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Interactive comment on "An On-line Monitor of the Oxidative Capacity of Aerosols (o-MOCA)" *by* Arantzazu Eiguren-Fernandez et al.

Anonymous Referee #2

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This paper presents an instrument for semi-continuous measurements of aerosol oxidative potential with the DTT assay. Generally, the paper is well written and the data (what there is of it) appears to be of good quality. The subject is of interest and this is an appropriate journal for publication. At times, however, the authors make rather broad (generally very positive), but unsupported statements regarding their method. They also fail to cite other work and seem to implicitly criticize other methods based on general statements. One gets the distinct impression of a highly biased view. This tends to diminish what could otherwise be a nice paper. I suggest the authors try to present a more balanced paper. I also suggest that the conflict of interest statement be seriously considered. The fact the the authors are from a company that aims to sell and profit from this instrument is surely a potential conflict of interest to be identified. It also tends to account for the tone of this manuscript.

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Discussion paper

Specific comments are below.

Line 14. It is rather odd in a paper that will ultimately be published to refer to it as a manuscript. Suggest minor edit.

Line 20, explicitly define extreme temperatures? What is the point of this line? What is it referring to? Why not just come out and state it; it is being asserted that this technique is better then steam based condensations systems (curiously this is often stated by these researchers but no data has every been shown to support this, this is acknowledged later in the paper, lines 84-85).

Line 61, the authors should cite papers on other methods for measuring DTT online and offline using a different approach [Sameenoi et al., 2013; Sameenoi et al., 2012]. Their method is not the first online DTT instrument; two others have come before. These other DTT analytical methods should also be discussed

Line 67-68. Please provide references showing how the DTT assay can distinguish between metals and organics to overall OP.

Line 68. Very few references are provided for DTT-health associations; also noted by the 1st reviewer regarding inflammatory markers. DTT-measured OP has also been associated with various health endpoints in recent epi studies. See for example, [Bates et al., 2015; Fang et al., 2016; Weichenthal et al., 2016; Yang et al., 2016].

Line 72 to 73: It states, that the DTT method is too time consuming to be widely applied. Exactly what does that mean? How do the authors know that and what is the proof to support this? Proof that seems to be counter to this statement is that sufficient DTT data has been generated for use in epidemiological studies, see above. This is a broad, imprecise and possibly largely incorrect statement.

Line 74, how does the filter extraction process alter the sample, whereas the method presented here does not? Be specific. For example, what specific components that contribute to DTT activity would be sensitive to differences between the two different

methods. Specific transition metals (Cu and Fe) and quinones are mentioned in the Intro. Eg, do Cu and Fe suffer from positive or negative artifacts? Charrier et al postulates that transition metals comprise much of the DTT activity at sites in California [Charrier and Anastasio, 2012].

Line 77, does the DCFH assay measure the oxidative capacity of PM? Be more specific distinguishing between what DCFH and DTT measures.

Line 78, Sameenoi reference does not belong in this list; it measures DTT. In fact in this paragraph the authors are mixing up two completely different assays and making broad statements that may not apply to both assays. Eg, heating the sample in the PILS may alter the peroxides on the particle in the DCFH assay, how does heating affect the components in the DTT case? Is there evidence to support these claims in other PILS data/comparisons? What specific DTT active components are affected (see note above)?

Line 84, a rather odd statement, mainly innuendo; i.e., line starting with While it is not known. . .

Lines 85 to 90 (or so), while total DTT is undoubtedly of value, being able to separately measure water-soluble vs insoluble components is also of value since they likely have differing physiological effects, see for example [Delfino et al., 2010].

The last line of the introduction is mainly speculation.

Section 2.1: It is repeatedly asserted that that this system quantitatively measures insoluble species, yet no proof for this is provided. Based on the design it does seem feasible, but to make this claim it should be shown that insoluble particles are quantitatively collected and transported through the particle collection and liquid handling system.

Line 107, what exactly does very gentle water condensation process mean?

Line 117-118. Again, speculation without support.

It might be worth pointing out that this particle growth method greatly limits the max sample flow rate. This has implications.

Section 2.2: The chemical module in this work is somewhat similar to that described by Fang et al [Fang et al., 2015]. The authors know of this paper as it is cited in line 165. Since Fang published the first automated analytical system for DTT analysis, and this paper uses a similar approach (dual syringe pumps with reaction vial), that work should be cited and comparisons made. How are they similar, how do they differ? What are the advantages of this system?

Line 273, this is a rather broad and largely incorrect statement. Cross contamination is not a significant issue for all online systems, instead being mainly an issue with only liquid based systems.

Line 260, too broad a statement, the results of Fig 4 apply only to this system.

Regarding the use of a filter (frit) to remove insoluble particles. In this approach all samples will then pass through the filter containing collected insoluble particles from all previous samples. It would seem that this arrangement could potentially lead to significant artifacts, depending on ambient conditions.

Line 339. Not sure what unattended means in light of the previous discussion on stability of the reagents? Were the reagents changed daily or were they sufficiently stable?

Field testing data to prove the performance of the instrument is very sparse consisting of only 3 days of operation and no comparison to other standard methods, such as filter collection and analysis. This is a major weakness of this paper. (As an aside, the time axis in Fig 6 is difficult to read). For example, in the field data analysis it is claimed that the measured DTT activity follows a similar trend as PM2.5 mass and BC concentrations. From Fig 6, this seems unlikely. Why not do a regression analysis and report the correlation to support this. Even better, run the instrument longer and

provide a stronger data analysis section truly demonstrating the power of the instrument. Essentially, the very limited field data provides little evidence that the instrument is accurately measuring DTT. That is, magnitudes seem reasonable compared to other studies, but really there is not evidence that the observed fluctuations in DTT are real. This is surprising given the emphasis afforded to this in the conclusions.

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