

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

Anonymous Referee #1

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This is a very detailed description of a novel scheme for calibration of a PAN-GC. While the level of detail makes the paper somewhat laborious to read, it is acceptable for a manuscript in AMT.

My only main comment is related to the use of TD-CRDS to derive mixing ratios of PANs from diffusion sources.

The authors use a TD-CRD to measure the NO₂ from thermal dissociation of a gaseous PAN sample and equate this to the original mixing ratio of the PAN, thus

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assuming that the TD-CRDS quantitatively measures PAN. This is THE central assumption and, given that the TD-CRDS method for measuring the sum of PANs can certainly not be described as established, more detail is needed here and not just a reference to the authors own work (a single paper, Paul et al from 2010).

The main issue is related to the fact that the authors are working at relatively high pressures and, unlike the TD-LIF studies of PANS made by the Berkely group, recombination is likely. This results in underestimation of the PAN mixing ratio.

The authors should therefore address in this paper the issue of recombination of acylperoxy radicals with NO₂ in the TD-CRD. This may be of reduced importance at low mixing ratios (where wall losses of the PA radical will win over reaction with NO₂ to reform PAN), but will be an issue at levels of up to 8 ppb (Figure 7).

Minor issues:

Some abbreviations can be removed to make the manuscript more readable (e.g. RF)

P 5955 The authors list and draw 5 PANs. Indicate why the list is restricted to these. Are they the most abundant, most important, most frequently measured ?

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