

This paper describes a two-channel cavity ring-down instrument for the measurement of NO_2 and the sum of peroxy nitrates (ΣPN), and the sum of alkyl nitrates (ΣAN), accomplished by selective thermal decomposition. These are potentially useful measurements, particularly the ΣPN s, and the authors have done a good job of characterizing the NO_2 , NO , and VOC radical dependences of the system and developed ways to correct them, except for one glaring omission (see below). The work done here is helpful to the other groups who use this method. This paper should be publishable, contingent on the response to the following general and specific comments.

General Comments;

There seems to be some confusion about whether the ΣPN inlet was at 450K or 473K, both appear at different places. Please clarify.

There is one large question mark that people have about this method, pertaining to the ΣAN measurement, and it would be extremely helpful if this group could explore this issue with some solid work in the laboratory. Nitric acid is the largest NO_y compound in well-processed air masses in the polluted lower troposphere, often reaching 40 to 60% of total NO_y , while ΣAN s are 5-15% of NO_y (depending if one can believe ΣAN measurements). HNO_3 uni-molecular thermal decomposition kinetics have been known for some time [Harrison et al., 1962 and references therein], and indicate that HNO_3 will be converted to only a very small extent at the ΣAN conditions, depending on convertor residence time (which needs to be specified in this paper). Indeed one needs a quartz convertor at a higher temperature to convert HNO_3 to NO_2 [Day et al. 2002, Wild et al., 2014]. However, heterogeneous and catalytic conversion in the presence of VOCs at the lower temperature is a real possibility, indeed the gold and molybdenum NO_y catalysts rely on this for conversion of HNO_3 to NO_2 at 573-598°K. There is a hint of such an effect in the results of Wild et al., [2014] who observed HNO_3 conversion at temperatures as low as 573K in their system. Only a small conversion of such a large NO_y component would make a big contribution to ΣAN , and would lend completely unrealistic characteristics to the ΣAN and HNO_3 signals obtained with this method, leading perhaps to one concluding that HNO_3 fluxes were coming out of a forest for example [Farmer and Cohen, 2008].

It is strongly urged that the authors look at HNO_3 in their system, and define its contribution to ΣAN , and possible catalytic and surface effects upon addition of CO and VOCs. This would be a tremendous service to the community.

A general comment on ambient measurements with this technique: In principle it is possible to scan convertor temperatures to see if one really is at a 'plateau', which is a necessary (but not entirely sufficient) condition to demonstrate selectivity between the various classes of NO_y species. There are some "scans" with laboratory samples that have been reported, but with only the NO_y species present. Why not scan in ambient air, especially above 723K, to demonstrate that such a plateau has been reached? Yes, there is variability in ambient air, but there are also times when concentrations are stable and such a scan is possible.

Specific Comments:

Page 11535, Lines 19-20. While it is true that the reaction of PAN with OH will not be competitive with thermal decomposition anywhere in the troposphere, photolysis is faster than

thermal decomposition above about 7km altitude, give or take, based on average (i.e. Springtime, mid-latitude) conditions.

Page 11536, Line 25, the peroxypropionic PAN compound is usually referred to as PPN, and indeed is referred to that way on page 11567 of this paper.

Page 11537, Line 1. Perhaps the original PAN TD-CIMS reference, Slusher et al., 2004, should be listed here?

Page 11537, Lines 9-11. It should be mentioned here that HNO_3 is sometimes 40-60% of NO_y .

Page 11540, Lines 23. From the conditions mentioned here, it would appear that the residence times of air with the heated zones were on the order of 0.2 to 0.4 sec, is that correct? What residence times were used for the model calculations?

Page 11541, Line 14. This text says i-butyl nitrate, which is $\text{CH}_3\text{CH}(\text{CH}_3)\text{CH}_2\text{ONO}_2$, and the Figure caption says 2-butyl nitrate, which is $\text{CH}_3\text{CH}(\text{ONO}_2)\text{CH}_2\text{CH}_3$. Which is it?

Page 11542, Lines 9-22. Ideally, one can predict the behavior of a given $-\text{NO}_2$ containing compound based on O-N bond dissociation energies; peroxy nitrates have been reviewed by Kirchner et al., [1999] and tend to range from 20 to 27 Kcal/mole; RO- NO_2 bonds tend to be on the order of 38 to 41 Kcal/mole [see for example Roberts 1990]; nitric acid has a HO- NO_2 bond strength of 47-49 Kcal/mole. The behavior of these compounds in the quartz convertors follows these trends, implying that these quartz surfaces are “inert”, at least under the laboratory conditions used here. This simple picture needs to be tested under real world conditions, to see if there is catalytic behavior due to the presence of other species, O_3 , VOCs etc.

Page 11545, Line 17. Should read “and its concentration was..”

Page 11546, Pyrolysis of O_3 . Not sure what to make of this section, Lee et al., [2014] found that this did have an effect, even at 380°C. Why the difference?

Page 11547, 473 K Inlet. The photolytic PAN source is typically run with a considerable excess of acetone. Does this have any effect on the chemistry?

Page 11549, Lines 11-14. I would be interested to see what the temperature profiles look like. The related issue is what residence times were associated with the convertors and do they make sense given the chemical simulations?

Page 11555, Line 12. This should read 10ppbNO, not NO_2 .

Page 11561, Line 27, Should read 893mb for consistency.

Page 11562, Line 6. The phrase “1 sigma precision increases for integration times up to 40s” is a bit confusing. One gets the point when looking at the graph, but really 1 sigma decreases, which corresponds to increased precision, or maybe a more appropriate word would be “better” precision.

Page 11565, TD-CRDS vs. CLD. Can the authors comment on how the results of Reed et al. 2015 might impact the intercomparisons?

Page 11567, MPN should be MPAN for consistency.

Page 11568, Conclusions and Outlook. I guess I want to make one more pitch for looking at the behavior of HNO_3 in these systems, especially under conditions of high CO and VOCs. For the good of the community, someone needs to do this.

Page 11578, The Yin-Nan, L. reference is wrong, Yin-Nan is actually his given name, same with Xian-Lang, so this reference should read: Lee, Y.-N., Zhou, X.-L., and Hallock, K.

Page 11596, The caption for Figure 18 should have the details about the red and green points in the ΣANs panel. Typo on Line 4, “when sampling from the...”. Was it a 450K or 473K inlet? Supplement. Figure SI 1, this says 450K, is that correct?

Reference List

Day, D. A., Wooldridge, P. J., Dillon, M. B., Thornton, J. A., and Cohen, R. C.: A thermal dissociation laser-induced fluorescence instrument for in situ detection of NO₂, peroxy nitrates, alkyl nitrates, and HNO₃, *Journal of Geophysical Research-Atmospheres*, 107, 4046, doi: 4010.1029/2001JD000779, 2002.

Farmer, D. K., and Cohen, R. C.: Observations of HNO₃, ΣAN, ΣPN and NO₂ fluxes: evidence for rapid HOx chemistry within a pine forest canopy, *Atmos. Chem. Phys.*, 8, 3899-3917, 10.5194/acp-8-3899-2008, 2008.

Harrison, H., Johnston, H. S., and Hardwick, E. R.: Kinetics of the thermal decomposition of nitric acid vapor. IV. A shock tube study between 800-1200°K, *J. Am Chem. Soc.*, 84, 2478-2482, 1962.

Kirchner, F., Mayer-Figge, A., Zabel, F., and Becker, K. H.: Thermal stability of peroxy nitrates, *Int. J. Chem. Kinet.*, 31, 127-144, 1999.

Lee, L., Wooldridge, P. J., Gilman, J. B., Warneke, C., de Gouw, J., and Cohen, R. C.: Low temperatures enhance organic nitrate formation: evidence from observations in the 2012 20 Uintah Basin Winter Ozone Study, *Atmos. Chem. Phys.*, 14, 12441–12454, doi:10.5194/acp-14-12441-2014, 2014.

Reed, C., Evans, M. J., Di Carlo, P., Lee, J.D., and Carpenter, L.J., Interferences in photolytic NO₂ measurements: explanation for an apparent missing oxidant?, *Atmos. Chem. Phys. Discuss.*, 15, 28699-28747, 2015.

Roberts, J.M., The atmospheric chemistry of organic nitrates, *Atmos. Environ.*, 24A, 243-287, 1990.

Slusher, D. L., Huey, L. G., Tanner, D. J., Flocke, F. M., and Roberts, J. M.: A thermal dissociation-chemical ionization mass spectrometry (TD-CIMS) technique for the simultaneous measurement of peroxyacyl nitrates and dinitrogen pentoxide, *J. Geophys. Res.*, 109, D19315, doi:10.1029/2004JD004670, 2004.

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, NO_y, together with NO₂, NO, and O₃ via cavity ring-down spectroscopy, *Environ. Sci. Technol.*, 48, 9609-9615, 10.1021/es501896w, 2014.