Response to public comments made by Jörg Kleffmann.

Comparison of Two Photolytic Calibration Methods for Nitrous Acid

Prepared by Andrew J. Lindsay and Ezra C. Wood

We are thankful for the public comments made by Dr. Kleffmann during the interactive discussion phase. Black text denotes comments made by Dr. Kleffmann, and blue text denotes our responses.

In the manuscript of Lindsay and Wood a new quantification method used for a former photolytic HONO source is described. In the source, HONO is formed by photolysis of water at 184 nm forming OH and by the consecutive reaction of NO+OH. HONO is quantified by measuring the additional reaction product NO_2 ("NO_2 proxy method"). In addition, to several comments by the three reviewers, I have also a few other comments to the manuscript.

In the introduction, I missed a short summary on other HONO sources used in former studies besides the Febo et al. source and the photolytic sources. First, there are recent modifications of the Febo source and second, also other types of HONO sources are completely missing (e.g. the one by Taira and Kanda, 1990 or the very recent one from our group, Villena and Kleffmann, 2022). In addition, in contrast to the statement by the authors in lines 54-56, the original Febo source can be operated down to a few ppbs (see the original publication) and in recent modifications of this source, HONO levels even in the sub-ppb range can be produced.

The Villena and Kleffmann, 2022 paper was cited within the fourth paragraph of the preprint's introduction focused on recent modifications to the Febo technique. We will add additional text regarding the ability of Febo-based sources to operate at lower concentrations. Specifically, we will reference a recent modification by Lao et al., 2020 that can operate down to tens of pptv.

In addition, the authors should highlight that their HONO source represents a complex NO_y mixture including NO (in excess), NO_2 (50% of HONO), HONO and HNO_3 and is not a more or less pure HONO source like in most former approaches (e.g. the purity of HONO from the original Febo source was >99%). This makes the use and quantification of this source more complicated.

Although the HONO calibration mixture does include NO_2, excess NO, and trace HNO_3, we respectfully disagree that this makes the calibration gas "complex". The NO, NO_2, and HNO_3 do not add any complexity to our CIMS measurements besides the higher background signal. We will clarify in the revision that the high NO could potentially preclude its use for other HONO measurement methods (while noting that it worked very well for iodide-adduct CIMS). We disagree that the use and quantification of

our source is complicated – in fact, as presented in the manuscript, the quantification of HONO using the proxy method is actually very simple!

For example, the absolute interferent-free quantification of NO_2 is absolutely necessary for the present approach, which is not trivial here. E.g. the typical chemiluminescence instruments with molybdenum converters ("NO-what-boxes") commonly used for the simply quantification of pure HONO sources cannot be used here. And even if a more selective photolytic converter is available, the quantification of NO_2 is highly uncertain, since a) there is the additional uncertainty in the NO_2-converter efficiency and b) NO_2 is quantified from the difference of two large signals (NO is in excess...). Thus, groups who want to use this source need to have a CAPS or any similar selective and direct NO_2 instrument. In addition, in this humid NO_y mixture, there may be significant secondary heterogeneous HONO formation ($NO+NO_2+H2O$, $2NO_2+H_2O$, heterogeneous photolytic NO_2 conversion…), which is dependent on the surfaces available (photoreactor, transfer lines, analyzer,…), the gas/surface reaction time and S/V ratio and which will affect both, the concentrations of HONO and of NO_2 used to quantify HONO.

We completely agree with these points regarding the need to use a direct NO_2 measurement (e.g., CAPS or CRDS), and this was already noted within the conclusion of the preprint. In the revision we will include additional mentions of this requirement in the introduction and abstract.

Non-photolytic heterogeneous HONO formation mechanisms are accounted for during the calibration procedure by obtaining the background signal by turning off and on the mercury lamp (i.e., any heterogeneous formed HONO will be present during both background and operation). In the revision we will discuss the possibility that additional HONO could be formed by exposure of the quartz photolysis tube to the UV radiation or heterogenous formation of HONO through photolytic NO_2 conversion. The results of several tests, some already conducted, will be included (e.g., turning the UV on/off without the excess NO flow under both dry and humid conditions, and turning a 254 nm-only source on/off with humidified N_2/air and excess NO).

Furthermore, we note that the alternative to using a humidified calibration gas is to only calibrate an instrument under dry conditions. The response of any HONO instrument to ambient humidity must be thoroughly characterized, so these issues regarding potential heterogeneous HONO formation may also apply to other HONO measurement methods.

Besides, the authors should specify the range of HONO levels, which can be obtained by the independent variation of the three variables (light intensity, humidity, reaction time). This is important, since for example the variation of the humidity may not be recommended when calibrating a CIMS instrument, caused by the strong, non-linear humidity dependence of these instruments (see Figure 4).

Different values of HONO can be prepared by varying light exposure, light intensity, and humidity. The multipoint calibration plot (Fig. 3) was obtained at a constant RH with HONO varied by altering photon flux (i.e., light intensity). There is a factor of seven difference between the greatest and smallest [HONO] values obtained. The caption of this figure will be updated to state experimental conditions (i.e., constant humidity with photon flux altered using a Variac Variable transformer) so that readers can get an idea of a potential concentration range by adjusting photon flux only.

The [HONO] values of Fig. 4 (i.e., the sensitivity-humidity plot) were adjusted by altering humidity only. We had a factor of 15 difference between the highest and lowest [HONO] values that were obtained by varying humidity between 4.1 % and 67 % (RH values within the photolysis tube). There is a proportional

relationship between [HOx] and [H_2O] and a near-proportional relationship between [HONO] and [H_2O] at constant lamp flux and exposure (i.e., both relative humidity and [HONO] were increased nearly 15 fold). In the revision of the text, the range in [HONO] and the photolysis tube humidity (both RH and mixing ratios) will be stated in the text to make the potential range in [HONO] by varying only humidity more apparent. The experimental conditions for Fig. 3 (the multipoint calibration) and Fig. 4 are both stated in the text.

Specific comments:

Line 31: Should be Jiang et al., 2020 (no 2022 paper in the reference list?)

Lines 88-90: Can you explain how the humidity dependence is accounted for the CIMS? This should be a non-linear correction, see Figure 4, the shape of which may be in addition HONO dependent (with decreasing sensitivity at high HONO levels (?) as this was observed for the CIMS used in the study of Jurkat et al., 2011, doi:10.1029/2011GL046884).

In addition, can the instrument's analytical parameters by specified (DL, precision, accuracy, linear range), see the variable signal background in Figures 2 and 3 and the significant noise at the 5 ppb HONO level in Figure 2.

Response to Specific Comments:

Reference issue: Thank you for noticing this issue. The Jiang et al., 2022 citation is correct but was missing from the references section.

Accounting for humidity: For ambient sampling, we constantly measure humidity and apply a function to determine the real-time CIMS sensitivity (similar to how almost all iodide-CIMS users operate). We use an exponential fit to describe the relationship between I-$HONO^-$ signal and CIMS IMR χ_{H2O}. We will add a sentence briefly outlining this procedure, but full details on our ambient measurements will be discussed an upcoming manuscript. We have not observed any decreases in sensitivity with [HONO].

Analytical parameters: We will include the below information regarding detection limit, precision, and linear response in the SI as this manuscript is focused on calibration techniques and not instrumental parameters.

- **DL:** We do not state or show a true HONO background signal within this paper (i.e., HONO signals were elevated from impurities in our NO cylinder). During sampling near Boise, Idaho, background I-$HONO^-$ counts were ~190 normalized counts per second (ncps). This led to a detection limit of 12.3 pptv for HONO at SNR = 2 (time averaging of 1 s).
- **Precision:** shot noise dominated (i.e., the square root of the signal in counts/s)
- **Accuracy:** The accuracy depends on the calibration method, which is one of the main points of this paper.
- **Linear range:** We show linear response using the multipoint calibration for a concentration range of 450 to 3,400 pptv. We have yet to discover a limit to the linear range.

- **Inconsistent background signal in Figures 2 and 3:** The time series figure (Fig. 2) was of an early experiment and used insufficient [NO] (low by a factor ~ 4). The time series figure has been updated for the revised version of the manuscript, and the background signal is now consistent with the Fig. 3 multipoint calibration intercept.
- **Figure 2 Noise:** The Fig. 2 time series plot shows 1 Hz data and we disagree that it shows "significant" noise for this concentration ~ 5 ppbv HONO. 60-sec averages would show markedly reduced noise.