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Sensitive photonic system to measure oxidative potential of airborne nanoparticles and ROS levels in exhaled air

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Abstract

A photonic system has been developed that enables sensitive quantitative determination of reactive oxygen species (ROS) – mainly hydrogen peroxide (H_2O_2) – in aerosol samples such as airborne nanoparticles and exhaled air from patients. The detection principle relies on the amplification of the absorbance under multiple scattering conditions due to optical path lengthening [1,2]. In this study, the presence of cellulose membrane that acts as random medium into the glass optical cell considerably improved the sensitivity of the detection based on colorimetric FOX assay (FeII / orange xylenol). Despite the loss of assay volume (cellulose occupies 75% of cell volume) the limit of detection is enhanced by one order of magnitude reaching the value of 9 nM (H_2O_2 equivalents). Spectral analysis is performed automatically with a periodicity of 5 to 15 s, giving rise to real-time ROS measurements. Moreover, the elution of air sample into the collection chamber via a micro-diffuser (impinger) enables quantitative determination of ROS contained in or generated from airborne samples. As proof-of-concept the photonic ROS detection system was used in the determination of both ROS generated from traffic pollution and ROS contained in the exhaled breath as lung inflammation biomarkers.

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Keywords: Oxidative potential; nanoparticle; oxidative stress; ROS; chemical sensor; photonic device; real-time detection

1. Introduction

Of the unintentional routes of human exposure to particulates, chemicals or mineral fibers, inhalation is considered the most significant. The lungs are an efficient entry portal for a variety of gaseous and aerosol-

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transported molecules, providing a large surface area and thin epithelial barrier, in addition to extensive vasculature. Inhalation of nanoparticles has already been documented to induce oxidative stress associated with the development of a plethora of pulmonary and cardiovascular diseases. More generally, the link between exogenous ROS generation and intracellular oxidative stress has been well identified in the context of NPs exposure [3]. In other words, the potency of a given NP to produce ROS – namely its ROS-generation capacity – can be seen as a predictive indicator of its potential to generate oxidative stress on cells.

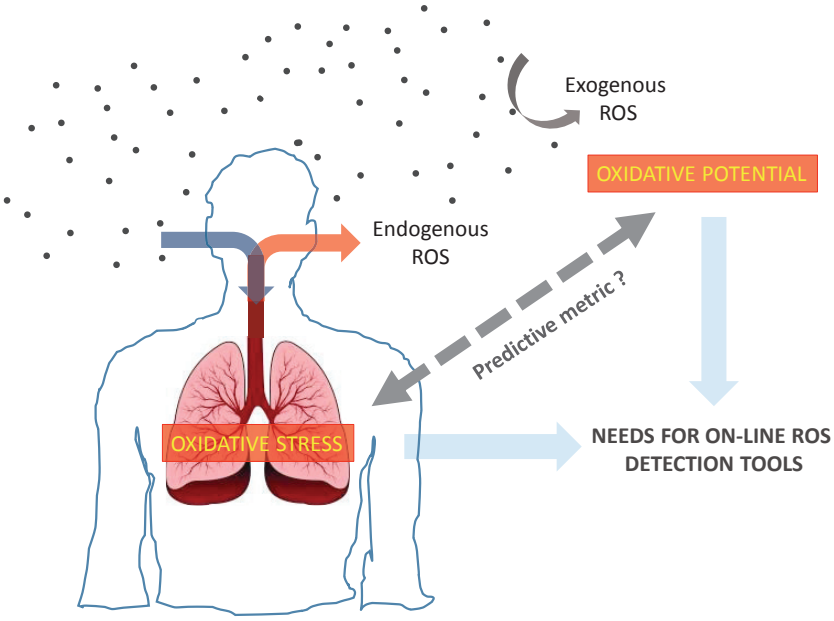

Figure 1: Schematic illustration of airborne ROS context : catalytic behavoir of NP can lead to the generation of exogenous ROS that, in turn, can licit oxidative stress and endogenous ROS formation.

2. ROS Detection strategy

The sensing cell was made of a glass tube (3 mm id) filled with scattering random medium such as glass fibres or cellulose membrane – as absorbance enhancers – and coated with a reflective Mylard film to further lengthen the optical path inside the cell. ROS detection principle relied on a colorimetric assay – namely FOX – based on the oxidation of Fe(II) into Fe(III) by ROS and the subsequent formation of a colorimetric complex with orange xylenol, OX-Fe(III) that strongly absorbs at 580 nm. Moreover, the addition of sorbitol in the assay solution results in a recycling of H2O2 and an increased sensitivity of the assay [4]. The optical chamber holds the optical fibres that ensure the illumination of the sensing cell and the analysis of the outcoming light via a miniature spectrometer (Thorlabs CCS100). An air sampling membrane pump and a compact peristaltic pump operate the impinger (aspiration mode) and drive the assay solution in closed loop through the sensing cell, respectively (Fig. 2). Spectral data are treated via developed software that calculates the normalized oxidative coefficient and its variation with time (periodicity from 5 to 15 s).

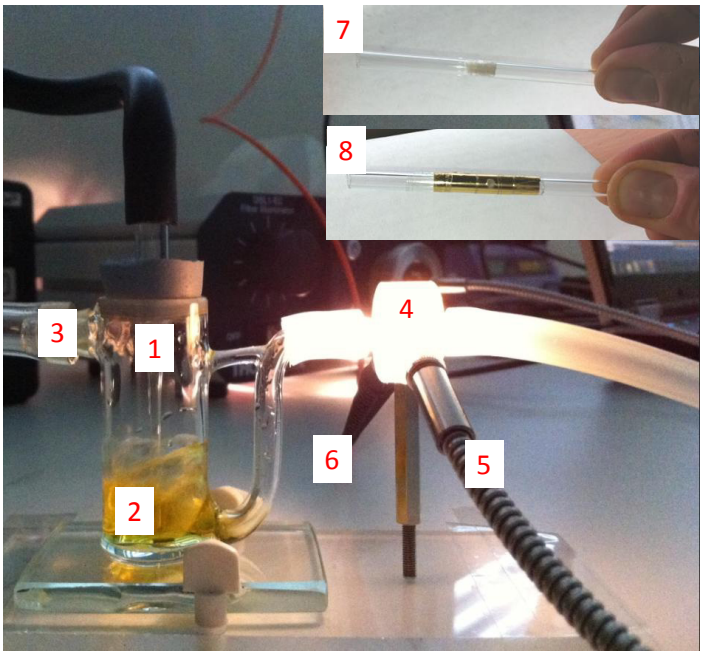

Figure 2: Airborne ROS photonic detection system that comprises of : 1) diffuser for air sample elution into assay ; 2) colorimetric FOX assay based on formation of colored Fe(III)-xylenol orange (absorption peak 580 nm) ; 3) connection to pump (aspiration) ; 4) optics holder in which the sensing cell is inserted ; 5) Light source ; 6) light output connected to miniature spectrometer ; 7) photonic cell made of glass tube filled with cellulose membrane (random medium) ; 8) and coated with reflecting material (Mylard).

3. Characterization

In order to characterize the efficiency of the multiple scattering approach calibration curves were established to estimate the optical gain resulting from the addition of glass fibers or cellulose membrane in the sensing cell tube. The calculated limit-of-detection obtained for the beer-lambert configuration (no random medium) – already low with 120 nM H_2O_2 – was further decreased to 50 and 9 nM after filling the sensing tube with glass fibres or cellulose membrane, respectively. It is worthily to notice that those effective sensitivity gains do not take into consideration the fact that the volume of assay present in the sensing cell – that is the number of molecules – only represents 25 % of the geometrical volume of the cell in the case of Beer-Lambert configuration. In other words, the optical gain seen as the efficiency of the multiple scattering to enhance absorbance measurements due to light path elongation versus Beer-Lambert situation is more than 40-folds when cellulose membrane acts as random medium in the sensing cell. In order to get dynamic information on [H_2O_2] evolution in time, the raw signal – normalized oxidative potential vs. time – is smoothed via multiple moving average approach and derivative is calculated. This data treatment enables time-resolution of the H_2O_2 concentration as shown in Fig. 3C) that can be a crucial requirement for many applications for which cumulative values are not sufficient for interpretation.

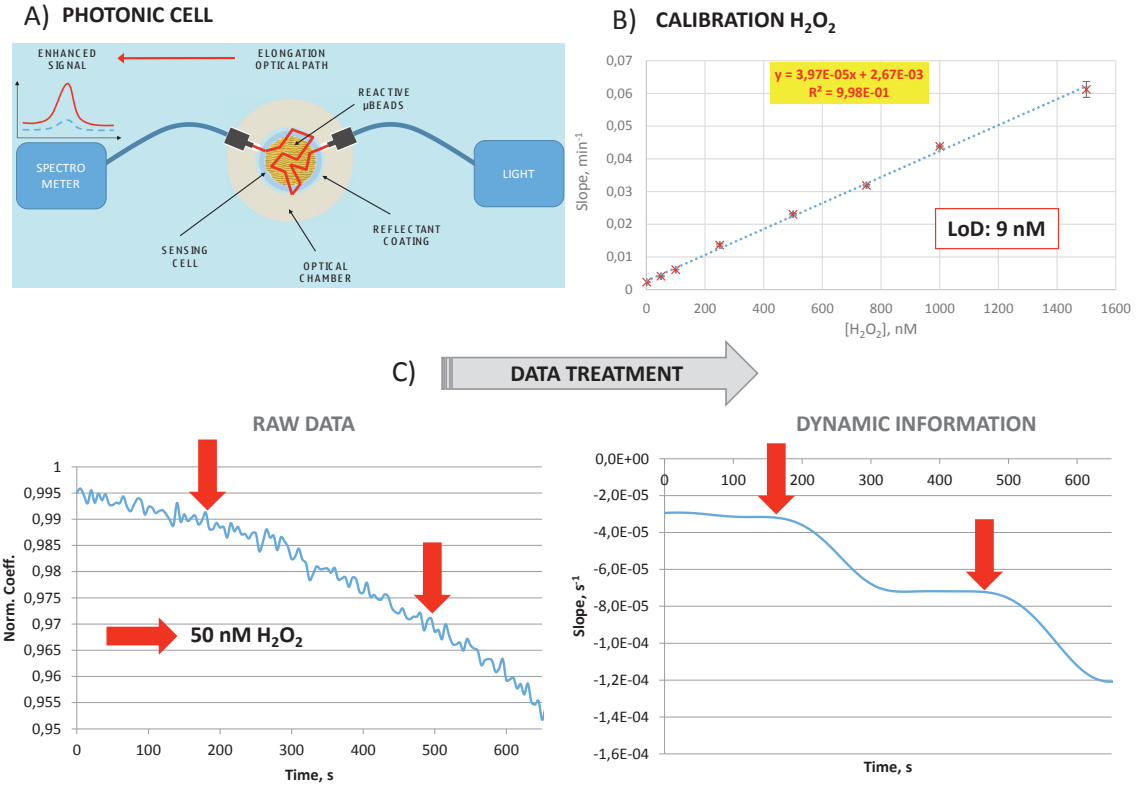

Figure 3: A) Schematic drawing of the optical path elongation occurring when light propagates through the cellulose membrane in the photonic cell. B) Calibration curve obtained with the developed ROS detection device in which the velocity of the Fe(III)-XO complex formation increases linearly with $[H_2O_2]$ present in the reaction chamber. C) Normalized coefficients calculated from raw spectra are treated via a smoothing function in order to generate the derivative which can directly be converted into $[H_2O_2]$ as a function of time.

4. Measurements

However, for proof-of-concept the photonic detection system was applied in the quantification of exogenous ROS originating from diesel engine combustion in urban environment with on-site air sampling using standard Tedlar bag approach. In this case, Tedlar air collection bags were filled (Vol: 5L; flow rate: 1L min^{-1}) either inside the Institute for Work and Health building or outside in the front of emergency department at Lausanne Hospital, nearby a road. Straight after collection, the air samples were eluted into 2 mL of H_2O mmQ via the impinger for analysis in the developed photonic system. For each situation, the time-evolution of the calculated normalized oxidative coefficient was measured for 5 min and the corresponding slope value enabled quantitative H_2O_2 analysis. As shown in Fig. 4A) the average slope corresponding to outdoor sample is almost twice the value obtained for air sample collected inside the Institute building. Moreover, the number concentration of nanoparticles were determined in parallel to air bag sampling using portable device (DISCmini; MatterAerosol). Not surprisingly the number concentration of nanoparticles was below the value of 1.10^3 in indoor situation while it reached a peak of 7.10^5 at the proximity of the road.

In another application the photonic detection system was used to evaluate the oxidative potential of human breath samples collected on healthy non-smoker volunteers. The collected exhaled air (10 L) was eluted into 2 mL of H_2O mmQ and analyzed with the detection system. The results summarized in Fig. 4B) show that for those two volunteers P1 and P2 the ROS level seems to be lower than in control air. A possible explanation could be due to the presence of antioxidants in exhaled air [5,6]. For sure, those preliminary results have to be considerably implemented via studies involving a significant number of smoker and non-smoker volunteers in order to evaluate the capability of the developed detection device to identify chronic lung inflammation. Furthermore, real-time ROS detection experiments are currently being carried out for H_2O_2 dynamic quantification at the workplace.

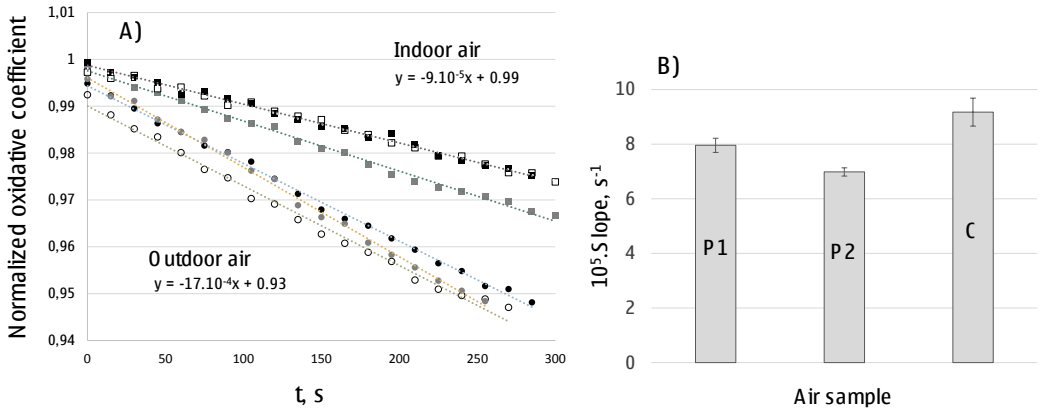

Figure 4: A) Time-evolution of normalized oxidative coefficient corresponding to exogenous ROS generated by ultrafine particles originated from traffic pollution. Samples collected in IST building (indoor; n=3) and close to the road (outdoor; n=3). The average calculated slopes are linearly linked to $[H_2O_2]$ via the calibration curve. B) Calculated slopes corresponding to the time-evolution of the normalized oxidative coefficient for exhaled air samples (n=3) collected on healthy volunteers (P1 and P2) and the ambient air as control (C).

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