Atmos. Chem. Phys. Discuss., 8, S862–S866, 2008
www.atmos-chem-phys-discuss.net/8/S862/2008/

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 #1

Received and published: 19 March 2008

General Comments:

This manuscript describes a short (5-day) deployment of an optimized LOPAP instrument to measure HONO at the Jungfraujoch. The authors address two main objectives: 1) determining whether the LOPAP has adequate sensitivity and stability to make fast and reliable measurements of HONO at the low mixing ratios (sub- to several pptv) reported for previous studies in polar and high altitude regions, 2) showing that known and unknown interferants causing positive artifacts in the measurement of HONO by the LOPAP technique are successfully recognized and accounted for by the technique (2-stripping coils in series). Objective one is based on the apriori assumption that

Full Screen / Esc
Printer-friendly Version
Interactive Discussion
Discussion Paper

HONO mixing ratios at Jugfraujoch are comparable to, and controlled by similar processes as, those in polar regions. Results of the reported campaign clearly confirm this assumption, and establish that the LOPAP technique is well suited for future campaigns where HONO mixing ratios are quite low, and dominated by snow pack emissions.

A third objective of the manuscript is to establish that other "wet", or chemical, techniques purporting to measure HONO are likely to suffer from similar positive artifacts, but that these are not adequately accounted for as the techniques have been implemented. This possibility has been recognized and discussed in the literature for some time. Evidence from previous studies consists primarily of poor agreement between HONO measured by wet chemical versus optical techniques (primarily active DOAS) in intercomparisons, and the inability of models to accommodate "HONO" measured by these wet techniques in a manner consistent with simultaneous measurements of HO_x and NO_x. Discrepancies with DOAS and models are largely apparent during mid-day hours when photochemistry is active. The present manuscript nicely summarizes these earlier findings, and points out that some instances of reported successful intercomparisons between DOAS and chemical measurements of HONO were not very rigorous. The authors then suggest that positive artifacts quantified in the second channel of the LOPAP instrument (used to correct the signal in first channel, hence yielding HONO meausrement) provide independent evidence about the importance and magnitude of unrecognized interferants that cause other wet chemical techniques to seriously overestimate HONO, especially during the day when mixing ratios are relatively low. The point that other HONO measurements need to quantify and correct for interferants is valid, and well made through the survey of published literature. However, differences between LOPAP and other techniques (described as fundamental advantages of LOPAP herein) make it extremely unlikely that quantitative insight about artifacts in the other techniques can be gained from the second channel, or the ratio of signals in the two channels, in the LOPAP instrument. Unfortunately, the authors try very hard to make the case that the magnitude of corrections made to channel one of the LOPAP during this campaign indicate the magnitude of uncorrected artifacts in HONO mea-

ACPD
8, S862–S866, 2008

surements by other wet chemical techniques. This point is not well established, and is also not integral to the main objectives. Trying too hard to make this point detracts from the rest of the paper.

Specific Comments:

Section 2.1 describes the LOPAP, and highlights “advantages” (this is the author’s term) compared to other chemical techniques that minimize artifacts. Chief among these are the use of a very acidic stripping solution in 2 coils in series. Each coil is quite short to keep residence time short. Combined, these result in nearly quantitative collection of HONO in the first coil, and inefficient (but nearly constant) collection of known interferants in both coils. This approach largely allows correcting for the interferants (shown in previous LOPAP intercomparisons), but also makes the signal in channel 2, and the ratio of the two LOPAP channels, hard to relate to measurements trapping HONO (and interferants) in neutral or alkaline solutions, in systems with longer contact times between sample air and the wet surfaces.

Despite convincing the reader that the LOPAP technique is fundamentally different than other chemical techniques, the authors use Figures 4 and 5 to attempt to constrain the magnitude of interferants impacting these other techniques. Figure 4 is particularly interesting, with the signals in the 2 LOPAP channels quite similar for 9-10 hours. The “relative” interference approaches 100%, and correcting for it reduces inferred HONO mixing ratio by a factor of 4. This is implied to be indicative of the size of unrecognized artifacts in HONO measured by other techniques.

It should be noted that the signal in channel 2 is essentially flat for the first 13 hours plotted in Figure 4, with increasing relative interference nearly entirely due to decreasing signal in channel 1, and high values of relative interference occur between about 22:00 and 7:00 (mainly in the dark). Significant night-time interference does not help to explain the “HONO problem” of being too high for models or compared to DOAS from late morning into afternoon.

ACPD

8, S862–S866, 2008

Figure 6 suggests that the authors realize (though they do not acknowledge) that the temporal pattern of interference in the LOPAP does not fit that in other techniques. The trend line suggests increasing abundance of compounds interfering with LOPAP at higher solar elevations. But, the trend is not terribly convincing, with reduced slope, or even a reversal, above 200 W m^{-2}. It is also not clear how the large fraction of time in the dark was weighted (well over 50% of the sample interval would have been at night in November). Further, comparing Figures 4 and 6 raise the question of how representative 5-6 November may have been, since channel 2 was at or slightly above 4 pptv all night (Fig 4), but apparently this was quite different from the other 4 nights, as Figure 6 shows nearly no points with mixing ratios so high in the dark.

A couple of statements in section 3.2 suggest the authors may have a bias, leading them to focus too strongly (my opinion) on trying to transfer LOPAP channel 2 findings to other techniques. Specifically, on pages 5 and 11 they note "significant chemical interferences, which are normally not corrected for by chemical instruments" followed on page 12 by the statement "that interferences are expected to be of even higher importance for other chemical instruments". The latter is not credited to anyone else, suggesting this is the authors expectation (perhaps well founded, but not necessarily established). The first statement is not generally true, since nearly all investigations using denuders employed paired denuders in series (like the 2 coils in LOPAP, with second one meant to account for interferences), as have several studies which used stripping coils coupled to HPLC for analysis. Apparently the authors feel that these efforts did not adequately account, then correct, for interferences but these other investigators (and referees of the published papers) felt that the techniques did make such corrections.

Technical Corrections:

Page 4, next to last line, "her called" should be "here called"

Page 5, it should be clarified whether Kleffmann et al., 2006 found relative or absolute

ACPD
8, S862–S866, 2008

interferences to be inversely correlated with pollution. Discussion later in present paper suggests the former (though it will be noted later that the distinction is not always made as carefully as it needs to be)

The sentence starting “Caused by these. . . ” is awkwardly constructed, hence harder to follow than it could be.

Page 6 next to last sentence of section 1. LOPAP channel 2 signals appear to do a good job of quantifying interferences in LOPAP channel 1. This is not the same thing as quantifying interferences in all chemical techniques purporting to measure HONO.

Page 10/11 The sentence bridging these 2 pages is awkward.

Page 12 “corrected for the small HONO losses in the first channel” probably should be “small losses from the first channel” or more precisely “corrected for the small fraction of HONO that passes through the first channel” (on page 6 it is stated that 99.4% of HONO is “lost” from the air stream in first coil)

First word in second sentence after above “In” should be “It”

Page 13 top, delete the comma in “more severe for instruments which”

Page 15 top “very high interferences of $>$ 100%” should be “relative interferences

Page 16 last sentence, here too, seems “interference” should be “relative interference”

Page 29, plot would be easier to read if labels for left hand axis $>$ 2.0 were deleted (as is done for those $<$ 0 on right hand axis)

Page 30, same comment as above, but for labels $>$28

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