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Ryan Caylor

Concordia University - Portland

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THE AGING EFFECT ON OPTICAL AND CHEMICAL PROPERTIES ON COLLECTED SOA

ABSTRACT

The enhanced greenhouse effect can be considered one of the greatest global environmental concerns. The amount of radiation absorbed by greenhouse gases is known to high certainty, absorbance from atmospheric aerosols particles is not. Experiments were aimed at the study of the chemical composition of secondary organic aerosols (SOA). The SOA were created in a temperature controlled chamber at Pacific Northwest National Laboratory (PNNL) and collected on filters. The SOA were then analyzed for chemical composition using Fourier Transform Spectroscopy (FTIR). Analysis of the FTIR showed that certain peaks were degrading over time while others had increased. Peaks at $>2350\text{ cm}^{-1}$ had decreases in absorbance overtime. However, at wavelengths $<1600\text{ cm}^{-1}$, absorbance increased. After relating the areas under these peaks, we were able to model a clear relationship between time and the individual absorbance peaks.

INTRODUCTION

The enhanced greenhouse effect is a result of an increase abundance of carbon dioxide and other radiation absorbing gases. The absorbance of radiation by greenhouse gases is known to high certainty. However the effect of aerosol particles is not known to high certainty [1]. For example current climate models do not take light absorbance by Secondary Organic Aerosols (SOA) into consideration. Therefore, research dealing with light absorption by SOA has become increasingly important.

Atmospheric aerosols can be chemically classified as carbon containing particles. These aerosol particles constitute to 40-90% of the particles in the atmosphere. The sources of these aerosols originate from fossil fuel combustion and biomass burning. The term “light absorbing carbon” (LAC) particles was coined by Bond and Bergstrom [2]. LAC particles in their definition are particles containing black carbon (BC). The optical properties of these particles are difficult to constrain, since they do not have a single chemical composition with consistent physical properties. Certain physical properties of BC are known such as how much light they absorb at 500 nm [2]. This is important to the enhanced greenhouse effect.

“Brown” carbon (BrC) is a second type of LAC that is a subset of OC, which is now being referred to as the light absorbing part of organic aerosol particles [3]. Studies such as Kirchstetter and Thatcher [4] calculated that 14% of the solar radiation (300-2500nm) was absorbed by BrC and 86% by BC created by wood smoke. The study

also showed that at wavelengths below 400 nm, radiation absorbed by BrC increased 49% [4]. Organic compounds have regularly been treated as purely scattering rather than absorbing. The absorption by BrC has not been accounted for, which can challenge the notion that BC and OC leads to an overall cooling effect in the atmosphere.

SOA particles are formed from oxidation of gas phase organic compounds in the atmosphere. These organic gases are emitted from either natural or anthropogenic sources. The oxidized gas phase compounds can condense into the particle phase due to a reduction in their vapor pressure. SOA is known to absorb between 300 to 500 nm which makes it a reasonable assumption that BrC is a component of SOA.

Since SOA particles are not part of current climate models, interest has risen in their optical properties. In our experiments SOA are formed in a chamber. After the SOA is formed they are impacted onto a filter to be analyzed. Our data suggests that the chemical composition of SOA can change. It is theorized that the change in chemical composition could affect SOA optical properties.

EXPERIMENTAL SECTION

Experiments were carried out at the Pacific Northwest National Laboratory (PNNL) under the supervision of Dr. John Shilling. The formation of SOA was done in dual Teflon bag chamber. Before each experiment, the chambers were flushed with purified air until the particle concentration was less than 10 cm^{-3} . A reaction vessel was then attached to the chamber and flushed

with the pure air. Once flushed, 1,2,4-trimethylbenzene (TMB) was injected into the reaction vessel, vaporized and then injected into the chamber. Sodium Nitrite and 99.999% Sulfuric Acid was added to the reaction vessel to create our oxidizing agents, NO and OH radicals. The chamber was then allowed to mix for approx. 1 hour or until the components were well-mixed. After mixing, UV lights were turned on to initiate photo oxidation. Reactions were done at 25 °C and at RH values of 5-30%. In one of the bags seed particles ((NH₄)₂SO₄) were used based on the experiment parameters. Before collection of the SOA particles, an infrared spectrum was taken of the Teflon background due to high absorbance from 600-700 and 1100-1200 wavenumbers cm⁻¹. Collection times (1-4 hrs.) varied based on the amount of available air in the bags. Aerosol particles collected from the chamber were impacted on Teflon filters.

The resulting SOA were analyzed by several instruments. A time-of-flight aerosol mass spectrometer was used to measure the chemical composition of non-refractory aerosol particles. A scanning mobility particle sizer (SMPS) was used to determine

particle concentration. The SMPS was used to determine the mass loading on filters. Fourier Transform Infrared Spectroscopy (FTIR) was used to determine chemical composition of the SOA particles.

Because two chambers were used during the course of experimentation, the chambers will be referred to as right (R) or left (L). The R chamber never had seed aerosols in its testing conditions while seed aerosols were sometime used in the L chamber. Collections of SOA particles were usually made in the latter half of the day so that H₂O₂ (peroxide) could be added to increase oxidation of the particles overnight for morning collections. Filters were immediately measured with FTIR to insure the strongest signal from fresh SOA. Samples were then sealed in containers and stored in a freezer to limit loss of volatile components.

RESULTS

Figure 1 is our spectrum collected to ensure the spectrometer was working properly. The distinguishable peaks at 1400, 1000, and 600 cm⁻¹ confirm that our FTIR instrument was functioning properly.

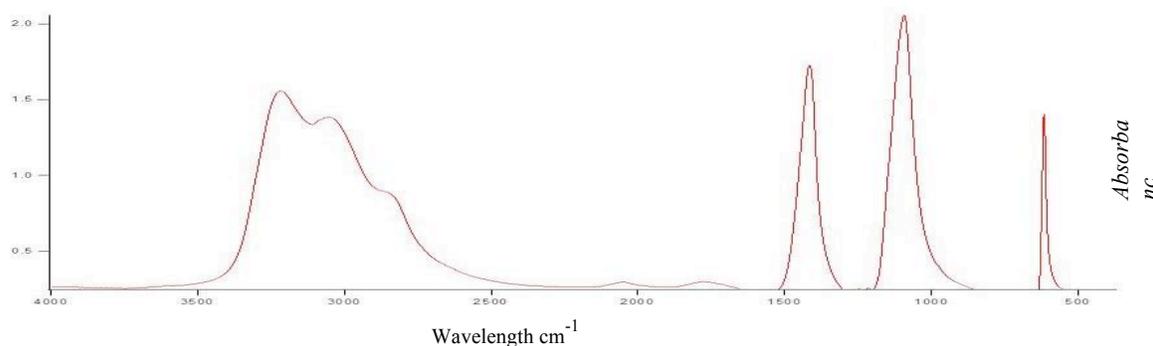


Figure 1. IR spectrum of ammonium sulfate.

The first SOA sample collected for analysis was on 6/04/14. This sample was collected in the R chamber. The chamber was filled with TMB and then oxidized by OH and NO radicals under UV light. Figure 2 is the spectrum of the collected SOA sample.

The peaks between at $3600-300\text{ cm}^{-1}$ are identified as a hydroxyl groups. In the spectrum at $849, 1281$ and 1644 cm^{-1} result from organonitrate functional groups. Other functional groups in the spectrum that indicate the presence of SOA are nitroaromatics (1559 cm^{-1}), carbonyls (1727 cm^{-1}), alkanes ($2942, 2996\text{ cm}^{-1}$), and cyclic alcohols (1090 cm^{-1}). The peaks at 2730 cm^{-1} and 2500 cm^{-1} have been denoted in green. These peaks require further analysis to

confirm the identity. It is theorized that these peaks result from absorption by aldehydes, amines, and peroxides.

A significant decrease in the peak absorbance near 3400 cm^{-1} , 2730 cm^{-1} , and 2500 cm^{-1} were apparent after 24 hours of storage. On the other end of the spectrum peaks at 1400 cm^{-1} and 1050 cm^{-1} appeared to increase. This result was surprising so a second experiment was conducted in the L chamber. Figure 4 shows the results from second SOA collection in the L chamber. Once again the same decreases and increases in peaks were observed. The only difference between the experiment carried out in the L chamber was the use of ammonium sulfate seed aerosol.

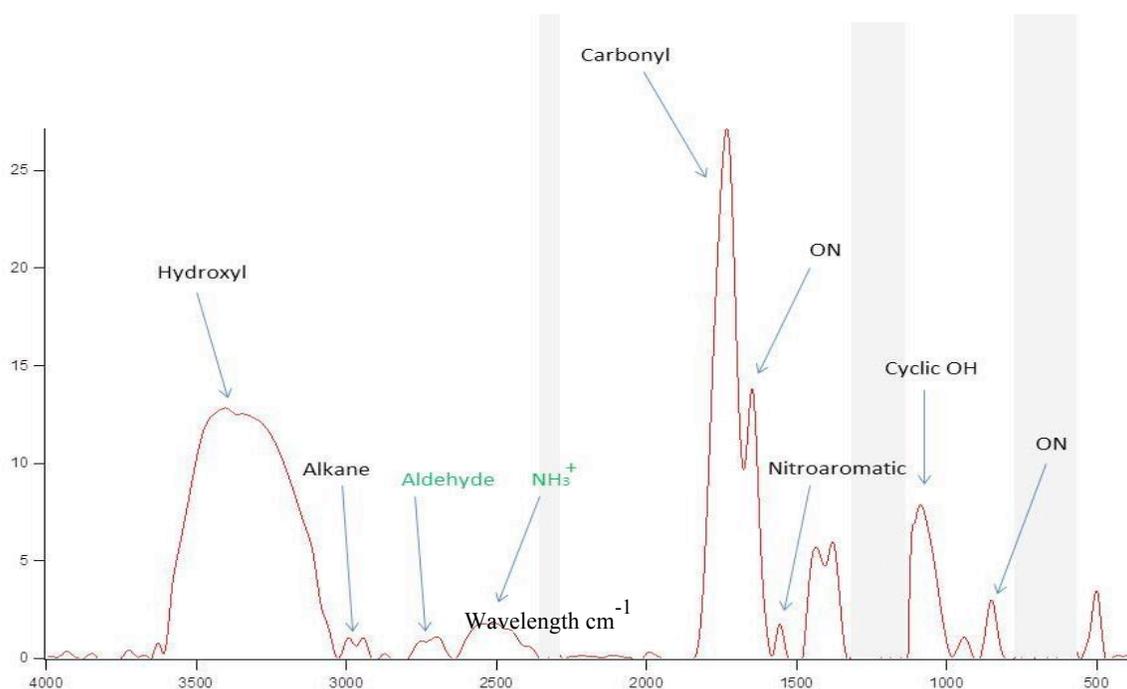


Figure 2. IR spectrum of SOA collected on 6-4-14. The SOA was analyzed immediately after collection.

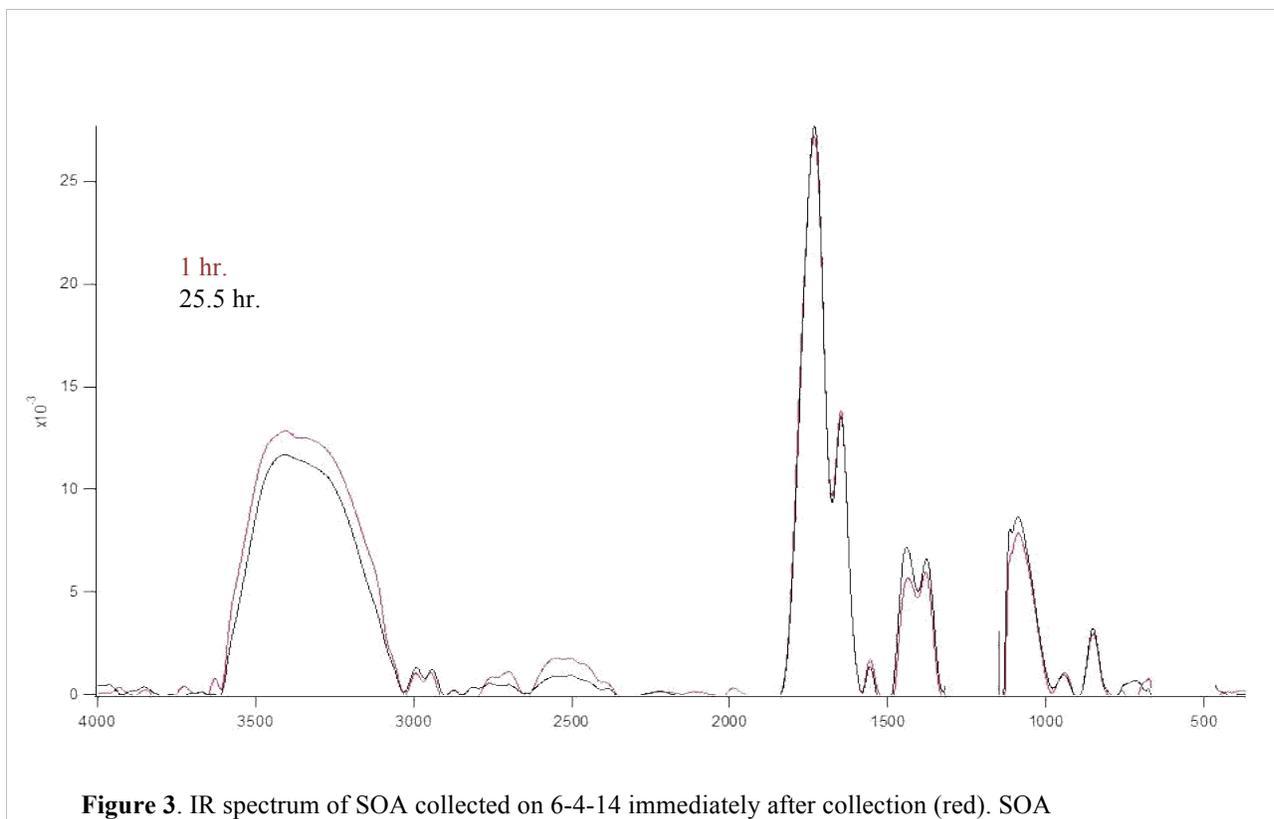


Figure 3. IR spectrum of SOA collected on 6-4-14 immediately after collection (red). SOA collected on 6-4-14 analyzed 25.5 hours after collection (black).

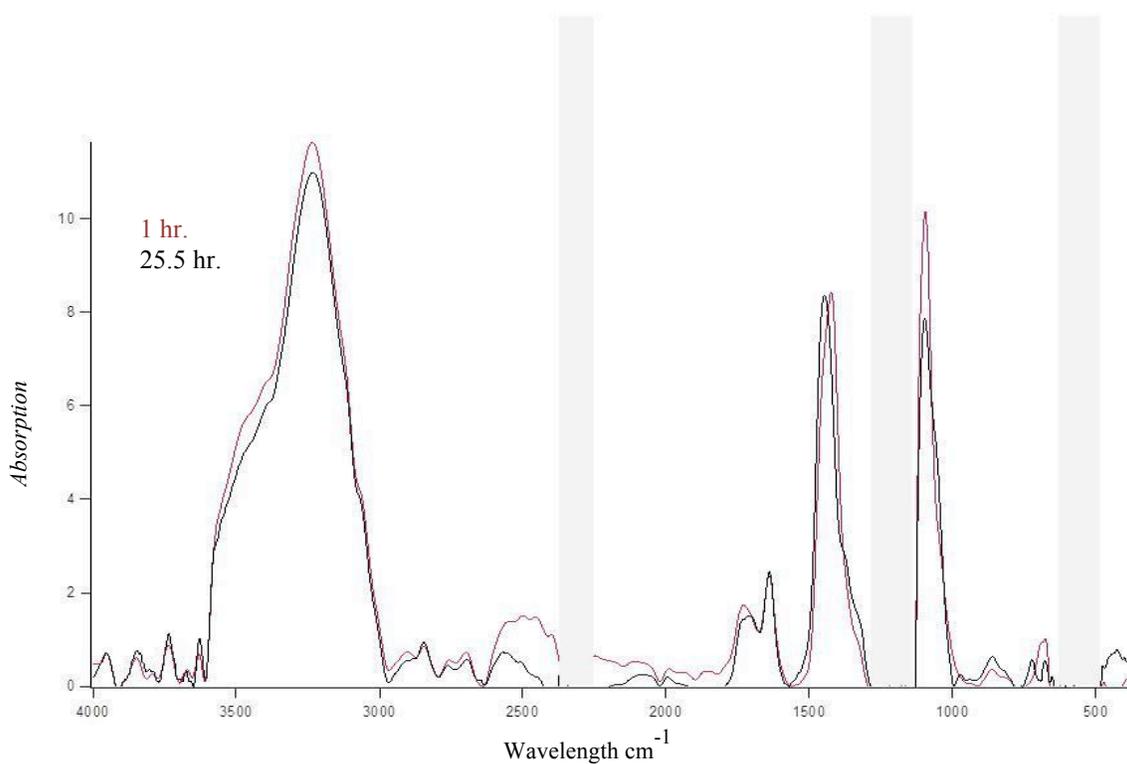


Figure 4. IR spectrum of SOA collected on 6-11-14 analyzed immediately after collection (red). SOA collected on 6-11-14 analyzed 25.5 hours after collection (black).

In order to determine if peaks underwent alterations while the SOA was in storage, a peak integration analysis was done. Two methods were used in assessment, ratio to peaks and ratio to baseline. These methods provide useful information about the area under a specific peak. Both methods were able to deliver consistent results within $\pm .002$ of each other.

The SOA collected in figure 4 was extremely important analyze using these methods. The SOA was created using seed particles which contain ammonium sulfate. The physical and chemical properties of ammonium sulfate cause it not to degrade over time. Figure 4 expresses a strong ammonium sulfate peak at 1400 cm^{-1} and when analyzed using the integration methods, the area under the peaks remain constant. This ultimately led to the decision for a longer and more extensive study on a freshly collected aerosol filter with controlled parameters.

On June 19, 2014, conditions were set in the chamber to produce light absorbing SOA through the use of high NO_x . The sample was then analyzed via FTIR. The sample was then stored in a dark freezer and only taken out at various time intervals to be scanned with the FTIR.

| Hour | Wavenumbers (cm^{-1}) | | | | |
|------|----------------------------------|-----------|-----------|-----------|-----------|
| | 3000-3600 | 2675-2800 | 2350-2650 | 1600-1525 | 1500-1300 |
| 1 | 7.181 | .144 | .338 | .037 | .899 |
| 25.5 | 5.715 | .031 | .171 | .04 | 1.159 |
| 82 | 4.458 | .013 | .023 | .045 | 1.311 |
| 111 | 2.088 | .009 | .014 | .113 | 1.368 |

Table 1. The relationship of time elapsed and peak area from SOA collected on 6-19-14.

Table 1 also shows change in peak areas over time. On the upper wavelengths of the spectrum, $>2350\text{ cm}^{-1}$, the peak area illustrates decreases over time. On the lower end of the spectra, $<1600\text{ cm}^{-1}$, peak area was observed to increase over time. The integrated peaks were then graphed on the basis of integration vs time.

Figure 5 shows time vs peak area between $3000\text{-}3600\text{ cm}^{-1}$. The data showed a linear decrease in peak area over time, however, it is expected to decrease over time. The correlation coefficient calculated is .9384 which is shows a strong relationship in the $\sim 94\%$ confidence interval.

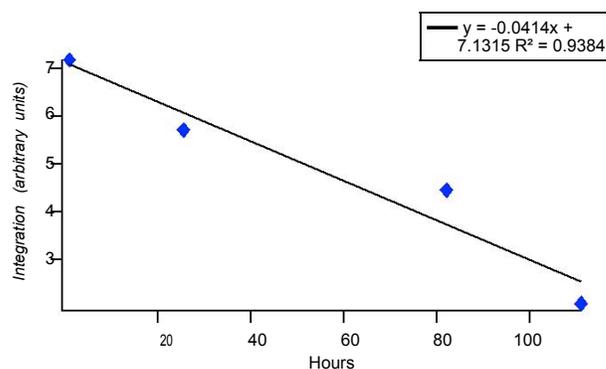


Figure 5. Integrated peak area vs time of $3000\text{-}3600\text{ cm}^{-1}$.

One explanation is that OH functional groups are being lost since OH absorbs between $3000\text{-}3600\text{ cm}^{-1}$. OH could

undergo further oxidation or could evaporate from the filter. With this being said, as the SOA is stored for a longer period of time the expectation is for it to reach a point where peak area no longer changes and reaches a minimum area.

In figure 6 a power function was used to fit the peak areas vs time data (2675-2800 cm^{-1}). This was used because the peak area rapidly decayed over time and then gradually flattened out.

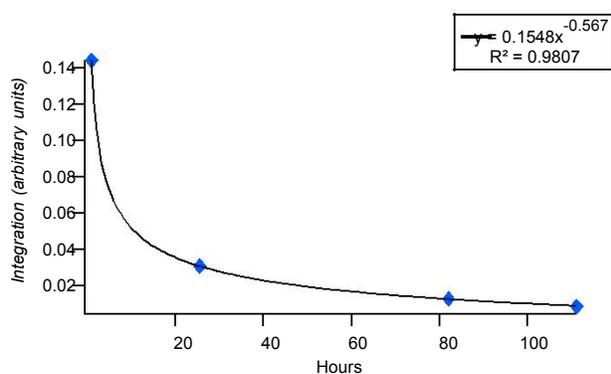


Figure 6. Integrated Peak Area vs time (2675-2800 cm^{-1}).

This absorbance in the spectra is thought to be an aldehyde functional group. This specific section of the spectra has never been analyzed with FTIR, so further studies of this functional group are required. However, the data shows that this stretch is lost at rapid rate. So further studies on this functional group must be done within 24 hours where the potential for loss of this stretch is high.

The final section analyzed was the peak between (1300-1500 cm^{-1}). At these wavelengths, the individual peak areas increased. This specific absorbance is thought to be polar nitro groups. Figure 7 shows the increasing peak areas.

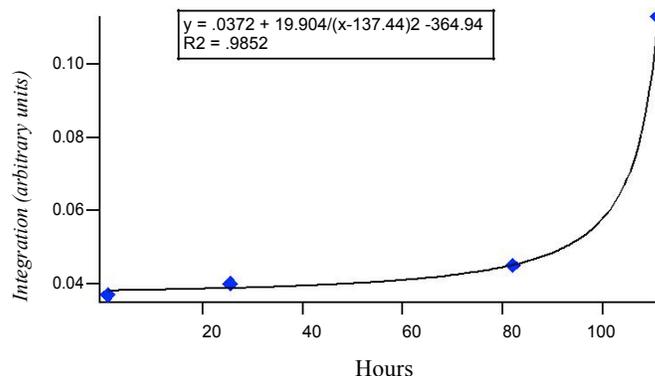


Figure 7. Integrated peak area vs time from (1300-1500 cm^{-1}).

The integral values from 1300-1500 cm^{-1} increase at an increasing rate. This equates to an increase polar nitro groups as time elapses. Possible reasons for the increase are oxidization of the functional groups that absorb at (3000-3600 cm^{-1}). Other uncertainties lie in whether or not the filter continues to react with itself in storage. Figure 8 is all the FTIR spectrum collected for SOA over a period of hours.

DISSCUSION

In the past there hasn't been concern with regards to storage and collection of SOA samples. Typical storage methods include placing the filters in a case then

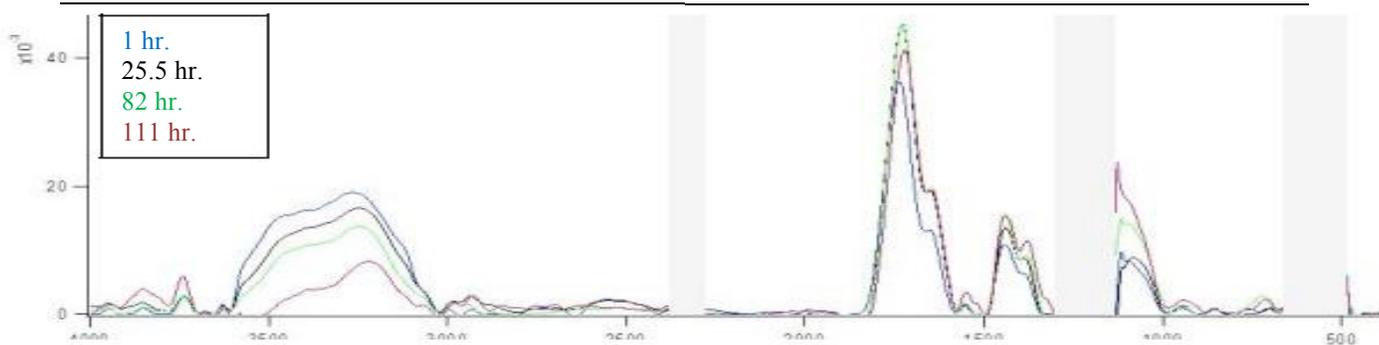


Figure 8. Comparison of all the FTIR taken over 111 hours for the 6-19-14 filter.

storing them in freezers. However, the data suggests current methods of storage may not be enough. More analysis needs to be done to understand what is happening to the specific functional groups are affected. However, our results show that future experimentation is warranted.

Current studies of SOA performed on SOA involve their formation, absorbance, and reaction in the atmosphere. To our knowledge there are no studies concerning the storage of SOA and the possibility of chemical changes as they are stored. This is important since absorbance is dependent on SOA composition. If the stored filters lose or gain the ability to absorb radiation while in storage, this can have an impact on climate models.

As previously stated there are more paths to be explored to fully understand the impact of storage on these SOAs. Future work involves the analysis of absorbance by freshly collected samples versus samples stored over a period of time. Recent data also suggest the formation of peroxides in collected samples. Peroxide identification has been an issue in determination of SOA composition. A recent collected sample showed peroxide concentrations through ultra violet visible spectroscopy(UV-VIS). However, testing this method on older collected samples have failed to produce results.

CONCLUSION

The enhanced greenhouse effect can be considered one of our greatest global environmental concerns. The amount of radiation absorbed by greenhouse gases is

known to a high degree, while absorbance due to aerosols particles is not. The current climate models do not incorporate the effect of SOAs. This raises the importance for understanding how these particles interact with the atmosphere; however, concerns of the storage of these collected SOAs has yet to be raised. The data collected suggests that further reaction and/or volatility continue to occur even after the samples have been “properly” stored. Significant loss and gains of functional groups throughout the spectrum. This data will hopefully be the foundation for the expansion on this area of study on SOAs.

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