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Utilizing Various Forms of Spectroscopy in Search of Unique Characteristics in Brands of Nail Polish

I. Abstract

Three different brands of red and blue nail polish were examined to determine if there was a way to identify each nail polish by using various forms of spectroscopy; Attenuated total reflection-Fourier transform infrared (ATR-FTIR), UV/Vis and fluorometry. UV/Vis and fluorometry were found to be best suited for quantitative analysis and do not assist in identifying differences in nail polish. ATR-FTIR has potential, but time and resources are needed to separate the various compounds that make up nail polish to get a more exact measurement of how much of each component are in the various nail polishes.

II. Literature Review

Small paint fragments from nail polish can be found at a crime scene due to chipping off. It may be sourced from walls or furniture where the nails rubbed against (Singh 1). The evidence collected at a crime scene will most likely be tiny flakes or smudges and are therefore noted as trace evidence. A quick identification can be made to have an idea of what color the nail polish is, but to go further than that, spectroscopy can be utilized. Nail polishes are complex samples that vary on formula based on color and brand. They contain ~15% film forming agents, ~7% plasticizers, ~70% solvent, ~1% suspending agents, and ~0-1% pigment (López-López 155). Currently Laser Desorption Mass Spectrometry (LDMS), Secondary Ion Mass Spectrometry (SIMS), Energy Dispersive X-ray

Fluorescence spectrometer (EDXRF) and principal component analysis (PCA) have been utilized to help identify nail polish colors and brands (Singh 2).

Attenuated total reflection-Fourier transform infrared (ATR-FTIR) spectroscopy is a non-destructive form of spectroscopy which is an advantage when using trace evidence. An infrared light is passed through the ATR crystal, the light will reflect off the crystal and an evanescent wave is formed. The beam ends at a detector and is analyzed. ATR-FTIR is fast and provides excellent quality data (Ausili 160).

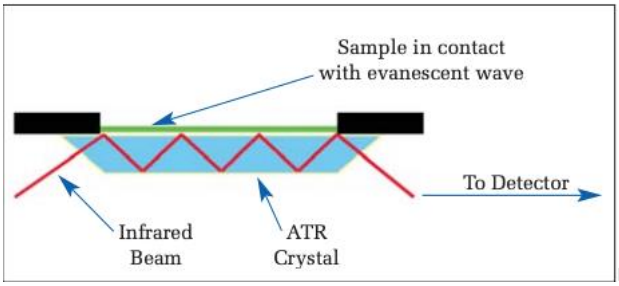


Fig 1. A multiple reflection ATR system

UV/Vis measures the absorbance of light energy. A light source is separated from the sample by a filter and a detector is at the other end (Raja 4.4). A fluorometer measures the intensity of the fluorescent signal from a sample based upon excitation and emission wavelengths (Wenzel 3.3). These two methods of spectroscopy will require the nail polish to be treated in a solution therefore they may be destructive unless a solvent is found that can easily be removed without changing the chemical makeup of the trace evidence.

In this study, three different types of spectroscopy (ATR-FTIR, UV/Vis and a fluorometer) will be utilized to analyze three different brands of nail polish. Each brand of nail polish will be represented by two colors, red and blue.

III. Methodology

Three different brands of nail polish were chosen to analyze. Each brand was represented with a shade of red and blue. The colors were chosen because they are primary colors and there would be less likelihood that any pigmentation would be similar between them. In order to replicate a crime scene, the nail polish was applied to glass microscope slides and allowed to dry for 2-3 hours. The dried polish was then scraped by using a scalpel and tested using ATR-FTIR spectroscopy. This process was repeated three times for each color to ensure accuracy.

A similar process was utilized for UV/visible spectroscopy and the fluorometer. Once the nail polish was dry, 0.050 ± 0.001 g was weighed. The dry nail polish was then placed into a 50 mL volumetric flask along with acetone and mixed until it was completely dissolved into the solution. A series of dilutions were then made to create a calibration curve.

To further testing, the acetone was evaporated from the solution and once the nail polish was dry again and the flask was allowed to cool, acetone was added. The solution was then retested to see if the results remained the same and if any product was lost. If the spectra remains the same, it allows for the retesting of nail polish trace evidence using liquid spectroscopy methods without destroying evidence.

All spectra will be analyzed to see any similarities/differences between nail polish brands and colors.

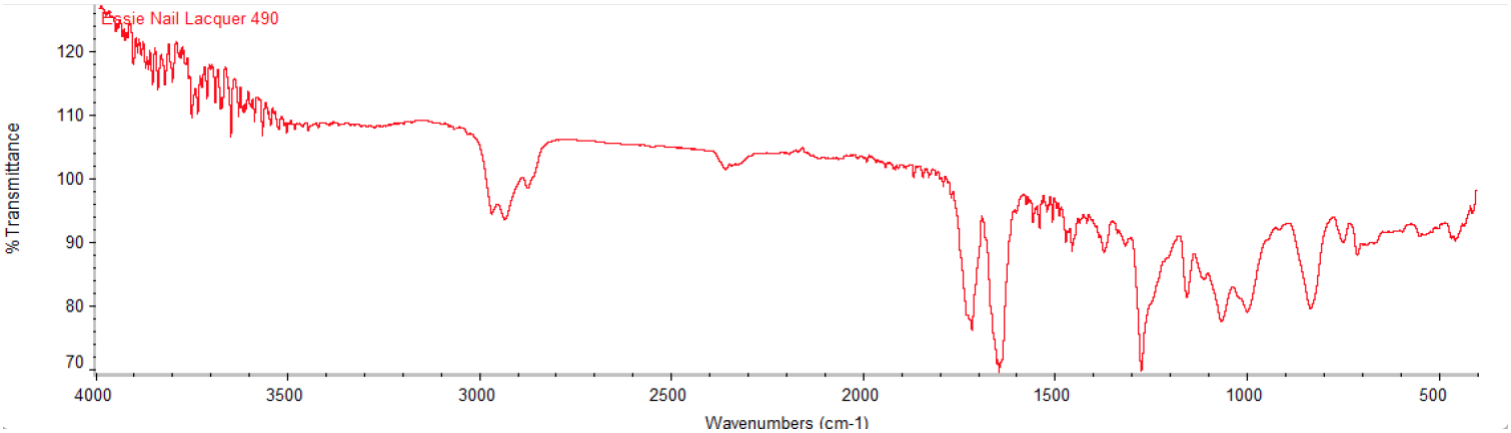
The nail polish that will be analyzed are:

Brand	Name
Essie #490	Not Red-y for Bed
Essie #772	Butler Please
OPI #1095	Red Hot Rio
OPI #0303	Mi Casa es Blue Casa
Sally Henson #299	Pucker Up
Sally Henson #479	Pacific Blue

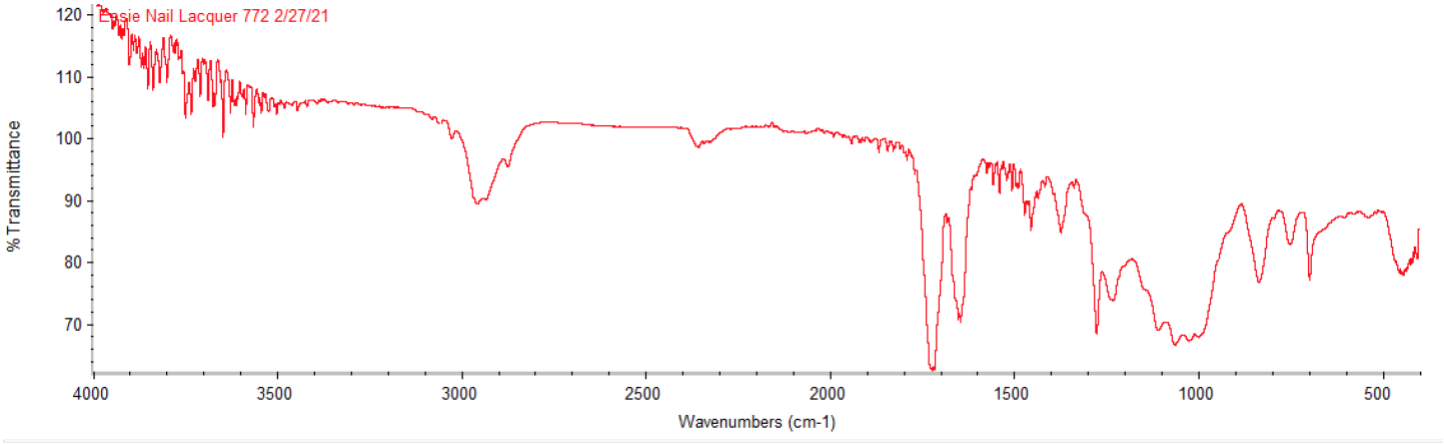
IV. ATR-FTIR

When analyzed, the dry nail polish revealed this IR spectra:

ESSIE #490



ESSIE #772



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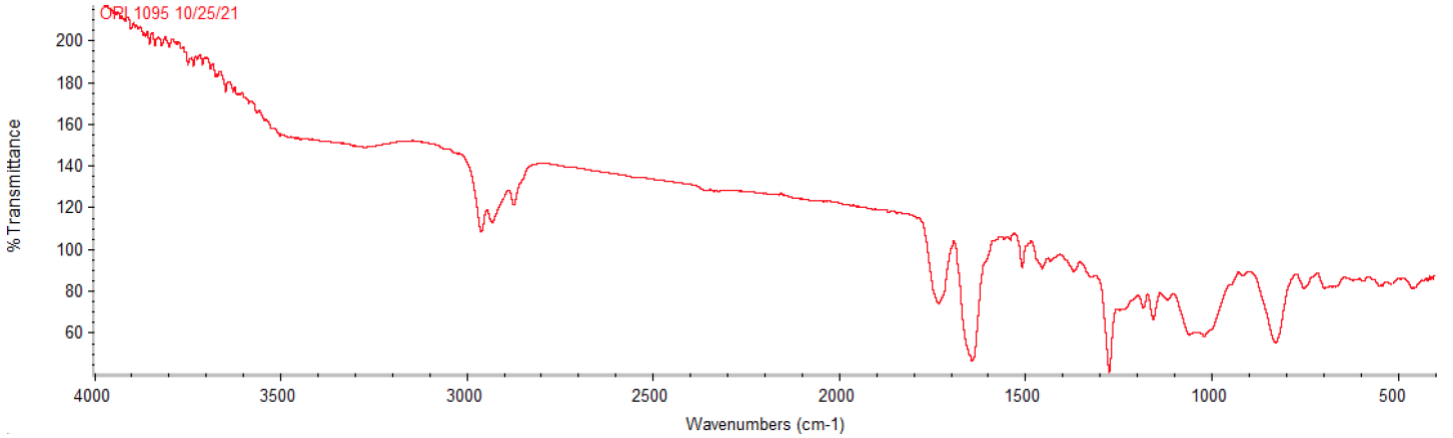
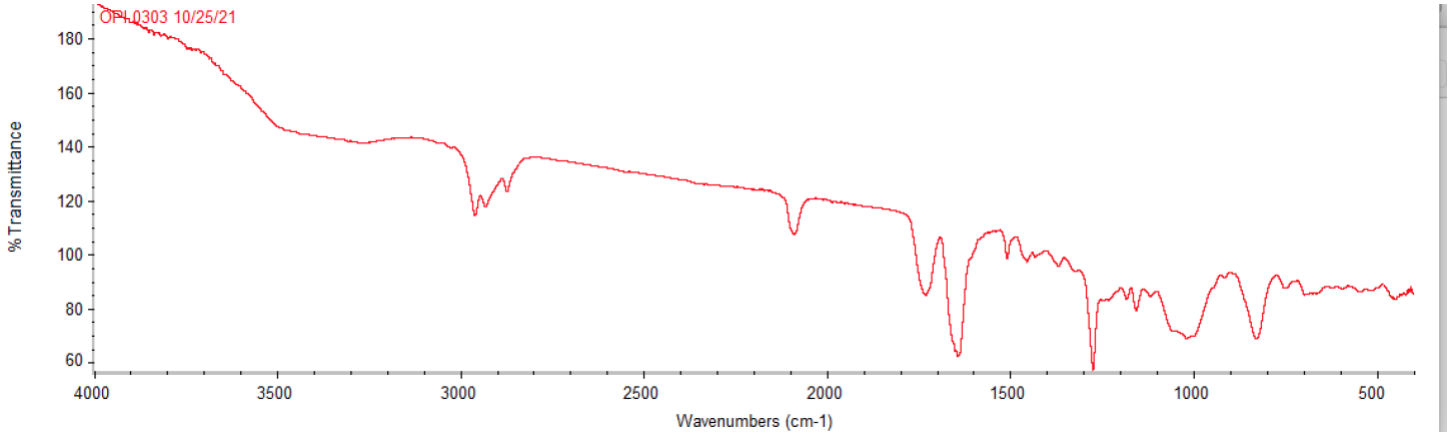
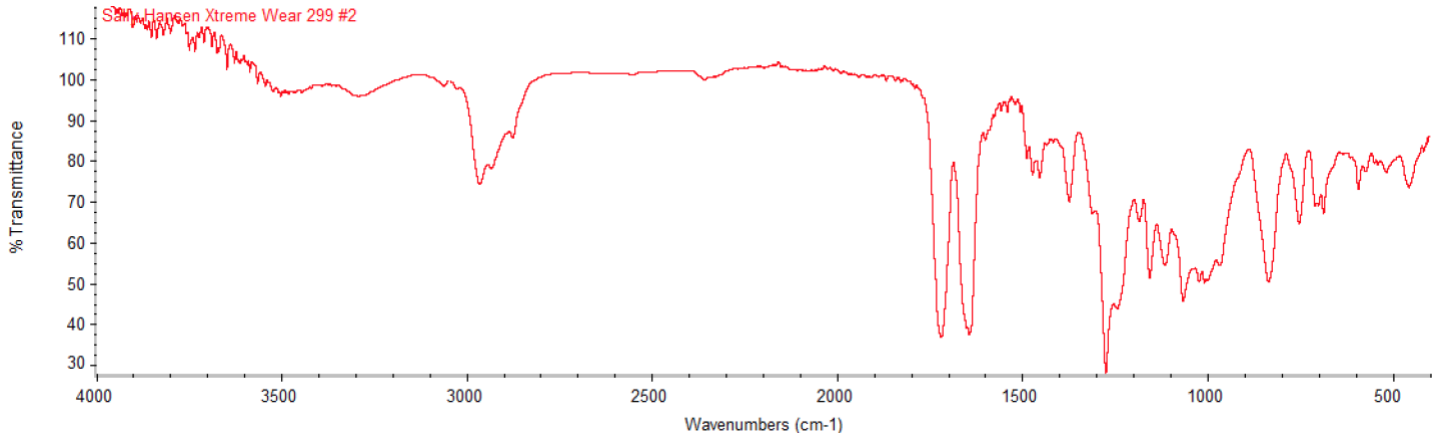


OPI #0303



SALLY HENSON #299



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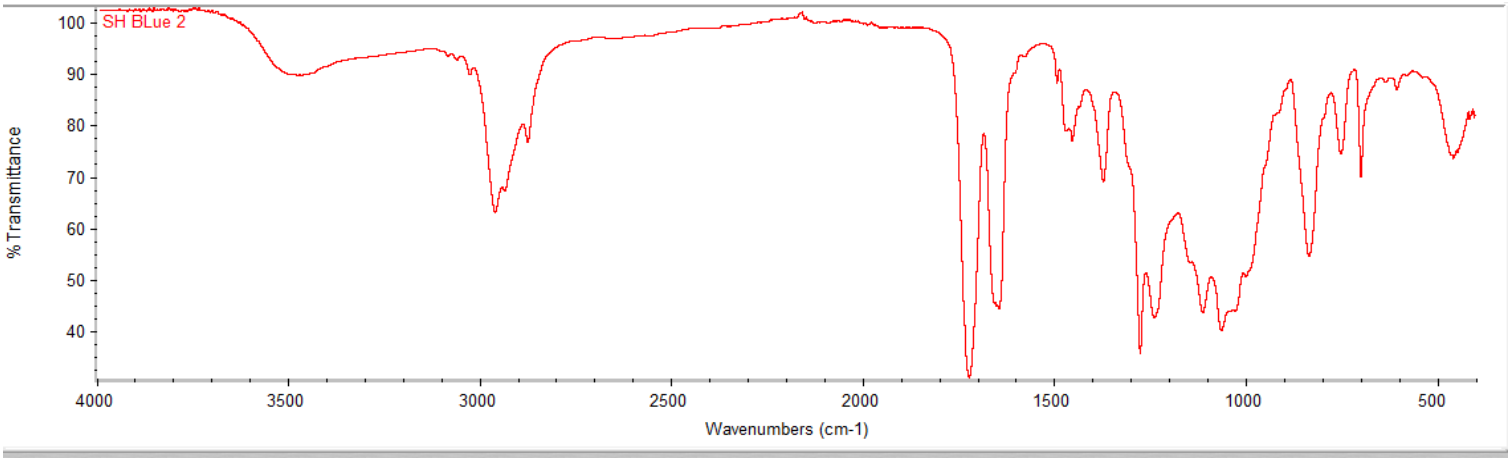
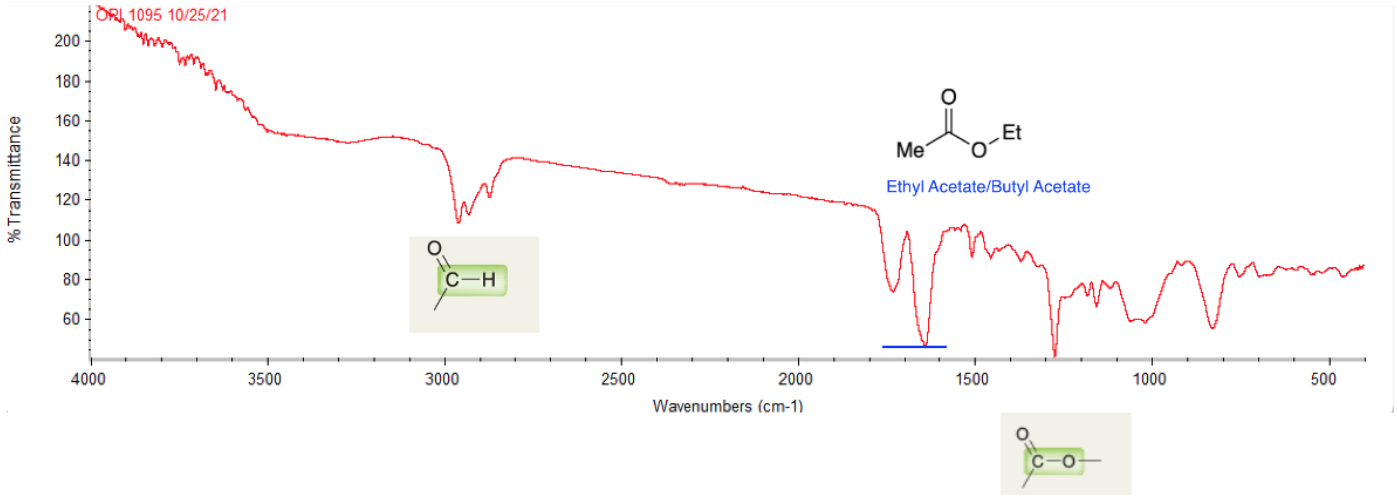
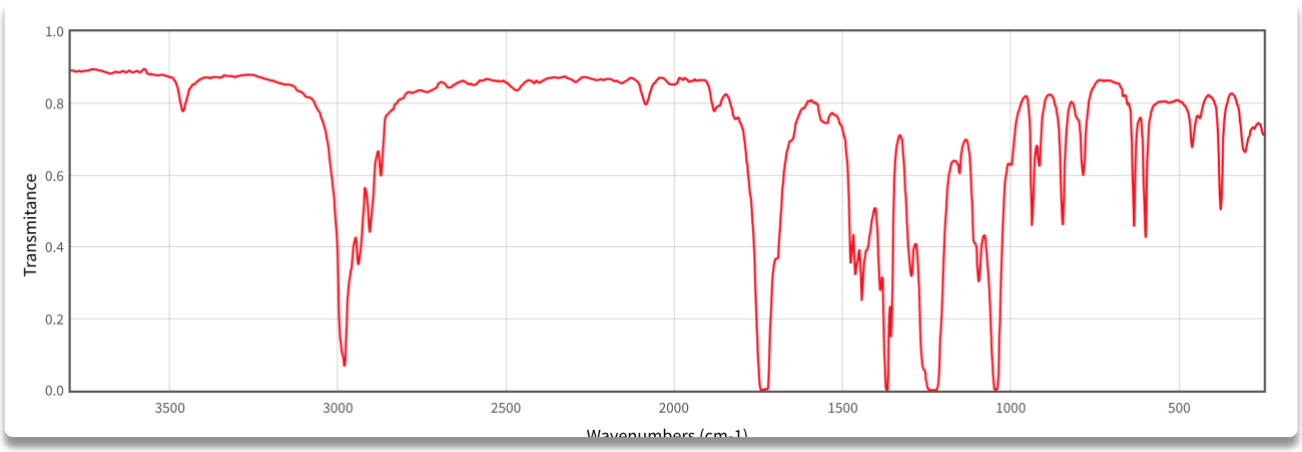


IR: 3000-2800 cm^{-1} (-COOH & =C-H stretch & C-H stretch & O=C-H stretch), 1700 – 1600 cm^{-1} (O=C-O stretch)

The spectra are all relatively similar. Revealing an aldehyde group at about 3000 cm^{-1} and an ether group at 1550 cm^{-1}. For the latter, that is mainly because of ethyl acetate and butyl acetate, which make up the majority of all nail polishes.



When examining the known IR of ethyl acetate, similar trends are observed:



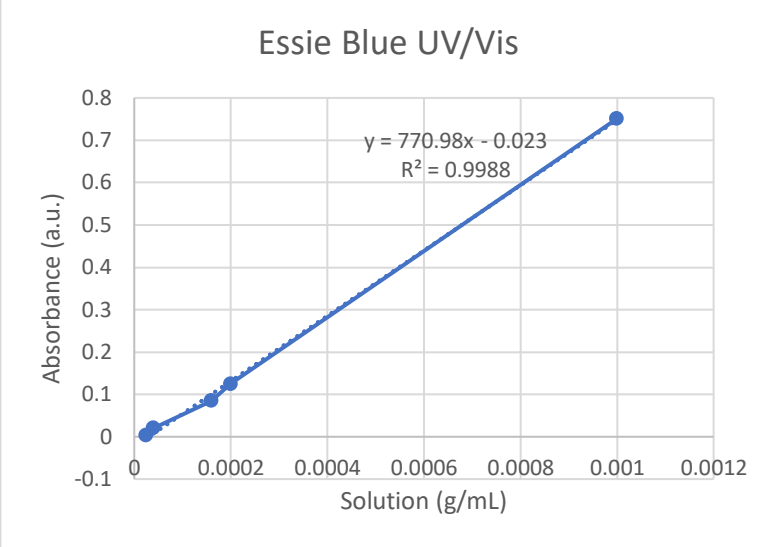
Source: https://webbook.nist.gov

When analyzing the IR spectra from literature, the same trends of the nail polish can be observed. Ethyl Acetate and butyl acetate are used as solvents in nail polish and make up roughly 70% of the makeup of nail polish. Then there are about 10 or more other compounds used. If more time and resources were available, a series of separations could be facilitated and each compound individually tested with ATR-FTIR spectroscopy. The amount of each compound would then be ascertained and a more detailed knowledge of each nail polish would be obtained. Unfortunately, in the day-to-day of forensics, time is a luxury.

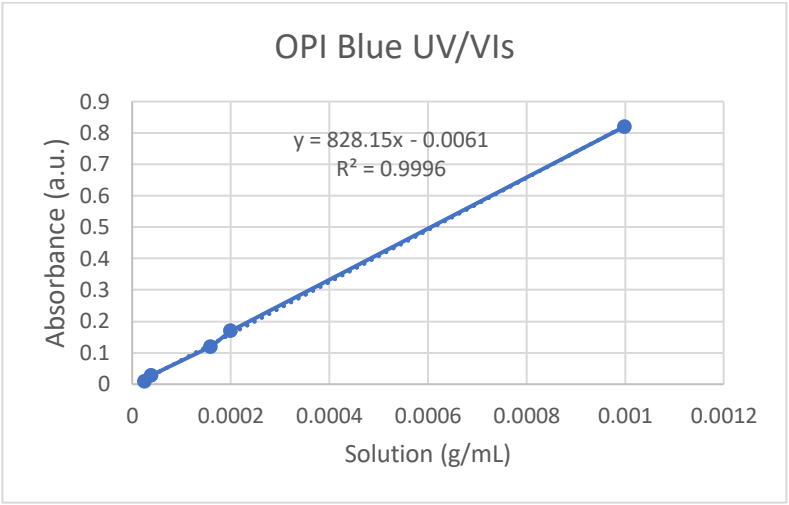
V. UV/Vis Spectroscopy

Several dilutions were made of the nail polish to create a calibration curve and the results were thus:

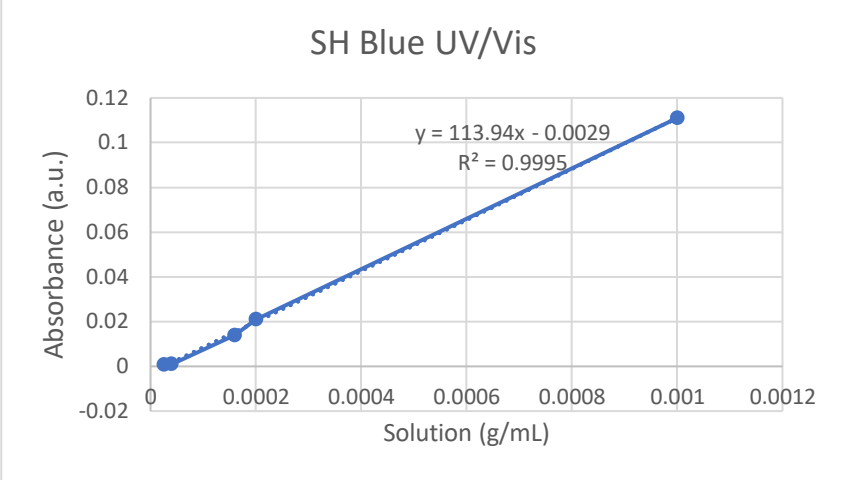
Wavelength	Solution (g/mL)	Absorbance (a.u.)
622.5	0.001	0.751
	0.0002	0.125
	0.00016	0.085
	0.00004	0.02
	0.0000256	0.003



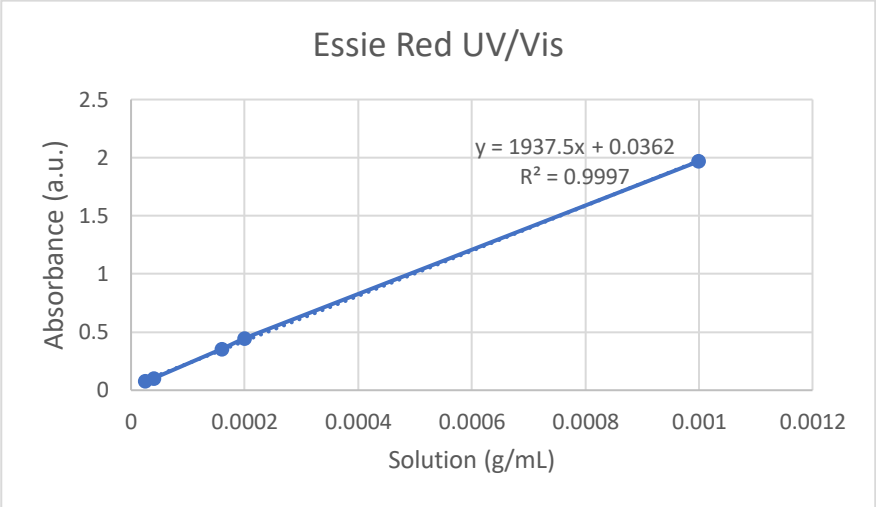
Wavelength	Solution (g/mL)	Absorbance (a.u.)
658	0.001	0.821
	0.0002	0.17
	0.00016	0.12
	0.00004	0.029
	0.0000256	0.01



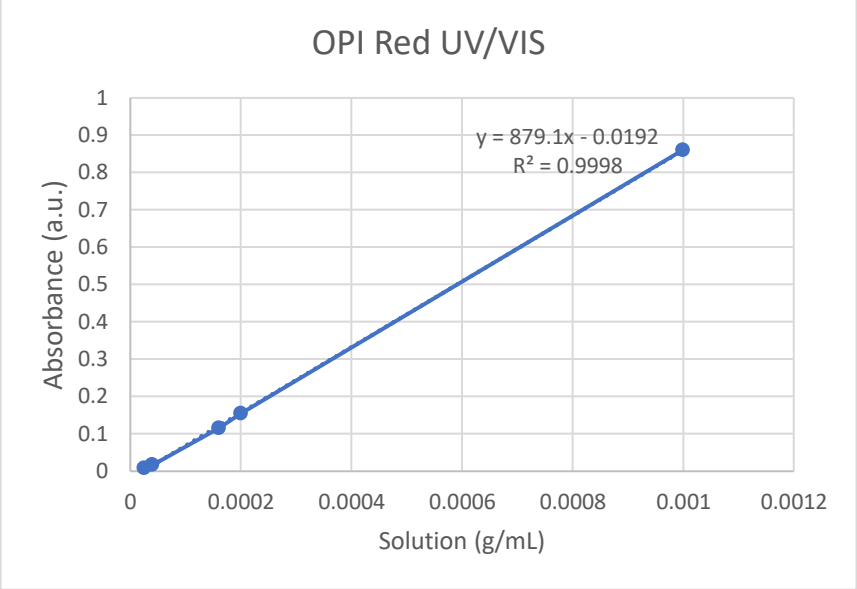
Wavelength	Solution (g/mL)	Absorbance (a.u.)
622	0.001	0.111
	0.0002	0.021
	0.00016	0.014
	0.00004	0.001
	0.0000256	0.0008



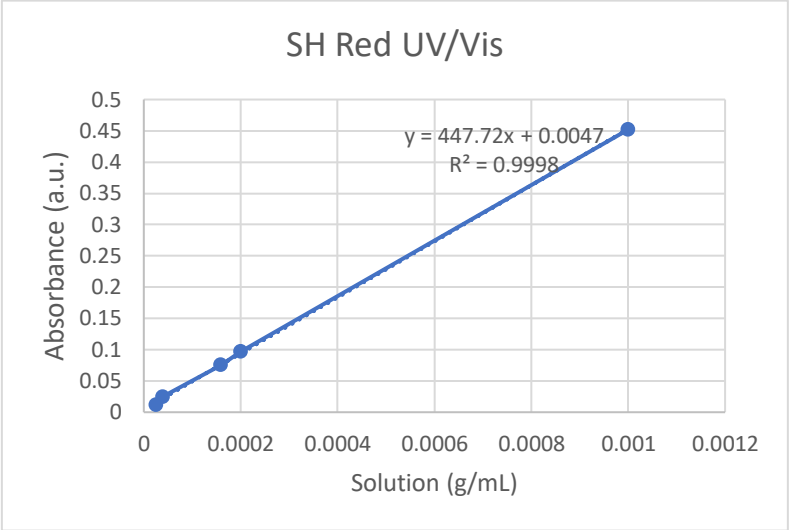
Wavelength	Solution (g/mL)	Absorbance (a.u.)
570	0.001	1.969
	0.0002	0.445
	0.00016	0.354
	0.00004	0.1
	0.0000256	0.075



Wavelength	Solution (g/mL)	Absorbance (a.u.)
547.5	0.001	0.861
	0.0002	0.155
	0.00016	0.115
	0.00004	0.017
	0.0000256	0.009



Wavelength	Solution (g/mL)	Absorbance (a.u.)
552.9	0.001	0.452
	0.0002	0.097
	0.00016	0.076
	0.00004	0.025
	0.0000256	0.012



UV/Vis spectroscopy is a great way for quantitative analysis. Unfortunately, when it comes to a substance that has a specific color that can be observed by the naked eye, it is not very helpful. However, if there was a substance that was being analyzed that is believed to contain nail polish, and the amount was trying to be determined, UV/Vis would be very helpful.

This analyzation can be done multiple times if there is enough trace evidence. The acetone was evaporated from the solution and the nail polish was back in dry form. The experiment was recreated by adding the acetone back in and obtaining the spectra. The data was gathered and although some nail polish was lost, the UV/Vis spectra was still obtained. For example, the Red OPI nail polish had an absorbance of 0.219 a.u. which concluded that there was about 0.00027 g/mL of nail polish in the solution which had begun at 0.001 g/mL. A loss of nail polish is not ideal in forensics, especially with trace evidence, but if there is enough, the data can be reexamined.

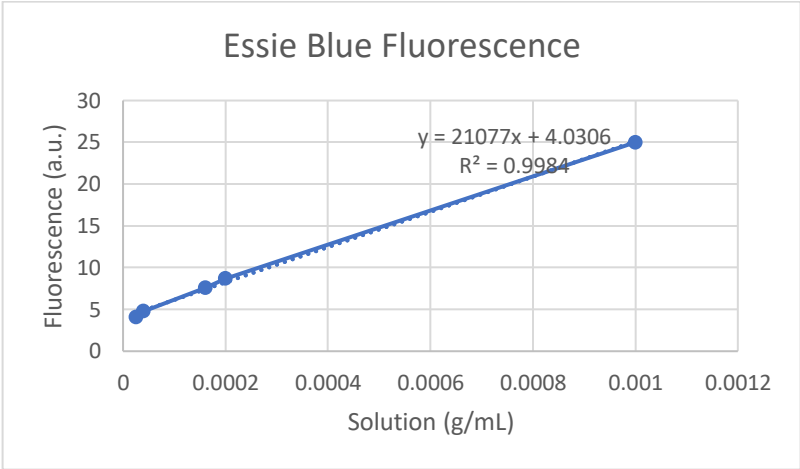
VI. Fluorometry

The settings for the fluorometer were:

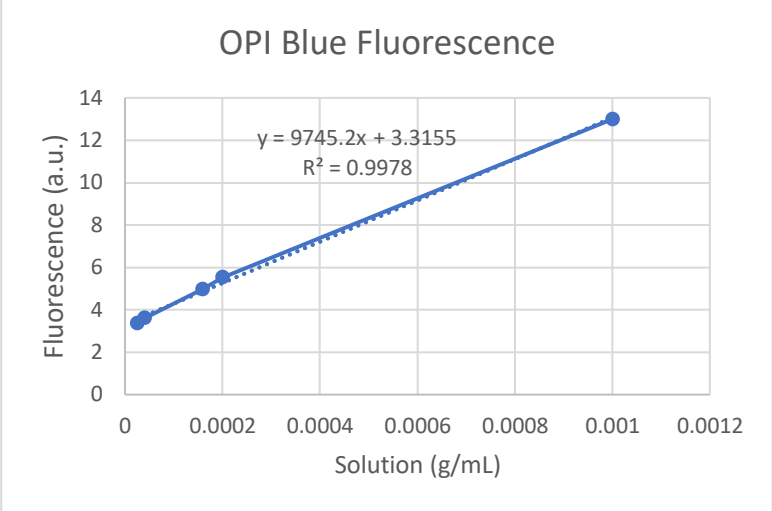
Wavelength: 680 – 750 nm

Excitation: 350

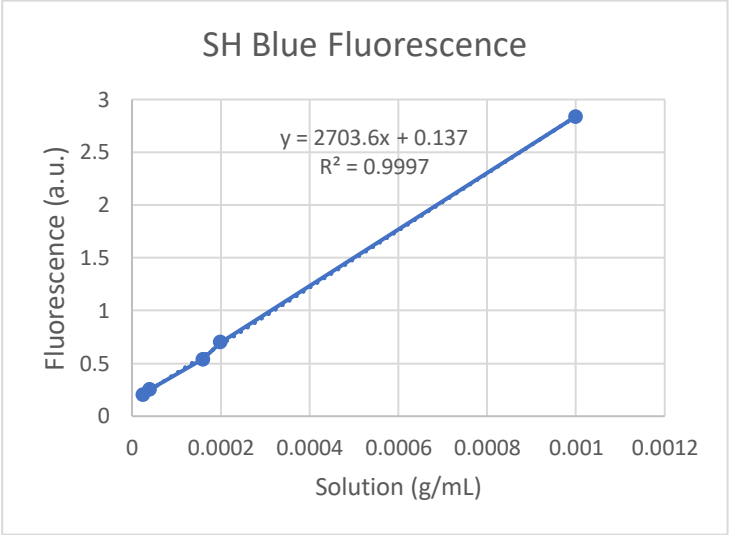
Wavelength	Solution (g/mL)	Fluorescence (a.u.)
703	0.001	25
	0.0002	8.7
	0.00016	7.6
	0.00004	4.8
	0.0000256	4.1



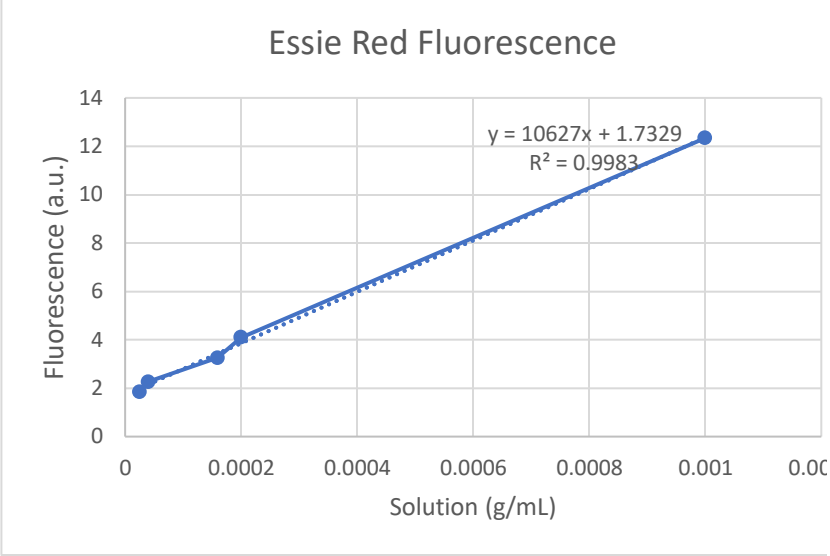
Wavelength	Solution (g/mL)	Fluorescence (a.u.)
702	0.001	13
	0.0002	5.53
	0.00016	4.98
	0.00004	3.61
	0.0000256	3.35



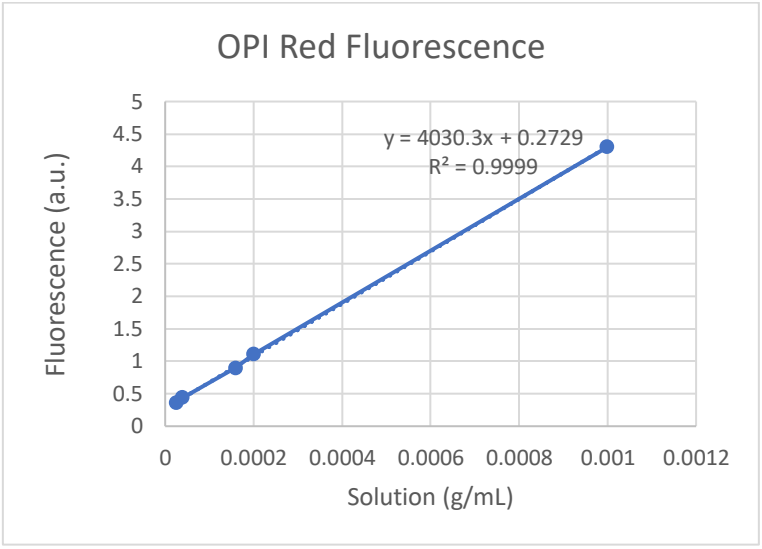
Wavelength	Solution (g/mL)	Fluorescence (a.u.)
702	0.001	2.84
	0.0002	0.702
	0.00016	0.541
	0.00004	0.252
	0.0000256	0.204



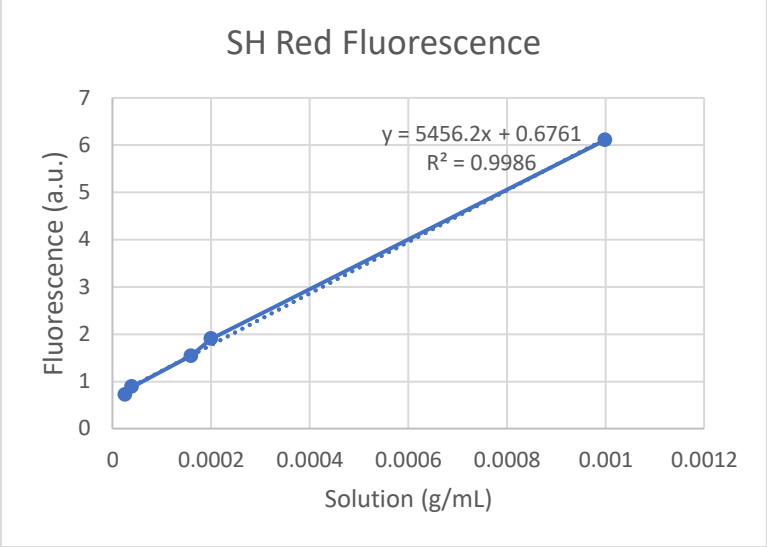
Wavelength	Solution (g/mL)	Fluorescence (a.u.)
702	0.001	12.34
	0.0002	4.1
	0.00016	3.255
	0.00004	2.27
	0.0000256	1.85



Wavelength	Solution (g/mL)	Fluorescence (a.u.)
702	0.001	4.3
	0.0002	1.11
	0.00016	0.9
	0.00004	0.44
	0.0000256	0.36



Wavelength	Solution (g/mL)	Fluorescence (a.u.)
703	0.001	6.11
	0.0002	1.9
	0.00016	1.54
	0.00004	0.886
	0.0000256	0.723



Fluorometry faces the same problems that UV/Vis spectroscopy does. They are both great forms to analyze quantitatively, but not qualitatively. However, a very interesting observation was made when using the fluorometer. The excitation was set to 350nm to analyze a range of 680-750 nm. Typically, the excitation should be much closer to the wavelength being examined, but when using higher wavelengths like 500 nm, there was no reading from the fluorometer.

The same extra step of evaporating the acetone and reintroducing it to the nail polish was done, just like with the UV/Vis spectra, but unfortunately the data was inconclusive. This shows that whatever was fluorescing in the nail polish originally was possibly tampered with when this extra step was done.

VII. Discussion and Conclusion

The initial intention of this research was to find a qualitative method to identify nail polish, but UV/Vis spectroscopy and fluorometry are much better suited for quantitative analysis when handling nail polish. If there is a solution that is suspected to have nail polish, these two methods

could be used to find the exact amount. Also, when the acetone was removed by evaporation, the UV/Vis results remained the same, but much of the nail polish was lost. Unfortunately, the fluorometry results did not come back as originally tested.

ATR-FTIR does have potential to analyze various nail polishes, but that would take more time and resources. There are over ten different compounds in nail polish. Time would allow the experiment to separate each compound and test individually and find the exact amount in each nail polish. However, in the forensic field, this is not a viable option because time is not necessarily an asset.

References:

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