The Analysis of Printer Ink Over Time Using Infrared Spectroscopy

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Overview

The effects of sunlight, darkness, and time on paper with printer ink were measured using IR spectroscopy over a period of forty days for 12 different types of paper. From this analysis came the conclusions that the age of ink does not appear to affect the resulting IR spectrum between five and nineteen days. However, there is a very evident increase in transmittance between the first and fifth day which could be helpful when aging a document. In terms of sunlight and darkness as factors, there is not enough information to concretely say whether or not the conditions affect the ink degradation.

Introduction

- Past analyses have been done on both printer ink and ballpoint pen ink, which indicate that ink will go through chemical changes over time. (Calcerrada, et al.)
- Keeping track of these changes would allow for a timeline to be made, which would then allow for the possibility of dating a document.
- Having this capability would also help in the determination of whether or not a document is forged.
  - A falsified document would have differently aged ink than the original document in many cases. This information would be extremely beneficial to forensic science due to the abundance of document examination present in the field.
- The changes that occur as ink ages on different types of paper were investigated using infrared (IR) spectroscopy.
  - The effect of sunlight/darkness on this aging process was also investigated to determine if this would affect the determination of the age of a document based on ink.

Materials & Methods

- Papers (12): Georgia-Pacific Standard Multipurpose Paper, Astrobrights Inkjet Laser Print Colored Paper (assorted: Yellow, Pink, Green, Orange, Lime), Astrobrights Laser Print Colored Paper (Stardust White), Southworth 100% Cotton Thesis Paper (Wove Finish White), Boise ASPEN 100 Recycled Copy Paper, Navigator Platinum Paper, JAM Paper Cardstock, WB Mason Blizzard Blinding White Copy Paper
- Ink: Canon PGI 270
- Baseline spectra of the individual papers were collected; three samples were run three times each (from different locations) for each individual paper.
- The papers with ink were prepared by creating a template with bullet points placed one after another all down the paper and three of these templates were printed for each individual paper.
- Of the three triplicates, one was placed in a lab bin, one was placed in the darkness (under a desk) and the final set was placed in the direct sunlight (by a window).
- To run on IR, bullet points were cut out one by one for each paper and run after being cut out. For each paper, there bullet points were sampled three times each at each time point.
- For the papers in darkness and sunlight they were sampled in the same way, however they were only sampled at one additional time point.
- Certain peaks were monitored over time to determine changes as the ink aged.

Results

Astrobrights Assorted yellow and WB Mason Blizzard Blinding White are two examples of papers analyzed. These papers appear to exhibit the same trends of change in percent transmittance found in the other papers observed as well.

Figure 1a.

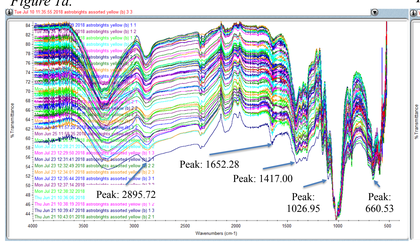
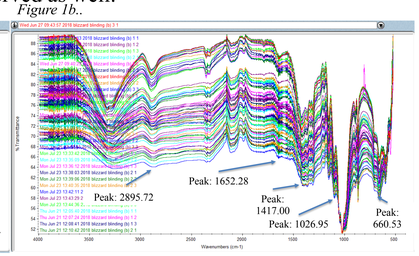


Figure 1b..



- All other Astrobrights paper and WB Mason Blizzard Blinding white paper exhibit similar trends to the figures below.
  - All other papers analyzed in the experiment also show similar trends to that of the figures below.
- Figures 2a, 2b, 3a, and 3b depict two of the specified peaks (1417.00 cm-1 and 2895.72 cm-1) over the forty day period and their changes in percent transmittance over time.

Figure 2a.

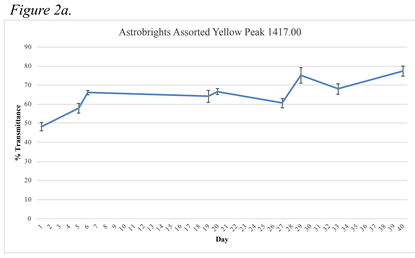


Figure 2b.

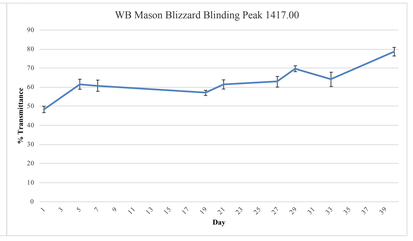


Figure 3a.

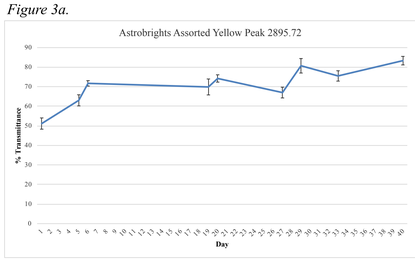
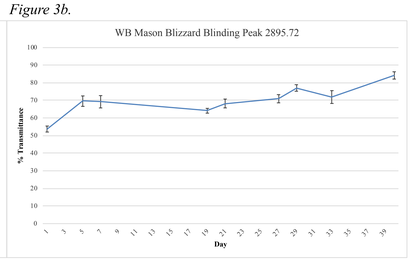
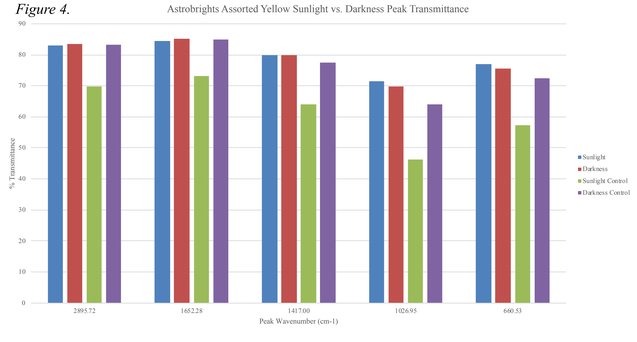


Figure 3b.



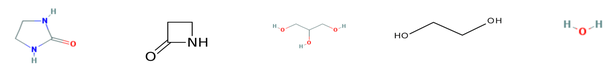
- Figure 4 shows the average peak transmittance values for the selected peaks in comparison to their respective controls.

Figure 4.



Conclusions

- There are noticeable differences over time for the IR signal obtained from black printer ink on various types of paper.
- The observed peaks were most likely from alkane stretching (2895.72), alkane bending (1417.00), amine bending (1652.28), ether stretching (1026.95), and alkene bending (660.53).



- The increase in transmittance seen within the first time point is due to a decrease in vibrational signal, likely caused by the ink solvent drying/evaporating.
  - Ink is made of many components, one of which is a solvent that makes it so it is liquid enough to be printed onto a paper.
- Other decreases in transmittance are caused by an increase in signal which is likely due to bonds stretching more after other bonds broke.
- For papers that were aged in the dark and direct sunlight, the ones in the sunlight had percent transmittances that were much different than those of their corresponding control. This could be due to an increased speed of ink degradation, but further experimentation would have to be conducted to determine such results. The paper left in the darkness for the most part remained similar in percent transmittances to that of its control.

Future Directions

- Investigate shorter time points between ones already ran to determine what happens during this time in the aging process.
- Add longer time points to determine if there are any other significant changes past 40 days.
- Use mass spectrometry to identify what the compounds within the ink are, and what they are changing into throughout the aging process.
- Use Raman spectroscopy to investigate the aging of ink to compare this method to another nondestructive method.

References

Canon Safety Data Sheet. http://sds.staples.com/msds/1804225.pdf.
Richter, G. A. *Industrial & Engineering Chemistry* **1935**, *27*(2), 177–185.
Calcerrada, M.; García-Ruiz, C. *Analytica Chimica Acta* **2014**.

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