Atmospheric Measurement Techniques Discussions

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Comment on amt-2022-157

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Community 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-CC1, 2022

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.

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.

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.

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).

Specify 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.