

Atmos. Meas. Tech. Discuss., referee comment RC1
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Comment on amt-2022-157

Anonymous Referee #1

Referee comment on "Comparison of two photolytic calibration methods for nitrous acid" by Andrew J. Lindsay and Ezra C. Wood, Atmos. Meas. Tech. Discuss., <https://doi.org/10.5194/amt-2022-157-RC1>, 2022

Nitrous acid (HONO) is a key atmospheric intermediate owing to its role in the production of OH, and for other reasons, and hence further examination of methods designed to calibrate field instruments for measurement of HONO is important and timely, and is certainly in scope for AMT. In this paper two calibration methods are compared, one widely used, the other novel and requiring a measurement of NO₂, with agreement providing confidence in both methods. The paper is succinct and well written, and is suitable for publication in AMT subject to consideration of the following points.

Abstract.

- State the range of HONO concentrations over which the calibration methods operate.

Introduction.

- HONO is very important indoors, given the wavelength cut off for window glass, and mention of HONO measurements indoors should be made
- Page 2, line 40. Some methods used to detect HONO are listed in this paragraph, with

a focus on intercomparisons. One method not listed is that of laser photofragmentation followed by detection of OH using laser-induced fluorescence spectroscopy, this ought to be listed having been used for both indoor and outdoor HONO measurements.

Instrumentation

- Page 3, line 75, state the range of O₃ over which the CAPS instrument was calibrated
- Although the manufacturer for the NO gas used is stated on page 4 (Airgas), manufacturers for other gases are not given, and none of the purities of the gases are stated, nor of the purity of the water used in the bubbler (electrical resistance) or other reagents (e.g. CH₃I). Given HONO is such a difficult molecule to measure, with impurity and interference problems, it is important to state the purity of the gases/reagents used in the calibration.
- State the manufacturer of the RH/ T probe. Quantification of water vapour is a central part of the calibration method, and water vapour is difficult to measure accurately. Was a dew-point hygrometer or other instrument for water vapour used, even if only to check the calibration of the RH probe (as these can drift).
- State the make and model of the CAPS NO₂ instrument and scroll pump

Calibration methods

- For reaction (R5), it is important that the fate of the H atom is only reaction with O₂. The H atoms be formed with excess energy via (R4) and Fuchs et al (2009) in a nice paper showed that 100% of the H atoms do result in HO₂ formation rather than reacting via other potential exothermic reactions – this paper should be referenced. Fuchs et al., AMT, 2009, 2, 55.
- Page 4, line 109. What is the length of the section of the flow tube exposed to the Hg lamp? State this – especially as the remaining length of the flow tube before sampling by the CIMS is stated later in the paper.
- Page 4, line 110 – state the range of lamp flux which was used to generate HONO (this can be estimated from the product of $F \times t$ divided by an approximate photolysis time).

Actinometric calibration

- Page 4, line 127, small w in where
- Page 5, line 137 and following. For the use of the O₂/O₃ actinometry method for calibration of HO_x instruments, where the gas mixture exiting the calibration flow tube is sampled at the centre of the flow by (usually) a pinhole and a supersonic expansion (e.g. for FAGE instruments), a profile factor (or P factor) needs to be used to reflect the laminar flow velocity profile across the flowtube (and hence a range of photolysis times) if the flow regime is laminar or partially turbulent. This is the case if the O₃ measurement is taken from the remaining flow that does not enter the FAGE sampling pinhole which samples the OH. If the flow is fully turbulent, as often used for the N₂O/NO actinometric method, then such a P-factor does not need to be taken into account as there is a flat velocity profile. In the case here, there is no pinhole for sampling, but there a short section of tubing before the excess flow goes to the CAPS instrument, and even if a profile factor does not need to be used, a discussion should be added regarding the nature of the flow in the photolysis chamber/flowtube and whether this needs to be taken into account in any way in the calibration.
- Page 5, line 140, state the value of the O₂ optical depth used in this calibration flow tube. Also, give some more further details about what is meant by "non-ideal overlap" between the lamp and the O₂ absorption spectrum.
- Page 5, line 146, in the equation, $(1 - (\beta/(1+\beta)))$ is the same as $1/(1+\beta)$ and might be simpler to write?
- Page 5, line 165, when only a low concentration of O₂ is used, state both the concentration of O₂ and also the lifetime of the H atoms by reaction with this O₂ to show it is still very short.

Results and Discussion

- Page 6, line 180. As well as the CIMS $\chi(\text{H}_2\text{O})$ which is the ratio of adduct to reagent, can the absolute water vapour concentration in the flow tube (as a mixing ratio) be stated also, as this will enable comparison with typically encountered levels of water vapour encountered in the atmosphere. Also, for completion, the total pressure of gas in the flow-tube and also the temperature should also be stated (it is on the figure caption)
- Page 6, line 180, the slope is discussed to give the sensitivity, can some discussion also be made of the intercept to figure 3, which is presumably from HONO impurities in the N₂ used?
- Page 6, line 199. I agree that the $\chi(\text{H}_2\text{O})$ is a useful quantity to compare CIMS instruments, but the level of water vapour (as a mixing ratio) also needs to be stated in order to gauge how the sensitivity of the instrument varies for different regions of the atmosphere.
- Page 7, Figure 2. Comment on the slower fall and rise of the NO₂ signal compared with that of HONO when the lamp is toggled off.
- Figure 2, also, state T and P conditions. State also the RH and absolute mixing ratio of

H₂O for this experiment.

- Page 8, Figure 3, the RH and [H₂O] are measured in the CIMS scroll pump exhaust. Was H₂O also measured closer to the exit of the photolysis region to check that the RH did not change (e.g. as a result of any temperature change after the pump or wall-losses of H₂O?) The measurement of water vapour is critical to the calibration.
- Figure 3, discuss the intercept in the text.
- Figure 3, the dotted line is clearly a linear least squares fit to the data, but this needs to be added to the caption.
- Figure 3. From the slope the sensitivity factor is obtained. Can the limit of detection of the instrument also be stated from the calibration and associated noise levels? Was a multipoint calibration also performed using the actinometric method?
- Page 9, figure 4. Discuss the shape of the graph and the possible reasons for this shape and increasing sensitivity at lower $\chi(\text{H}_2\text{O})$
- As well as IMR $\chi(\text{H}_2\text{O})$, the x-axis also should have the mixing ratio of H₂O vapour in the photolysis tube used to provide HONO to the instrument. This will allow how the instrument sensitivity changes with ambient water vapour levels.
- Does the shape of the curve have any implications for use of this type of instrument in various regions of the atmosphere? Although not the primary focus of the paper, which is about the agreement of the 2 methods of calibration, which is very good, the shape of the calibration plot with water vapour will be of interest, and might have implications for measurement of HONO using CIMS.
- The error bars for the proxy method multipoint calibration (dark blue point) is similar to the error bar for the adjacent single point calibration method (light blue point), whereas I might have expected it to have been smaller given it is based on a slope of several points. Is there any reason for that?

References

- Subscripts have not come out, probably a problem with endnote.

Supplement

- Line 9, small w in "where"
- Variables in the text, for example *T* and *P* should be in italics (as they are in the equations)
- The supplement is quite short, and consideration might be given to combining this with the main paper (which is fairly short).