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Comparison of two photolytic calibration methods for nitrous acid

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Supplementary Information

S1 Detection of HONO by Chemical Ionization Mass Spectrometry

The following sections detail the analytical parameters and humidity effects of the chemical ionization mass spectrometry (CIMS) HONO measurements.

S1.1 Analytical Parameters

The signal-to-noise ratio (SNR) and limit of detection (LOD) for our CIMS measurements of HONO are determined by the precision of the total and background signals, both of which are dominated by shot noise. The SNR is given by $SNR = (S_T - S_B)/(\sigma^2_T + \sigma^2_B)^{½}$ where S_T is the total signal, S_B is the background signal, σ_T is the precision of the total signal, and σ_B of the background signal. For our lab experiments the background signal was elevated due to HONO impurities associated with the high NO mixing ratios used (1.58 ppmv). For field measurements from 2019 in Boise, Idaho, our unnormalized $I(HONO)^-$ background signal was 228 counts/s, corresponding 76 ncps. With a sensitivity of 2 ncps ppt^{-1} (that of a typical ambient humidity), the resulting 1 s LOD was 8.0 pptv (SNR = 2). An upcoming manuscript focused on the 2019 field measurements will have further discussion of limit of detection.

The CIMS $I(HONO)^-$ signal responds linearly to [HONO] for a given humidity as demonstrated by the multipoint calibration curve in the main text (Fig. 3). We have yet to experience HONO concentrations that deviate from a linear trend. Linear response in $I(HONO)^-$ signal is shown in the multipoint calibration figure (Fig. 3) for a 450 to 3,400 pptv range, and past multipoint calibrations have shown linear response for wider ranges that extend above 10,000 pptv.

S1.2 Humidity Effects

The ionization chemistry utilized is sensitive to humidity. HONO can be ionized by reaction with either I^- or the iodide-water adduct $I(H_2O)^-$ to form the detected adduct $I(HONO)^-$:

$$I^- + HONO \rightarrow I(HONO)^- \quad \text{RS1}$$

$$I(H_2O)^- + HONO \rightarrow I(HONO)^- + H_2O \quad \text{RS2}$$

The reverse reaction of S2 also occurs:

$$I(HONO)^- + H_2O \rightarrow I(H_2O)^- + HONO \quad \text{RS3}$$

Reactions RS2 and RS3 lead to variation in the sensitivity depending on ambient water vapor levels. The CIMS sensitivity to HONO decreases with ambient water vapor concentration as shown in Fig. 4 of the main text. Many compounds sampled by I^- CIMS exhibit similar sensitivity-water vapor trends, though to varying degrees (Lee et al., 2014). As a result, sampling in dry conditions with low ambient water vapor mixing ratios allows for more sensitive detection of many compounds by I^- CIMS including HONO. Drastic changes in sensitivity from atmospheric variability can be suppressed by constant dilution of the IMR with humidified nitrogen (as performed here) or by maintaining constant water vapor concentration (Veres et al., 2020).

S2 Impact of Product Branching Ratio for HO_2 + NO

We account for the impact of the small yield of HNO_3 from the HO_2 + NO reaction (R6b in main text) on the two HONO calibration methods. The branching ratio for these reactions is determined using literature temperature, pressure, and humidity dependences. Butkovskaya et al. (2007) present the quantity β, which is the ratio of reaction rates (k_{R7b}/k_{R7a}), rather than a traditional branching ratio ($k_{R6b}/(k_{R6a} + k_{R6b})$. First, we determine β *under dry conditions* using only the temperature and pressure dependences. This first form will be referred to as β^*.

$$\beta^*(T,P) = 0.01\ (\frac{530}{T} + 6.4\ x\ 10^{-4} \cdot P - 1.73) \quad \text{(S1)}$$

where T is temperature in Kelvin and P is pressure in Torr. The 2σ uncertainties for the constants of the three numerical terms are ±10, ±1.3 and ±0.07, respectively. A humidity factor f_{H2O} is then applied to β^* to determine β (Butkovskaya et al., 2009).

$$f_{H2O} \approx (1 + 2\ \text{x}\ 10^{-17}[\text{H}_2\text{O}]) \quad \text{(S2)}$$

$$\beta = f_{H2O} \cdot \beta^* \quad \text{(S3)}$$

Here, $[H_2O]$ is expressed in number concentration (molecules cm^{-3}). β is useful for accounting for the $[HNO_3]$ if the final $[NO_2]$ is observed after all HO_2 is processed by R6a and R6b:

$$\beta = \frac{k_{R6b}}{k_{R6a}} = \frac{[HNO_3]}{[NO_2]} \quad \text{(S4)}$$

$$[HNO_3] = \beta \cdot [NO_2] \quad \text{(S5)}$$

In the photolytic calibration involving standard O_3 actinometry, the [HOx] generated at the point of H_2O photolysis is quantified. Therefore, a branching ratio is required to account for the small portion of the HO_2 initially formed that does not form HONO because of R6b. Here, we define branching ratio as β_{BR}.

$$\beta_{Br} = \frac{k_{R6a}}{k_{R6a}+k_{R6b}} = \frac{[NO_2]}{[NO_2]+[HNO_3]} \quad \text{(S6)}$$

Substituting Eq. (S5) into the $[HNO_3]$ of Eq. (S6) yields Eq. (S7):

$$\beta_{Br} = \frac{1}{1+\beta} \quad \text{(S7)}$$

This branching ratio appears in Eq. (4) in the main text.

S3 Uncertainty Propagation for Actinometric Calibration

The uncertainty in [HONO] quantified by the actinometric method involves adding in quadrature the relative uncertainties of each variable in Eq. (3) (see Sect. 2.2.1 of main text) as shwon in Table S1. The resulting [HONO] relative uncertainty is 26.9 % (2σ). A small uncertainty is also associated with the term β used in the correction equation that converts [HOx] to [HONO] (Eq. (4) in the main text). Because of this small correction, we round up and assign an overall uncertainty of 27 % (2σ) to the calibration. The σ_{O2} uncertainty is the largest contributor to this overall [HONO] uncertainty and was determined experimentally. The uncertainty in σ_{H2O} was the same as used by Dusanter et al. (2008). We choose a $[H_2O]$ uncertainty of 5 % (2σ) because the Vaisala HMP60 RH/T probe used for $[H_2O]$ quantification in this manuscript had not recently been factory calibrated but agreed to within 1.1 % with a brand new Vaisala HMP60 sensor that has a manufacturer-stated accuracy of 3 %. In a separate experiment, the RH/T probe was compared to the CIMS exhaust RH/T probe (also a Vaisala HMP60) and agreed to within 3.5 %. The $[O_2]$ uncertainty is based on the range stated by the gas manufacturer (Airgas), and the uncertainty of $[O_3]$ is that of the CAPS NO2 instrument (see main text Sect. 2.2), which effectively measures Ox (O_3 + NO_2).

Table S1 Relative Uncertainties (2σ) for Variables Used to Quantify [HONO] By Chemical Actinometry

Variable	Relative Uncertainty (%)
$[H_2O]$	5
σ_{H2O}	6
$[O_3]$	4
$[O_2]$	4.8
σ_{O2}	25
[HONO]	26.9

S4 Uncertainty Propagation For NO_2 Proxy Calibrations

Uncertainty calculations for the NO_2 proxy calibrations are mentioned in Sect. 3 of the main text. In the following sections, uncertainty equations are provided for the multipoint calibration curve (Fig. 3 of main text) and the sensitivities shown in Fig. 4 (spanning several humidity values) determined by single point calibrations.

S4.1 Multipoint Calibration Uncertainty Calculations

The multipoint calibration plot (normalized CIMS HONO signal vs quantified [HONO]) includes uncertainty in both axes. The normalized CIMS signal uncertainty (σ_{CIMS}) is quantified in Eq. (S8) by combining the 15 s average precision of the CIMS $I(HONO)^-$ and I^- signals.

$$\sigma_{\mathrm{CIMS}} = \sqrt{\left(\frac{\sigma_{I(HONO)^-}}{S_{I(HONO)^-}}\right)^2 + \left(\frac{\sigma_{I^-}}{S_{I^-}}\right)^2} \quad \text{(S8)}$$

Absolute uncertainties are represented by σ, and the CIMS signals in counts per second are represented with *S*. Normalized CIMS HONO signals are scaled by a 10^6 factor for this manuscript, in which the relative error calculated by Eq. (S8) is maintained.

This quantified [HONO] uncertainty (σ_{HONO}) is calculated by Eq. (S9).

$$\sigma_{HONO} = \sqrt{\left(\frac{(\sigma_{NO_2}^2+\sigma_{NO_2}^2)^{\frac{1}{2}}}{S_{NO_2}-bkg_{NO_2}}\right)^2 + 0.03^2 + \left(\frac{\sigma_\beta}{2+\beta}\right)^2} \quad \text{(S9)}$$

The terms added in quadrature are 1.) the background subtracted $[NO_2]$ relative uncertainty, 2.) the CAPS NO_2 measurement accuracy (i.e. 3%), and 3.) the relative uncertainty of β as applied in Eq. (5) of the main text (i.e. including the addition of 2 as a constant). The uncertainty propagation for the NO_2 background subtraction is accomplished by combining absolute NO_2 uncertainties in quadrature (see numerator of first term) using a set value of 27 pptv for σ_{NO2} based on the 5 s average precision. The resulting absolute uncertainty in NO_2 is converted to relative uncertainty by its quotient with the background subtracted $[NO_2]$ value (i.e. the denominator where *S* and *bkg* represent the signal and background values of $[NO_2]$, respectively). The relative uncertainty of the third term in Eq. (S9) is very small (typically 0.14%, 2σ) due to the constant addition of 2. The value of σ_β is determined by combining the uncertainties for the variables of Eq. (S1).

S4.2 Single Point Calibration Uncertainty Calculations

The CIMS sensitivities in the Fig. 4 (of main text) single point calibration plot (showing humidity dependence) were determined by the quotient of respective background subtracted CIMS measurements with quantified [HONO] values. Therefore, the Fig. 4 uncertainties were quantified by combining in quadrature the relative errors of these two variables. The uncertainty in quantified [HONO] is calculated with Eq. (S9) - the same as discussed in Sect. S2.1. The background subtraction for the CIMS measurement is a new step (not conducted for the multipoint calibration at a single humidity) and thus requires a slightly different uncertainty calculation (Eq. (S10)) compared to Eq. (S8).

$$\sigma_{\mathrm{CIMS}} = \sqrt{\left(\frac{\left(\sigma^2_{IHONO^-} + \sigma^2_{\overline{IHONO^-_{bkg}}}\right)^{\frac{1}{2}}}{S_{IHONO^- - bkg_{IHONO^-}}}\right)^2 + \left(\frac{\sigma_{I^-}}{S_{I^-}}\right)^2} \qquad \text{(S10)}$$

The first term shown in quadrature of Eq. (S10) represents the uncertainty propagation for the CIMS background subtraction process. This uncertainty propagation is handled similarly to that of the background subtraction for quantified [HONO] (see Sect. S2.1 and Eq. (S9)). First, the absolute 1 Hz uncertainties of the $I(HONO)^-$ signal and background are added in quadrature (see numerator). Then, the absolute uncertainty is converted into relative error (i.e. dividing by the background subtracted signal) to add in quadrature with the relative uncertainty of the I^- reagent signal.

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