Atmospheric Measurement Techniques Discussions

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Comment on amt-2022-157

Anonymous Referee #3

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-RC3, 2022

This manuscript presents a calibration method for HONO instruments that was recently proposed in the literature, relying on the photolysis of water vapor to produce OH and HO2 radicals that are then quickly converted into HONO through the addition of NO in the calibration apparatus. In the existing literature, the concentration of HONO exiting the calibrator is computed from O2 actinometry. In this publication, the authors propose to take advantage of the formation of NO2, which is concomitant to the formation of HONO, to assess the HONO concentration from NO2 measurements. The authors demonstrates that the proposed approach helps to reduce the calibration uncertainty. While the paper is relatively short in terms of new results, this work will be of interest for groups working on HONO measurements and deserves to be published once the authors have addressed the following comments:

The authors mention the use of two photolytic HONO calibration methods. It seems to this reviewer that only one calibration method is used in this publication, namely the water photolysis method for the generation of OH and HO2 radicals with the implementation of an additional step to convert both OH and HO2 into HONO. There are however two different approaches used to quantify the amount of generated HONO. The authors should revise the text accordingly.

L41-44 : " For a Beijing, China based study, a comparison of several HONO measurements showed an overall mixed agreement with major differences observed for a few techniques (Crilley et al., 2019). Measurements in Houston, Texas showed several instruments to mostly agree in capturing variations in HONO, though there were differences in the magnitude of presented [HONO] values (Pinto et al., 2014)." – Please indicate the level of disagreement.

L74-76: "The CAPS instrument was calibrated using a 2B 75 Technologies Model 306 O3 Calibration Source, which agreed to within 2.5% with a Thermo Environmental

Instruments 49C O3 Calibrator. We assign an uncertainty of 3% (2σ) to the NO2 measurements" – The authors indicate that the CAPS instrument is calibrated using an O3 calibration source. How was the gas phase titration of O3 into NO2 performed? The stated 2σ uncertainty of 3% is rather low. How was it inferred?

L88-90: "We account for the humidity dependence of the instrumental response by determining the mole fraction of H2O(g) (χH2O) in the IMR by measuring the RH and temperature of the IMR in the exhaust of the scroll pump." – Why is there a humidity dependence?

L140: "We use a value of 1.4 x 10-20 cm2 molec-1 for σO2 for the mercury lamp used for these experiments." – Was σO2 determined experimentally? If not, how did the authors estimate the uncertainty associated to σO2? Was it factored in error bars shown in Fig. 4 for the actinometric approach?

Fig. 2: Please indicate the HONO mixing ratio derived from NO2 in the caption.

Fig. 3: Why is there a significant y-intercept when HONO=0 in Fig. 3? This intercept is approx. 3000 ncps, while in Fig. 2, measurements performed without HONO provide a normalized background signal of approx. 1000 ncps. Why are these "background" signals different? From Fig. 3, the normalized CIMS signal extrapolated for a HONO mixing ratio of approx. 5000 ppt (similar to that generated in Fig. 2, ΔNO2 of approx. 2500 ppt à HONO of approx. 5000 ppt) would be approx. 17500 ncps, which is approx. 14500 ncps after subtraction of the "background" signal. This does not compare to that reported in Fig. 2 since the background subtracted CIMS signal is approx. 5000 ncps. This difference of a factor of 2.9 does not seem to be only due to the humidity-dependence of the CIMS response reported in Fig. 4 since the sensitivity decreases by a factor of 1.4 when humidity varies from 0.39% to 0.56% (water mixing ratio estimated by the reviewer for data shown in Fig. 2, estimation based on reported RH values for the photolysis cell and assuming that temperature was the same for experiments displayed in Figs. 2 and 3). Could the authors comment on this?

Edits:

L111: "humidified ZA/N2" should read "humidified zero air/N2"

L136: "ΦO2" should read "ΦO3"

L171: "40% within the H2O photolysis cell" & L178 "28% within the photolysis cell and 18% within the CIMS IMR" – Please indicate the temperature for each RH measurement. Other instances in the text. Temperature should be provided each time RH is reported.

Fig. 2 vs. Fig.3: please use the same title for the y-axis

Supplementary material:

L5-6: "(kR7b/kR7a" should read "(kR6b/kR6a" & "(kR7b/(kR7a + kR7b)" should read "(kR6b/(kR6a + kR6b)"