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Intrinsic hydroxyl radical generation measurements directly from sampled filters as a metric for the oxidative potential of ambient particulate matter

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ABSTRACT

The reactive oxygen species (ROS) generation capacity of ambient particulate matter (PM) represents a promising predictor for particle induced adverse health effects. An intrinsic method to determine ROS generation, adaptable for environmental monitoring is introduced here. The approach is based on the aligned electron paramagnetic resonance spectroscopy technique with 5.5-dimethyl-1-pyrroline-N-oxide (DMPO) as spin trap and hydrogen peroxide as substrate and is specifically sensitive to Fenton-type reaction mediated generation of hydroxyl radicals. Previous studies demonstrated the usefulness of this method to screen ambient PM samples collected on Polytetrafluoroethylene and cellulose filters after their suspension in deionised water. We demonstrate the suitability of direct measurements on quartz fibre filters, which are commonly used for routine environmental monitoring of PM, by revealing coefficients of variances $<12\%$ in duplicate analysis. Direct incubation of the filter with DMPO shortened the analysis time to about 15 min per sample avoiding complicated extraction procedures. Among the various possible positive controls copper sulphate and BCR 723 Road Dust were found to be the most suitable materials to enable intra- and inter-laboratory comparability as well as to ensure reproducibility of the measurements by revealing coefficients of variances $<8\%$ and $\leq 5\%$, respectively.

1. Introduction

The interest in the measurement of reactive oxygen species (ROS) generation by particles increased over the last decade, because toxicological studies demonstrated a link between particles induced ROS formation and different adverse health effects (Donaldson et al., 2003; Schins et al., 2004). As a result, ROS are considered currently to play a major role in adverse health effects induced by ambient air particles and to be a promising health relevant metric, in addition to the commonly

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used mass based metric (Borm et al., 2007). The evaluation of ambient mass concentrations of particulate matter (PM) involves weighing of glass or quartz fibre filters prior and after sampling at defined conditions (EU Directive 2008/50/EC, 2008). Using a combination of hydrogen peroxide (H_2O_2) and spin trap based electron paramagnetic resonance (EPR) technique, Shi et al. (2003) demonstrated the applicability of ambient PM induced ROS detection method collected on Polytetrafluoroethylene (PTFE) and cellulose filters. Several other methods to assess the oxidative properties of ambient PM have been proposed (Ayres et al., 2008) and most if not all of these have substantial limitations for application in a routine monitoring network. Toxicological investigations have demonstrated clear associations between the intrinsic ROS generation of PM and an increase of inflammatory markers or oxidative DNA damage (Schaumann et al., 2004; Shi et al., 2006; Wessels et al., 2010). In the current study an adaptation of the original method was investigated in order to show a more general applicability of this EPR method, e.g. for commonly used quartz fibre filters. PTFE filters are not commonly used in Europe due to their high costs, the high pressure drop and difficulty in handling. Hence tests were focused on quartz fibre filters being frequently used for mass concentration measurements and subsequent chemical analysis, especially for elemental and organic carbon analysis. Investigations were extended to test the potential of the analytical method for standardised ambient air quality monitoring and to determine its reproducibility. The normalisation to a standard or reference is crucial for data comparability and hence for the use of this metric for monitoring ambient air quality. Not only inter-laboratory, but also intra-laboratory variances caused by slightly different basic raw material, (im)purities or sample preparation and handling, as well as instrument sensitivity differences may lead to daily variances. No official reference materials for the applied EPR method are available yet. In this study, three different materials were identified as candidate reference and normalisation materials: (1) copper sulphate ($CuSO_4$) solution – a well known Fenton like reaction triggering transition metal, (2) Road Dust BCR 723 (Certified Standard Material for inorganic metal analysis, Zischka et al., 2002) and (3) Tempol (4-hydroxy-2.2.6.6-tetra-methylpiperidinyloxy) – a common used paramagnetic spin probe.

2. Materials and methods

2.1. Materials

DMPO (5.5-dimethyl-pyrrolineN-oxide) and Tempol (4-hydroxy-2.2.6.6-tetramethyl-piperidinyloxy) were purchased from Enzo Life Sciences (Lörrach, Germany). All other reagents, such as H_2O_2, $Cu(II)SO_4$, $Ni(II)SO_4$, $Fe(II)SO_4$, $Fe(III)SO_4$ and the BCR 723 Road Dust (all solid) were purchased from Sigma-Aldrich (Munich, Germany). The solutions of DMPO and H_2O_2 were prepared and used in a chloride and calcium free phosphate Buffer (PBS, Sigma-Aldrich).

2.2. Methods

PM2.5 samples were collected on filters at an urban background station ($n=5$) in Rotterdam and near a motorway ($n=10$) in Amsterdam (Netherlands) for 15 days (Yang et al., 2014). At each location, PTFE (37 mm diameter, 2 μm pore size, PVC support ring, Pall Corp., NY, USA) and quartz fibre filters (37 mm diameter, QMA, Whatman – GE Healthcare Biosciences Corp.) in duplicates (2 × PTFE = 1 duplicate and 2 × quartz = 1 duplicate) were collected parallel with a Harvard impactor (Air Diagnostics and Engineering Inc., Naples, Maine, USA) operating at 10 L/min flow. In sum 30, quartz and 30 PTFE filters in duplicate at the same 15 days were sampled.

Additionally, PM10 samples, at an urban background ($n=3$) location in Muelheim-Styrum (Germany), and PM10 samples ($n=2$) at a motorway near Meckenheim (Germany), were collected on large quartz fibre filters (⌀ 150 mm, Whatman GmbH) using a high volume sampler (700 L/min, Digitel DHA80, Switzerland) (Beuck et al., 2011; Quass et al., 2008). The mass of the filters was determined by the weighing procedure after equilibration in accordance with the European standard (DIN EN 12341: 1998).

The hydroxyl radical ($OH^{\bullet}$) generation capacity of the sampled PM were measured by using the EPR-technique based on the method by Shi et al. (2003). However the method was slightly changed by skipping the filtering step prior EPR analysis and avoiding resuspension preparation when using quartz fibre filters. In consequence two approaches, an “original” and an “adapted” approach, described as following were applied (shown in Fig. 1).

The method, here named as “original” approach, briefly summarised: the PTFE filters (⌀ 47 mm) on which the PM were collected are placed in deionised water (dH_2O) and the PM resuspended by three preparation steps. In the first step, the samples are shaken by hand for five minutes, followed by sonication for further five minutes in a sonication water bath (Bandelin Sonorex RK-52, 60/120 kW, 35 kHz). Finally, the samples are vortexed (IKA LabDancer, 2800 rpm) again for five minutes. The prepared PM suspensions are then mixed with the ingredients and incubated prior to EPR analysis (Fig. 1, original approach). In the present study, the “original” method was also tested for its applicability for quartz fibre filter. Furthermore an “adapted” approach avoiding a separate resuspension preparation step was tested (Fig. 1, adapted approach).

The principle of ROS detection is here in all cases based on the trapping of PM elicited $OH^{\bullet}$, which is mainly generated via Fenton-type reaction in presence of H_2O_2. Especially transition metals are sensitive to H_2O_2 oxidation, generating $OH^{\bullet}$ that transform DMPO into a DMPO-OH adduct for which the first derivative of its absorption signal results in a typical quartet EPR spectrum as shown in Fig. 1. The suspension preparation procedure used in the “original” approach showed already visually high amounts of fibres after the sonication of the quartz fibre filters. The energy input by sonication destroys the