

Atmos. Meas. Tech. Discuss., author comment AC1
<https://doi.org/10.5194/amt-2021-332-AC1>, 2021
 © Author(s) 2021. This work is distributed under
 the Creative Commons Attribution 4.0 License.

Reply on RC1

Guillermo Villena and Jörg Kleffmann

Author 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-AC1>, 2021

A continuous source for the generation of pure HONO mixtures from the sub-ppb range up to 500 ppb is developed and characterized. nitrite is almost completely converted into HONO due to the acidic conditions of the aqueous phase ($\text{pH} \approx 2.5$). The source shows a fast time response of ~ 2 min (0-90 %) at higher concentrations and an excellent long-time stability. A general equation based on Henry's law is developed, whereby the HONO concentration of the source can be calculated using measured experimental parameters, i.e. nitrite concentration, liquid flow rates, gas flow rate, pH of the solution and temperature of the stripping coil. For the calculation of the effective Henry's law constant, the acid dissociation equilibrium of HONO/nitrite is used as a variable to adjust the theoretical HONO concentration to the measured values. A standard deviation between all measured and theoretical HONO concentrations of only ± 3.8 % is observed, for the first time, a stable HONO source is developed. I believe this study is of great interest to readers. There are some comments that the authors should consider, then the manuscript can be accepted to publish.

We would like to thank referee #2 for her/his interest and helpful comments, which will improve the quality of the paper.

1. Lines 161, " the theoretical and not the experimental pH values were used for $\text{pH} < 2$ in Figure 2" Why use theoretical values instead of experimental pH values here?

Answer: As explained in lines 157-161 of the manuscript, at $\text{pH} < 2$ we were not able to measure the theoretical pH-values, expected assuming a reasonable quantitative dissociation of the strong sulfuric acid. Here, the measured pH was significantly larger than the theoretical values. This deviation is a known artefact for electrochemical glass electrodes when using strong acids ("the acid error": Bates, 1973). In contrast, for $\text{pH} > 2$ theoretical and experimental pH values agreed very well in the present study. Since quantitative dissociation of the strong sulfuric acid can be assumed in the pH range 0-2, we decided to use the theoretical values here. However, for the present HONO source, this artefact is no issue, since a fixed pH of ca. 2.5 is recommended, for which measured and theoretical pH agreed well (e.g. for the measured pH of 2.49 in Figure 2 the theoretical value was 2.44).

2. Lines 200, in figure 3, HONO should be added an ordinate.

Answer: Thanks for pointing to this error. In a first version of this figure, we originally showed the measured NO_y signal and not the calculated HONO ($\text{NO}_y - 2 \times \text{NO}$). The ordinate title will be changed to "NO, HONO [ppb]".

3. Lines 271, the English usage in the statement of " A HONO source was developed and characterized, where HONO is produced by the reaction of diluted nitrite and H_2SO_4 solutions in a temperature-controlled stripping coil " is not understandable and the sentence should be rephrased.

Answer: We rephrased the sentence as follows: "In the present study a new HONO source was developed and characterized. In contrast to most recent studies (Ren et al., 2010; Reed et al., 2016; Gingerysty and Osthoff, 2020; Lao et al., 2020), HONO is produced by the reaction of nitrite and H_2SO_4 in the liquid phase. In a stripping coil reactor HONO partitions to the gas phase according to its known moderate solubility in acidic solutions."

4. Lines 280, why the time response depending on the HONO concentration levels?

Answer: Indeed, the time response of the source slightly increased with decreasing HONO levels. The effect was however only observed at concentrations in the very low ppb range (see Figure 3). A possible explanation for this observation is the adsorption of HONO on humid surfaces behind the HONO source (glass surfaces of the exit of the stripping coil, PFA lines, PFA-T, inlet of the chemiluminescence instrument), which leads to some delayed response of the NO_y signal. It is well known, that adsorption of gases plays a larger role at lower concentrations, as the time needed to saturate the surfaces increases at low concentrations. E.g. at the end of the experiment shown in Figure 3, the source was first switched to water (at 16:09), which should make the HONO source to a perfect "zero-gas generator" after a short time. However, after a first fast decrease of the HONO mixing ratio, there was a significant tailing of the signal at lower HONO levels. We think that this tailing does not results from the HONO source or the PFA surfaces behind the source, as the slope of the decreasing HONO levels did not significantly change, when the HONO source was physically disconnected and the chemiluminescence instrument was operated by pure nitrogen (at 16:59). Possibly, HONO adsorbed on the inlet particle filter or on the stainless-steel inlet surfaces of the instrument is still desorbing to the gas phase even after longer time. Thus, most probably this changed time response is an adsorption problem of the chemiluminescence instrument and not a problem of the HONO source. As reasons for this observation are however not fully clear, we did not discuss this issue in the manuscript. However, it should be highlighted that even a time response of 7 min at a low HONO mixing ratio of 1 ppb is superior compared to any HONO source yet developed and we do not consider this issue too important.

With respect to a similar comment by referee #1, we have added the following information to section 3.2, where Figure 3 is explained: "The increasing time response at low HONO levels is explained by adsorption/desorption of HONO on the surfaces behind the HONO source, which gets less important with increasing HONO levels, leading to faster saturation of the surfaces. From the experiment shown in Figure 3, we conclude that most of this adsorption/desorption took place on the surfaces of the chemiluminescence instrument used (inlet particle filter, stainless-steel lines) and not on the PFA transfer lines. At 16:09 the HONO source was switched from reagents to pure water, for which the HONO emissions should quickly decrease to zero. However, after a first fast decrease of the HONO concentration there was a significant tailing of the signal. Here the slope of the

decreasing signal did not change when the HONO source was replaced by pure nitrogen at 16:59. This can only be explained when the tailing is caused by desorption of HONO from the surfaces of the chemiluminescence instrument, as all other PFA surfaces were removed. This conclusion is also in agreement with our experience with pure HONO mixtures, for which adsorption losses in PFA transfer lines of up to 20 m length were found insignificant."

5. In the part of 3.2, is it calibrated with Nitrogen (N₂) as the background? What is the gas flow in this part?

Answer: As described in line 81 of the manuscript, the source was operated with pure nitrogen from our in-house nitrogen line for all experiments shown, but can be also operated with synthetic air. We used nitrogen here, as the nitrogen is expected to have smaller impurities compared to synthetic air. Although both have an original purity of better than 99.999 % (purity: "5.0"), the nitrogen is produced by evaporation from the liquid nitrogen tank of the chemistry department. It can be expected that most impurities (e.g. any NO_x) will stay in the liquid nitrogen at the low temperatures (77 K). In addition, the NO calibration gas used is also provided in pure nitrogen. Thus, the NO_x-instrument is exactly calibrated with the same buffer gas as used in the experiments, not affecting its sensitivity by any different quenching of the NO₂^{*} formed in the chemiluminescence cell. In the experiments described in section 3.2, a nominal gas flow rate of 2 l/min was used for the flow controller of the HONO source, leading to a calibrated standard flow rate (298.15 K, 1 atm) of 2104 ml/min, see figure captions 3 and 4.

6. In the part of 3.6, the source was operated at a low liquid pump speed of 10 rpm to get 2s noise is 0.76 %. Can you get the same value at the liquid pump speed of 20 rpm? Or the same value in the next experiment at 10 rpm?

In this study, the long-time precision was only tested in the experiment shown in Figure 8, for which a liquid pump speed of 10 rpm was used. However, years ago we made similar tests with 20 rpm using a HONO-LOPAP instrument to quantify the output of the source and found a similar precision of 1.0 % (the slightly higher value is most probably caused by the lower precision of the HONO LOPAP compared to the chemiluminescence instrument used in the present study). Furthermore, when looking to the short-time precision during the liquid flow rate dependence (see section 3.4, with each step only ca. 30-45 min) the precision was found to be independent of the liquid flow rate. Also, for the longest HONO step shown in Figure 3 at a much higher HONO concentration compared to Figure 8 (with a corresponding better relative precision of the NO_x instrument), an even better 2σ precision of only 0.4 % was observed at 20 rpm, (although again at a much shorter duration of only 50 min). And finally, with respect to the second question, the same high precision is also obtained when the source was operated on two different days by two different operators, for which a mean deviation between the two sets of experiments of only 0.67 % was observed for HONO concentrations >20 ppb (see section 3.2 and Figure 4). Thus, the given upper limit precision error, which will also result from the precision of the chemiluminescence instrument should well describe the general stability of the HONO source.