

Online instrument for detection of particle oxidative potential

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Introduction

While the adverse health effects of the airborne ultrafine aerosol particles are widely known, the underlying mechanisms are not yet fully understood. It has been suggested (e.g. Dellinger et al., 2001) that the particle bound reactive oxygen species (ROS) has a significant role in the health effects causing oxidative stress. The ROS content of the aerosol particles are measured as oxidative potential, and it is typically expressed normalized to the hydrogen peroxide (H_2O_2) equivalent concentration.

The oxidative potential is typically measured using a chemical probe, which properties change during the oxidation under the influence of ROS. The most commonly used probes are dichlorofluorescein (DCFH) and dithiothreitol (DTT). In the DCFH method (used for instance in Fuller et al, 2014) the particles are first immersed in horse radish peroxidase (HRP), which is then mixed with the DCFH. After a set reaction time the fluorescence intensity of the DCF+HRP mixture is measured. The oxidative potential of the particles can then be calculated based on the fluorescence intensity, the reaction time, the solution concentrations and the amount of particles collected into the liquid. The DTT method operates similarly. The particles are first collected into the DTT solution and then after a set oxidation time a quenching agent is mixed to the sample together with a developing agent (DTNB). After this the light absorption of the 412 nm light is measured revealing the remained DTT concentration. By comparing this to the DTT concentration in the beginning the consumed DTT concentration is obtained and combining that information with the collected particle concentration the oxidative potential is obtained (Cho et al, 2005). Both of these methods need several steps for the measurement and accurate timing for the reaction time. The reaction time for both methods is usually in the order of few minutes. Another time consuming aspect in the measurement is the particle collection. Depending on the method the collection times can be from few minutes to tens of minutes. This is especially challenging in the oxidative potential measurement, since the oxidative species are chemically active and they react very rapidly.

While most of the ROS measurements are done with off-line analysis, Fuller et al (2014) introduced an online CFH assay based instrument for the measurement of the particle bound ROS concentration. In the instrument the particle collection was integrated to an automated liquid sampling and detection system. The reported response time was around 15 minutes. Fang et al (2015) reports an automated DTT assay system for the oxidative potential measurement of collected particle samples.

The goal of this study was to design and build an on-line measurement instrument prototype for the measurement of the oxidative potential of aerosol particles. The targeted temporal resolution for the instrument is in the range of one minute with the operational particle size range from 30 nm to 1 μ m. A picture of the build prototype instrument is shown in figure 1.

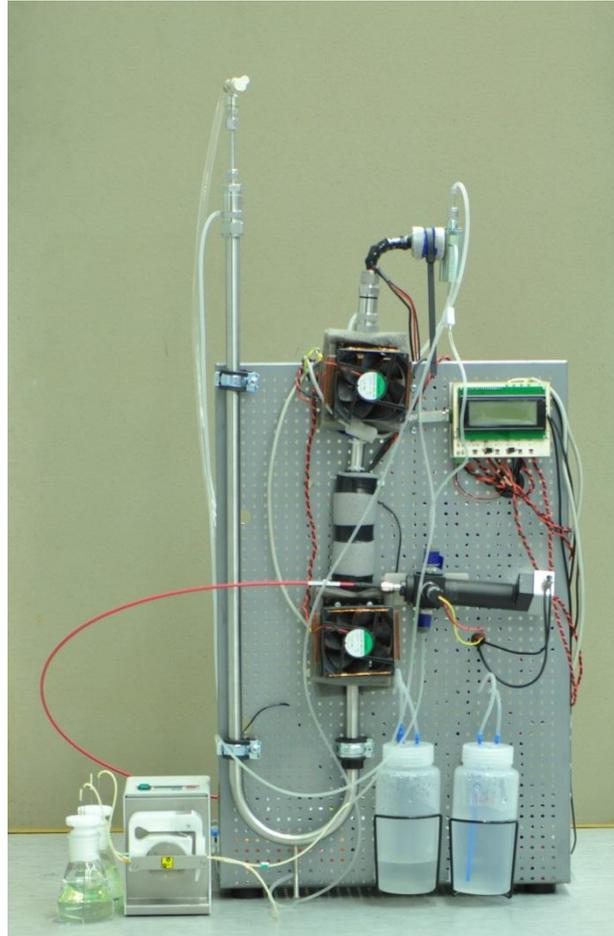


Figure 1. Prototype instrument for measuring the oxidative potential of fine aerosol particles.

Instrument design

The operation of the instrument is based on a liquid fluorescent nitroxide (9,10-bis(phenylethynyl)anthracene-Nitroxide, BPEAnit) probe, developed in Queensland University of Technology (Stevanovic et al, 2012). The key advantage of the BPEAnit probe is that it does not require the use of additional compounds in the detection. The ROS concentration is obtained by measuring the fluorescence intensity under UV excitation. In the instrument the particles need to be first grown with water in order to enable inertial particle collection. After the particle growth the particles are collected into the probe by their inertia. As a final step the fluorescence intensity is measured from the particle containing probe. The instrument operation principle is illustrated in figure 2.

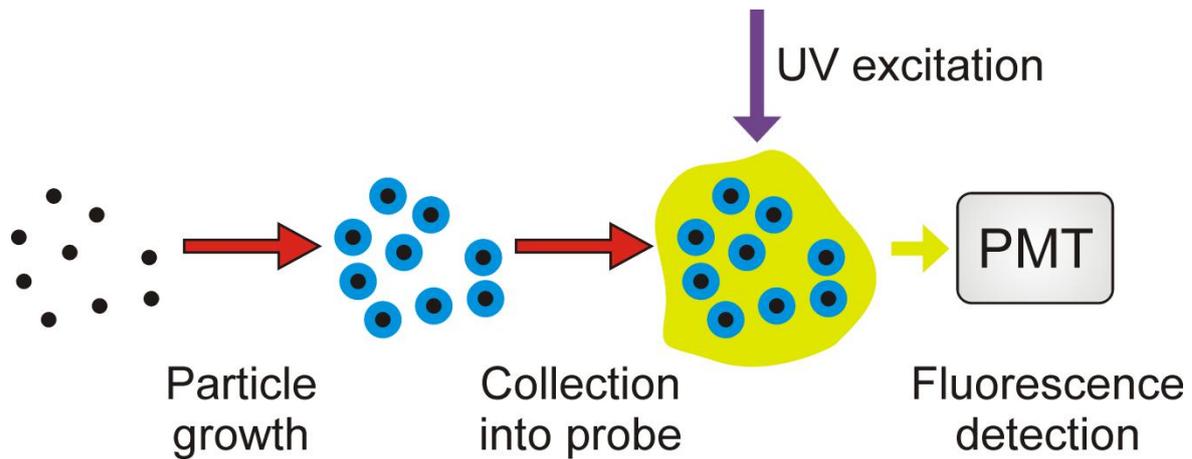


Figure 2. Basic principle of the instrument

For the particle collection a commercially available particle into liquid sampler (PILS, Orsini et al, 2003) system could be used. However the PILS system has a one major drawback, the water content of the sample after the growth is very high. This would significantly dilute the sample, which would make it necessary to have compensation for the amount of excess water. This in turn would be difficult, since the water amount is not constant. For this reason, systems that use this kind of particle collection need to use a tracer compound to measure the probe dilution after the collection (eg. Sameenoi et al, 2012). In order to overcome aforementioned drawback and maintain simplicity, a customized particle collection system was designed for the instrument.

Particle growth system

The particle growing part of the instrument is based on the design by Hering et al (2014). A schematic view of the particle growing part is shown in figure 3. As the first step in the growth process the aerosol is cooled down in the conditioner while flowing in a wetted wall channel. After the cooling the high relative humidity flow enters the heated saturator, where water vapor is introduced to the flow by heating the wetted walls of the flow channel. Since the diffusion coefficient of the water molecule is higher than the thermal diffusivity of the air, the center of the flow becomes supersaturated and the particle growth is initiated. As the final step the particles flow through the moderator, where excess water vapor is removed from the sample. A small flow of air is also drawn from the bottom of the growth system in order to drain out the excess water fed to the system. The particle growth characteristics of the growing part can be controlled by varying the temperatures of the different sections.

The targeted particle size after the growth is above 1 μm . The growth system performance is a compromise between the particle end size and the particle penetration through the system. Additionally while the particle number concentration increases the particle size after the growing decreases. This is due to the local temperature rise caused by the latent heat released in the condensation (Lewis et al., 2013). A set of operational parameters were searched so that the growth system is able to grow the particles large

enough with high penetration efficiency for particle concentrations below $1 \times 10^5 \text{ 1/cm}^3$. The operational parameters of the particle growth system are collected to table 1.

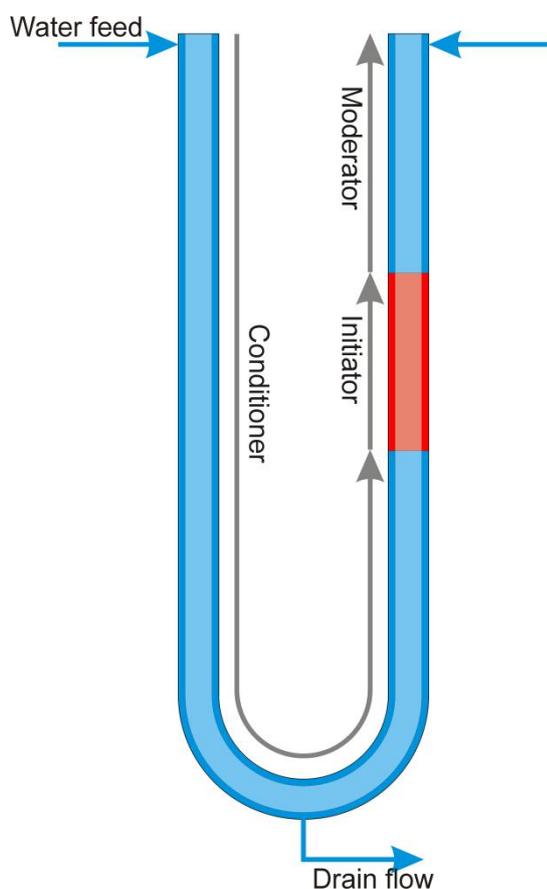


Table 1. Operational parameters of the particle growth system

Sample in flow rate	6.2 lpm
Sample out flow rate	5.0 lpm
Drain flow	1.2 lpm
Conditioned temperature	6°C
Initiator temperature	80°C
Moderator temperature	15°C
Water feed rate (total)	30 ml/h
Particle size after the growth	> 1 μm

Figure 3. Schematic view of the particle growth system

Particle collection into probe

A wetted wall cyclone was chosen for the particle collection, because the cyclone construction allows easy handling of the collection liquid. The cyclone is located directly after the particle growth system and it is connected with a heated sample line. This was necessary in order to avoid water condensation and particle losses caused by the condensed water. A cross section of the cyclone is shown on the left hand side in figure 4 together with a picture of the prototype cyclone on the right. The designed cutpoint of the cyclone is $1 \mu\text{m}$ and the liquid feed is located to the point where the sample enters the cyclone cone. The liquid is drawn from the bottom of the cone to the analysis. For the operation of the cyclone, it is essential that the liquid feed rate is exactly equal to the feed rate drawn from the cyclone, in order to avoid liquid buildup or wall drying in the cyclone. The prototype was made from titanium, since it allows very good chemical compatibility with the dimethyl sulfoxide (DMSO) solvent used for the probe. In order to enhance

the surface wetting inside the collection area the whole cyclone was coated with titanium dioxide (TiO_2) in an atomic layer deposition (ALD) process. The surface must be illuminated with UV light before the use, after which the surface becomes superhydrophilic.

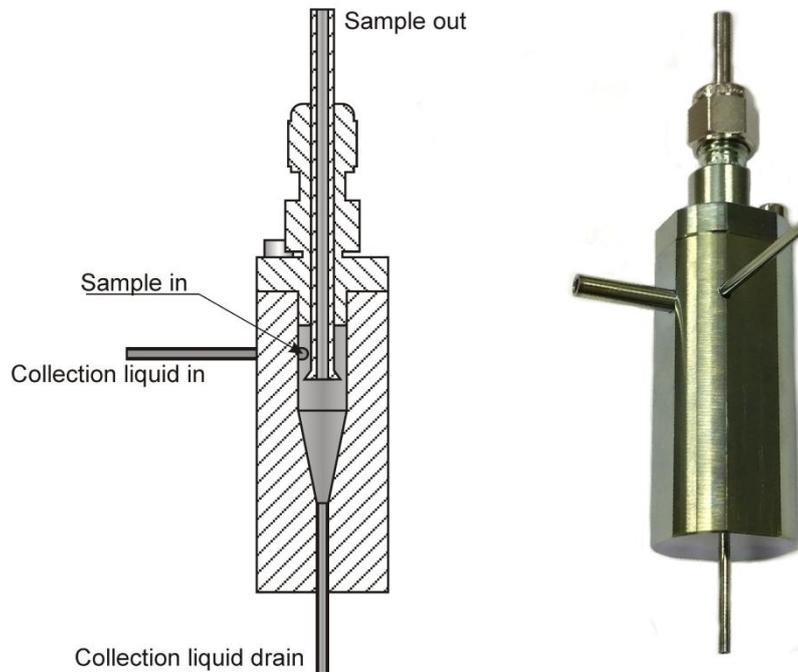


Figure 4. Cross section view of the wetted wall cyclone on the left and picture of the prototype on the right. Note that the cyclone is not in the same position in the two pictures.

Fluorescence detection

After the particles are collected to the probe, the liquid probe is pumped through the fluorescence unit, pictured in figure 5, where the fluorescence intensity is measured under UV excitation. A continuous wave laser diode with wavelength of 405 nm and a power output of 100 mW is used as the light source. The excitation beam travels through a narrow bandwidth 405 nm bandpass filter with a bandwidth of 10 nm and a focusing optics. The emitted fluorescence is measured with a photo multiplier tube (PMT). In front of the PMT, there is a light collecting optics together with an optical long pass filter limiting the spectral range to above 442 nm in wavelength. A good quality filters were selected in order to avoid the scattering to interfere the measurement. The focal points of the excitation beam and the detection optics are aligned together. The liquid flows through that focal point inside a quartz glass tube. The tube inside diameter is 1 mm and the liquid flow rate is 0.5 ml/min. The diameter of the excitation focal point is approximately 2 mm. Based on these numbers the detection volume is approximately $2 \mu\text{l}$ resulting to a theoretical time

resolution of 0.2 s for the fluorescence measurement. The time resolution of the fluorescence measurement is however limited to 1 s in the measurement electronics.

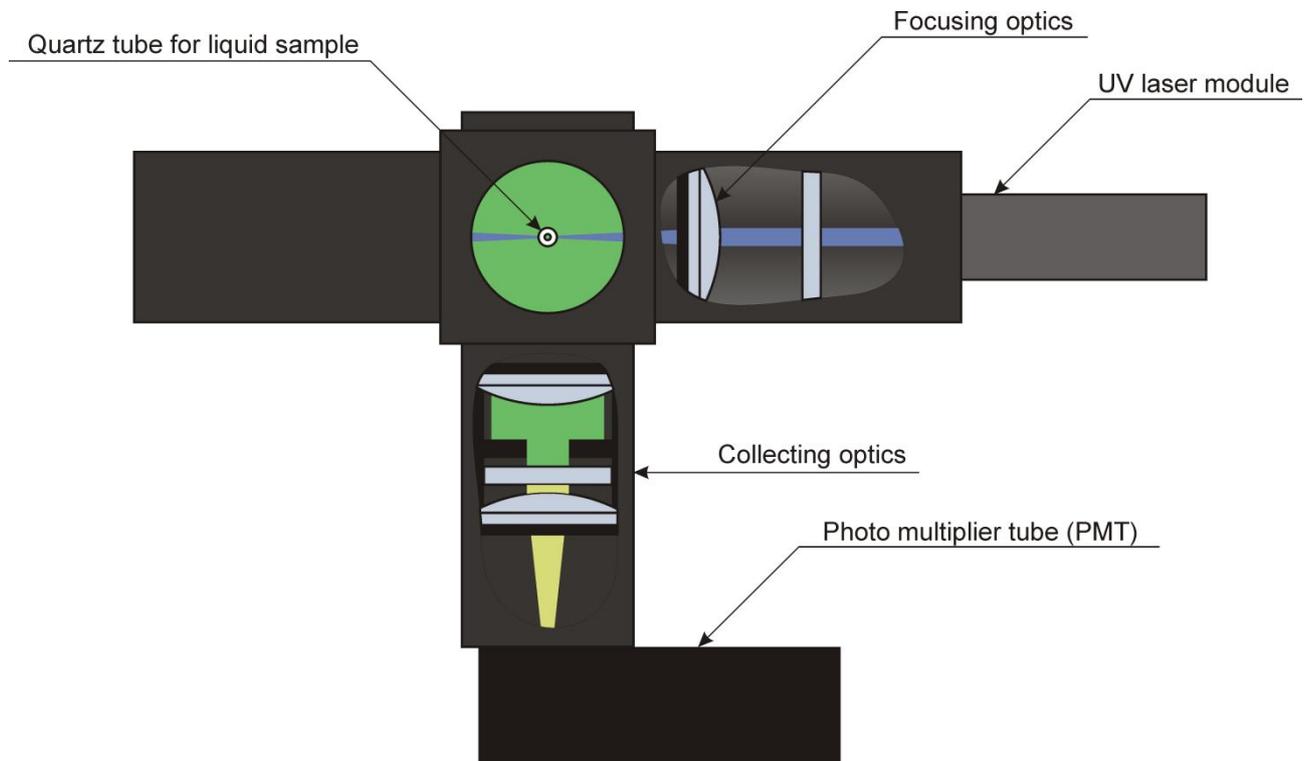


Figure 5. Schematic view on the fluorescence unit

Prototype performance

The particle into liquid collection efficiency depends heavily on the performance of the growth system. Since the growth conditions are not fully homogeneous due to the temperature and water concentration profiles in the growth region, the particles grow at different rates. This results to differences in the particle size after the growth. For the best performance it is important to have as many particles as possible to grow to a size that is collected by the cyclone, but at the same time limit the growth so that the maximum size is low enough to avoid inertial losses in the system. It turned out that the window for the optimal growth conditions is really narrow. With the parameters listed in the table 1, particle collection efficiency to the cyclone is above 90 % for particle number concentrations up to $1e5 \text{ 1/cm}^3$

The overall performance of the system in the oxidative potential measurement depends on the particle into liquid collection efficiency, the fluorescence detection efficiency and the efficiency of the probe used. The detection efficiency of the fluorescence unit depends on the optical background in the system. While the background level was managed to keep relatively low, thanks to the high quality filters used, the background from the unreacted probe is relatively high. The background level depends on the age,

temperature and pH of the probe, but is typically in the order of 10 % of the measurement range. This limits the system overall performance significantly.

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