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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Technical Note: Quantification of interferences of wet chemical HONO measurements under simulated polar conditions" *by* J. Kleffmann and P. Wiesen

Anonymous Referee #2

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General Comments:

The authors are to be commended for methodically characterizing performance of a 2-channel LOPAP instrument for analysis of HONO under conditions relevant to the Arctic. The manuscript includes a detailed review of past evaluations of measurement techniques for HONO and presents a convincing case that the 2-channel approach used to correct for background influences minimizes interferences in HONO measured using the LOPAP "chemical" technique. Temporal variability in the background correction is quite interesting.

Although the authors cite several studies that report positive interferences associated

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with other chemical techniques for measurement of HONO, they present no direct evidence that would allow the magnitude of the background correction for the 2-channel LOPAP to be interpreted in terms of these interferences. For example, on page 3507 (lines 11 to 24), the authors indicate that, based on results from other studies, the background correction for the LOPAP may not be directly comparable to the magnitude of bias in other chemical techniques because of differences in inlet configurations, contact times with upstream surfaces, sampling media, sample integration times, and/or ambient conditions.

In addition, the authors question the reliability of intercomparisons that report minor to negligible interferences in measurement of HONO using other wet-chemical techniques. Unfortunately, as detailed under specific comments below, these assessments are based in part on misunderstanding regarding methodological details and selective interpretation of results.

All new results presented in the manuscript are specific to the 2-channel LOPAP and associated variability in the background correction. Based on the above, however, the background correction for the LOPAP is not directly comparable to bias in other techniques and, consequently, results presented in the manuscript are not relevant to "quantification of interferences" for other types of chemical methods. Thus, the current title seems inappropriate and the general applicability of the interpretation of these admittedly interesting results seems rather limited. I encourage the authors to consider rewriting the manuscript to focus on interpreting new measurements and evaluating factors that influence the background correction in their instrument.

As indicated below, the manuscript contains numerous qualitative descriptors that detract from the presentation. I encourage the authors to replace these with quantitative information. In addition, the manuscript contains several spelling and grammatical errors that should be corrected.

Specific Comments:

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Abstract, line 2. The acronym "LOPAP" should be defined when first used. Other acronyms that appear in the text should also be defined.

Abstract, lines 3 and 5. If the DL is 0.2 pptv (line 3), why does the lower limit for the specified range on line 5 indicate $<$5 pptv?

Abstract, line 7. Here and elsewhere throughout the text (see additional comments below), the use of qualitative descriptors detracts from the presentation. How low is "very low?"

Pages 3501-3502, first paragraph. How sensitive is "very sensitive;" how fast is "very fast;" how short is "very short."

Page 3506, lines 15-17. These correlations are consistent with but do not "confirm" the hypothesis that HONO is produced photochemically on ground surfaces.

Page 3507, line 3. How high is "extremely high?"

Page 3507, line 10. What specifically was "very complex" about these conditions?

Page 3508, par. 1. The description of the intercomparison in HONO measured in parallel by DOAS and mist chambers [Keene et al., 2006] contains several erroneous statements that require correction. First, the reported "condensation of analytes on inlet surfaces" was specific to sampling fresh (rapidly cooling) biomass-burning emissions from the stack of a burn facility in Germany; the reported median loss of HONO under those conditions was 3%. As described in the paper, the HONO intercomparison was conducted in ambient air on the coast of Maine, USA using established procedures detailed in a cited publication; to my knowledge, condensation in the inlet has not been reported when sampling ambient air using these procedures. Second, as described in the paper, the conversion of HONO to HNO3 in aging mist solutions was evident in samples of biomass-burning emissions only because fresh samples contained virtually no NO3-. This process could not be evaluated explicitly based on samples of polluted continental outflow containing high concentrations of HNO3 (for example, see Keene

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et al., 2004, cited in the paper; Fischer et al., 2006, JGR). During the intercomparison, NO3- (virtually all of which originated from dissolution of HNO3) was present in exposed mist solutions at substantially (many factors) higher concentrations relative to NO2-; NO3- was not added to NO2- to estimate HONO. Third, during the intercomparison, NO2- in exposed mist solutions was analyzed immediately (not several hours) after recovery. Keene et al [2006] characterized the HONO data generated by the mist-chambers technique as semi-quantitative (due to limited testing) and upper limits (due to published evidence for positive artifacts). Despite these limitations, results intercompared well with HONO measured in parallel with a long-path DOAS suggesting that artifacts were not a large source of positive measurement bias for the mist-chambers technique under those conditions. These results contrast sharply with the poor intercomparison of paired measurements based on a mist-chamber technique and LIF instrument (reported in the manuscript starting at the bottom of page 3500) for which data generated by the MC averaged 7 times higher.

Page 3508, lines 20-21. The characterization of HONO measurements by HPLC as "significantly higher" than paired measurements by DOAS implies that a statistical evaluation was conducted but the details are not reported. Differences between median values and distributions for paired data should be evaluated statistically and reported in the manuscript to justify the authors' assertion that data generated during daytime by the HPLC technique were associated with significant positive bias. In addition, the selective interpretation of paired data is potentially misleading. For example, the authors report that HONO measured by HPLC during daytime was higher than that measured in parallel by DOAS on 7 of the 11 days. How do the data compare on the other 4 days and what were the absolute and relative magnitudes of differences? Are these differences statistically significant? Similarly, the reported maximum relative difference ("up to a factor of four") is not a particularly useful sample statistic. Does this comparison correspond to a single set of paired data over the full 17-day period? What is the corresponding absolute difference? If near DLs, such large relative differences may be insignificant.

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Page 3509, lines 4-7. Based on the above, the authors have not, in my view, demonstrated that the background correction for the LOPAP instrument provides a representative diagnostic for "the general importance of chemical interferences for remote measurements" of HONO by other "chemical" techniques. As such, I question this central premise of the manuscript.

Page 3509, lines 10-15. These relationships may be inconsistent with the hypothesis but they do not "disprove" it.

Page 3509, last line. How "excellent" was the agreement?

Page 3510, line 4. Suggest replacing "strong" with "significant" and specifying the correlation coefficient.

Page 3510, lines 10-11. The results of this study are specific to the LOPAP. The statement should be revised to so indicate (e.g., "... demonstrate the importance of using a 2-channel LOPAP instrument ...").

Interactive comment on Atmos. Chem. Phys. Discuss., 8, 3497, 2008.