Atmos. Meas. Tech. Discuss., 7, C3706–C3713, 2014
www.atmos-meas-tech-discuss.net/7/C3706/2014/

Atmospheric Measurement Techniques Discussions

Interactive comment on "A new airborne laser-induced fluorescence instrument for in situ detection of Formaldehyde throughout the troposphere and lower stratosphere" *by* M. Cazorla et al.

M. Cazorla et al.

thomas.hanisco@nasa.gov

Received and published: 12 November 2014

Anonymous Referee #1

General Overall Comments: This is a very nice paper reflecting a very thorough assessment of a new airborne HCHO instrument. The authors did a very nice job of discussing the instrument, the data acquisition procedures, gas handling, data reduction, sensitivity, precision, detection limits, and time response. The paper is well written and should be published after the following minor points below are addressed. However,

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper

there are two shortcomings with the ISAF instrument in its present form that should be addressed in future versions and require authors comments here: the present instrument does not have provisions for chemically zeroing the inlet/sampling cell to mitigate the effects of HCHO wall outgassing and the present instrument does not add HCHO standards to the inlet during flight to periodically cross check wall losses and potential instrument sensitivity changes. Providing such capabilities are common practices with many airborne instruments and future improvements to ISAF should incorporate these practices. Specific comments further discussing these issues are provided below. Because these two issues can affect measurement accuracy, this reviewer strongly urges the authors to provide comments.

We thank the reviewer for the positive comments and acknowledge the issues brought up regarding the calibration and zeroing of the instrument in flight. The instrument design that we present here does not preclude the implementation of a zero air and/or calibration standard in flight. We simply find in practice the addition of zero air is unnecessary and the use of calibration gas on the aircraft is not accurate enough to be useful. These points are addressed in detail below.

Page 2, Lines 12 – 15: The statement that: direct sources of HCHO are minor compared to secondary production is a little misleading and needs to be modified. Although secondary sources of HCHO typically dominate over primary combustion sources globally, locally, primary sources (e.g., fires) can also be important. In addition, one sometimes characterizes immediate HCHO formation from combustion, such as in flares, as pseudo-primary, due to the very rapid formation. Since this is an area of debate, I would simply state here that direct and pseudo-direct sources of HCHO could also be important.

Yes, we have clarified the phrasing to reflect the fact that primary point sources can be important locally.

Page 2, Line 16: The 2-3 hour lifetime is around noon, and I would add this. The HCHO

AMTD

7, C3706–C3713, 2014

lifetime dramatically increases as the sun's UV radiation decreases. The statement that wet deposition is a minor sink is also misleading since uptake by liquid drops and rain out can be an important sink process locally, and this needs to be modified. Page 3, Line 2: The authors should include the rather extensive HCHO intercomparison study by Gilpin et al. (Intercomparison of six ambient [CH2O] measurement techniques, JGR, 102 (D17), 21,161 – 21,188, 1997).

We have added the wet deposition mechanism and the reference. Page 3, Line 5: The TDLAS technique is more accurately reflected by the Fried et al. (2008) study and the Weibring et al., 2007 reference refers to a similar technique called Difference Frequency Generation Absorption Spectroscopy (DFGAS). I would site both references here with their appropriate names.

We have added the reference.

Page 4, Line 17 – 19: In theory the combination of differential on-line-off-line pumping, followed by time gated and long-wavelength wavelength selective filtering should be sufficient to ensure high selectivity. However, the UV region contains a wealth of electronic absorption features from numerous hydrocarbons and potentially high overtones and combination bands of row-vibrational transitions. It is thus important to convince the reader that high selectivity is achieved by listing all the different gases and their concentrations that have been examined. After all, up until several years ago it was thought that the same high degree of selectivity ensured that LIF measurements of OH were interference-free. However, recent more thorough analysis revealed that this was not the case.

The interference with OH instruments is an OH generation problem from the non-resonant photolysis of O3 to produce O1D and the subsequent reaction of O1D with H2O to produce OH. There is no "spectroscopic" interference with OH measurements. We do not know of any spectroscopic interference with HCHO LIF. The scans like that shown in Figure 6 that are acquired periodically in flight do not show any absorption

AMTD

7, C3706–C3713, 2014

feature other than HCHO. This is not suprising. Unlike absorption experiments, an interfering species must absorb at the same wavelength and fluoresce in the same window (400 - 450 nm). NO2, for example, absorbs at 353 nm, but it does not fluoresce. Likewise, we are not aware of any photolytic interference involving non-resonant excitation. These types of interferences require two-photons (photolysis + detection) and are easily identified by the laser power squared dependence. This has been added to Section 3.4. There is a sampling interference with OH, possibly due to alkenes reacting with ozone in the low-pressure expansion used in the detection of OH. The same could be possible for HCHO. We are aware of the possibility that ISOPOOH can be converted to HCHO on hot metal surfaces (Armin Wisthaler, personal communication). We do not think that this is occurring in our instrument, but we have not completed the tests to say what the impact is.

Page 6, Line 20: In the statement regarding the same absorption line width in the reference and sample cells, does the significantly different self broadening of HCHO relative to air broadening come into play here? In the IR HCHO self-broadening is about a factor of 4 times higher than air-broadening.

The concentration of HCHO in the reference cell is very low, on order ppm, and does not affect the linewidth.

Page 6, Line 24: How well does the second power monitor outside the sample cell Reflect the actual alignment in the sample cell? As the detected fluorescence efficiency critically depends upon the precise alignment of the laser relative to the detection zone, the authors need to give some indication of how well the monitoring beam tracks movement of the sample beam.

The ratio of the two laser power monitors is constant to +/- 3.4%. The text in Section 4.1 has been updated to include this. Also, a clarification is needed: The detection efficiency does not depend critically on the laser alignment. With this single-pass design the sensitivity is not very sensitive to the alignment at all. That is why the system is so

AMTD
7, C3706–C3713, 2014

stable. Regardless, the alignment is also extremely stable. Alignment is rarely needed, even after long distance shipping. The measurement of the laser power outside of the sample cell is a critical parameter because it is used to normalize the fluorescence signal. We minimize the effect of beam movement on the power monitors by using large area detectors (A = 1 cm2). We use the ground-fused silica diffusers to minimize the effects of inhomogeneity of the detector. This has been added to Section 3.2.

Page 7, Line 1: change “oxegenated to ”oxygenated “ Done.

Page 7, discussion of sampling: It is important to note that the present setup has no provisions for inlet chemical zeroing. As shown by the inlet study of Wert et al., even silicosteel and PFA Teflon tubing can outgas significant amounts of HCHO after exposure to high ambient concentrations. This becomes particularly true after sampling very high HCHO levels in smoke plumes. One would expect that after sampling such large plumes one should expect erroneously high ambient HCHO measurements at high altitudes when the HCHO concentrations drop. Even the HCHO intercomparison study by Kaiser et al. (Atmos. Meas. Tech., 2014) between a comparable LIF system and a Hantzsch system reveals outgassing from the LIF system, which was likewise not chemically zeroed. The online-offline subtraction scheme does not account for this potential error source. Comparisons with other HCHO instruments during field campaigns, despite showing good overall agreement and correlations, do reveal issues in the upper troposphere and lower stratosphere most likely from this cause as there is significant surface area in the sampling zone from the numerous light baffles. The authors need to add some statements about this.

The effect of reversible adsorption and desorption is a function of mass flow and the volume/surface area of the instrument detection system. A large mass flow and low volume/surface area are ideal to minimize adsorption/desorption effects. We use large mass flow through the bypass to minimize the impact of adsorption/desorption in the inlet. We furthermore use a very small detection volume (<60 cm3) that is flushed rapidly (115 ms). The sample flow is not exposed to the baffles prior to detection.

AMTD
7, C3706–C3713, 2014

These baffles are on the exhaust side of the detection region. This is a very different design than the instrument in Kaiser et al. The Wisconsin instrument is a multi-pass cell with the larger volume and sensitivity to alignment typical of multi-pass designs. In regards to zeroing, we have not seen significant contamination or outgassing in the measurements to date. When we add air with zero HCHO to the inlet, we measure zero +/- 20 ppt. We frequently add up to 10 or 20 ppb HCHO during calibrations and do not see significant outgassing after reducing HCHO back to zero. Perhaps another figure can illustrate this point better. We have added a new figure 12 to show the time response and the recovery after exposure to large concentrations of HCHO. In this example, a flight through the Ring Fire plume near Yosemite, CA on Aug 26, 2103 we measured over 200 ppbv HCHO. We show the recovery from high HCHO to background levels in just a few seconds. We have included the raw 10 Hz data in expanded views to better illustrate the fast response of the instrument. There are several instances where a change in HCHO by two orders of magnitude are observed in one or two seconds and an order of magnitude in less than a second.

Page 8, Line 6-13: This is a nice discussion of the line locking procedure employed. The authors should add a very brief discussion of how specifically the small absorption changes during wavelength shifting are corrected. Also, the authors state in a previous section (Page 6, line 21) that Section 3.5 will discuss how the reference absorption cell is used to correct sample cell data. Although line 26 on page 8 in Section 3.5 mentions this, it would be helpful for the non-informed reader specifically how this is accomplished.

We have added a few sentences in Section 3.4 to describe this in more detail.

Page 9, Discussion on Sensitivity: The authors did a very nice and thorough job of comparing UV and IR measurements as well as their standards measurements in the lab. However, the assessment of sensitivity and its stability would be even more convincing if standard additions to the sample cell were further carried out periodically in flight, as is the common practice with many airborne instruments. In part this relates to the

AMTD
7, C3706–C3713, 2014

comment above (Page 6, line 24); in part to inlet/cell HCHO losses; and perhaps most importantly, to the potential of sensitivity changes due to varying quenching of the LIF signal by water vapor. In fact, in their discussion of precision on page 11, lines 16-18, the authors note the possibility of changing HCHO surface desorption during calibration from various surfaces due to changes in temperature. Could this be a problem in flight during ambient acquisitions? How stable is the temperature of various components in flight? How stable is the sensitivity of 75 counts s-1 mW-1 ppbv-1? We originally designed an in-flight HCHO addition system to be used with the ISAF instrument. The benefits, as you mention above are potentially significant. However, in practice, we find that calibrations performed in these conditions are not consistent enough to improve accuracy. The reason is that the sensitivity of the instrument is more stable than the calibrations. In fact, we do not use calibrations that we perform between flights to adjust the sensitivity of the instrument during a field campaign. These calibrations are simply used as diagnostics to check the overall performance of the instrument.

In regards to quenching, HCHO fluorescence is not significantly affected by H2O abundance. In regards to inlet adsorption/desorption, see discussion above.

Although not stated but implied, the authors use their reference cell response facto and the implied stability of their HCHO glue emission source as a means of providing in-flight checks on their sensitivity. Is this correct? To first order this is reasonable. However, the authors should further provide additional evidence as to how well the reference cell calibration factors track the sample cell calibration factors. Potential differences in broadening (self broadening in the reference cell versus air broadening in the sample cell), water vapor quenching in the sample cell, and potential differences in beam alignment between the two cells (see comment page 6, line 24 above) can all result in systematic errors.

No, this is not correct. The reference cell is strictly to maintain wavelength accuracy.

This reviewer is only suggesting that the above issues may be potential problems, and

AMTD

7, C3706–C3713, 2014

the authors need to provide additional evidence in this paper to indicate why they are not important here. Again, in the future it would be much more convincing to simply add in-flight standards directly into the sample cell periodically. Page 12, lines 1 -12: This is a nice discussion of S/N and measurement precision for both theory and actually achieved in the laboratory and in the UT during flight in Fig. 11. Also, it would be helpful if the authors can provide any additional information, if available, on instrument stability during aircraft pitch, roll, and yaw maneuvers. Can the authors expound on their reduction in operating laser power from 20mW to 10mW (lines 11 and 12)? Is this a fundamental problem? The pump diodes and nonlinear crystal (PPLN) should have relatively long lifetimes unless the crystal does not have a MgO coating to prevent bleaching. Which component are the authors trying to protect?

The instrument is not sensitive to pitch, roll or yaw maneuvers. The optical bench is supported on vibration damping mounts. The description of the optical bench in Section 3.2 has been modified to include this statement. The reduction in power is motivated by the PI's experience that all lasers have a finite number of photons in them. By turning the laser power down all of those components have a better chance of lasting longer.

Please also note the supplement to this comment:
http://www.atmos-meas-tech-discuss.net/7/C3706/2014/amtd-7-C3706-2014-supplement.pdf

---

Interactive comment on Atmos. Meas. Tech. Discuss., 7, 8359, 2014.

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper