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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 #2

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The paper describes a modified version of the CIMS instrument introduced by Slusher et al. for measurements of peroxy acetyl nitrate and its homologues in ambient air based on thermal decomposition followed by electron transfer reaction of the peroxyacyl radicals with iodide ions and detection of the resulting anions. Modifications of the instrument include the introduction of an octopole filter instead of the lens stack and technical modifications (e.g., pumps, pressure control) in order to reduce weight and power consumption to make it suitable for deployment aboard research aircraft. An in-situ calibration for PAN based on photolysis of 13-C acetone in the presence of NO has

also been added. The major part of the paper addresses a laboratory characterisation of the sensitivity of the instrument to various PAN homologues s and discusses reasons for the observed differences, including temperature dependence and influence of humidity. The paper should be of great interest to experimental researchers engaged in the measurement of PANs and in CIMS technology. It also provides important information for evaluating future measurements made with the instrument in the field. As the paper is heavily weighted towards instrumental issues, I feel that it would be better placed in AMT than in ACP. The review below would still remain effective and the paper should be published after the comments below have been successfully implemented. I hope that the suggested changes will be of help to the authors to enhance the clarity of the message.

Major Comments

My major comment is that the paper contains many unnecessary repetitions and structural deficits that make it difficult to read, in particular due to the wealth of information contained. Particularly, the mixture of introductory statements with experimental facts and discussion of mechanistic explanations in some chapters should be restructured and separated so that the reader can more easily depict the essentials for each calibration experiment or compound and hence can develop his/her own opinion of the facts before appreciating the explanations provided by the authors. To me, the best solution would be to separate the "Discussion" completely from the "Results". If the authors feel that this would introduce too much overhead, however, I would urge to go through the different sections and do the separation one by one. I have tried to list several examples under "Specific and technical comments".

The FTIR measurements should be included in Figure 4 and results for PPN should be included in Fig 5.

The paper leaves somewhat unclear how the different calibration methods were used exactly and which weight they had on the final results. I assume this is mainly a problem

of structure and wording. I would suggest to improve the description of the use of the different sources for PANs more clearly (or clearly state that all results for homologues are based on the environmental chamber studies). The discussion on HPAN is rather speculative and hence difficult to accept. It should be reworded and removed from the conclusions except for its non-detectability.

The conclusions are not entirely backed up by the results and discussion. Because of the many factors influencing the sensitivity for a given compound, the calibration scheme may not prove as "reliable" as stated in line 9 (should be deleted).

Specific and technical comments:

Headings / structure:

Chapter 2.1:

The readability could be greatly improved by restructuring as follows:

1. CIMS description of main components (Fig 1) and their function (without argumentation).

2. Changes from Slusher's design with reasons; addition of a 13-C PAN source for in-situ calibration.

3. introduce a subheading : 2.2. Reference instruments (NOxy and Pan GC) for easier reading.

Chapter 3:

- move CPAN behind MPAN (as in heading) and remove "(see below)" Alternatively, change order in heading and move the last part starting with . . ." but about 10 times more sensitive than MPAN. . .. . .reagent ion." into the MPAN section. - introduce/change numbering of headings for

3.2.4 Phenyl-substituted PANs (had no number)

3.2.5 Mass 75 (was 3.3)

Change subsequent headings to: 3.3 Influence of ambient humidity 3.4 Interference of on-situ calibration 4. Discussion (see comment above)

Language and clarity of text(main examples only):

I would suggest to define short names for the NOxy (e.g. CLD) and the NCAR-Fast-PAN-GC (e.g., GC) which should then be used from thereon (the lengthy names disrupt the sentences unnecessarily). Remove "thorough(ly)" at all occurrences (this judgement should be left to the reader). Remove duplications of text throughout the paper. The photolytic source seems to be described twice (or have two version s of this source been applied, one with 13-C and one with 12-C acetone?). Should be spelled out more clearly.

8465, line 21: delete "species"

8466, line 18ff: Who has assumed? Wording should be improved or reference added..

Line 24-26: change PANs to homologues; sensitivities to sensitivity; are to is

8467 line 11: the passus: . . ." by an in-line stainless steel MKS instruments model 640 pressure controller." is the outstanding example for the need to improve wording. I would suggest to follow the common approach by putting company and partnumber information in brackets.

Line 24: 0.86 mm diameter orifice made of aluminium Line 25: what is a "flow tube ion-molecule reactor"? 8468, line 11/12: provides instead of provided (check also further down and next page for correct tense!)

8471: line 1ff: Remove "thorough". The paragraph is difficult to understand (was it a comparison of two different PAN sources or of 13-C with 12-C acetone in the same source? Please explain exactly what you mean by "and the NO2 was determined . . .." Is it a photo source, a photolysis source or a photolytic source ? (use the same wording

throughout the paper, I suggest to use photolytic source) Was there any evidence for impurities in the deuterated acetone, e.g. by the GC measurements ?

First sentence of 2.2.3: Reword to what has been done, e.g., “PAN compounds were synthesized in an environmental chamber. Describe the chamber with periphery, i.e. FTIR, followed by the description of the experiments. Question: Are the literature values for cross sections of PANs really more accurate than using the measurements provided in this study using prep-GC and NO2/NOy instruments?

p. 8479, line 17ff: I would think that this paragraph belongs into “Conclusions” or into the “Discussion” chapter if my suggestion above is adopted)

Chapter 3.2: The introduction should be reworded. It reads as if there was no heading in between this and the previous paragraph. It is “Because..” and not “Even though” the sensitivities vary with inlet conditions, that a standard procedure is required! Just state the facts!

Chapter 3.2.1: Remove the repetition regarding the PAN source, or clarify as outlined above.

p.8481, section on PPN: It would be important for strengthening the argumentation for the other compounds if the T dependence for PPN relative to PAN could be shown as well. Should be included in Figure 4!

p.8482, line 10ff: Are you saying the prep GC didn’t work as expected? This needs more explanation. The statements starting in line 15 are not convincing and the potential for radical losses being different for different species opens another can of worms, which would require more explanation. If there is no sound explanation for the earlier results being so different, this should be clearly stated and the entry possibly removed from Table 3, or at least put in brackets.

Tables:

Table 1: meaning of last column is not clear and I didn’t find it mentioned in the text.

Delete or explain.

Table 2: In the footnote a 93% efficiency id mentioned, whereas in the text 95.5% are stated. Needs explanation.

Table 3: Why is CIMS/GC missing for PPN? Add uncertainty to the column “Preferred value”.

Figures:

Axis labels on several figures (particularly 4, 5, 6, 10, 11, 14, 15) are hardly readable and should be enlarged.

Fig. 1: A legend should be added to the caption explaining the different items (pumps, pressure controller, CDC etc. The term “Zero Volume” is somewhat misleading as it is in realiter a heated SS- tube filled with SS-wool which serves as a catalytic PANs destructor. The description of the components should be consistent (either always with company information or just name of part, e.g. scroll pump, turbo pump, etc. or just a number with the explanation given in figure caption). Caption needs to include, e.g., . . .and photolytic PAN source used for primary calibration, and the description of items above as necessary.

Fig. 2 should show details for the GC-column (bore, length, material) and possibly the sizes of the FCs. The diffusion tube should be labelled (the “fork” above the tube is not clear to me) and the thermostat is missing.

Fig. 3: Volume of chamber should be given

Fig. 4. include FTIR measurements

Fig.6: error in legend of lower right panel (should read PnBN instead of PiBN)

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