

The author's present a methodology where they incorporate a dithiothreitol (DTT) based assay into a previously established online method for particle composition analysis (MARGA). The authors make alterations compared to previous online DTT methods in the literature, including the use of nitrogen carrier gas and shielding from light in order to reduce the DTT background signal. The optimised DTT method is compared to current methods existing in the literature and deployed in ambient measurement campaigns where they correlate DTT activity with a range of inorganic ions, trace gasses and black carbon. However, there is a lack of technical detail in places, and the comparison between online and offline measurements requires additional clarification. I would recommend publication after addressing the following comments:

Line 111-113 - There is a lack of technical details in general in this section – is nitrogen continuously flowed through, if so what flow rate? How is the DTT reaction vial actually protected from light? As these are key modifications, there should be substantially more technical details added.

Line 172 – Additional details should be given regarding how offline PQN experiments were performed.

Line 174 – What are traditional samples, please specify.

Line 184 – What are the PM_{2.5} mass loadings on the filters collected for analysis?

Line 204 – Again, more detail required here regarding the nitrogen and light-reducing modifications.

Line 223 – If the slope is lower compared to Puthussery et al, does this not mean the response as a function of PQN concentrations is less, and thus the method is less sensitive to PQN? Is this slope corrected for baseline, accounting for background DTT consumption? This should be elaborated in more detail in the manuscript.

Line 231 – How does this LOD compare to the other methods mentioned in the literature? And how does this compare to the LOD of the offline method used?

Line 254 – It is unclear to me what the purpose of the “PQN correction” is? Please elaborate.

Line 257 – Referring to the comparison of online and offline measurements in Figure 5. The authors state in the introduction that online methods are advantageous due to the online method capturing reactive components that offline methods currently do not, which is valid. Therefore, we would expect the online DTT signal to be higher than that of the offline method for an equivalent sample once normalised, due to the rapid capture of particles in the online method compared to offline. This is not the case in Figure 4 where the PQN slopes are the same, but the offline values are higher compared to online, why? Is this due to the optimisation of the online method? It is not clarified clearly. In Figure 5, the ambient samples measured offline have a higher DTT activity compared to online, and after the “PQN correction”, the offline DTT activity is roughly equivalent to the online, if not still slightly higher for some samples. Puthussery et al (2018), frequently cited in this manuscript, for instance show a higher online signal compared to offline. There is really limited description of the data in Figure 4 and Figure 5 in the manuscript, and as the online vs offline comparison is a key feature of implementing

the DTT assay into an online methodology, this should be explained more clearly and in more detail.

Line 522 – Figure caption 1 is not sufficient to describe the method, please expand substantially to include more technical detail.

Technical corrections:

The manuscript could benefit from an additional proof reading for English as there are confusing and, in some cases, incomplete sentences throughout the manuscript.

Line 26 – reactive oxygen (species?) typo?

Line 150 – deionized water (deionised water) typo.

Line 180 – the amount of what?

Line 294-296 – ng m⁻³, typo? ug m⁻³?

Line 526 – no x-axis title on Figure 2 (left), label both graphs (e.g. A and B)

Line 533 – error given in Figure 3 but not in Figure 4 for the same data?