

Interactive comment on “A gas chromatograph for quantification of peroxy-carboxylic nitric anhydrides calibrated by thermal dissociation cavity ring-down spectroscopy” by T. W. Tokarek et al.

Anonymous Referee #2

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This is a detailed, well-written manuscript describing a method for calibrating a “tried and true” chromatographic method to analyze PAN compounds in the ambient atmosphere. As the authors note, calibration of GC methods for this measurement has historically been its Achilles heel. This paper describes a means of quantifying authentic synthesized standards that has some significant advantages over other methods that have been used. The GC and calibration systems were demonstrated to be effective in two ambient environments with good detection limits and chromatographic resolution.

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The ambient data described in this paper is consistent with measurements of these compounds made in a variety of other sites and adds to our body of knowledge of the distribution of these compounds. However, the novelty of the work described in this paper for AMT is using CRD for calibration. This point seemed to get buried in the text at times and was distracted by discussion of issues that do not hinge on this effectiveness. For example, the fitting routine for the GC data (something all chromatographers in the field have to choose) is described in detail but the authors do not give motivation for using their routine over a commercially available package nor do they give a detailed comparison of any advantages of their routine, especially as it reflects on the improvement by CRD. A clear description of the reason for going with their routine would strengthen the paper. Some details are given starting on L 599, which I think should be moved up to Section 2. If this routine is a major finding, it should be described in the abstract. Also, the discussion of the TD-CIMS measurements is natural given that they were made at the same time as the GC measurements, but this again is distracting from the main topic of the paper. Changes in the title and abstract could shift that main topic to make it fit better, but that may not be advisable.

I like this paper, which I think should be published, and it would be improved with some organizational changes that might focus attention better on the main innovation of using CRD for quantification. I would separate the Experimental descriptions of CRD and CIMS into different paragraphs. CRD is used for calibration while CIMS is used for ambient sampling. The subject of the paper is CRD, yet the experimental description is a third of the size of CIMS, which is of most value for this paper as a “check” against the GC data. To support the ultimate conclusion that CRD is “easily implemented” for fieldwork, more detail of what implementation would entail should be given in this paper.

Specific questions/comments

L 113 What is the volume of the sample loop? Was it the same for both field studies? Was there a pressure drop experienced in the loop as a result of 115 sccm?

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L 125 How long does the CuSO₄ column last?

L 149 typo "EC"

L 253 How was the conditioning time for the FEP tubing determined? Especially given the evidence described in this paper of memory effects of PAN compounds with Teflon, is 30-60 minutes enough time to achieve a consistent output?

L 263 How was the amount of time the calibration run on the CRD determined? The traces in Fig 4 look like they are still sloping upward when the GC is injected.

L 349 I'm a little uncomfortable with the speculative nature of this paragraph. For instance, the authors mention that a fragment is consistent with HPAN without giving any evidence (from their experiment or from the literature) that this is plausible or supported. What exactly are we supposed to learn from these results?

L 356 I assume that the response factors were determined from multi-point calibration curves. How were the different PAN concentrations achieved for these? What range of concentrations were used? In L 370 the authors say the concentrations were "deliberately varied" without mentioning how.

L 374 I'm not clear how the corrections for PAN contamination were made. Was the amount of PAN in the sample determined by GC, which was calibrated by the system that needs to be corrected?

L 414 This is the first mention of detection limit. I think detection limits should be included in the abstract and discussed in the Section 2 along with the method used, rather than burying it starting on L 468 and L 609.

L 542 typo "alas"

L 996 Can the authors explain what the advantage of a 10-port valve for this configuration is over a 6-port valve?

L 1000 The valve manifold for switching the cal sources into and out of the sampling

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line is confusing. Should the 2-way valves be where the 'tee' fittings are shown?

L1049 GC details are redundant and should be removed from the caption.

Interactive comment on Atmos. Meas. Tech. Discuss., 7, 5953, 2014.

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