Calibration of an airborne HOX instrument using the All Pressure Altitude based Calibrator for HOX Experimentation (APACHE)

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Abstract. Laser induced fluorescence (LIF) is a widely used technique for both laboratory-based and ambient atmospheric chemistry measurements. However, LIF instruments require calibrations in order to translate instrument response into concentrations of chemical species. Calibration of LIF instruments measuring OH and HO2 (HOX), typically involves the photolysis of water vapor by 184.9 nm light thereby producing quantitative amounts of OH and HO2. For ground-based systems HOX instruments, this method of calibration is done at one pressure (typically ambient pressure) at the instrument inlet. However, airborne HOX instruments can experience varying cell pressures, internal residence times, temperatures, and humidity during flight. Therefore, replication of such variances when calibrating are essential to acquire the appropriate sensitivities. This requirement resulted in the development of the APACHE (All Pressure Altitude-based Calibrator for HOX Experimentation) chamber. It utilizes photolysis of water vapor, but has the additional ability to alter the pressure at the inlet of the HOX instrument thus relating instrument sensitivity to the external pressure ranges experienced during flight (275 to 1000 mbar). Measurements supported by COMSOL multiphysics and its computational fluid dynamics calculations revealed that, for all pressures explored in this study, APACHE is capable of initializing homogenous flow and maintain near uniform flow speeds across the internal cross-section of the chamber. This reduces the uncertainty regarding average exposure times across the mercury (Hg) UV ring lamp. Two different actinometrical approaches characterized the APACHE UV ring lamp flux as 6.3 x 1012 (± 0.9 x 1012) s⁻¹ depending on pressure. Data presented in this study are the first direct calibrations, performed in a controlled environment using APACHE of an airborne HOX system instrument.

1 Introduction

It is well known that the hydroxyl (OH) radical is a potent oxidizing agent in daytime photochemical degradation of pollutants sourced from anthropogenic and biogenic processes thus accelerating their removal from our atmosphere. The hydroperoxyl radical (HO2) also plays a central role in atmospheric oxidation as it not only acts as a reservoir for OH, but is involved in formation of other oxidants such as peroxydes and impacts the cycling of pollutants such as NOX (= NO + NO2) (Lelieveld et al., 2002). Therefore, measurements of OH and HO2 (HOX) within the troposphere are essential in understanding the potential global scale impacts of pollutants in both the present day and in climate predictions. One common HOX measurement method is Laser Induced Fluorescence (LIF) (Stevens et al., 1994; Brune et al.,...
1995; Hard et al., 1995; Martinez et al., 2003; Faloona et al., 2004; Hens et al., 2014; Novelli et al., 2014). However, other methods have been successfully implemented to measure HOX. Chemical Ionization Mass Spectrometry (CIMS) (Sjostedt et al., 2007; Dusanter et al., 2008; Kukui et al., 2008; Albrecht et al., 2019) and Differential Optical Absorption Spectroscopy (DOAS) (Brauers et al., 1996; Brauers et al., 2001; Schlosser et al., 2007) have also been used in the measurement of HOX in the field and in intercomparisons with LIF instrumentation. However, low-atmospheric concentrations of HOX (Schlosser et al., 2009) and potential interferences (Faloona et al., 2004; Fuchs et al., 2011; Mao et al., 2012; Hens et al., 2014; Novelli et al., 2014; Fuchs et al., 2016) can make HOX measurements especially challenging. Airborne LIF-FAGE (LIF-Fluorescence Assay by Gas Expansion) instruments experience large variability in pressure, humidity, instrument internal air density, and internal quenching during flights, which cause a wide array of instrumental sensitivities (Faloona et al., 2004; Martinez et al., 2010; Regelin et al., 2013; Winiberg et al., 2015). Therefore, it is critical to utilize a calibration system that can suitably reproduce in-flight conditions to determine the instrument response to known levels of OH and HO2 to acquire robust HOX measurements. The first stage of our Hydroxyl Radical measurement Unit based on fluorescence spectroscopy (HORUS) inlet is an inlet pre-injector (IPI), used to determine the concentration of background OH interferences by removing atmospheric OH from the signal via addition of an OH scavenger such as propane. IPI draws 50-230 sL min^{-1} depending on altitude and is susceptible to temperature and pressure-driven changes in internal reaction rates and residence times under flight conditions. This has implications for the removal of atmospheric OH in the inlet and for the characterization of background interference signals in HORUS. Therefore, a device capable of providing stable high flows whilst reproducing a wide range of pressures and temperatures is needed in order to calibrate the airborne HORUS instrument.

2 Experimental design and set up

2.1 APACHE design overview

Figure 1 shows the overview of the APACHE system. In front of the APACHE inlet, a series of mixing blocks were installed where multiple dry synthetic air additions were injected into a controlled humidified air supply ensuring thorough mixing of water vapor before being measured by a LI-COR 6262 CO2/H2O (figure 1a). This air is then fed into a large mass flow controller (MFC). The construction of the APACHE chamber itself is shown in figure 1b. The first section contains the diffuser inlet with a sintered filter (bronze alloy, Amtag, filter class 10). This 2 mm thick sintered filter, with a pore size of 35 μm, which initializes a homogeneous flow and further improves the mixing of water vapor before passing over the UV ring lamp (described further in section 4). The water photolysis section contains a low-pressure, 0.8 A, mercury ring lamp (uv-technik, see supplementary, figure S.1) which produces a constant radial photon flux at 184.9 nm, situated 133 mm after the sintered filter and separated from the main APACHE chamber by an airtight quartz window. Between the lamp and the quartz window there is an anodized aluminum band with thirty 8 mm apertures, which blocks all light apart from that going through the apertures, which reduces the amount of UV flux entering APACHE and controls the size of the illuminated area. The HORUS inlet is clamped down 169.5 mm after the photolysis section in such a way that the instrument sample flow is perpendicular to the airflow passing over the inlet. The inlet protrudes 51.5 mm into the APACHE cavity much like it is when installed in the aircraft shroud system (see figure 2), and is made air tight with the use of O-rings. Opposite the HORUS inlet, there is an airtight block attachment containing a series of monitoring systems.
One system being a pitot tube attached to an Airflow PTSX-K 0-10Pa differential pressure sensor (accuracy rating of 1% at full scale, 1σ), which is used to monitor the internal flow speeds within APACHE. A 3 kOhm NTC-EC95302V thermistor is used to monitor the air temperature and an Edwards ASG2-1000 pressure sensor (with an accuracy rating of ± 4 mbar, 2σ) monitors the static air pressure. Additionally, there are two one-quarter inch airtight apertures in the monitoring block that can be opened to enable other instrumentation to be installed.
2.2 Pressure control

For this study, the operational pressure range of APACHE used was 250 – 900 mbar, with precision of ± 0.1% (1σ) and accuracy of ± 2% (1σ) with mass flows ranging from 200 to 990 sL min⁻¹. This was achieved by an Edwards GSX160 scroll pump controlling the volume flow, which resulted in air speeds of 0.9 to 1.5 m s⁻¹ through APACHE at 250 and 1000 mbar respectively at 25 °C, used in combination with a MFC (Bronkhorst F-601A1-PAD-03-V) capable of controlling a mass flow of up to 2000 sL min⁻¹ dictating the mass flow of air entering APACHE and thus controlling the pressure. Although not critical for this study, the operational pressure range of APACHE can be extended by changing the draw speed of the Edwards scroll pump. However, that may cause the flow speeds and potentially the flow speed profiles across the UV ring lamp to vary in between different pressure calibrations.

2.3 The airborne HORUS instrument

The LIF-FAGE instrument developed by our group (HORUS), is based on the original design of GTHOS (Ground Tropospheric Hydrogen Oxide Sensor) described by Faloona et al. (2004) and is described in further detail by Martinez et al. (2010). The airborne instrument is a revised and altered design to perform under conditions experienced during flight and conform to aeronautical regulations. It was primarily developed for installation on the High Altitude and Long Range Research Aircraft (HALO). The system comprises of an external inlet shroud, detections axes, laser system, and a vacuum system (figure 2). Additionally, this is the first airborne LIF-FAGE instrument measuring HOₓ with a dedicated inlet pre injector (IPI) system installed for the purpose of removing atmospheric OH enabling real time measurements and quantification of potential chemical background OH interferences. The airborne IPI system is redesigned to fit within the shroud inlet system, whilst maintaining similar operational features as the on-ground IPI installation (Novelli et al., 2014).

To prevent excessive collisions of OH and HO₂ with the IPI orifice and internal walls, thus limiting losses of HOₓ, the momentum inertia of the air passing through the external shroud system had to be overcome to promote flow direction into the instrument. This was achieved by installing in the shroud a choke point behind the instrument inlet, resulting in air flow to decrease from ~ 200 to < 21 m s⁻¹, which is sufficiently below the sample velocity of HORUS (44 – 53 m s⁻¹). Additionally, it limits non-parallel flows across the HORUS inlet created by variable pitch, roll and yaw changes of the aircraft. As the aircraft changes pitch, roll and yaw, the measured OH variability increases by ± 4.51 x10⁶ cm⁻³ (1σ), which is only 10 to 15 % higher than the natural variability of OH on average. This increase in variability is negligible as represents, depending on internal pressure, 19 to 30 % of the detection limit of the instrument. Both these effects of the external shroud improve the measurement performance by reducing variable wall losses of HOₓ at the HORUS inlet under flight conditions.
As with other LIF-FAGE HO\textsubscript{X} instruments, HORUS measures an off-resonance signal to discern the net OH fluorescence signal. This is achieved by successive cycling of the laser tuning from on-resonance (measuring the total signal of OH fluorescence and the signal originating from other fluorescence and electronic sources), to off-resonance (measuring all the above except the OH fluorescence). The HORUS instrument utilizes the Q\textsubscript{1}(2) transition \(X^2\Pi \frac{3}{2}(v'' = 0) \rightarrow A^2\Sigma^+(v' = 0)\) (Dorn et al., 1995; Holland et al., 1995; Mather et al., 1997).

The net OH signal (\(S_\text{OH}\)) is thus the difference between the on-resonance and off-resonance signals. The OH sensitivity (\(C_\text{OH}\)) and average laser power within the detection axis (\(W_{z1 \text{ pwr}}\)) are then used to calculate the absolute OH mixing ratio (see Eq. (1)). HO\textsubscript{2} is measured indirectly through the quantitative conversion of atmospheric HO\textsubscript{2} to OH by injection of nitric oxide (NO) under the low-pressure conditions within HORUS.

\[ \text{HO}_2 + \text{NO} \rightarrow \text{NO}_2 + \text{OH} \quad (R1) \]

When NO is injected into the instrument, both ambient OH and HO\textsubscript{2} are measured in the second detection axis. The net HO\textsubscript{2} signal (\(S_{\text{HO}_2}\)) in the second axis is therefore derived from subtracting the net OH signal from the first detection axis normalized by the ratio of the OH sensitivities for the two detection axes (\(C_{\text{OH}_2} / C_{\text{OH}}\)) from the net HO\textsubscript{X} signal (\(S_{\text{HO}_X}\)). Then \(S_{\text{HO}_2}\) is corrected by the sensitivity to HO\textsubscript{2} (\(C_{\text{HO}_2}\)) and laser power (\(W_{z2 \text{ pwr}}\)) to reach absolute HO\textsubscript{2} mixing ratio (see Eq. (2)).
\[ \text{OH} = \frac{S_{\text{OH}}}{(c_{\text{OH}} \cdot W_{z1\text{pwr}})} \]  
\[ \text{HO}_2 = \frac{1}{(c_{\text{HO}_2} \cdot W_{z2\text{pwr}})} \cdot \left\{ S_{\text{HO}_2} - \frac{c_{\text{OH}_2}}{c_{\text{OH}}} \cdot S_{\text{OH}} \right\} \]

\(W_{z1\text{pwr}}\) is the laser power in the first detection axis, \(W_{z2\text{pwr}}\) is the laser power in the second detection axis and \(c_{\text{OH}}\) and \(c_{\text{HO}_2}\) are the calibrated sensitivity factors for OH and \(\text{HO}_2\) (cts s\(^{-1}\) pptv\(^{-1}\) mW\(^{-1}\)) respectively. By calibrating using a known OH mixing ratio, the instrument sensitivity \(c_{\text{OH}}\) can be determined by rearranging Eq. (1) to:

\[ c_{\text{OH(\text{cal})}} = \frac{S_{\text{OH(cal)}}}{(\text{OH} \cdot W_{z1\text{pwr}})} \]

The sensitivity of HORUS depends on the internal pressure, water vapor mixing ratios, and temperature, which are subject to change quite significantly during flight. Therefore, further parameterization when calibrating is required to fully constrain the sensitivity response of the instrument at various flight conditions. Eq. (4) shows the terms that affect the sensitivity of the first HORUS axis that measures OH.

\[ c_{\text{OH}}(P, T) = c_0 \cdot \rho_{\text{int}}(P, T) \cdot Q_{\text{IF}}(P) \cdot b_c(T) \cdot W_{z\text{pwr}} \cdot [\alpha_{\text{IPI}}(P, T) \cdot \alpha_{\text{HORUS}}(P, T)] \]

Where \(c_0\) is determined by calibrations and is the lump sum coefficient of all the pressure independent factors affecting the HORUS sensitivity, for example, OH absorption cross section at 308nm, the photon collection efficiency of the optical setup and quantum yield of the detectors, as well as pressure independent wall loss effects (cts cm\(^3\) molecule\(^{-1}\) s\(^{-1}\)). \(\rho_{\text{int}}\) is the internal molecular density. \(Q_{\text{IF}}\) is the quenching effect of \(\text{N}_2, \text{O}_2\) and \(\text{H}_2\text{O}\) occurring inside the detection axis, which is normalized to 1 % water mixing ratio. Both are pressure dependent terms as denoted in Eq. (4). The Boltzmann correction \((b_c)\) has a temperature dependency as it corrects for any OH molecules that enter the HORUS instrument in a thermally excited state and are therefore not measurable by fluorescence excitation at the wavelength used. \(W_{z\text{pwr}}\) is the measured laser power entering the white cell in the detection axis. \(\alpha\) is the pressure dependent OH transmission, which is the fraction of OH that reaches the point of detection. This term is separated for the two-tier pressure conditions present in the instrument. The term \(\alpha_{\text{IPI}}\) represents the correction for pressure and temperature dependent OH loss on the walls within IPI (post pinhole, pre-critical orifice). The term \(\alpha_{\text{HORUS}}\) is the correction for pressure dependent OH loss to the walls within the HORUS detection axes post critical orifice. Whilst the quenching effects, internal densities and Boltzmann corrections can be quantified, and the power entering the measurement cell is measured, the two factors that need to be determined through calibration are \(c_0\) and OH transmission. Once the \(c_0\) coefficient and \(\alpha\) terms are known, the final in-flight measured OH mixing ratio (pptv) is found:

\[ \text{OH} = \frac{S_{\text{OH}}}{(c_0 \cdot \rho_{\text{int}} \cdot Q_{\text{IF}} \cdot b_c \cdot W_{z\text{pwr}} \cdot [\alpha_{\text{IPI}} \cdot \alpha_{\text{HORUS}}])} \]

As depicted in both figure 1b and figure 2, the complete system is calibrated with IPI attached and operating as it did when installed in the aircraft. Therefore, the combined losses of OH within IPI and in the low pressure regime post critical orifice contribute to the overall calibrated \(c_{\text{OH}}\) sensitivity factor in the same way during measurement and calibrations,
meaning that the OH transmission of HORUS can be quantified with both OH transmission terms (\(\alpha_{\text{IPI}} \) and \(\alpha_{\text{HORUS}}\)) combined into one term (\(\alpha_{\text{Total}}\)).

\[
\text{OH} = \frac{S_{\text{OH}}}{(c_0 \cdot \rho_{\text{Int}} \cdot Q_{\text{IF}} \cdot b_c \cdot W_{\text{pwr}} \cdot [\alpha_{\text{Total}}])}
\]  

(6)

Figure 3 shows the graphical representation of the different factors described above and their impact on the overall sensitivity.

![Graphical representation of factors affecting LIF sensitivity.](image)

**Figure 3.** Pressure dependent components affecting LIF sensitivity. Internal density (solid green line), OH transmission (dotted blue line), and quenching (dotted red line). The product of these factors produce the expected pressure dependent sensitivity. (Modified after Faloona et al., 2004).

3  
**Calibration method and theory**

As an overview, table 1 shows common calibration techniques for OH instruments. The APACHE system is based on the production of known quantified and equal concentrations of OH and HO\(_2\) via photolysis of water vapor in pure synthetic air using a Hg ring lamp emitting UV radiation at 184.9 nm.

\[ \text{H}_2\text{O} + \text{hv} \xrightarrow{\lambda=184.9 \text{ nm}} \text{OH} + \text{H}^* \]  

(R2)

\[ \text{H}^* + \text{O}_2 \xrightarrow{} \text{OH} + \text{O}_3 \]  

(R3)

\[ \text{H}^* \xrightarrow{\text{M}} \text{H} \]  

(R4)

\[ \text{H} + \text{O}_2 \xrightarrow{\text{M}} \text{HO}_2 \]  

(R5)

Stable water mixing ratios with a variability of < 2 % were achieved by heating 300 sL min\(^{-1}\) flow of synthetic air to 353 K and introducing deionized water using a peristaltic pump into this heated gas flow causing it to evaporate before entering a 15 L mixing chamber. This prevents re-condensation and humidity spikes when the pump is introducing the water. The humidified gas flow is then diluted (to around 3 mmol mol\(^{-1}\)) and mixed further with additional dry pure synthetic air via a series of mixing blocks to achieve the required and desired stable water vapor mixing ratios. The photolysis of H\(_2\)O has only one spin-allowed and energetically viable dissociation channel at 184.9 nm (Engel et al., 1992), meaning the quantum yield of OH
and H* are unified (Sander et al., 2003). Even though reaction R3 is possible particularly since the H* atoms can carry transitional energies of 0.7 eV at 189.4 nm (Zhang et al., 2000), the fast removal of energy by reaction R4 allows for the general assumption that all H* atoms produced leads to HO2 production. The use of water photolysis as a OH and HO2 radical source for calibration of HOX instruments has been adopted in a number of studies (Heard and Pilling. 2003; Ren et al., 2003; Faloona et al., 2004; Dusanter et al., 2008; Novelli et al., 2014; Mallik et al., 2018). As an example, the factors required to quantify the known concentrations of OH and HO2 during calibrations are shown below:

\[
[OH] = [HO_2] = [H_2O] \cdot \sigma_{H_2O} \cdot F_{184.9 \text{ nm}} \cdot \Phi_{H_2O} \cdot t \tag{7}
\]

Table 1. Various known methods for OH instrument calibrations.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Method</th>
<th>Quoted (1σ) Uncertainty</th>
<th>Limitations</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>(I) Water UV-Photolysis</td>
<td>See section 3.1</td>
<td>10-30%</td>
<td>Dependent on lamp, photon flux measurement, and absorption</td>
<td>(Creasey et al., 2003; Heard and Pilling, 2003; Holland et al., 2003; Ren et al., 2003; Faloona et al., 2004; Smith et al., 2006; Martinez et al., 2010; Mallik et al., 2018)</td>
</tr>
<tr>
<td>(II) Pulsed N2-H2O RF discharge</td>
<td>At low pressure (0.1 Torr); OH and NO produced using a low power RF discharge. Concentrations of NO and OH are closely linked</td>
<td>20%</td>
<td>Requires NO measurement using stable ambient air calibrations</td>
<td>(Dilecce et al., 2004; Verreycken and Bruggeman, 2014)</td>
</tr>
<tr>
<td>(III) Low-pressure flow-tube RF discharge</td>
<td>OH radical production by titration of H atoms with NO2. Known amount of H atoms produced using microwave discharge using low pressure flow tube</td>
<td>30%</td>
<td>Stable ambient air calibrations</td>
<td>(Stevens et al., 1994)</td>
</tr>
<tr>
<td>(IV) Continuously Stirred Tank Reactor</td>
<td>In a CSTR, OH produced through UV-irradiation of specific Hydrocarbon in presence of H2O and NO. Concentration of OH relates to loss of the Hydrocarbon</td>
<td>36%</td>
<td>Time intensive, systematic wall loss of OH in reactor</td>
<td>(Hard et al., 1995; Hard et al., 2002)</td>
</tr>
<tr>
<td>(V) Steady-State O3-alkene</td>
<td>A steady state OH concentration produced from ozonolysis of a known concentration of an alkene</td>
<td>42%</td>
<td>Time consuming, large uncertainties compared to other methods</td>
<td>(Heard and Pilling, 2003; Dusanter et al., 2008)</td>
</tr>
<tr>
<td>(VI) Laser photolysis of Ozone</td>
<td>Photolysis of O3 with 284 nm light producing O(1D). Which then reacts with H2O producing OH</td>
<td>40-50%</td>
<td>Requires large apparatus</td>
<td>(Tanner and Eisele, 1995)</td>
</tr>
</tbody>
</table>

Where in Eq. (7), the OH and HO2 concentrations are a product of photolysis of a known concentration of water vapor [H2O], \( \sigma_{H2O} \) is the absorption cross section of water vapor, 7.22 \(( \pm 0.22) \times 10^{-20}\) cm² molecule⁻¹ at 184.9 nm (Hofzumahaus et al., 1997; Creasey et al., 2000).
$F_{184.9 \text{ nm}}$ is the actinic flux (photons s$^{-1}$) of the mercury lamp used for photolysis, $\phi_{\text{H}_2\text{O}}$ is the quantum yield and $t$ is exposure time. The quantum yield of water vapor photolysis at the 184.9 nm band is 1 (Creasey et al., 2000).

4 APACHE conditions and parametrizations

4.1 Flow conditions

With any calibration device, the flow conditions must be characterized to inform subsequent methods and calibrations. Regarding APACHE, the two main factors to be resolved are (i) how uniform are the flow speed profiles and therefore exposure times in respect to the APACHE cross section, and (ii) the impact of OH wall losses.

To this end, experimental and model tests were performed to determine whether the combination of the sintered filter, and the stainless steel perforated plates and wool arrangement could provide a homogeneous flow. This means that under operation the flow speeds should be uniform along the cross section of APACHE to within the uncertainty of the measurements. This is to ensure that the air masses passing across the lamp have the same exposure times irrespective of where they are in the cross section. Additionally, model simulations can provide an indication of, as a function of APACHE pressure, the development and scale of boundary air conditions where air parcels experience extended contact time with the interior walls of APACHE, and so have pronounced OH wall losses. This highlights potential flow conditions where there is sufficient time between the photolysis zone and the HORUS inlet to allow APACHE boundary air to expand into and influence the OH content of the air being sampled by HORUS.

4.1.1 Flow speed profiles

During calibration, the pressures within the HORUS instrument had to be controlled and monitored to replicate the inflight conditions. The APACHE chamber pressure is equivalent to the inflight pressure in the shroud where the HORUS system samples. The pressure of the detection axes depends on the pressure at the inlet and the efficiency of the pumps. For IPI however, the airflow through it is dependent on the pressure gradient between the shroud and the ambient pressure at the IPI exhaust or alternatively the APACHE pressure and pressure in front of the XDS 35 scroll pump (post IPI blower). During the campaign, the exhausts of all blowers and pumps of the HORUS system were attached to the passive exhaust system of the aircraft and were thus exposed to ambient pressure. Therefore, in the lab and throughout the calibrations, the pressure at the exhaust for every blower and pump involved in the HORUS instrument was matched to the respective in-flight ambient pressures by attaching a separate pressure sensor, needle valve and XDS35 scroll pump system. Figure 4 shows the lab setup described above.
To limit the effect of wall loss, HORUS samples air from the core of the APACHE flow system and draws only a fraction of the total air flow as shown in figure 5. At 900 hPa the HORUS instrument takes 20% and at 275 hPa HORUS takes 30% of the total volume flow entering APACHE. To validate that this proportional volume flow into HORUS does not disturb the flow conditions within APACHE, flow speed profiles were performed using the Prandtl pitot tube installed directly opposite the HORUS inlet, which can be positioned flush against the internal wall up to 60.5 mm into the APACHE cavity, which is 15 mm from the APACHE center. Figure 6 shows the measured flow speed profile (blue data points) when the APACHE pressure was 920 hPa. As the distance between the APACHE wall and the pitot tube inlet increased, no significant change in the flow speed was observed. The largest change observed was between 46.6 and 60.5 mm where the flow speed increased by 0.16 m s$^{-1}$, which is 22.8% smaller than the combined uncertainty of these two measurements ± 0.21 m s$^{-1}$ (2σ). Compared to the other four measurement points performed at 920 mbar, the 1.54 m s$^{-1}$ measured at 60.5 mm is not significantly different. However, when performing the speed profile tests at the low pressures, the pressure difference measured was close to or below the resolution of the differential pressure sensor. Consequently, the flow inside APACHE and the HORUS inlet system was simulated using the computational fluid dynamics (CFD) model from COMSOL multiphysics to gain a better understanding of the flow speed profiles at all pressures. The CFD module in COMSOL uses Reynolds Averaged Navier-Stokes (RANS) models (COMSOL. 2019). The standard k-epsilon turbulence model with incompressible flows was used for this study as it is applicable when investigating flow speeds below 115 m s$^{-1}$ (COMSOL. 2019). An extra fine gridded mesh of a perforated plate with a high solidity ($\sigma_s = 0.96$) was implemented in the turbulence model to generate the turbulence and replicate the flows created.
by the bronze sintered filter (Roach. 1987). The model was constrained with the pressures measured within APACHE and the HORUS inlet. The volume flow was calculated from measured mass flow entering APACHE and temperatures were constrained using the thermistor readings. To gain confidence in the model, the flow speed output data was compared to the available measured flow speed profile, see figure 6. Overall, the modelled flow speed profile did not differ significantly from measured. The only point where the model significantly disagreed with measurements was at the boundary (< 4 mm away from the APACHE wall), where the model predicted a flow speed of 1.3 m s\(^{-1}\), which is 6 % lower than the minimum extent of the measurement uncertainty 1.38 m s\(^{-1}\). However, as this is occurring within a region that ultimately does not influence the air entering HORUS, see section 4.1.2, the disagreement between modelled and measured flow speeds at distances less than 4 mm from the APACHE wall is ignored.

Figure 5. The percentage of the total volume flow entering APACHE, which is sampled by HORUS as a function of pressure within APACHE. All error bars are quoted to 1\(\sigma\).

Figure 6. The measured (blue) and COMSOL simulated (red) flow speed profiles within APACHE, at 920 hPa. The x-axis is the distance from the internal wall of APACHE. The error bars are quoted to 2\(\sigma\).
Figure 7 shows the simulated flow speeds at six discreet pressures within APACHE. The black lines depict the streamlines of the HORUS sample flow and the color gradient relates to the flow speed. The flow conditions in the center flow within the HORUS inlet, post pinhole, the center of the streamlines and the undisturbed flow airflow not influenced by the sample flow of HORUS are indicated. The figure shows the internal APACHE dimensions starting from the sintered filter to the first perforated stainless steel plate 0.135 m and 0.601 m from the APACHE inlet, respectively. From the simulations, the centerline flow speed differs by less than 0.1 % compared to the undisturbed flow, which is also the case at 275 mbar when HORUS is drawing in the highest percentage of the total volume flow entering APACHE. After the sintered filter the high calculated Reynolds numbers (Re > 2300) support the statement that a turbulent flow regime is created. Additionally, the measurements in conjunction with simulations show that the small pores of the sintered filter release a uniform distribution of small turbulent elements across the diameter of APACHE, which remain prevalent all the way up to the HORUS inlet.

4.1.2 HOx losses in APACHE

The modelled OH mixing ratios (pptv) in figure 8 show the change in OH content as the air flows along the length of APACHE. Mixing ratios were used as they are independent of the changing density within APACHE. In every simulation, the OH and HO2 concentrations were initialized at zero, and losses at the walls were fixed to 100 % for both OH and HO2. The radial photolytic production of OH and HO2 as calculated using Eq. (7) and Eq. (8), occurred when the air passed the UV ring lamp. For all simulations, the HOX radical-radical recombination loss reactions, (reactions R6-R8), and the measured molecular diffusion coefficient of OHdm in air (Tang et al., 2014) was used:

\[
\text{OH}_{\text{dm}} = 179 \pm 20 \text{ Torr cm}^2 \text{ s}^{-1} \quad (238.65 \pm 26.7 \text{ hPa cm}^2 \text{ s}^{-1})
\]

In literature, there have been no reports of successfully performed tests that accurately measure HO2 diffusivity coefficients in air. However, calculations of HO2 diffusion coefficients using the Lennard-Jones potential model have been performed (Ivanov et al., 2007). Ivanov et al. (2007) performed a series of measurements and Lennard-Jones potential model calculations to quantify the polar analogue diffusion coefficients for OH, HO2 and O3 in both air and pure helium. The calculated OH and O3 diffusion coefficients in air from the Lennard-Jones potential model were in good agreement with the recommended measurement values in Tang et al., (2014) well within the given uncertainties. Therefore, to best replicate the diffusivity of HO2 within the simulations, the following diffusion coefficient of HO2 in air from the Ivanov et al., (2007) paper was used:

\[
\text{HO2}_{\text{dm}} = 107.1 \text{ Torr cm}^2 \text{ s}^{-1} \quad (142.8 \text{ hPa cm}^2 \text{ s}^{-1})
\]

It is clear from figure 8, that irrespective of pressure the air masses at the boundary (where wall losses are 100 %) do not have sufficient time to expand into the HORUS sample flow streamlines, and influence HOX content entering HORUS. Lateral exchanges between air at the walls of APACHE and the free air in the center are suppressed due to the preservation of the small turbulence regime between the sintered filter and the HORUS inlet. Table 2 provides, for six pressures, the evolution of OH along the length of APACHE, within the streamlines created by the HORUS sample flow as depicted in figure 8.
The L term represents OH mixing ratios on the left most streamline, C represents OH mixing ratios in the center of the streamlines, and R represents OH mixing ratios on the right most streamline. The mean mixing ratio at each APACHE pressure does not change significantly and is thus independent of the distance from the lamp. Conversely, the standard deviations of the OH mixing ratios within the HORUS sampling streamlines decrease as the distance from the lamp increases, indicating that the air is homogenizing. However, figure 8 and table 2, with support from available measurements, indicate that the OH-depleted air masses (i.e. air masses
that have experienced loss of OH at the APACHE walls) do not expand into and influence the OH content of air that is being sampled by HORUS. The main loss process that influences HOX entering HORUS is the wall loss at the HORUS inlet itself. On average, 22.2 (± 0.8) % of OH and HO2 is lost at the inlet, which will form part of the \( \alpha_{\text{PI}} \) loss calculation in section 5.

**Figure 8.** COMSOL Multiphysics output data, simulating OH conditions at 6 discreet pressures within APACHE ranging from 275 to 894 mbar, between the sintered filter and the first perforated stainless steel plate. The color is OH mixing ratio (pptv), with initial OH production occurring at the lamp (0.26 m from APACHE inlet), using Eq. (7) and Eq. (8). The black lines are the streamlines created by the HORUS sample flow. The black arrows depict the flow direction. The x-axis is the distance from the center of APACHE in meters. The y-axis is the distance from the APACHE inlet. The centerline within HORUS Inlet tags represent the flow and OH concentrations in the center of the fully formed flows after the HORUS pinhole. The undisturbed tags show the flow conditions outside of the HORUS streamlines, and the centerline tags show the flow conditions in the center of the streamlines (i.e. the area of flow influenced by HORUS sampling).
Table 2. The evolution of OH within the HORUS sample flow streamlines, along the length of APACHE at all six pressures, within the streamlines created by HORUS sampling as depicted in figure 8. The L term represents OH mixing ratios on the left most streamlines, C represents OH mixing ratios in the center of the streamlines, and R represents OH mixing ratios on the right most streamline. The centerline within HORUS inlet column shows the OH mixing ratios in the center of the flow in the HORUS inlet. All standard deviations are quoted to 1σ.

<table>
<thead>
<tr>
<th>APACHE Pressure (mbar)</th>
<th>OH (ppbv) At the lamp</th>
<th>OH (ppbv) 4.2 cm from lamp</th>
<th>OH (ppbv) 8.4 cm from lamp</th>
<th>OH (ppbv) 12.8 cm from lamp</th>
<th>OH (ppbv) 2 cm before HORUS Inlet</th>
<th>OH (ppbv) In Centerline within HORUS Inlet</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>L</td>
<td>C</td>
<td>R</td>
<td>Mean</td>
<td>Std (1σ)</td>
<td>L</td>
</tr>
<tr>
<td>894</td>
<td>438</td>
<td>445</td>
<td>513</td>
<td>465</td>
<td>41.4</td>
<td>442</td>
</tr>
<tr>
<td>735</td>
<td>502</td>
<td>508</td>
<td>572</td>
<td>527</td>
<td>38.8</td>
<td>506</td>
</tr>
<tr>
<td>524</td>
<td>611</td>
<td>617</td>
<td>672</td>
<td>633</td>
<td>33.6</td>
<td>615</td>
</tr>
<tr>
<td>439</td>
<td>652</td>
<td>657</td>
<td>706</td>
<td>672</td>
<td>29.8</td>
<td>656</td>
</tr>
<tr>
<td>335</td>
<td>760</td>
<td>765</td>
<td>805</td>
<td>777</td>
<td>24.7</td>
<td>764</td>
</tr>
<tr>
<td>275</td>
<td>866</td>
<td>871</td>
<td>907</td>
<td>881</td>
<td>22.4</td>
<td>870</td>
</tr>
</tbody>
</table>
4.2 UV conditions

The photolysis lamp is housed in a mount with the side facing into the chamber having an anodized aluminum band with thirty 8 mm apertures installed between it and a quartz wall. The housing was flushed with pure nitrogen to purge any O₂ present before the lamp was turned on. The nitrogen flushing was kept continuously thereafter. After approximately one hour, the lamp reached stable operation conditions, i.e. the relative flux emitted by the lamp as measured by a photometer (seen in Figure 1b at the UVL on the underside of the APACHE chamber) was constant. The flux ($F_\text{b}$) entering APACHE is not the same as the flux experienced by the molecules sampled by HORUS ($F$). Factors influencing the ratio between $F_\text{b}$ and $F$ are as follows. (i) Absorption of light by O₂, which is particularly important as O₂ has a strong absorption band at 184.9 nm and the O₂ density changes in APACHE when calibrating at the different pressures. (ii) The variable radial flux, which is dependent on the geometric setup of the ring lamp and on the location within the irradiation cross section where the molecule is passing. These factors were resolved through the combination of two actinometrical crosscheck methods. The advantage of actinometrical methods is that the flux calculated is derived directly from the actual flux that is experienced by the molecules themselves as they pass through the APACHE chamber. Therefore, allowing direct calibration of the flux inside APACHE itself.

The first actinometrical method (A) used the ground based calibration device (Martinez et al., 2010) to calibrate the HORUS instrument to be used as a transfer standard. Only for the purpose of this experiment, the critical orifice diameter was changed from the airborne configuration of 1.4 mm to a 0.8 mm on-ground* configuration to adapt HORUS to the mass flow that the ground based calibration device is able to provide. The asterisk discerns terms that were quantified when the smaller 0.8 mm critical was used. The calculated instrument on-ground* sensitivity was then used to translate OH and HO₂ concentrations produced by the uv-technik Hg ring lamp into a value for $F_\text{b}$. Take note that for the calibrations discussed in section 5, the initial 1.4 mm diameter critical orifice used during the airborne campaign was re-installed.

The HORUS on-ground* sensitivity at 1010 mbar for OH and HO₂ are 12.79 (± 1.8) and 16.59 (± 2.3) cts pptv⁻¹ mW⁻¹ respectively, with the uncertainties quoted to 1σ. This sensitivity was then used to calculate the OH and HO₂ concentrations at the instrument inlet with the APACHE system installed and operating at 1010 mbar. To ensure sufficient flow stability during calibration at this high pressure, the Edwards GSX160 scroll pump was disengaged. Additionally, the water mixing ratios were kept constant (~3.1 mmol mol⁻¹) and oxygen levels were varied by adding different pure N₂ and synthetic air mixtures, via MFCs. The OH and HO₂ concentrations at the HORUS inlet were 1.51 (± 0.01) and 1.43 (± 0.01) x 10¹⁰ molecules cm⁻³ respectively when only pure synthetic air and water vapor were injected into APACHE, the uncertainties here are quoted as measurement variability at 1σ. Using these values, the OH and HO₂ concentrations at the lamp were back calculated accounting for radical-radical loss reactions (R6-R8) using rate constants taken from Burkholder et al. (2015) with temperature (T) in Kelvin.

\[
\begin{align*}
\text{OH} + \text{OH} & \rightarrow \text{H}_2\text{O} + \text{O}(^3\text{P}) & k = 1.8 \times 10^{-12} \cdot \exp\left[\frac{-2}{T}\right] & \quad \text{(R6)} \\
\text{HO}_2 + \text{HO}_2 & \rightarrow \text{H}_2\text{O}_2 + \text{O}_2 & k = 3.0 \times 10^{-13} \cdot \exp\left[\frac{-4600}{T}\right] & \quad \text{(R7)}
\end{align*}
\]
OH + HO₂ → H₂O + O₂  k = 4.8 x 10⁻¹¹ ∙ exp[250/T]  (R8)

The chemical losses of OH and HO₂ were found to be 32% and 30%, respectively, yielding OH concentrations of 2.2 (± 0.02) x 10¹⁰ molecules cm⁻³ and HO₂ concentrations of 2.0 (± 0.02) x 10¹⁰ molecules cm⁻³ at the lamp, at 1010 mbar, using a water vapor mixing ratio of 3.1 mmol mol⁻¹ in pure synthetic air. The uncertainties are quoted as measurement variability at 1σ. The photon flux (F) experienced by the air sampled by HORUS, quantified using the OH and HO₂ concentrations stated above, ranged from 3.75 x 10¹⁴ photons cm⁻² s⁻¹ to 6.1 x 10¹⁴ photons cm⁻² s⁻¹ depending on oxygen concentrations and considering the chemical losses. As described before, Eq. (7) shows how the production of OH at the lamp is calculated:

\[
[OH] = [H₂O] ∙ σ_{H₂O} ∙ F_{184.9 \text{ nm}} ∙ ϕ_{H₂O} ∙ t
\]

(7)

\[
F_{184.9 \text{ nm}, \text{L}} = F_{β} ∙ e^{-(γ_{H₂O[H₂O]} + γ_{O₂[O₂]})}
\]

(8)

Where \(F_{β}\) is the flux intensity entering APACHE from ring lamp, with:

\[
γ_{O₂} = R_β ∙ ω ∙ σ_{O₂}
\]

(9)

Where \(R_β\) is the radial distance of the sampled air parcel to the ring lamp of APACHE, \(ω\) a correction factor replicating the integrated product of the absorption cross section and the ring lamp’s emission line as modified by the effect of the absorption of O₂ present in between the lamp and the flight path of the sampled air, normalized by \(σ_{O₂}\) is the effective cross section of O₂. When combining Eq. (7) and Eq. (8) the OH concentration produced at the lamp is quantified as:

\[
[OH] = [H₂O] ∙ σ_{H₂O} ∙ ϕ_{H₂O} ∙ t ∙ F_{β} ∙ e^{-(γ_{H₂O[H₂O]} + γ_{O₂[O₂]})}
\]

(10)

Eq. (10) can be rearranged to:

\[
\ln \left[ \frac{[OH]}{[H₂O] ∙ σ_{H₂O}} \right] = \ln(F_{β} ∙ t ∙ ϕ_{H₂O}) + (γ_{H₂O} ∙ [H₂O] - γ_{O₂} ∙ [O₂])
\]

(11)

Figure 9, shows the measured production of OH, (left side of Eq. (11)) plotted against oxygen concentration. Given that the other terms within Eq. (11) are constant with regards to changing oxygen levels, the plotted gradient of the linear regression in figure 9 yields \(γ_{O₂}\) as a function of oxygen concentration being 1.3 x 10⁻¹⁹ (± 0.05 x 10⁻¹⁹) cm⁻³ molecule⁻¹.
Given that, the y intercept of the linear regression, 29.61, is equal to the natural logarithm of \( F_\beta t \phi_{H2O} \), the flux entering APACHE \( F_\beta \) can be characterized:

\[
F_\beta = \frac{e^{29.61}}{t \phi_{H2O}} = 6.9 \times 10^{14} (\pm 1.1 \times 10^{14}) \text{ s}^{-1}
\]  
(12)

The accuracy in \( F_\beta \) from this method, which we call method A, is 15.9\% (1\σ).

Table 3. Parameters and uncertainties involved in method A, using HORUS as a transfer standard. The total uncertainty is the sum of the quadrature of the individual uncertainties.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Comments</th>
<th>Total 1σ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NO Monitor (TEI)</td>
<td>Calibration uncertainty</td>
<td>5.2</td>
</tr>
<tr>
<td>NO standard (NPL)</td>
<td>Purity and concentration of the gas</td>
<td>1</td>
</tr>
<tr>
<td>( \text{N}_2\text{O} ) cross section</td>
<td>JPL recommendation</td>
<td>2</td>
</tr>
<tr>
<td>( \text{H}_2\text{O} ) cross section</td>
<td>JPL recommendation</td>
<td>2</td>
</tr>
<tr>
<td>( \gamma_{O2} )</td>
<td>From method A</td>
<td>3.5</td>
</tr>
<tr>
<td>( \text{O}(1D) ) yield</td>
<td>Martinez et al. (2010)</td>
<td>1</td>
</tr>
<tr>
<td>Kinetic rate coefficients</td>
<td>JPL recommendation</td>
<td>12</td>
</tr>
<tr>
<td>( F_\beta ) Variability</td>
<td>From method A</td>
<td>3.5</td>
</tr>
<tr>
<td>Photolysis chamber dimensions</td>
<td>Specifications of in-house workshop</td>
<td>3</td>
</tr>
<tr>
<td>( [\text{H}_2\text{O}] )</td>
<td>From calibration with NIST standard Dew point generator</td>
<td>2</td>
</tr>
<tr>
<td>( [\text{O}_2] )</td>
<td>From method A</td>
<td>3.4</td>
</tr>
<tr>
<td>Mass flow controllers</td>
<td>Calibration with NIST DryCal</td>
<td>2</td>
</tr>
<tr>
<td>Pressure and Temperature sensors</td>
<td>Validated against NIST standard</td>
<td>2</td>
</tr>
<tr>
<td>Overall Experimental Stability</td>
<td>Variability of measured terms</td>
<td>4</td>
</tr>
<tr>
<td></td>
<td>Overall uncertainty</td>
<td>15.9</td>
</tr>
</tbody>
</table>

The second actinometrical method (B) involved using an ANSYCO O3 41 M ozone monitor to measure the ozone mixing ratio profile between the HORUS inlet and the wall surface of APACHE, at ground pressure (1021 mbar). This method utilizes \( \text{O}_2 \) photolysis at 184.9 nm,
which produces two O(3P) atoms capable of reacting with a further two O₂ molecules to produce O₃.

O₂ + hv → O(3P) + O(3P)  \quad (R9)

O₂ + O(3P) + M → O₃ + M  \quad (R10)

The value of 1.3 x10⁻¹⁹ cm³ molecule⁻¹ for γO₂ found in the previous method was used to calculate the actinic flux entering APACHE:

\[ F_β = \frac{[O₃]}{[O₂] \cdot γO₂ \cdot \phiO₂ \cdot t \cdot e^{-(γO₂}[O₂]}) \quad (13) \]

ΦO₂ is the quantum yield of O₂ at 184.9 nm, which has been determined to be 1 between 242 and 175 nm (Atkinson et al., 2004). As in method A, the ozone produced at the lamp is quantified by back calculating from the ozone measured at the ANSYCO O₃ 41 M inlet position. Typical ozone mixing ratios ranged from 45 – 72 ppb depending on the oxygen concentration. From this approach, the calculated \( F_β \) is 5.7 x 10¹⁴ (± 0.74 x 10¹⁴) s⁻¹ with a total uncertainty of 12.9 % (1σ). From the combination of the two experiments, the final values taken for the UV environment within APACHE are:

Actinic flux (\( F_β \)) = 6.3 x 10¹⁴ (± 0.9 x 10¹⁴) s⁻¹

Accuracy in \( F_β \) = 14.4 % (1σ)

Table 4. Parameters and uncertainties involved in Method B, using ANSYCO O₃ 41 M monitor. The total uncertainty is the sum of the quadrature of the individual uncertainties.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Comments</th>
<th>Total Uncertainty 1σ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O₃ calibrator</td>
<td>Calibrated against a primary standard</td>
<td>2</td>
</tr>
<tr>
<td>[O₃]</td>
<td>Calibration of ANSYCO O₃ 41 M monitor</td>
<td>4</td>
</tr>
<tr>
<td>[O₂]</td>
<td>From method A</td>
<td>3.4</td>
</tr>
<tr>
<td>γO₂</td>
<td>From method A</td>
<td>3.5</td>
</tr>
<tr>
<td>( F_β ) Variability</td>
<td>From method A</td>
<td>3.5</td>
</tr>
<tr>
<td>Mass flow controllers</td>
<td>Calibration with NIST DryCal</td>
<td>2</td>
</tr>
<tr>
<td>Pressure and Temperature sensors</td>
<td>Validated against NIST standard</td>
<td>2</td>
</tr>
<tr>
<td>Experimental Stability</td>
<td>Variability of values</td>
<td>10.1</td>
</tr>
<tr>
<td>Overall uncertainty</td>
<td></td>
<td>12.9</td>
</tr>
</tbody>
</table>

5 Results and discussion

5.1 Evaluation of instrumental sensitivity

Figure 10 shows the sensitivity curve of HORUS, the quenching effect, the linear fits used to quantify the pressure independent sensitivity coefficients, and relative HOₓ transmission values for OH, OH in the second axis, and HO₂ plotted as a function of the HORUS internal density. Table 6 shows the pressure independent sensitivity coefficients for OH in the 1st axis, OH in the 2nd axis, and HO₂ in the 2nd axis found from the slopes in figure 10 row C. As
described in section 3.2, the pressure driven wall losses in IPI and post critical orifice both
contribute to the overall sensitivity curve. The OH transmission terms (α_{IPI} and α_{HORUS}) can
be considered together as the total OH transmission (α_{Total}). According to the COMSOL
simulations, the losses of HOX occur mainly at the inlet itself resulting in for both OH and HO₂
to be 78 (± 0.8, full range) %. To calculate the loss of HOX within IPI, the following was used:

$$\alpha_{IPI\_OH} = 1 - \frac{\text{OH}_\text{DM}(P_r \cdot t_{IPI}(P,T) \cdot \pi)}{P_{IPI} \cdot P_{IPI}}$$ (14)

$$\alpha_{IPI\_HO_2} = 1 - \frac{\text{HO}_2\_\text{DM}(P_r \cdot t_{IPI}(P,T) \cdot \pi)}{P_{IPI} \cdot P_{IPI}}$$ (15)

Where \( t_{IPI} \) is the transit time within IPI, i.e. the time it takes air to flow from the IPI inlet to
the critical orifice of HORUS. IPI \( A \) is the internal cross sectional area of IPI and \( P_{IPI} \) is the
measured pressure within IPI. The \( \text{OH}_\text{DM} \) and \( \text{HO}_2\_\text{DM} \) terms are the OH and HO₂
diffusion coefficients as described in section 4.1.2. By applying Eq. (14) and Eq. (15), \( \alpha_{IPI\_OH} \) and \( \alpha_{IPI\_HO_2} \)
ranged from 0.98 to 0.995 and 0.99 to 0.997 respectively across the pressure range within IPI
of 210 – 1010 mbar and IPI transit times of 90 – 120 milliseconds. Summing the inlet wall
loss found from the COMSOL simulations (78 ± 0.8 %) and \( \alpha_{IPI\_OH} \) and \( \alpha_{IPI\_HO_2} \) calculated from
Eq. (14) and Eq. (15) results in a combined \( \alpha_{IPI} \) term for OH of 76.7 (± 2.2, full range) and for
HO₂ of 77.3 (± 1.6, full range). However, to calculate \( \alpha_{Total} \), the OH transmission post critical
orifice, \( \alpha_{HORUS} \), must be resolved. \( \alpha_{HORUS} \) regarding OH and HO₂ can be calculated by adapting
Eq. (14) and Eq. (15) to the internal HORUS conditions producing:

$$\alpha_{HORUS\_OH} = 1 - \frac{\text{OH}_\text{DM}(P_r \cdot t_{1}(P,T) \cdot \pi)}{P_{int} \cdot P_{int}}$$ (16)

$$\alpha_{HORUS\_OH_2} = 1 - \frac{\text{OH}_2\_\text{DM}(P_r \cdot t_{2}(P,T) \cdot \pi)}{P_{int} \cdot P_{int}}$$ (17)

$$\alpha_{HORUS\_HO_2} = 1 - \frac{\text{HO}_2\_\text{DM}(P_r \cdot t_{2}(P,T) \cdot \pi)}{P_{int} \cdot P_{int}}$$ (18)

Where \( t_{1} \) and \( t_{2} \) are the transit times within HORUS from the critical orifice to the 1st and
2nd detection axis respectively. HORUS \( A \) is the internal cross sectional area of HORUS and \( P_{int} \)
is the measured internal pressure within HORUS. The OH transmission from the critical orifice
to the 1st detection cell (\( \alpha_{HORUS\_OH} \)) ranged from 0.84 to 0.96, the OH transmission from the
critical orifice to the 2nd detection cell (\( \alpha_{HORUS\_OH_2} \)) ranged from 0.59 to 0.88, and the HO₂
transmission from the critical orifice to the 2nd detection cell (\( \alpha_{HORUS\_HO_2} \)) ranged from 0.82 to
0.96. These ranges are quoted under the HORUS internal pressure range of 3.7 to 18.4 mbar
and internal transit times to the 1st detection axis (3.8 to 4.3 milliseconds) and 2nd detection
axis (23.5 to 27.8 milliseconds). The combined \( \alpha_{Total} \) values for OH, OH at the second detection
axis, and HO₂ are plotted in figure 10 row D as a function of the internal density of HORUS.

The two actinometric methods used to calibrate the flux entering APACHE from the uv-
technik ring lamp, yielded encouraging and comparative results. The \( F_p \) found from ozone
actinometric method (5.7 ± 0.74 x 10^{14} \text{ s}^{-1}) and from the HORUS transfer standard actinometric
method (6.9 ± 1.1 x 10^{14} \text{ s}^{-1}) agree with the difference of 1.2 x 10^{14} \text{ s}^{-1} representing only 60
% of the combined 1σ uncertainty in \( F_p \), ± 2 x 10^{14} \text{ s}^{-1} from the two methods.
5.2 Absolute Calibration Uncertainty

The contribution of parameter uncertainties to the respective sensitivities are summarized in tables 5 to 8.

Table 5. Parameters within APACHE, their ranges and uncertainties, contributing to the uncertainty in the three measurement sensitivities within HORUS.

<table>
<thead>
<tr>
<th>Parameter (unit)</th>
<th>Range or typical value</th>
<th>Precision (1σ)</th>
<th>Total Uncertainty (1σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$F_0$ at 184.9 nm (s$^{-1}$)</td>
<td>6.3 x 10$^{14}$</td>
<td>3.5 %</td>
<td>14.4 %</td>
</tr>
<tr>
<td>$\sigma$H$_2$O (cm$^2$ molecule$^{-1}$)</td>
<td>7.22 x 10$^{-20}$</td>
<td>-</td>
<td>2 %</td>
</tr>
<tr>
<td>$\gamma$O$_2$ (cm$^3$ molecule$^{-1}$)</td>
<td>1.30 x 10$^{-19}$</td>
<td>1.8 %</td>
<td>3.5 %</td>
</tr>
<tr>
<td>[O$_2$] (x10$^{18}$ molecules cm$^{-3}$)</td>
<td>1.1 - 4.8</td>
<td>1.4 %</td>
<td>3.4 %</td>
</tr>
<tr>
<td>[H$_2$O] (x10$^{16}$ molecules cm$^{-3}$)</td>
<td>2.00 - 7.41</td>
<td>1.2 %</td>
<td>2 %</td>
</tr>
<tr>
<td>Mass flow controller (sL min$^{-1}$)</td>
<td>203 - 988</td>
<td>&lt; 2 %</td>
<td>2 %</td>
</tr>
<tr>
<td>Pressure sensors (mbar)</td>
<td>275 - 894</td>
<td>&lt; 1 %</td>
<td>2 %</td>
</tr>
<tr>
<td>Temperature sensors (K)</td>
<td>282 - 302</td>
<td>&lt; 1 %</td>
<td>2 %</td>
</tr>
<tr>
<td>Overall</td>
<td></td>
<td>5 %</td>
<td>16.2 %</td>
</tr>
</tbody>
</table>

Table 6. Pressure independent sensitivities and their overall uncertainty from calibrations with APACHE.

<table>
<thead>
<tr>
<th>Parameter (cts cm$^{-3}$ molecule$^{-1}$ s$^{-1}$)</th>
<th>Value</th>
<th>Precision (±1σ)</th>
<th>Total Uncertainty (1σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>c0 for OH in OH axis</td>
<td>1.44</td>
<td>4 %</td>
<td>6.9 %</td>
</tr>
<tr>
<td>c1 for OH in HO$_2$ axis</td>
<td>0.68</td>
<td>4 %</td>
<td>6.9 %</td>
</tr>
<tr>
<td>c2 for HO$_2$ in HO$_2$ axis</td>
<td>1.3</td>
<td>2 %</td>
<td>5.6 %</td>
</tr>
</tbody>
</table>

Table 7. Pressure dependent OH and HO$_2$ transmission and their overall uncertainty from calibrations with APACHE.

<table>
<thead>
<tr>
<th>Parameter (%)</th>
<th>Value</th>
<th>Precision (±1σ)</th>
<th>Total Uncertainty (1σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\alpha$Total (for OH to OH axis)</td>
<td>61 - 72</td>
<td>2.8 %</td>
<td>14.3 - 11.4 %</td>
</tr>
<tr>
<td>$\alpha$Total (for OH to HO$_2$ axis)</td>
<td>35 - 65</td>
<td>4.3 %</td>
<td>14.1 - 11.5 %</td>
</tr>
<tr>
<td>$\alpha$Total (for HO$_2$ to HO$_2$ axis)</td>
<td>54 - 70</td>
<td>2.9 %</td>
<td>7.9 - 4.7 %</td>
</tr>
</tbody>
</table>

Table 8. Pressure dependent sensitivities for the three measurement within HORUS, their overall uncertainty from calibrations with APACHE. The range in the precision relates to the numbers quoted in the value column.

<table>
<thead>
<tr>
<th>Parameter (unit)</th>
<th>Value</th>
<th>Precision (±1σ)</th>
<th>Total Uncertainty (1σ)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C$_{OH}$ (cts s$^{-1}$ pptv$^{-1}$ mW$^{-1}$)</td>
<td>7.9 - 26.4</td>
<td>1.1 - 0.5 %</td>
<td>17.6 %</td>
</tr>
<tr>
<td>C$_{OH}$ (2) (cts s$^{-1}$ pptv$^{-1}$ mW$^{-1}$)</td>
<td>3.9 - 10.5</td>
<td>2.0 - 0.3 %</td>
<td>17.6 %</td>
</tr>
<tr>
<td>C$_{HO2}$ (cts s$^{-1}$ pptv$^{-1}$ mW$^{-1}$)</td>
<td>7.5 - 22.3</td>
<td>0.4 - 0.7 %</td>
<td>17.1 %</td>
</tr>
</tbody>
</table>
Figure 10. The determination of the pressure based sensitivity of OH in both axes and HO2. The data shown are one-hour averages for the tested pressures, all plotted with the internal density on the x-axis. The top row (A) is the overall sensitivity curve, the second row (B) is internal quenching by N2, O2, and water vapor, and row (C) is internal density and cN (c0 for OH 1st axis, c1 for OH 2nd axis and c2 for HO2). (D) is the total OH and HO2 transmissions, all plotted against internal density. The error bars represent measurement variability (1σ), for rows B and C. In rows A and D, the error bars represent the total uncertainty (1σ).
6 Conclusions

The overall goal of this study was to develop and test a new calibration system capable of providing the high flows required by the airborne HORUS system whilst maintaining stable pressures across the pressure ranges experienced during flight. Such systems are critical to suitably characterize airborne systems, (such as a LIF-FAGE measuring HOX), that have a strong pressure dependent sensitivity. In addition, this system is purely based on the use of water-vapor photolysis, which is a frequently adopted technique for HOX instrument calibration (Martinez et al., 2003; Faloona et al., 2004; Dusanter et al., 2008). The COMSOL multiphysics simulations constrained by temperature, pressure and mass flow measurements demonstrated that air masses at the boundary of the APACHE system do not have sufficient time to expand into the streamlines created by the HORUS sample flow and influence the HOX content entering HORUS. The main HOX wall losses occurred at the HORUS inlet where on average 23.3 % (± 1.6, full range) of OH and 22.7 % (± 0.9, full range) of HO2 are lost. While the application of these factors contribute to the uncertainty in the overall calibration factor, they proved to be critical in understanding and constraining the UV conditions within APACHE. The largest uncertainties result from constraining the flux ($F_\beta$) entering APACHE ($6.3 \pm 0.9 \times 10^{14}$ s$^{-1}$, 1σ) and the total uncertainty in the pressure independent sensitivity coefficients (ranging from 5.6 to 6.9 %, 1σ). The two actinometrical methods used to derive $F_\beta$ proved to be in good agreement with one another, with the HORUS transfer standard method yielding $6.9 \pm 1.1 \times 10^{14}$ s$^{-1}$ (1σ) and the ozone monitor method yielding $5.7 \pm 0.74 \times 10^{14}$ s$^{-1}$ (1σ). Furthermore, the APACHE system enabled the total OH and HO2 pressure dependent transmission factors to be characterized as a function of internal pressure using both COMSOL simulations and calculations of HOX diffusivity to the walls within IPI and the low-pressure regime within HORUS. Overall, the APACHE calibration system sufficiently able to calibrate the airborne HORUS system across the pressure range experienced during flight. The relatively low overall uncertainty of 17 - 18 % (1σ) demonstrates the suitability of this calibration approach, particularly when compared to other calibration methods described earlier.

Author contributions. K.H, C.E, M.M, H.H, U.J, and M.R formulated the original concept and designed the APACHE system. D.M, H.H, and U.J prototyped, developed, and characterized the APACHE system. T.K, D.M, and H.H developed and performed the CFD simulations. D.M prepared the manuscript with contributions from all coauthors.

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References


COMSOL, Multiphysics Documentation, version 5.4, [software], 2019.


instrument using the Highly Instrumented Reactor for Atmospheric Chemistry (HIRAC)."
