< 6	< 5	< 5	< 6	< 6	< 6	< 5	< 5	< 6	< 6	< 6	< 5	< 5
1-3-5-trimethylbenzene	< 6	< 10	< 6	< 6	< 10	< 10	< 10	< 6	< 6	< 10	< 10	< 10	< 6	< 6
1-2-4-trimethylbenzene	< 2	< 16	< 2	< 2	< 16	< 16	< 16	< 2	< 2	< 16	< 16	< 16	< 2	< 2
1-2-3-trimethylbenzene	< 2	n.a.	< 2	< 2	n.a.	n.a.	n.a.	< 2	< 2	n.a.	n.a.	n.a.	< 2	< 2

Table 1. Continued for monoterpenes and OVOCs and acetonitrile.

Residual monoterpenes [pmol/mol]:

Purifier:	**In-house zero**	**Adsorption cartridge**		**Palladium catalyst**		**Platinum catalyst**	
Testing lab:	**DWD**	**DWD**		**DWD**		**DWD**	
Supplied amount of m.terpenes [nmol/mol]:	**0**	**0**	**1.2**	**0**	**1.2**	**0**	**1.2**
alpha-pinene	< 4	< 4	< 4	< 4	< 4	< 4	< 4
myrcene	< 3	< 3	< 3	< 3	< 3	< 3	< 3
3-carene	< 2	< 2	< 2	< 2	< 2	< 2	< 2
cis-ocimene	< 2	< 2	< 2	< 2	< 2	< 2	< 2
p-cymene	< 2	< 2	< 2	< 2	< 2	< 2	< 2
limonene	< 2	< 2	< 2	< 2	< 2	< 2	< 2
camphor	< 2	< 2	< 2	< 2	< 2	< 2	< 2
1,8-cineole	< 5	< 5	< 5	< 5	< 5	< 5	< 5

Residual OVOCs and acetonitrile [pmol/mol]:

Purifier:	**In-house zero gas (air)**			**Adsorption cartridge**						**Palladium catalyst**						**Platinum catalyst**	
Testing lab:	**DWD**	**VSL**	**INRIM**	**DWD**		**VSL**		**INRIM**		**DWD**		**VSL**		**INRIM**		**DWD**	
Supplied amount of OVOCs [nmol/mol]:	**0**	**0**	**0**	**0**	**10**	**0**	**10**	**0**	**20 to 70**	**0**	**10**	**0**	**10**	**0**	**20 to 70**	**0**	**10**
methanol	< 77	< 110	< 3	< 77	< 77	< 110	< 110	n.a.	67 ± 11	< 77	< 77	< 110	< 110	n.a.	73 ± 10	< 77	< 77
acetaldehyde	124 ± 19	< 110	n.a.	< 84	< 84	< 110	< 110	n.a.	n.a.	< 84	< 84	< 110	< 110	n.a.	n.a.	< 84	< 84
ethanol	< 26	< 120	< 11	< 26	< 26	< 120	< 120	n.a.	< 11	< 26	< 26	< 120	< 120	n.a.	< 11	< 26	< 26
acetone	52 ± 15	< 80	< 11	< 31	< 31	< 80	< 80	n.a.	57 ± 10	< 31	< 31	< 80	< 80	n.a.	63 ± 9	< 31	< 31
MEK	< 2	< 180	n.a.	< 2	< 2	< 180	< 180	n.a.	n.a.	< 2	< 2	< 180	< 180	n.a.	n.a.	< 2	< 2
methacrolein	n.a.	< 110	n.a.	n.a.	n.a.	< 110	< 110	n.a.	n.a.	n.a.	n.a.	< 110	< 110	n.a.	n.a.	n.a.	n.a.
acetonitrile	< 6	n.a.	n.a.	< 6	< 6	n.a.	n.a.	n.a.	n.a.	< 6	< 6	n.a.	n.a.	n.a.	n.a.	< 6	< 6

4 Conclusions

~~The suitability of a gas purification system depends on the requirements for the zero gas. In a zero gas for air monitoring application, the target components to be measured have to be zero or below the detection limits of the measurement systems. 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. A possible blank change over time has to be monitored.~~

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.~~ It was shown that it is important to conduct a cleaning procedure of the catalysts as they can emit some VOCs in early stages of use. Consequently, they were flushed with zero gas and held at operation temperature for at least two hours without connecting them to the measurement instruments. Subsequently, it is necessary to check the purity of the catalysts output again. Only this way it is guaranteed to have a working set up to characterise the purifier efficiency correctly.~~

The tested adsorption cartridge was not suitable to remove light NMHCs (C_2 to C_4). 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 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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