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Determination of Total Peroxide Content in Secondary Organic Aerosol Particles

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Determination of total peroxide content in secondary organic aerosol particles

Abstract

Secondary organic aerosol particles (SOA) formed from the oxidation of monoterpenes can impact the Earth's radiation balance, act as cloud condensation nuclei and negatively affect human health. In the initial Visiting Faculty Program application, we proposed the use of an ultraviolet-visible spectrometer equipped with a liquid waveguide capillary flow cell to determine the extent to which SOA absorb visible light. The inclusion of Concordia University in the Secondary Organic Aerosol From Forest Emissions Experiment (SOAFFEE) laboratory campaign at PNNL necessitated a change in the proposed experiments. An iodometric-spectrophotometric (IS) technique was developed to quantify the total peroxide content in SOA. The experimental technique was validated by measuring the peroxide content in commercially available products. After the validation of the experimental technique, the total peroxide content of SOA formed from a variety of experimental conditions was quantified. It was found that the amount of peroxides in the SOA generated at PNNL was similar to that found in previous research studies. The research carried out at PNNL will be included in an undergraduate senior thesis at Concordia University - Portland (CU). It is also expected that the research will be included in peer-reviewed journal articles. It is our hope that the success of our work will result in future collaborations between PNNL and CU.

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1. Introduction - Background and Research Objectives

Monoterpenes, such as α−pinene and Δ-carene, are a class of hydrocarbons that are emitted into the atmosphere in the gas phase from vegetation. It is estimated that monoterpene emissions account for approximately 10% of the global biogenic hydrocarbon budget. Furthermore, their emissions are approximately equal to hydrocarbon emissions from anthropogenic sources [1,2]. In the atmosphere monoterpenes can react with other species such as ozone and hydroxyl radicals. The products from the gas phase oxidation of monoterpenes can be low in volatility. If the vapor pressure of the products is low enough, compounds can be transferred from the gas phase to the particle phase. These particles are termed secondary organic aerosol particles (SOA).

SOA can impact the atmosphere in several different ways. Lambe et al. [3] studied the relationship between the level of oxidation and the optical properties of different types of SOA. The various types of SOA were created in a flow reactor by the OH oxidation of gas phase precursors mimicking anthropogenic (naphthalene and tricyclodecane), biomass burning (guaiacol) and biogenic (α-pinene) volatile organic compounds (VOC). It was found that the SOA created in the Lambe et al. [3] study could contribute significantly to the amount of light absorbing brown carbon in the atmosphere. Therefore, climate models that do not include the influence of SOA in their calculations could be drastically underestimating their warming potential.

A second way SOA can impact the atmosphere is regional air quality. Because SOA particles are relatively small (diameter <2.5 μm), they can have profound effects on human health. Studies have found relationships between the amount of fine particle mass in the atmosphere and increased human morbidity and mortality [4]. When monoterpenes are oxidized in the atmosphere a multitude of organic compounds (e.g., aldehydes, ketones, carboxylic acids and alcohols) can partition from the gas phase to the particle phase. Additionally, organic hydroperoxides are expected to make a significant contribution to SOA mass [5]. Organic hydroperoxides are highly reactive and thus could play a major role in the effects on human health [6].

During the summer of 2015, the Secondary Organic Aerosol From Forest Emissions Experiment (SOAFFEE) laboratory campaign took place at the Pacific Northwest National Laboratory (PNNL). Researchers from several different universities and national laboratories travelled to PNNL to conduct experiments with SOA created and collected in Dr. John Shilling's aerosol chamber. We were given the task of quantifying total peroxide content of the SOA. It is this task that gives rise to the study conducted for the VFP appointment.

In the summer of 2014, Dr. Matthew Wise (Associate Professor of Chemistry, Co-PI) and two undergraduate chemistry students at Concordia University – Portland (CU) worked with Dr. Shilling to determine the optical properties of SOA produced in his lab at PNNL. The research was conducted over a period of ten weeks and was funded by the VFP at PNNL. The experiments proposed for the 2015 VFP were intended to extend the work Dr. Shilling and Dr. Wise started in 2014. At the time the 2015 VFP proposal was written, the details of the SOAFFEE laboratory campaign were not available. Once our inclusion in the SOAFFEE study was confirmed, the deliverables had to be modified. The new deliverables for the 2015 VFP are:
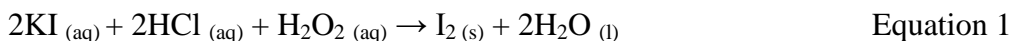
1) the optimization of an iodometric-spectrophotometric (IS) technique to quantify total peroxide content in aqueous solutions
2) determination of the total peroxide content in SOA created during the SOAFFEE laboratory campaign

2. Progress: Scientific Approach, Impacts and Accomplishments

2.1 Development of the IS procedure to detect peroxides in SOA particles

The experiments carried out during the VFP at PNNL utilized an UV/Vis spectrometer and a 100-cm liquid waveguide capillary flow cell (LWCC) to determine total peroxide content of SOA particles. Because this type of experiment was not previously performed at PNNL, the experimental procedure was developed and validated using aqueous hydrogen peroxide solutions.

The experimental procedure and setup were modified from Mertes et al. [7]. Chemical compounds containing peroxides do not absorb in the UV/Vis portion of the electromagnetic spectrum. Therefore, the IS technique was used to quantify total peroxide content. Equations 1 and 2 are the chemical reactions that take place during the IS procedure (when the identity of the peroxide is hydrogen peroxide).

$$2KI_{(aq)} + 2HCl_{(aq)} + H_2O_{2\,(aq)} \rightarrow I_{2\,(s)} + 2H_2O_{(l)} \qquad \text{Equation 1}$$

$$I_{2\,(s)} + KI_{(aq)} \rightarrow KI_{3\,(aq)} \qquad \text{Equation 2}$$

In these reactions, the colorless reactants are converted into solid molecular iodine which subsequently forms yellow colored triiodide ions (I_3^-) in solution. The absorbance at 470 nm due to the triiodide ions (subtracted from the baseline absorbance of the solution at 540 nm) was used to quantify hydrogen peroxide concentration.

Molecular oxygen reacts with aqueous potassium iodide in the same way as hydrogen peroxide. Therefore, the reaction must take place in an oxygen-free environment. The experimental setup used to maintain an oxygen-free environment during the reaction is schematically shown in Figure 1. A cylinder of pre-purified nitrogen gas was connected to ¼ inch stainless steel tubing. Three "purging" stations were connected to the stainless steel tubing using stainless steel T-fittings. Prior to each T-fitting, a valve (represented by black circles in Figure 1) was placed to control the flow of nitrogen to each purging station.
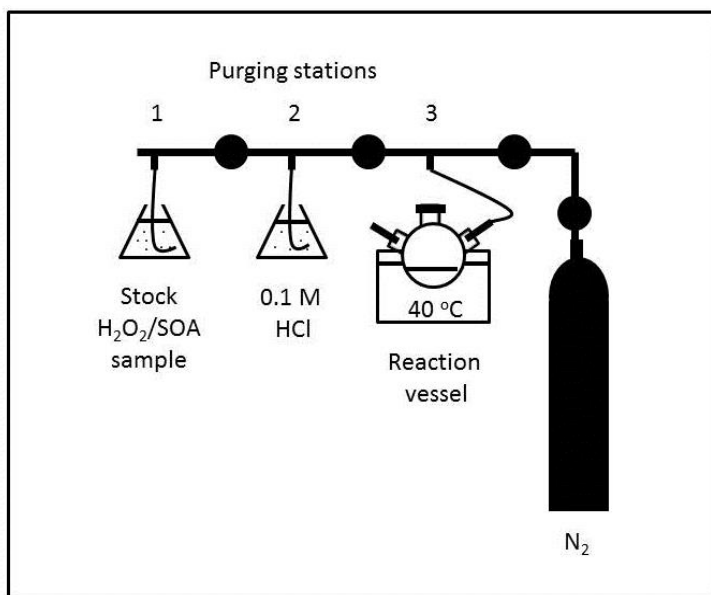
Two ¼ inch teflon tubes (with the

Figure 1. Experimental setup for the IS procedure.

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ends sealed) were attached to purging stations 1 and 2 and coiled into Erlenmeyer flasks containing a stock solution of ~176 µM hydrogen peroxide and 0.1 M hydrochloric acid respectively. Numerous small holes were punched into the submerged portion of the Teflon tubes so a steady stream of bubbles were created when the nitrogen was flowing. In this way, dissolved molecular oxygen was removed from each solution. The solutions were purged with nitrogen for 10 minutes before the IS reactions were initiated.

The IS reactions took place in a custom made 100-mL reaction vessel. The vessel consisted of a thick-walled glass bulb with three necks. Approximately 0.11 g of solid potassium iodide was placed in the reaction vessel through the middle neck. After the addition of the potassium iodide, the neck was sealed with a rubber septum. ¼ inch stainless steel tubes were coupled to the reaction vessel via vacuum compression fittings in the outer two necks. Purging station 3 was attached to the ¼ inch stainless steel tube in the right-hand neck of the reaction vessel using flexible stainless steel tubing and a vacuum fitting. The reaction vessel was placed in a 40 ^{o}C water bath and purged with a steady flow of nitrogen for 10 minutes.

After sufficient purging, approximately 10-mL of 0.1 M hydrochloric acid from station 2 was drawn into a gas-tight glass syringe and introduced into the reaction vessel via the left-hand neck. Depending on the final concentration of hydrogen peroxide desired, between 0.1 and 1.25-mL of hydrogen peroxide was transferred from station 1 to the reaction vessel. The left and right-hand necks of the reaction vessel were capped and the reaction was allowed to proceed for one hour.

Once the reaction time was completed, the solution in the reaction vessel was drawn up into a gas-tight glass syringe and injected into a 100-cm path length LWCC (World Precision Instruments model LWCC-3100). The absorbance of the solutions, at wavelengths ranging from 250-700 nm, was measured using a high resolution UV/Vis spectrometer (Ocean Optics, Inc. Jaz model UX-83500-20) coupled with a miniature Deuterium-Tungsten Halogen light source (Ocean Optics Inc. model DH-mini). The spectrum was saved and the difference in the absorbance at 470 nm and 542 nm was calculated.

The solid line in Figure 2 is the absorbance spectrum of a 15.62 µM hydrogen peroxide solution. As expected, the increase in absorbance at the shorter wavelengths of the spectrum was due to presence of the triiodide ions. For the 15.62 µM hydrogen peroxide sample, the difference in absorbance at 470 nm and 542 nm was 0.853. Figure 3 is the absorbance of various hydrogen peroxide solutions plotted as a function of concentration (1 to 20 µM), The linear least squares regression fit to the data yields a slope of
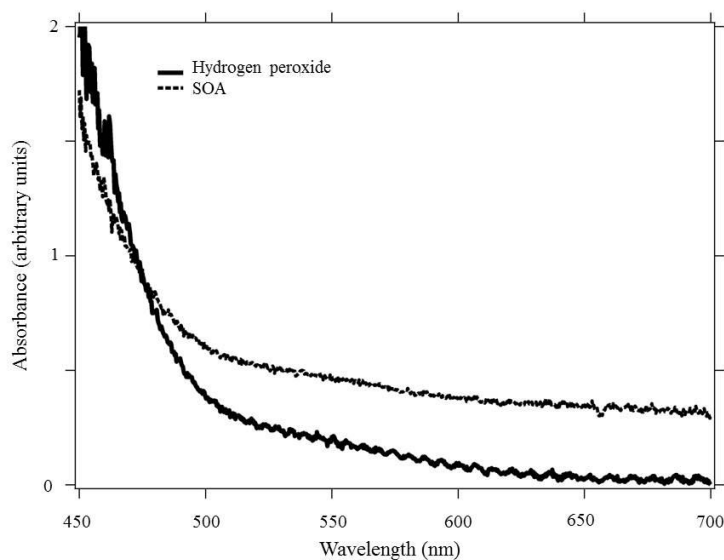

Figure 2. UV/Vis absorption spectrum of 15.62 µM hydrogen peroxide and SOA.

0.0389 ± 0.0020 and a y-intercept of 0.280 ± 0.022 (R^2 = 0.984). Because the data approximates a straight line very well, it can be used as a calibration curve to determine the concentration of an unknown hydrogen peroxide solution.

It was impossible to remove all the molecular oxygen in the samples using the purging technique. Furthermore, it was possible that there were impurities of iodine in the solid potassium iodide. Therefore when there was no hydrogen peroxide present a small absorbance at 470 nm

Figure 3. Hydrogen peroxide calibration curve.

existed. Measurements of solutions containing no hydrogen peroxide yielded a blank signal of 0.140 ± 0.051. Using this data, a limit of detection of 3.47 μM was calculated.

The slope of the calibration curve generated here agrees well with that determined by Mertes et al. [7] (0.0379 ± 0.0005). However, the calibration curve generated by Mertes et al. [7] had a y-intercept of 0.00581±0.0081. The presence of molecular oxygen and iodine in the potassium iodide are reasons why the calibration curves do not intersect the y-axis at the origin. Mertes et al. [7] performed their experiments in an air-tight PVC housing whereas the experiments performed here were not. Thus, it is not surprising that the Mertes et al. [7] calibration curve intersects the y-axis at a value closer to zero than the calibration curve in this study.

2.2 Determination of the peroxide content in commercially available products

Prior to experimentation with SOA particles, several commercial products were tested for total peroxide content using the procedure outlined in Section 2.1. The impetus for experimentation with these products was two-fold. First, it was important to validate the experimental procedure for solutions containing compounds other than hydrogen peroxide and water. Second, there was not enough mass to perform more than one peroxide measurement on the same SOA sample. Therefore the accuracy and precision of the procedure was determined by performing multiple measurements on products containing known amounts of peroxide.
The peroxide content measured here is close to the content reported by the manufacturer of the products. Therefore, we are confident the experimental procedure can be used for solutions containing compounds other than hydrogen peroxide and water.

2.3 Determination of total peroxide content in SOA particles

SOA (using ammonium sulfate as seed particles) were generated in the PNNL environmental chamber as part of ongoing research under the Atmospheric Systems Research (ASR) program. The PNNL chamber design and general experimental method are provided in Liu et at. [8]. Briefly, the chamber consisted of two 10' x 5' x 7' Teflon reaction bags enclosed in a single
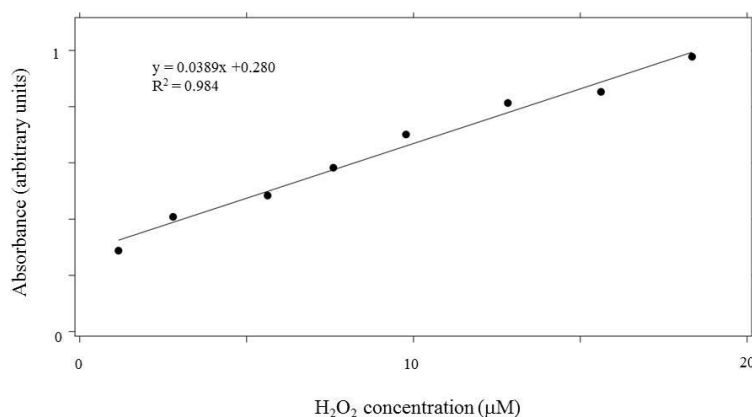
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temperature controlled room (15 − 45 °C). Both chambers were operated independently and could operate either in the traditional batch mode or in a continuous-flow mode [9]. Constant light flux was provided by 110 UVA-340 fluorescent lamps which surrounded the chamber. Volatile organic compounds (VOC) were typically injected into the chamber by pipetting the VOC into a gently heated glass bulb with a syringe. Vapors were transferred to the chamber via a flow of pure air. A variety of oxidants were used to initiate SOA formation from the vapors. OH was generated by photolysis of either H_2O_2 or HONO (depending on whether experiments were run under high-NO_x or low-NO_x conditions). Additional NO was sometimes injected from a pre-mixed gas cylinder to further control the NO_x concentrations, which determined the fate of generated organic peroxy radicals. A suite of analytical instrumentation analyzed the particle and gas phases in real time including an Aerodyne HR-ToF-AMS, an Ionicon PTR-MS, and a TSI SMPS.

SOA samples, generated using the procedure outlined above, were collected on 37-mm Teflon filters. Collection times ranged from 3 to 16 hours. After collection, the SOA was extracted from the filters via ultrasonication in 0.1 M hydrochloric acid for 15 minutes. The total peroxide content was determined using the IS procedure and the hydrogen peroxide calibration curve described in Section 2.1.

During the SOAFFEE campaign, several different types and concentrations of VOC were used in conjunction with various concentrations of hydrogen peroxide, NO_x and ozone to create SOA. In all, fifteen conditions were studied and the peroxide content quantified. Figure 2 shows the absorbance spectrum (dotted line) after the IS reaction of 61 μg SOA created from one reaction condition: 10 ppb α-pinene, 1 ppm H_2O_2 and 5 ppb NO. The increase in absorbance at the shorter wavelengths is due to presence of peroxide compounds in the SOA particles. For the SOA, the difference in absorbance at 470 nm and 542 nm is 0.551. Using the hydrogen peroxide calibration curve, a total peroxide content of approximately 7.0 μM was calculated.

Docherty et al. [10] created SOA using α-pinene, ozone and hydroxyl radical scavengers. The conditions used to create SOA in the Docherty et al. [10] study were not the same as the conditions used in this study. However, it is interesting to compare the total peroxide content found in their experiments to the amount found during the SOAFFEE study. Docherty et al. [10] found 29-58 wt % of their SOA was comprised of organic peroxides (assuming a molecular weight of 300 g/mol). The 7 μM peroxide concentration found in the SOA used in Figure 2 corresponds to approximately 26 wt% of the particles. Therefore, the peroxide content in the SOA found here is a reasonable value.

3. Future Work

The research described here is not sufficient to fully quantify the peroxide content of SOA. More UV/Vis absorbance measurements must be collected using SOA generated under different conditions. Furthermore, it is not clear if a hydrogen peroxide calibration curve is sufficient to predict total peroxide content in SOA aerosol particles. Additional experimental methods can be used to validate the IS procedure. For example, the absorption of the O-O stretching vibration in peroxides is weak in the infrared spectrum but has an intense band from 700-900 cm^{-1} in the Raman spectrum. Therefore, Raman spectroscopy could be used to quantify the peroxide content in SOA and validate the experimental procedure described here.

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4. Impact on Laboratory or National Missions

Climate change science is a key research area for both PNNL and for the Department of Energy's (DOE) Office of Science programs. Growth of atmospheric nanoparticles to climatically-relevant size is governed largely by deposition of secondary organic aerosol (SOA). Because a large fraction of the particle mass is composed of this secondary organic material, many of the properties of atmospheric aerosol particles are also influenced or even determined by the properties of the condensing SOA. Atmospheric models have struggled to accurately model these properties, in large part due to the difficulty in modeling SOA formation. The goal of DOE's Atmospheric System Research Program is to advance the process-level understanding of the aerosol lifecycle with one major component being SOA research. At PNNL, the Atmospheric Sciences and Global Change division is invested in improving scientific understanding of SOA formation.

A large laboratory campaign with 10 PI groups conducted collaborative experiments at the PNNL environmental chamber from June 15th – July 31st to investigate the chemistry of SOA formation from monoterpenes and isoprene. The campaign brought together PIs with individual expertise in a wide range of aerosol chemistry and property measurements allowing for an extensive understanding of the mechanistic chemistry driving photooxidation of biogenic VOC's, formation of secondary organic aerosol (both gases and particles), partitioning between gas and particle phases, SOA volatility, and SOA CCN properties. The experiments were motivated by the desire to explain the mechanistic chemistry driving observations from the DOE-funded field campaigns, including CARES, GoAmazon, and BAECC. As part of these collaborative experiment, PI Wise collected filter samples of the produced SOA and analyzed the material for organic peroxide content and with IR spectroscopy to determine their functional groups. The ultimate goal of these experiments is to gain mechanistic insight into SOA formation mechanisms, chemistry, volatility, and CCN activity that will advance understanding of the SOA lifecycle.

5. Conclusions

The IS technique, used to measure the total peroxide content of SOA, was optimized. The hydrogen peroxide calibration curve constructed during the optimization process agreed well with the literature. Several commercial products were tested for total peroxide content using the hydrogen peroxide calibration curve. The measured peroxide content of the products were close to the content reported by the manufacturer. SOA created during the SOAFFEE study were analyzed to determine their peroxide content. It was found that the SOA particles had similar amounts of peroxide as those created in different experimental studies.

Without the VFP, the undergraduate student working on this project, Ryan Caylor, would not have the ability to work in a cutting edge research environment. Furthermore, he would not have the ability collect the data needed to complete his senior research thesis. We are very grateful to DOE, PNNL, VFP administrators and Dr. Shilling for the opportunity to conduct this research. It is our hope that future collaborations between PNNL and Concordia University students will occur.

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6. References

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Appendix

Participants

Name	Institution	Email	Role
Dr. John Shilling	PNNL	john.shilling@PNNL.gov	Co-PI
Dr. Matthew Wise	Concordia University- Portland	mawise@cu-portland.edu	Co-PI
Ryan Caylor	Concordia University- Portland	rcaylor@livecom	Student

Dr. Shilling was a co-PI on the project and the contact person for our work at PNNL. He dictated the SOA generation procedures and conditions in the aerosol chamber. We sampled and analyzed the particles created in the chamber. Dr. Wise was a co-PI on the project and oversaw data generation and collection by an undergraduate student Ryan Caylor. Ryan was responsible for the data generated by the UV/Vis instrument. Each participant helped with all facets of data generation and collection at some point during the 10-weeks.

Scientific Facilities: No scientific user facilities at PNNL were used in the proposed project.

Notable Outcomes: It is expected that this research will be included in a peer-reviewed journal article. However, at this time there are no archival peer-reviewed journal articles, patent disclosures, laboratory technical reports, etc. from research performed under this appointment.

Research Vibrancy: The work done at PNNL during the summer of 2014 was the impetus for the successful proposal submitted for the VFP during the summer of 2015. It is possible to use the 2015 experience to generate a VFP proposal for the summer of 2016. However, it is our intention to write a proposal to the M.J. Murdock Charitable Trust to obtain money for a research project carried out on the Concordia University campus. If the proposal is successful, we will not be able to return in the summer of 2016. Even if we do not return to PNNL in 2016, the working relationship between Concordia University and PNNL is expected to continue.

Connection to Programs at Home Academic Institution: Concordia University is a small liberal arts institution with very little experience with cutting edge research. Last summer we purchased an instrument called a differential scanning calorimeter (DSC). The DSC was used to study phase transitions (i.e., liquid to solid) in small particles. We have already discussed the possibility of studying phase transitions of SOA particles generated in Dr. Shilling's aerosol chamber. Concordia University does not collaborate very often with high level research institutions. Therefore the possibility of this collaboration is very exciting!

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