

A portable, automated online instrument to quantify reactive oxygen species (ROS) in ambient aerosol

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Epidemiological studies have linked urban aerosol levels with mortality and hospital admissions due to respiratory and cardiovascular disease. It is often hypothesised that these negative health effects could be due to particle-bound reactive oxygen species (ROS) or particle-induced formation of ROS, and subsequent oxidative stress of lung cells. ROS are defined as including families of oxygen-centred or -related free radicals (HO[•], HOO[•] or ROO[•]), ions (HOO⁻) and molecules (H₂O₂, organic and inorganic peroxides).

Established methods to quantify ROS mostly rely on particles being collected on filters or impactors, followed by subsequent extraction steps and chemical analysis. These procedures are labour intensive and have poor time resolution. In addition, a long delay between collection of particle-bound ROS and their analysis might underestimate true total ROS concentrations because many ROS components are highly reactive and thus short-lived. To overcome these limitations, we developed a technique to allow on-line, continuous measurement of particle-bound ROS using the fluorescence probe 2',7'-dichlorofluorescein (DCFH), in conjunction with catalytic enzyme horseradish peroxidase (HRP), via fluorescence spectroscopy (Fuller, 2014).

In this study we describe the design and characterisation of a portable instrument using the DCFH/HRP reaction system to quantify ROS. The new instrument allows for an automated, unattended operation of about 15 hours. Though this operation time is extended if an operator is present.

In our instrument, ambient air is drawn into the instrument at 5 l/min through the aerosol conditioning unit, which consists of a stainless steel cyclone (2.5 µm cut-off) and an activated-charcoal denuder to remove any oxidizing gases such as ozone or organics. After the charcoal denuder the aerosol particles enter the custom-built particle collector. The particle collector allows extracting soluble components of aerosol under mild room temperature conditions and within seconds of entering the particle collector. Should water soluble ROS not be extracted at the initial spray-formation stage, they will further come into contact with the HRP solution on the filter stage within the particle collector. After the particle collector, the ROS extract/HRP solution is combined with the DCFH solution in a continuous liquid flow reaction system and the DCF fluorescent intensity is detected spectroscopically to quantify ROS.

Calibration of our new instrument was achieved using known concentrations of ROS model hydrogen

peroxide (H₂O₂). The response of a range of other organic peroxides and oxidizing aerosol components were tested to characterize their response to the DCFH/HRP assay.

The long-term stability of the instrument, essential to perform ambient measurements, was evaluated using a flow tube where secondary organic aerosol was generated at constant concentrations. We show that the instrument could be operated over many hours with only minimal maintenance.

The detection limit of the instrument is about 3 nM [H₂O₂] equivalents/m³ air, which is suitable for ambient studies at polluted urban sites. A high time resolution of about 10 min allows tracking fast changes in atmospheric conditions e.g. changes in meteorological conditions or traffic pattern.

The new instrument was tested at a roadside air monitoring station in London (Marylebone Road) and ROS concentrations of about 4 to 30 nM [H₂O₂] equivalents/m³ air were detected and ROS concentrations correlated reasonably well with total PM_{2.5} concentrations in the range of 5 to 25 µg/m³.

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