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Techniques

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Discussions

Interactive comment on "HONO Measurement by Differential Photolysis" *by* C. Reed et al.

Anonymous Referee #2

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Review of Reed et al., "HONO measurement by differential photolysis" MS No.: amt-2016-17

General comments.

This is a clearly written paper that describes an interesting and novel approach to measuring atmospheric HONO. This species couples the HOx and NOx cycles and its accurate measurement has been the subject of some controversy.

In principle this is a compelling idea. The paper is clearly written and its logic is easy to follow. The differential photolysis technique described in this paper depends on differencing three numbers (detector response for ambient NO, NO plus some fraction of NO2 photolysed at 385 nm, and NO plus a different fraction of NO2 photolysed at 395 nm plus some fraction of HONO) to accurately derive HONO. Crucially, the chemiluminescence selectivity for NO, the photolytic selectivity for NO2, and the photolytic

selectivity for HONO will determine the atmospheric applicability of this technique. In principle this might be tractable, but in practice this paper does not do a sufficiently thorough job in characterizing the uncertainties in these three measurements. With some additional work this could be suitable for publication, as described below.

This approach may not necessarily require an accurate NO2 measurement in order to measure HONO (although that would greatly simplify the analysis, and seems to be assumed). This approach does require that any interferences in the NO2 measurement at 385 nm are unchanged when HONO is measured at 395 nm. This assumption is implicit, but should be stated explicitly, and defended at some level in the text.

A paper in review at ACPD by these authors shows that undesired thermal decomposition of PAN presents an interference in their NO2 measurement (http://www.atmos-chem-phys-discuss.net/acp-2015-789/). Further, possible interferences from thermal decomposition of methyl pernitrate (CH3O2NO2) (Browne et al., ACP, 11, 4209–4219, doi:10.5194/acp-11-4209-2011, 2011) may also compromise the NO2 measurement in certain regions. Are these an issue for the HONO measurement by difference from NO2 in this approach, and if not, why not?

Further, no discussion is given of the spurious NO2 "artifact" signal that can be generated when illuminating NO2-free air at UV wavelengths (e.g., Kley and McFarland, J. Atmos. Technol., 1980). This NO2 "artifact" signal can be large and variable, and if different at the different wavelengths used to infer HONO in this technique, can represent a major bias in inferred HONO unless accounted for. Are there similar "artifact" signals for HONO when HONO-free air is irradiated at 395 nm? The authors should discuss these issues, quantify them in their instrument, and include them in a comprehensive uncertainty analysis before this paper is acceptable for publication.

Specific comments.

P4, line 7: change to read "...gives a sample residence time of 0.96 seconds assuming plug flow..." How good is the plug flow assumption?

P5, lines 9-10: "It is noted that at both 385 nm and 395 nm there is potential interference from BrONO2 (or in fact any other compounds which photolyse to give NO at either wavelength)..." A point that first comes up here: the potential interferences also include spurious NO chemiluminescence when the photolysis cell is illuminated at either wavelength in the absence of gas-phase nitrogen compounds. This has been termed an "artifact" signal in NO2 photolysis and is thought to arise from undesired photolysis of nitrogen compounds (likely nitric acid or ammonium nitrate, but others are possible) adsorbed on the photolysis cell walls. At times this artifact signal has been substantial (e.g. on the photolytic NO2 measurement flown on the NASA ER-2 aircraft described in Del Negro et al., JGR, 1999) and should not be neglected. I did not find any discussion of the NO2 "artifact", or the possibility of its being different at the different wavelengths used to infer HONO abundance. The "artifact" needs to be quantified fully and its uncertainties discussed as a possible source of error in HONO inferred by this technique.

P8, lines 2-5: "This 2 apparent HONO conversion determines the limit of detection, which is the ability of the analyser to discriminate the difference in signal arising from photolysis at the two different wavelengths from photon counting noise." Because this method is a difference of three numbers (NO, NO2, and HONO) that can vary independently, the effective limit of detection should also depend on the NO concentration, the NO-to-NO2 ratio, and the NO-to-HONO ratios. For example, when ambient NO is very low (e.g. after dark in remote regions) the 'background' signal (really, ambient NO plus the fraction of NO2 photolysed at 385 nm) from which HONO is determined will be relatively low, and the effective HONO LOD will improve due to better precision in the 'background' signal according to photon counting statistics. Conversely, when ambient NO is very high (e.g. in urban areas at the surface, close to traffic sources) the 'background' signal can be very high, thus the effective HONO LOD must be degraded. Please include a more rigorous treatment of the HONO limit of detection.

P8, lines 9-11: "The effect of the back reaction of OH + NO, reforming HONO, before

detection of NO, thus reducing the NO signal in the NOx/HONO measurement in the presence of HONO was calculated using a box model..." The ensuing discussion uses a reaction time of 0.11 seconds, which assumes this reaction begins only after the sample exits the photolysis cell. Is it really that simple? There is a similar back-reaction that involves NO + O3P, reforming NO2, which if not accounted for will bias the NO2 measured at 385 nm and thus HONO inferred by this technique. Further, what about HONO and/or NO2 that are photolysed immediately upon entering the photolysis cell? The reaction time to reform either HONO or NO2 can take place in the photolysis cell as well. Both back-reactions, including those occurring in the photolysis cell residence time of about 1 second, should be modeled.

P12, line 23: "...NO offset was taken between these times." What does this mean? Please rephrase for clarity.

P13, lines 1-2: "There is reasonable agreement between the established LOPAP method of HONO measurement 1 and that provided by the pHONO instrument without correction or calibration." This is a value judgement and should be changed to express a quantitive measure of agreement.

P13, lines 3-4: "During 2 the high ozone and high HONO events observed on the 1st and 2nd especially there is very good 3 agreement between the two." Yes, but what about the data observed on June 30 shown in Figure 6? The measurements diverge by a factor ~2 and lines 21-22 suggest the June 30 data were not plotted in Figure 7. I find the focus on days characterized as "high HONO" to be troubling. The comparison at low values is equally useful and should be included. Please include all the available data in Figures 6 and 7, and explain why a subset was chosen for the linear fit in Figure 7. Is the linear fit single-sided or does it allow for uncertainties in both X and Y values, as it should? Please confirm that a bivariate fit weighted by instrument precisions was used. If at times the two measurements disagree systematically by a factor of two, what does this imply for the accuracy and selectivity of either measurement? It would help to also show the time series of NO and NO2 data in Figure 6, because it is likely the

pHONO measurement will be at its best at relatively low NOx and high HONO values.

P14, lines 11-13: "During 11 field tests the photolytic HONO instrument agreed reasonably well with the established LOPAP 12 instrument,.." This is a value judgement and should be changed to express a quantitive measure of agreement.

Figures.

Fig. 1. For clarity please use colored text to identify the different spectra. The caption describes the colors, but is cut off after line 2 in my PDF version.

Fig. 2. The error bars should show the standard error of the mean – please confirm in the caption.