# Measurement of $NO_x$ and $NO_y$ with a thermal dissociation cavity ring-down spectrometer (TD-CRDS): Instrument characterisation and first deployment.

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## *Supplement*

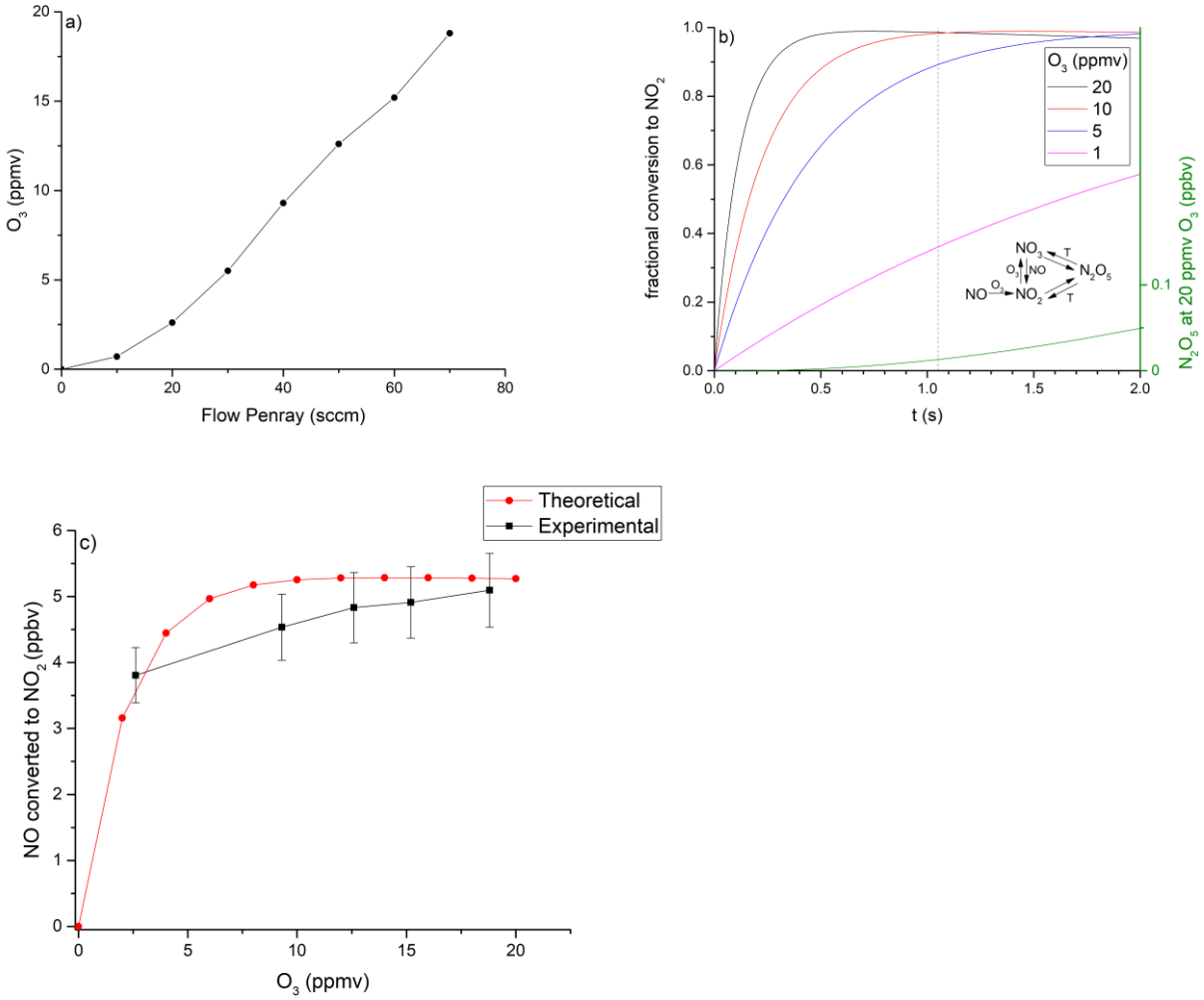


**Figure S1:** Optimisation of NO to $NO_2$ conversion via the addition of $O_3$. *a)* Ozone generated by passing synthetic air over the Pen-Ray lamp as a function of the flow rate. *b)* Box model results for the fractional NO conversion as a function of reaction time and a chemical scheme showing reactions included in the model. High concentrations of $O_3$ can lead to the formation of significant amounts of $N_2O_5$ (50 pptv at 20 ppmv $O_3$ and 2 s reaction time). *c)* Conversion of 5.3 ppbv NO to $NO_2$ as a function of $O_3$ in 1.05 s reaction time. Both laboratory results and predictions of a numerical simulation are shown. Quantitative conversion is achieved for $O_3$ concentrations above 15 ppmv. The error bars indicate total overall uncertainty.

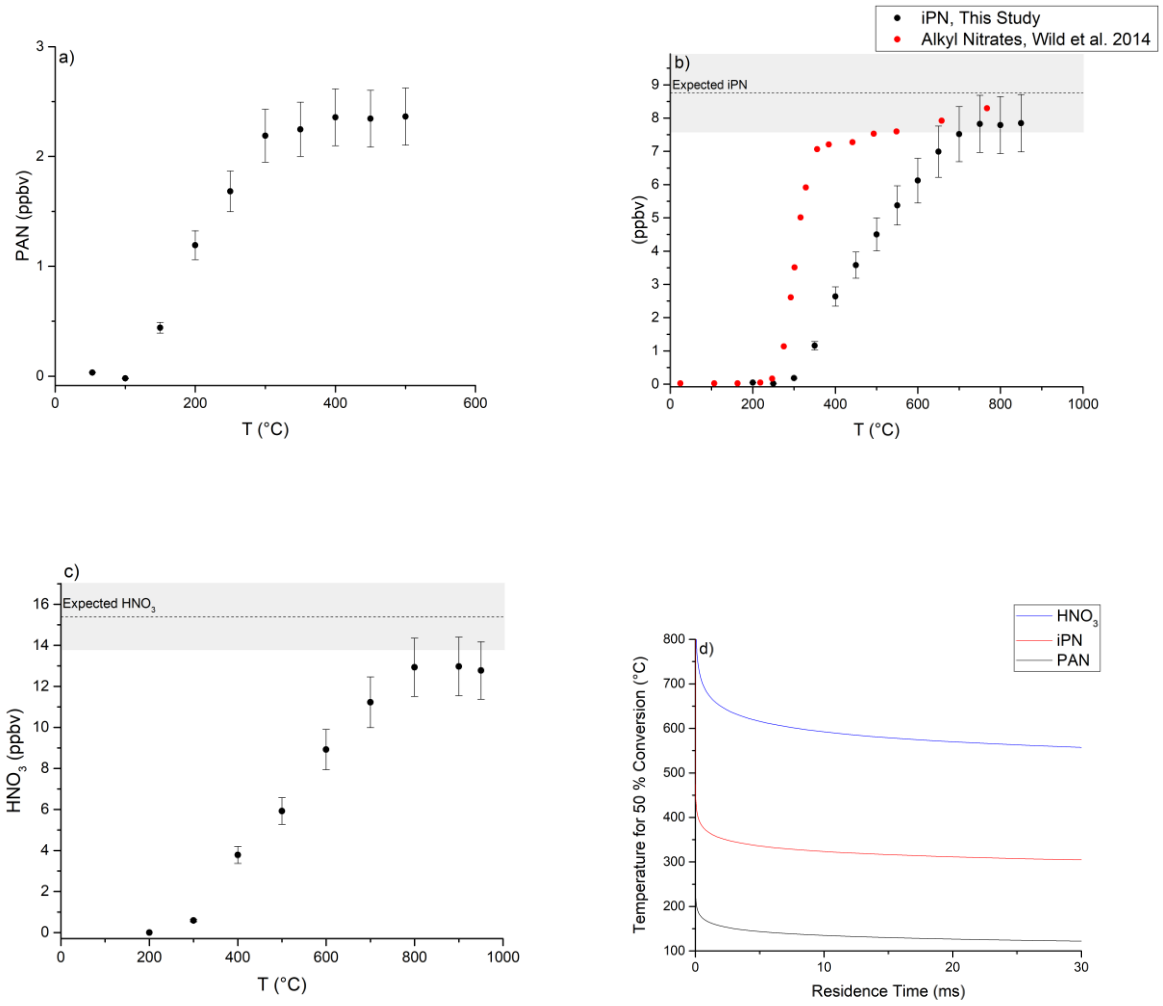


**Figure S2:** Individual absolute thermograms of PAN *(a)*, iPN *(b)* and $HNO_3$ *(c)*. Error bars represent the total uncertainty of the TD-CRDS measurements. Shaded areas show the estimated uncertainty ranges for the expected iPN and $HNO_3$ concentrations, based on errors during sample preparation and gas stream dilution. Considering these uncertainties, quantitative conversion of PAN, iPN and $HNO_3$ to $NO_2$ can be concluded at the TD-CRDS set temperature of 850 °C. *(b)* also includes readout data points for an alkyl nitrates mixtures from Wild et al. (2014), to illustrate broader dissociation steps for ANs species, observed in the literature. *d)* Calculated threshold temperature for 50 % conversion of PAN, iPN and $HNO_3$ to $NO_2$ relative to the residence time in the heated inlet and based on kinetic parameters of their thermal dissociation (see Sect. 3.1.3). For $HNO_3$, the threshold temperature increases by 40 °C when the residence time decreases from 30 to 10 ms.

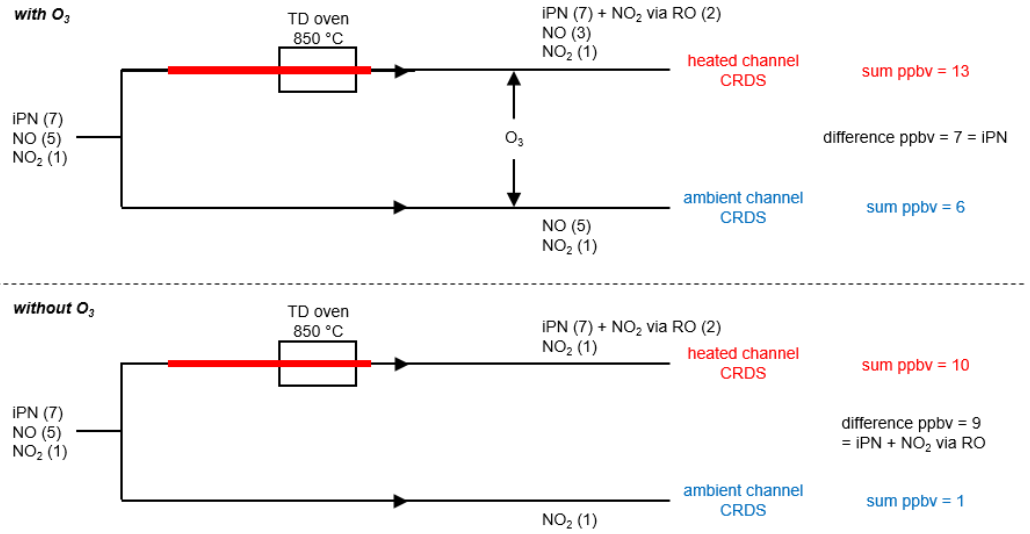


**Figure S3:** Graphical representation of the bias caused by $RO_2$ + NO reactions in detecting iPN. In both cases an initial mixing ratio of 7 ppbv iPN is present, along with 5 ppbv NO and 1 ppbv $NO_2$. When passed through the oven the iPN is converted to 7 ppbv $NO_2$ and (in this scenario) 2 ppbv of NO are converted to $NO_2$ via reaction with $HO_2$. In total 13 ppbv of $NO_2$ are detected in the cavity sampling via the oven. In the cavity at ambient temperature 6 ppbv of $NO_2$ are detected so that a (correct) iPN mixing ratio of 7 ppbv is derived. In the lower part of the figure, the same initial conditions apply, but $O_3$ is not added. The conversion of 2 ppbv NO to $NO_2$ occurs as above, so that 10 ppbv $NO_2$ are detected when sampling from the oven. The $NO_2$ mixing ratio in the cavity sampling at ambient is 1 ppbv, resulting in a derived (incorrect) $NO_2$ iPN mixing ratio of 9 ppbv.

## *References*

Wild, R. J., Edwards, P. M., Dube, W. P., Baumann, K., Edgerton, E. S., Quinn, P. K., Roberts, J. M., Rollins, A. W., Veres, P. R., Warneke, C., Williams, E. J., Yuan, B., and Brown, S. S.: A measurement of total reactive nitrogen, NOy, together with $NO_2$, NO, and $O_3$ via cavity ring-down spectroscopy, Env. Sci. Tech., 48, 9609-9615, doi:10.1021/es501896w, 2014.