Atmos. Meas. Tech. Discuss.,
doi:10.5194/amt-2018-113-RC2, 2018

Atmospheric Measurement Techniques Discussions

Interactive comment on "Quantification of peroxynitric acid and peroxyacyl nitrates using an ethane-based thermal dissociation peroxy radical chemical amplification cavity ring-down spectrometer" *by* Youssef M. Taha et al.

Anonymous Referee #2

Received and published: 5 June 2018

This paper describes laboratory characterization of a new method for quantifying peroxynitric acid (PNA) and peroxyacyl nitrates. Overall the article is well written and describes important results and I recommend publication after the mostly minor issues below are addressed.

Line 79: "The measurement of peroxy radicals by PERCA is prone to interferences", but the text proceeds to discuss that the amplification must be determined by calibrations and that it varies with relative humidities. These are not interferences! Later in the text an actual interference by ozone for TD-PERCA_CRDS is well described.... But

variation of calibration factor with RH is not an interference. Same for 89: replace "interference" with "disadvantage" or "property"?

Ling 143 – "Teflon" – what kind – PFA? PTFE?

Section 2.3.2 – clarify that the concentration of PNA is determined by the NO2 mixing ratio, correct? Ie, NO2 is the limiting reagent and HO2 is in excess. Line 190-191 – O2 is not readily photolyzed to form O3 by 254 nm – replace with "...generated by photolysis of O2 by 185 nm radiation from a low-pressure mercury lamp"?

Box model simulations (in SI) The SI discusses formation of C2H5ONO and C2H5O2NO2, but what about the temperature dependence of C2H5ONO2? That is, ethyl nitrate, formed by C2H5O2 + NO.

Section 3.2 and figure 5. This is overall very good demonstration of the technique. It is a bit confusing that, apparently, both the inlet heater and PERCA chamber can be heated separately. This should be more explicitly pointed out in the earlier experimental sections.

Ling 281: the text in the parenthesis, though likely true, makes the sentence awkward to read

Section 3.5: interestingly the amplification factor for PNA (yielding HO2) is less than that for PAN (which forms CH3CO3). The following sections address details of the chain length with T, RH, but is there is a conclusion for why the PNA vs. PAN results are so different?

Line 309: "...operated under optimal conditions and ..." – this assumes that the optimal conditions do not change under varying circumstances. Might it be possible that the optimum NO or ethane concentrations are different at different temperatures or RH values?

SEction 3.7.2: The observed interferences are very interesting, and are likely relevant not only to TD-PERCA-CRDS but also to non-amplified thermal dissociation methods,

e.g. TD-LIF.

Section 3.8 , discussion of detection limit. Some of the terms here are confusing. 1. Do the authors actually mean precision when they have written LOD? LOD needs to be defined – is it for signal to noise ratio of 2? Or 3? The LOD is quoted as 87 ppt (1 sigma, 1 sec), but this seems much more like a description of the precision, not the LOD (ie, 1 sigma for precision, signal to noise ratio for LOD). 2. The authors have taken the "LOD" for the CRDS of 87ppt (1 sigma, 1 s) and divided by the CL of 69 to come up with the LOD for PANs of 1.3 ppt. Realistically, measuring PANs involves measuring NO2 twice - in amplification mode and in reference mode (either sequentially in a single channel instrument, or simultaneously with in a multi-channel instrument), so there should probably be another factor of sqrt(2). Also, the authors point out that the precision of the CRDS NO2 measurement is affected by the presence of NO and ethane reagent gases. For measurement in ambient air, or laboratory air, what is the precision of measuring NO2? The LOD (and precision) for an actual PNs measurement in ambient air would be affected by the precision of the CRDS NO2 measurement at the actual measurement conditions. For example, if O3 is 25 ppb, some portion of the O3 will react with the NO to give up to 25 ppb NO2 – is the precision the same at 0 ppb and 25 ppb? This has likely been addressed in earlier NO2 CRDS papers but should be mentioned for the reader's sake.

Interactive comment on Atmos. Meas. Tech. Discuss., doi:10.5194/amt-2018-113, 2018.