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Atmospheric Measurement Techniques Discussions

Interactive comment on "An instrument for the rapid quantification of PM oxidative potential: the Particle Into Nitroxide Quencher (PINQ)" *by* R. A. Brown et al.

Anonymous Referee #2

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This paper reports on the development of a steam-particle-growth system coupled to a cyclone for droplet collection followed by analysis of the liquid for particle bound ROS with a fluorescence probe. Recently, a number of papers have been published describing various designs aimed at measuring particle-bound ROS. This paper adds an additional method to this group. The authors have done a series of careful experiments testing the performance of the instrument, however there are a number of major issues to address. 1) The particle collection system of the instrument is nearly identical to other instruments already reported in the literature, with the exception that the cyclone design differs; exactly how it differs is not totally clear since exact details are not provided. 2) The instrument described measures only ROS associated with particles, yet

it equates measurements of particle bound ROS with other assays that measure completely different particle species associated with the aerosols ability to induce oxidative stress. This conflation adds to the confusion that seems to exist in the new field of aerosol research. Prior to publication, these two major issues should be addressed. Details are provided below, along with other minor issues to consider.

Major Issues

A major issue is that the instrument described in this paper is essentially identical to a PILS with a cyclone droplet collector instead of impactor. Orsini et al (2008) describes an instrument with PILS coupled to a cyclone (which the authors cite), and Peltier et al (2007) specifically describes and tests a PILS-mini cyclone system (not cited in this work). Since the proposed instrument is so similar to these existing instruments, details of how the new instrument differs, such as what are the technical advances in this new instrument over existing technology. For example, why not just utilize the existing methods? It appears that the authors are implying that the cyclone design is novel, ie, that it produces what they call a standing vortex. If this is indeed the main novel feature, the exact details of how the cyclone was designed and constructed to achieve this should be discussed in more detail. As it stands it is doubtful a reader could reproduce the results of this paper due to insufficient detail.

A second major issue with this paper is the conflation of particle bound ROS and aerosol species that produce ROS in vivo, which is now often referred to as oxidative potential (OP). The title states that this is a method to measure PM OP, but it is more precisely a measure of ROS associated with particles. The title should be more specific, eg, possibly changed to something like. . . rapid quantification of ROS associated with particles... Also, in the abstract it should be clearly stated that particle bound ROS is being measured. Throughout the paper care should be taken to delineate the two. Thus, it would be best not to equate what is being measured in this work with OP, eg, Pg 2 line 17 states: In order to achieve ROS quantification, termed herein oxidative potential, ...

The two, particle ROS and OP should be delineated as they are associated with different aerosol chemical species and have potentially different health effects. Particle ROS, what the authors call exogenous ROS is what this paper is measuring and which has not been associated with any adverse health effects in population studies; at least this reviewer does not know of any. Maybe the authors can add citations supporting why particle-bound ROS is an important thing to measure. An example may be direct inhalation of combustion products, like cigarette smoke? In contrast to particle-bound ROS, endogenous ROS, which is often referred to as OP and typically measured with the DTT or GSH assay, has been associated with adverse cardiorespiratory adverse health effects in some studies (Abrams et al 2018; Bates et al., 2015; Weichenthal et al., 2016; Yang et al., 2016). Thus, it is strongly suggested that the term oxidative potential be removed throughout the paper and replaced with particle-bound ROS, or similar notation, except in the cases where DTT assay is specifically referenced, eg, Table 1. Overall, the point is that this research area lacks an agreed upon terminology, but no matter what the authors decide to call what they measure, it is very important that it be made clear that it is fundamentally different than certain other assays that measure aerosol chemical species that generate ROS in vivo (eg, DTT or GSH, etc).

Related to this, if particle-bound ROS is so reactive and has a short life-time, the justification for this instrument, why would one expect it to be a significant health hazard to a large segment of the population? It seems the instrument is most useful for measuring particle-bound ROS associated with very fresh combustion emissions. Where specifically would one then expect to deploy this instrument. A discussion along these lines should be added. This would further help clarify the difference between what this instrument is measuring vs methods using the DTT or GSH assays (ie, methods measuring aerosol oxidative potential not particle bound ROS).

Minor Issues

Pg 2 last line is not correct as two online DTT systems have been developed, see Puthussery et al. (2018), and Eiguren-Fernandez, et al, (o-MOCA), which is cited.

Last paragraph of section 1.3.4: There is a difference between a solid insoluble particle and a hydrophobic particle. Can the authors give an example of an insoluble particle bound ROS species? For oxidative potential, this is extensively discussed in Fang et al, (2017) This is an important question since the authors are using this as design criteria. (More on this below).

Section 2.2.4, What specific system used a copper steam generation system the authors refer to? This is not common practice in most steam systems, including the commercially available PILS. References to the copper system should be removed unless specific instruments using it can be identified.

In the particle mass collection efficiency method was the aerosol neutralized after nebulization for the IAC leg, as done for the SMPS leg? If not the reason for not doing this and implications should be discussed since one may expect highly charged particles. Also, how is the impactor affected by these highly charged particles (if there was no neutralization)?

Why is the impactor installed before the particles are dried? Was the cut size of the impactor actually 0.1 um or did it remove larger droplets, but ended up effectively removing dried particles with diameters less than 0.1 um?

Pg 16, line 8, if the particles are dried, depending on the RH achieved, the ammonium sulfate may not be spherical. Why not do a sensitivity test to see how the findings change if say the DMA sizing is corrected assuming non-spherical particles.

Pg 16, line 10, why does the the Dp log scale make the area under the curve not proportional to fraction of overall mass when the size distribution is plotted as dN/dlogDp? That is precisely the point of the size distribution function.

Pg 17 line 4, typo, 0?

Section 4.1.3. What is the difference between a hydrophobic particle and an insoluble particle? Is DEHS insoluble in very dilute systems? Does DEHS remain as the original sizes generated in the droplet collection system (ie, cyclone)? The point is the one thing that is unique about this instrument is the claim that it can measure at near 100% efficiency insoluble particles, but only one form is tested. What about collection efficiency of solid particles? Will the instrument actually collect solid particles and thus have the ability to measure ROS associated with solid particle surfaces, say for example, fresh soot particles. Are comparisons of this vortex cyclone to the Orsini et al or Peltier et al mini-cyclone valid since their test were done with truly solid particles (PSL or soot)?

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