Supporting Information

An instrument to measure and speciate the total reactive nitrogen budget indoors: description and field measurements

Leigh R. Crilley¹, Melodie Lao¹, Leyla Salehpoor¹, and Trevor C. VandenBoer^{1,*}

¹ Department of Chemistry, York University, Toronto, ON, Canada.

*Correspondence to: tvandenb@yorku.ca

S1. Components of the tN_r instrument

The components of the tNr instrument are housed in a standard 19" rack that is approximately 1.8 m tall to fit through a standard doorway. It is designed to be quiet with the pumps housed in a sound proofed shelf with fans to facilitate cooling, and unobtrusive from its small footprint so that it can be used continuously in occupied indoor areas. The frame of the tNr instrument was constructed from T-slotted framing rails (5537T101, McMaster Carr, Aurora, OH, U.S.A) to form the 19-inch rack (length x width x height is 8 x 53 x 175 cm) to mount the five modules (Fig. S1). Three modules (DAQ control box, HONO calibration source, and tNr oven) are enclosed in separate black 19-inch rack-mounted cases (RMCV190713BK1, Hammond Manufacturing, Guelph, ON, Canada). The instrument requires an electrical outlet capable of providing 110 V AC and 20 A, which is commonly used for indoor appliances and such outlets are often located in kitchens, bathrooms, or laundry rooms. Two outlet strips are mounted vertically to the rack, one outlet strip uses a NEMA 5-20 plug (71515K34, McMaster Carr, Aurora, OH, U.S.A).

Details of the electronics and wiring for the DAQ control box are provided in Fig S2. The components and construction of the HONO calibration source is provided in the Supplemental Information of Lao et al.¹. The zero-air generator provides gas flow through the HONO calibration source and also dilutes the generated HONO to adjust its calibration quantities based on the environment and expected range of measured HONO levels. The zero-air generator was custom-built, consisting of a small pump, water filter (¼" NPT, AFR-2000, SPK603, Thailand), membrane air dryer (IDG1-N02, Proax Technologies Ltd, Oakville, ON, Canada), and cartridges (400 cc, ¼" fitting, Scrubbing Media Cartridge, Chromatographic Specialties Inc.) filled with a mixture of molecular scrubbing media (CP Blend, Purakol, Purafil Inc., Doraville, GA, U.S.A) to remove trace gases like NO_x, ammonia (NH₃), ozone (O₃), water, and volatile organic compounds (VOCs). The mass flow controllers (MFCs; MKS Instruments, Inc.) control the diluent zero air flow for HONO calibrations as well as the total sample flow through the system via an additional inlet pump. To increase or decrease the flow rate of zero air for background/blank measurements in addition to diluting calibration gases, the flow through MFC1 was modified (Fig 1). An optional second MFC is to modify the residence time of a real air sample through the system and can be installed prior to the NO_x analyser inlet in the Fig 1 flow schematic.

The sampling inlet consists of ¼" perfluoroalkoxy alkane (PFA) tubing (51805K72, McMaster Carr, Aurora, OH, U.S.A) and a polytetrafluoroethylene (PTFE) filter in a holder assembly (47 mm single-stage, ¼" x ¼" PFA Clamp, Savillex, Eden Prairie, MN, U.S.A) which is attached to the sample inlet to remove particles. Throughout the system, a minimized amount of PFA tubing is used by insertion of ¼" PTFE tees and elbows (T-420-3, T-420-9, Swagelok, Mississauga, ON, Canada). Gaseous compounds are diverted into different branches of the inlet as they enter the three-way ¼" PTFE solenoid valves (12V DC, Galtek®, Chaska, MN, U.S.A) by either the normally open (NO) or normally closed (NC) port and exit through the common (COM) port to reach the NO_x analyser. Annular denuders (URG-2000-30x150-3CSS, URG Corporation, Carrboro, NC, U.S.A) selectively scrub nitrogenous species based on their coating solution, as described in Section 2.1.4 of the main manuscript. Instrument noise is reduced by installing mufflers (4450K3, ¼" NPT Male Steel Fitting, McMaster Carr) on the pumps (GAST, Cole-Parmer Canada) and enclosing them in shelving lined with adhesive acoustic insulation (5692T26, 90 % Adhesive backing polyurethane foam, McMaster Carr, Aurora, OH, U.S.A).



Fig S1. Physical layout of tN_r instrument components.



Fig S2: Example time series of raw NO_x measurements for a single 20 minute duty cycle. For reference, colour coding is same as for Fig 1 and Table 1.



S2. tN_r instrument control and Data Acquisition (DAQ)

Fig S3. Electronic diagram of the DAQ control box. The closed circles represent the junction of the wiring. Throughout the wiring scheme, the orange lines represents the positive wiring (+), yellow is negative wiring (-), and green is ground (GND). A cooling fan (5 V DC) was inserted to provide temperature management of the electronics and it was powered by a 12 V DC transformer. The 12 V DC transformer also supplies power to the solenoid valves by converting a 120 V AC power input to a 12 V DC output. The power switching board (green square; PS12DC, LabJack, Lakewood, CO, U.S.A) was wired in parallel to distribute power to the solenoids and remove the need for multiple solid-state relays. The power switching board was attached to the red DAQ board (T7, LabJack, Lakewood, CO, U.S.A) through the DB15 connector (15 pin D-sub). An analog output expansion module (LJTick-DAC, LabJack, Lakewood, CO, U.S.A) was connected to the DAQ board to provide communication with the mass flow controllers (MFC). The custom 15 V DC power source supplies power to the two MFCs and is organized through a screw terminal block for power distribution. The wiring of the MFC communication cables requires a 15 pin D-sub male and female assembly for connection of the cable to the case (DACA and DACM) and the connections are numbered and configured as: 1. No Connection (NC); 2. Flow out (0-5 V, purple wire); 3-4. NC; 5. Ground (0 V, green wire); 6. Neutral (-15 V, yellow wire); 7. Live (+15 V, orange); 8. Flow rate set (0-5 V, blue wire); 9-10. NC; 11-12. Signal common (brown wire); and 13-15. NC. The grey lines show the analog input and

ground connections between the DAQ board and the NO_x analyser to synchronize and log its measurements, the date, and time.



Figure S4. The graphical user interface of the custom-LabVIEW program for the YorkU tN_r instrument. The VI code for the LabVIEW program can be found on the GitHub repository²

S3. Data processing of tN_r data

The tN_r instrument graphical user interface was designed to control the flow rate, valving switching, and time resolution of each pathway. The date and time, valve state, and measurements from the NO_x analyser are logged into a text file via the LabView program. Text files were typically saved in redundant copies every 1-2 days to prevent data loss/corruption. A custom R script was written to automate data processing of the files from the LabVIEW program in RStudio. A summary of the data processing (focusing on NO_2^* , NO_2 , and HONO as example, but with a similar procedure for tN_r and basic N_r) in the R script includes:

- 1. Organizing tN_r datasets by each sampling pathway and the number of cycles through the inlet configuration.
- 2. Separating each cycle number into multiple data frames and integrating it into a large list for each inlet configuration.
- 3. Calculating an average at one minute time-resolution for each data frame located in the list.
- 4. Removing the first minute of each data frame to account for the time response of the tN_r instrument, which is limited by the NO_x analyser.
- 5. Concatenating data from each sampling pathway and sorting by date and time to have a total of four data frames per pathway (i.e., assembled all measurements of NO₂* into one data frame).
- 6. Filling in missing date and times and then applying linear interpolation for each sampling pathway to estimate mixing ratios in observation gaps of 16 min.

- 7. Calculating the difference of NO_2^* and NO_2 to determine the mixing ratio of HONO.
- 8. Generating data plots for quick QA/QC visualization and then saving processed datasets into the assigned directory.
- 9. Combining daily processed datasets into one large dataset for the entire campaign.
- 10. Removing interpolated data when they do not make physical or chemical sense. For example, if NO_2 levels that are greater than NO_2^* , as this would result in negative values for calculated HONO.
- 11. Calculating the rate of change between measured data points of NO₂* and NO₂; if it is ±50 %, then flag for manual removal of interpolated values of NO₂*, NO₂, and calculated values of HONO. The rate change was calculated to determine the percent change in mixing ratio over a period of time (e.g. 1 min). This identifies strong emission events for our measurements determined by difference (e.g. HONO) that may have a duration shorter than the time resolution of the instrument inlet cycling time.

Linear interpolation was incorporated into the R script to fill in missing gaps of ~16 min from removed data points from Step 4 and modulated inlet pathways for each pollutant. This data analysis method utilizes two observation periods bracketing the gap and infers the unobserved mixing ratios between the measured series of points with a straight line. The linearly interpolated data could underestimate or overestimate the mixing ratio of pollutants, depending on the distribution of measured values and length of time gap. Linear interpolation assumes the rate of change is uniform, which could be unrealistic in a highly ventilated indoor environment with activities that result in short duration emission spikes (e.g. the commercial kitchen in this work).

Interpolated points generated under such conditions are manually removed when plumes/events shorter than our total instrument cycle time of 20 minutes were encountered. This prevents gross systematic bias in our final dataset by not assuming pollutants levels are stable when they are known to be rapidly increasing or decreasing. Such instances were identified in this work by comparing the tN_r measurements (NO, NO₂*, and NO_x*) to those of the second chemiluminescence analyser. Steps 10 and 11 in the R-script were written to speed up the data finalization process based on these unexpected insights. Step 11 flags gaps between our measured data points with a rate change of \pm 50 % to guide and speed up manual removal of interpolated data points.

For example, if the first data point measured from cycle 2 has increased/decreased in mixing ratio by 50 % compared to the last data point measured from cycle 1, then this will be flagged to have the interpolated points removed between measured cycle 1 and cycle 2. Flagging the rate change of \pm 50 % will work even better in indoor facilities with stable or lower AER. The commercial kitchen in this work had very high AER throughout the day, so rapid changes in mixing ratio of 50 % were more challenging to identify due to the short duration of the emission plumes. When this manual correction is performed, the measured data points (NO, NO₂, NO_x, NO₂*, and NO_x*) are retained during such events since they are real measurements. As a result, the majority of direct HONO emissions during the rapid cooking events here were removed from the final dataset and the presented HONO levels are lower-limit representations that do not fully capture the peak values.

The final dataset that results from this processing has a one minute time resolution with 4 minutes of data measured and the remaining data points either linearly interpolated or left unreported based on these interpretation and processing criteria.

S4: Time response and conversion efficiency experimental data

Table S1. Calculation of the time response of NO, NO_2 , and HONO through the NO_x pathway at 630 ccm by double exponential fit.

N _r species	τ_1 (min)	τ_2 (min)	D (%)	Input mixing ratio (ppbv)
NO	1.1	1.1	46	18 ± 1
NO_2	0.2	1.5	39	18 ± 1
HONO	1.0	1.0	44	20 ± 1



Figure S5. (a) Response time experiments at various flow rates for NO (red), NO₂ (black), and HONO (green) with their linear trends. **(b)** Response time plot of HONO to zero at 630 ccm (12 s averages). The circles represent HONO measurements and their exponential decay (95 – 0%). Each colored circle and line represent a response time experiment replicate. **(c)** Response time of replicate experiments (n=3) as a function of varied HONO mixing ratios with an inlet flow of 630 ccm. The green circles represent the averaged HONO mixing ratio analyzed – ranging from 2-20 ppbv. The weighted line of best fit (black) suggests the response time of HONO lies within one minute regardless of a change in HONO mixing ratio sampled (slope = -0.007 ± 0.026 min ppbv⁻¹).



Fig S6. Response time through the total Nr pathway of the instrument for HONO (13 \pm 2 ppbv) as function of flowrate, with a slope of -6.55 x10⁻⁵ \pm 2 x10⁻⁴ min² cm⁻³.



Fig S7. Normalised decay to baseline levels after addition of zero air for NH₃ (green inverted triangles), monomethylamine (MMA; red circles), diethylamine (DEA, orange triangles) and dimethylamine (DMA, blue squares).



Fig S8. HONO calibration through a Na_2CO_3 denuder, the slope is horizontal (slope of -1.27 x 10⁻³ ppbv min⁻¹) consistent with all HONO being collected by reaction onto the surface of the denuder.



Fig S9. Normalised decay when NH_3 (blue circles) and DEA (red squares) were scrubbed with a H_3PO_3 denuder.



Fig S10. Passing a known mixing ratio of NO through the Na₂CO₃ denuder (yellow shaded regions) resulting in a slope not significantly different from zero of -7.66 x $10^{-5} \pm 7.52 \times 10^{-5}$ ppbv min⁻¹, indicative of no reactive loss of NO.



Fig S11. Passing a known mixing ratio of NO₂ through the Na₂CO₃ denuder (yellow shaded regions) resulting in a slope between exposure and bypass replicates of $-3.42 \times 10^{-6} \pm 5.25 \times 10^{-5}$ ppbv min⁻¹ (from n=3 experiments depicted).



Fig S12. Scatter plot of NO₂ added to inlet and then measured after the Na₂CO₃ denuder in humid air (42-50 % RH) representative of indoor conditions.

Table S2. Percent difference of the mixture of NO ₂ and humid air scrubbed by the Na ₂ CO ₃ denuder at	630
ccm shown in Fig S11.	

RH	Input NO ₂	NO ₂ after	NO ₂ lost	%
(%)	(ppbv)	denuder (ppbv)	(ppbv)	Difference
50	24.0 ± 0.6	23.3 ± 0.6	0.7 ± 0.8	2.9
49.5	51.9 ± 0.8	50.1 ± 0.8	1.8 ± 1.1	3.5
41.5	107.1 ± 1.2	105.3 ± 1.3	1.8 ± 1.8	1.7
50.0	206.4 ± 1.4	204.6 ± 1.9	1.8 ± 2.4	0.9
49.5	305.2 ± 1.8	301.6 ± 2.1	3.6 ± 2.8	1.2



Fig S13. Conversion efficiency as function instrument flowrate through the tN_r instrument for NO₂ as function of mixing ratio and flowrate. Linear fits are $1.01 \pm 0.005x - 0.5 \pm 0.3$; $1.02 \pm 0.009x - 2.6 \pm 0.6$; and $1.007 \pm 0.02x - 1.3 \pm 1.1$ for 630, 1000 and 1460 ccm, respectively. All r² >0.99.



Fig S14. NH_3 conversion efficiency to NO_x as a function of flowrate in the tN_r oven.

S5. Proof of concept measurements in a commercial kitchen

Table S3. GANNT chart indicating the typical frequency and order of quality control checks for the tN_r instrument during field operation. Note the blocks are not to scale with respect to time and are indicative of the typical order of operations when used in the field. Generally, the addition of zero air or $NH_3/HONO$ to the respective pathways was for 15-20 minutes each. Addition of zero air to the oven was allowed to vary in order to ensure the measured tN_r levels returned to baseline.

Procedure	Day 1				Day 2					Day 3						Day 4						Day 5					
tN _r indoor																											
measurement																											
Denuder swap																											
Denuder check																											
Addition of zero																											
air to oven																											
Addition of NH ₃																											
to oven																											
Addition of zero																											
air to NOx																											
pathway																											
Addition of																											
HONO to NOx																											
pathway																											



Fig S15. Comparison of NH_3 and amines measured by passive samplers to the average basic N_r fraction during the same period. Variability shown is one standard deviation of the average measurement.

References

- M. Lao, L. R. Crilley, L. Salehpoor, T. C. Furlani, I. Bourgeois, J. A. Neuman, A. W. Rollins, P. R. Veres, R. A. Washenfelder, C. C. Womack, C. J. Young and T. C. VandenBoer, A portable, robust, stable, and tunable calibration source for gas-phase nitrous acid (HONO), *Atmos. Meas. Tech.*, 2020, **13**, 5873–5890.
- 2 M. Lao and L. Crilley, tNr instrument software, https://github.com/data-lao/tNrInstrument.