

Review of Duncianu et al., 2016

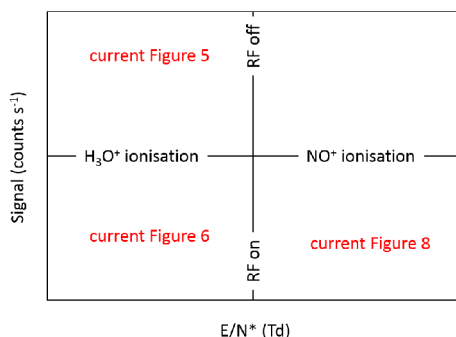
General Comments:

This paper presents interesting work on the application of proton transfer reaction mass spectrometry to the measurement of speciated organic nitrates using different compounds that represent different classes of organic nitrates (2 alkyl nitrates, 1 hydroxyl nitrate, 2 keto nitrates and PAN). The paper is well written, the data appears to be of good quality and the results are of scientific interest. I would support publication subject to corrections outlined in the comments below.

Specific Comments:

- (1) On line 370 the purities of the synthesised keto-nitrates by FTIR should be given? Were these comparable to the commercially purchased alkyl nitrates? If not what were the major impurities and what are the likely effects on the results presented?
- (2) On line 444, it is mentioned that the abundance of water clusters were higher than typical during this study. Is there a reason for this?
- (3) In my opinion there are too many figures and the way they are shown prevents a more straightforward comparison of the different ionization schemes, RF modes and E/N ratios. The paper would be greatly improved if the results for each of the different types of organic nitrates (alkyl nitrates, hydroxyl nitrates and keto nitrates) were presented in a similar way to Figure 1 where operational differences can be clearly seen and compared. For example:

e.g., 10H3C3



I note that the NO+ mode without RF (top right quadrant of this diagram) was less favourable to NO+ adduct formation and thus was not pursued in this work (lines 409-414). However, I would recommend including that data for completeness. With the same reasoning as above I would combined the mass spectra figures for the different ionization modes, e.g., for 10H3C3 figures 7 and 9. Again, if the data were available I would include the mass spectra for all modes and RFon/off, for the optimised E/N ratio in each case to give the complete picture.

- (4) The optimised conditions appear to be slightly different for each class of organic nitrates and this clearly limits this technique in terms of which compounds can be observed simultaneously as I believe this is a parameter that is not possible to change 'on the fly' in contrast to the reagent ion that can be switched as in the switchable reagent ion (SIR) versions of the PTRMS instrument. Table 2 summaries the optimisation work and shows the sensitivities. However, I think there is a final step missing here. To be the most useful analytical tool it is better to encompass the widest range of analytes, in this case all of the organic nitrates. Thus it seems that what should also be included is a recommendation for

operation of the PTRMS to best detect all the different types of organic nitrates discussed here. What are these conditions, i.e., NO^+ with E/N of ~ 40 , what are the sensitivities of the different types (alkyl nitrates, hydroxyl nitrates, keto nitrates and PANs) under this single set of analytical conditions?

- (5) In the introduction there is discussion of the limited measurements of speciated organic nitrates (especially multifunctional ones) and thus some of the motivation for developing this approach is to provide a method to measure these compounds in the atmosphere. However, data is only presented from a smog chamber containing the specific target compounds and not a more complex mixture of compounds that would present an analytical challenge. However, to really convince the reader of the application of this approach to ambient measurements there really needs to be some actual ambient measurement data included in the manuscript. This would really strengthen the paper and I strongly encourage the authors to do it. If not then at the very least there needs to be a very convincing discussion with reference to published ambient measurement data to demonstrate how unique the mass fragments/molecular ions are relative to the mass fragments/molecular ions of other constituents of the ambient atmosphere that are also ionized within this instrument. For example, line 471 (H_3O^+ ionization of AlkC3) mentions RO^+ m/z 59, in the atmosphere this signal is likely dominated by acetone. Without this it is difficult to assess the applicability of this approach to ambient measurements.
- (6) The data presented only refers to unit mass resolution data, was the high accuracy mass data also used? I could imagine that it might be useful in distinguishing the organic nitrates from other atmospheric compounds that are also ionised by the PTRMS.
- (7) PAN type compounds are sensitive to thermal decomposition. With the inlet at 40 degrees C one might expect some thermal decomposition of PANs (dependent on residence time in the inlet)? Can the authors comment on this and whether this may be a reason for the high detection limits observed for these compounds with this method.

Technical Corrections:

Line 25 – reword ‘...allows to easily identify the organic nitrate (R) with the....’ to read ‘...allows the easy identification of the organic nitrate (R) from the....’.

Line 30 – reword ‘This method exhibits however lower capabilities for the detection.....’ to read ‘However, this method exhibits much lower capabilities for detection....’.

Line 34 – reword ‘Organic nitrates are important....’ to read ‘Organic nitrates are an important....’.

Line 35 and throughout the manuscript – subscript of x in the abbreviation NO_x

Line 39 – reword ‘They play therefore...’ to read ‘They therefore play....’.

Line 41 – reword ‘....impact of organic nitrates chemistry on ozone budget....’ to read ‘impact of organic nitrate chemistry on the ozone budget....’.

Line 44 and throughout the manuscript - subscript of y in the abbreviation NO_y

Line 46 – reword ‘They are monofunctional alkyl nitrates, PANs but also....’ to read ‘They are not only monofunctional alkyl nitrates and PANs but also....’.

Line 48 – reword ‘These latter include i) hydroxynitrates which are formed by the oxidation of alkenes initiated by OH radicals and by isomerisation processes of alkoxy radicals....’ to read ‘The

latter include i) hydroxynitrates formed by the OH oxidation of alkenes followed by isomerisation processes of the resultant alkoxy radicals....'.

Line 51 – reword ‘...alkenes but are also second-generation....’ to read ‘...alkenes and also as second-generation....’.

Line 57 – remove ‘then’

Line 58 – replace ‘commercial’ with ‘commercially available’.

Lines 71 to 75 – these lines are confusing as written. Suggest rewording ‘The thermal dissociation (TD) properties of different classes of nitrates was used as an analytical tool to sketch the global chemistry of RONO_2 , same as the Laser-Induced Florescence (LIF), cavity ring down spectroscopy (CRDS)(Paul et al., 2009), or cavity attenuated phase shift (CAPS)(Sadanaga et al., 2016), were used to quantify the NO_2 issued from the organic nitrates decomposition.’ to read something like ‘The thermal dissociation (TD) properties of different classes of nitrates was used as an analytical tool to probe the global chemistry of RONO_2 utilizing Laser-Induced Florescence (LIF), cavity ring down spectroscopy (CRDS)(Paul et al., 2009), or cavity attenuated phase shift (CAPS)(Sadanaga et al., 2016) to quantify the NO_2 evolved from organic nitrate thermal decomposition’.

Line 151 – replace ‘Worth noticing...’ with ‘It is worth noting...’

Line 178 (also Line 638) – replace ‘Worth notice...’ with ‘It is worth noting...’

Line 273 – replace ‘thoughtful’ with ‘well thought out’ or ‘carefully thought out’.

Line 312 – LISA, define abbreviation on first use.

Line 377 – replace ‘leads’ with ‘leading’.

Line 522 – replace ‘..used as template...’ with ‘...used as an example...’ or ‘...used as a reference....’

Line 742 – Missing citation, there appears instead an error (Erreur! Source du renvoi introuvable)

Line 778 and throughout manuscript – use of the word ‘sensibility’ should be replaced with ‘sensitivity’. (e.g., lines 665, 667,

Line 780 – reword ‘...signals corresponding to the adduct formation is barely noticed....’ to read as ‘...signals corresponding to adduct formation are barely noticeable....’.

Line 807 – replace ‘...deployment of the...’ with ‘...using this...’