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Atmospheric Measurement Techniques Discussions

Interactive comment on "Calibration of an airborne HO_X instrument using the All Pressure Altitude based Calibrator for HO_X Experimentation (APACHE)" *by* Daniel Marno et al.

Anonymous Referee #2

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In this paper Marno et al. demonstrate the first results from the "APACHE" chamber designed to calibrate and characterise the Mainz airborne "HORUS" OH and HO2 instrument. The results show the APACHE chamber operating on the ground under controlled conditions to calibrate HORUS, but it is designed also to be operated on the HALO aircraft when OH and HO2 measurements will be made, in order to calibrate in flight.

The development of a device to calibrate for OH and HO2 measurements in flight is a very difficult challenge, not only does the sensitivity of the instrument vary with a change in the pressure and temperature sampled (which changes with altitude),and also the level of water vapour, but also the losses between the point of OH and HO2 generation in the calibrator and sampling by HORUS change also (there would be losses also for ambient OH and HO2 which are to be measured). For the former, the change in sensitivity owing to changes in parameters with altitude after the HORUS inlet can be experimentally determined via the calibration – but in this paper these are investigated through calculations also. For the latter, i.e. losses in OH from the point of generation (lamp) and the HORUS inlet need to be characterised experimentally – and understood. CFD calculations are used to simulate the flowfield within APACHE for comparison with experiment.

The description of a device to generate known concentrations of OH and HO2, and its characterisation and comparison with simulations, given the range of parameters, is complex. Likewise the sensitivity of the instrument measuring OH and HO2 and how this varies with sampling pressure is also complex – and so naturally this paper is complex and many parameters have to be explained and how they change with pressure explained. However, this is critical, as OH and HO2 are highly reactive and can be lost both in the gas-phase and at surface. The authors have made the paper fairly clear – as the characterisation is quite complex – but some further clarity is needed. The experiments appear to have been carefully performed, and many of my comments are aimed to help improving clarity for the reader.

It is not clear from the paper whether the APACHE/HORUS device has been used in flight already, as this reports experiments done in a controlled environment on the ground – and perhaps something about how it performs in flight would be useful to include, and comparison with the ground performance. The paper is an impressive piece of work – and the APACHE/HORUS is quite a feat of engineering and the thorough characterisation of APACHE and HORUS is critical to give confidence in the OH and HO2 measurements from HORUS on HALO. The paper is suitable for AMT, and the development of a calibration source for use inflight for OH measurements is very important, and a considerable achievement. There is a lot covered in this paper, but

some further details/clarifications are needed in some places. See comments below.

More specific comments.

Abstract.

A key result is that the two actinometric approaches agree fairly well, and as well as the average it would be good also to give the level of agreement also. Say what the two approaches are. What pressure is relevant for the value stated, as you say “depending on pressure”, which is not clear?

Stated what the two approaches are, their values, and agreement in the form of zeta score. We have removed the mention of pressure as the actinic flux of the lamp is not pressure dependent, this information is discussed at greater length in the text. Not relevant here in the abstract.

Although the paper is about APACHE and its characterisation, I think readers will want to know what the sensitivity is of HORUS determined with APACHE. Could the expected C factors be stated for OH and HO2, and the derived limits of detection, and how these are predicted to vary with altitude, also be given in the abstract.

The overall accuracy of the calibration ought to be stated also in the abstract from the use of APACHE. This is given in some detail in the paper but there is nothing here. A few more numbers summarising actual performance needed in the abstract.

We have included sensitivity values and the calibration accuracy. Regarding the limits of detection we have included a figure and discussion at the end of the paper, describing how they changing during flight.

Also, “controlled environment” is a bit unclear, please make clear that this is on the ground, rather than results being presented of APACHE used under “a controlled environment” on the aircraft in flight.

We have stated here that calibrations with APACHE were performed in the lab.

Introduction.

46. The referencing is rather selective, please also include Juelich and Leeds LIF references (zeppelin and aircraft measurements also). For CIMS include some Eisele group references also (and subsequent including Mauldin/Cantrell which have also flown).

Included these references

Figure 1. The APACHE shown here is for the controlled environment on the ground – make clear in the figure caption. Looking at Figure 2, the left hand side of APACHE would be a bit different when on the aircraft? (no inflow from mixing blocks?)

We do not characterize the inlet shroud, but the HORUS instrument starting at the inlet(IPI Nozzle). In APACHE we provide a homogenous flow profile with a characterized OH profile to HORUS.

96, replace “being” with “is”

Replaced “being” with “is”.

107. Is the 0.9 to 1.5 ms-1 in APACHE over the pressure range the same as the flow velocity at the same pressure when sampling on the aircraft. In line 132 the “choke” on the aircraft nacelle is used to lower the flow velocity to < 21 ms-1, but not clear if < 21 ms-1 means it will be similar to the 0.9-1.5 ms-1 as in the controlled experiments on the ground? < 21 ms-1 could cover a wide range.

We have looked into periods during take-off and landing where there are large changes in flow speed (1 to 12 m s^{-1}) within the shroud and we find no change in our signal that is attributable to flow speed changes across the IPI nozzle. Therefore, there is no uncharacterized loss, at a detectable level, occurring at the IPI Nozzle when flow speeds are 0.9-1.5 m s^{-1} in APACHE when compared to 21 m s^{-1} during flight.

124 – say also there is a critical orifice at the end of the IPI, this was not clear (and not labelled in Figure 2).

Improved the labelling in figure 2.

There is both a HORUS inlet, and a IPI critical orifice, and I think the presence of these two needs to be clearer. In figure 2 I suggest, that both the HORUS inlet and also the IPI critical orifice have a label. Also both "IPI orifice", "HORUS inlet" and "IPI critical orifice" are used. In line 128, is "IPI orifice" the "HORUS inlet" which samples from APACHE, or the "IPI crictical orifice" which is between the IPI and the 2 fluorescence cells? I think the former as the choke point is then mentioned which slows the flow from the aircraft speed to a slower flow in APACHE?

The IPI nozzle/ inlet is not a critical orifice. The critical orifice sits between IPI itself and the first detection cell. The choke point is at the end of the inner inlet shroud. We have changed the labelling throughout the paper to ensure consistency.

132. "sample velocity of HORUS", this means the flow within APACHE at which HORUS sampled perpendicularly? Is 44-53 ms-1 what is expected on the aircraft? Figure 2. label the critical orifice in the IPI and also HORUS inlet for clarity (as discussed above).

This means the sample flow speed within IPI ranged between 44-53 ms-1 during flight. We have also include at the end of this paragraph a statement explaining that the location of the critical orifice allows HORUS to sample (~ 3 - 17 sL min^{-1}) from the central flow that is moving through IPI (~ 51 - 230 sL min^{-1}) . The excess flow is removed via a perforated ring that surrounds the base of the critical orifice cone evacuated by a blower. All discussion in section 2.3 is regarding parameters and occurrences during flight. We have also included "during flight" statements here to emphasize we are talking about processes happening in and around HORUS when airborne. We have also adjusted the labelling in Figure 2 (see above).

144. As an IPI is used, it would be worth mentioning OH-WAVE (on to off resonance) and OH-CHEM, otherwise not clear of the purpose of the IPI. All the experiments performed here are OH-WAVE – presumably results of OH-CHEM in a controlled environment (to show all OH removed etc.) will be discussed in another paper. The IPI is present here but not used.

We have included the OH-WAVE and OH-CHEM discussion here. IPI was operated during calibrations as it would have been during flight as it does impact the overall sensitivity. But, as you have indicated, the inflight performance of IPI with regards to scavenging efficiency and OH-CHEM in flight will be discussed in a different publication. For this paper OH-CHEM is not the focus.

149. Again the referencing of papers is selective to a couple of groups only who use LIF.

We have included primary references that discuss directly the OH absorption spectrum. We have left the LIF references because at this point we are only discussing HORUS as a LIF instrument.

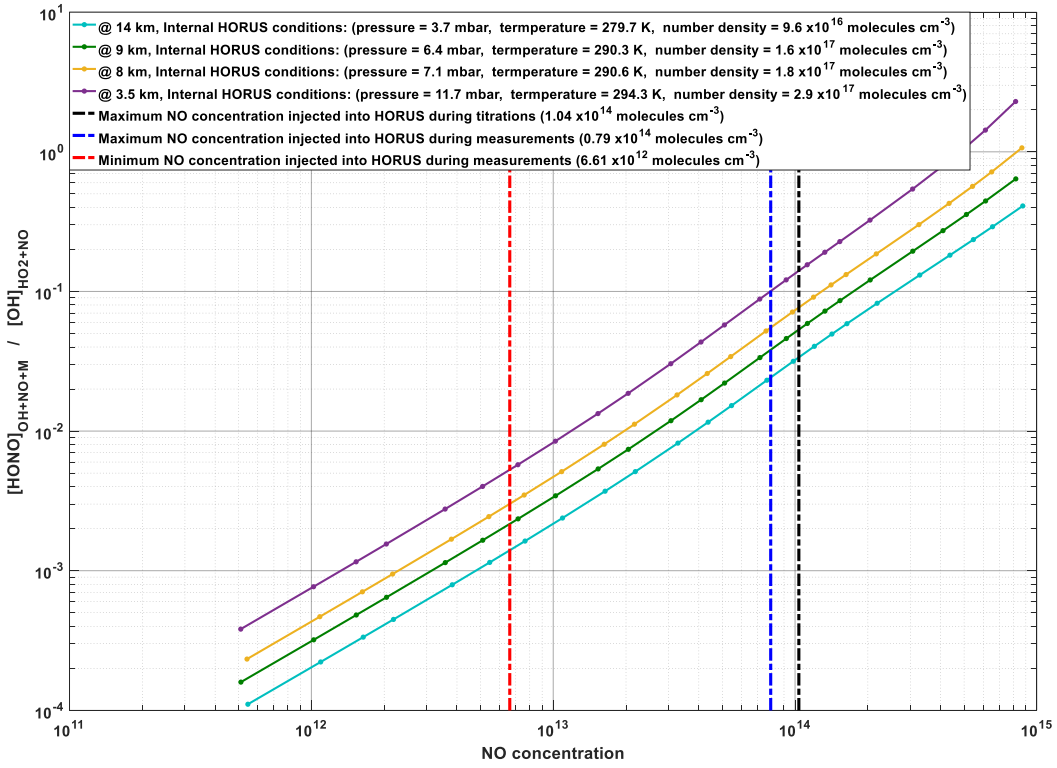
153. Quantitative conversion is mentioned here. can a % be given, as it is not possible

to achieve 100% owing to OH+NO + M = HONO + M meaning that not all of the HO2 conversion to OH remains as OH. What is the % that is achieved here? What flow of NO is added?

We have calculated the internal HONO formation in our instrument using the caaba/mecca box model initializing with HO2 and NO at the corresponding low pressure conditions experienced in flight. Note that here any reference to [OH] is in regards to OH formed from the reaction of HO2 with NO. The following figure shows the fractional HONO concentrations formed compared to the formed OH concentrations at different flight altitudes i.e. [HONO] from the reaction $k_{OH+NO+M}$[NO][OH][M] divided by [OH] from k_{HO2+NO}[HO_2][NO]. This is to show at flight altitudes of 14 km, 9 km, 8 km and 3.5 km what percentage of OH formed from HO_2 + NO undergoes further reaction forming HONO internally within HORUS. The black dotted-dashed line is the maximum NO concentration (1.04 x10^{14} molecules cm^{-3}) injected into HORUS when we are performing in-flight NO titrations. The blue dotted-dashed line shows the maximum NO concentration (0.79 x10^{14} molecules cm^{-3}) injected into HORUS when performing normal measurements, the red dotted-dashed line shows the minimum NO concentration (6.61 x10^{12} molecules cm^{-3}) injected into HORUS. When measuring we toggle our NO injection between these two

concentrations to resolve for RO_2 interference. At the low NO mode any RO2 interference in the signal is heavily suppressed as there is not sufficient NO present in HORUS to promote production of OH via RO2+NO. The higher NO addition has a better signal to noise ratio, however contains a more significant RO2 contribution. To resolve for this we perform NO titrations to resolve our HO2 conversion efficiency at every pressure level and NO concentrations being injected into HORUS. If the high NO injection signal (once corrected for conversion efficiency) is significantly higher (i.e. consistently above by more than the detection limit) than the low NO concentration signal (once corrected for conversion efficiency) we use the signal from the low NO injection mode for atmospheric HO2 measurements. If the high NO injection is not greater than the low NO injection mode (i.e. higher by more than the detection limit of HORUS) we use the high NO injection mode as the signal to noise ratio is better.

When titrating to maximum NO concentrations, 3.3 % of formed OH is converted into HONO at 14 km, 5.4 % of formed OH is converted into HONO at 9 km, 7.8 % of formed OH is converted into HONO at 8 km, and 13.8 % of formed OH is converted into HONO at 3.5 km. These values are the upper limit of HONO formation, as the calculations assume perfect mixing of NO. Additionally in this figure for all altitudes, the low NO injection measurement mode results in less than 0.5 % of the formed OH being lost via HONO formation, which further limits the influence of HONO formation on the HO2 signal.



We have also determined what NO concentrations are required to cause HONO formation to have a detectable influence on the HO2 signal in HORUS, i.e. at what NO concentration does the drop in [OH] (caused by HONO formation) from the maximum titrated OH concentration value exceed the detection limit of the instrument. The table below shows these values:

Altitude (km)	Required NO concentration in HORUS (x10^{14} molecules cm^{-3}), to cause HONO formation to have a detectable influence
14	2.36
9	1.52
8	1.14
3.5	0.82

Note: The NO concentration values quoted here are the lower limit, as these are calculated under the assumption of perfect NO mixing, and taking the minimum characterized detection limit at each altitude level.

This table shows that given the strong pressure dependence of the termolecular reaction that forms HONO, significantly higher NO concentrations (>14% than the maximum titrated concentration) are required to result in a detectable influence on the HO_2 signal via HONO formation. Only at flight altitudes 3.5 km and below can HONO formation have a detectable influence. However, this is only in the cases when we are titrating at these low altitudes which is not the main focus of the OMO-ASIA 2015 campaign in which HORUS took part and this study, where the main focus was and is on altitudes exceeding 8 k km. Even in the high HO2 conversion mode, applying NO in the order of 0.79 $x10^{14}$ molecules cm^{-3}, the HONO formation still falls below this lower limit.

This discussion regarding HONO forms part of a later publication where instrument performance (e.g. OH-CHEM and RO_2 interferences etc) is the focus. Alongside intercomparison with the LIF instrument from Jülich. As the too flew on HALO during the same OMO-ASIA 2015 campaign.

180 “where” small w

Changed to lower case w.

202 – state the size of the critical orifice here. (diameter)

Stated the diameter. 1.4 mm.

Fig 3 – make clear this is a schematic only – rather than any actual performance of the HORUS. Could point to fig 10 where this is shown. Also in the caption, the dotted blue line is for “OH transmission”, whereas in the figure it is “wall loss”.

Corrected the labelling in the figure. Explicitly describe it as a schematic.

219 – split – and 1 in the units

Corrected.

230. Juelich showed that the reaction of H* with O2 did not lead to OH, rather that 100% of H went to HO2, so worth referencing that.

Added Jülich reference.

Table 1. For (IV) CSTR, was the OH generated through UV irradiation of the VOC, or of another precursor? Certainly the decay rate of the VOC is used to determine the OH. Also reference Winiberg et al. 2015 (in the reference list) who used the decay of a hydrocarbon to calibrate for OH in a chamber with a LIF instrument (agreeing well with method I, water paper photolysis).

We have altered the description to match how they are described in the referenced publications. Added Winiberg et al., 2015 to the reference list, including what hydrocarbons were used in that study.

238, “where”, small w

Changed to lower case w.

268. The exhaust from the pumps are at a different pressure when in flight compared to when the exhausts are exposed 1 atm, and this is taken account of by matching to ambient pressures in flight – that is good. Was the same pumping system used for the APACHE testing on the ground as the pumps that will be used (or are used) in flight (which might be 400 Hz pumps from the aircraft power)? (different pumps or pumps used with different motors may have different capacities).

Clarified here that the pumps used during calibrations with APACHE are the same ones that were installed on the aircraft. Also that we used a 3 phase mission power supply unit that provides the same power as on the aircraft.

305 “from the measured...”

Corrected

Figure 6. Can it made clear what is meant by “internal wall of APACHE”, perhaps by cross-referencing to figure 1?

We added a small caption in figure 6 showing what we mean by Internal wall of APACHE

240. The number of sig figs in the error 179 +/-20 does not seem consistent with the sig figs quoted in the errors in brackets for the other units.

Changed the sig figs, so that they match.

361. L, C, and R term are introduced, to make clearer, say which figure they are in – otherwise not clear what referring to.

Clarified in what sense to the L, C and R terms relate to, i.e the streamlines created by the HORUS sample flow in figure 7 and 8.

371. How is 22.2 % loss known for OH and HO2 the inlet? (HORUS inlet). Also, one might expect the loss to be higher for the more reactive OH? Please expand a little.

We have adapted our discussion regarding this variable. According to the model irrespective of pressure the IPI nozzle is 22 %, suggesting that this loss is pressure independent. This value is not utilized any further. The true/characterized/measurable pressure independent loss is now characterized within the pressure independent sensitivity coefficients, which do differ between OH and HO2 at the second axis.

Figure 8. What [H2O] the same for all the pressures? Perhaps add this value.

We have included the water mixing ratio. It was kept constant at 3.2 mmol/mol.

Tabel 2. Right hand column – OH (ppt) also?

Yes pptv. Units added to this column.

395. The IPI critical orifice diameter is given here – but needs to be given earlier as well when this orifice is first introduced. What is the reason that the diameter of this orifice is changed from 1.4 mm to 0.8 mm for the controlled experiments on the ground?

This adaptation was done to enable use to relate the flux of a pre-calibrated penray lamp used on the ground based calibration device to F_β entering APACHE

Adapted and expanded upon the reasoning:

"Since the pre-characterized ground based calibration device is designed to supply only 50 sL min^{-1}, and the sensitivity of airborne HORUS instrument is optimized for high altitude flying, the critical orifice diameter in HORUS was changed from the airborne configuration of 1.4 mm to a 0.8 mm on-ground* configuration. Additionally, the IPI system was switched to passive (i.e. the exhaust line to the IPI blower was capped using a kf 40 flange). This was to adapt HORUS to a mass flow that the ground based calibration device is able to provide and reduces the internal pressure within HORUS (from 18 mbar to 3.5 mbar) to optimize the sensitivity towards OH at ambient ground level pressures (~1000 mbar). The asterisk discerns terms that were quantified when the smaller 0.8 mm critical orifice was used. The calculated instrument on-ground* sensitivity was then used to translate OH and HO_2 concentrations produced by the uv-technik Hg ring lamp into a value for F_β."

439 and 441, another "where" to change

Changed to lower case w

457 and elsewhere, for the units of flux of the light should this be "photons s-1", or even also per unit area?

All flux units have be corrected "photons cm^{-2} s^{-1}).

Section 5 is the results, and quite a few are shown, but compared with the rest of the paper this is fairly short, and the discussion ought to be extended a little to fully exploit the results – what behaviour is therefore expected from aircraft measurements based on the lab work?

We have expanded section 5 into section 4. We have also provided additional context and discussion in the section, including instrument behavior during a typical flight.

495. The losses at the inlet were the same for OH and HO2? Some further discussion of this as might expect OH to lost more.

See response 371.

498 "where"

Page 20 – I found this page difficult to follow, there were a lot of losses discussed, quantified by the alpha values, for various stages of the airflow, e.g. the meanings of equations 16-18 and the discussion around this was confusing.

We have expanded on points here and explicitly stated which alpha term is which and how they are summed to together to acquire the total OH and HO2 pressure dependent transmission terms.

522. Remind reader of the two actinometric methods again (as not much detail was give on these two methods earlier).

Removed this paragraph as it did not sit well within the context of the discussion at this point. We talk about the two actinometric methods again within the conclusions.

Section 5.2 seems to be a series of tables 5-8, and a big figure, and there is virtually no text to go with this? Some further discussion is needed to bring this all together, given it is the main results from the paper. From the C factors presented , e.g. in Table 8, can the LOD of the instrument be presented, and this compared with expected levels of OH and HO2 in the atmosphere during the flights?

We have expanded section 5 into section 4. We have also provided additional context and discussion in the section, including instrument behavior during flight. Including LOD.

Figure 10. For the second row on quenching, link this to an equation used in the text – the label of the plot "Overall quenching" is unclear – and some link to the relevant part of the text is needed. Likewise for the other panels. for the first row, the y label is "Overall sensitivity" which I assume is the C(OH) factors etc., and an explicit link should be made. Likewise ALHPA (total) – refer to the equation where that is in the text.

We have included an equation explaining how the quenching is calculated. Within the text and figure explicit links have been included regarding quenching, C(OH), and $ALPHA_{Total}$.

554. The losses of HOx is discussed for the operation of APACHE during the controlled conditions ground testing. Can this be compared with the expected losses during flight when the flow velocity within APACHE may be a somewhat different (or a statement making clear the velocity within APACHE will be the same as here, or similar).

We have included a figure for inflight conditions to allow for discussion and direct comparison, between controlled ground testing and in-flight losses.

566 "is" missing after "system"

Corrected the statement to "However, in this study, the APACHE calibration system has demonstrated that, within the lab, it is sufficiently capable of calibrating the airborne HORUS instrument across the pressure ranges the instrument had experienced in-flight during the OMO-ASIA 2015 airborne campaign."

567 – experienced in flight is mentioned, but make clear again that the tests presented here are on the ground.

See comment above

568. 17-18% overall uncertainty (1 sigma) – explain why this is "suitable" for a calibration approach. Mention is needed of what the measurements will be used for – to compare with OH and HO2 calculations from an atmospheric model – for which there is an uncertainty also – and a robust comparison can only be done if the measurements are accurate to a certain %, etc.

The overall uncertainty is now 22.1 – 22.6 % (1 sigma). We have adjusted this statement to be a direct comparison to the other calibration methods shown in table 1. As of this study we are not addressing an overarching scientific question, and therefore making no statement regarding the "suitability" of this uncertainty.

"The overall uncertainty of 22.1 – 22.6 % (1σ) demonstrates that this calibration approach with APACHE compares well with other calibration methods described earlier in Table 1. Accurate calibrations of instruments, particularly airborne instruments that have strong pressure dependent sensitivities, are critical to acquiring concentrations of atmospheric species with minimal uncertainties. Only through calibrations can the accuracy of measurements be characterized and allow for robust comparisons with other measurements and with models to expand our current understanding of chemistry that occurs within our atmosphere."

The paper focusses on pressure and water vapour, can any comments be made about the expected change in performance (e.g. losses on surfaces, or lamp) with changes in temperature during flights?

The APACHE system is an on ground setup, built to replicate conditions in flight . It is not installed on the aircraft. However, we have highlighted future developments of APACHE to adapt it for temperature control as well as pressure control.

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