2023

Investigation of Unexpected Purple Substance Extracted from Newsprint Paper

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INVESTIGATION OF UNEXPECTED PURPLE SUBSTANCE EXTRACTED FROM NEWSPRINT PAPER

A Thesis Submitted

In Partial Fulfillment

of the Requirements for the Designation

University Honors with Distinction

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May 2023

This Study By: Raquel Wilhelm

Entitled: Investigation of Unexpected Purple Substance Extracted from Newsprint Paper

Has been approved as meeting the thesis or project requirement for the

Designation University Honors with Distinction

_________ ____

Date Dr. Shoshanna Coon, Research Advisor, Department of Chemistry & Biochemistry

_________ ____

Date Dr. Jessica Moon, Director, University Honors Program

ACKNOWLEDGMENTS

This honors thesis was made possible through the support of the following departments and faculty:

Department of Chemistry & Biochemistry

Dr. Shoshanna Coon

Dr. Kirk Manfredi

Anne Marie Gruber

University of Northern Iowa Honors Program

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ABSTRACT

In an attempt to extract a green dye from newsprint advertisements, it was serendipitously discovered that a purple substance can be extracted from newsprint paper using methanol or acetic acid.[1] Further investigations involving blank newsprint paper showed that the purple substance was a part of the paper itself rather than a component of the ink in the advertisements. Soxhlet extraction was used on the blank newspaper print to obtain the compound. Using different analytical instruments, characteristics of the compound were determined such as potential structures, functional groups, and percent composition. The ultimate goal was to determine the compound and its structure.

INTRODUCTION

In a previous research project, there was an attempt to extract ink from newsprint paper and an advertisement with green ink was chosen for the extraction. When it was placed in methanol, the methanol turned purple which was unexpected as the dye was green. The process was repeated but this time a piece of newspaper print with black ink was used. When placed in methanol the purple compound was once again extracted. An extraction was then performed on a blank piece of newsprint paper and the purple compound was extracted again. This indicated that the purple compound was a component of the paper, rather than a component of the ink.[1]

With this new information, blank newsprint paper was placed in various solvents to determine how successful they were at extracting the purple compound. Methanol and acetic acid were used in these tests. While acetic acid was able to extract the purple compound faster, it was also extracting more than just the purple compound. This led to using only methanol as the solvent. In these tests methanol was placed in a beaker and several small squares of newsprint paper were placed in the methanol. Overtime, the purple compound would be extracted. This technique was very slow and produced low yields. For continuation of this project, a more efficient extraction method would need to be developed. Soxhlet extraction was chosen to improve efficiency and yields.

The previous research project ended before any characteristic tests could be performed on the unknown purple compound. The goal of this project was to produce a more efficient way to extract the purple compound and to run characterization tests on it to see what characteristics could be determined. Initially the end goal was to determine the mass and structure of the compound. As the research progressed it became clear that this was too ambitious of a goal.

LITERATURE REVIEW

Before research was conducted to determine what the unknown purple compound in newsprint paper is, it was important to investigate what is already known about the subject. There was no literature available on a purple compound found in newspaper print. As a result, this literature review was focused on investigating the newsprint paper itself, effective methods of extraction, and the serendipitous discovery of the purple compound.

Like other kinds of paper, newsprint paper is made from trees. The wood from trees is mechanically broken down into a pulp which is used in the manufacturing process. To keep the process as inexpensive as possible, lignin is not removed from the pulp.[2] Lignin is a biopolymer in plant cell walls that aids in growth and development. Lignin has a molecular formula of $C_{18}H_{13}N_3Na_2O_8S_2$ and consists of phenolic and aliphatic hydroxyl groups.[3] Another major component of newsprint paper is cellulose. Cellulose is a long chain molecule made from glucose monomers that are a major component of plant cell walls. The molecular formula of cellulose is $(C_6H_{10}O_5)_n$ in which the n is dependent on how long the chain is. When cellulose is extracted from newsprint paper it results in a green mixture that can be formed into green crystals. This indicates that the unknown compound is not cellulose as the compound is purple and not green.[4] Both cellulose and lignin darken when exposed to sunlight which accounts for the yellowing that occurs in newsprint paper when it is exposed to the sun for a long period of time. The mechanical pulp used in newsprint paper allows for the opaqueness and quality that is customary in newsprint. The pulp can be bleached and chemically treated to improve the strength and integrity of the paper.[2]

In previous research it was found that methanol and acetic acid can be used as solvents to extract the purple compound from the newsprint paper. In previous set ups, several beakers were filled with solvent and newsprint paper clippings were placed in the beakers. The purple compound would slowly leech out of the paper. This process was time consuming, resulted in low yields, and required large amounts of solvents.[1] As a way to improve upon these negatives, a Soxhlet extractor was used. Soxhlet extractors are commonly used in extractions because they allow for solvent to be recycled and minimize the amount of time it takes for the extraction to occur.[5] Using a Soxhlet extractor in conjunction with a condenser and round bottom flask filled with solvent allows for the newsprint paper to be extracted multiple times. Once the paper has been extracted from it is easy to exchange with a new piece of paper without having to replace the solvent. The Soxhlet extraction technique was tested and resulted in yields that were 40 times greater than the previous methods used while using less solvent overall.

RESEARCH QUESTIONS TO BE ANSWERED

The research question to be answered is “What is the purple compound that can be extracted from newspaper print?”. The end goal of this project is to find the molar mass, elemental composition, and a possible structure of the compound. The compound will be extracted using a Soxhlet extractor with methanol as a solvent. Once it has been extracted several analytical techniques and instruments was used to determine the characteristics of the unknown compound.

METHODOLOGY

To obtain the unknown purple compound an extraction was performed on blank newsprint paper. To optimize the amount of solid that could be extracted while using a minimal amount of solvent Soxhlet extraction was used. Figure 1 shows the the Soxhlet extraction set up and Figure 2 shows a close up of the newsprint paper in the apparatus.

Figure 1. Soxhlet extraction set up.

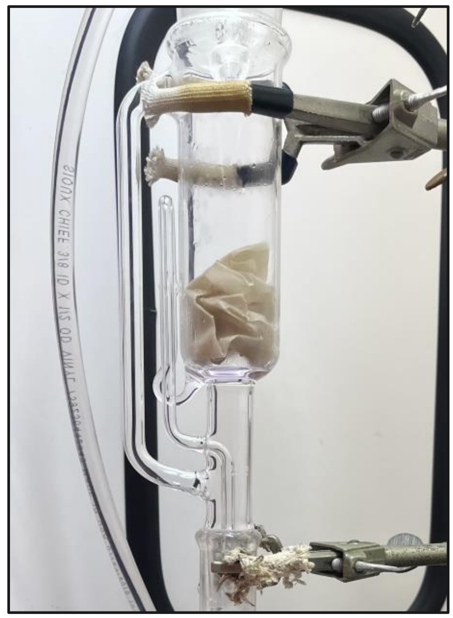

Figure 2. Close up of Soxhlet extraction set up.

A Soxhlet extraction works similarly to a regular extraction. The sample that is extracted from is added to the thimble and a solvent is added to the distillation flask. The solvent is gently heated and as it begins to evaporate it travels up the side passage of the middle column. The evaporated solvent then condenses at the base of the condenser which has cold water running through it. The warm solvent falls onto the paper and is then able to extract the sample. Once enough solvent has been acquired in the thimble it siphons back into the distillation flask. This allows for the sample to be reused and for the concentration of the extracted compound to be higher than if new solvent was used each time. Figure 3 shows the compound dissolved in methanol following extraction. Once the mixture has cooled, a rotary evaporator was used to remove most of the solvent. The rest of the compound was transferred to a 50mL round bottom flask and the remaining solvent was blown off using nitrogen gas. Figure 4 shows the dried compound in the flask. The process was repeated with blank copy paper.

Figure 3. The unknown purple compound dissolved in methanol.

Figure 4. Dried sample of the unknown purple compound.

Several analytical instruments were used to run characterization tests on the unknown compound once it had been extracted. The first technique that was used was attenuated total reflectance Fourier Transform Infrared Spectroscopy (ATR-FTIR). This technique works by sending an infrared beam through a crystal with a high refractive index causing total internal reflection where the crystal is in contact with the sample. This reflectance results in an evanescent wave that goes through the sample. The infrared beam then leaves the crystal and is picked up by the detector which records the signal as an IR spectrum.[6] ATR-FTIR is a valuable analytical tool because the spectra shows what functional groups exist in the sample. Figure 2 shows how an attenuated total reflectance FTIR instrument works.

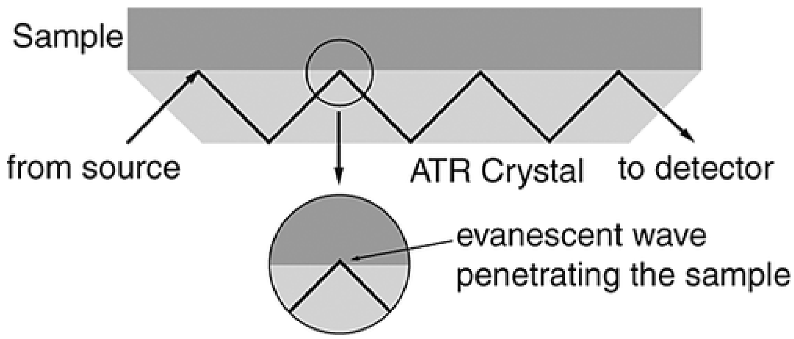

Figure 2. Diagram of attenuated total reflectance FTIR. [6]

The next technique that was used was nuclear magnetic resonance (NMR) spectroscopy. NMR works by capitalizing on the fact that the isotopes of carbon and hydrogen have nuclei with magnetic dipoles. These magnetic dipoles act differently in the magnetic field of the NMR and will resonate at different frequencies. These frequencies are translated into chemical shifts on an NMR spectrum.[7] These shifts are indicative of some of the molecular structural elements of a compound. Figure 3 shows the schematic diagram of an NMR instrument.

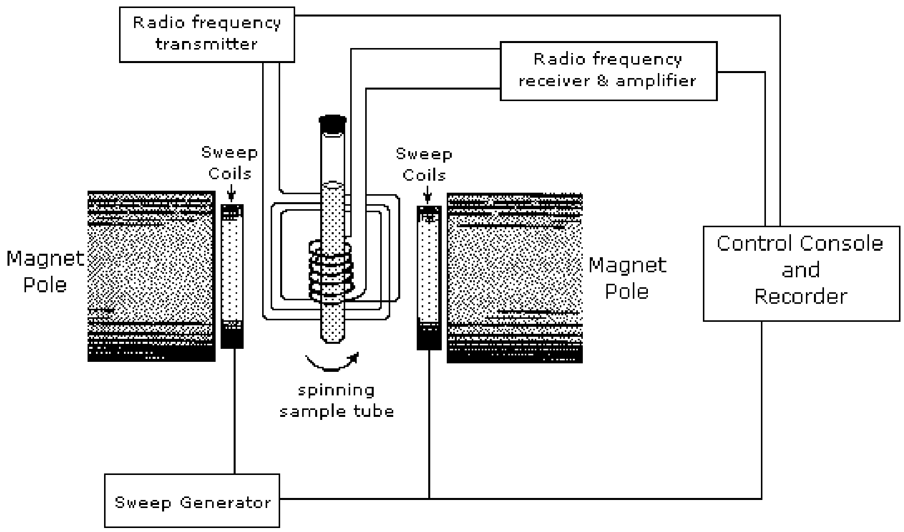

Figure 3. Diagram of an NMR instrument.[8]

Ultraviolet-visible (UV-VIS) spectroscopy was another analytical tool used to characterize the compound. This technique utilizes the fact that some molecules will change electronic energy levels when they interact with light. Only certain wavelengths of light will cause different molecules to change their electronic energy levels and UV-VIS spectroscopy measures the absorbance vs the wavelengths.[9] The UV-VIS spectrometer works by sending a light source through a monochromator which allows for a single wavelength of light to hit the reference sample and the sample being tested. Detectors pick up the light that has made it through the sample and that is output as an absorbance vs wavelength spectrum.[9] Figure 4 shows a basic internal schematic of a UV-VIS spectrometer.

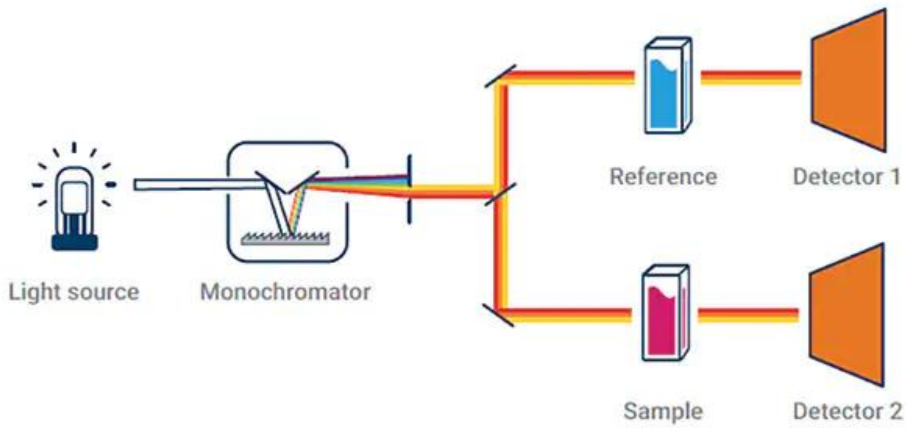

Figure 4. Basic diagram of the internal schematic of a UV-VIS spectrometer.[9]

Liquid chromatography mass spectrometry (LC-MS) was also used to evaluate the sample. LC-MS is used to determine the molecular weight of an unknown compound. Liquid chromatography is used to separate a compound into its components and a mass spectrometer detects charged ions. A spectrum is produced which depicts the mass to charge ratio which corresponds to unique molecular compounds.[10] Figure 5 shows how an LC-MS works.

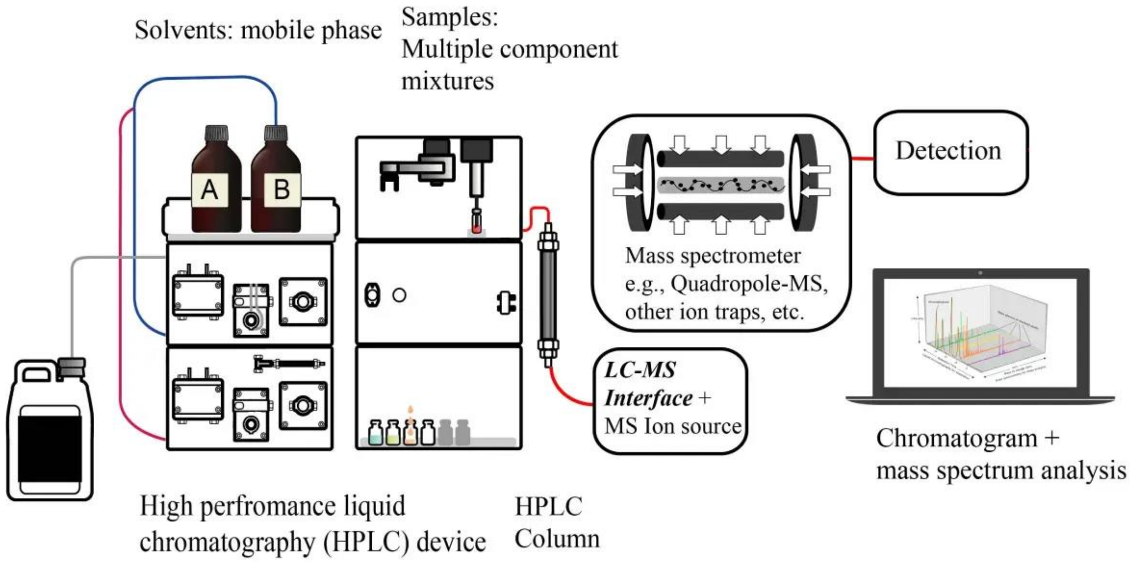

Figure 5. Schematic representation of an LC-MS.[1]

The final analytical instrument that was used was a fluorometer. Fluorometry measures how much a compound fluoresces. When a specific wavelength of light hits a sample, it excites the electrons which fluoresce light themselves. This emitted light is of a different wavelength. The emission spectrum that is emitted goes through a monochromator and then a spectrophotometer. This emission is then translated into an intensity vs wavelength spectrum. Fluorescent compounds have a unique type of light that they excite at and emit.[12] Figure 6 shows a diagram of a fluorometer.

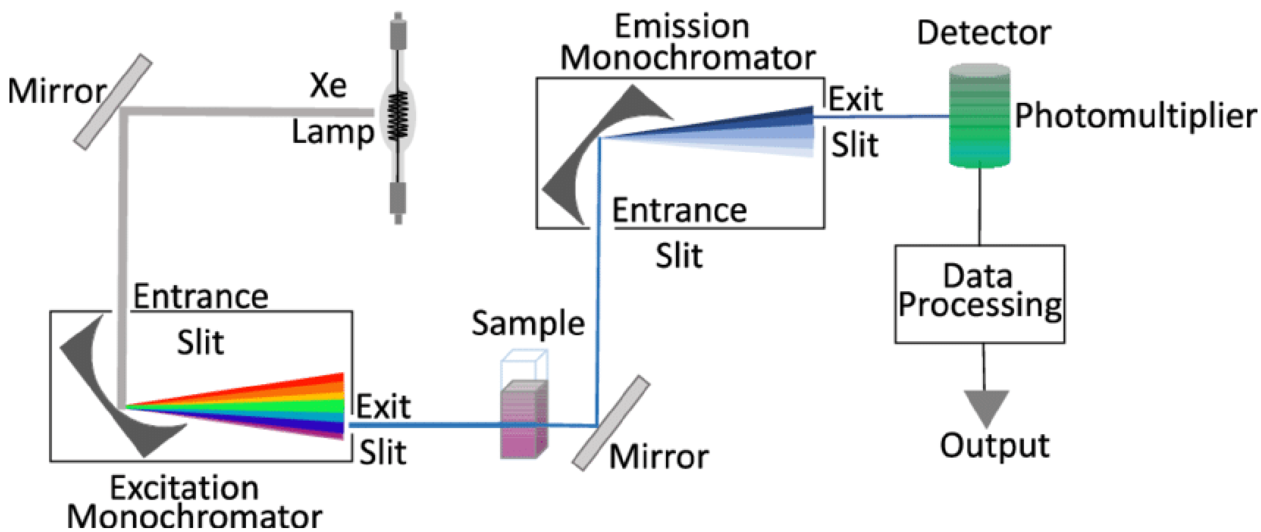

Figure 6. Schematic representation of a fluorometer.[12]

EXPERIMENTAL

For each extraction roughly 250 mL of methanol was added to the round bottom flask. A piece of blank newsprint paper was obtained, massed, and crumpled into a ball. It was then placed in the extraction chamber. Due to the fact that an unknown compound was extracted from the paper and would end up in the methanol a thimble was unnecessary. The condenser was connected to water via rubber tubes and the heating mantle was then turned on. Once the piece of blank newsprint paper had been extracted from twice the paper was removed and a new piece was added. This process was repeated on four total pieces of paper. Table 1 shows the masses that were taken of the four pieces of newsprint paper that were extracted from.

	Mass
Newsprint Paper #1	1.1128g
Newsprint Paper #2	1.4881g
Newsprint Paper #3	1.7393g
Newsprint Paper #4	1.8310g

Table 1. Masses of the newspaper print that was extracted from.

The methanol with the purple substance was then placed on a rotary evaporator to remove the methanol. Once most of the methanol was removed the remaining methanol and unknown purple compound were transferred to a 50 mL round bottom flask. The remaining methanol was removed using nitrogen gas. The mass of the solid was then recorded.

The process was repeated on four pieces of blank copy paper to compare to the blank newsprint paper. Table 2 shows the masses of the pieces of blank copy paper that were extracted from.

	Mass
Copy Paper #1	2.3834g
Copy Paper #2	2.1164g
Copy Paper #3	2.2875g
Copy Paper #4	2.2173g

Table 2. Masses of the copy paper that was extracted from.

For ATR-FTIR spectroscopy a solid tip on an attenuated total reflectance diamond was used. The solid, dried sample was placed on the crystal, enough to cover the surface, and the tip was lowered onto the sample. A signal vs wavenumber spectrum was generated. To prepare the sample for NMR spectroscopy 0.0189g of sample were placed in an NMR tube with deuterated chloroform. The sample was placed in the NMR instrument and ^{1}H proton NMR and ^{13}C NMR were run. For UV-VIS spectroscopy the sample was dissolved in methanol and placed in a cuvette. A spectra of absorbance vs wavelength was produced. For LC-MS the sample was dissolved in methanol and a positive esi was used. To run fluorescence, the sample was dissolved in methanol and diluted accordingly depending on the intensity of the signal.

RESULTS

The total mass of the newsprint paper used was 6.172g and the total mass of the purple sample that was extracted was 0.1192g. This means that the unknown purple substance makes up 1.93% of newsprint paper. The total mass of blank copy paper used was 9.004g and the mass of purple substance extracted was 0.0487g. The percentage of the purple substance in blank copy paper was 0.541%. Figures 7 and 8 show the dried solids of the newsprint paper and blank copy paper respectively. Figures 9-14 show the results of the characterization tests.

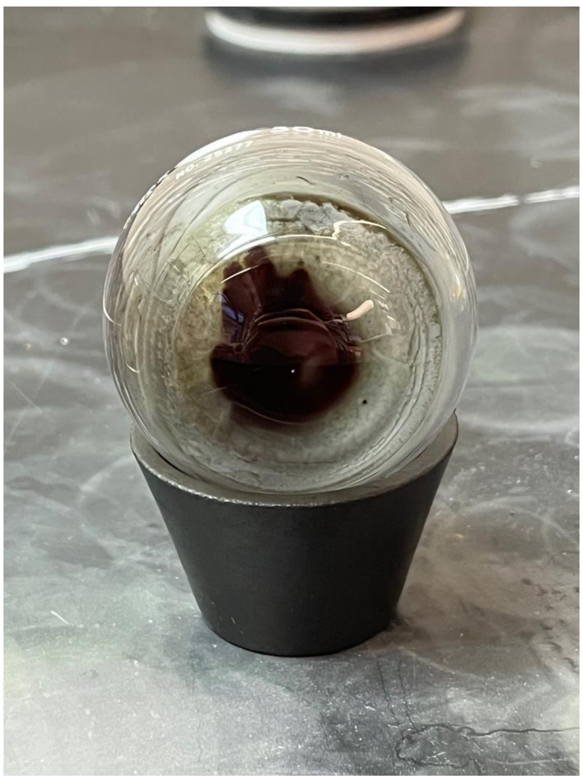

Figure 7. Dried compound extracted from newsprint paper.

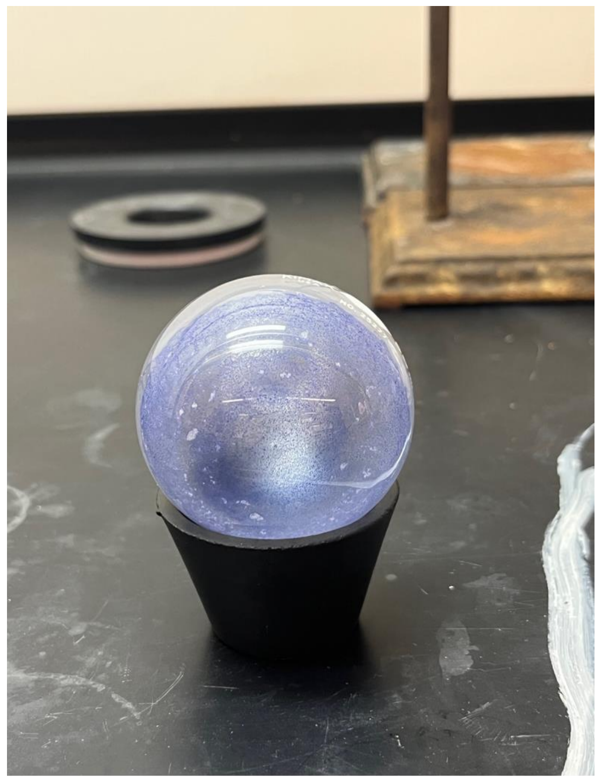

Figure 8. Dried compound extracted from Blank copy paper.

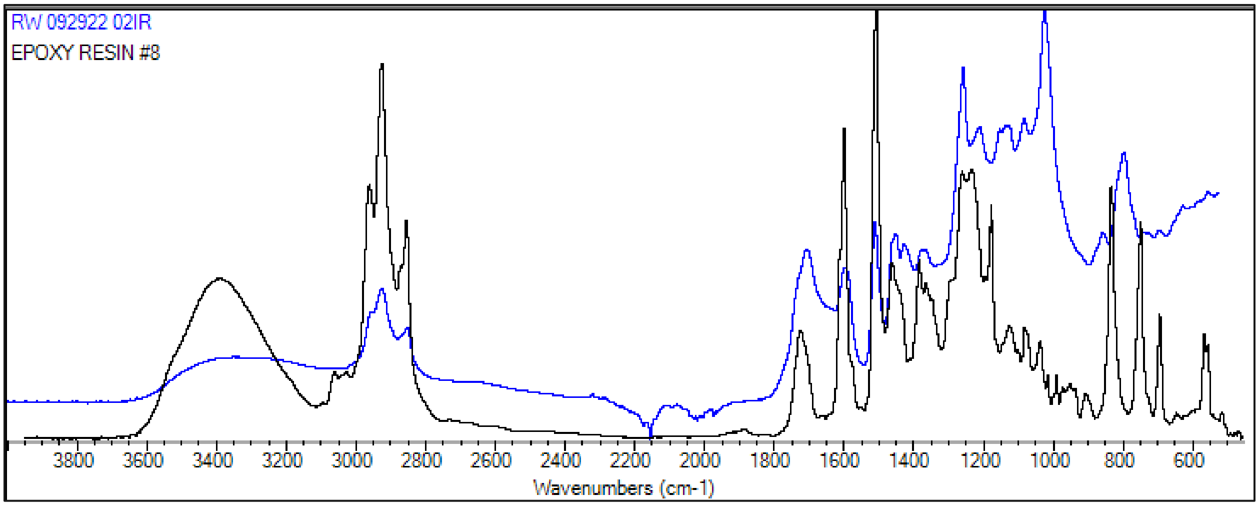

Figure 9. ATR-FTIR spectra of the unknown purple compound (blue) overlaid with the IR spectra of epoxy resin (black).

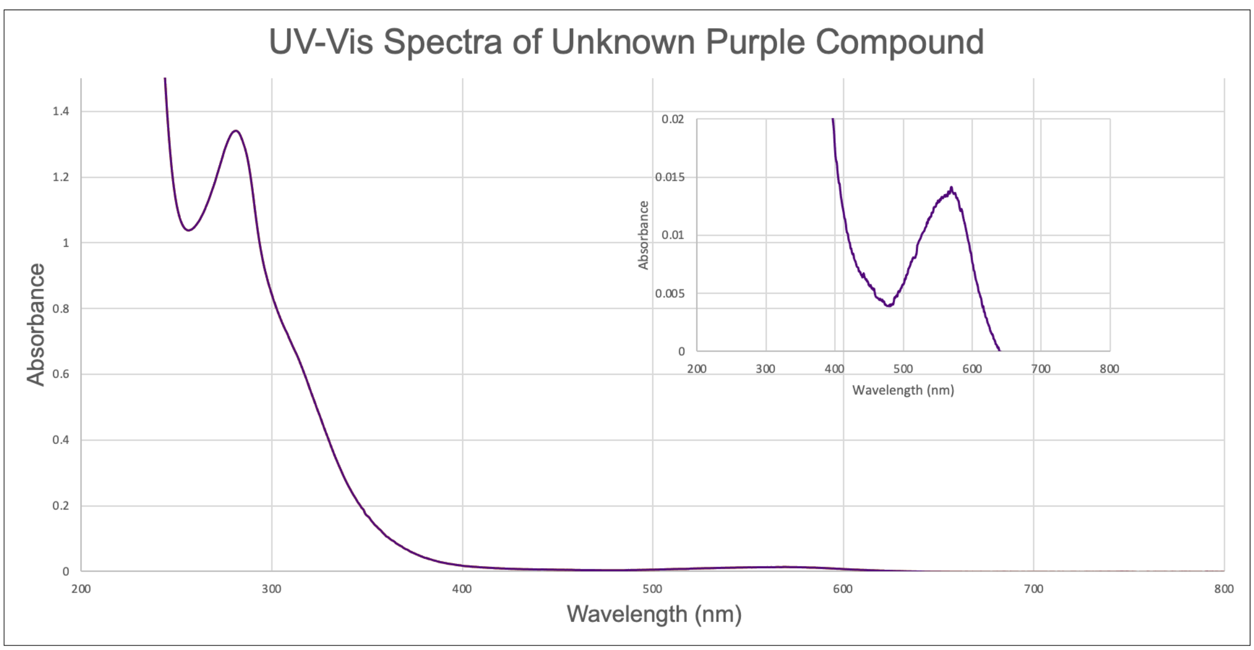

Figure 10. The UV-Vis spectra of the unknown purple compound with peaks at 280 nm and 560 nm.

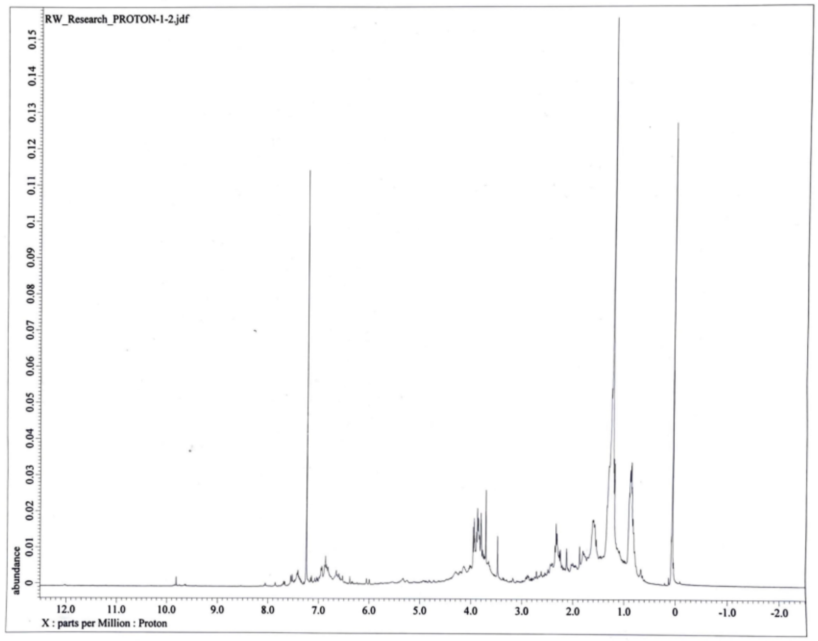

Figure 11. The NMR spectra of the unknown purple compound extracted from newsprint paper.

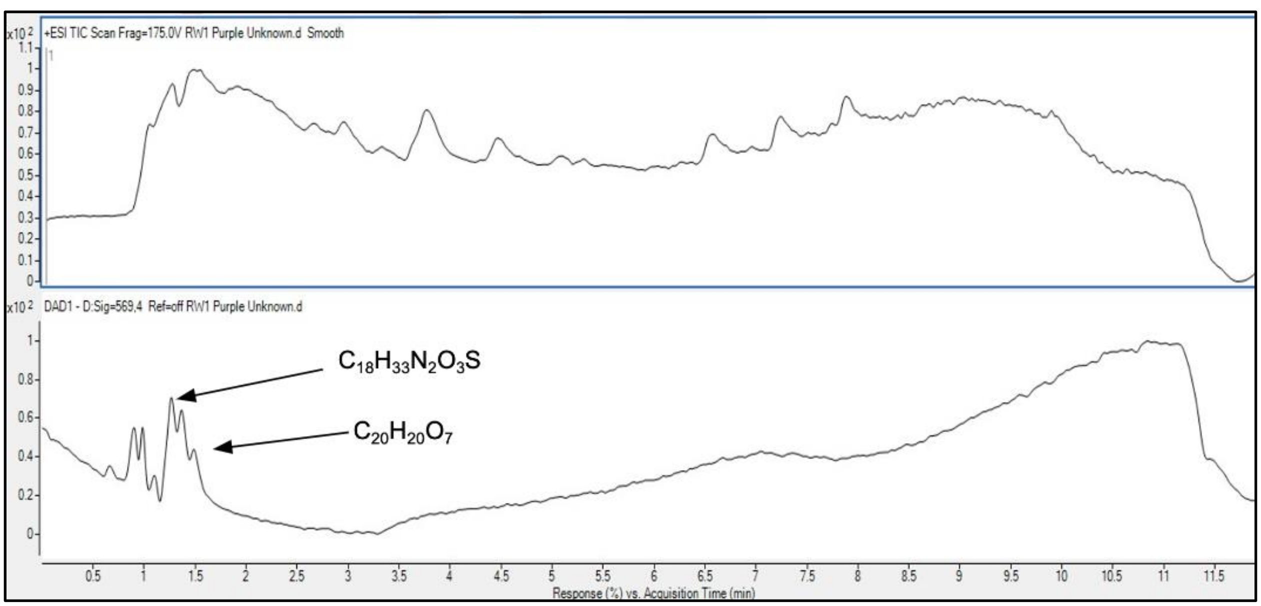

Figure 12. LC-MS spectra of the unknown purple compound extracted from newsprint paper. Top: Total Ion Chromatogram. Bottom: Diode array detector signal at 569 nm.

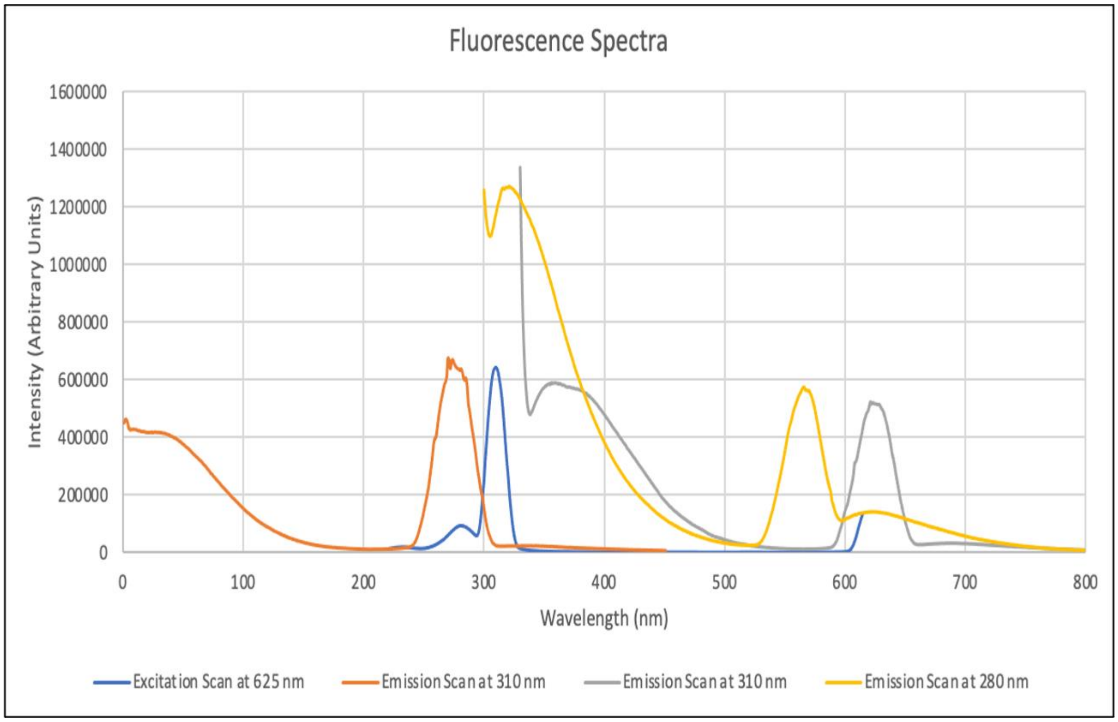

Figure 13. Fluorescence spectra of the unknown purple compound. Excitation at 280 nm corresponded to emission peaks at 310 nm, 565 nm, and 625 nm.

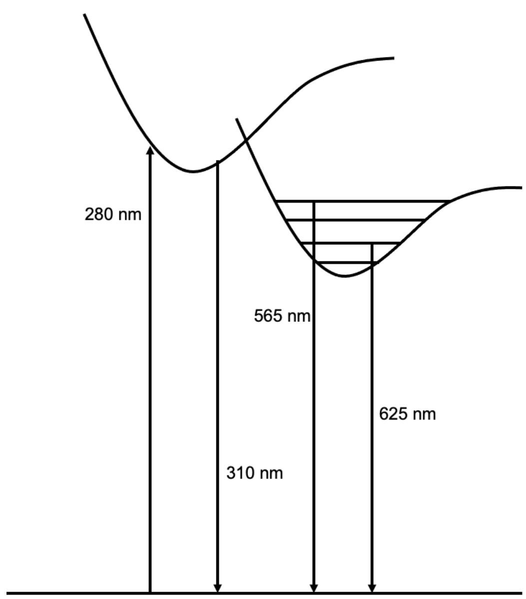

Figure 14. Energy level diagram corresponding to the fluorescence data above.

DISCUSSION

While no definite structure was determined for the compound, useful information was still obtained. Looking at the dried sample in the round bottom flask it is apparent that there is more than one compound in the sample. This is indicated by the fact that while the center is a dark purple color along the periphery there is a green solid. Different colors mean different substances.

The IR spectra of the unknown compound extracted from newsprint paper had peaks at 3500 cm^{-1}, 1750 cm^{-1}, and 1600 cm^{-1}. A broad peak at 3500 cm^{-1} is an OH stretch. The peak at 1750 cm^{-1} is indicative of C=O stretching and a peak at 1600 cm^{-1} is the result of C=C stretching. When the spectra that was obtained was compared to known IR spectra in a database the closest match was to resin. Resin is a logical result because it is used as a coating on paper to make it shiny and smooth.

The NMR spectra has peaks at 6.8 ppm, 4.0 ppm, 1.2 ppm, and 0.1 ppm. The peak at 7.3 ppm is from the solvent, deuterated chloroform ($CDCl_3$). The shift at 6.8 ppm is indicative of an alkene and the shift at 4.0 ppm is an OH group. The peak at 1.2 ppm is an alkyl group and 0.1 is most likely grease that came into the solution from the Soxhlet extraction apparatus.

The UV-VIS spectra shows that the compound had a peak at 280 nm and a much smaller peak at 560 nm. The LC-MS peaks were compared to known peaks in a database. Some potential peaks are $C_{18}H_{33}N_2O_3S$ and $C_{20}H_{20}O_7$. This data also indicates that the sample is more than one compound.

The fluorescence data reveals that exciting the compound at 280 nm corresponds to emissions at 310 nm, 565 nm, and 625 nm. A blue shift in the excitation of the compound results in a blue shift in the emission data that is obtained. The values for fluorescence indicate that this would not be considered a fluorescent compound.

CONCLUSION

When the purple compound was extracted from newsprint paper, looking into the literature very quickly demonstrated that there was a lack of research concerning newsprint paper. This research attempted to help bridge that gap and to provide any information possible about the unknown purple compound. While the compound was not identified at this time, valuable information was still learned, and it opened the door for further research to be completed.

This research was able to conclude that not all papers yield the same result when they are extracted from. This was evidenced by the different color compounds that came from newsprint paper and blank copy paper. The research also suggests that more than one compound is being extracted. The different colors of the solid, as well as the LC-MS data, indicate this. Finally, potential structures and functional groups were determined using LC-MS and IR data.

While the conclusions obtained from this research are important, they are far from complete. Further research could be continued to expand upon what has already been learned. For example, an NMR spectrum was obtained using deuterated chloroform as a solvent. The purple compound did not dissolve fully. It is known that the compound dissolves in acetic acid so another NMR sample could be taken using deuterated acetic acid. Further research could also involve doing extractions of different types of paper. Due to limited time, the project only extracted from one type of newsprint paper and blank copy paper. Further research could involve extracting from different types of newsprint paper, as well as other types of paper. Characterization could then be done on these compounds to see how they compare to the original newsprint paper used.

This research is important because there is not much in the available literature concerning newsprint paper, specifically regarding a purple compound extracted from newsprint paper. All new research is valuable because it contributes to an area that is lacking in information. By shedding light on an area of chemistry that has less information, this research may spark the interest of future researchers to continue investigating newsprint paper and eventually other kinds of paper.

\

LITERATURE CITED

1. Carter, Briyana; Coon, Shoshanna; and Manfredi, Kirk, "Investigating the Unknown Purple Substance from Newsprint Paper" (2021). Summer Undergraduate Research Program (SURP) Symposium. 14.
2. PaperIndex Academy. https://www.paperindex.com/academy/paper-grades/newsprint-primer (accessed Oct 14th, 2022).
3. Liu Q, Luo L, Zheng L. Lignins: Biosynthesis and Biological Functions in Plants. Int J Mol Sci. 2018 Jan 24;19(2):335. doi: 10.3390/ijms19020335.
4. M.A. Mohamed, W. N. W. Salleh, J. Jaafar, S.E.A.M. Asric, and A. F. Ismail. Physicochemical properties of “Green”- Nanocrystalline Cellulose isolated from recycled newspaper. RSC Advances, 1-12. (2012).
5. M.D Luque de Castro, L.E García-Ayuso. Soxhlet extraction of solid materials: an outdated technique with a promising innovative future. Analytica Chimica Acta, Volume 369, Issues 1–2, Pages 1-10. (1998). doi.org/10.1016/S0003-2670(98)00233-5.
6. Blum, M.-M. and John, H. (2012), Historical perspective and modern applications of Attenuated Total Reflectance – Fourier Transform Infrared Spectroscopy (ATR-FTIR). Drug Test. Analysis, 4: 298-302. doi-org.proxy.lib.uni.edu/10.1002/dta.374
7. Kwan, A.H., Mobli, M., Gooley, P.R., King, G.F. and Mackay, J.P. (2011), Macromolecular NMR spectroscopy for the non-spectroscopist. The FEBS Journal, 278: 687-703. oi-org.proxy.lib.uni.edu/10.1111/j.1742-4658.2011.08004.x
8. Libre Texts NMR. https://chem.libretexts.org/Bookshelves/Analytical_Chemistry/Physical_Methods_in_Ch

emistry_and_Nano_Science_%28Barron%29/04%3A_Chemical_Speciation/4.07%3A_NMR_Spectroscopy. (Accessed April 4, 2023).

9. Agilent UV-VIS. https://www.agilent.com/en/support/molecular-spectroscopy/uv-vis-uv-vis-nir-spectroscopy/uv-vis-spectroscopy-spectrophotometer-basics (Accessed April 2, 2023).
10. Agilent LCMS. https://www.agilent.com/cs/library/support/documents/a05296.pdf (Accessed April 6, 2023)
11. Nebiolab LCMS Diagram. https://www.nebiolab.com/complete-guide-on-liquid-chromatography-mass-spectrometry-lc-ms/ (Accessed April 6, 2023).
12. Fluorometer Diagram. https://www.researchgate.net/figure/Major-components-of-fluorescence-spectrophotometry_fig1_333437881 (Accessed April 4, 2023).