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

J. Kleffmann and P. Wiesen

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Reply to Anonymous Referee #1

We are very grateful for the reviewer's interest in our manuscript and the detailed comments and suggested corrections. The concerns raised by the reviewer are addressed below.

General comments, "third objective":

We completely agree with the referee's comment that it should be clear by now that chemical HONO measurements are affected by interferences "through the survey of published literature", which should be considered/corrected in recent and future stud-

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ies. The motivation to publish the somewhat limited data from the Jungfraujoch campaign arose only after we realized that this is simply not the case and for example, still unreasonably high HONO/NO_x ratios of up to 100 % were recently published from a campaign performed under polar conditions and using a chemical instrument. Thus, the objective of our manuscript was also to summarize and highlight the very likely overestimation of some former HONO measurements and to bring to peoples attention that these data should not be used further without critical assessment, for example by modellers.

We also completely agree with the referee's comment that the absolute interference signals measured by the LOPAP instrument cannot be transferred directly to other instruments using different sampling conditions (e.g. with respect to inlet lines, higher pH of sampling solution, longer gas/liquid contact time, etc.), see below. Thus, we later conclude (page 3510, lines 10-11) that other instruments should also be used as two channel instruments to correct for their individual interferences. However, since all known interferences are expected to be of similar or even higher importance for other instruments, caused by their longer gas/liquid contact time and higher pH of the sampling solution (for details, see page 3507, lines 11-24), at least similar or even higher interferences are expected for these instruments. This is confirmed by unsuccessful intercomparison studies and the 5-20 times higher HONO/NO_x ratios reported for similar conditions as those presented here for the LOPAP instrument. Although we agree to emphasize in the revised manuscript that the absolute correction of interferences applied for the LOPAP instrument cannot be directly used for other instruments (referee #2 raised the same concern...), we still see the necessity to highlight the importance of the active correction when using chemical instruments for measuring HONO, in order to improve the quality of future HONO data. The presentation of our interference data as the potential lower limit of interferences of other instruments may help to estimate at least the lower limit of the magnitude of potential overestimations. This is for example done by comparing our corrections (up to factor of four) with a recent intercomparison study also performed under remote conditions (factor of seven higher HONO concen-

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trations for the chemical instrument) and by comparing published remote HONO/NO_x data with ours (factor of 5-20 higher values by other chemical instruments). Since also the inverse dependency of the relative importance of interferences observed for the LOPAP (see Fig 7 from Kleffmann et al., 2006 and Fig. 5 from this study) fits very well with former published intercomparison studies (good agreement for high HONO concentrations and/or night-time urban, strong overestimation by the chemical instruments for low concentrations and/or daytime urban...), it is at least very likely that the same tendency of relative interferences is to be expected for other chemical instruments. For example, in the study of Spindler et al., 2003, good agreement between a DOAS and a chemical instrument was observed during night-time for ca. 1 ppb HONO, for which we would only expect on average <10 % correction based on former LOPAP interference measurements (see Fig 7 from Kleffmann et al., 2006). However, during daytime a factor of 2-4 higher values compared to the DOAS were observed in Spindler et al. for DOAS concentrations of 50-100 ppt. For these conditions, we also would expect higher interferences of ca. 50 % (see Fig 7 from Kleffmann et al., 2006 and Fig. 5 from this study). Therefore, the tendency is similar, although the magnitude of the relative interferences is different (ca. 50 % LOPAP to be expected, 200-400 % difference to the DOAS in Spindler et al.). Another example is given below, under "specific comments". In conclusion, if possible we would like to leave the "third objective" in the manuscript and would only like to clarify that the correction of interferences applied for the LOPAP instrument should be considered as a lower limit of the overestimation of HONO concentrations by other chemical instruments.

Specific Comments:

Section 2.1 and Figures 4+5:

Although we have demonstrated that our instrument is different to other chemical instruments it still uses an aqueous surface for the sampling of HONO. Thus, any reactions taking place in the aqueous phase or on an aqueous surface, which lead to nitrite formation will influence any aqueous sampling instrument. The difference between the

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LOPAP and other instruments (shorter contact time, lower pH) causes only that some interfering reactions are of lesser importance for the LOPAP. But this may not be always the case and absolute interferences by specific reactions may be of similar magnitude compared to the LOPAP. For example, PAN hydrolysis is generally slow for $\text{pH} \leq 7$, which is applied in many instruments. In addition, the pH dependency of the reaction $2\text{NO}_2 + \text{H}_2\text{O}$ is also weak in the pH range $0 - \leq 7$. Thus, for instruments sampling under neutral conditions these interferences may be of similar magnitude compared to the LOPAP. Nevertheless, as already mentioned above, we will point out in a revised manuscript that the absolute magnitude of the interference correction applied for the LOPAP may be only a lower limit of the overestimation of other instruments.

High interferences during night-time in Fig 4:

As referee #1 correctly pointed out, our highest relative interferences (400 %) were observed during night time when the HONO concentrations were extremely low. This observation is not in line with the typical daytime differences between chemical instruments and DOAS measurements. However, these intercomparison studies were all performed under urban conditions (caused by sensitivity limitations of the DOAS...), for which the minimum HONO levels are observed during daytime. In contrast, in this study and in all other mountain site and polar studies the lowest HONO concentrations are observed during dark periods. Since we found that the absolute interference signal in channel 2 increases much more slowly than the concentration of HONO itself (see Fig. 5, absolute interference signal variability: factor ca. 3 vs. HONO variability: >factor 10), the relative correction of interferences is of importance at low HONO concentrations and not necessarily only during daytime (only for urban conditions this is the same...).

Figure 6 suggests...:

We do not fully understand the referee's first sentence. Why does Figure 6 suggest that interferences of the LOPAP are different to interferences of other instruments? Other

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instruments typically do not measure interferences and have for sure not measured the irradiance dependency of interferences.

We agree with the referee, that the trend observed in Fig. 6 is small (only a factor of two from light to dark...), but that is the data... In addition, the data were not weighted, thus the intercept is almost only given by the average of the night-time values (which is lower than the average of the daytime values, inline with our conclusion...).

In addition, the night 5-6 November is certainly not representative, since it was chosen as the most extreme case to demonstrate how high relative interferences can get for low HONO concentrations. Normally the values are lower; see average relative interference data from Fig. 5.

Couple of statements in section 3.2:

We will emphasize in the revised manuscript that the absolute correction applied for the LOPAP instruments cannot be directly transferred to other instruments (see above). However, as shown in the example of Spindler et al. (see above) the magnitude of interference correction of other instruments is expected to be equal or even higher compared to the LOPAP. This can be also deduced from the lower HONO/NO_x ratios from the present study compared to similar mountain site studies using other instruments. For example, the average HONO/NO_x ratio of ca. 5 % from this study is 4-6 times lower than the average 20-30 % observed by an HPLC system for other mountain site measurements (Huang et al., 2002, and Zhou et al., 2007) and also much lower than published polar data. For those conditions, we would expect average interference corrections of 50-150 % based on the data shown in Figure 5. Again this correction is lower than the difference between the LOPAP HONO/NO_x data and similar data from other chemical instruments. Thus, it is very likely that interferences are similar or even higher for other instruments for remote conditions.

The correction of interferences is, indeed, done by dry sodium carbonate (alkaline) denuders, which typically also use two denuders in series. However, also data from

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these measurements are not in agreement with DOAS data (see Appel et al., 1990). This might be explained by the very alkaline surface properties, by which for example interfering phenols (phenols+NO₂) would be completely sampled on the first denuder (in contrast to the LOPAP). Thus, corrections of interferences by two channel denuder systems will fail for those interferences. In addition, denuders are different to aqueous sampling instruments, since the same surface is used for very long sampling periods and surface properties can change over time. We often observed this in smog chamber studies, for which denuders could not be used to remove HONO after some sampling time caused by the uptake of other trace gases. In contrast, in aqueous instruments the sampling surface is continuously renewed and the magnitude of specific interferences will not change over time.

For the HPLC system we are not aware of any field measurements for which two stripping coils are used in series. In the interference tests performed by Huang et al. only a dry carbonate denuder was used, which will underestimate interferences (see above).

Technical corrections:

Page 4: done

Page 5: done

The sentence starting "caused by these..." will be changed in the revised manuscript.

Page 6: not changed, see discussion above

Page 10/11: will be changed in the revised manuscript.

Page 12 (11): done

First word...: done

Page 13 top: done

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

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