Title: FTIR Analysis of Polymer Films, Edible Oils, HATE document, CBD, Vape oils, and Engine Oils.

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Submitted: November 5, 2019, Due Date: November 5, 2019 Section 3

Abstract:

Using Fourier-Transform Infrared spectroscopy, unknown films labeled as 1, 2, 3, 4 were found to be polytrimellitamide imide, polyester terephthalate, polypropylene atactic, and polycarbonate bisphenol A respectively. Three unknown brand films were analyzed and their compositions were found to be polyethylene with brand A having a thickness of 22.0 microns, brand B having a thickness of 19.0 microns and brand C having a thickness of 15.0 microns. Multiple samples of oils were analyzed using attenuated total reflection (ATR) including fish oil capsules, hemp oil, CBD oil, vape oils, canola oil, extra virgin olive oil, synthetic motor oil and conventional motor oils. Other than oils, paper samples were analyzed as well under ATR which required a slip clutch to put pressure onto these samples. The samples were plastic money with clear security stripes, and a HATE document with five suspect ink pens. The ATR determined that the pen that was used was either suspect pen 2 only or a combination of suspect pen 2 and suspect pen 4. A final sample that was analyzed was adulterated oil that was created by the laboratory manager where it was to be found that Linoleic Acid Methyl Ester was the suspect ingredient.

Keywords: Fourier-Transform Infrared spectroscopy, thickness, samples, oils, analyze, attenuated total reflection, ATR.

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I. Introduction

In this experiment, we used Fourier Transform Infrared (FT-IR) spectrometry to determine the composition of course supplied unknown polymer films, cooking oil (both used and unused), olive oil, fish oil capsules, adulterated olive oil, 2 engine oils (both synthetic and conventional), CBD, and vape oils. Using FT-IR, a hate document was analyzed and a suspect pen, out of five, was determined to be the hate document writer's pen of choice.

For my pre-laboratory report, Li et. al [1] used FT-IR to determine the effectiveness of synthesizing Dawsonite from . I also read two additional peer-reviewed journal articles that were published in 2019 and they are summarized together with my pre-laboratory report journal article in Table 1. The first additional article that I read was by Peng et al [2] where raw electroplating sludge and calcined electroplating sludge was used to determine the amount of Ni(2+) that was adsorbed from waste water. To do this, the sludge has alcohol groups and carboxylate anions where FT-IR was used to determine if Ni(2+) was adsorbed by looking at the peaks in the IR if they are changed. Peng et al concluded that both the RES and CES adsorbed more Nickel(2+) than commercially available adsorbents. The second additional article that I read was by Babu et al [3] where a clay-semiconductor system was synthesized by a $SnO_2/Bentonite$ coprecipitation method. To determine that if the clay-semiconductor system was created successfully, FTIR was used to determine the Sn-O bands. Babu et al concluded that the semiconductor that was deemed to be a low cost, eco-friendly, and an efficient photocatalyst.

Table 1. My refereed journal articles.

Corresponding Author	**Date Submitted**	**Date Accepted**	**Samples**	**My reference number**
Bing Li	August 4, 2019	October 14, 2019	Dawsonite standard and Dawsonite with varying Copper(II) concentrations	1
Guilong Peng	April 15, 2019	October 17, 2019	Raw electroplating Sludge (RES) and Calcined electroplating Sludge (CES) adsorping Ni(2+) from wastewater	2
Avius Tresa Babu	January 26, 2019	September 20, 2019	Clay-Semiconductors with Sn-O bonds embedded	3

From page 243-250 of the textbook [4], infrared spectroscopy is introduced. Infrared spectroscopy of interest happens between the wavelengths of 2 μm to 20 μm which includes part

of the Near-IR range and the whole of the mid-IR range. An equation helps determine the IR frequency from the IR wavelength range where

$$\lambda = \frac{c}{\nu} \qquad (1)$$

λ is the wavelength, c is the speed of light, and ν is the frequency. Using this equation, the relationship between wavelength and wavenumber can be stated to be

$$Wavelength\ (\mu m) * Wavenumber\ (cm^{-1}) = 10,000 \qquad (2)$$

where the wavelength is in microns and wavenumber is in inverse centimeters. For a molecule to absorb IR radiation, the molecule is required to have a change in **dipole moment** during its vibration. This correlates to polar bonds where one atom has a partial negative and the other is said to have a partial positive charge. There are two common types of vibrations that occur during the excitation process by IR, stretching and bending. Stretching changes bond lengths within the molecule, like a spring, while bending involves a change in bond angle or positional change for an atom or group of atoms compared to the rest of the molecule. If the molecule, under vibration, creates symmetric stretch then that molecule is said to be IR inactive. There are special cases to find the amount vibrational modes there are. For linear molecules, there are

$$3N - 5 \qquad (3)$$

and for non-linear there are

$$3N - 6 \qquad (4)$$

modes where both N correspond to the number of atoms within that molecule. Vibrational motion can also be determined from equations where

$$\nu = \frac{1}{2\pi}\sqrt{\frac{f}{\mu}} \qquad (5)$$

with ν is the frequency of vibration, f is the force constant of the spring, and μ is the reduced mass. The reduced mass is given to be

$$\mu = \frac{M_1 M_2}{M_1 + M_2} \qquad (6)$$

where M_1 is the mass of one vibrating body and M_2 is the mass of the other. Using equation 5, ν can be replaced with $\bar{\nu}$ which is the wavenumber of the absorption maximum in cm^{-1}. The equation becomes

$$\bar{\nu} = \frac{1}{2c\pi}\sqrt{\frac{f}{\mu}} \qquad (7)$$

where c is the speed of light, f is the force constant of the spring, μ is the reduced mass in grams. From pages 275-276 of the textbook [4], a separate method of is introduced called attenuated total reflectance where a crystal is used to determine the amount of light the sample can absorb while bouncing through. The ZnSe used has a Spectral Range of 15,000-650 cm^{-1} and has a refractive index of 2.4. If the sample does not absorb any of the light, then all of the light is reflected in the crystal, but if any is absorbed, the beam reduces in intensity at the locations where the sample absorbs. A final equation was used to determine the thickness of films from unknown brands that were analyzed. The equation is as follows:

$$t = \frac{n}{2} * \frac{1}{(\nu_1 - \nu_2)} \quad (8)$$

where t is the thickness in cm that is to be reported in microns, n is the number of bands counted between ν_1 and ν_2 that are the wavenumbers in inverse centimeters of the first and last peaks counted that is not within the polymer absorption bands.

II. Experimental

Equipment:

Instrumentation: ThermoFisher Nicolet iS10 FT-IR Spectrometer (Waltham, Massachusetts) equipped with transmission and attenuated total reflection (ZnSe crystal) sampling compartments. The instrument was controlled by Omnic Spectra Software by ThermoFisher (Waltham, Massachusetts).

Instrument operating parameters are summarized in Table 2.

Table 2. FT-IR Instrument operating parameters.

Parameter	**Value**
Resolution	4 cm^{-1}
Number of Scans	32
IR Scan Region	4000-400 cm^{-1}

Reagents: Spectro grade acetone

Samples: Course supplied unknown polymer films, cooking oil (both used and unused), olive oil, fish oil capsules, adulterated olive oil, 2 engine oils (both synthetic and conventional), CBD, Vape oils, HATE document, and several suspect ink pens.

Table 3 Summarizes the samples that were analyzed.

Table 3. Sample Inventory

Sample Description	**Manufacturer**
Extra Virgin Olive Oil	California
Extra Virgin Olive Oil	Colavita
CBD Oil 10mg	Garden Of Life

Table 3 cont. Sample Inventory

Sample Description	**Manufacturer**
Hemp Oil	Manitoba
Peachy Punch 0mg Nicotine	Keep It 100
Peachy Punch 5mg Nicotine	Keep It 100
Fish Oil Capsule	Kirkland
Fish Oil Capsule	Trunature
New Canola Oil	Wesson
Used Canola Oil	Wesson
Full Synthetic Oil	Mobil 1
Conventional Oil	Pennzoil

Brief Description of Procedure:

There were two weeks for this experiment using the Nicolet iS10 FT-IR spectrometer. The first week consisted of using the transmission device with the Nicolet iS10 spectrometer by taking background first, then a film was inserted into the transmission device which plotted the spectra on the computer subtracting the background which contains carbon dioxide and water vapor. The second week used the attenuated total reflection (ATR) with a ZnSe crystal module that passed a laser through the sample that was to be analyzed. The process involved both solids and liquid samples where a background was collected first, then the sample was placed over the laser that measured the absorbance through the sample. For a solid, a pressure was required to push the sample onto the crystal for the best result, but for a liquid, no pressure was needed since the liquid spread with the help of gravity that allowed for enough spread on the crystal to be analyzed.

III. Results

Figure 1 shows the IR spectrum of one of the unknown films in transmission device.

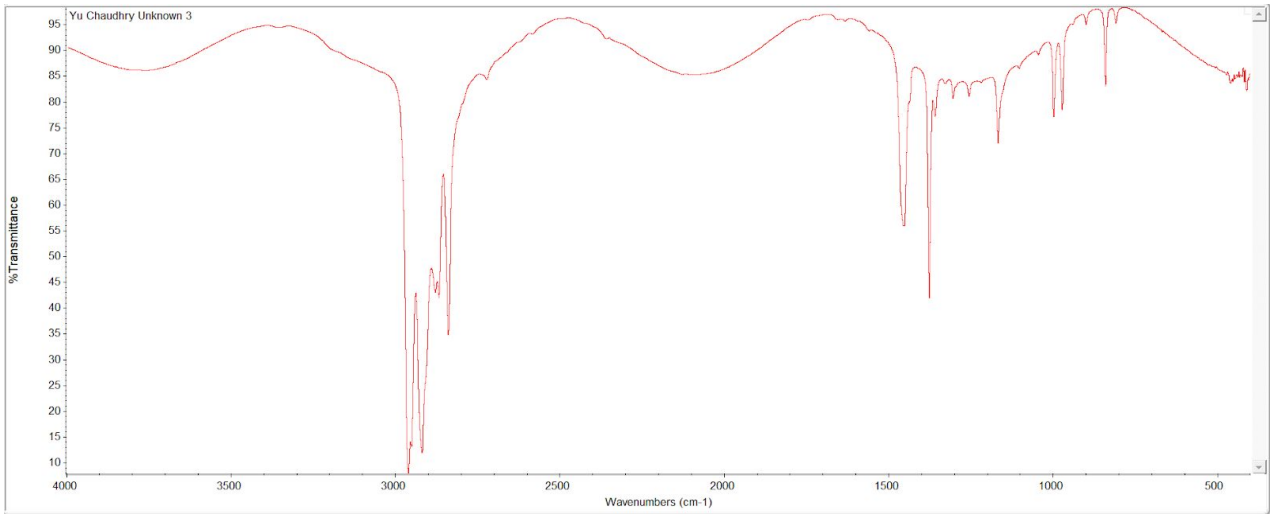

Figure 1. IR Spectrum of unknown 3.

Figure 2 shows the results of the library search for unknown 1 that I chose to illustrate searching a polymer library to identify unknowns.

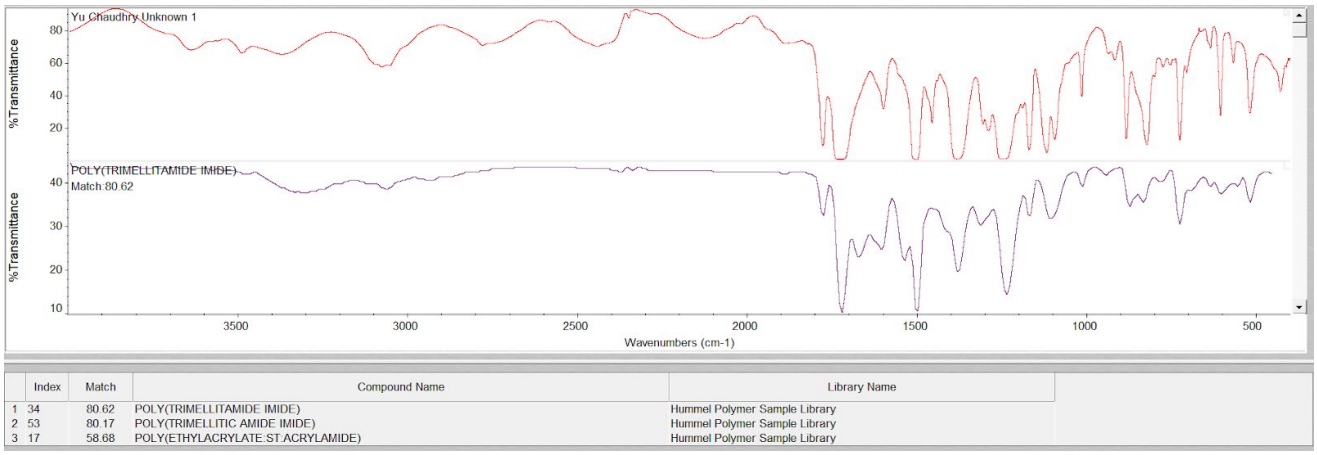

Figure 2. Screenshot of unknown polymer library search.

Table 4 summarizes the identity, for unknown polymer films, and thickness of the branded polymer films.

Table 4. Identity and thickness of unknown polymer films.

Sample ID	**Polymer**	**Thickness (microns)**
Unknown 1	POLY(TRIMELLITAMIDE IMIDE)	Not requested.
Unknown 2	POLYESTER, TEREPHTHALATE	Not requested.

Table 4 cont. Identity and thickness of unknown polymer films.

Sample ID	**Polymer**	**Thickness (microns)**
Unknown 3	POLY(PROPYLENE), ATACTIC	Not requested.
Unknown 4	Polycarbonate, Bisphenol A	Not requested.
Brand A	Poly(Ethylene)	22.0
Brand B	Poly(Ethylene)	19.0
Brand C	Poly(Ethylene)	15.0

Table 5 summarizes the identity of the plastic used in the plastic banknotes.

Table 5. Identity of the plastic used in the plastic banknotes.

Banknote	**Polymer (Clear)**	**Polymer (color)**
Mexico 20 Pesos	Poly(ethylene:propylene:diene)	Poly(ethylene:propylene:diene)
NZ 5 Dollar	Poly(ethylene:propylene:diene)	Poly(ethylene:propylene:diene)

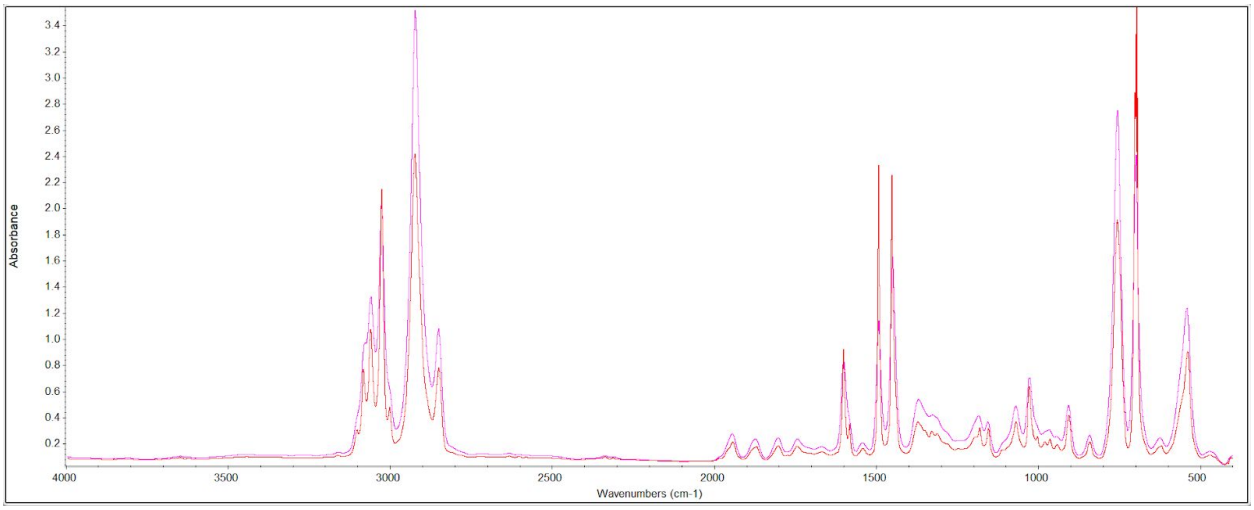

Figure 3. Comparison of resolution at 4 cm^{-1} vs 16 cm^{-1} for polystyrene film. Top spectra (pink) is the 4 cm^{-1} resolution and bottom spectra (red) is the 16 cm^{-1} resolution.

Based on the two plots, the 4 cm^{-1} has more bands than that of 16 cm^{-1} which could be much more useful in determining different bands in shorter areas since the 4 cm^{-1} resolution means a 2 cm^{-1} interval of acquiring data while 16 cm^{-1} is an interval of 8 cm^{-1} which can skip some of the

more minute details within the spectra. With 16 cm^{-1} , the spectra that is acquired has sharper bands, but with 4 cm^{-1} , the bands acquired are less sharp.

Figure 4 compares the IR spectra of the three different brands of polyethylene polymer films.

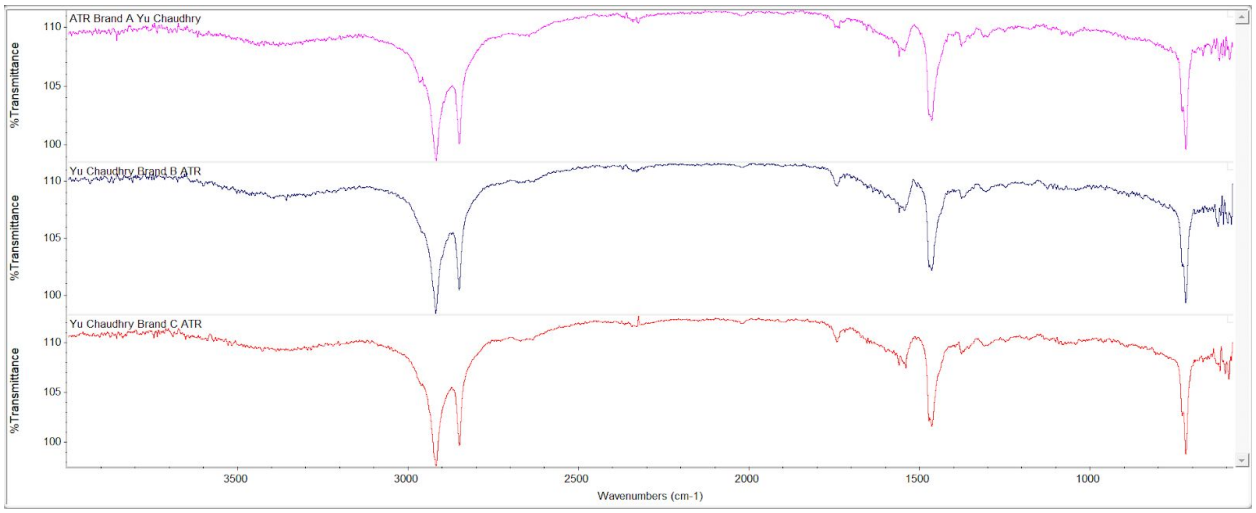

Figure 4. IR Spectra of polyethylene polymer films from brands A, B, and C under ATR conditions.

Figure 5 compares the IR spectra of the adulterated olive oil with that of virgin olive oil. From the IR spectra of the oils that I analyzed, the adulterated olive oil contains Linoleic Acid Methyl Ester, or this and a combination of other oils such as vegetable oil.

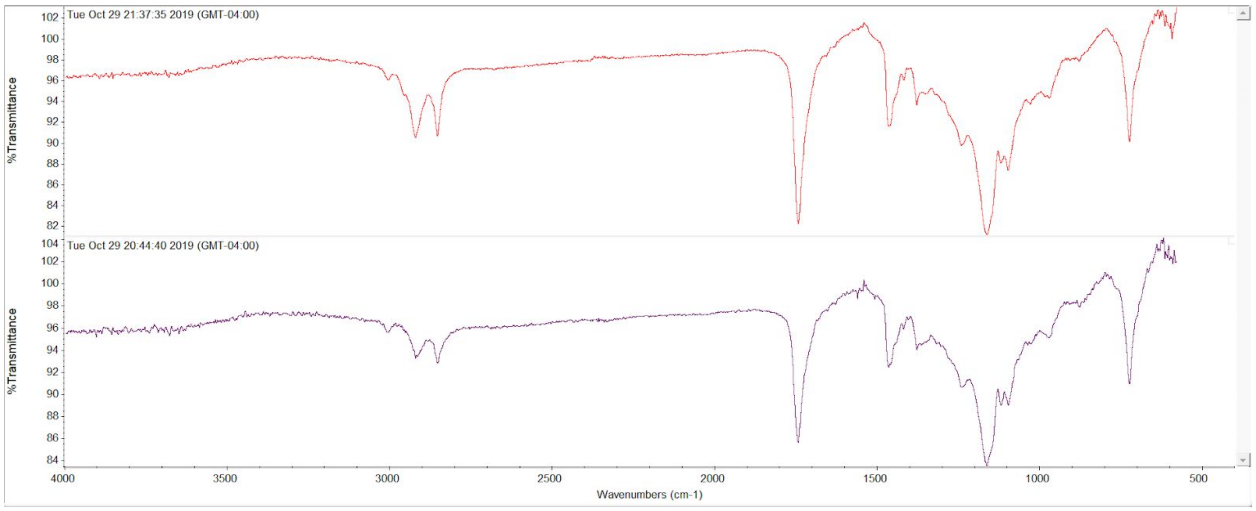

Figure 5. IR spectra of adulterated and extra virgin olive oil. Top one is adulterated olive oil and the bottom is Colavita extra virgin olive oil.

Figure 6 compares the IR spectra between the vape oil with and without nicotine.

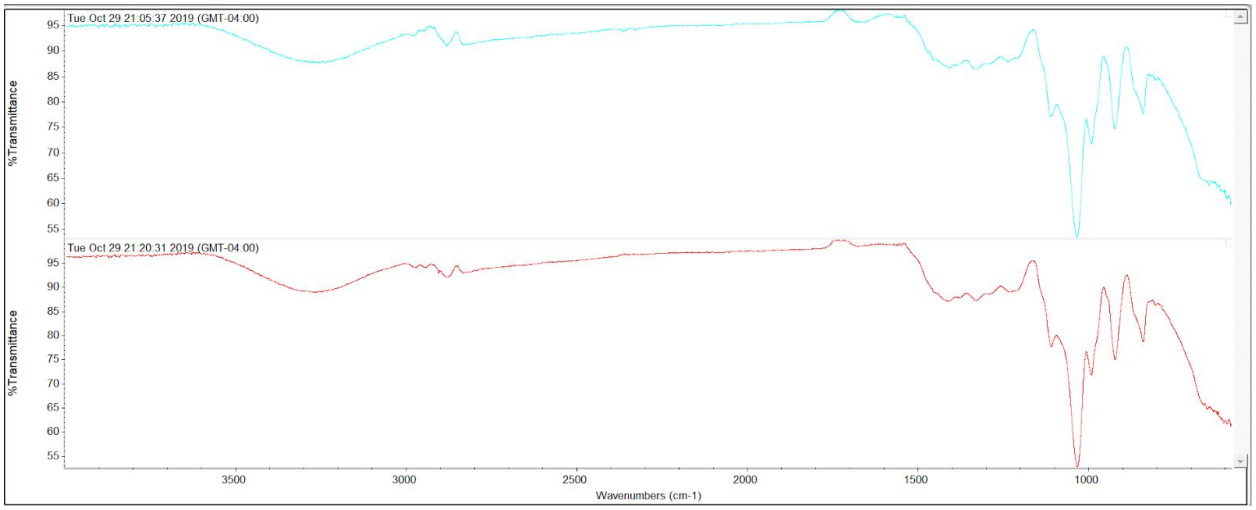

Figure 6. Comparison of vape oils, top is 0mg Nicotine and the second has 5mg Nicotine which both are from Keep It 100.

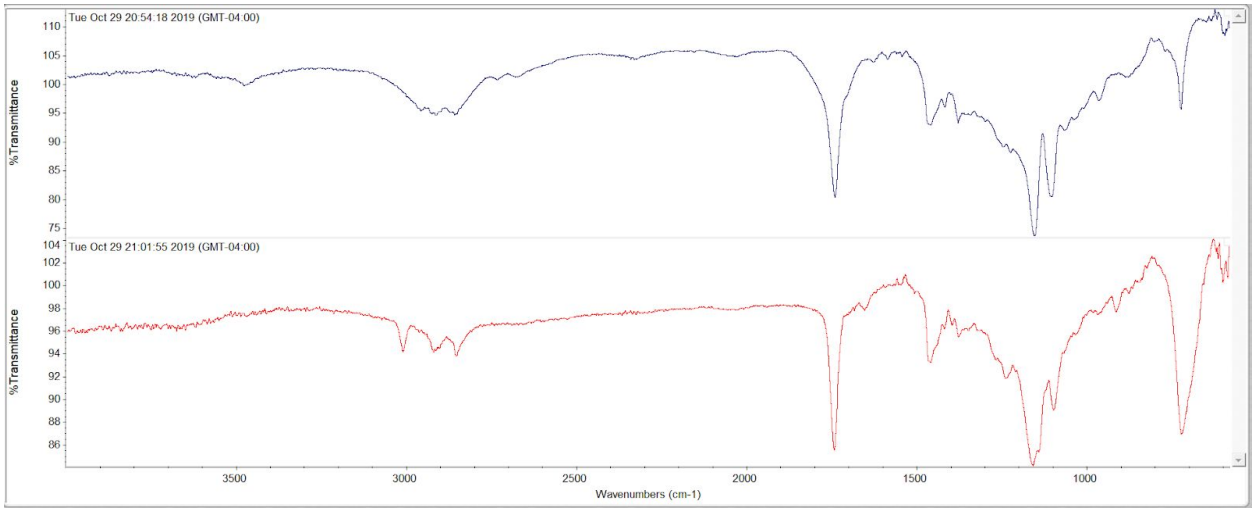

Figure 7. Comparison of CBD and Hemp oil. Top is 10mg CBD from Garden of Life and bottom is Hemp oil from Manitoba.

Between the CBD oil and Hemp oil, to tell the difference between each other, in the structure of THC, there is an ether compared to that of CBD which has an alcohol where the ether group should be. The ether bands happen around 1250-1050 cm^{-1} and the alcohol band happens around 3600-3200 cm^{-1} .

Table 6 Summarizes the major components in the oil samples.

Table 6. Major chemical compounds in oil samples

Sample	**Chemical Compound**
Kirkland Fish Oil Capsule	Linoleic Acid Methyl Ester
Trunature Fish Oil Capsule	Linoleic Acid Methyl Ester
Keep It 100 Peachy Punch 0mg Nicotine Vape Oil	Glycerol
Keep It 100 Peachy Punch 5mg Nicotine Vape Oil	Glycerol
Manitoba Hemp Oil	Linoleic Acid Methyl Ester
Garden Of Life 10mg CBD Oil	Methacrylic acid, isobutyl ester
California Extra Virgin Olive Oil	Linoleic Acid Methyl Ester
Colavita Extra Virgin Olive Oil	Linoleic Acid Methyl Ester
Adulterated Olive Oil	Linoleic Acid Methyl Ester
Canola Oil	Oleic Acid
Mobil 1 Synthetic Oil	Poly(ethylene:propylene)
Pennzoil Conventional Oil	Poly(ethylene:propylene)

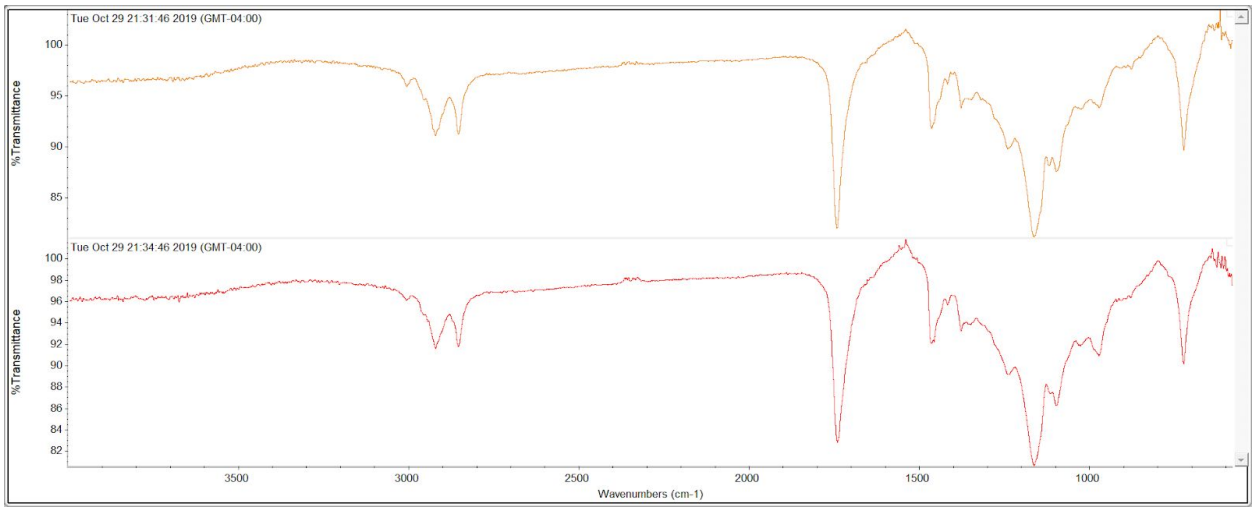

Figure 8. IR spectra of used and new cooking oil. Top is new Wesson cooking oil and bottom is used Wesson cooking oil.

Figure 9 compares the spectra of polyester, terephthalate polymer film collected in transmission mode vs. that collected in the ATR (attenuated total reflection) mode.

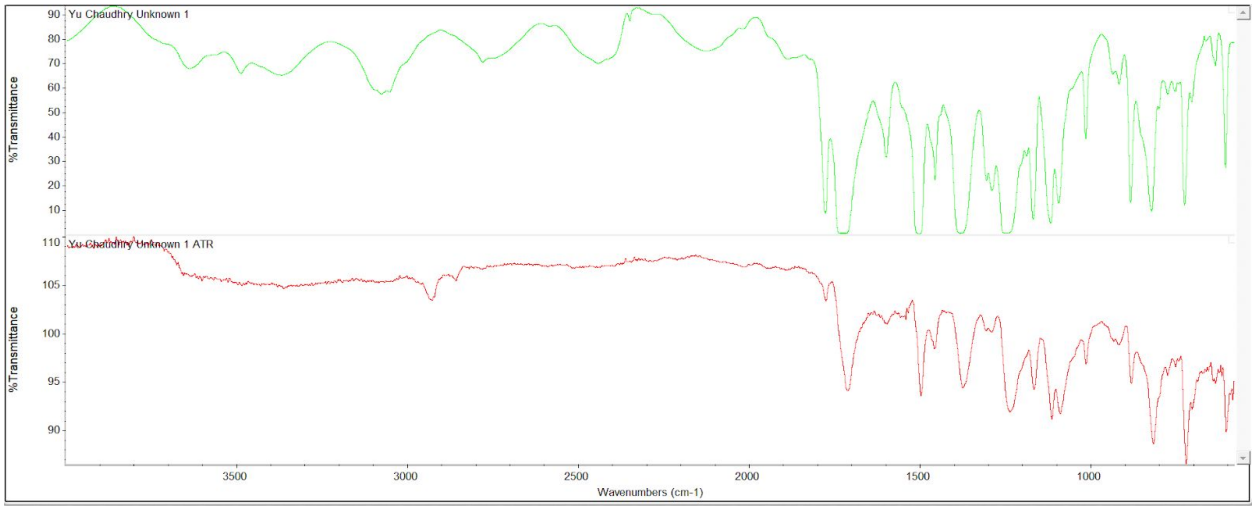

Figure 9. IR spectra of polyester, terephthalate polymer film in transmission and ATR mode. Top is film under transmission conditions and bottom is film under ATR conditions.

Figure 10 compares the IR spectrum of the HATE document compared to the suspect pen ink. The background chosen was the background of the paper since the ink that was measured was on something that was not sought after. Based on the subtraction of the HATE document spectra and each pen ink's spectra, pen 2 was determined to be the suspect. This doesn't correlate with what was actually observed on the HATE document. The HATE document was gray/black in color while pen 2 was blue in color. Going off observations, the next best subtraction that was yielded was pen 4 and that matches with the color observed on the paper. Using the two subtractions, another possibility could have been that there was more than one pen involved, which could mean that since pen 2 gave a great subtraction and pen 4 was the second best for the subtraction, these two pens could have been used together to create the HATE document.

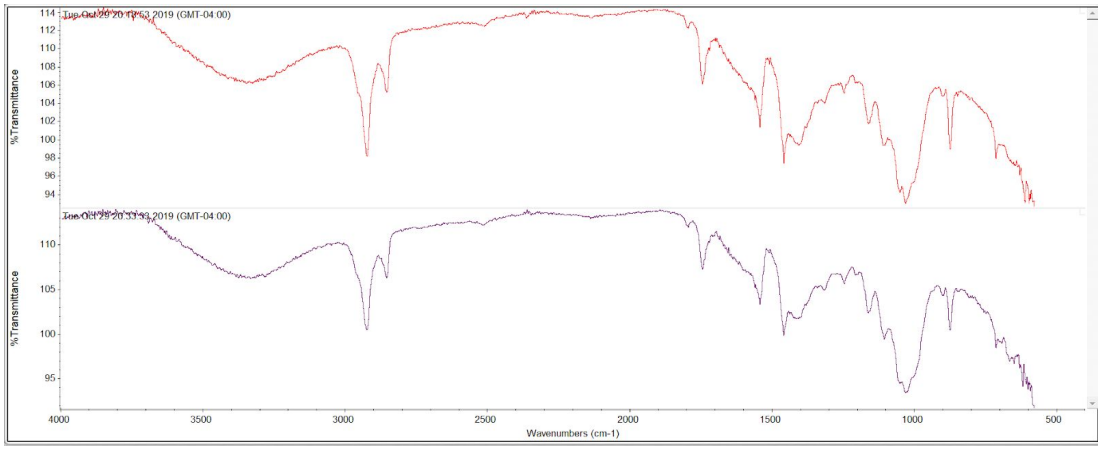

Figure 10. IR spectra of HATE document ink vs suspect pen ink. Top is HATE document and bottom is suspect pen 4 ink.

Figure 11 is the IR spectrum of Keep It 100 Vape oil showing band assignments (functional groups) of the major compounds in Keep It 100 Vape oil.

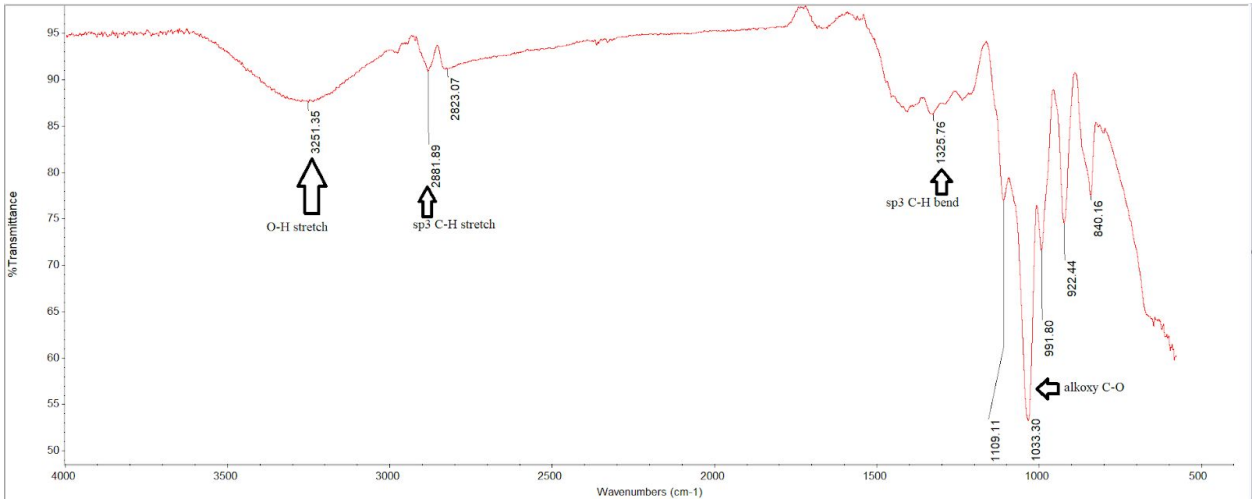

Figure 11. IR spectrum of Keep It 100 Vape oil with band assignments.

IV. Conclusions

From the spectra that was acquired during the experiment, the three unknown brands of polymer film was found to be polyethylene based on a library search. The library search had a match percentage on all three to about 93% accuracy. The thickness of Brand A was calculated to be 22.0 microns, Brand B was 19.0 microns, and Brand C was 15.0 microns. This displayed that all three of the brands, if they are all different are not made the same, and if all three brands are the same, then the films aren't made to a standard, but to an error margin. From the spectra of all three, around the 1575 cm^{-1} range for all three, Brand C has two bands there about the same height while Brand A has a brand that is larger than the adjacent bands in the region.

From Library searches, the fish capsules, Kirkland and Trunature, were found to contain Linoleic Acid Methyl Ester as a major compound. The Keep It 100 Peachy Punch vape oils were found to contain glycerol as a major compound and the Manitoba hemp oil was found to contain linoleic acid methyl ester. In the Garden of Life CBD oil, methacrylic acid, isobutyl was found to the major component. Both extra virgin olive oils, from California and Colavita, was found to contain Linoleic Acid Methyl Ester as a major compound whereas the adulterated olive oil contained linoleic acid methyl ester, or a combination of multiple other seed oils. Canola oil was found to have oleic acid and both the synthetic oil and conventional oil contained poly(ethylene:propylene).

In the used and new cooking oil spectra in Figure 5, the used cooking oil has bands that seem weaker than the bands from the new cooking oil. An example band is a display of two bands around the 2900 cm^{-1} region where in the used oil spectra, the bands are shorter than that

of the ones in the new oil spectra. Another band that could be shown to be weaker is around the 1700 cm^{-1} region where again the used oil spectra is shorter with a % transmittance about 86 than that of the new oil with a % transmittance of 82.

V. References

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