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Technical note

An improved method for the quantification of SOA bound peroxides

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ABSTRACT

An improvement is made to a method for the quantification of SOA-bound peroxides. The procedure is based on an iodometric-spectrophotometric method that has been commonly used for the determination of peroxides in a wide range of biological and environmental samples. The improved method was applied to determine the peroxide content of laboratory-generated SOA from α-pinene ozonolysis. Besides main improvements for the detection conditions, the use of more environmentally sound solvents is considered instead of carcinogenic solvents. In addition to the improved method for peroxide determination, the present study provides evidence for artefact formation caused by ultrasonic agitation for the extraction of organic compounds in SOA filter samples. The concentration of SOA-bound peroxides in the extracts from ultrasonic agitation were up to three times higher than those from a laboratory orbital shaker under the same extraction conditions, indicating peroxide formation caused by acoustic cavitation during extraction. In contrast, pinic acid, terebic acid and terpenylic acid showed significantly lower concentrations in the sample extract prepared using ultrasonic agitation, indicating that these compounds react with OH radicals that are formed from acoustic cavitation. Great care should be taken when extracting SOA samples and the use of ultrasound should be avoided.

1. Introduction

HO_2 and organic peroxy radicals are important products in the oxidation of volatile organic compounds (VOCs). The ozonolysis of alkenes is one of the major sources for peroxy radicals in nighttime (Simonaitis et al., 1991) and daytime chemistry. In the absence of NO, the fates of peroxy radicals are largely controlled by HO_2–HO_2, HO_2–RO_2 and RO_2–RO_2 radical recombination reactions (Atkinson, 2000). The HO_2–HO_2 reaction in the presence of water leads to the formation of hydrogen peroxide, and the HO_2–RO_2 reactions yield organic hydroperoxides. In addition, photochemical reactions in atmospheric aqueous phase can be an important source of hydrogen peroxide (Faust et al., 1993). These hydroperoxides are highly reactive, and known to play an important role in atmospheric chemistry such as the oxidation of SO_2 to H_2SO_4 in atmospheric aqueous droplets (Penkett et al., 1979). So far the impact of atmospheric peroxides on human health is not well understood but an excess of particle-bound reactive organic species (ROS) is suggested to cause oxidative stress that influences human morbidity and mortality (Ayres et al., 2008). Furthermore, peroxides are suggested to account for a significant fraction of laboratory-generated secondary organic aerosol (SOA) (Docherty et al., 2005). It has been proposed that heterogeneous reactions of hydroperoxides and aldehydes can form higher molecular weight (HMW) compounds such as peroxyhemiacetals in SOA (Tobias and Ziemann, 2000). Recent results from smog chamber experiments have shown that peroxides account for up to 85% of the SOA mass produced from β-pinene ozonolysis and 47% from α-pinene ozonolysis (Docherty et al., 2005). There are a number of methods available to detect peroxides including fluorescence (e.g. Lazarus et al., 1985), chemiluminescence (e.g. Kok et al., 1978), electrochemical (e.g. Sanchez et al., 1990) and spectrophotometric (e.g. Kieber and Helz, 1986) detection. Among those, an iodometric-spectrophotometric method has been commonly used to quantify SOA-bound peroxides (Docherty et al., 2005; Nguyen et al., 2010; Mertes et al., 2012). This method is based on the reaction of the peroxide with iodide (I^-) to form I_2 molecules that react further producing triiodide (I_3^-). The absorbance of I_3^- can be measured at $\lambda = 351$ nm with an extinction coefficient $\varepsilon = 26{,}400$ L mol^{-1} cm^{-1} (Awtrey and Connic, 1951). This wavelength is chosen because this corresponds to the highest absorption for I_3^- and the lowest for I_2 whereas the extinction coefficients of both I_2 ($\varepsilon = 745$ L mol^{-1} cm^{-1}) and I_3^- ($\varepsilon = 975$ L mol^{-1} cm^{-1}) at $\lambda = 460$ nm used by Docherty et al. (2005) are much lower than that of I_3^- at $\lambda = 351$ nm. Within the present study, the iodometric method for SOA-bound peroxide determination was improved.

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First, a two-phase solvent was replaced by a less toxic and non-carcinogenic one-phase solvent system. Second, the method uses an orbital shaker instead of ultrasonic agitation to avoid artefact formation from acoustic cavitation. Consequently, the modified method presented in this study is simpler and more reproducible than the previously used method.

2. Experimental

2.1. Chemicals and standards

Hydrogen peroxide (30% in water), sulphuric acid (98%), potassium iodide (≥99.5% purity) were obtained from Merck (Darmstadt, Germany) and acetic acid from Fluka (puriss, eluent additive for LC–MS, St. Louis, USA). Terebic acid, pinic acid and pinonic acid are purchased from Sigma–Aldrich (St. Louis, USA). Synthesised standards were available for terpenylic acid (Claeys et al., 2009), 3-methyl-1,2,3-butanetricarboxylic acid (Szmigielski et al., 2007) and diaterpenylic acid acetate (Iinuma et al., 2009). Methanol for chromatographic separation was obtained from Fluka (Chromasolv LC-MS). Ultrapure water was used for the filter extraction (Milli-Q gradient A 10, 18.2 MΩ cm^{-2}, 3 ppb TOC, Millipore, USA).

2.2. Chamber experiments

α-Pinene ozonolysis SOA was generated using the 19 m^3 PTFE smog chamber of IfT Leipzig (LEAK). The conditions used for chamber experiments are summarised in Table 1. Carbon monoxide (CO) was used as an OH scavenger. A detailed description of the smog chamber can be found elsewhere (Iinuma et al., 2009).

After 2 h reaction time 1.8 m^3 of chamber air was sampled using a denuder-filter-device (Kahnt et al., 2011). A DNPH (2,4-dinitrophenylhydrazine) coated denuder (5 channel, 400 mm length, URG, Chapel Hill, USA) was used to avoid positive sampling artefact on the PTFE-filter (47 mm diameter, PALLFEX T60A20, Pall, NY, USA). The samples were stored in a freezer (−22 °C) until analysis.

2.3. Sample preparation

One quarter of the filter was used for the peroxide test and another quarter was used to determine the blank value. Each quarter was cut into small pieces and extracted with 3 mL ultrapure water using either an orbital shaker (700 rpm) or ultrasonic agitation for 15 min. Insoluble materials were removed using a syringe filter (Teflon, 0.2 μm pore size, Acrodisc, Pall). The resulting extract was acidified with acetic acid to pH 3. Afterwards the extract was sparged with nitrogen for 5 min to remove oxygen. During the degassing procedure, potassium iodide (KI, 30 mg, 0.18 mmol) was added to the extract, capped directly and slightly pressurized with nitrogen. For the filter blank value determination, no KI was added to the filter extract. After 1 h of reaction the absorption was measured with a UV/VIS spectrophotometer at $\lambda = 351$ nm. The peroxide content was calculated using a series of H_2O_2 solutions ranging from 0.75 to 25 μM. The H_2O_2 stock solution was prepared freshly at the beginning of each analytical day. Another quarter filter was cut into small pieces and extracted in 500 μL methanol using either ultrasonic agitation or an orbital shaker for 15 min. The extract was filtered through a syringe filter and the filter residue was extracted again with 500 μL MeOH. The extract was dried under a gentle stream of nitrogen and reconstituted in 250 μL CH_3OH/H_2O (50/50, v/v).

2.4. Instrumentation

The UV–VIS spectra were measured with a Lambda 900 UV/VIS spectrometer (Perkin Elmer, Waltham, USA). The data were recorded from $\lambda = 200$ to 600 nm in 1 cm path length disposable cuvettes (Brand, Wertheim, Germany).

The filter extracts were analysed using a 1100 Series HPLC system (Agilent Technologies, Santa Clara, USA) connected to an electrospray ionisation time-of-flight mass spectrometer ((-)ESI-TOFMS, Bruker Daltonics, Bremen, Germany). The separation was carried out on an Agilent ZORBAX C18 column (3.0 × 150 mm, 5 μm particle size). The eluent composition was (A) 0.1% acetic acid in ultrapure water and (B) methanol with the following gradient: 10% B for 2 min, increased from 10% B to 100% B in 20 min, held constant for 3 min and re-equilibrated for 5 min.

3. Results

3.1. Improvement of the method

The method described by Docherty et al. (2005) was evaluated using a series of H_2O_2 standard solutions and α-pinene ozonolysis SOA samples. For the determination of SOA-bound peroxides it was approximated that the water-soluble peroxide fraction accounts for the whole peroxide content. This is consistent with the results reported by Nguyen et al. (2010). Since the target analytes were water-soluble, the extraction solvent (ethyl acetate) was substituted with ultrapure water to avoid side reactions during the extraction. Furthermore, the solvent based reaction mixture described by Docherty et al. (2005) (acetic acid-chloroform-water (0.53:0.27:0.20)) was substituted by ultrapure water to improve the handling of the samples and to avoid a carcinogenic constituent (chloroform). In addition, this avoids streak formation from the different refractive indices of chloroform, water and ethyl acetate that can interfere with the absorption.

Parameters that influence the quantification of SOA-bound peroxides were varied to optimise reaction conditions. This includes the pH value, potassium iodide concentration, degassing duration, and reaction time. The exact conditions used for evaluation are summarised in Table 2. The extraction efficiency and reproducibility were determined for the optimised method ($n = 3$).

The influences of the pH values and added amounts of KI are shown in Fig. 1. The pH value was varied from pH = 1 to pH = 7, adjusted using sulphuric acid, acetic acid and sodium hydroxide depending on the desired pH value. Reproducible results were obtained for all pH values, especially at lower pH values. The hydroperoxide concentration was significantly underestimated at pH 5 and no absorption maximum was observed in the UV/VIS spectrum at pH 7. This can be explained by the slow reaction of peroxides with KI under neutral to mildly acidic conditions that is caused by the pH-dependency of the oxidation potential of H_2O_2

Table 1
Reaction conditions for the ozonolysis of α-pinene.

Set	HC_{ini} [ppb]	O_{3ini} [ppb]	CO_{ini} [ppm]	Relative humidity [%]	Temperature [°C]	ΔHC [ppb]	No. of repetition
1	60	35	105	0	20 ± 1	20 ± 1	2
2	60	35	105	50	20 ± 1	20 ± 1	1
3	60	35	105	75	20 ± 1	20 ± 1	1