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Atmospheric Chemistry and Physics Discussions

Interactive comment on "Characterization of a thermal decomposition chemical ionization mass spectrometer for the measurement of peroxy acyl nitrates (PANs) in the atmosphere" *by* W. Zheng et al.

Anonymous Referee #1

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This paper describes efforts to characterize the performance of a thermal dissociation chemical ionization mass spectrometer (TD-CIMS) for detection and quantification of peroxyacyl nitrates. The specific instrument in question was apparently constructed and used by NCAR scientists in collaboration with a group responsible for the first description of a TD-CIMS for such an application. The sensitivity of the instrument to various homologues of PAN was determined through use of standards synthesized via wet chemistry or a photochemistry chamber. The authors also examined how the sensitivity depended on certain instrument and sampling conditions such as dissociation

temperature and water vapor. In some cases quantitative results were obtained, in other cases only qualitative results are described. The conclusions are reasonably in line with the results obtained, although, in a few cases a slight change in wording will be required to remain fully consistent in my opinion. The paper overall well written, but it contains a lot of information that took significant time to ingest. The general importance of peroxyacyl nitrates in atmospheric chemistry makes this paper of some interest to readers of this journal.

My most significant comment, however, is that the paper contains relatively little in terms of scientific advances while being a nice comprehensive description of issues related to an important measurement technique. I think this paper is an obvious one for Atmospheric Measurement Techniques (AMT) - less obvious for Atmospheric Chemistry and Physics. This decision is up to the editor in my opinion. It is certainly publishable after revisions within one of these two journals.

My second most significant comment is that there are parts of the manuscript where fairly broad or significant conclusions are drawn about the capabilities (or causes of a lack thereof) that seem inconsistent with results or at least not strongly supported. In some cases, clear quantitative results couldn't be obtained or the results appear to be quite different from those found with other instruments the authors cite in the paper. Possible instrumental configuration effects are mentioned as possible explanations but then not really followed up. I would thus suggest, where possible, the authors distinguish between issues related to "the technique" or "the method" and their specific "implementation" of that technique. In the rest of the comments that follow, I try to highlight these areas.

Specific Comments (in order of which they appear): 1. 2nd line of abstract word "chemical" is missing

2. 6th line of abstract the phrase "to give a specific and quantitative measurement of each PAN species" seems at odds with many of the findings presented in this

ACPD

11, C2529–C2533, 2011

manuscript, .e.g. MPAN, HPAN?

3. Lines 16 – 20 of abstract: I would say the authors have postulated that such reactions are important for explaining their results but haven't really proved them. Indeed a different set of experiments would be needed. I suggest adding qualifying phrases here. For example "We postulate that. . ." etc.

4. Last paragraph of the abstract – is the finding of the sensitivity being a factor 10 higher for I-(H2O)n than for I- actually new? Later in the paper the authors say the result is similar to that described by Slusher, et al. Perhaps it need not appear in the abstract?

5. Lines 18 – 25, pg 8466: If I understand the flow of knowledge correctly, Slusher et al reported a lower sensitivity to MPAN (see reference on line 3, pg 8485). Is it really true then that the general assumption has been that all PAN compounds can be detected by this method with equal efficiency? The implication of the wording is that this paper presents new data that invalidates the assumption – but it would seem that assumption couldn't have been valid from the first description of the technique?

6. Pg 8467, line 11 – the authors mention later that other versions of the method may use different pressures, temperatures, flows, etc. It would seem pressure during dissociation might be rather important if unimolecular dissociation of the peroxy radicals (as inferred here) is a potential problem?

7. Pg 8468, line 11 – 16: Does the collisional dissociation process not potentially induce unimolecular decomposition of the carboxylate ions? It is unclear what the actual electric field strength in the CDC is – a factor of two range is given in the equivalent collision energy. Is it not better controlled typically? Also, 48kcal/mol collision energy at 0.2 Torr seems like it could due something towards decomposition. Why is this issue not considered in the list of reasons for not detecting some PAN compounds or for different responses instrument to instrument? Are all CDC's the same in these instruments?

ACPD

11, C2529–C2533, 2011

8. Pg 8469 Line 5-6. The authors mention later that carboxylic acids are a possible interference. Is it reasonable to expect such acids pass this hot steel mesh filled tube with 100% efficiency?

9. Pg 8474 Line 10: It appears the Environmental Chamber was filled with completely dry air – the technique is water vapor dependent. Was water vapor added to the sampling lines or elsewhere in the instrument during these studies?

10. Pg 8475 line 25: perhaps add stability of the carboxylate anion?

11. Pg 8476, reading through the discussion here, it seemed like words to the effect of "some fraction of the peroxy radicals could" are needed. It reads too much as though this is the way it occurs. Critical of course is the branching through R9 vs to R10 and R11, but no information was given for the relative branching (expected or otherwise) through those channels in the current instrument.

12. Pg 8479 line 8 – 10: doesn't this explanation presume that the higher surface/volume of the transit tube relative to the chamber isn't also a factor? Later, inlet transmission is blamed for PBZN and another compound, so why not HPAN?

13. Pg 8485 line 5 -6: The sentence begins with "it is more likely," but then ends with "as well," ass though such an interference from methacrylic acid would be in addition to other possible causes instead of being the more likely explanation. Which is it? Also, I'm not sure I understand how these calibrations are done. This paper implies it is the presence of acetate ions from PAN detection that induces the interference to carboxylic acids. Were the calibrations to MPAN in the references cited done in the presence of PAN as well? Would there not have to be acetate ions for the methacrylic acid to be confused for MPAN signal?

14. pg 8489, Line 1 (of Summary), I suggest the following wording "A TD-CIMS instrument, based on the technique developed by Slusher, et al, . . ."

15. pg 8489, Line 4 – 5, I think a more appropriate sentence might be, "The sensitivity

ACPD

11, C2529–C2533, 2011

to each PAN-type compound was found to be highly dependent upon inlet condition, i.e., . . .” The “lifetime of the PA radical” argument isn’t supported strongly enough. The sentenced could be followed by “. . .perhaps due to differences in the lifetime of the corresponding PA radical. . .”.

16. pg 8489, Line 10 – 11. The statement “It was demonstrated that the TD-CIMS method is able to selectively detect and precisely quantify PAN homologous in the atmosphere” seems to be at odds with much of the findings presented in this work and what is described below in this paragraph. At the very least, the word “some” has to be inserted between quantify and PAN.

17. pg 8489, Line 19: in reference to the interference by methacrylic acid on MPAN isn’t unique to MPAN – isn’t interference by carboxylic acids a problem for all homologues?

18. pg 8489 Line 21: The conclusions about HPAN seem rather unsupported. Clearly the TD-CIMS couldn’t detect it from the chamber; but it is unclear exactly why that wasn’t possible – only speculation. Also, the statement that it won’t be important in the atmosphere seems quite a stretch. Is this conclusion based only on the decay of HPAN observed by FTIR in the Environmental Chamber? There wasn’t even a figure presented of that data, much less a discussion of the possible sources of uncertainty therein.

Interactive comment on Atmos. Chem. Phys. Discuss., 11, 8461, 2011.