

A new on-line monitor for in-situ, time-resolved characterization of the ability of ambient particles to generate reactive oxygen species

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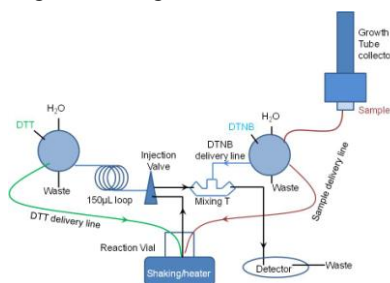
Oxidative stress has been associated with widely-spread diseases such as Alzheimer's, atherosclerosis, diabetes, and myocardial infarction. Despite ample evidence linking exposure to air pollution and the incidence of these diseases, the mechanism by which air pollution exposure leads to health effects remains unclear. One possible pathway is the ability of inhaled aerosols to generate reactive oxygen species (ROS). *In-vivo* and *in-vitro* studies have shown a correlation between the oxidative potential of airborne particles and the production of biological markers of ROS formation and oxidative stress. Yet, these studies are costly, time consuming, require long exposure protocols and high particle concentrations. To reduce costs, increase throughput, and obtain faster results, new chemical assays have been developed. Among them, the dithiothreitol (DTT) assay is widely used for the assessment of the capacity of ambient aerosols to generate ROS (Cho *et al.* 2005). The DTT assay is based on the ability of particle-bound redox-active chemicals to oxidize the DTT to its disulfate form. The rate of DTT loss is determined as the slope of its sample regression line which is then used as a relative measure of the oxidative capacity of the sample.

Here we present a new system for the in-situ, time-resolved measurement of the capacity of airborne particles to generate ROS using the DTT assay. The on-line monitor of the oxidative capacity of ambient aerosols (o-MOCA) consists of a liquid sample collector (Eiguren-Fernandez *et al.* 2015) coupled to an on-line chemical module.

The o-MOCA system

The o-MOCA (Figure 1) provides a new approach for on-line measurement of the ability of particles to generate ROS.

Figure 1. Diagram of the o-MOCA



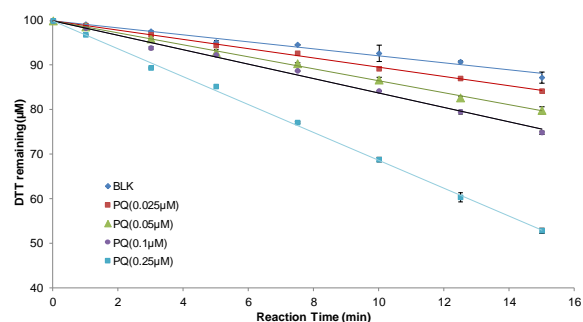
Airborne particles are collected directly into water using the condensation growth tube. The suspension is transferred to the reaction vial, where the DTT reagent is added. This solution is incubated at 37°C with gentle shaking. At designated times an aliquot of the reaction solution is delivered to the mixing T, where it is mixed with 5,5'-dithiobis-2-nitrobenzoic acid (DTNB) to form a complex, which absorbance was measured at 412nm.

Results

Optimization of the automated method

The on-line DTT assay and the automated chemical module were optimized using 9,10-phenanthraquinone (PQ), a highly active redox compound. Figure 2 shows the DTT consumed over time for four PQ concentrations and blanks. The calculated DTT consumption rate per unit PQ was similar for all samples with an average rate (\pm STDEV) of $3.13 \pm 0.12 \mu\text{M DTT}/\text{min} \cdot \mu\text{M PQ}$, which indicated a linear correlation between DTT loss and PQ concentration in solution.

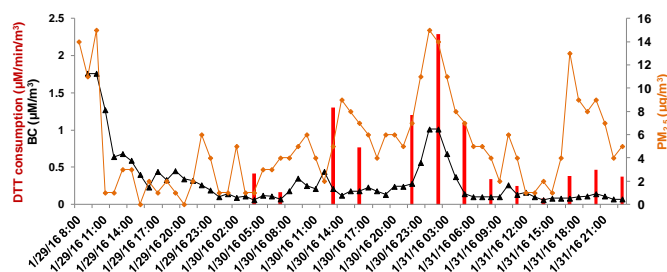
Figure 2. DTT consumption overtime for blanks and PQ



Oxidative capacity of ambient particles in Berkeley

The o-MOCA run unattended for 3 consecutive days in our laboratory collecting 3-hr $\text{PM}_{2.5}$ samples. Measured DTT consumption rates and $\text{PM}_{2.5}$ and BC concentrations (nearby Air Quality Management District Station data) are shown in Figure 3. Important diurnal and daily differences were observed. Also, the oxidative potential of particles followed similar trends to PM and BC concentrations.

Figure 3. DTT consumption rate ($\mu\text{M DTT}/\text{min} \cdot \text{m}^3$); $\text{PM}_{2.5}$ and BC ($\mu\text{g}/\text{m}^3$); *: <LOD



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