

Atmos. Meas. Tech. Discuss., referee comment RC3
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Comment on amt-2021-332

Anonymous Referee #3

Referee comment on "A source for the continuous generation of pure and quantifiable HONO mixtures" by Guillermo Villena and Jörg Kleffmann, Atmos. Meas. Tech. Discuss., <https://doi.org/10.5194/amt-2021-332-RC3>, 2021

Overall Comments

This manuscript provides the operational details of a commercial nitrous acid (HONO) calibration source that has previously been undescribed in the literature to allow replication and validation. As such, it has not been widely used for the calibration of in-situ atmospheric instrumentation. A nice instrumental intercomparison to show the utility of the source is made with the pairing of a chemiluminescent NO_x monitor and a LOPAP, particularly because they are calibrated orthogonally. A stable and pure HONO source is demonstrated in the 10s of ppbv mixing ratio range along with tunability, but operational validation at mixing ratios relevant to the atmosphere are either neglected for discussion entirely or glossed over. It is confusing why the Authors have enumerated so many points on the excellent performance of the calibration source, drawing off their extensive measurement experience, to emphasize that those values apply at concentrations that are an order of magnitude (or more) higher than would be delivered for the operating range of an instrument (assuming no more than ten-fold dilution). Subject to inclusion of that information, since it has been collected, the manuscript is fit for publication in AMT once minor and technical revisions have been made.

Minor Revisions

- Alphabetized lists are present throughout the manuscript and significantly detract from the quality of the points being made. In many places these are formatted badly and make the logic challenging to follow. In most cases, these can simply be replaced with a structured paragraph to address each point and some minor reorganization.
- The Authors are mixing metrics in their comparisons with other instruments in several instances that give misleading impressions on their performance. In most cases these can be corrected by clearly separating the terms being discussed (see technical corrections below).
- Present the performance metrics for the calibration source at output mixing ratios of 5

ppbv and below. This is the range that will be required to calibrate instruments for ambient measurements, as it will set instrumental accuracy and precision. It is critical to present the stability of the instrument that is applicable. Of course the metrics look great over 10 ppbv, just like every other high-output HONO source, but that applies to very few real situations (e.g. wildfire plumes or tunnels).

Technical Corrections

Page 1, Lines 24-25: Source stability has been solved for a long time (since Febo, ~2%), so this point that it is the first is not accurate. The statement on providing the first absolute calibration source is accurate and the most noteworthy contribution of this work. Revise the statement to prevent it from being misleading.

Page 3, Lines 68-70: This is another misleading sentence that needs rewriting to accurately represent the current state of knowledge. Varying the temperature and HCl concentrations are required only once to identify the required working range of the system and are not varied once that fact has been established. There are no reports of this system being modified in real-time to change HONO output of a calibration system, except for proof-of-concept to help end users know their options for obtaining a desired HONO output. Further, varying temperature is trivial and permeation tubes are prolific across many industries for gas calibrations. The Authors are being disingenuous by calling either of these complicated, but are correct that each could require some time to either acquire (permeation tubes require certification by manufacturers) or reach a programmed setpoint with a PID controller (temperature). It is fairly standard practice to expect such time requirements from a calibration system, especially given the time that one must commit to pipette solutions into cleaned labware to set up the calibration source, then prime the peristaltic pump (and so on) in the work presented here.

Page 3, Lines 85-87: This sentence is hard to follow. There is fragmentation and mixing of ideas. Revise into two sentences that are complete.

Page 3, Lines 94-95: The elasticity of peristaltic tubing degrades over time and can lead to poor flow control or a total loss of flow. Can the Authors please add some instruction on this for the presented system to the discussion where they are commenting on the volume requirements for the calibration source, so readers have an idea of the necessary maintenance? Can the Authors also provide some sort of objective metric to identify that the peristaltic tubing may be compromised in function?

Page 4, Line 128: This list is not necessary. Write with full sentences and paragraphs.

Page 4, Line 131: Units should be given in parentheses. Also, why is the molar concentration of HONO not presented as [HONO] in Equation (I)?

Page 5, Lines 157-159: There are too many ideas intermixed in this sentence. Please revise into two or three sentences for clarity.

Page 6, Lines 196-199: What about below 5 ppbv output? It's been long demonstrated that it is easy to get reproducible and stable HONO outputs for sources with high concentrations. These are not found in the real atmosphere, so the instruments would not be calibrated in their working range. It is also not reasonable to perform subsequent dilutions greater than a factor of 10 with MFCs as most users will not commit to the very large gas requirements (or potential pressure issues).

Page 7, Lines 210-211: Clarify that the NO_x monitor requires at least 1 L min⁻¹ here. The way this is written makes it seem like the instrument can only handle flows of 1 L min⁻¹, but a higher flow could be directed to it with an appropriate atmospheric vent or waste line used for the excess gas.

Page 8, Line 233: The point here is that higher flows generate higher concentrations of HONO, which can then decompose to NO_x. Revise this sentence so it does not seem that a separate issue of NO_x production that depends on flow exists (e.g. due to turbulent flow dynamics).

Page 9, Lines 244-245: As a standalone statement about RH, I do not understand the value of having a water vapour saturated in the calibration gas flow. If anything, this is a problem. The Authors point out that problem as well, saying that condensation can occur if the ambient temperature is below that of the dew point compared to the stripping coil. I'd suggest removing this sentence or making a clear point on why the water vapour in the calibration flow is useful.

Page 9, Lines 247-248: Does this imply that the backreaction is exothermic? Such that the elevated temperature is reducing the decomposition pathway to NO_x despite the higher HONO being produced? I'm not sure the current statement is accurate in terms of explanatory power despite the observed relationships being correctly stated.

Page 9, Line 259: What about the variance at lower mixing ratios? This evaluation is way above even the highest ambient mixing ratios observed in the real world, excepting extreme cases like wildfire plumes. The duration over which the variance was determined (as presented in Figure 8) also seems to be selected arbitrarily, rather than reflecting a typical span of time that one would conduct a calibration over (e.g. 1-2 hours). As a result, the additional data points from ~12 hours of observations make the variance seem much smaller than the more relevant timescale. It would be more useful to see the application-relevant performance of this calibration source at 5 ppbv, 2 ppbv and ~100 pptv, as suggested is possible in Figure 4B.

Page 9, Lines 262-263: This continuous duration is shorter than reported for other sources. That should be stated clearly and the point that this system can be shut down, flushed with deionised water, and restarted easily emphasized. The major contribution of this work is quantitative HONO production by mixing the two reagent solutions together on-demand with very little stabilization time required. It would be nice to see a depiction of that 'start-up' from instrument measurements over which the HONO is produced rapidly and with high stability. Apologies if this is what is being shown in Figure 8, but the initial and final conditions are not clearly stated as having changed the nitrite solution for deionised water or articulating a valve to deliver clean air to the instrument instead of the HONO source flow.

Page 10, Lines 275-276: This is true only over a few hours. The Authors state that pump flow rates drift over such periods, which means that they need to be recalibrated nearly daily. It is true that this task is simple, but one could argue that this is just as much of a malfunction as those observed in other sources. It would also be instructive to indicate how long the prepared nitrite solutions are stable for and under what conditions somewhere.

Page 10, Line 281: The Authors are conflating changing the HONO output from their source with the ability to easily dilute the HONO generated by others. Other sources can have their outputs rapidly modified on timescales of seconds using mass flow controllers, so the comparison being made is not fair-minded. The initial range for other sources simply requires proper setup. In fact, the Authors do not present good reasons to me why one would want to generate >50 ppbv of HONO for calibration purposes? As such, why not identify the correct nitrite concentration to obtain an output that is easily diluted into the ambient range of observed HONO mixing ratios? If a change in nitrite concentration in minutes then can give access to even lower stable mixing ratios (<10 pptv), that would be very attractive.

Page 10, Line 284: This work reports 2 hours for stability under the recommended operation conditions. Correct this statement.

Page 10, Lines 285-286: As stated above, permeation devices have been commercially produced for a very long time. They are sold with stabilized outputs that are certified, which requires no stabilization time to use. There are reviews on this cited in the work they are referencing. Here, the Authors are commenting on homemade permeation devices being stabilized on much shorter timescales compared to certified commercial options (days instead of 6 weeks). One could easily produce dozens of these at once and have stable HCl permeation devices for years, negating the statement made here. How long does it take to order and prepare the reagents for this source? Why are those timelines not considered in this comparison? Given the prevalence of permeation devices in use, the Authors are recommended to reduce their focus on this point, as HCl emissions with 5% accuracy could easily be obtained from a commercial manufacturer in perpetuity, with only the initial waiting period to consider.

Page 10, Lines 287-289: This is a separate discussion point, not a contrasting one. Move

to a separate part of the discussion. As suggested above, it would be great to show this performance in action where water and nitrite are exchanged in real time to demonstrate the start up and shut down periods that the system can achieve.

Page 10, Lines 292-294: For the Febo-style source, changing the temperature of the entire HCl solution is indeed time consuming, but it is easily done with a PID controller, so not particularly difficult. Also, if the relevant temperature to obtain HONO mixing ratios relevant to the operating range of an atmospheric instrument is identified, why would one be changing this regularly? They would simply be diluting the output with a mass flow controller and zero air. The Authors are putting a lot of emphasis on obtaining a wide dynamic range of HONO mixing ratios, particularly those above the observed atmospheric range. Why?

Page 11, Line 295: The NO_x decomposition is still occurring, the mixing ratios are simply below the detection limit of the monitor. Revise for accuracy.

Page 11, Line 297: The purities cited from these two works are the lower limits, when the sources were challenged to their limits or that of the instrumentation being used to determine impurities. While that is also the case with the value being discussed here, perhaps an additional point to make is that all three of these sources have >98 % purity when operated under ideal conditions in the environmentally relevant range of outputs? This would be a more balanced evaluation.

Page 11, Lines 300-301: Give quantitative advantages. These do not seem particularly specific. The Authors point out limitations in the discussion that impedes some of these statements (e.g. reagent consumption rate can be a major drawback). Also, for instruments like a ToF-CIMS utilizing CH₃I reagent ion chemistry, the RH variance in the calibration flow would make the calibrations more difficult due to the water-dependence of the ionisation scheme.

Page 11, Lines 302-304: This is by far the biggest contribution of this source to the field. Should be the first point.

Page 11, Lines 330-331: Yet again, atmospheric mixing ratios of HONO are typically below 5 ppbv. This systematic evaluation of the system by exclusion of the atmospherically-relevant mixing ratio range is not reporting the true performance of the system. Please revise throughout the manuscript to provide performance metrics for the data collected at only 5 ppbv and lower.