The Exploration of Spectroscopic and Physical Sorting Techniques to Sort Plastic Recycling

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This work is dedicated to my parents, who raised me to work hard and to care for the environment. I hope that I will be able instill such care in others as we all do our part to fight climate change.

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List of Abbreviations and Symbols

ATR	attenuated total reflectance
CAD	computer aided design
cm^{-1}	wavenumber
CPVC	chlorinated polyvinyl chloride
EPS	expanded polystyrene
FTIR	Fourier Transform infrared spectroscopy
g/cm^3	grams per cubic centimeter (density unit)
GPPS	general-purpose polystyrene
HDPE	high-density polyethylene
HIPS	high-impact polystyrene
HIS	hyperspectral imaging
ICI	industrial, commercial, and institutional
LDPE	low-density polyethylene
LLDPE	linear low-density polyethylene
mL	milliliters
MSW	municipal solid waste
NIR	near infrared reflectance spectroscopy
nm	nanometer
PE	polyethylene
PEI	Prince Edward Island
PET	polyethylene terephthalate

PP	polypropylene
PS	polystyrene
PVC	polyvinyl chloride
PVC-M	modified polyvinyl chloride
PVC-O	molecular oriented polyvinyl chloride
PVC-P	plasticized polyvinyl chloride
QCM	quick compare method
RGB	red, green, blue
RIC	resin identification code
UPVC	unplasticized polyvinyl chloride
µm	micrometer

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Abstract

Plastic consumption has skyrocketed in recent decades, but the development of disposal and recycling of these products has not kept pace. The biggest challenge to recycling plastic products is the inability to efficiently sort them. Six different types of plastics are commonly recycled and since they are mostly incompatible with one another they need to be accurately sorted.

In recent years, researchers have begun to explore the use of spectroscopic instruments to sort these plastics. Fourier transform infrared spectroscopy and Raman spectroscopy were used to see how well a variety of household plastic waste could be sorted. Parameters such as colours, labelling, instrument resolution, and spectral region were considered. Raman was only able to identify some of the plastic types but could identify through the label, whereas FTIR was able to identify all the plastic types but was unable to identify plastics through the label.

A physical sorting technique was also explored. The sink-float tank was able to sort plastics into two categories based on their densities and the density of the sorting medium. Polyethylene terephthalate and polyvinyl chloride always sank, high- and low-density polyethylene and polypropylene always floated and polystyrene sank or floated depending on the density of the medium used.

Chapter 1 Introduction

1.1 Background

The world's industrialization has meant that global consumption of plastic has dramatically increased in recent years. Once these plastics, much of which is single-use plastic such as packaging, reach the end of their life, they are discarded, creating enormous amounts of plastic-related waste. In 2019, 1.810 million tonnes of plastic were sent to Canadian landfills, compared to the estimated 0.215 million tonnes recycled. [1] The carelessness with which these plastics are thrown away has led to many issues worldwide. The Great Pacific Garbage Patch is arguably the most well-known collection of waste, but landfills worldwide are filling up alarmingly quickly. An additional unintended side-effect to full landfills is the possibility of groundwater contamination. About 1% of the plastic waste leaks into the environment every year in Canada. [1]

To begin remedying this situation, it is vital to understand the current waste management systems. Municipal solid waste (MSW) is the technical term for "waste generated by the residential and industrial, commercial, and institutional (ICI) sources." [2] MSW includes organics, waste, and recycling. Waste is collected in three different ways: source separation, single-stream, and no separation. Prince Edward Island employs a source separation system with three streams: compost, waste, and recycling. On Prince Edward Island, plastics are sorted and sent off-island for further processing, incinerated for waste-to-energy recovery, or sent to the landfill. [3]

A few other key statistics must be presented to accurately portray the Canadian and Prince Edward Island waste and recycling landscape. Canada produced 34 million tonnes of MSW in 2016. Of that 34 million tonnes, 9 million tonnes (27%) were diverted for recycling and composting. The remaining 73%, 25 million tonnes, was sent to landfills or incineration facilities. [4] For plastic waste, only 9% was recycled, and 4% was incinerated, leaving 87% in landfills. [1] In PEI, 56,795 tonnes of MSW were diverted from landfills in 2018. Organics (20,445 tonnes), paper fibres (12,214 tonnes), and various metal products (12,992 tonnes) were the largest sectors diverted. Comparatively, 939 tonnes of plastics were recycled. That represents only 1.7% of the waste diverted in the province. [5]

1.2 Challenges of Recycling

Plastics are part of daily life and will not soon be eliminated. Therefore, to continue living a similar lifestyle, the world needs to transition to a circular economy. Two parts of a circular economy are relevant to this project: the development of more efficient sorting of plastic recycling and the innovation of cost-effective ways to reuse the sorted plastics so they do not end up in landfills. There are five waste management pathways for plastics: upgrading, closed-loop recycling, downgrading, waste-to-energy, and dumping. [6]

Currently, there are three main challenges to the recycling of plastics. First of all, plastic product designs can be incompatible. Plastics are modified with fillers and additives, such as plasticizers, to improve product flexibility and colour dyes to suit the manufacturers' specifications. The variety of these modifications makes it difficult to sort the plastics in recycling plants and challenging to reuse since the additives might not be compatible with one another. [6]

The second challenge is to maintain and guarantee the purity and quality of the plastic. Contaminants such as food smells, inorganic contaminants, or other types of plastics can ruin the quality and purity of large volumes of plastic. [6] For example, polyethylene needs to be 97% pure to maintain structural integrity in new products. [7] A batch of polyethylene terephthalate can be ruined by 50 ppm of polyvinyl chloride. [8] Additionally, every time a plastic is reprocessed, it deteriorates; therefore, a many-time recycled piece of plastic will eventually lose its structural integrity, and the quality of a batch of recycled plastic cannot be guaranteed. [6]

The economics of recycling represents the third challenge. When oil prices are low, it is more affordable for companies to buy virgin plastics. Even when the prices are comparable, virgin plastic can guarantee a quality that recycled plastics cannot beat. There are also problems of supply and demand. Since virgin plastic is more commonly purchased, there is less demand for recycled plastic, leading to less plastic being correctly sorted for recycling purposes. Finally, the cost of repurposing used plastics is greater since collection, cleaning, and sorting must be added to the manufacturing costs. [6]

Recycling systems commonly use manual sorting processes, which are inefficient and labour intensive. Given that the job is physically gruelling and low-paying, it is not easy to maintain a skilled workforce. A high turnover can significantly slow down the productivity of a sorting facility.

1.3 Plastics

After addressing the challenge posed to recycling systems, one must also understand the intricacies of the plastics to be recycled and how they are identified. A plastic refers to a product made from a polymer through various methods ranging from injection moulding to thermoforming. Polymers are referred to as plastic resins in the plastic industry, and the terms will be used interchangeably in this paper. The molecular weight and length of the polymer chain is determined by the manufacturing method and polymerization conditions. [9]

1.3.1 Thermoplastics vs Thermosets

Plastics can be divided into two categories: thermoplastics and thermosets. The main difference between thermoplastics and thermosets is that thermoplastics are recyclable, and thermosets are not. Thermoplastics can be amorphous or semi-crystalline. They can be melted, re-shaped, and hardened to create a new product. Thermoplastics are typically linear polymers and are usually made through addition polymerization. The crystallinity of the structure is what gives thermoplastics their strength. Conversely, thermosets have cross-linked structures, which means that once the product has been set, it cannot be reheated and shaped into a new design. Thermosets are usually network polymers characterized by their cross-linking. Thermosets also do not have discrete molecular weights; their size is instead measured by cross-linking density which is also the source of their strength. Thermoplastics are more often used in packaging and consumer plastics due to their ease of production, whereas thermosets are used in construction as adhesives and coatings. [9]

1.3.2 Addition and Condensation Polymerizations

There are primarily two ways to form polymers through addition or condensation polymerizations. Addition polymers, also known as chain-growth polymers, are formed by adding monomers to the reactive end of a growing chain. The reactive end can be a radical, a cation or an anion, and there are three phases to the polymerization: initiation, propagation, and termination. [10]

Condensation polymers are also known as step-growth polymers. In this type of polymerization, a small molecule such as H_2O, alcohol, or HCl is lost when the functional groups react. The polymerization occurs between two different bifunctional monomers. One monomer has two functional groups A, and the other has two functional groups B. The A and B functional groups condense and form a dimer. Monomers and short chains continue to react in no specific order. High concentrations of monomers are required to prevent the premature termination of polymerization through the formation of cyclic molecules. Very high yields are required to obtain the desired long-chain polymers. [10]

1.3.3 Resin Identification Codes

In 1988, the US Society of the Plastic Industry developed the Resin Identification Codes (RIC) to identify the type of plastic a product was made of. The RIC divides plastics into seven numbered categories. The RIC symbols have been the category number surrounded by a triangle of chasing arrows. [11] The symbol has changed to an equilateral triangle surrounding the category number. Numbers one through six each represent a single type of plastic resin. RIC #1 corresponds to polyethylene terephthalate (PET), high-density polyethylene (HDPE) is RIC #2, polyvinyl chloride (PVC) is RIC #3, low-density polyethylene (LDPE) is RIC #4, polypropylene (PP) is RIC #5, and polystyrene (PS) is RIC #6 (Figure 1.1). The seventh category, represented by the number 7, is a catch-all category for many other types of plastics and products that contain a mixture of plastics.[11] RIC #7 includes a variety of lesser-used plastics such as polylactic acid (PLA), acrylonitrile butadiene styrene (ABS), and polycaprolactone (PCL). Products such as Ziplock bags contain a mixture of plastics, so they would also be in that category. So-called biodegradable plastics have RIC #7 because they often require specific composting processes and would contaminate the plastic recycling stream. [12]

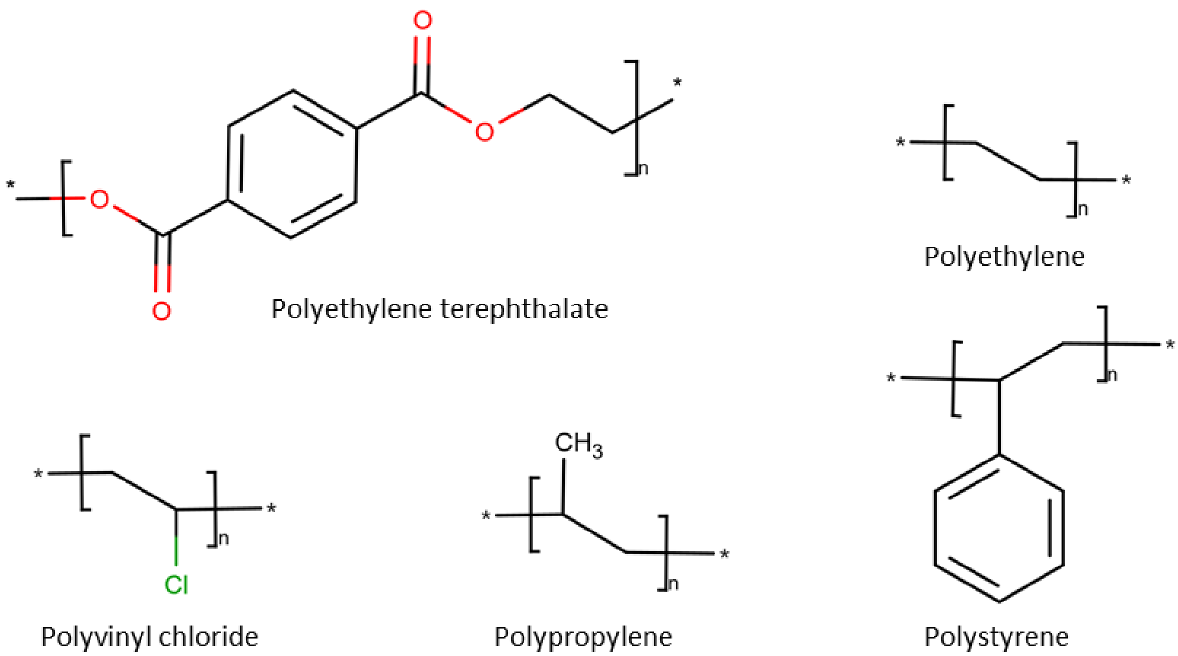

Figure 1.1 Structures of plastic resins

Contrary to popular belief, the RIC system only identifies the type of plastic; it does not indicate which plastics are recyclable. [11] In reality, the common term "recycling number" is a misnomer. That being said, typically, the lower the RIC number, the easier and more commonly recycled the plastic. [1] In Canada, municipalities or private corporations are responsible for the collection, diversion and disposal of MSW, provinces and territories create waste reduction policies and monitor the waste management facilities, and the federal government manages the movement of hazardous materials across provincial and national borders. [13]

1.3.4 Polyethylene Terephthalate

PET is a thermoplastic polyester known by its brand names Dacron or Mylar when referring to the film form. [10] It is distinguishable from its thermoset counterpart because it is saturated, whereas the thermoset is unsaturated-polyester. This polymer is formed through the condensation polymerization of dimethyl terephthalate and ethylene glycol and has a density of

1.300-1.400 g/cm^3. [9,14] PET has high crystallinity and clarity and is used to make drink bottles, clear hard packaging, and fruit containers. PET is also a polyester widely used as a fibre to make synthetic clothing. [9]

Between 25% and 30% of PET collected in Canada is recycled, making it the most recycled plastic resin in the country.[12] PEI and many other provinces have deposit and return programs to motivate the return of beverage containers for recycling. [12,15] PET can be recycled into fibres, food or beverage applications, or film and sheet plastic. [9]

1.3.5 Polyethylene

Polyethylene is the world's most-consumed plastic material by volume. [9] As previously mentioned, HDPE and LDPE are high- and low-density polyethylene, respectively. Both HDPE and LDPE are addition polymers. While they have identical base monomers, these two types of plastics have very different structures. HDPE is formed by Ziegler-Natta catalyst polymerization, creating a single chain that is easily packed together, making it a highly dense polymer. LDPE is formed by free radical polymerization and is less dense due to branching off the main chain. [9] The radical end of the growing chain will occasionally reach back and attack one of the hydrogens on a -CH_2- group, converting that carbon to a secondary radical in a move called "backbiting." The chain will continue growing from the secondary radical, leaving a branch that is usually four carbons long (Figure 1.2). [16]

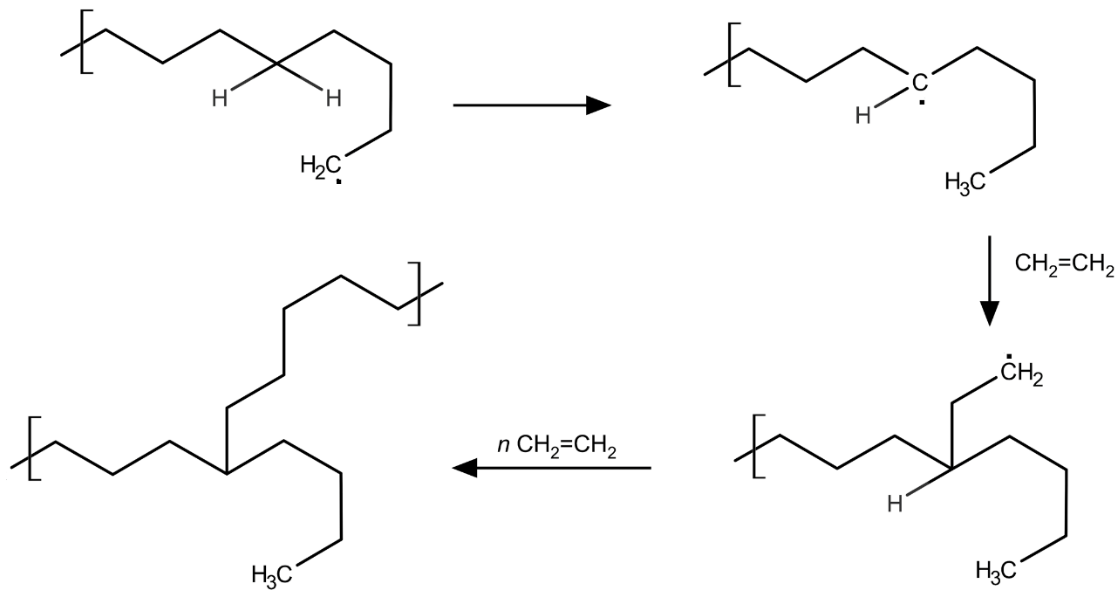

Figure 1.2 Polyethylene backbiting

A third type of polyethylene is called linear low-density polyethylene (LLDPE). LLDPE is synthesized through the copolymerization of ethylene and α-olefins. These α-olefins such as 1-butene or 1-hexene limit the frequency and length of side chains which gives LLDPE properties in between HDPE and LDPE (Figure 1.3).[9] HDPE has a density of 0.940-0.970 g/cm^3, LLDPE had a density of 0.915-0.950 g/cm^3, and LDPE has a density of 0.917-0.940 g/cm^3. [14]

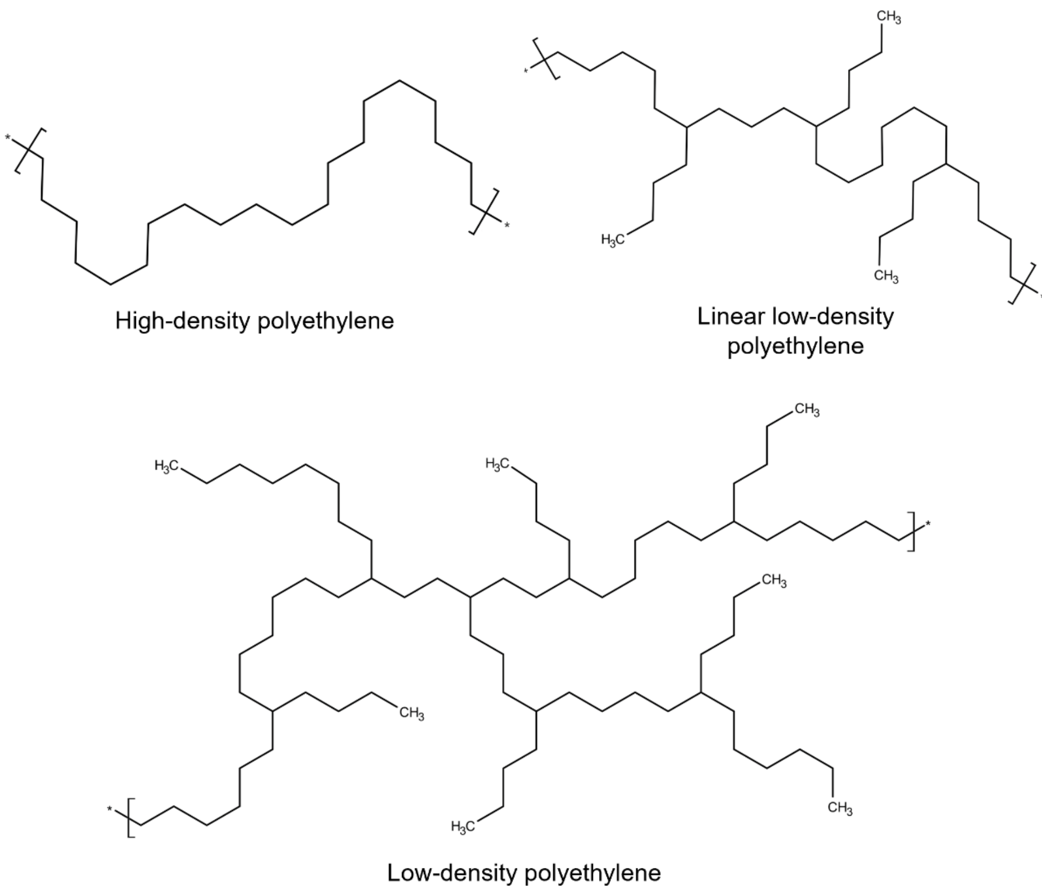

Figure 1.3 Structures of polyethylene

PE is highly flexible and does not require the addition of plasticizers which contributes to the ease of production and recycling. HDPE is used to make shampoo bottles, milk jugs, and covers of yogurt containers, among other things and is the second most recycled plastic in Canada at 10-15%. [12]

LDPE has a lower crystallinity causing it to have greater flexibility. LLDPE is included in the LDPE category recycling. LDPE is usually used for shopping bags, food packaging films, or as cable insulation. LDPE has an estimated recycling rate in Canada of 5-10%. [12]

1.3.6 Polyvinyl Chloride

PVC is formed in two steps. First, the vinyl monomer is formed through the chlorination of ethylene and its subsequent pyrolysis in a cracking unit. Then the polymer is formed through addition polymerization. [9] There are two main types of PVC, Flexible and Rigid, however there are also three other types: chlorinated PVC (CPVC), molecular oriented PVC (PVC-O), and modified PVC (PVC-M). Flexible PVC, also known as Plasticized PVC (PVC-P), has various plasticizers added to lower the crystallinity and make it more transparent and flexible. Rigid PVC is unplasticized and sometimes called Unplasticized PVC (UPVC). [17] PVC has between 10%-15% crystallinity due to the bulky chlorine atoms and is highly amorphous. [9] PVC-P has a density of 1.100-1.350 g/cm^3, and UPVC has a density of 1.300-1.450 g/cm^3. [17]

The most common use of PVC is for plumbing pipes and cable insulation, but it is also used in plastisol form, where powdered PVC is suspended in liquid plasticizers. Plastisol is used for dip-coating and roto-moulding. [9] Another use of PVC is in medical devices. [17] PVC is not generally accepted for recycling in Canada and has an estimated recycling rate of less than 5%. [12]

1.3.7 Polypropylene

PP is the second most-consumed plastic resin in the world. [18] PP is a rigid crystalline resin produced from the propylene monomer. PP is commonly polymerized by the Ziegler-Natta polymerization or through Metallocene catalysis polymerization. PP can have three different chain structures: atactic, isotactic and syndiotactic, where the methyl groups are arranged irregularly, on one side of the carbon chain, or alternatingly respectively. [18] PP has the lowest density of the six plastics recycled with a density of 0.90-0.91 g/cm^3. [14] PP homopolymer is the most common type of PP. It is commonly used in packaging, healthcare, automotive and electrical applications. [18] PP is estimated to have a 5-10% recycling rate in Canada, but for some products like plastic straws, they are either too small or risk food contamination. [12]

1.3.8 Polystyrene

PS is another addition polymer and is formed through free radical polymerization. PS is available in three forms: general-purpose PS (GPPS), high-impact PS (HIPS), and expanded PS (EPS). GPPS is brittle and stiff and is commonly used in plastic cutlery, coffee lids, CD cases, and blister packs. HIPS is a copolymer with butadiene that has greater impact strength. IT is often used to make yogurt cups. EPS is the foam form of PS commonly known as styrofoam. EPS contains a blowing agent that helps add air into the foam. EPS is used in hot and cold cups and clamshell take-out trays. [9] PS has a density of 1.040-1.050 g/cm^3. [14] PS is generally not accepted at recycling facilities. [12]

1.4 Sorting Techniques

Currently, most recycling is sorted manually. It might be sorted by colour or by resin type, however a significant amount of research has been done to improve recycling sorting systems worldwide. The new techniques can be separated into two general categories: physical and spectroscopic sorting methods. Some physical sorting methods include sink-float tanks, hydrocyclone, magnetic density separation, and froth floatation. Many of these systems have been automated and use the material properties to sort the plastics directly. [19] The spectroscopic methods that have been developed are near-infrared spectroscopy (NIR), Fourier Transform infrared spectroscopy (FTIR), and Raman spectroscopy, as well as hyperspectral imaging (HIS) using either NIR or FTIR. [20]

1.5 Innovative Uses of Recycled Plastics

There is so much potential for these plastics to be reused on Prince Edward Island if only the system for recycling them was more effective and efficient. Research has been conducted to explore the wide variety of different uses for recycled plastics. Moreno-Sierra et al. looked at using recycled plastics to build adaptable temporary shelters for post-natural disaster scenarios, so low-income countries can utilize the materials already on hand instead of having them shipped in.[21] Gu and Ozbakkaloglu reviewed the significant literature on the use of recycled plastics in concrete. [22] Najafi reviewed the work that has gone into the use of recycled plastics in wood-plastic composites. [23]

Many companies have been making their products from recycled plastic for years. From outdoor patio furniture to clothing, popular brands like C. R. Plastic Products and Patagonia have been turning recycled plastic into new products in a feasible manner proving that it is possible to create quality products using recycled plastics. [24,25]

While an improved sorting system will not completely solve the problems of transitioning to a circular economy, by developing identification and sorting technology that minimizes plastic cross-contamination, digitalizing it, and setting up the necessary infrastructure, significantly larger amounts of plastic could be properly sorted and recycled.

1.6 Objectives

This honours project is the first part of a larger project with the overall goal of implementing an automated recycling sorting plant in Prince Edward Island that can sort by resin type and by colour so that plastics can be recycled into new products on PEI. However, as this project is in its beginning stages; therefore, the objectives of this research project were to determine which of the spectroscopic techniques tested provided the correct identification of plastic resin types with the greatest efficiency. Additionally, a second objective was to collect the information needed to build a proof of concept for the sink/float tank and colour-sorting conveyor belt. These systems were tested using samples of typical household recycling objects with RIC numbers 1-6.

Chapter 2 Fourier Transform Infrared Spectroscopy

2.1 Introduction

2.1.1 Principles of FTIR

FTIR is a spectroscopic technique that irradiates the sample with infrared light which is absorbed into the molecule. The energy in the infrared light region is associated with the rotational and vibrational frequencies of different chemical bonds in a molecule. When irradiated with infrared radiation, a sample absorbs certain resonant frequencies and transmits others. The raw signal is then passed through a mathematical technique called the Fourier transform to create a spectrum as a function of wavelength generally between 4000 and 400 cm^{-1}. The absorption and transmission of resonant frequencies are associated with specific types of bonds, allowing for characterisation and assignment of bonds to elucidate structures.[26]

One of the standard FTIR techniques is attenuated total reflectance (ATR). ATR is used to measure solid or liquid samples. To do so, an infrared beam of light is emitted at a certain angle into an optically dense crystal with a high refractive index which creates an evanescent wave that extends into the surface of sample 0.5μm - 5μm deep.[27] The depth of penetration of the evanescent wave depends on the refractive index difference between the crystal and the sample.[28] The evanescent wave continues to reflect within the crystal until it reaches the other end of the crystal and the detector.[27] Good contact of the sample with the crystal is necessary to acquire a good reading. ATR FTIR is preferred for its reproducibility and simple sample preparation.[28] The most intense absorption of infrared light is caused by asymmetric vibrations that cause a change in the dipole of the molecule.[29]

Near infrared spectroscopy (NIR) is another type of spectroscopic instrumentation that has been studied with regards to sorting plastic polymers. NIR is able to differentiate between resin types except when the samples are black or dark coloured according to Roh et al.[30] Instead of reflecting the near-infrared light to show the overtones and combination bands of the rotational and vibrational frequencies, the light is absorbed into the plastic and there is no legible spectrum produced.[30] FTIR in the mid-IR region (4000-400cm^{-1}) is far enough away from the visible light region to avoid the interference seen with black plastics in NIR. [26]

2.1.2 Use of FTIR in recycling

As interest in improving recycling systems has grown, the research and application of spectroscopic sorting techniques has expanded as well. Kassouf et al. and Bae et al. have both used ATR FTIR to explore the chemometrics of plastic waste sorting with near 100% accuracy.[26] Signoret et al. have used their laboratory-based ATR FTIR work to develop FTIR Hyper Spectral Imagery (HSI) which has can simulate industrial conditions such as shorter acquisition time and diminished resolution. [31]

The FTIR spectroscopy research had mainly been lab-based and the majority of FTIR machines have not yet been adapted for industrial use.[31] NIR is currently the most used spectroscopic technology for sorting in industrial conditions.[32] However, a NIR spectrometer was inaccessible during the time-line of this project and will therefore be outside the scope of this project.

2.2 Methods

2.2.1 Sample Preparation

Fifty-two plastic samples were collected from household waste and recycling with RIC numbers 1-6. Table 2.1 has the sample name, the sample number given during the experiments and a description of the samples referred to in this chapter. A complete list of the samples with descriptions and property characterization can be found in the appendix. The samples were obtained directly from household recycling and while they might have been washed before being placed in the recycling, they were not washed after acquisition. The samples were cut into flat pieces, approximately 4cm by 1cm.

Table 2.1 List of samples used in FTIR work

Sample name	Sample number	Description
PET 1	1	Hand soap refill bottle
PET 2	30	Disposable water bottle
PET 3	43	“Celebration” cookie tray
HDPE 1	2	Shampoo bottle
HDPE 2	7	Carpet spot cleaner bottle
HDPE 3	20	“Activia” yogurt container cover
HDPE 4	4	Vitamin bottle
HDPE 5	11	Generic packaging sleeve
HDPE 6	9	Flyer sleeve
PVC 1	53	PVC pipe
PVC 2	50	Vinyl glove
PVC 3	47	Shower curtain
LDPE 1	5	Milk carton seal
LDPE 2	24	“Superstore” plastic bag
LDPE 3	14	“Wonder” hotdog bun bag
PP 1	3	Hand soap refill bottle cover
PP 2	8	Carpet spot cleaner bottle cover
PP 3	13	Carpet cleaner bottle cover
PP 4	23	Grape bag
PP 5	31	Protein powder scoop
PP 6	29	“Liberte” yogurt container cover
PS 1	41	“Tim Horton’s” hot drink cover
PS 2	42	Take-out drink cover

2.2.2 Spectrum Acquisition

All FTIR measurements were conducted on a Bruker Alpha-P ATR FTIR spectrometer with a diamond crystal. OPUS software by Bruker was used to process the spectra. The spectra were obtained using four scans at a resolution of 0.9 cm^{-1}. Baseline correction and peak picking were completed for all FTIR spectra.

The initial spectra of the samples were obtained using the parameters outlined above.

The next set of spectra was taken to measure the effect of labels. Samples were cut to include the label. A spectrum of the label was collected then superimposed with a spectrum of the inside of the sample. The interior and exterior without any labelling were also collected for each sample.

The third group of spectra was taken to determine if the different types of plastic could be identified based on a small section of the spectrum. Four spectral regions were identified for having significant spectral differences between the different types of plastic. The first region was the C-H stretching region between 2800-3000 cm^{-1}; the second was the C=O region from 1600-1800cm^{-1}; the third region was the C-H bending region between 1300-1550 cm^{-1}; and the fourth region was the overtone, out-of-plane bending, and halogen region between 700-900 cm^{-1}. A preliminary visual assessment was conducted, and the 1600-1800cm^{-1} region was discarded as some of the spectra were too similar. Using the initial spectra of samples PET 1, HDPE 1, PVC 1, PP 1, and PS 1, spectral references were created using the OPUS software’s Quick Compare Method (QCM). Three reference methods were created for each reference sample, one for each of the remaining spectral regions.

Nine samples were chosen to compare with the references, PET 2 and 3, HDPE 2 and 3, LDPE 1 and 2, PP 2 and 3, and PS 2. Each sample was compared to the reference of the same type of plastic. Since HDPE and LDPE present identical characteristic peaks, both types of plastic were referenced with the HDPE 1 reference. The samples were compared using the QCM.

Correlation values were obtained, and the results were individually saved. The mean of the correlation values for each spectral region was calculated. The spectral region between 1300-1550 cm^{-1} was determined to identify the plastic types with the greatest accuracy and precision. Each sample was then measured against each reference in the 1300-1550 cm^{-1} spectral region using the QCM, and the correlation values were recorded.

The final set of FTIR experiments explored the effects of resolution and the number of scans used to make up a spectrum. One sample of each resin type was measured using the routine four scans, then with two scans, then with one scan. These samples were PET 2, HDPE 2, PVC 1, LDPE 1, PP 2, and PS 2. Then these samples were measured at the standard 0.9cm^{-1} resolution, 2cm^{-1} and 5cm^{-1} with a single scan. The sample spectra were then compared in the 1300-1550cm^{-1} spectral region with the references of each resin type using the QCM.

2.3 Results and Discussion

2.3.1 Sample Procurement

When collecting the samples for this project, there were two goals in mind. The first goal was to obtain at least two samples of each type of plastic corresponding to the RIC 1-6. While it a small sample size, this study was simply exploratory and does not require statistical significance. The second was to obtain samples with a variety of colours, rigidity, and types of labelling. The sample pool was to reflect the variety of products that a household uses.

There were some difficulties in finding the desired variety in products. All the PET samples collected were either clear or in one case a transparent brown. Only one of the LDPE samples was not in film form. Finally, it was quite difficult to obtain a sample of PVC sourced from household recycling. Shower curtain liners are usually made of PVC [33], however when a sample was obtained and measured using FTIR, the sample proved to be made of a type of polyethylene (PE). Then, a vinyl glove was used as a sample and the FTIR spectrum for this sample did not resemble any of the resin types. It is possible that the glove either has a powder coating or plasticizers that are interfering with the PVC spectrum. Finally, a piece of PVC pipe was obtained from a non-recycling source in order to have a PVC sample for the experiments.

2.3.2 Initial Spectra

The initial FTIR spectra were collected, analyzed in an assignment table, and examined for characteristic peaks for each type of plastic (Figure 2.1 and Table 2.1).

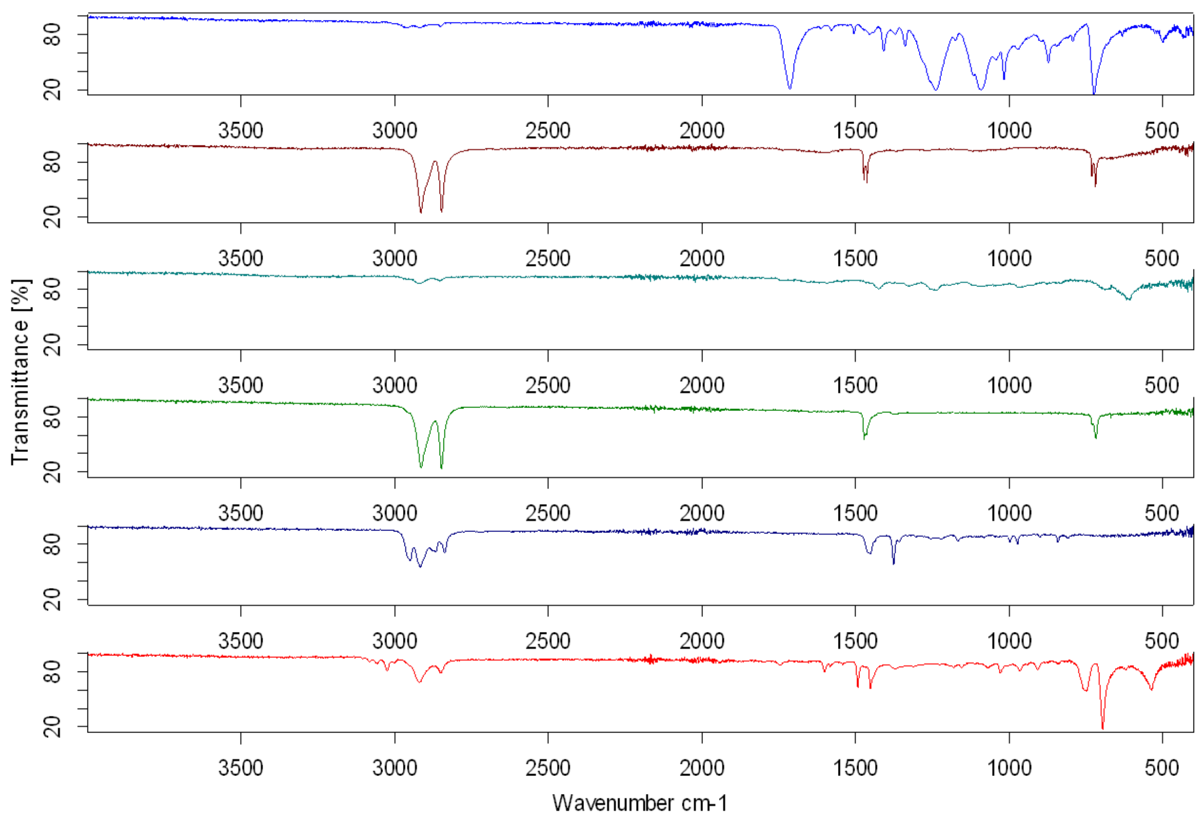

Figure 2.1 FTIR spectra of PET, HDPE, PVC, LDPE, PP, and PS

Table 2.2 Characteristic FTIR peaks for each type of plastic resin (cm^{-1})

PET	**HDPE**	**PVC**	**LDPE**	**PP**	**PS**
1713	2915	2918	2915	2949	2918
1239	2847	1424	2847	2916	2850
1093	1462	1239	1462	2837	1492
723	730	607	719	1457	1451
	719			1375	750
					695

Each resin type had peaks that that enable them to be easily differentiated. For PET, the peak at 1713cm^{-1} corresponded to an ester carbonyl. The peaks at 1239 cm^{-1} and 1093cm^{-1} corresponded to the C-O bond. PET was the only one of the six polymers that had the carbon-oxygen double and single bonds which were the stronger signals compared to any C-H bond vibrations. The fingerprint region in the PET spectrum was the busiest of any of the polymers.

The spectra for HDPE and LDPE plastics presented peaks at the same wavenumbers and with similar intensities. As the difference between the two types of plastic was purely structural and not chemical, it was expected that the spectra were the same and was consistent with the results from Rozenstein et al. [34] The PE spectra had the strongest C-H vibrations, both stretching at 2915cm^{-1} and 2847cm^{-1} and bending at 1462cm^{-1}.

The intensity of the PVC spectrum was the lowest of the six polymers, however the distinguishing factor in this spectrum was the peak at 607cm^{-1} for PVC that corresponded to the chlorine atom attached to the carbon.

In the PP spectrum, the peaks at 1457cm^{-1} and 1375cm^{-1} corresponded to the C-H bending vibrations of the methyl side group of PP. There were significant C-H stretching vibration between 2800cm^{-1} and 3000cm^{-1}.

Finally in the PS spectrum, the peaks at $695cm^{-1}$ and $750cm^{-1}$ represent the characteristic aromatic out-of-plane bending vibrations for a mono-substituted benzene ring.

Based on these initial spectra, the different resins appeared to have peaks that were unique and distinguishable.

2.3.3 Label Comparison

Labels cover a large portion of most plastic products, especially plastic packaging. Other than the PVC samples and PP 5, all the other samples were plastic packaging of some sort. Thirty-three of the samples had some sort of labelling. As the spectra were obtained it became clear that there were three different result scenarios when measuring the effect of labels on the accurate identification of the resin type of the sample. In the first scenario, there was a label on top of the plastic of the sample and it was made of a different material than the sample as seen in Figure 2.2 where PET 1 is shown with and without its label. The labels produced a completely different spectrum from that of the actual sample. Based on these FTIR scans of the label, it was not possible to accurately identify the resin type.

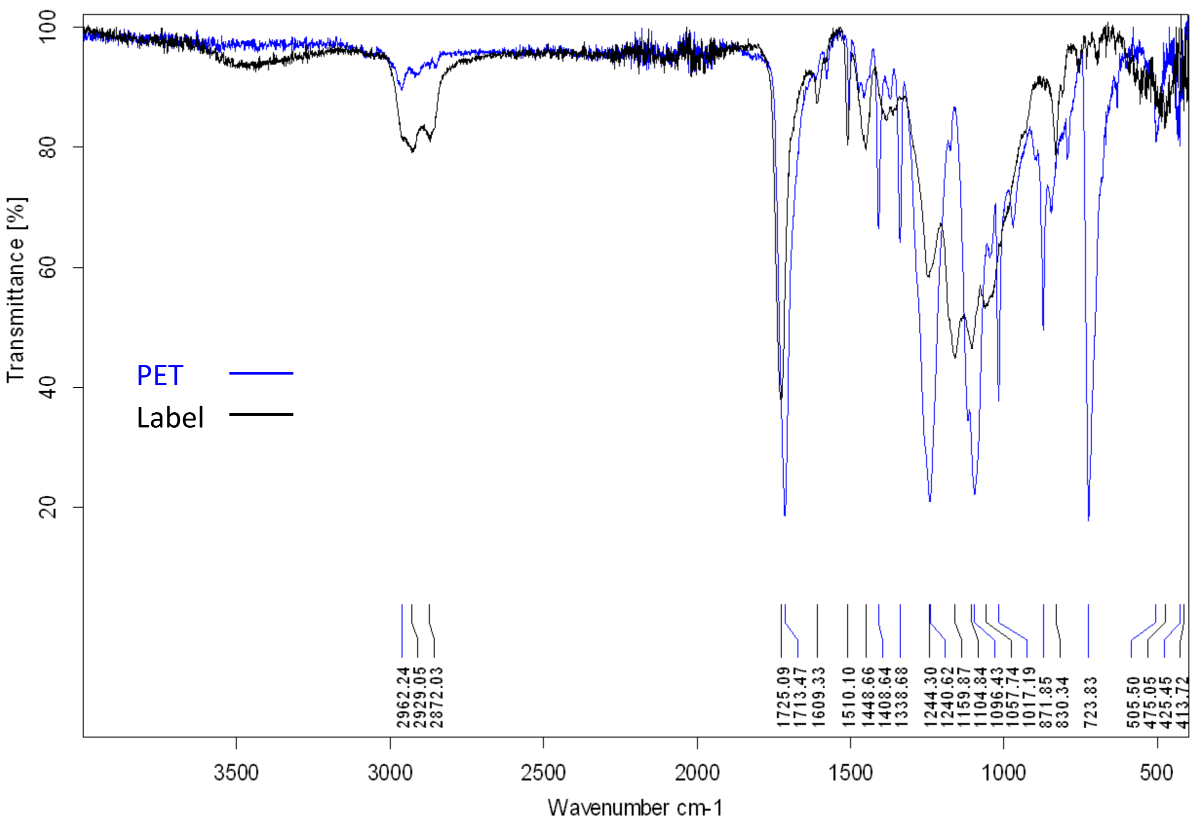

Figure 2.2 FTIR spectrum for the label comparison of PET 1

In the next scenario, samples had their colourful labels printed directly onto the surface of the sample. Included in this group were yogurt containers and bread bags. This exterior coating was made of a different material and created a completely different FTIR spectrum from the interior of the sample (Figure 2.3). This label often covered the entire exterior of the plastic product, rendering the identification of the resin via the that surface impossible.

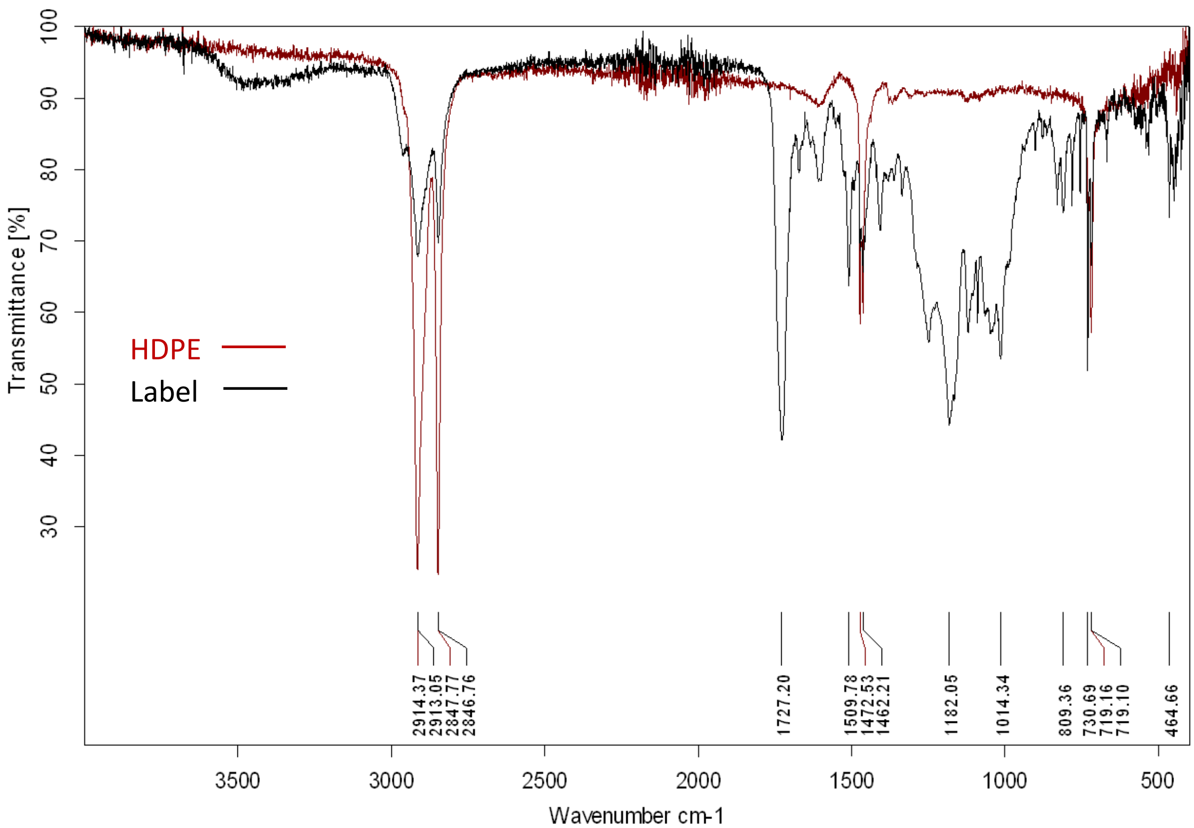

Figure 2.3 FTIR spectrum for the label comparison of HDPE 3

The third scenario was one where there was writing printed on a film plastic. To clarify, samples in this scenario only have black writing and were typically flyer sleeves or the bags online shopping products are shipped in. In these cases, the writing did not have a big impact on the FTIR spectrum. There was an increase in noise in the spectrum, however it was always possible to identify the resin type despite the writing (Figure 2.4).

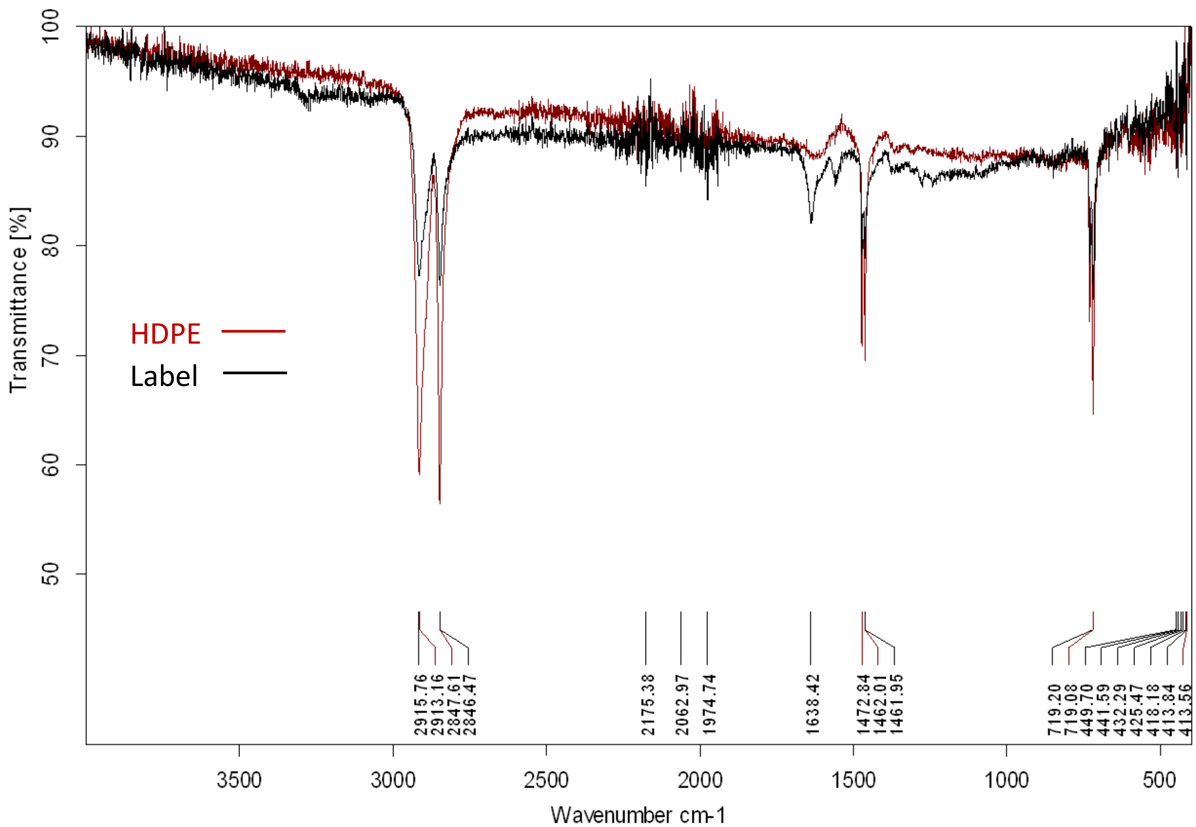

Figure 2.4 FTIR spectrum for the label comparison of HDPE 6

In conclusion, for the FTIR measurements, most labels had an effect on the sorting outcomes of the sample. When the label was a separate sticker, it did not cover the entirety of the sample, making it possible to sort the sample by measuring another part of the sample. The labels printed directly into the surface posed a larger problem. It was also not possible to determine the plastic type through the label using this technique, however the label covered the exterior making it difficult to measure a different part of the sample. Finally, samples that were a film with printed writing were able to be sorted without the label having any significant impact.

2.3.4 Exploration of a Shorter Spectral Region

A method to simplify to the identification process was to look at a smaller spectral region. To determine if the use of a smaller spectral region was possible, spectra for each plastic type were manually visually compared. Four regions were determined to have potential as being unique. These regions were 2800-3000cm^{-1}, 1600-1800cm^{-1}, 1300-1550cm^{-1}, and 700-900cm^{-1}. Upon further exploration, PET was the only sample with a significant peak in the carbonyl region between 1600-1800cm^{-1}. The other spectra were too similar in the region of 1600-1800cm^{-1} so that option was discarded. The other three regions had the peaks in the spectral regions that were unique for each plastic. Correlation values for the accuracy of comparison in these regions is displayed in table 2.3.

Table 2.3 Correlation values at different spectral regions with a reference of the same resin type

Sample #	**2800-3000 cm^{-1}**	**1300-1550 cm^{-1}**	**700-900 cm^{-1}**
PET 2	77.80%	97.70%	99.56%
PET 3	83.48%	90.08%	99.24%
HDPE 2	99.98%	99.44%	96.29%
HDPE 3	99.64%	98.05%	98.08%
LDPE 1	99.07%	94.39%	93.45%
LDPE 2	99.73%	98.65%	98.98%
PP 2	99.85%	99.86%	87.89%
PP 3	99.75%	99.64%	45.37%
PS 2	99.39%	99.01%	98.23%
Mean	95.41%	97.42%	90.79%

The means of the correlation values were 95.41% for 2800-3000cm^{-1}, 97.42% for 1300-1550cm^{-1} and 90.79% for 700-900cm^{-1}. The 2800-3000cm^{-1} region did not have good correlation for PET samples but had 99% correlations for the other resin types. The 1300-1550cm^{-1} region had more variability in correlation, but the correlations were all above 90% and the majority above 97%. The 700-900cm^{-1} region did not have good correlation for PP samples and had some variability among the other resin types. It was decided that a lower correlation that extended to all resin types was more important than having a high correlation for four of the five plastic types measured at this step. Based on these results, it was determined to compare a variety of samples of all resin types with the references of the different resin types within the 1300-1550cm^{-1} spectral region to observe the comparison correlations (Table 2.4).

Table 2.4 Correlation values for 1300-1550cm^{-1} for different reference samples

Sample#	Ref PET 1	Ref HDPE 1	Ref PVC 1	Ref PP 1	Ref PS 1
PET 2	97.58%	2.09%	36.33%	5.45%	0.00%
PET 3	90.08%	0.53%	38.40%	23.84%	9.77%
HDPE 2	4.94%	99.46%	0.00%	47.96%	16.97%
HDPE 3	2.57%	97.62%	0.00%	50.01%	23.05%
LDPE 1	2.08%	95.03%	0.00%	50.72%	21.70%
LDPE 2	2.28%	98.77%	5.56%	52.83%	23.24%
PP 2	9.93%	47.09%	6.59%	99.63%	45.20%
PP 3	11.02%	47.28%	9.44%	99.67%	45.27%
PS 2	0.00%	7.89%	5.12%	41.89%	99.06%

The correlations for the correct identifications were always above 90%. The PET samples had correlations with PVC in the high 30% range but did not have very high correlation with any of the other references. It is very interesting that PET and PVC have significant correlation considering that their structures are quite different.

Both the HDPE and LDPE samples had correlations with the PP 1 reference around 50% and the PP samples had nearly 50% correlation with the HDPE 1 reference. The high correlations between HDPE and LDPE and PP are expected because the polymers are only one methyl side-chain different. PP and PS also have correlations in the 40% range with the opposite reference.

The high correlation could be because both polymers are regularly substituted and made from α-olefins, a methyl group compared to a benzene ring.

The PET 2 sample had 0% correlation to PS, but PET 3 sample had 9.77% correlation. Both the PET 3 sample and the PS 1 reference were brown; therefore, it is possible the colour is the cause for this higher correlation. The brown colour of the PET 3 sample could also be the reason for the 90.08% correlation which is the lowest correlation between a sample and the reference of the same type of plastic.

2.3.5 Resolution Tests

One of the challenges of this project is to identify the resin type with high accuracy but trying to do so with less expensive and more accessible tools. FTIR can measure samples at different resolutions and with more of less scans. Correct resin identification with a lower resolution means a recycling sorting facility could use a machine with lower resolution that costs less for their sorting.

The standard settings for the FTIR machine used in this project were four scans at a resolution of $0.9cm^{-1}$. Samples were run with four, two, and one scan to see how the spectrum maintained its integrity. A lower number of scans did not have a great impact on the quality of the spectrum. There was an increase in noise in the spectrum.

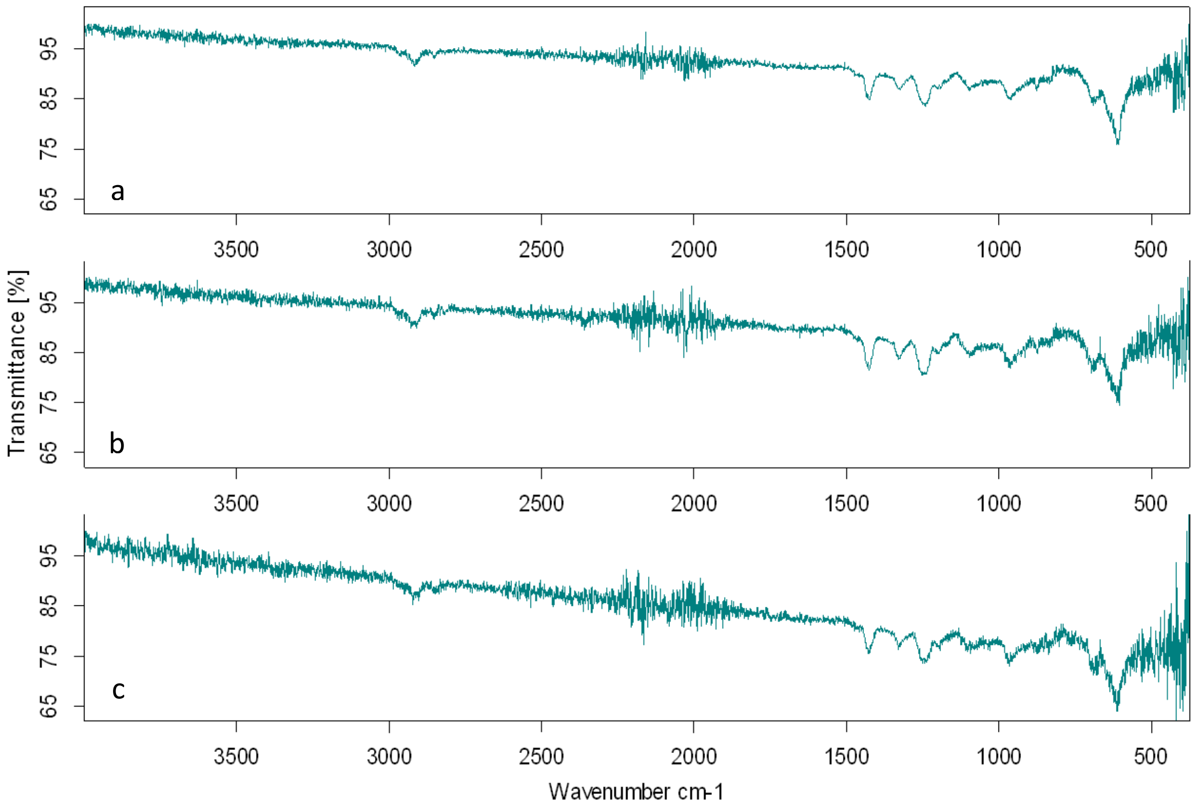

Figure 2.5 FTIR spectra of PVC 1 with a) four scans, b) two scans, c) one scan

The next part of these experiments was to explore the effects of lower resolution on the ability to identify the spectrum. As the resolution was lowered to $2cm^{-1}$, then to $5cm^{-1}$, the spectrum became smoother and smoother, but it retained the general outlines of the peaks that were crucial to the identification process. These tests were also run with one scan to use the minimal setting possible.

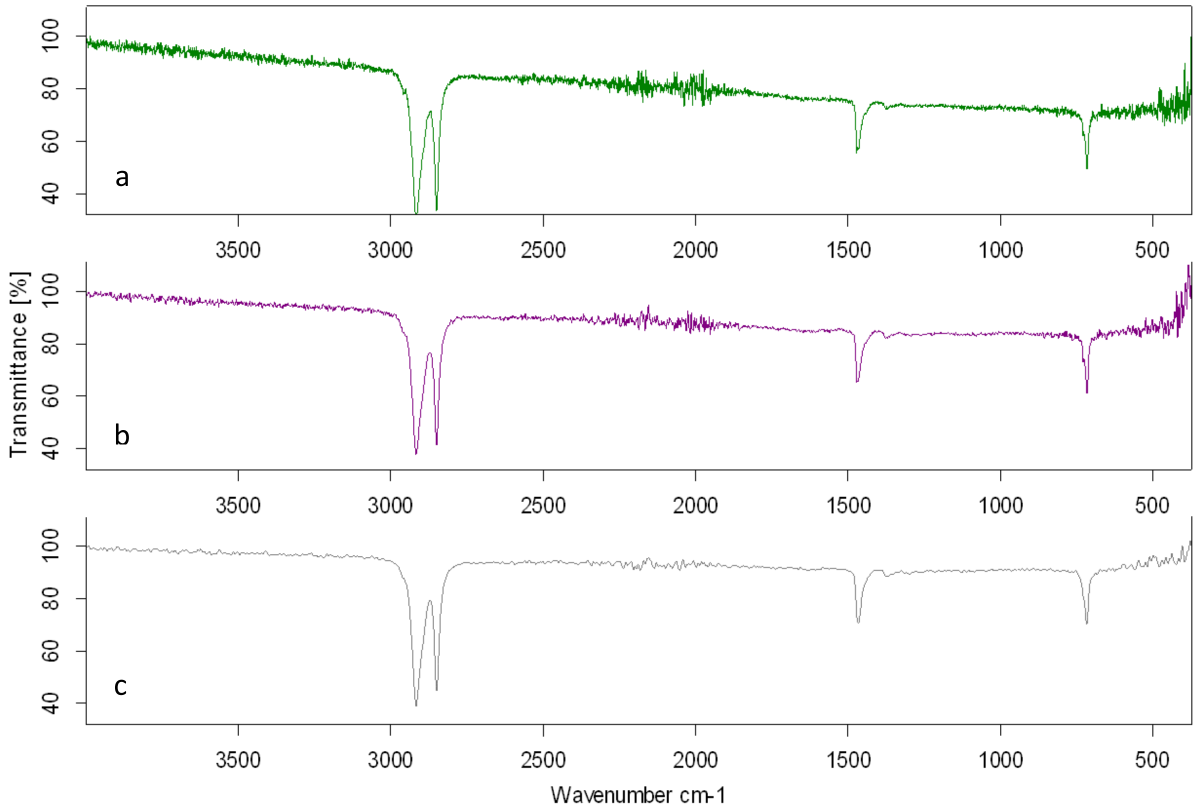

Figure 2.6 FTIR spectra of LDPE 1 a) 0.9cm^{-1} resolution, b) 2cm^{-1} resolution, c) 5cm^{-1} resolution

Finally, the spectra with a 5cm^{-1} resolution were run through the QCM for the 1300-1550cm^{-1} spectral region to ensure that identification accuracy was not lost. As seen in Table 2.5, the correlation factors remained high for all resin types, meaning the lower resolution and less scans do not affect the identification process.

Table 2.5 QCM correlation values of FTIR spectra with one scan and 5cm^{-1} resolution between 1300-1550cm^{-1}

PET 2	**HDPE 2**	**PVC 1**	**LDPE 1**	**PP 2**	**PS 2**
95.83%	99.81	99.59%	99.04%	99.86%	98.18%

Chapter 3 Raman Spectroscopy

3.1 Introduction

3.1.1 Principles of Raman Spectroscopy

The vibrational energy of a molecule can be measured through the irradiation of a molecule with infrared light. The light will move in one of three ways. If the incident photons of light have an energy that fits between the energy gap of the ground and excited states, it will be absorbed into the molecule and raise the molecule to a higher excited energy state. The second way photons proceed is through scattering. Scattered light photons are collected at an angle to the incident light beam. The energy of the photon does not need to match the energy gap of the molecule. Finally, it is possible for the light to pass right through a molecule and not interact with it.[35]

Raman spectroscopy is a complementary technique to infrared spectroscopy. This technique measures the bond vibrational energy through light scattering. Light photons can scatter elastically or inelastically. Elastic scattering does not produce a change in photon energy whereas inelastic scattering has a different frequency from the incident light causing a change in photon energy. The elastic scattering is called Rayleigh scattering, and the inelastic scattering is called Raman scattering. Inelastic scattering was first experimentally observed by C.V. Raman in 1928, thus the name. The vast majority of scattering photon are elastic; approximately one out of every 10^6-10^8 photon that scatters is inelastic Raman scattering. Raman scattering is more intense, coming from vibrations that cause a change in the polarizability of the electron cloud around the molecule. Symmetric vibrations generally cause the largest changes. [35]

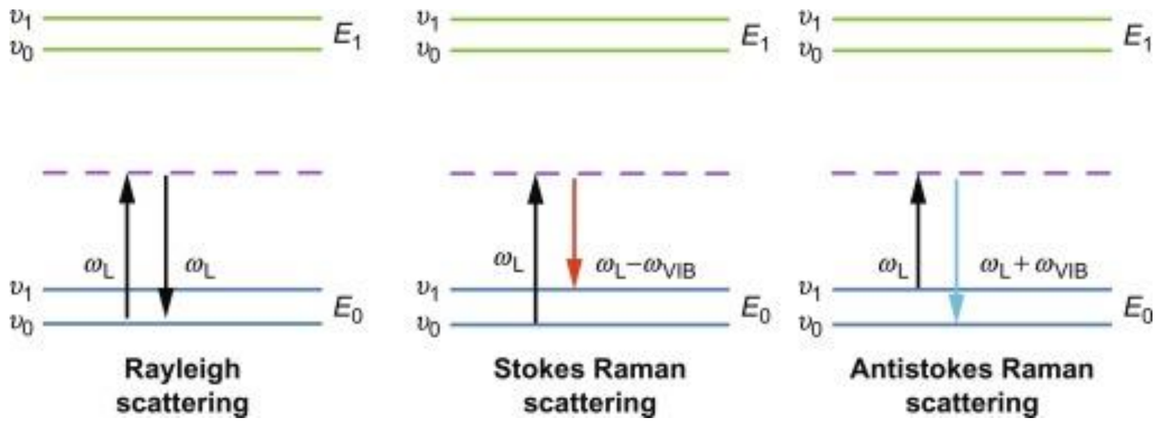

Figure 3.1 Rayleigh, Stokes Raman, and Anti-Stokes Raman scattering energy levels [36]

Raman spectroscopy uses optical filters to distinguish the scattered radiation with an altered frequency and energy from the incident light. [35] There are two types of Raman scattering, Stokes and Anti-Stokes. Stokes Raman scattering occurs when the energy released by the emitted photon is less than the energy of the incident light. Anti-Stokes Raman scattering occurs when the energy released by the emitted photon is greater than the energy of the incident light, relaxing the molecule down to a lower vibrational state in the electronic ground state. [36] Raman spectroscopy is also measured in frequency and wavenumbers (cm^{-1}). Each peak represents the energy shift or difference between a lower vibrational energy state and excited vibrational energy states for specific molecular bond in a molecule. The area of interest on a Raman spectrum is usually a range of 3600-400 cm^{-1} however Raman spectroscopy can detect shifts down to 100 cm^{-1} or lower with the correct equipment. [35] Since Raman spectroscopy is more impacted by the symmetric vibrations of a molecule and FTIR is more impacted by asymmetric vibrations, the spectra of the two methods are quite different but have complementary end results.

One of the biggest challenges of Raman spectroscopy is fluorescence interference. The lasers used in Raman spectroscopy are often within the visible light region. 795nm and 785nm lasers are common choices. Lasers with wavelengths of 1064nm or 1280nm reduce fluorescence to a minimum but the scattering efficiency lowers through the infrared region. [35] Even weak fluorescence from a sample is often stronger than the Raman scattering causing a large background in the spectrum. These fluorescence backgrounds are difficult and sometimes impossible to remove. They can occasionally even overpower the spectrum completely. [37] Fluorescence can also cause degradation. In modern Raman instruments, it is possible to burn out an impurity by exposing a sample for a few minutes, however, it is possible for that absorption to be too intense and cause sample degradation. [35]

3.1.2 Uses of Raman in Recycling

According to Neo et al., Raman is becoming known as the technique that can overcome NIR's inability to process black plastics and poor spectral resolution. However, Raman is used less widely than either NIR or FTIR because of the fluorescence interference. They also presented eight papers where Raman was used to measure and sort plastics. These papers typically looked at three or four different plastic types instead of the six used in this project. [26]

It was Florestan et al. who first discovered the potential of Raman in plastic sorting and significant advances have been made using chemometric tools such as neural networks or partial least-square regression models. Currently, the research has been limited to polymers of interest instead of wider variety used in the plastics industry. Pigmentation and fluorescence are also hindering the efforts to industrialize the use of Raman spectroscopy in plastic sorting for recycling.[26]

3.2 Raman Methods

All Raman measurements were completed using the B&W TEK NanoRam Handheld Raman Spectrometer. The NanoRam uses a 785nm laser with a TE-regulated charge-coupled device for detection. The integration time is automatically optimized by the instrument for each measurement to maximize the signal to noise ratio. This instrument was designed for product identification in the pharmaceutical industry. [38] As a result, the instrument determined if the measured sample was a match for a reference in the pre-loaded or machine libraries and showed the identification of the match or failure to match, by-passing the presentation of a complete spectrum. The raw data was obtained as a series of data points from 176cm^{-1} to 1800cm^{-1}.

Table 3.1 List of samples used in Raman work

Sample name	Sample number	Description
PET 1	1	Hand soap refill bottle
PET 2	30	Disposable water bottle
PET 3	43	“Celebration” cookie tray
HDPE 1	2	Shampoo bottle
HDPE 2	7	Carpet spot cleaner bottle
HDPE 3	20	“Activia” yogurt container cover
HDPE 4	4	Vitamin bottle
HDPE 5	11	Packing sleeve (generic)
HDPE 6	9	Flyer sleeve
HDPE 7	21	“Activia” yogurt container cover #2
HDPE 8	45	4-pack drinks cover red
HDPE 9	49	“Tide” laundry detergent
PVC 1	53	PVC pipe
LDPE 1	5	Milk carton seal
LDPE 2	24	“Superstore” plastic bag
LDPE 3	14	“Wonder” hotdog bun bag
PP 1	3	Hand soap refill bottle cover
PP 2	8	Carpet spot cleaner bottle cover
PP 3	13	Carpet cleaner bottle cover
PP 4	15	“Source” yogurt container
PP 5	23	Grape bag
PP 6	31	Protein powder scoop
PP 7	16	“Source” yogurt container cover
PP 8	18	Feta cheese container cover
PS 1	41	“Tim Hortons” hot drink cover
PS 2	42	Take-out drink cover

3.2.1 Initial Spectra

Five methods were created to be references, the samples used were PET 1, HDPE 1, PVC 1, PP 1, and PS 2. Since HDPE and LDPE presented the same in FTIR spectra, it was assumed that they would present the same in Raman spectra as well. The creation of a method involved a minimum of twenty scans. With each scan, a background scan was obtained and subtracted to eliminate as much fluorescence and incident light as possible.

Once the methods were created, eight samples were used to conduct investigation tests: PET 2, HDPE 3 and 4, LDPE 1 and 3, PP 2 and 4, and PS 1. These samples were chosen because they were mostly white samples and initial speculation was that the white samples had good Raman peaks with minimal fluorescence. There were no white PET samples and there was only one other PS sample. Each sample was inserted into the vial holder attachment and an investigation mode was run. The orientation or placement of the sample within the sample holder varied. The samples were always approximately perpendicular to the laser beam but would occasionally be off axis just to get the sample to stay in place. The investigation mode did a single scan of the sample and acquired a background to be subtracted. The NanoRam then calculated the similarities to the machine library as well as all the reference methods that were created for each plastic type and listed any matches.

3.2.2 Spectrum Processing

The raw data file was obtained. The highest intensity value of each data set was determined and used to calculate the relative intensity values. Using the relative intensities of the four-hundred and seven data points provided, a Raman spectrum from 176 cm^{-1} to 1800 cm^{-1} was created using an X Y scatter plot with straight lines. The high intensity peaks were gathered from the data set and spectra. The spectra were able to be superimposed upon one another to compare the shape of the peaks.

Some samples had higher fluorescence interference in the spectrum. To correct this fluorescence, a polynomial trendline was plotted along the spectrum and the order of magnitude of the function was increased until there was a good fit of the curve while using the lowest possible order of polynomial. Then the equation of the polynomial function is used to calculate the baseline correction for the sample where x is the wavenumber for each point in the data set.

The baseline correction is then subtracted from the spectral intensity to provide a new spectrum with less fluorescence interference.

3.2.3 Effects of Colour on the Spectra

In order to explore the effect of coloured samples on the clarity of the Raman spectra, a variety of coloured samples of different resin types were measured. Investigation mode was used, and the spectra were processed as described above.

Table 3.2 Sample name and colour for samples used in the colour comparison tests

Sample name	Colour
PET 3	Brown
HDPE 2	Dark blue
HDPE 7	Blue
HDPE 8	Red
HDPE 9	Orange
LDPE 2	Green
PP 3	Green
PP 7	Red
PP 8	Blue

3.2.4 Other Spectra

As a significant number of the samples were clear plastics, 16 of 52 samples, it was important to explore how Raman performed with clear plastics compared to white plastics. PET 2, HDPE 9, PP 5, and PP 6 were measured and compared to their white reference sample.

The next set of spectra was to measure the effects of labels on the spectrum. PET 1, HDPE 1, HDPE 3, and HDPE 5 were measured on both sides and the spectra were superimposed.

3.3 Results and Discussion

The Raman measurements obtained for this experiment provided data in the fingerprint region, from $176cm^{-1}$ to $1800cm^{-1}$. Interestingly, the Raman machine seemed to melt small circles in some of the coloured samples and, depending on the thickness of the plastic, sometimes even created a hole in the sample.

Figure 3.2 Holes melted in PS 1 while taking Raman spectra

3.3.1 Initial Spectra

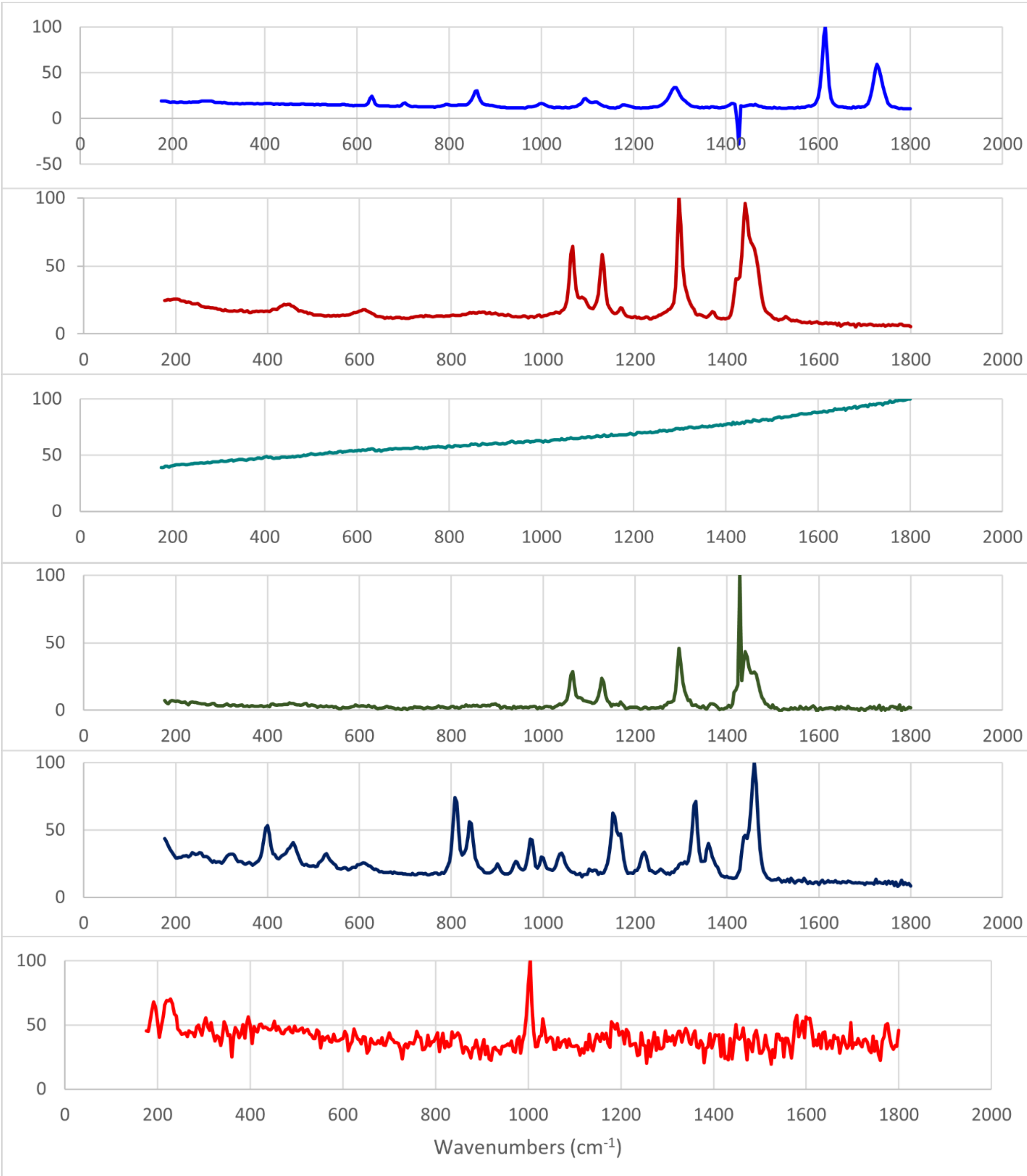

Figure 3.3 Raman Spectra of PET, HDPE, PVC, LDPE, PP, and PS

Table 3.3 Characteristic peaks from the Raman spectra for each resin type (cm^{-1})

PET	**HDPE**	**PVC**	**LDPE**	**PP**	**PS***
632	448	No peaks	1064	400	1004
860	608		1128	808	
1096	1064		1296	840	
1292	1128		1440	1152	
1616	1296			1332	
1728	1440			1460	

*PS sample was referenced to acetaminophen

The spectrum of PET 2 presented strong Raman signals. The strongest peak was at 1616$cm^{-1,}$ and the second strongest was at 1728cm^{-1}. These peaks are the most prominent and bring uniqueness to the spectrum. The spectrum of PET 2 also had a strange peak. There was a large negative peak at 1428cm^{-1} (intensity of -6,273.11). The baseline of that spectrum was around 3000 intensity units making this peak approximately 9000 intensity units below the baseline. The intensity of 1424cm^{-1} was -354.69cm^{-1} but the intensities of 1420cm^{-1} and 1432cm^{-1} were 3474.98 and 3075.21 respectively. This peak was determined to be an error as it appeared in multiple other spectra, notably LDPE 1 and 2, HDPE 6 and PS 1.

The PET 3 sample was a transparent brown and relatively thin. It was one of the samples that had a hole melted through it. The sample absorbed so much of the light and heated up, causing the hole instead of reflecting the light. The sample did not present any Raman active signals.

HDPE 3 had a green side and a white side. For the initial tests, the white side was used. Both HDPE 3 and HDPE 4 had many strong Raman peaks. These peaks were at a consistent wavenumber.

LDPE 1 had a noisier baseline and was closer to 0 than HDPE 3 or 4. This spectrum had the error at 1428cm^{-1}, which had an intensity of 6943.64, which was more than double the intensity of any other peak, skewing the appearance of the spectrum slightly. There are two broad weak peaks at 448cm^{-1} and 608cm^{-1} in the HDPE spectrum that do not appear in the LDPE spectra. The other four peaks, at 1064cm^{-1}, 1128cm^{-1}, 1296cm^{-1}, and 1440cm^{-1} are present in both spectra with the same peak ratio. LDPE 3 did not produce any Raman scattering peaks.

The PVC 1 Raman spectrum did not show any Raman peaks. The spectrum produced a baseline that increased in intensity at the wavenumber increased. This baseline can be attributed to fluorescence interference. An investigation mode scan and the creation of a reference method were attempted, however partway through the scans to create the method, the PVC 1 sample began to smoke and showed marks of burns. The sample was significantly thicker than any of the other samples, which could explain why there was no hole burned completely through the plastic. Due to the smoke, all further Raman experiments with PVC were suspended.

The Raman spectrum of PP 2 had many peaks; therefore, it was important to identify the strongest peaks and most likely to be seen in a spectrum with high fluorescence. After comparing a clear spectrum with a spectrum with significant background fluorescence, it can be confirmed that the peaks at 400, 808, 840, 1152,1332, and 1460cm^{-1} can be clearly seen through the fluorescence interference. In a clear spectrum, it is also possible to see peaks at 608, 972, 1220, and 1360cm^{-1}.

PS is used as the reference for the NanoRam machine. Therefore, when the first PS sample was measured, it presented a spectrum with only two negative peaks, one of which was at 1428cm^{-1} and deemed to be an error. A second spectrum was obtained and this time the machine was calibrated with acetaminophen, another standard reference material. The acetaminophen referenced PS spectrum only had one peak, at 1004cm^{-1}.

PET and HDPE and LDPE have peaks between 1290-1300cm^{-1}, HDPE and LDPE and PP have peaks at 1440cm^{-1} and 1460cm^{-1}, respectively, making differentiating these peaks more difficult. However, it is the peak patterns that set the resin types apart.

3.3.2 Effects of Colour on the Spectra

As previously mentioned, fluorescence can cause significant interference with the Raman spectrum. Many of the plastic samples were vibrant or dark colours which are commonly fluorescent. Of the nine coloured samples explored, two were minorly affected by fluorescence and produced a spectrum similar to a white sample. These were HDPE 8 and PP 3.

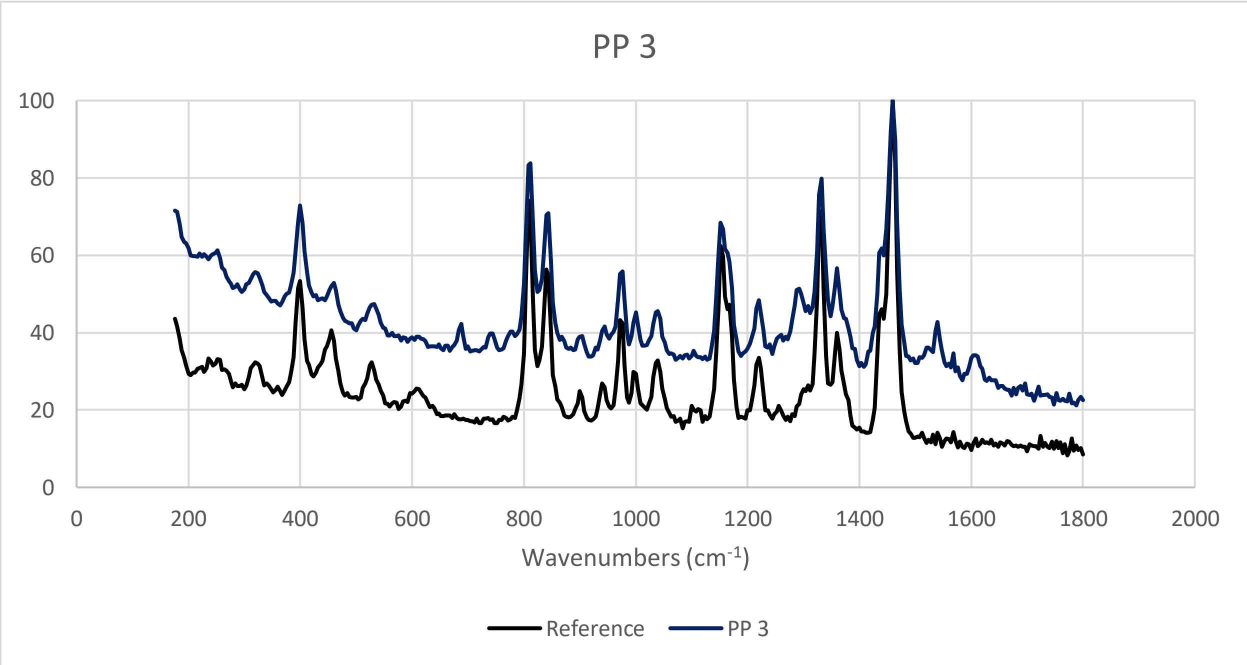

Figure 3.4 Raman spectrum of PP 3 with PP reference

As seen in Figure 3.3, the baseline of PP 3 was significantly higher than the baseline of the reference PP 1. The peaks were also less intense. These factors were attributed to the fluorescence interference. Despite these factors, the peaks from PP 3 lined up with the reference, and the sample was definitively identifiable as PP.

PP 8 had a spectrum with a significant amount of fluorescence interference. In order to clarify the peaks, the fluorescence interference was removed using the analysis methods described in section 3.2.2. Once the fluorescence was removed, six peaks were observed, however when compared to references, the wavenumbers of the peaks did not align with any of the references. In conclusion, this sample is unidentifiable based on this spectrum and the analysis completed.

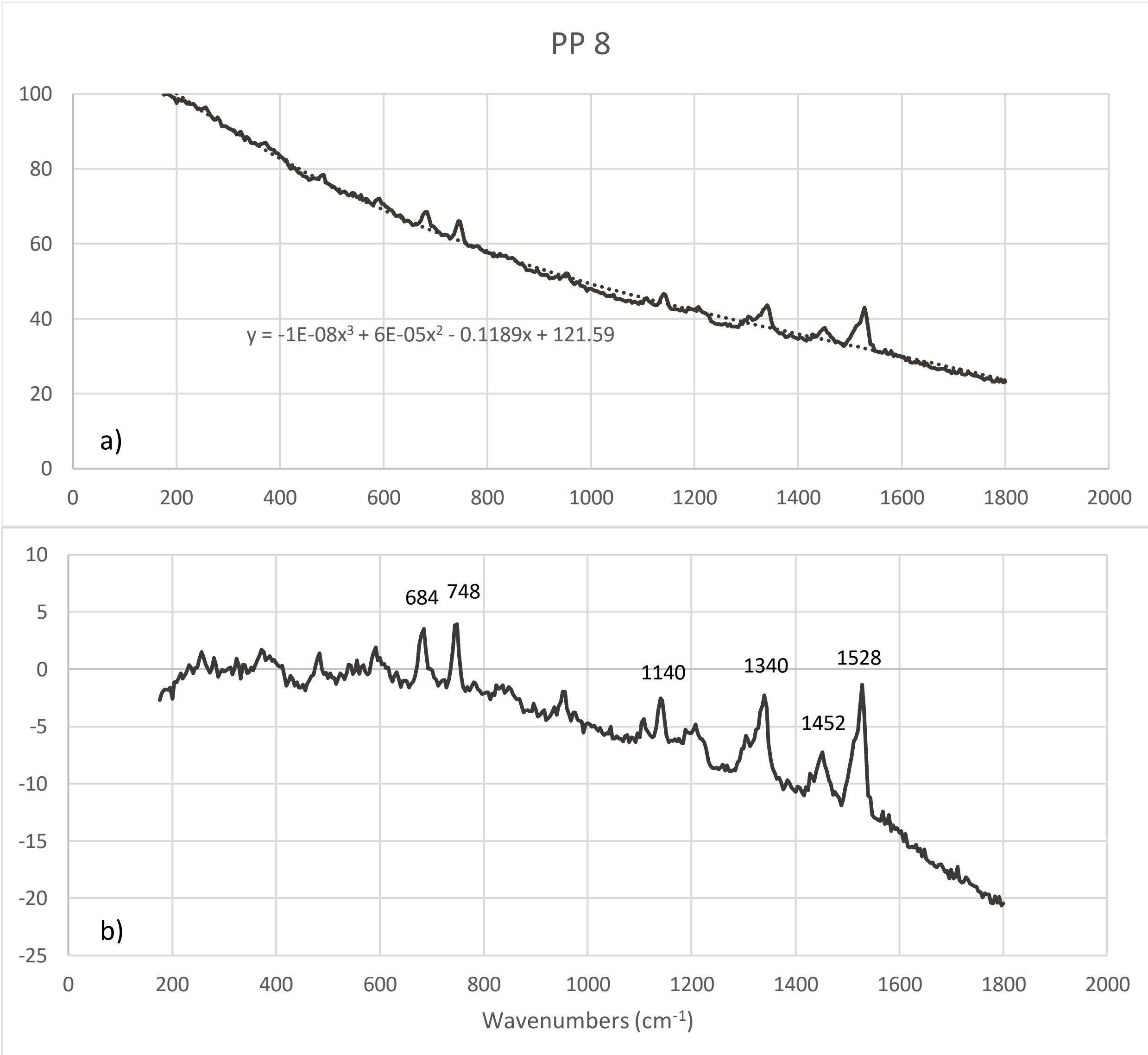

Figure 3.5 Raman spectra of PP 8 a) as obtained b) after fluorescence interference removed

Similarly, HDPE 7 showed significant fluorescence interference. The removal of the fluorescence interference did not improve the identification of the Raman peaks. However, based on the raw peak wavenumbers, HDPE 7 had similar peaks to PP 8 and cannot be identified based on this analysis.

Like PP 8 and HDPE 7, HDPE 9 showed significant fluorescence, however it remained identifiable based on their stronger peaks. The fluorescence interference was removed to enhance the peaks, but it was not necessary to identify the sample's resin type.

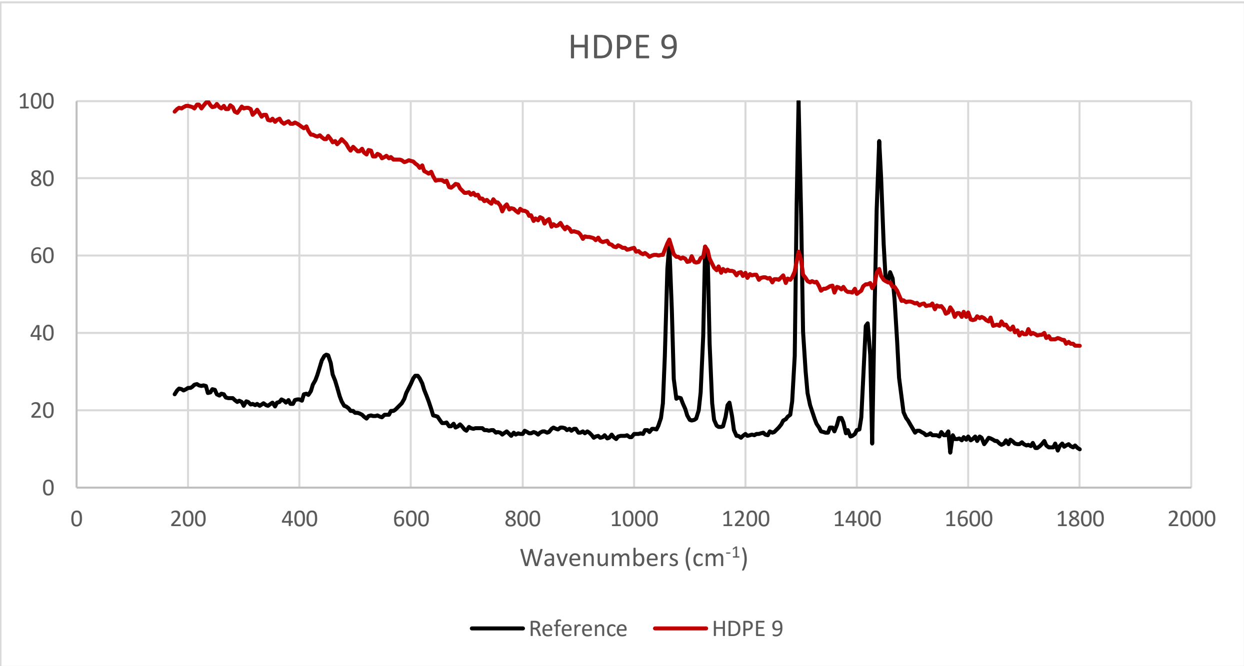

Figure 3.6 Raman spectrum of HDPE 9 with reference

The Raman spectrum of HDPE 2 had so much fluorescence interference that any Raman signals were lost. PET 2 did not provide any Raman or fluorescence signals. It was simply a noisy baseline.

3.3.3 Clear Samples

Four clear samples were tested to see if the transparency had any effect on the spectra. These samples were different resin types and had a variety of thicknesses. The results were varied in their clarity. The thicker samples of PP 6 and PET 2 gave clear spectra, similar to results with white samples. PP 5 produced a noisy spectrum that can be distinguished as PP with difficulty (Figure 3.7). The spectrum for HDPE 6 had similar results to PP 5.

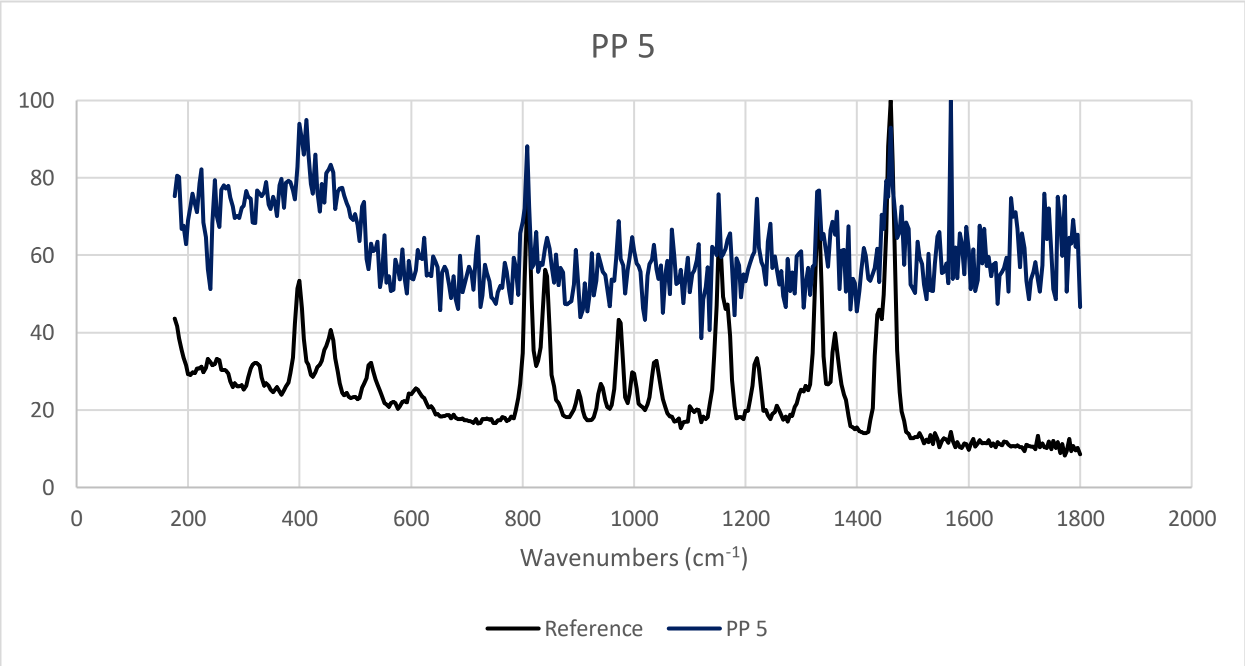

Figure 3.7 Raman spectrum of PP 5 with PP reference

3.3.4 Label Comparison

Three different types of labels were measured using Raman. First, there was HDPE 1, where there was a sticker label attached. As seen in Figure 3.8, the baseline is significantly higher than the reference and quite noisy. All the characteristic peaks of HDPE were present, but there were also many other peaks. These peaks line up with the PP spectrum. Based on these results, it can be concluded that the label was made of PP since the sample is HDPE.

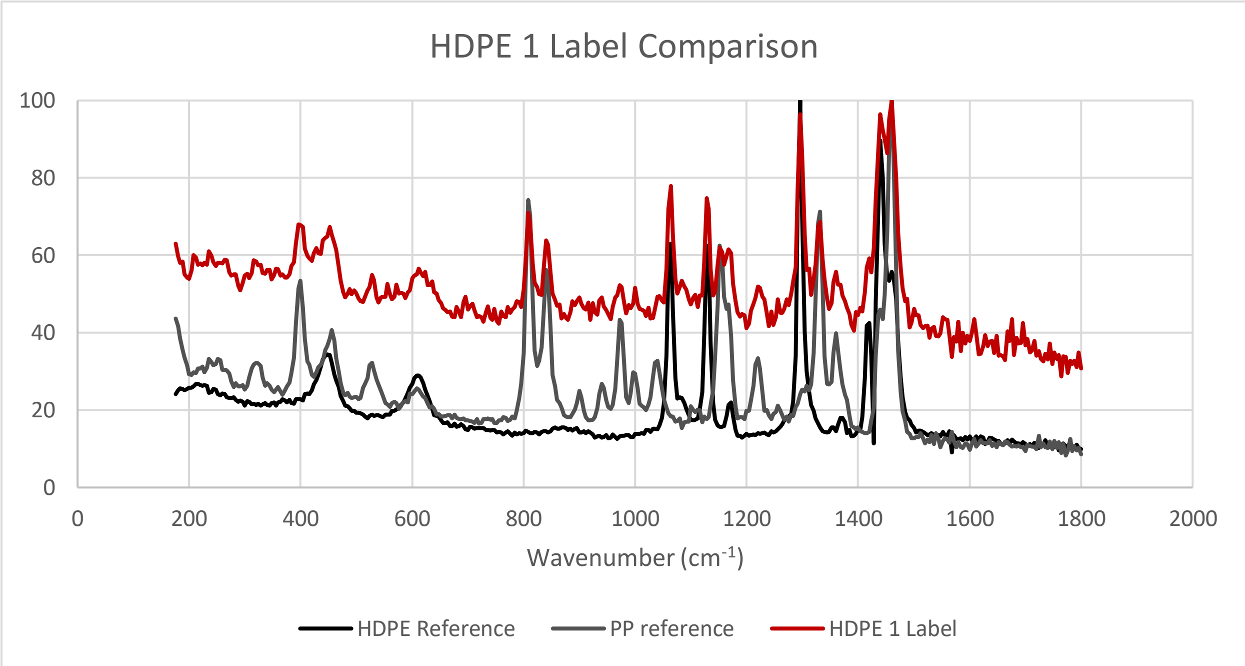

Figure 3.8 Raman spectrum of HDPE 1 with HDPE and PP references

Figure 3.9 Raman spectra for the white and green sides of HDPE 3

HDPE 3 is the cover of a yogurt container with a label printed directly onto the surface of the plastic. Figure 3.9 shows the spectra for either side of the sample. The interior was white and produced a strong and clear spectrum, whereas the label was green and had significant fluorescent interference. After enhancing the peaks, they ended up having similar wavenumbers to the spectrum of PP 8 seen in Figure 3.5.

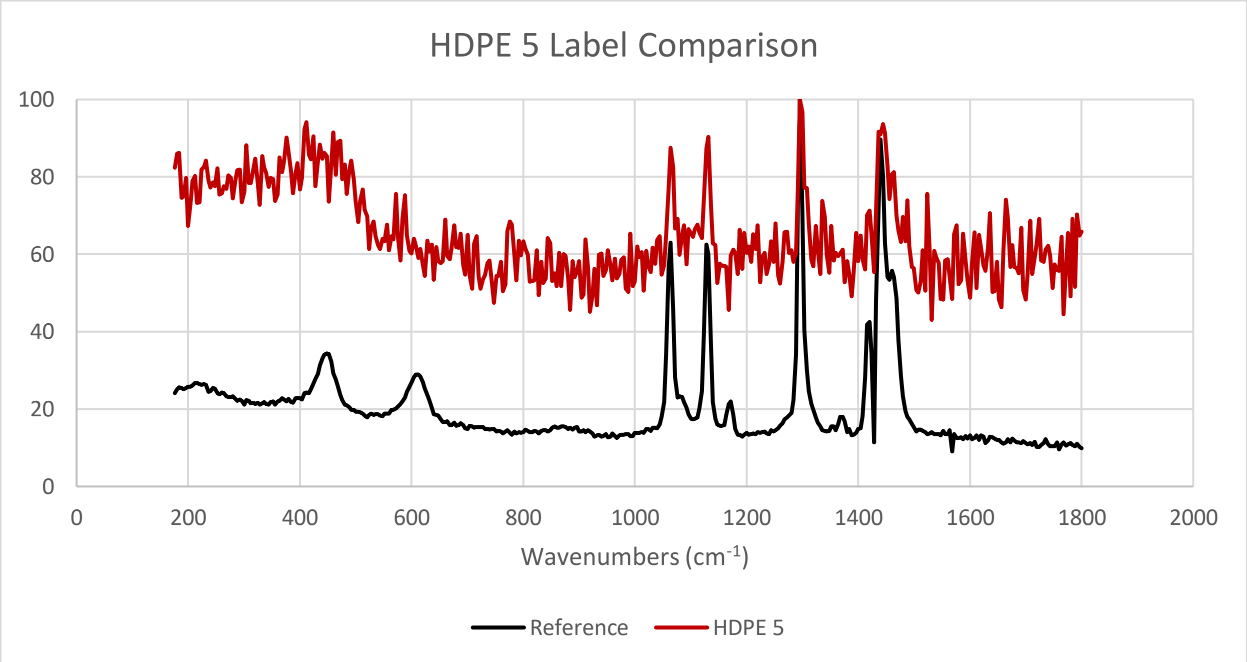

Figure 3.10 Raman spectrum of HDPE 5 with HDPE reference

The third type of label was printed black writing. The peaks were not very strong compared to the baseline, however based on these peaks, it is still easy to identify this sample as HDPE.

Chapter 4 Physical Sorting Techniques

4.1 Introduction

A secondary part of this project was to explore some of the simpler physical sorting techniques being used to sort plastics. Some of these techniques were mentioned in Chapter 1. Plastic sorting by sink-float tank was the main physical sorting technique explored.

Density sorting has been used in other industrial processes such as mineral processing. The separation medium can be modified by adding chemical solutions, brines, or suspending fine, chemically inert particles in the fluid. Unless the samples are being sorted in a water-only medium, the samples need to be washed and then these chemicals are hopefully recovered. However, the extra washing and water processing is costly in time, energy, and money. [39]

A sink-float tank is becoming a more common physical sorting method for recycling systems. Since the resins have different densities, it is possible to separate them when suspended in a liquid of medium density, usually water. PP, LDPE, and HDPE have a lower density than water whereas PS, PVC, and PET are denser than water. A mixture of plastics is added to the sink-float tank and as the tank fills the plastics are agitated. The PP, LDPE and HDPE should float on the surface of the water and PS, PVC, and PET should sink. The floating plastics can be scooped out of the tank before the others are removed. [40]

Sink-float tanks cannot achieve the accuracy of the spectroscopic techniques explored in earlier chapters, however, there is potential to quickly and roughly sort plastic into two groups before beginning a more exact sorting.

4.2 Physical Sorting Methods

Polymers can be sorted based on their densities. The most basic medium for this sorting is water, however it is possible to manipulate the density of the sorting medium to change which plastics float or sink. The plastics were first tested in tap water, then in a second solution with a lower density. Ethanol was a good solvent to add to water to lower the density. It is non-toxic, miscible with water and readily accessible. Ethanol has a density of 0.7893 g/cm^3 at 20°C. [41]

Table 4.1 List of samples used in Mechanical sorting work

Sample name	Sample number	Description
PET 1	1	Hand soap refill bottle
PET 2	30	Disposable water bottle
PET 3	43	"Celebration" cookie tray
HDPE 1	2	Shampoo bottle
HDPE 2	7	Carpet spot cleaner bottle
HDPE 3	20	"Activia" yogurt container cover
PVC 1	53	PVC pipe
PVC 2	50	Vinyl glove
PVC 3	47	Shower curtain
LDPE 1	5	Milk carton seal
LDPE 2	24	"Superstore" plastic bag
PP 1	3	Hand soap refill bottle cover
PP 2	8	Carpet spot cleaner bottle cover
PP 6	31	Protein powder scoop
PS 1	41	"Tim Hortons" hot drink cover
PS 2	42	Take-out drink cover

For the first set of tests, 100mL of room temperature tap water was placed in a beaker. Each sample was individually placed into the beaker of water and agitated with a stir stick for approximately 5 seconds, making sure that the sample was fully submerged at least once. The sample was then allowed to settle, either floating to the top or sinking to the bottom.

Table 4.2 Densities of the plastic polymers [14]

Resin Type	**Densities (g/cm^3)**
PET	1.300-1.400
HDPE	0.940-0.970
PVC	1.300-1.450
LDPE	0.915-0.950
PP	0.90-0.91
PS	1.040-1.050

For the second solution, the goal was to lower the density of the medium enough to ensure the PS samples would sink. Based on the densities of the resins, 0.97 g/cm^3 became the target density. Perry's Chemical Engineer's Handbook 8th Ed. has a table of the densities of mixtures of ethanol and water at 20°C. 19% w/v or 23.4% v/v ethanol would give a density of 0.96991 g/cm^3. [42]

23.4mL of 95% ethanol was added to 76.6mL of room temperature tap water in a beaker. The solution was gently stirred to ensure uniformity. The same samples were individually placed in the solution and agitated for approximately 5 seconds making sure the sample was fully submerged at least once. The sample was then allowed to float to the top or settle at the bottom of the beaker.

4.3 Results and Discussion

Table 4.3 Results from the sink-float tests with water and with water-ethanol mixture

Sample name	Water	Water-Ethanol mixture
PET 1	Sink	Sink
PET 2	Sink	Sink
PET 3	Sink	Sink
HDPE 1	Float	Float – somewhat suspended
HDPE 2	Float	Float
HDPE 3	Float	Float – somewhat suspended
PVC 1	Sink	Sink
PVC 2	Float	Float
PVC 3	Sink	Float/ Sink
LDPE 1	Float	Float
LDPE 2	Float	Float
PP 1	Float	Float
PP 2	Float	Float
PP 6	Float	Float
PS 1	Float – slow rise	Sink
PS 2	Float – slow rise	Sink

As expected, the PET samples all sank in both sets of tests as PET has a density significantly greater than 1 g/cm^3. The HDPE samples floated; however, some of the HDPE samples acted oddly in the water-ethanol mixture test. After agitation, the sample floated and the length of one side was at the surface, but rest of the sample remained submerged at an approximate 45° angle. This occurred for HDPE 1 and HDPE 3.

PVC 1 sank, which is the expected outcome for PVC based on its density. The results of PVC 2 floating further prove that the sample was not actually made of PVC. PVC 3 had interesting results. It was initially tested in the water-ethanol mixture first, where it floated. Then it was tested in the water solution, which has a higher density. The sample sank in the water.

This result was puzzling, so the sample was tested in the water-ethanol mixture again and this time it sank. It is unclear why the PVC 3 sample floated the first time before sinking later, however there are a few possibilities. First, there could have been a powder on the surface of the sample, which is a vinyl glove, that might have created miniscule bubbles helping it float. After being submerged in a water-ethanol mixture, the powder could have washed off causing the sample to sink in further tests. The second possibility is that since the sample is a film, the surface tension was not sufficiently broken during the agitation or there was an air bubble caught underneath the sample that went unnoticed.

LDPE and PP were expected to float, and both did for all their samples. PS floated in the water tests but rose to the surface very slowly, the samples were almost suspended in the water. It was this result that led to the idea of a second set of tests with a lower density to see if it was possible to get PS to sink. In the water-ethanol mixture tests, the PS samples did sink after the agitation.

Occasionally the sample would float on the surface when added to the beaker but would sink after. It is presumed that the surface tension was holding up a sample that should and would otherwise sink. This happened with both sets of tests.

Chapter 5 Conclusion and Future Work

After completing an exploratory analysis of both FTIR and Raman spectroscopy a number of conclusions can be attained. A similar number of samples were tested with each technique however the software used for the FTIR was significantly more comprehensive which enabled more extensive spectrum analysis. If a similar software was obtained for the Raman analysis it is likely that equally comprehensive analysis could be achieved.

One of the limitations of this project was the difficulty to acquire a variety of samples that would reflect the range of MSW produced by a household with each of the six resin types represented. PVC and PS were the hardest to acquire. Any future work should have these resin types represented with greater number and variety.

The effect of labels on the identification of a plastic sample was measured with both techniques. While FTIR could not see through a sticker label on a sample, Raman presented a spectrum that combined the spectrum of the sample and of the label. When measuring HDPE 3, a yogurt container with green labelling, neither technique could identify the sample plastic type when measuring the green exterior of the sample. The FTIR spectrum showed another material while the Raman spectrum was overpowered by fluorescence obscuring any Raman activity.

The colour of the sample did not seem to have a large effect on the FTIR results; however, this was not intensely studied like it was studied in the Raman work. Fluorescence had a ranging effect on the Raman spectra of the coloured samples. For some samples, there was a higher baseline with greater background noise but still easily identifiable, then there were samples that produced Raman peaks that were not characteristic of any of the plastics being studied. There were samples with extremely high fluorescence interference, but a few peaks remained visible to identify the sample, and samples where the fluorescence completely overpowered the Raman signals. Finally, there were a few samples that were Raman inactive.

The FTIR spectra had a much larger spectral range compared to the range used in Raman however, for both techniques the key findings were seen between 700-1700cm^{-1} approximately. While the Raman analysis did not extend to the exploration of use of a smaller spectral region, the majority of the characteristic peaks were within the region outlined above, more specifically greater than 1000cm^{-1}. The FTIR analysis of a shorter spectral region determined that the 1300-1550cm^{-1} region correctly identified the resin type with the highest correlation values and was able to definitively identify the resin type when compared to each of the different plastic types. In future, there is potential to try to identify plastics based on a shorter Raman spectral region as was successfully completed with the FTIR analysis.

A series of resolution tests were completed using FTIR where it was determined that a single scan with a resolution of 5cm^{-1} in the shorter spectral region of 1300-1550cm^{-1} was still able to identify the correct resin type with at least 95% correlation. A similar resolution test was not conducted using the Raman spectrometer however would certainly be an area of interest for future experimentation.

There are many factors to consider when concluding which of these spectroscopic techniques would be most effective in a proof of concept and later fully industrial sorting model. The advantages of FTIR are that it can be used to definitively identify samples using a smaller spectral region and lower resolution and number of scans than the standard setting and colour does not seem to have a significant impact. The advantages of Raman are that it is able to identify the resin type through some of the sticker labels and Raman is already commonly used in other industrial settings such as pharmaceuticals or mining. At the moment, it is not possible to choose one technique over the other. Additionally, a final decision would be faulty if it did not consider NIR spectroscopy as an option. Therefore, before making a decision a similar series of tests need to be conducted using NIR.

With respect to the physical sorting techniques, the sink-float tank with water and with the water-ethanol mixture gave mostly expected results. PET and PVC sank in both media. HDPE, LDPE, and PP floated in both media. PS floated in the water but was slow to rise to the surface after the agitation since its density was very similar to the density of water. PS sank in the water-ethanol mixture as the density was lowered. Any future work on sink-float tanks would need to consider buoyancy in greater depth and how the shape and size of the samples affects the results.

The larger scope of this project is jointly headed by Dr. Nola Etkin and engineering professor Dr. Nadja Bressan. Dr. Bressan is focusing on the removal of plastics from the sink-float tank, colour sorting, and the overall automation of the project. She has been working on this project with one of her classes and the students are designing ways to remove plastic samples from the tank. The samples Dr. Bressan and her students are using are the same samples that were collected for this project. Many ideas from the physical sorting chapter were also worked out with Dr. Bressan. It was hoped that there would be some results to share from this work. A number of delays from COVID-19 meant that Dr. Bressan and her students have not yet finished their work however, a general idea of the plans will be provided below.

For the removal of the plastics from the sink-float tank, Dr. Bressan’s students created a basket that can be submerged into the tank at different levels using a robot to separate the floating plastics from the plastics that have sunk. Figure 5.1 shows a computer aided design (CAD)

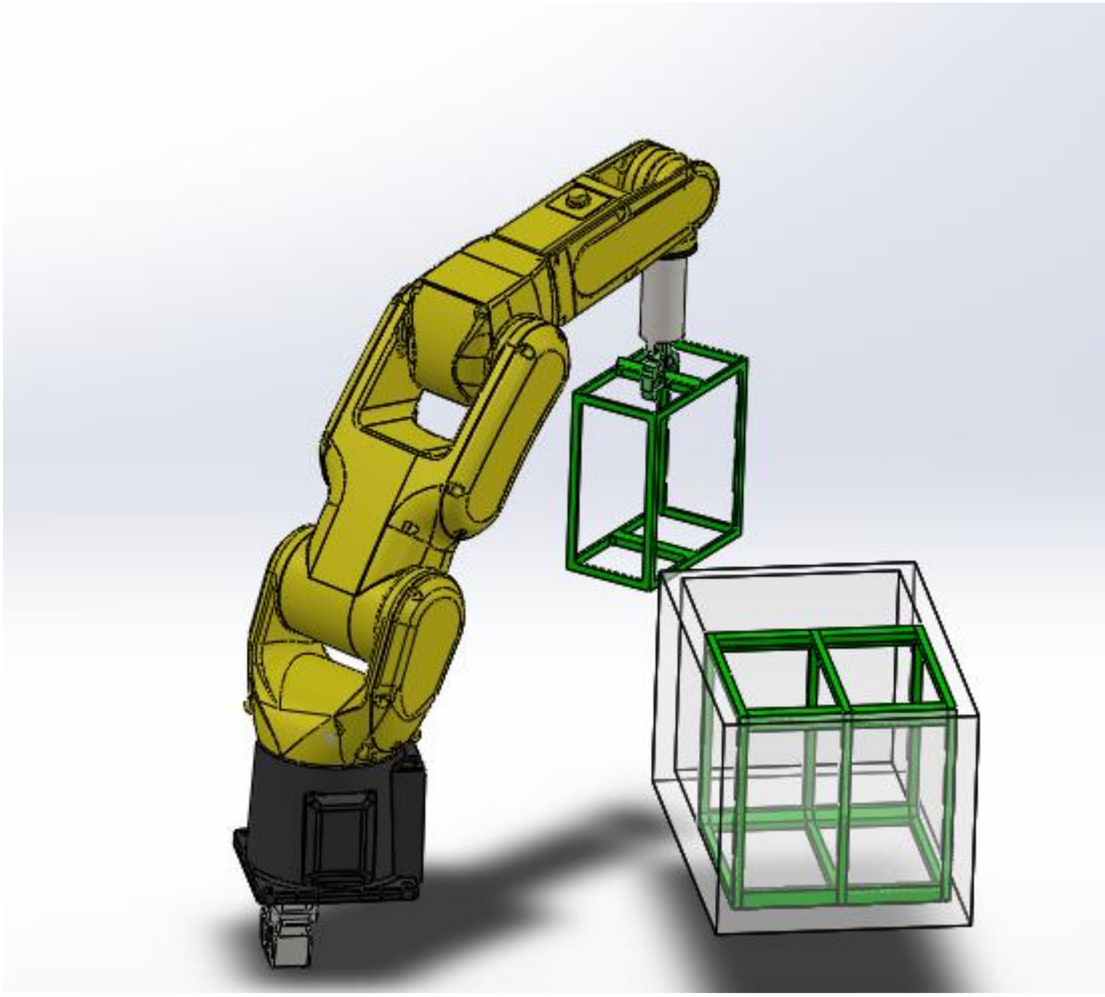

Figure 5.1 CAD model of the proposed baskets and the robot used to remove plastics from the sink-float tank

The colour sorting will involve the plastic samples being placed on a conveyor belt. The samples will pass by colour sensor and be sorted by colour with a flipper arm. The colour sensors will be red, green, blue (RGB) sorting sensors that use a logic gate system. These colour sensors can sort samples into nine different colour categories: red, green, blue, yellow, cyan, magenta, white, and black.

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Appendix A – Sample List

Sample number #: number given during the experiments

Size: small (s), medium (m), or large (l)

Rigidity : soft, medium, or hard

Label/writing size : small (s), medium (m), large (l)

Table AP.1 All samples with description and properties

Sample name	#	Description	RIC #	Colour	Size	Rigidity	Label size
PET 1	1	Hand soap refill bottle	1	clear	l	med	s
PET 2	30	Disposable water bottle	1	clear	m	med	n/a
PET 3	43	"Celebration" cookie tray	1	clear brown	m	med	n/a
PET 4	32	Packaging (generic) #2	1	clear	s	med	n/a
PET 5	34	"Tim Hortons" juice bottle	1	clear	s	med	m
HDPE 1	2	Shampoo bottle	2	white	m	med	m
HDPE 2	7	Carpet spot cleaner bottle	2	dark blue	m	hard	m
HDPE 3	20	"Activia" yogurt container cover	2	white	s	med	m
HDPE 4	4	Vitamin bottle	2	white	m	hard	l
HDPE 5	11	Packing sleeve (generic)	2	clear	l	soft	m
HDPE 6	9	Flyer sleeve	2	clear	s	soft	s
HDPE 7	21	"Activia" yogurt container cover #2	2	blue	s	med	m
HDPE 8	45	4-pack cover red	2	red	m	hard	n/a
HDPE 9	49	"Tide" laundry detergent	2	orange	l	med	m
HDPE 10	10	Milk carton	2	white/blue	m	med	m
HDPE 11	6	Milk carton cover	2	white	s	hard	n/a
HDPE 12	12	Carpet cleaner bottle	2	dark blue	l	hard	m
HDPE 13	26	Margarine container cover	2	white	m	med	m
HDPE 14	33	2L carton	2	opaque	l	med	n/a
HDPE 15	35	"Tim Hortons" juice bottle cover	2	opaque	s	hard	n/a
HDPE 16	44	6-pack cover purple	2	purple	m	hard	n/a

Sample name	#	Description	RIC #	Colour	Size	Rigidity	Label size
HDPE 17	46	6-pack cover blue	2	blue	m	hard	n/a
HDPE 18	48	“Arm and hammer” laundry soap	2	yellow	l	med	m
PVC 1	53	PVC pipe	3	gray	s	hard	n/a
PVC 2	47	Shower curtain	3	opaque	m	soft	n/a
PVC 3	50	Vinyl lab glove	3	opaque	m	soft	n/a
LDPE 1	5	Milk carton seal	4	white	s	med	n/a
LDPE 2	24	“Superstore” plastic bag	4	green	m	soft	m
LDPE 3	14	“Wonder” hotdog bun bag	4	clear/white	m	soft	l
LDPE 4	52	Shipping packaging	4	gray	l	soft	s
LDPE 5	22	Tortilla bag	4	clear	m	soft	l
LDPE 6	36	Idared apple bag	4	clear	m	soft	m
LDPE 7	37	Carrot bag	4	clear	m	soft	l
LDPE 8	38	Brown sugar bag	4	clear	m	soft	l
LDPE 9	39	Multigrain bread bag	4	clear	m	soft	l
LDPE 10	40	Raisin bread bag	4	clear	m	soft	l
PP 1	3	Hand soap refill bottle cover	5	white	s	hard	n/a
PP 2	8	Carpet spot cleaner bottle cover	5	white	s	hard	n/a
PP 3	13	Carpet cleaner bottle cover	5	green	s	hard	n/a
PP 4	15	“Source” yogurt container	5	white	m	hard	l
PP 5	23	Grape bag	5	clear	m	soft	l
PP 6	31	Protein powder scoop	5	clear	s	hard	n/a
PP 7	16	“Source” yogurt container cover	5	red	s	hard	m
PP 8	18	Feta cheese container cover	5	blue	s	hard	m
PP 9	29	“Liberté” yogurt container cover	5	black	s	med	m
PP 10	17	Cream cheese container	5	white	s	hard	l
PP 11	19	“Activia” yogurt container	5	white	m	med	l
PP 12	25	Margarine container	5	white	m	med	m
PP 13	27	“Iogo” yogurt container	5	white	m	med	l
PP 14	28	“Liberté” yogurt container	5	white	m	med	m
PS 1	41	“Tim Hortons” hot drink cover	6	brown	s	med	n/a
PS 2	42	Take-out drink cover	6	clear	s	med	n/a

Appendix B – FTIR Spectra

Initial Tests

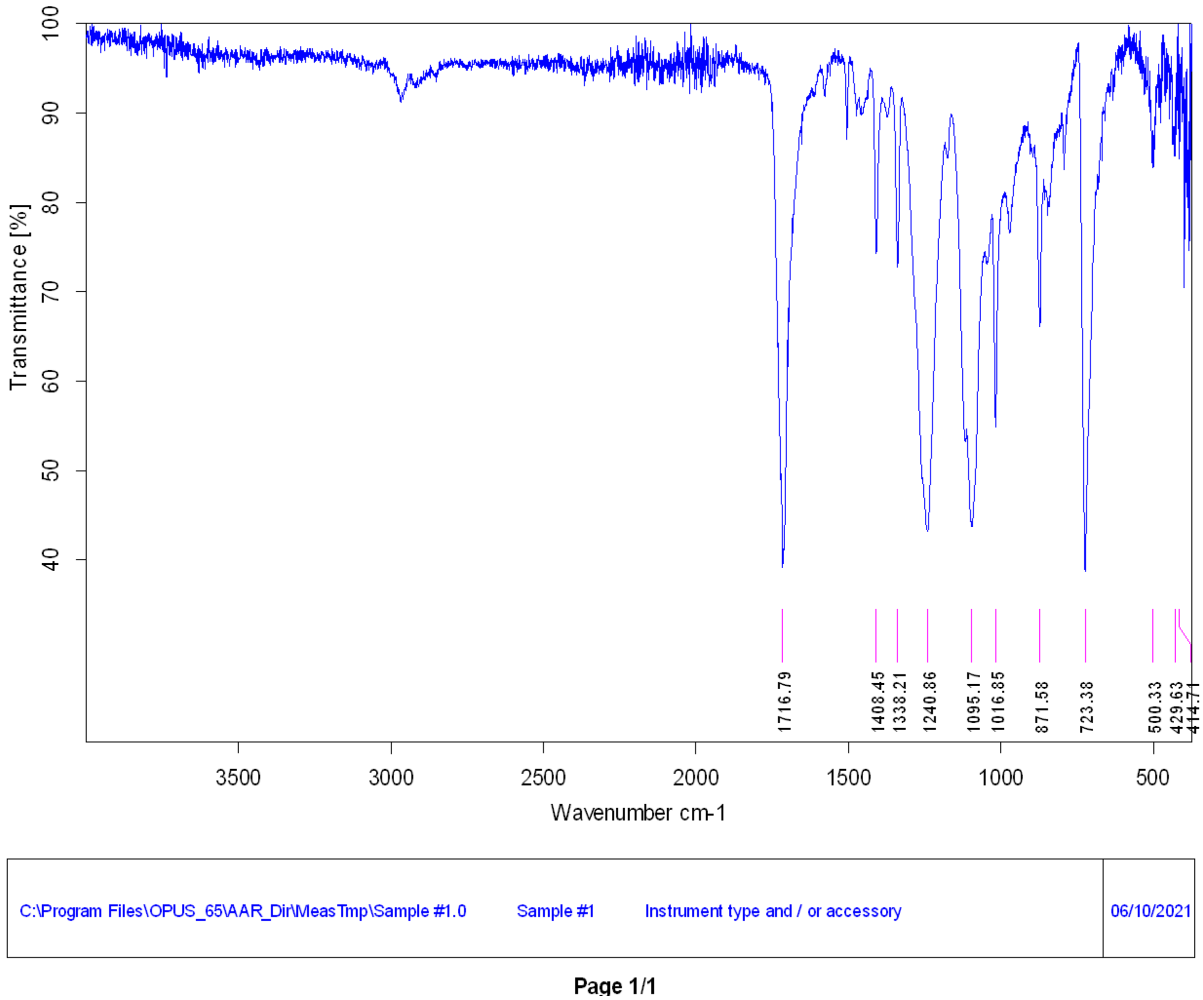


Figure AP. 1 FTIR spectrum of PET 1

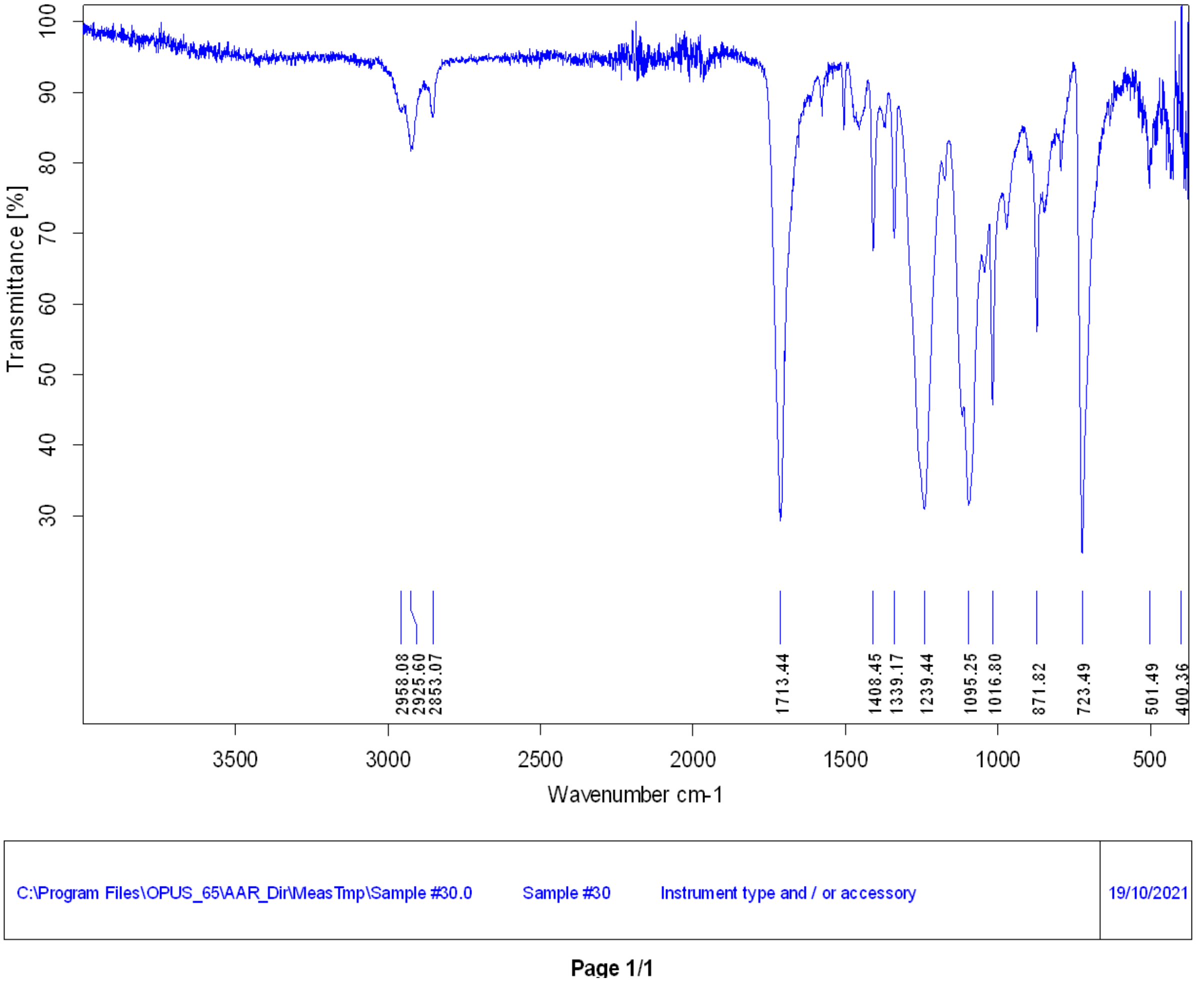


Figure AP. 2 FTIR spectrum of PET 2

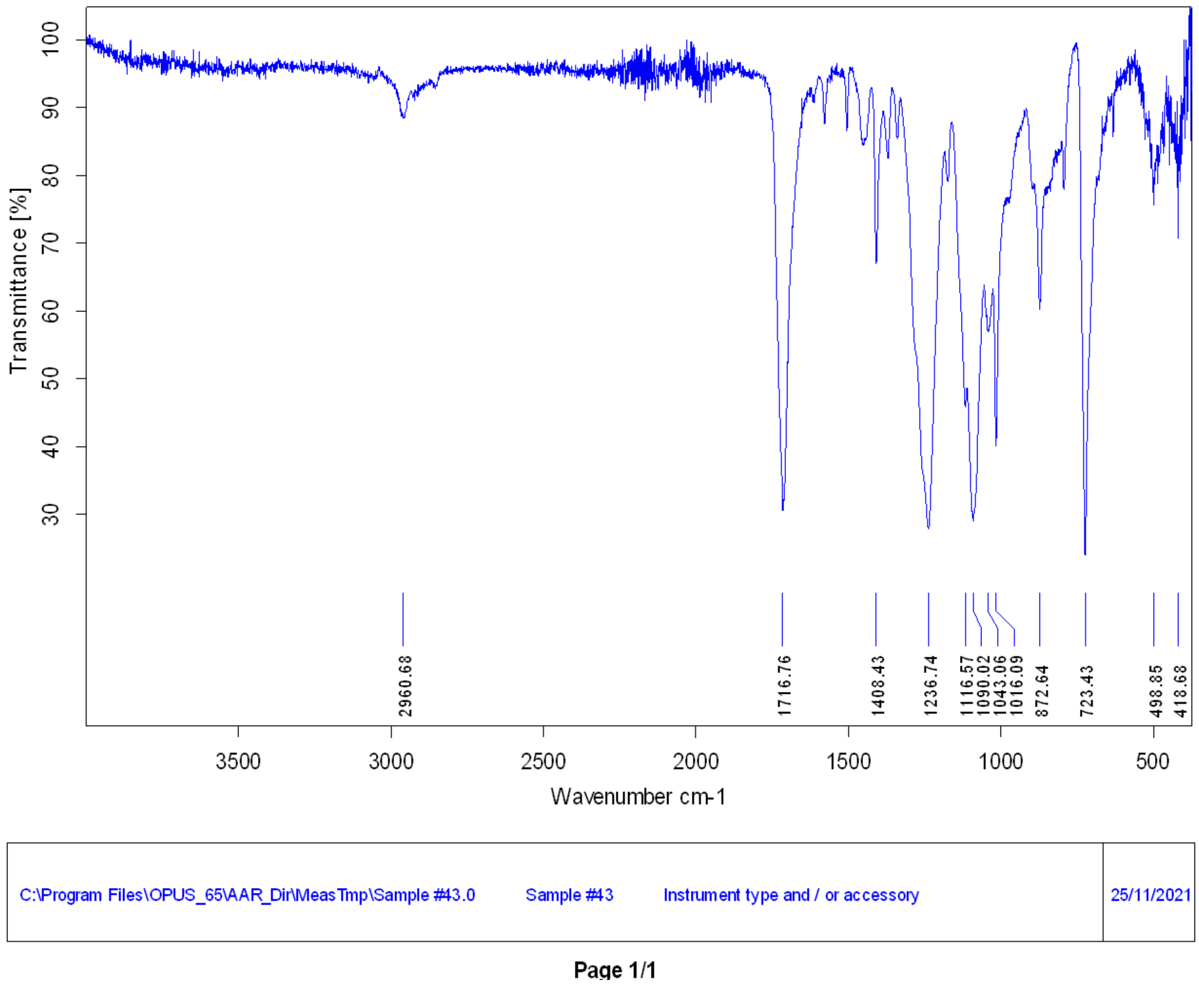


Figure AP. 3 FTIR spectrum of PET 3

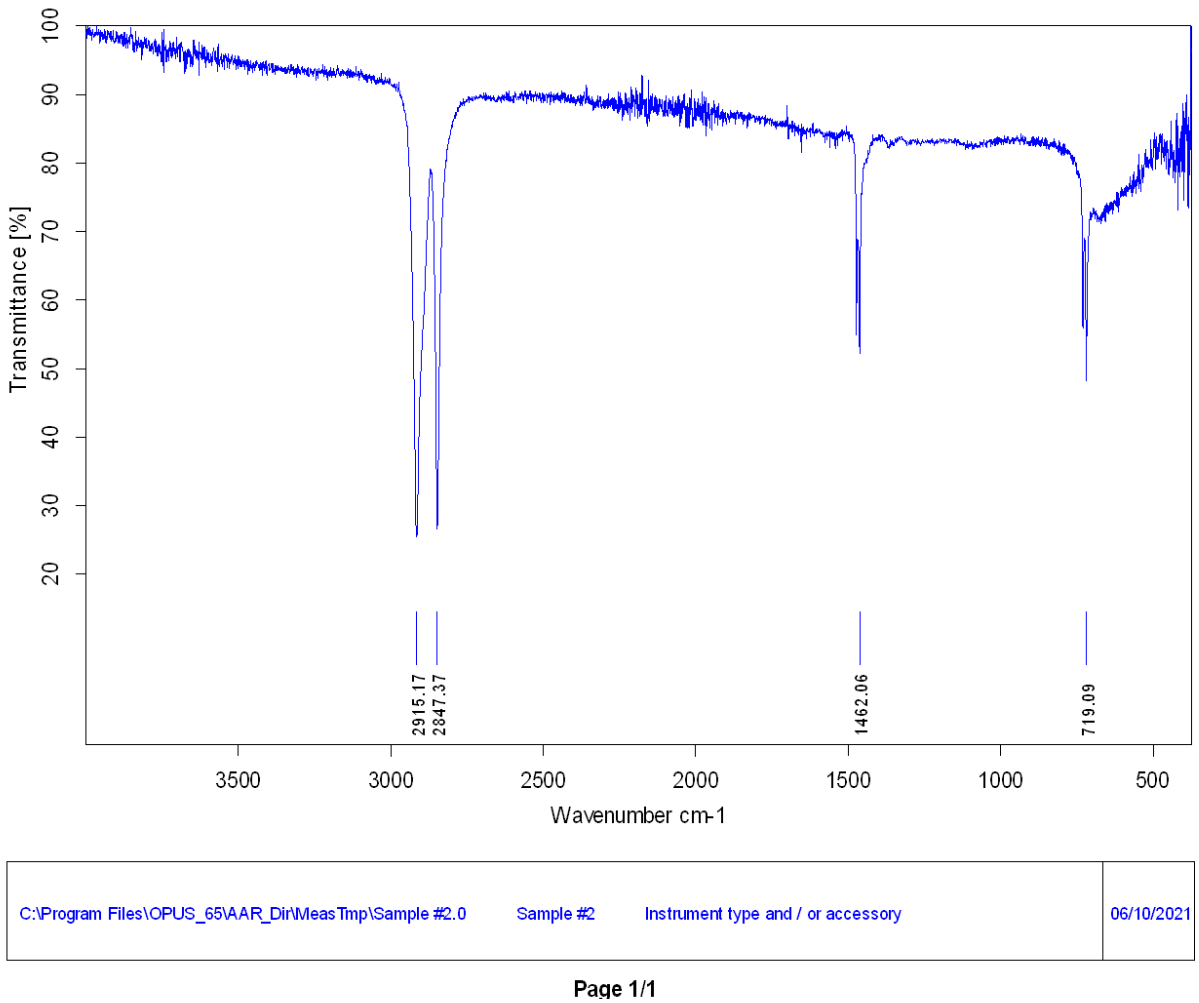


Figure AP. 4 FTIR spectrum of HDPE 1

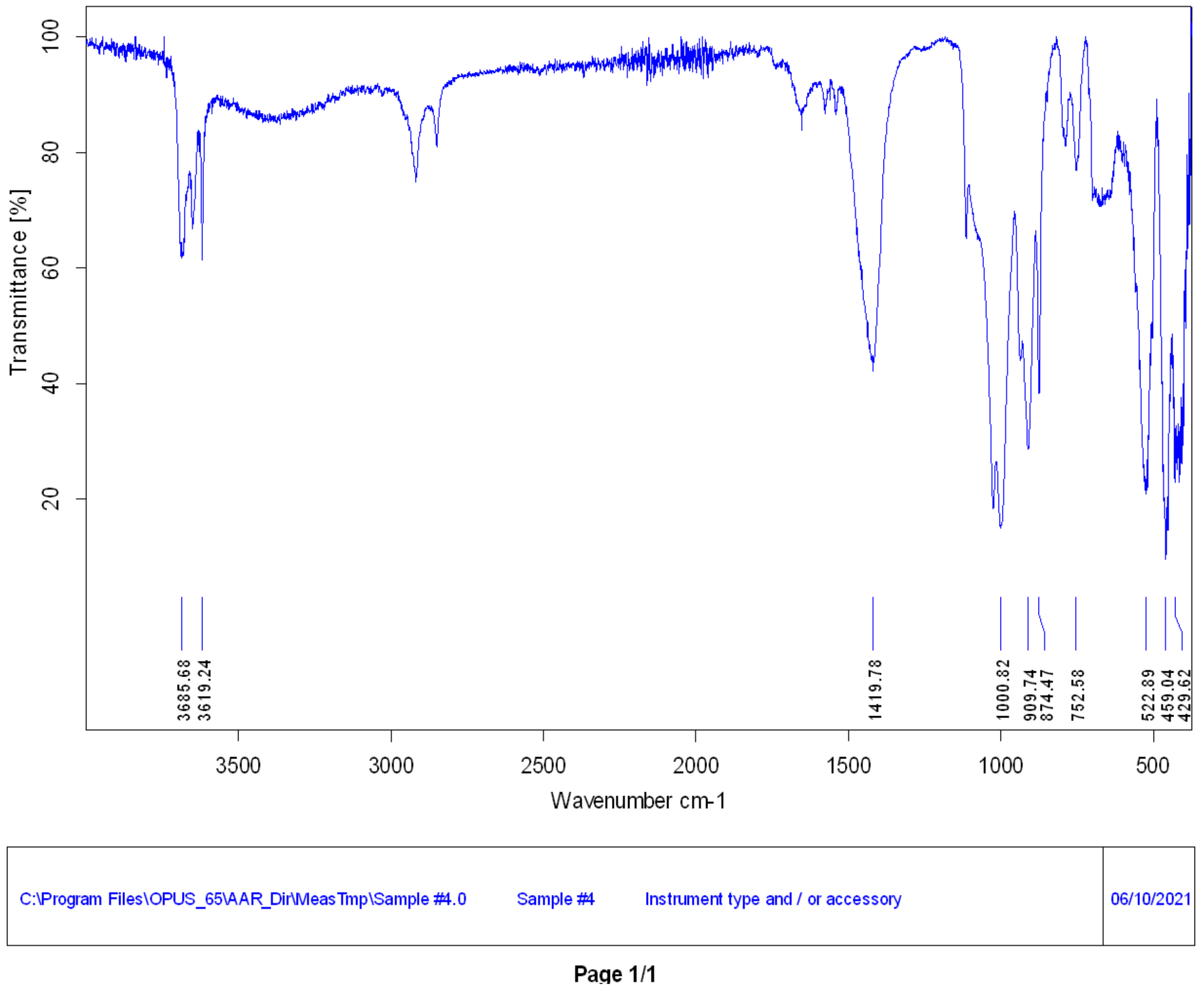


Figure AP. 5 FTIR spectrum of HDPE 4

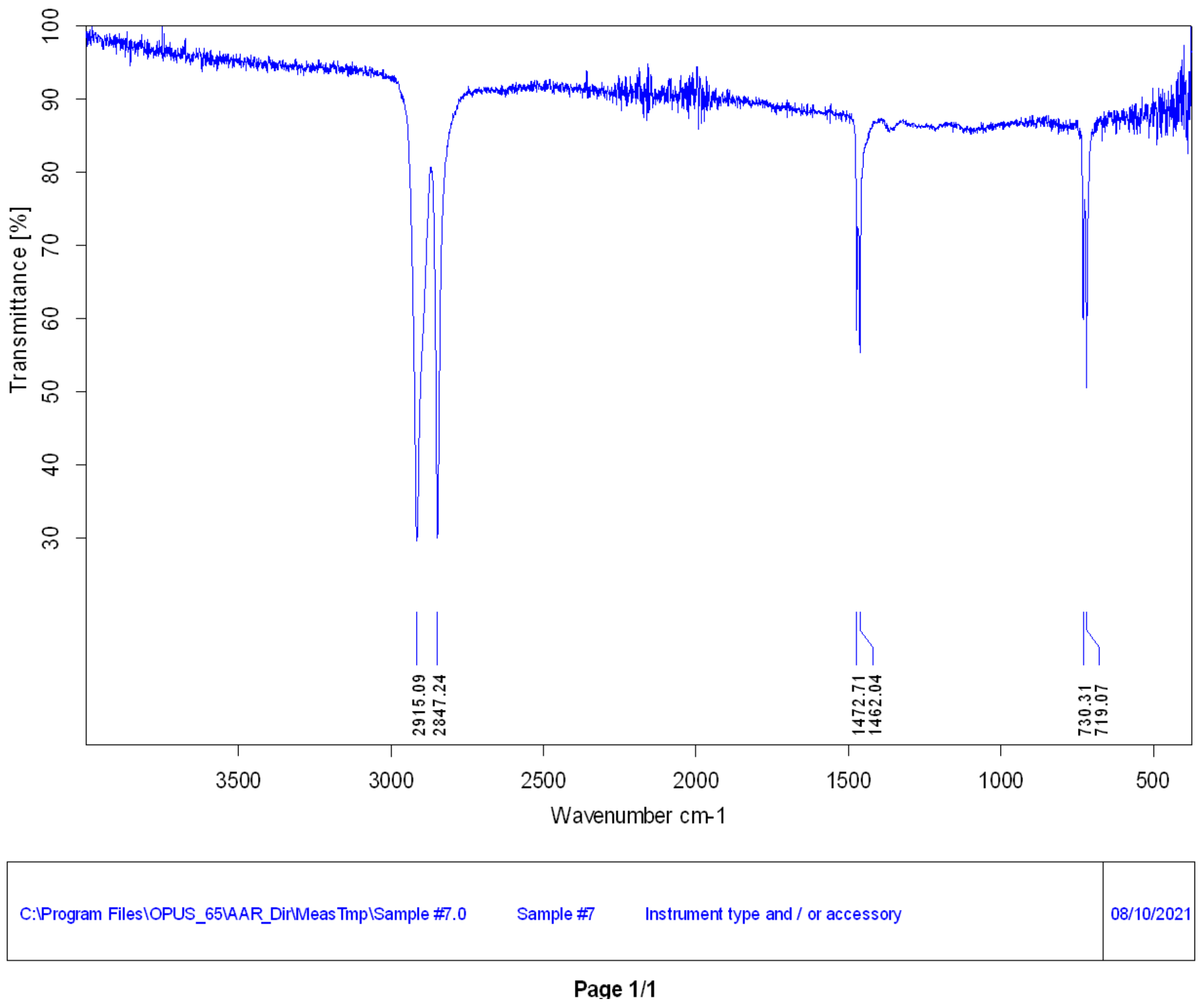


Figure AP. 6 FTIR spectrum of HDPE 2

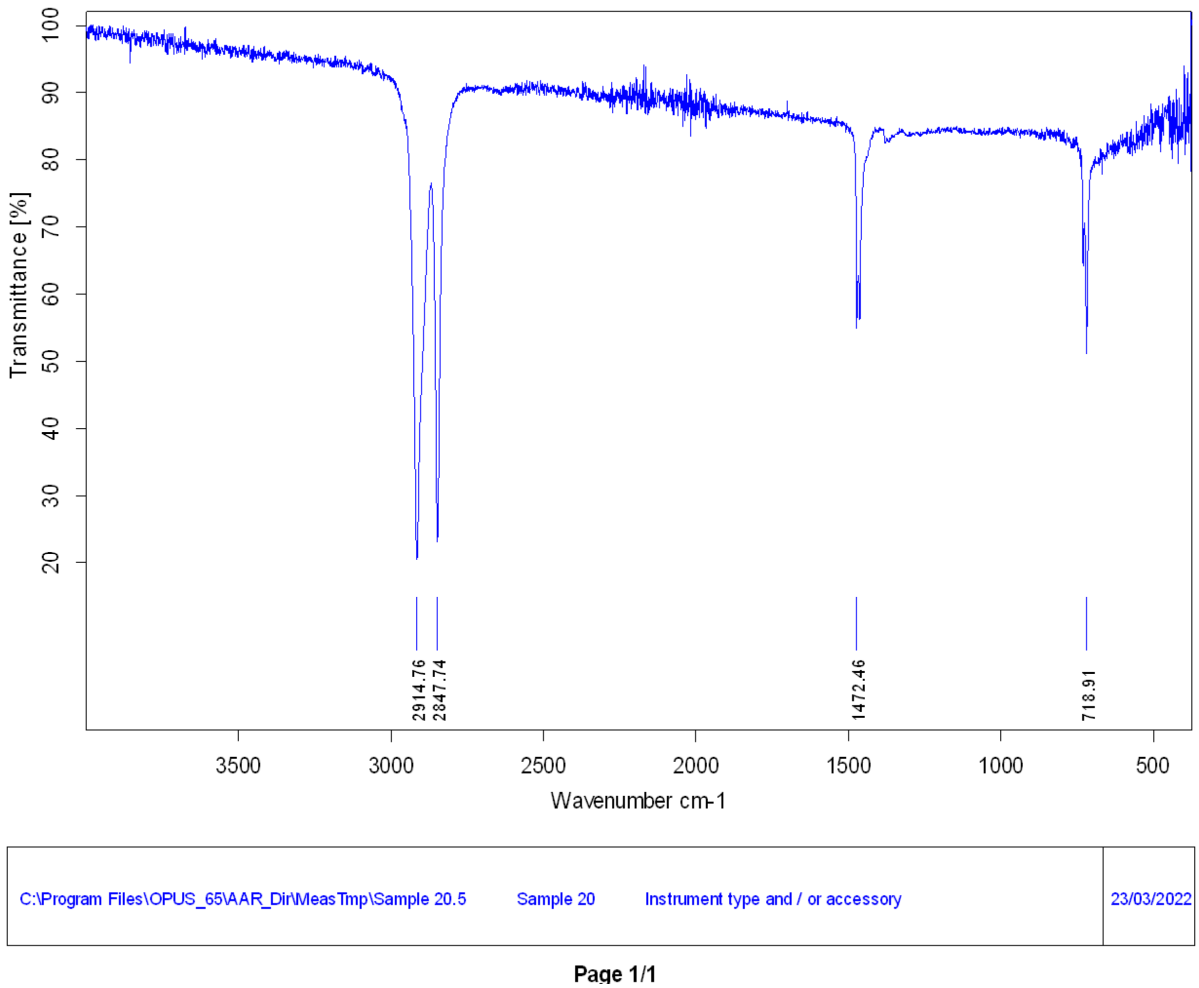


Figure AP. 7 FTIR spectrum of HDPE 3

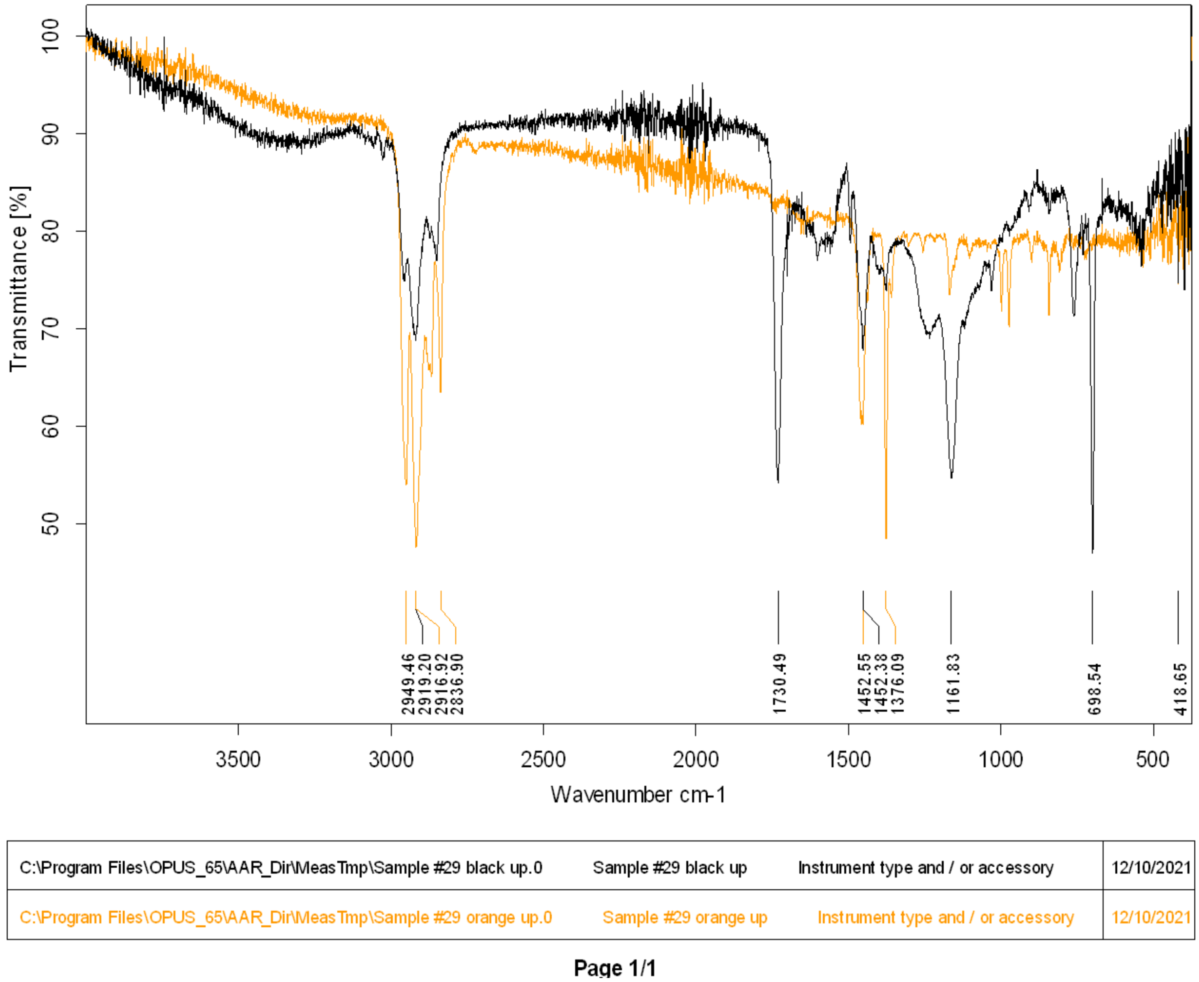


Figure AP. 8 FTIR spectrum of HDPE

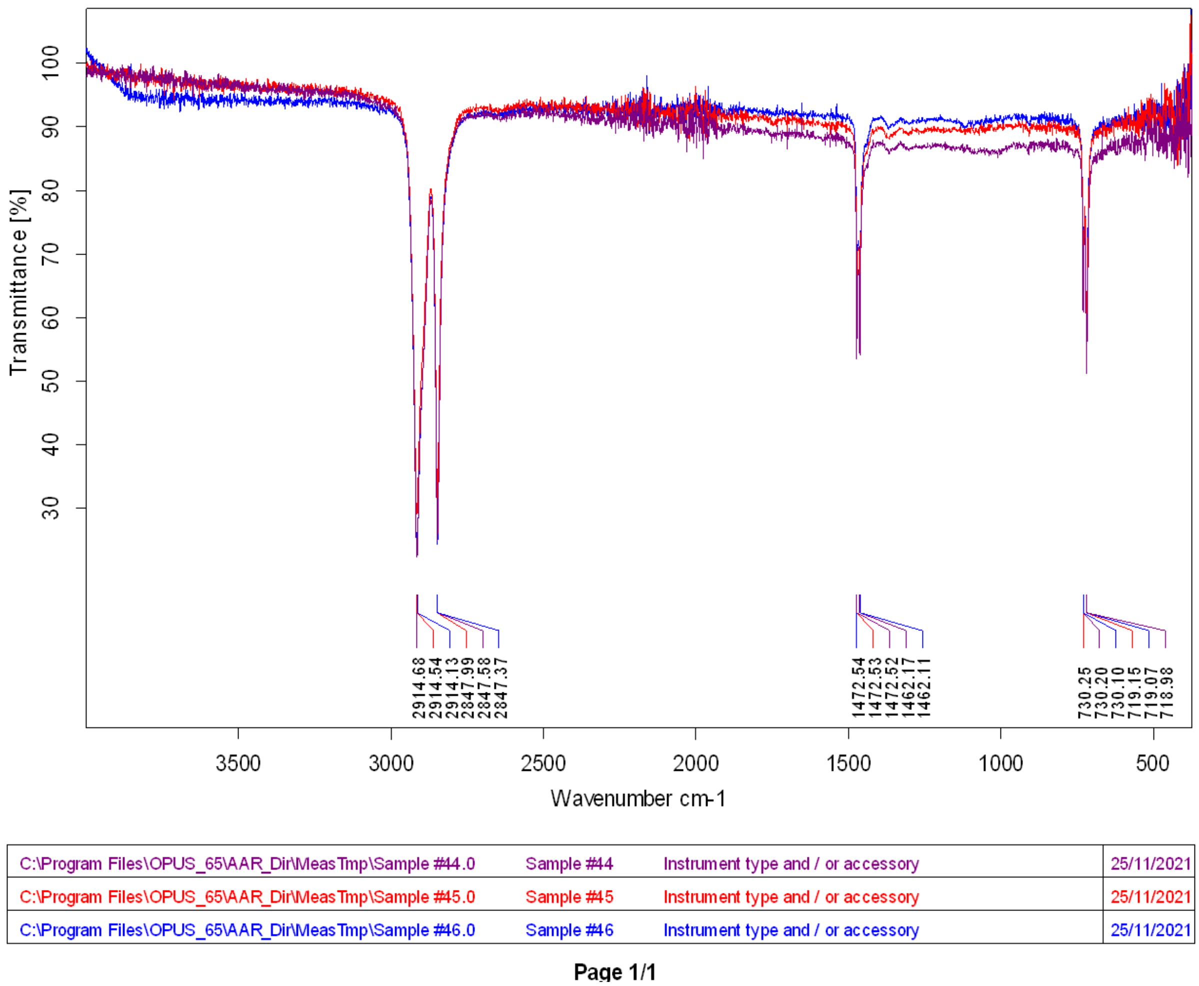


Figure AP. 9 FTIR spectra of HDPE

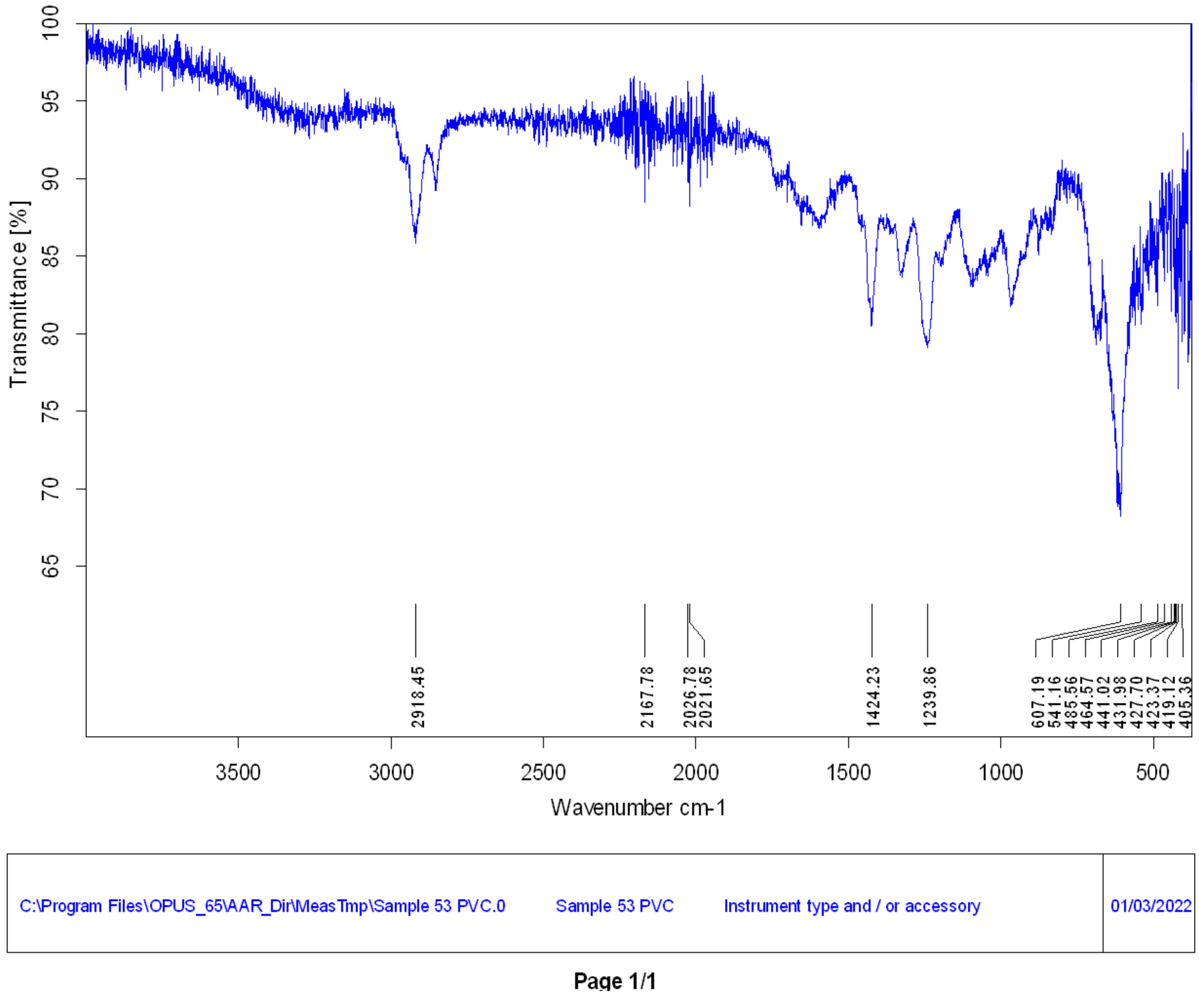


Figure AP. 10 FTIR spectra of PVC 1

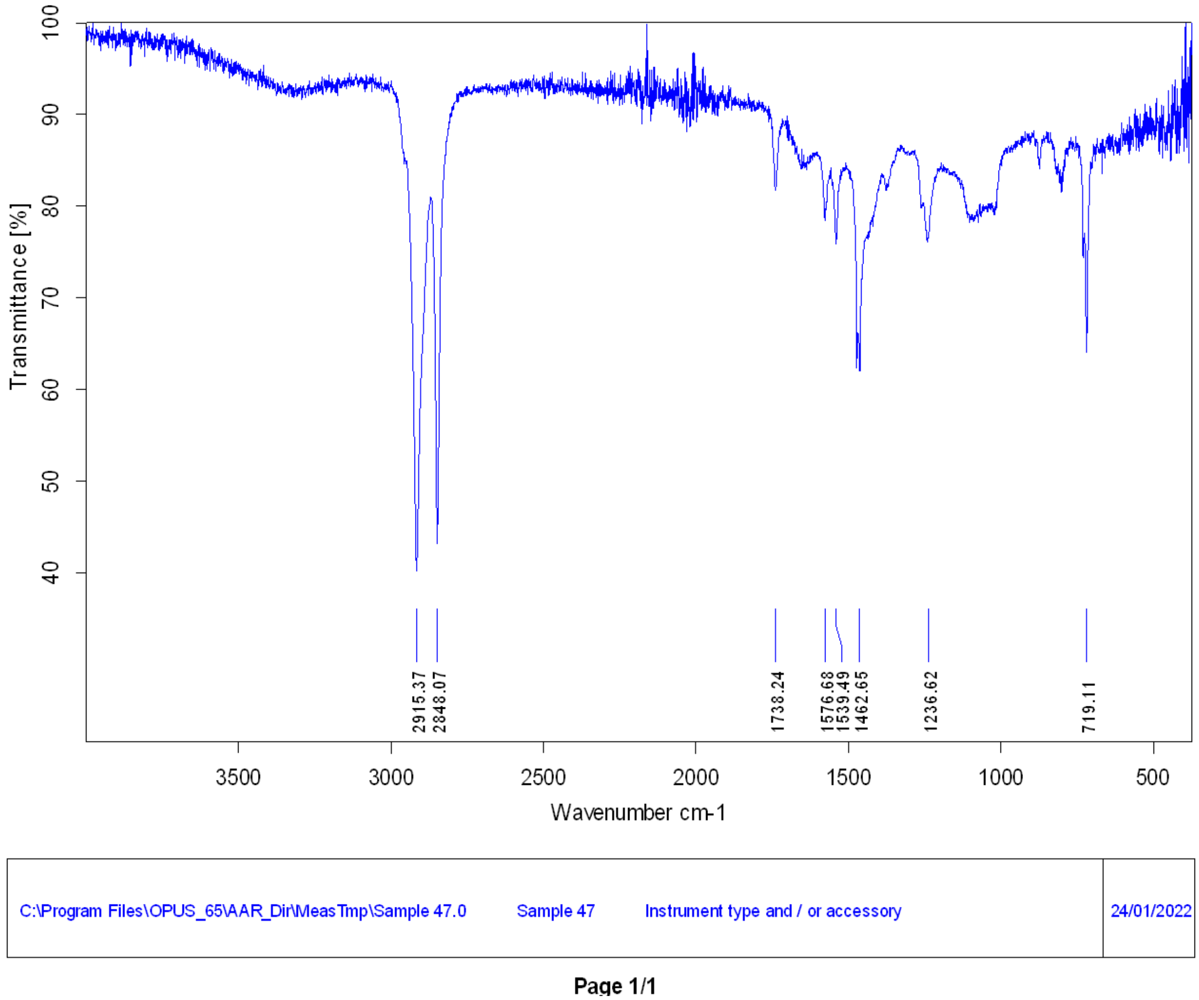


Figure AP.11 FTIR spectra of PVC 2

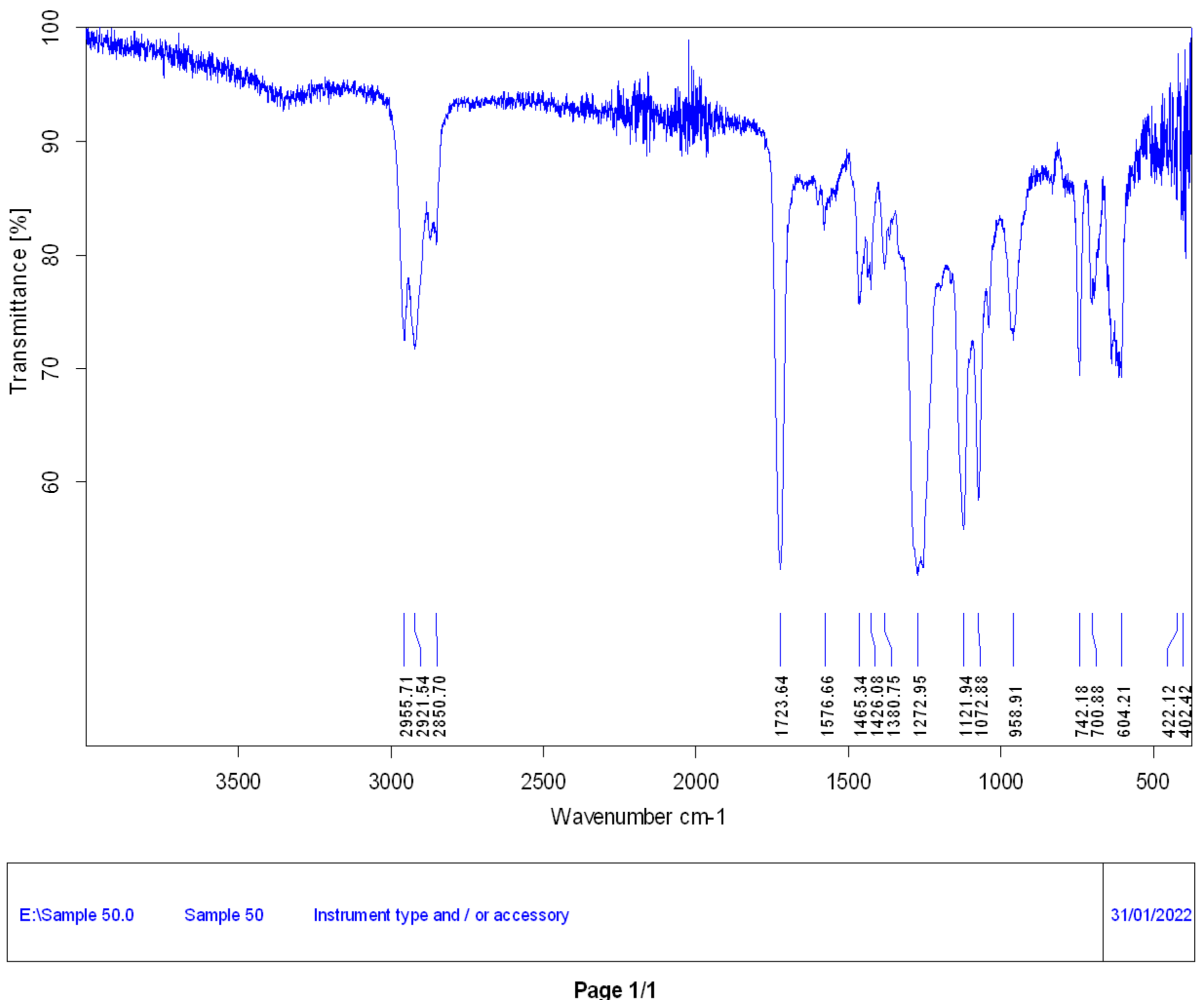


Figure AP. 12 FTIR spectra of PVC 3

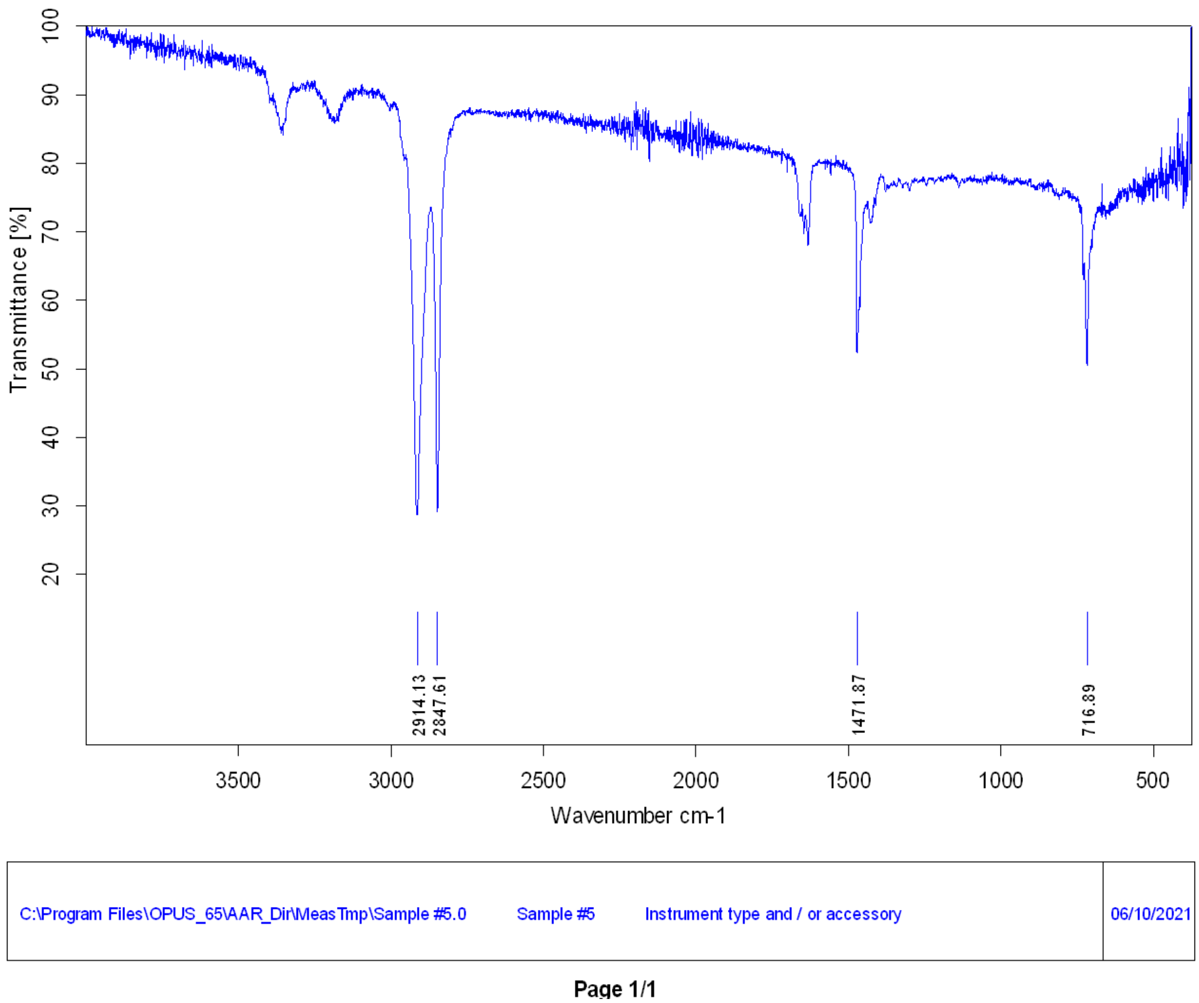


Figure AP. 13 FTIR spectrum of LDPE 1

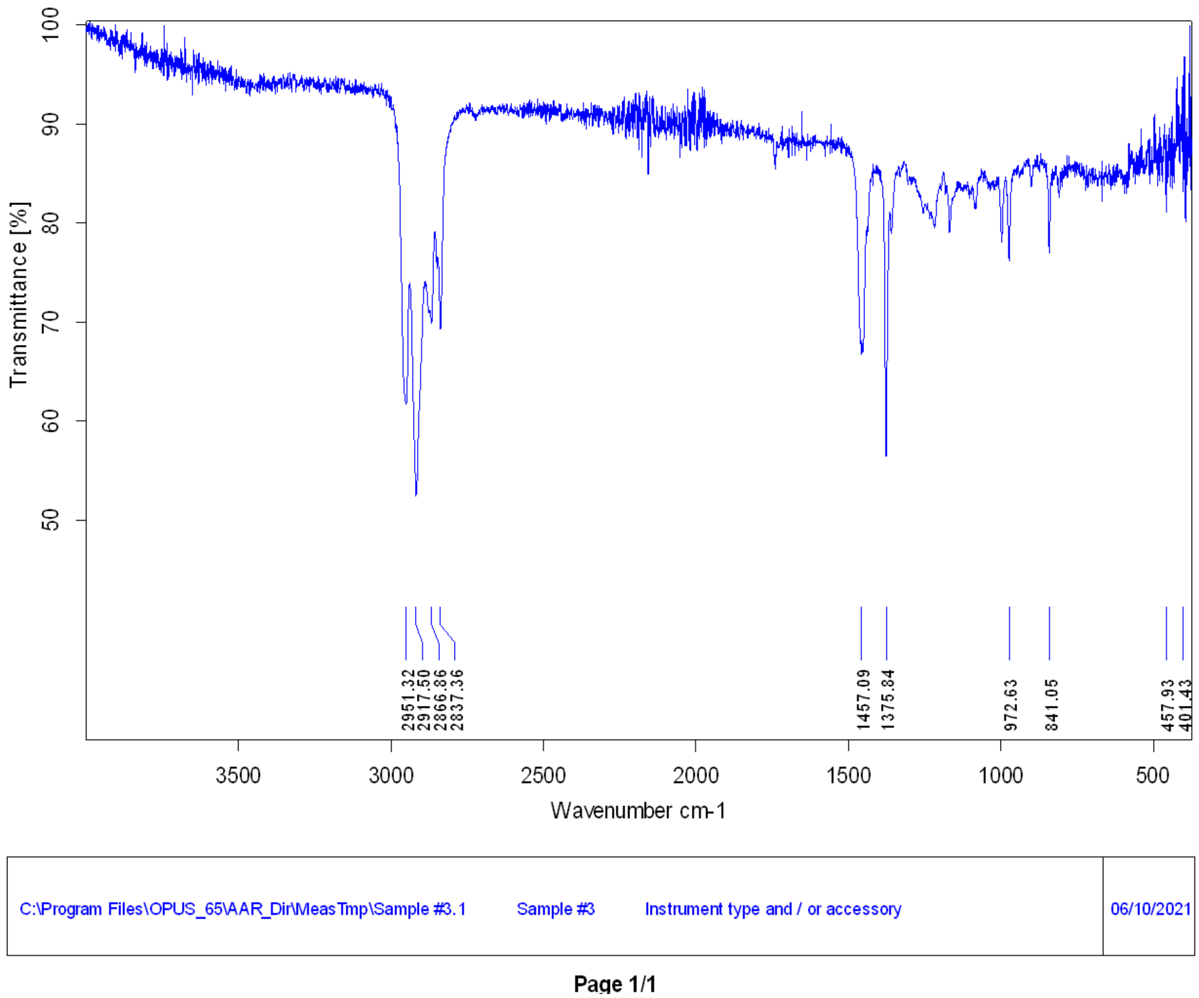


Figure AP. 14 FTIR spectrum of PP 1

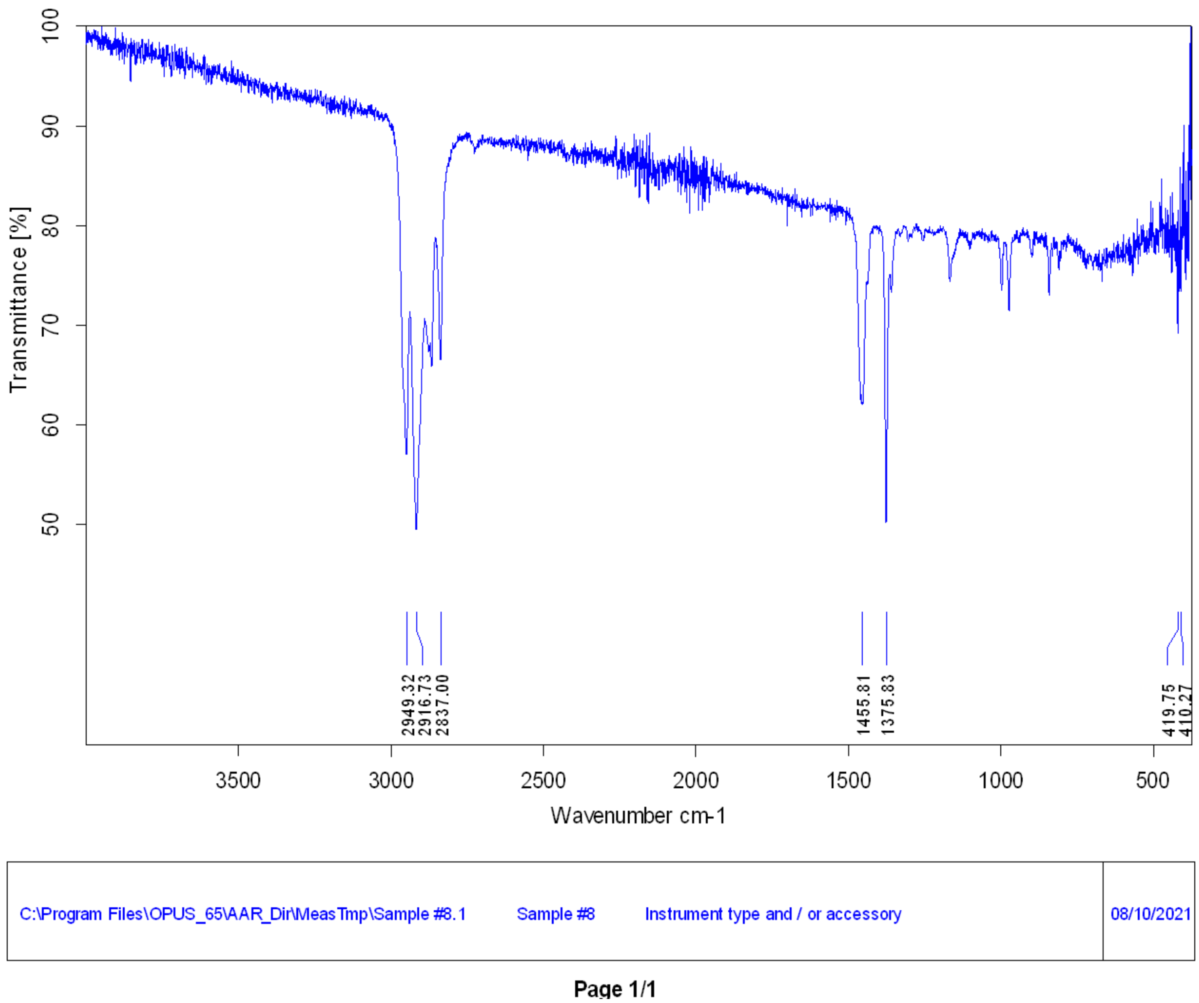


Figure AP. 15 FTIR spectrum of PP 2

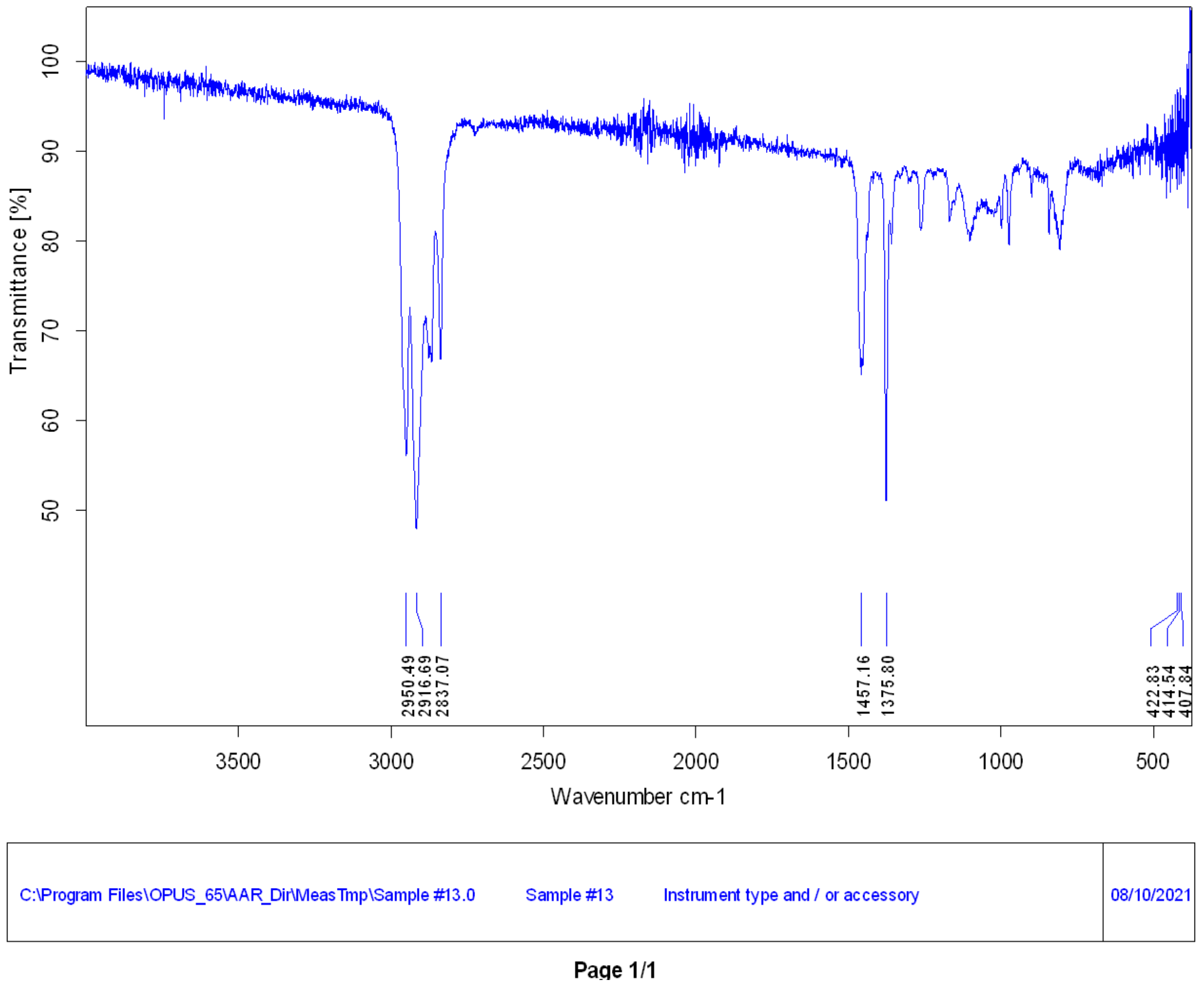


Figure AP. 16 FTIR spectrum of PP 3

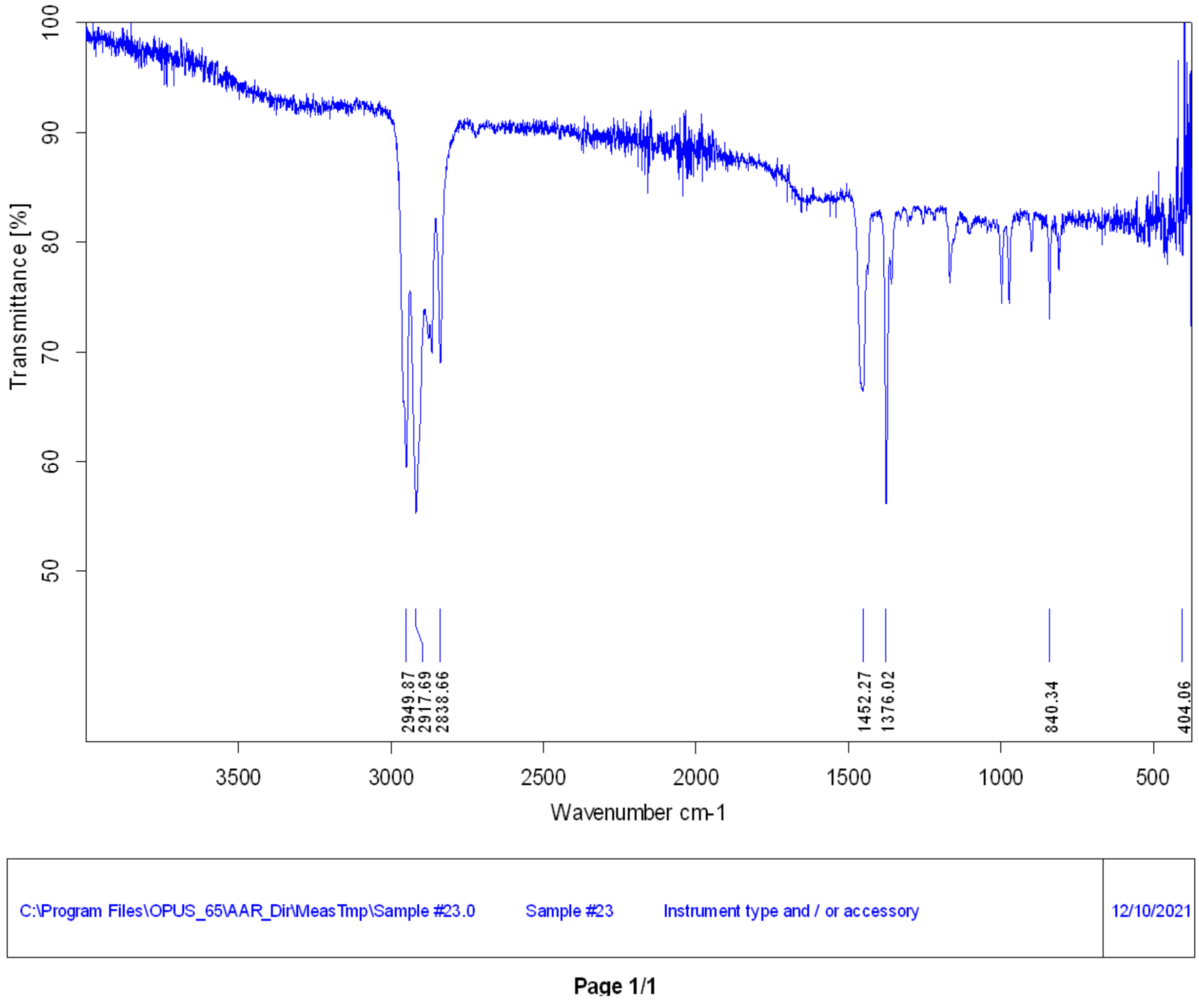


Figure AP. 17 FTIR spectrum of PP 5

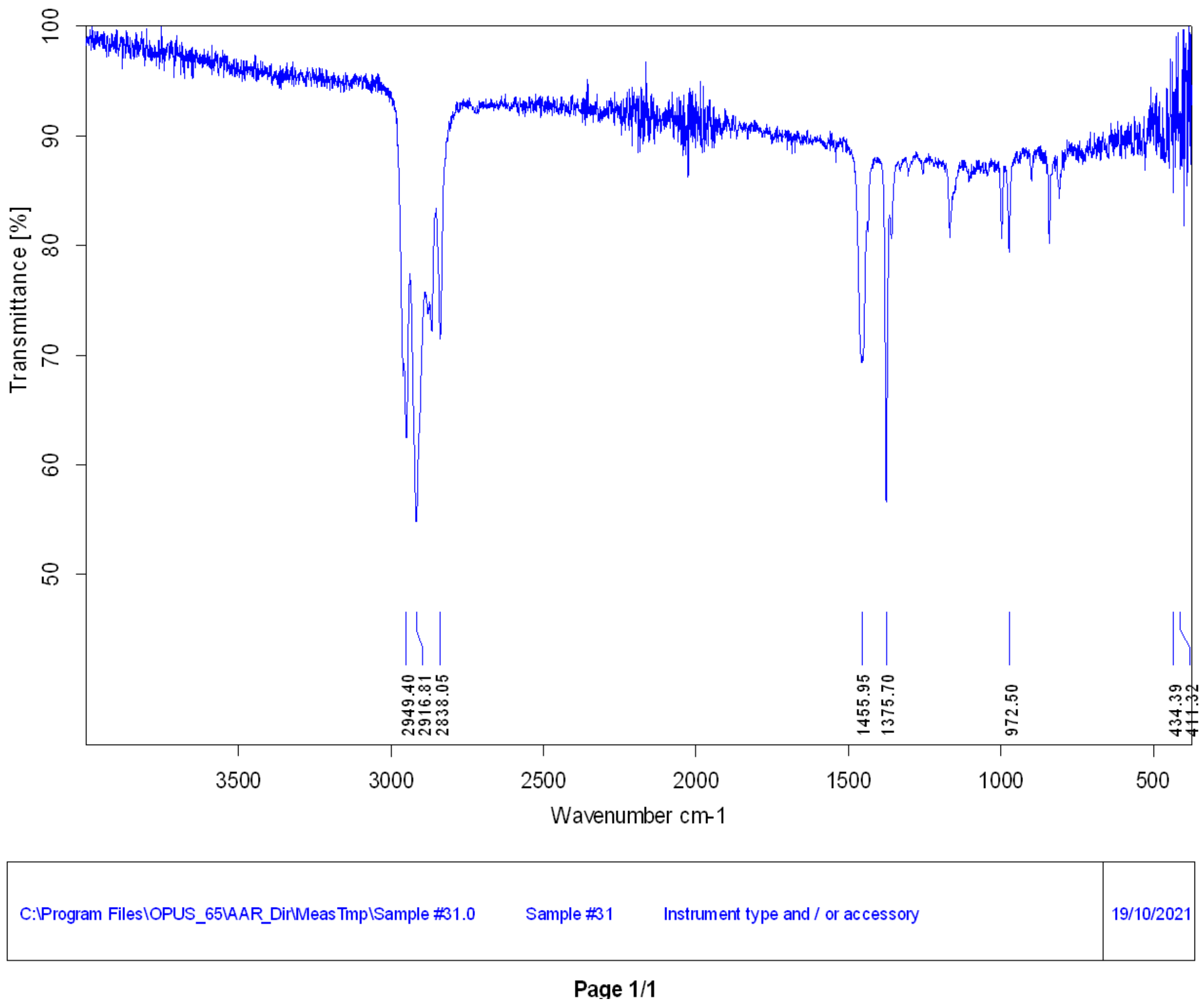


Figure AP. 18 FTIR spectrum pf PP 6

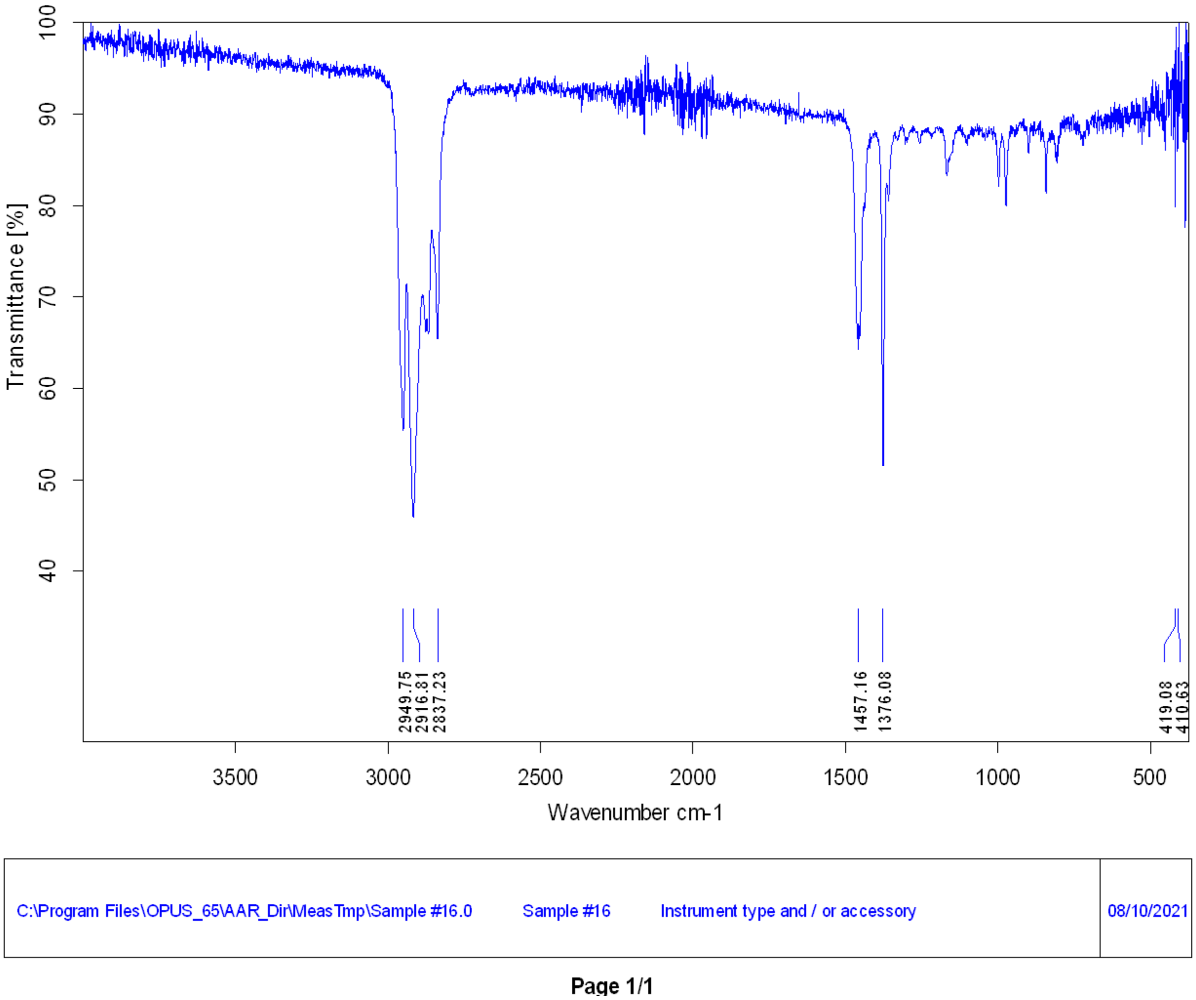
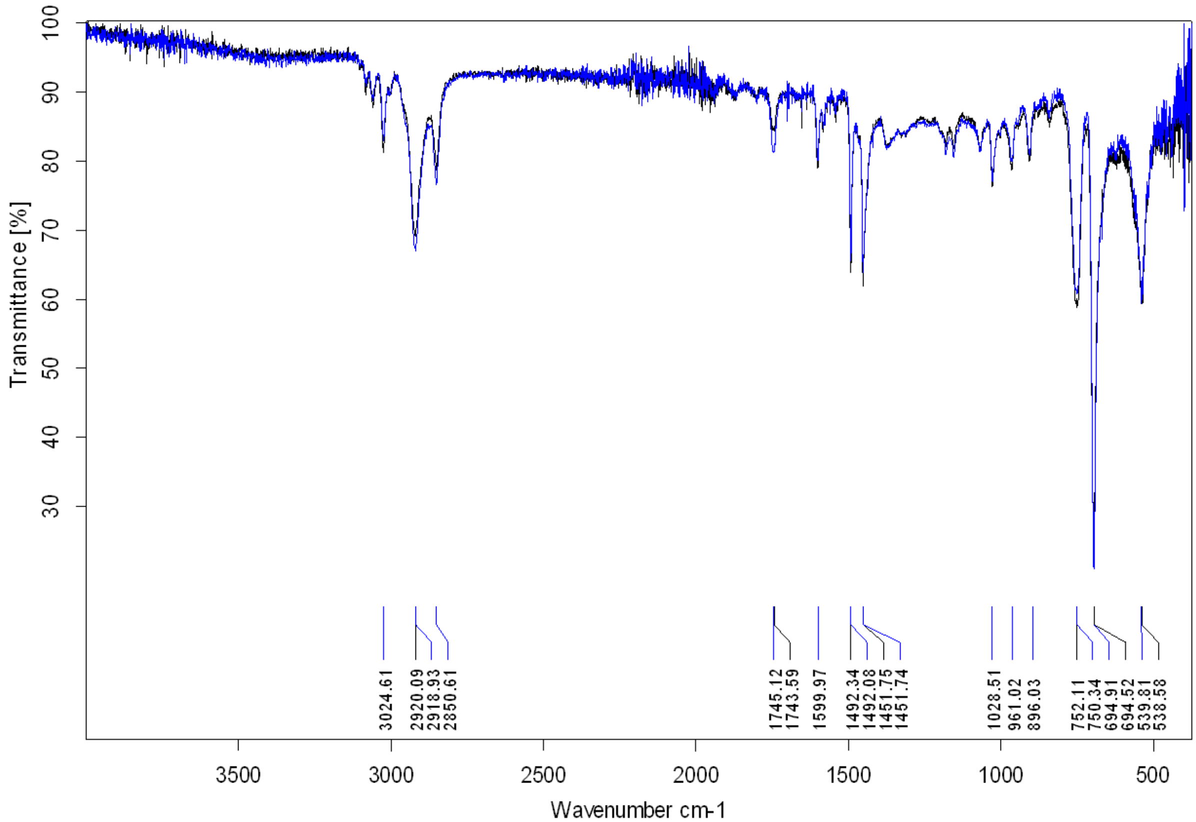


Figure AP 19. FTIR spectrum of PP 7



C:\Program Files\OPUS_65\AAR_Dir\MeasTmp\Sample #41.0	Sample #41	Instrument type and / or accessory	25/11/2021
C:\Program Files\OPUS_65\AAR_Dir\MeasTmp\Sample #41outside down.0	Sample #41outside down	Instrument type and / or accessor	25/11/2021

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Figure AP. 20 FTIR spectrum of PS 1

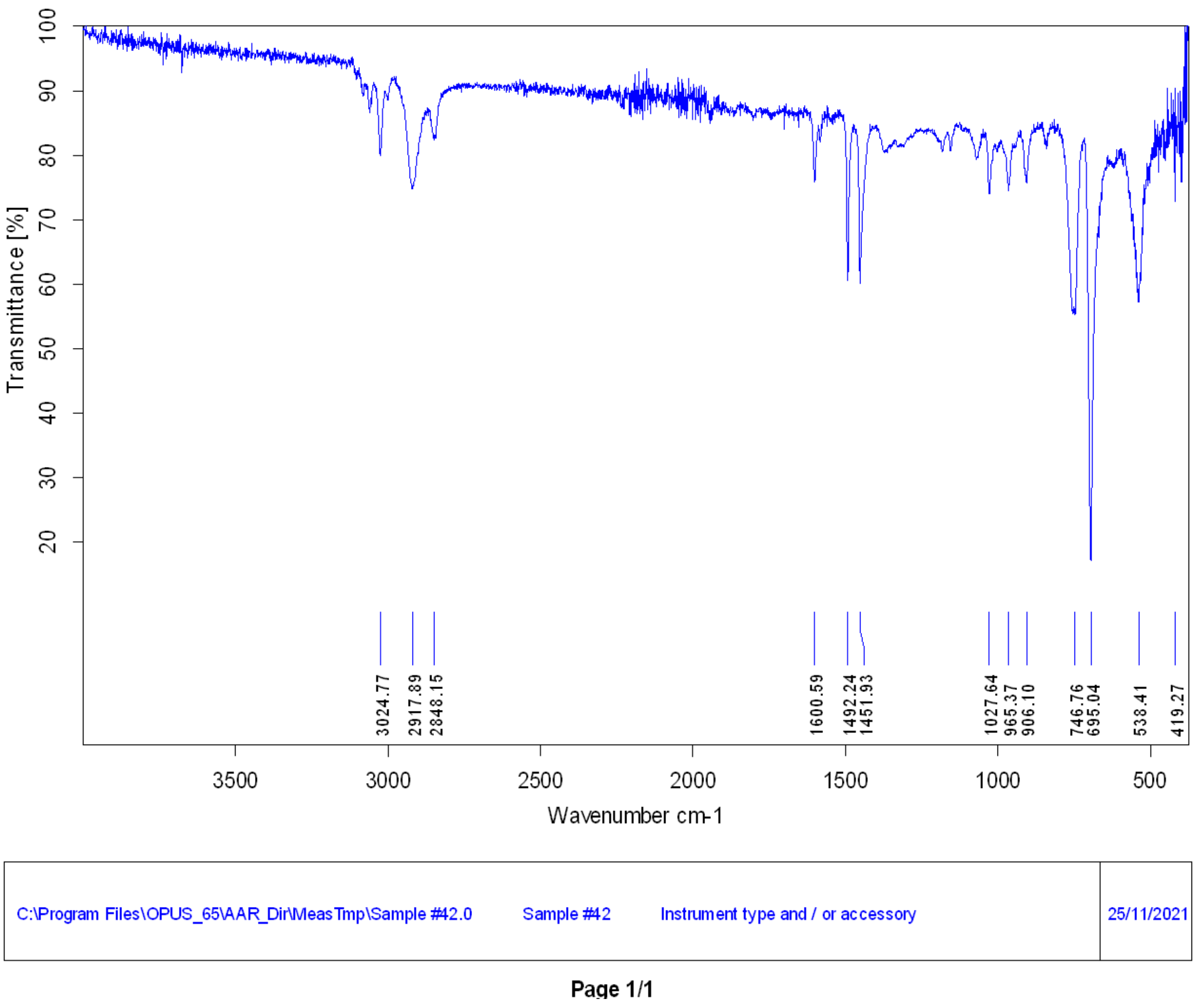
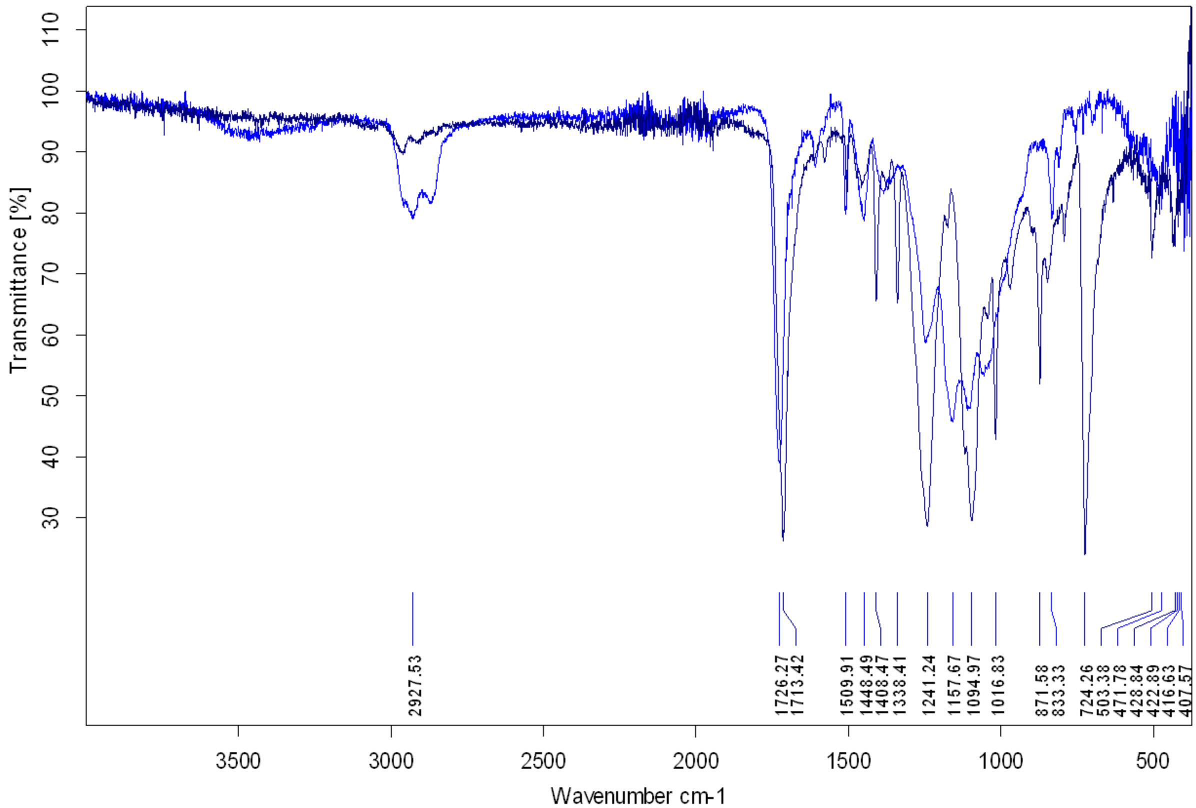


Figure AP. 21 FTIR spectrum of PS 2

Label Comparison



C:\Program Files\OPUS_65\AAR_Dir\MeasTmp\sample #1 blue label up.0	sample #1 blue label up	Instrument type and / or accessory	21/10/2021
C:\Program Files\OPUS_65\AAR_Dir\MeasTmp\sample #1 blue label down.0	sample #1 blue label down	Instrument type and / or acces:	21/10/2021

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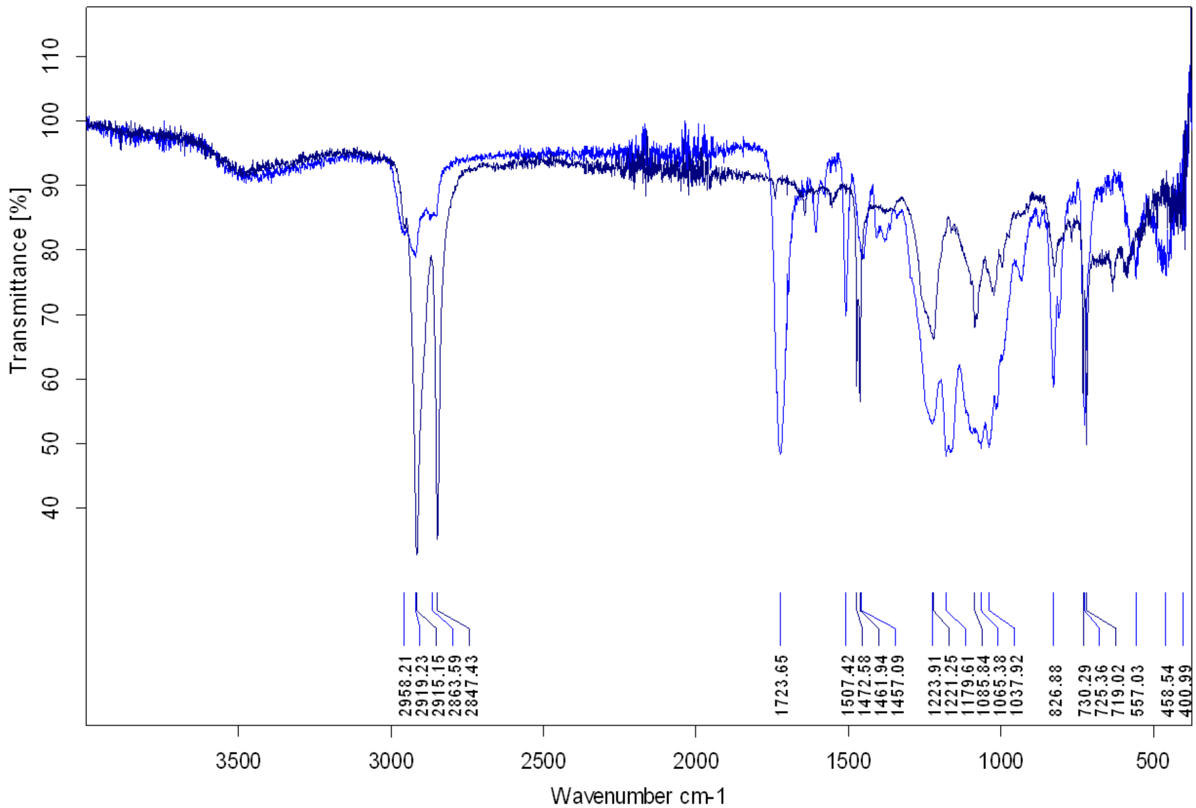
Figure AP. 22 FTIR label comparison of PET 1



C:\Program Files\OPUS_65\AAR_Dir\MeasTmp\sample #2 blue label up.0	sample #2 blue label up	Instrument type and / or accessory	21/10/2021
C:\Program Files\OPUS_65\AAR_Dir\MeasTmp\sample #2 blue label down.0	sample #2 blue label down	Instrument type and / or acces	21/10/2021

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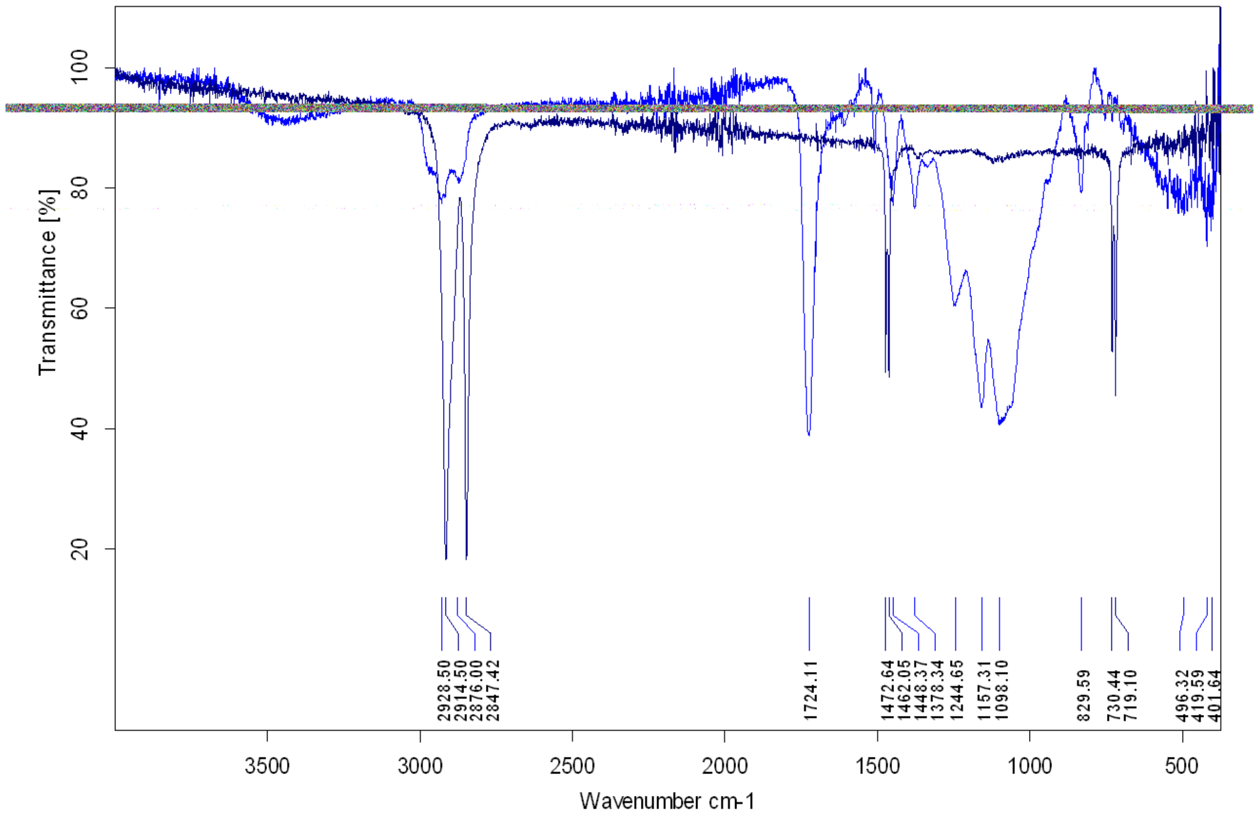
Figure AP. 23 FTIR label comparison of HDPE 1



C:\Program Files\OPUS_65\AAR_Dir\MeasTmp\sample #7 dark blue label up.0	sample #7 dark blue label up	Instrument type and / or ac	21/10/2021
C:\Program Files\OPUS_65\AAR_Dir\MeasTmp\sample #7 dark blue label down.0	sample #7 dark blue label down	Instrument type and /	21/10/2021

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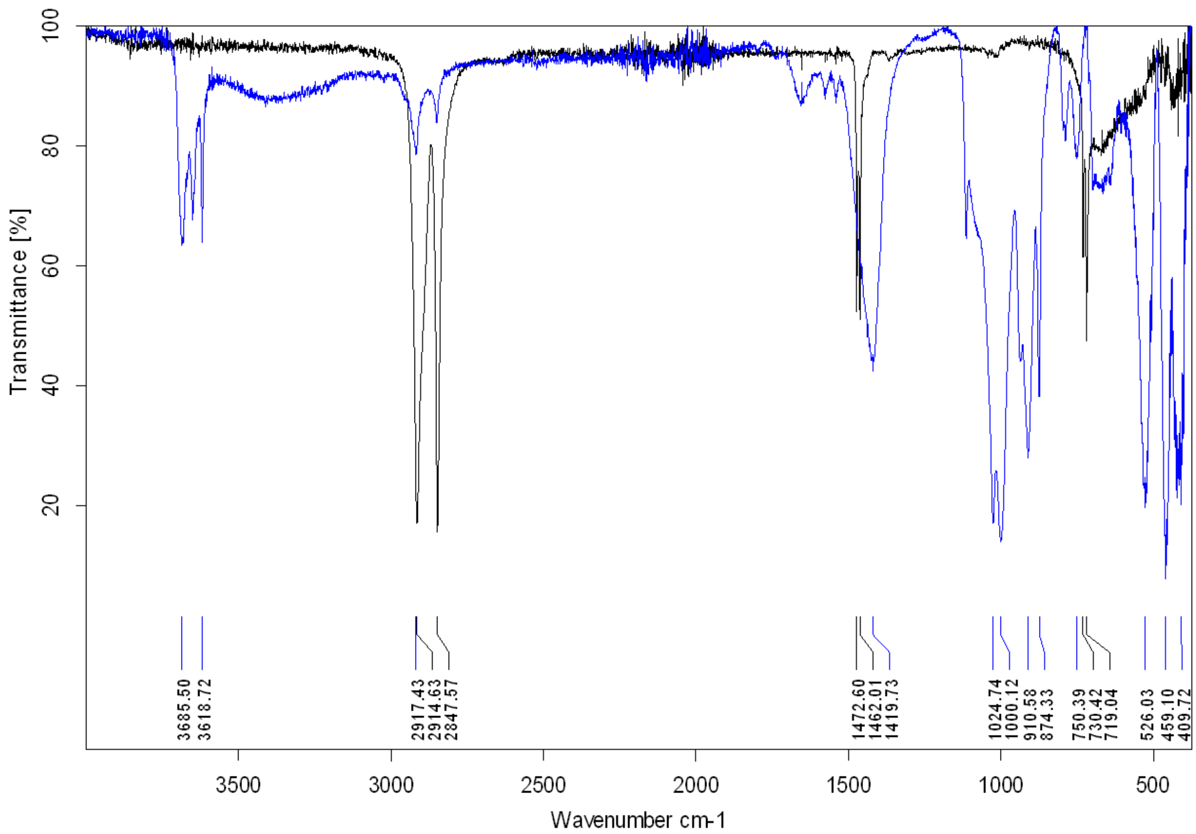
Figure AP. 24 FTIR label comparison of HDPE 2



C:\Program Files\OPUS_65\AAR_Dir\MeasTmp\sample #4 white label down.0	sample #4 white label down	Instrument type and / or acce	21/10/2021
C:\Program Files\OPUS_65\AAR_Dir\MeasTmp\sample #4 white label up.0	sample #4 white label up	Instrument type and / or accessory	21/10/2021

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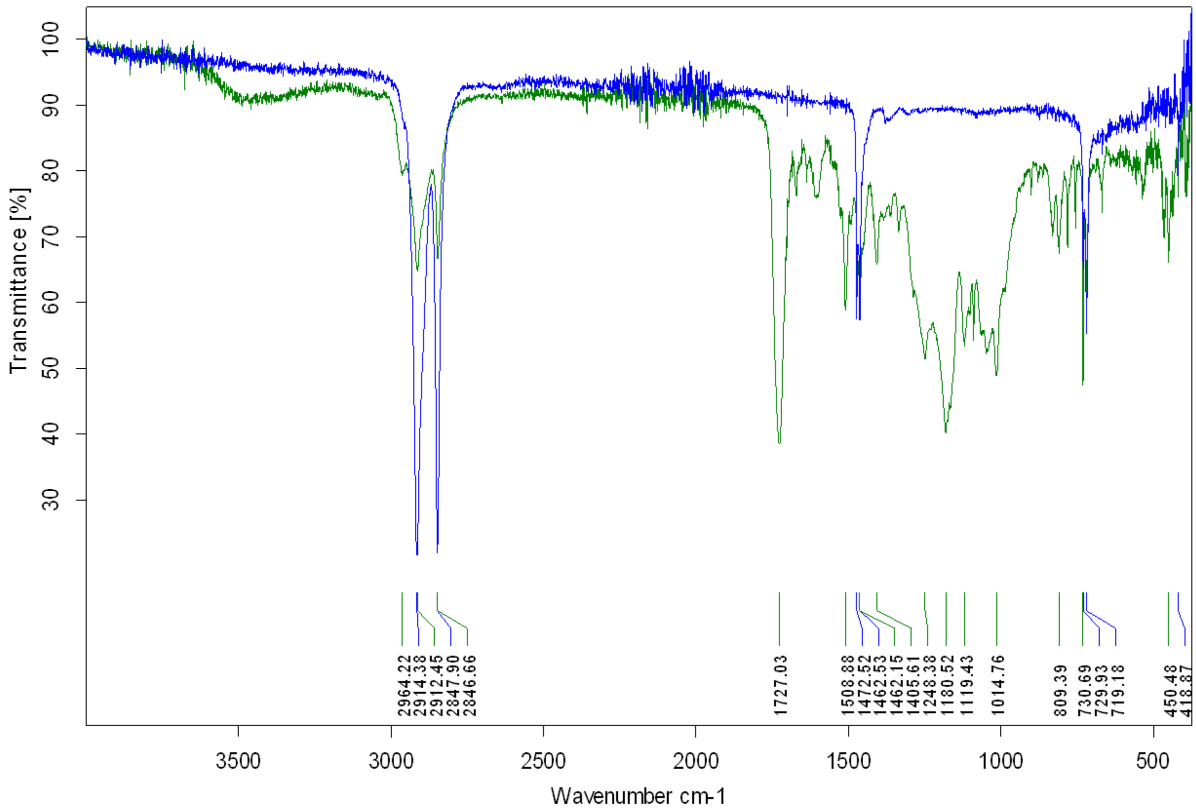
Figure AP. 25 FTIR label comparison of HDPE 4



C:\Program Files\OPUS_65\AAR_Dir\MeasTmp\Sample #20 inside.0 Sample #20 inside	Instrument type and / or accessory		28/10/2021
C:\Program Files\OPUS_65\AAR_Dir\MeasTmp\Sample #20 green label.0 Sample #20 green label	Instrument type and / or accessory		28/10/2021

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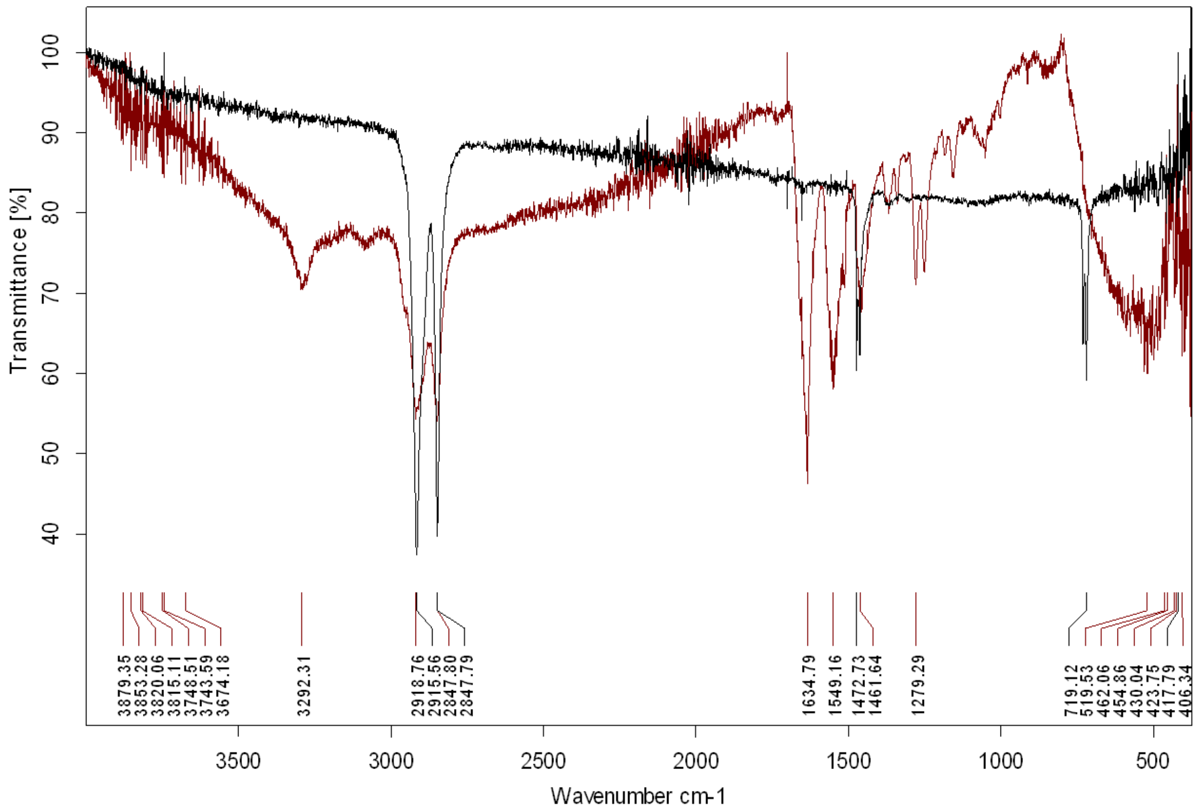
Figure AP. 26 FTIR label comparison of HDPE 3



C:\Program Files\OPUS_65\AAR_Dir\MeasTmp\Sample #14 dark brown up.0	Sample #14 dark brown up	Instrument type and / or acces	22/10/2021
C:\Program Files\OPUS_65\AAR_Dir\MeasTmp\Sample #14 dark brown down.0	Sample #14 dark brown down	Instrument type and / or a	22/10/2021

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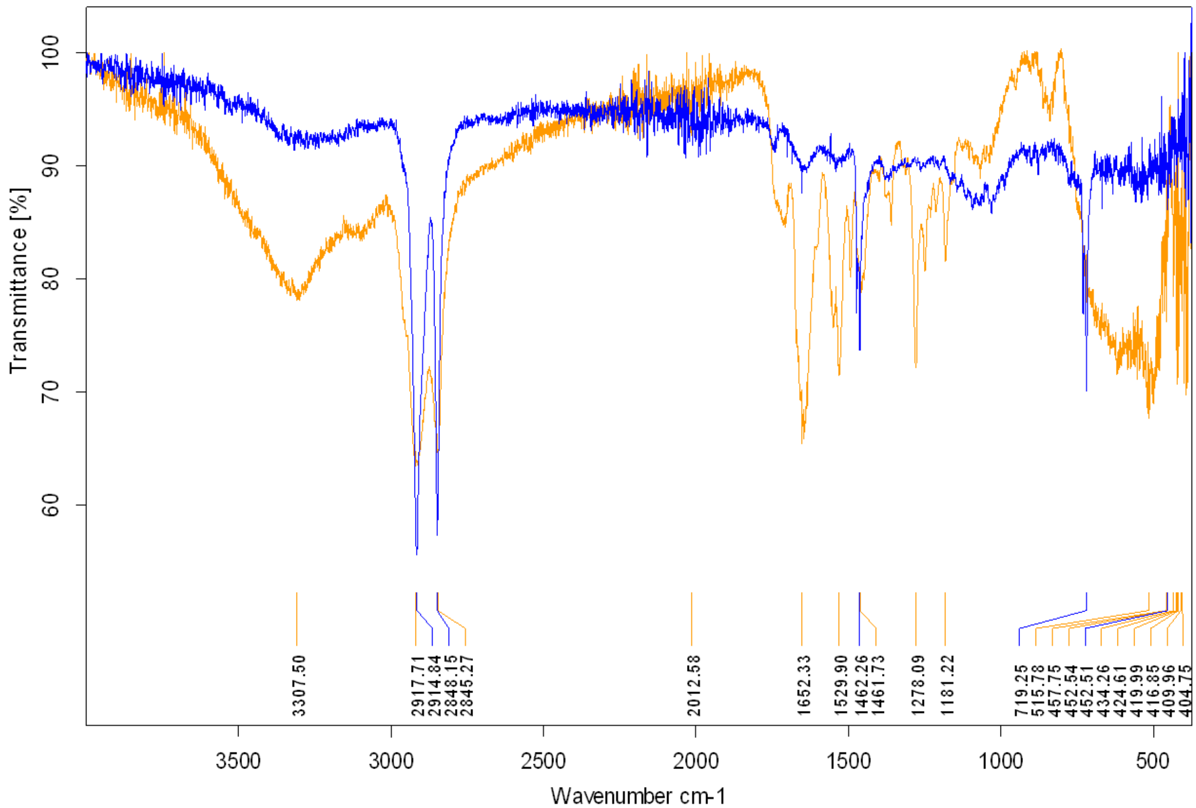
Figure AP. 27 FTIR label comparison of LDPE 3



C:\Program Files\OPUS_65\AAR_Dir\MeasTmp\Sample #22 orange label up.0 Sample #22 orange label up	Instrument type and / or acc	29/10/2021
C:\Program Files\OPUS_65\AAR_Dir\MeasTmp\Sample #22 orange label down.0 Sample #22 orange label down	Instrument type and / c	29/10/2021

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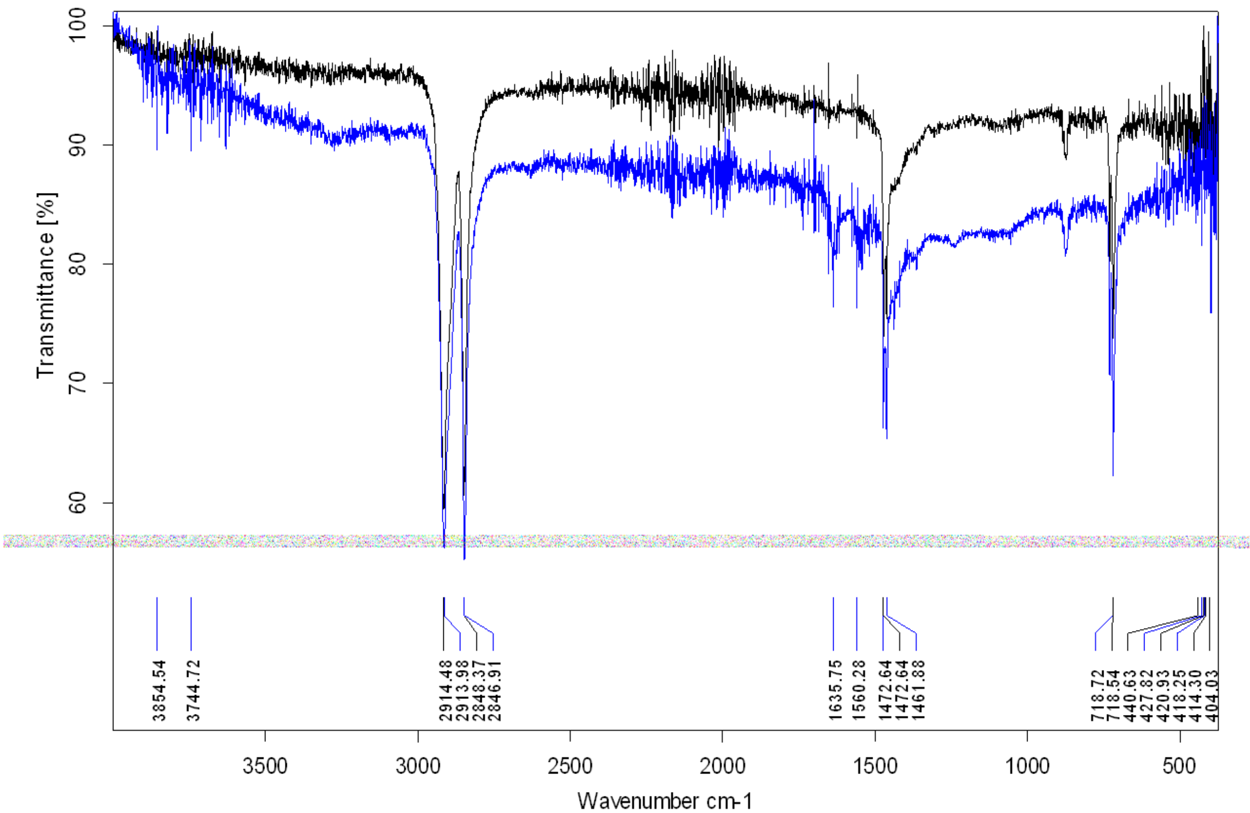
Figure AP. 28 FTIR label comparison of LDPE 5



C:\Program Files\OPUS_65\AAR_Dir\MeasTmp\Sample #9 writing down.0	Sample #9 writing down	Instrument type and / or accessory	22/10/2021
C:\Program Files\OPUS_65\AAR_Dir\MeasTmp\Sample #9 writing up.0	Sample #9 writing up	Instrument type and / or accessory	22/10/2021

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Figure AP. 29 FTIR label comparison of HDPE 6

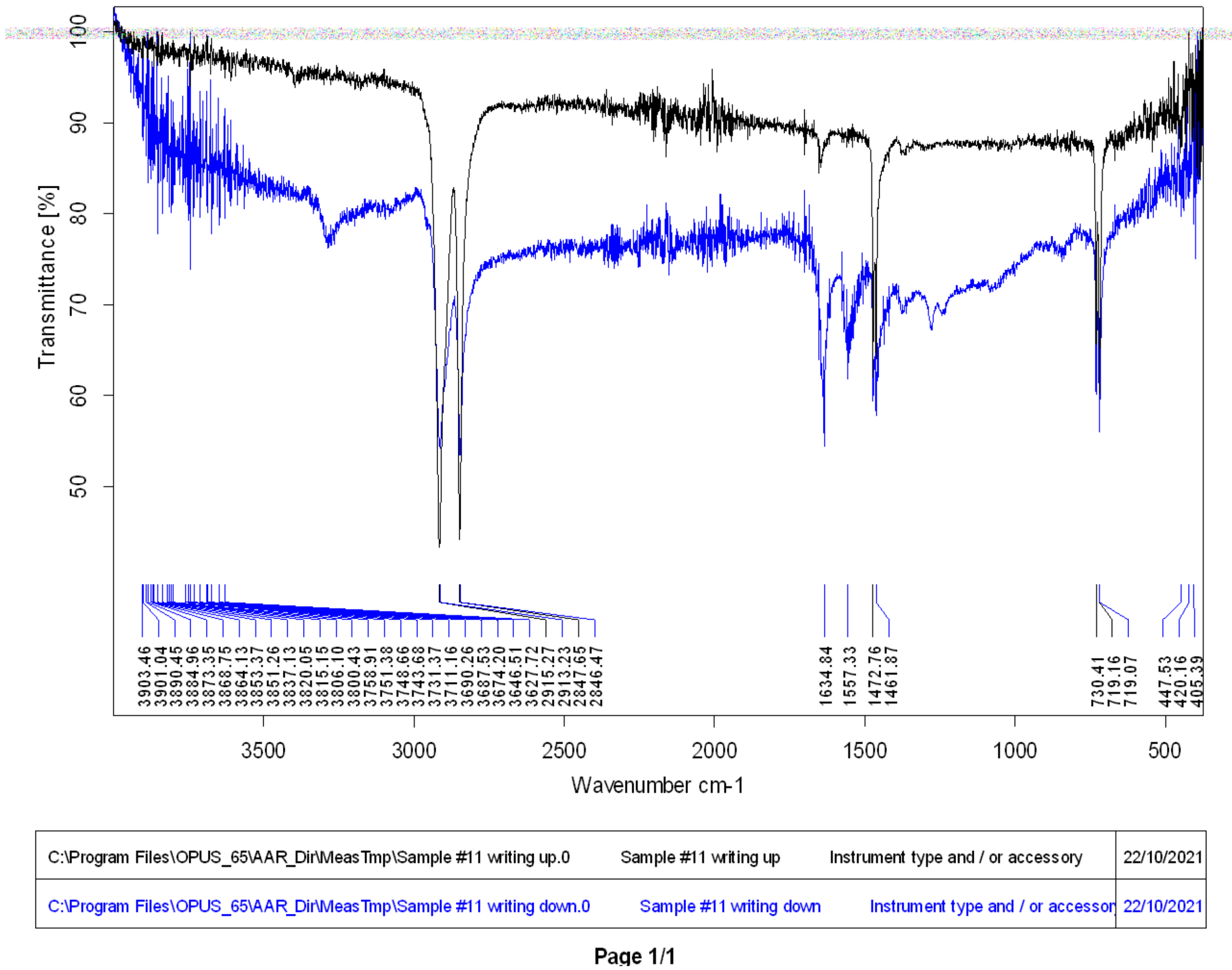
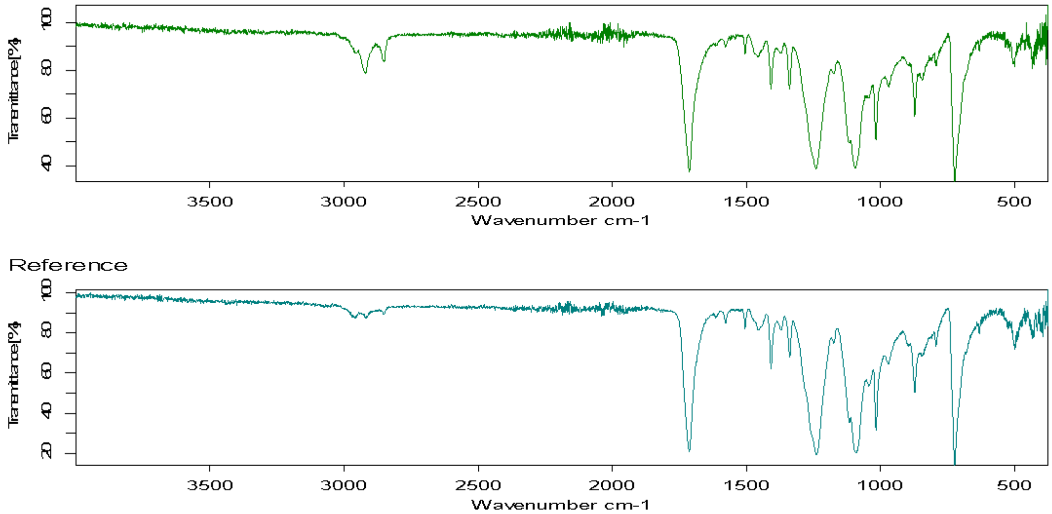


Figure AP. 30 FTIR label comparison of HDPE 5

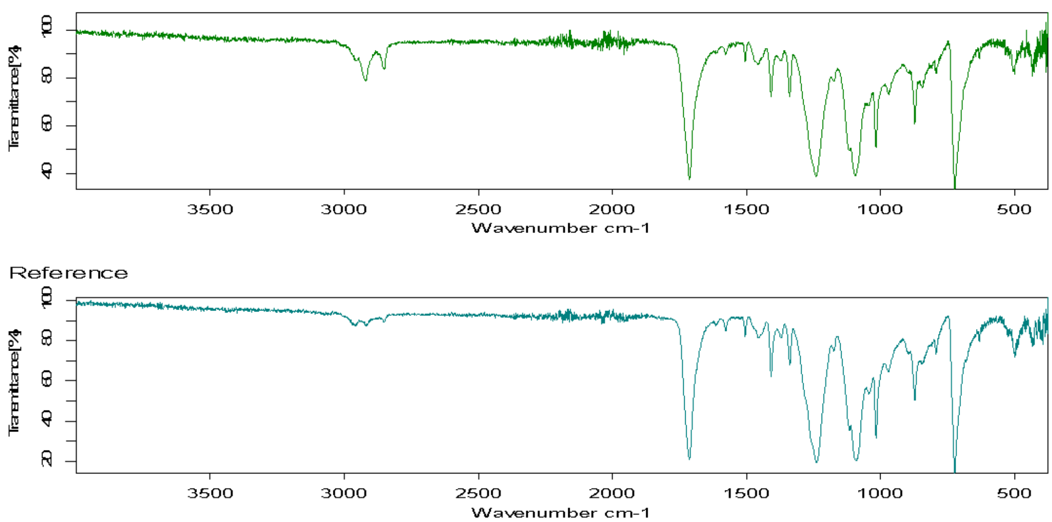
Three Spectral Regions



Result: OK

Correlation: 99.56 %
Threshold: 95.00 %
Sample: Sample 30.1

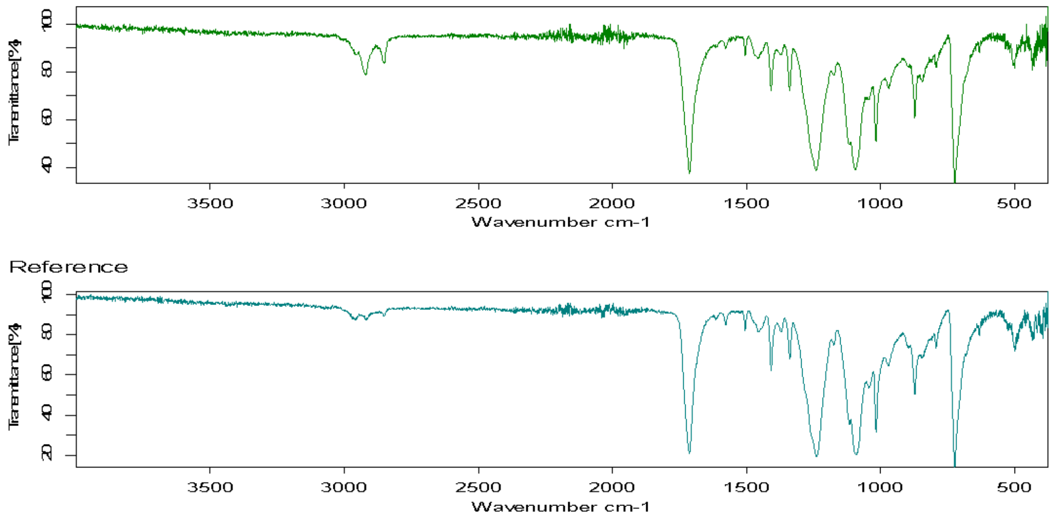
Figure AP. 31 FTIR QCM of PET 2 between 700-900cm^{-1}



Result: OK

Correlation: 97.70 %
Threshold: 95.00 %
Sample: Sample 30.1

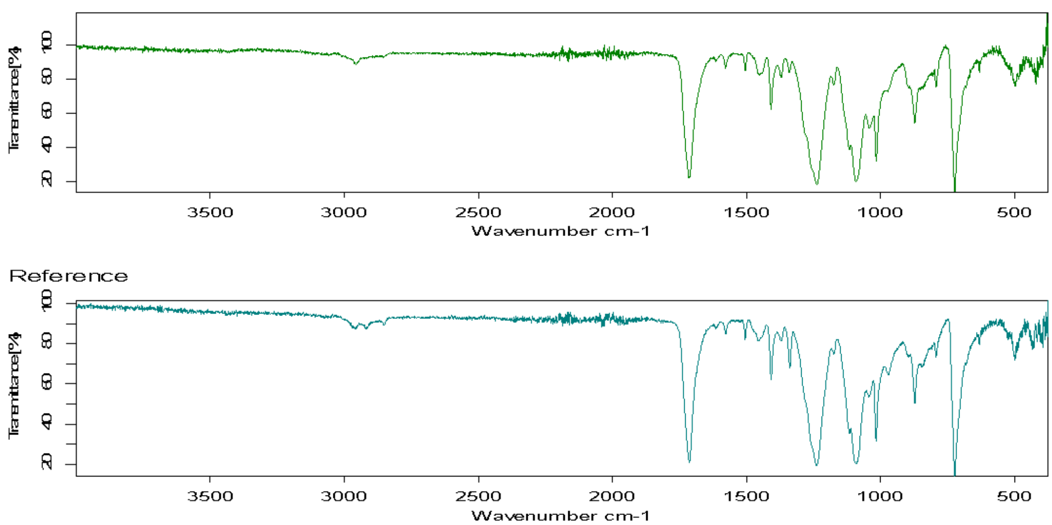
Figure AP. 32 FTIR QCM of PET 2 between 1300-1550cm^{-1}



Result: NOT OK

Correlation: 77.80 %
Threshold: 95.00 %
Sample: Sample 30.1

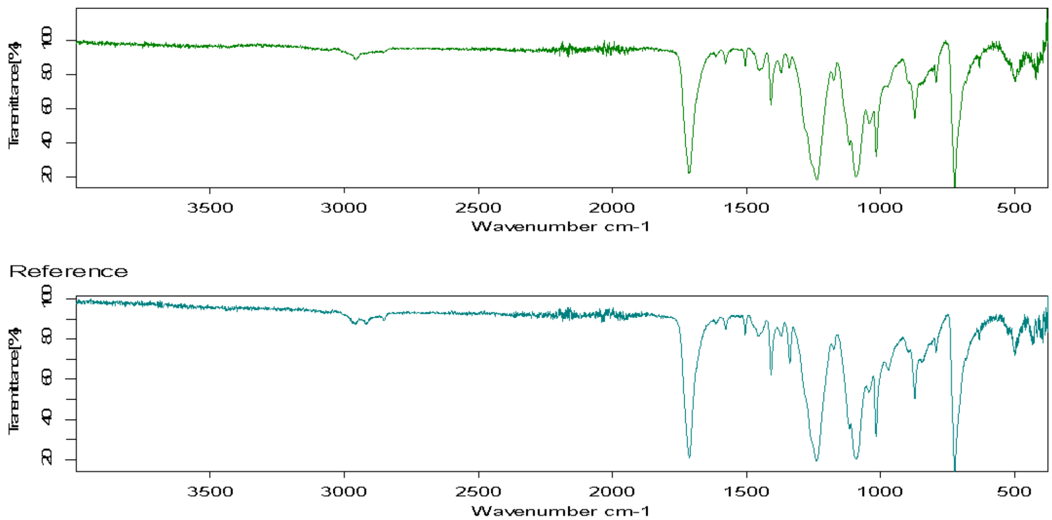
Figure AP. 33 FTIR QCM of PET 2 between 2800-3000cm^{-1}



Result: OK

Correlation: 99.24 %
Threshold: 95.00 %
Sample: Sample 43.1

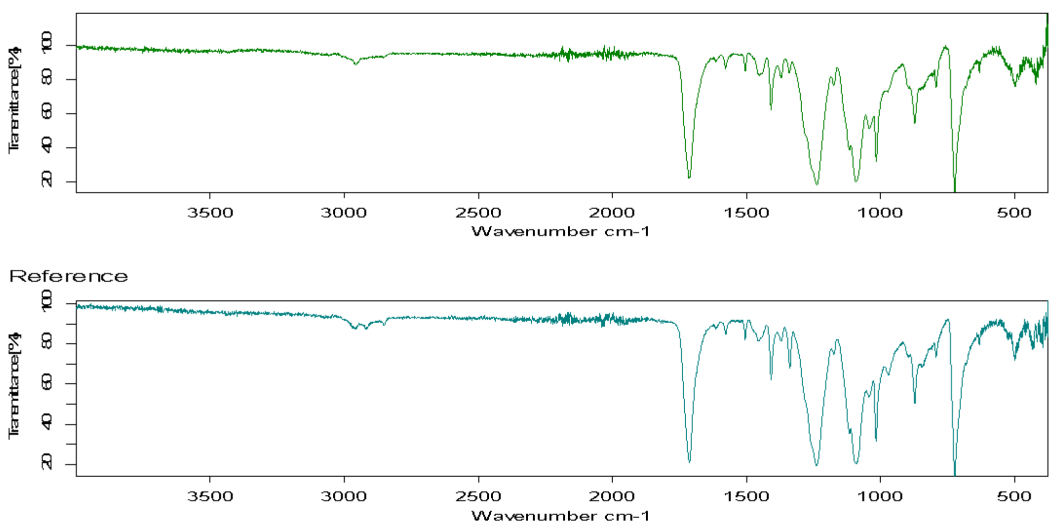
Figure AP. 34 FTIR QCM of PET 3 between 700-900cm^{-1}



Result: NOT OK

Correlation: 90.08 %
Threshold: 95.00 %
Sample: Sample 43.1

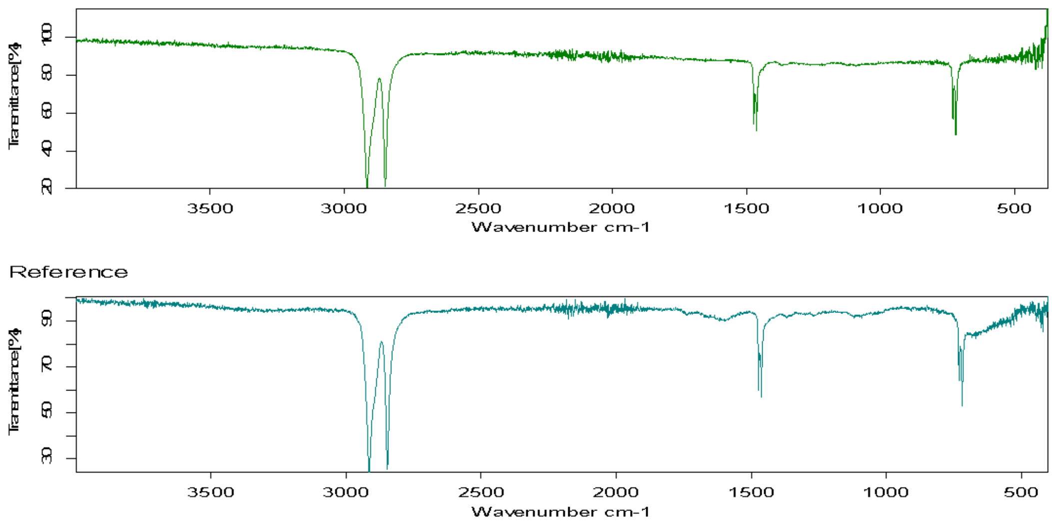
Figure AP. 35 FTIR QCM of PET 3 between 1300-1550cm^{-1}



Result: NOT OK

Correlation: 83.48 %
Threshold: 95.00 %
Sample: Sample 43.1

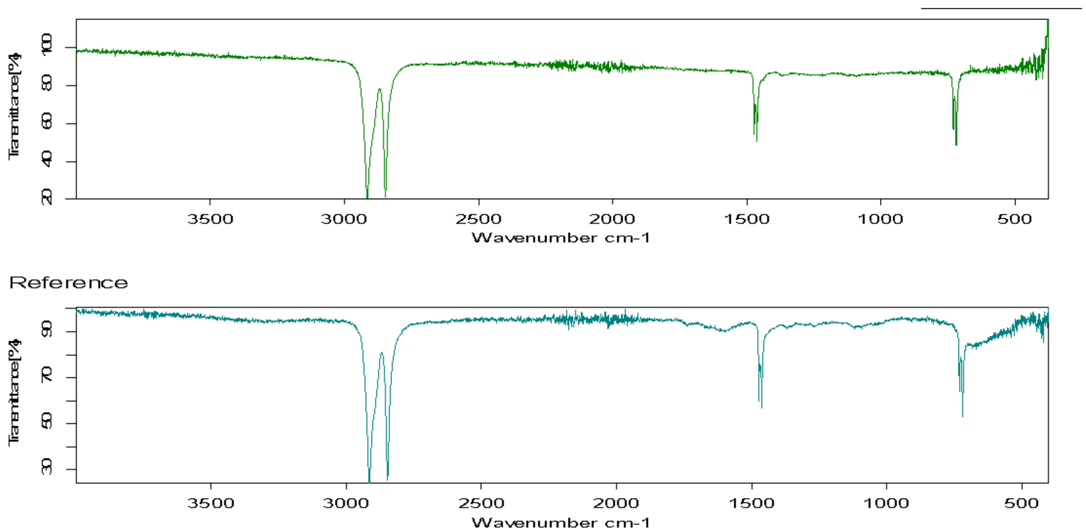
Figure AP. 36 FTIR QCM of PET 3 between 2800-300cm^{-1}



Result: OK

Correlation: 96.29 %
Threshold: 95.00 %
Sample: Sample 7.3

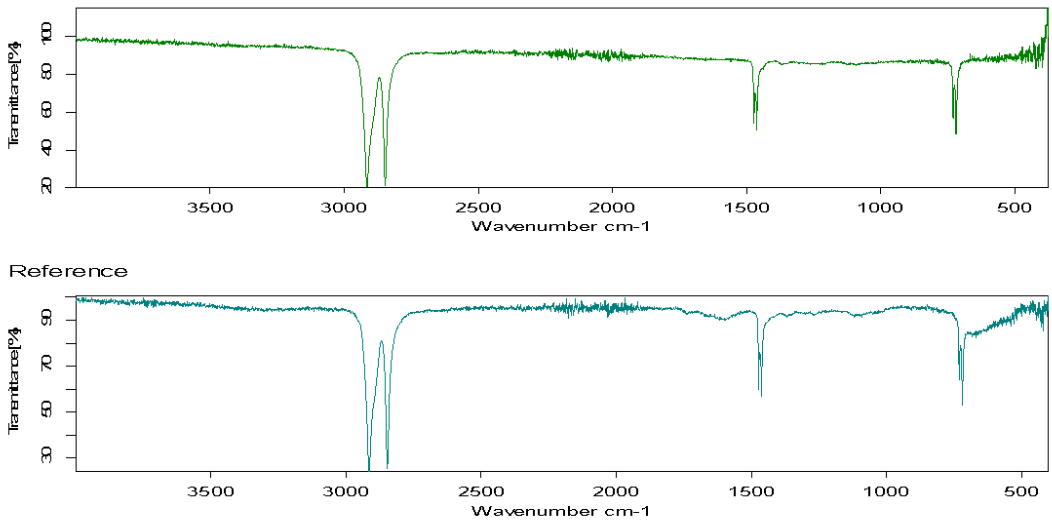
Figure AP. 37 FTIR QCM of HDPE 2 between 700-900cm^{-1}



Result: OK

Correlation: 99.44 %
Threshold: 95.00 %
Sample: Sample 7.3

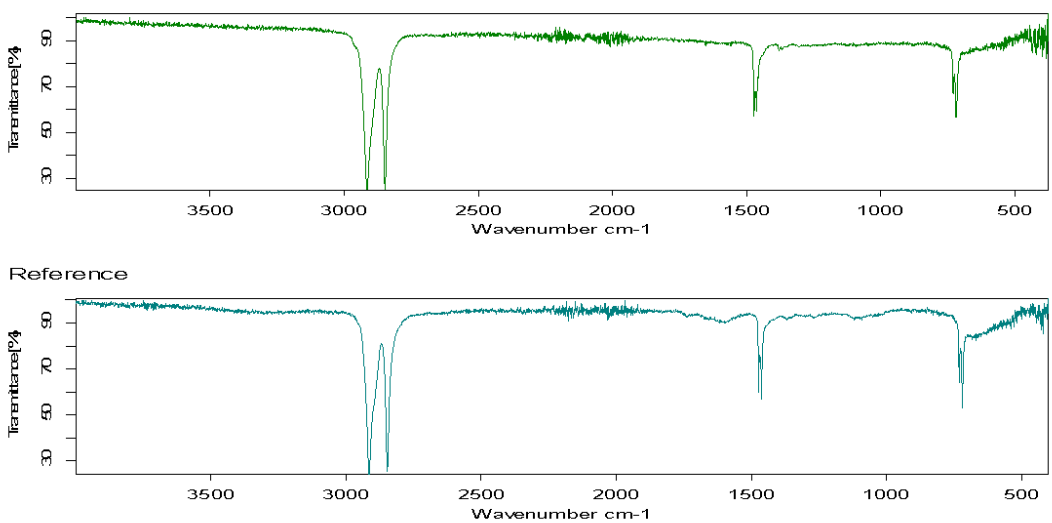
Figure AP. 38 FTIR QCM of HDPE 2 between 1300-1550cm^{-1}



Result: OK

Correlation: 99.98 %
Threshold: 95.00 %
Sample: Sample 7.3

Figure AP. 39 FTIR QCM of HDPE 2 between 2800-3000cm^{-1}



Result: OK

Correlation: 98.08 %
Threshold: 95.00 %
Sample: Sample 20.1

Figure AP. 40 FTIR QCM of HDPE 3 between 700-900cm^{-1}

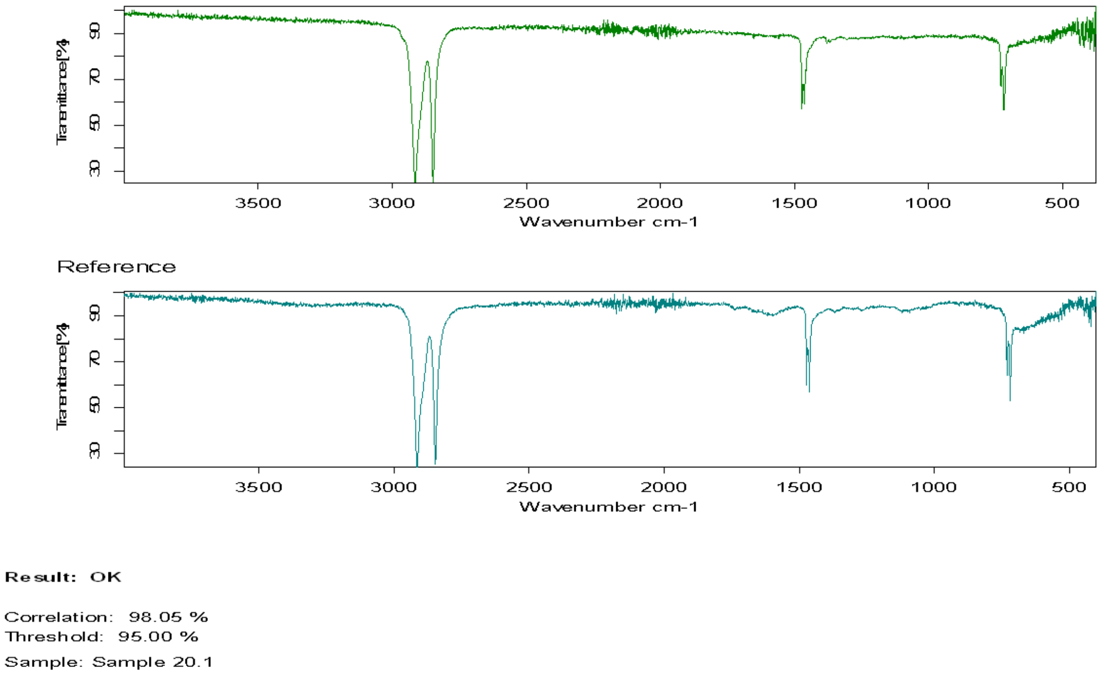


Figure AP. 41 FTIR QCM of HDPE 3 between 1300-1550cm^{-1}

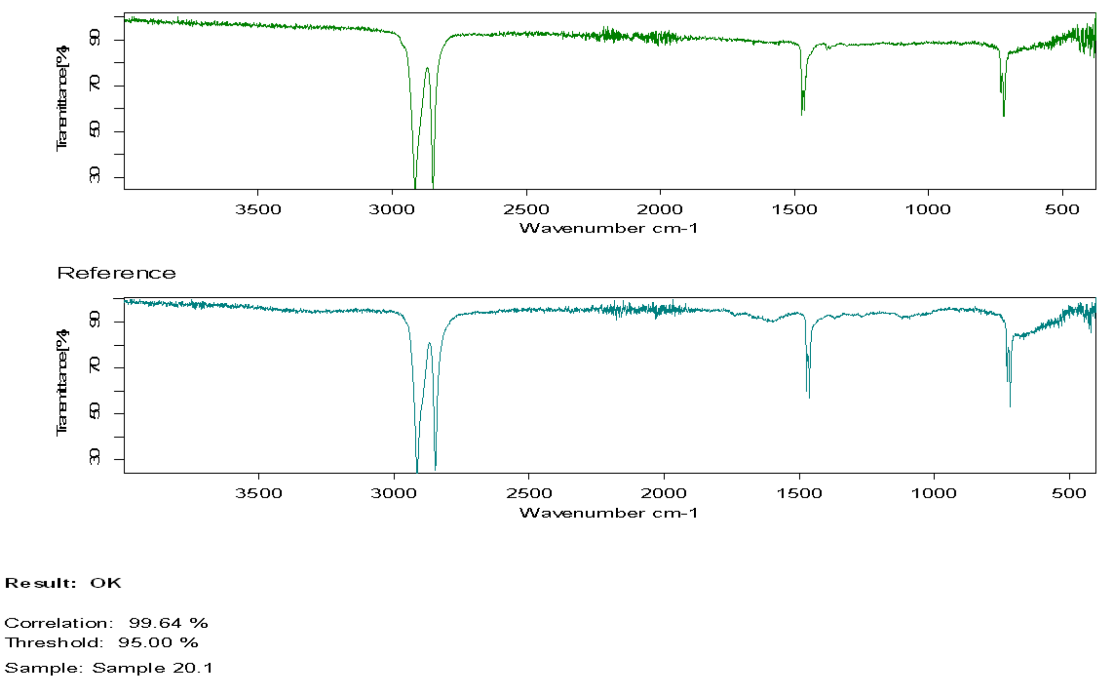


Figure AP. 42 FTIR QCM of HDPE 3 between 2800-3000cm^{-1}

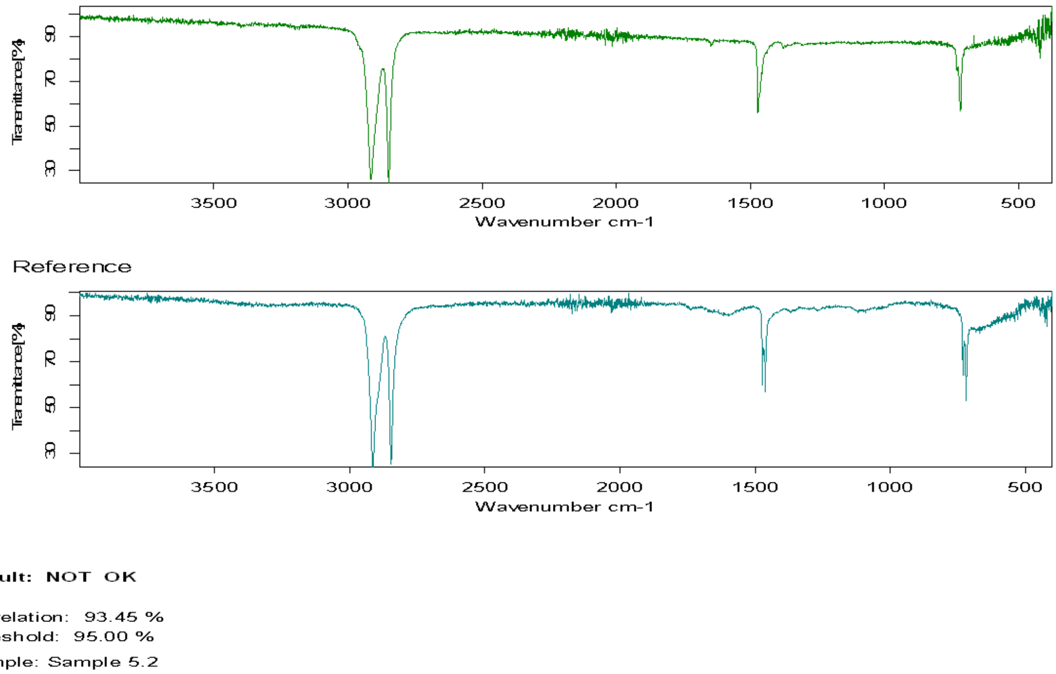


Figure AP. 43 FTIR QCM of LDPE 1 between 700-900cm^{-1}

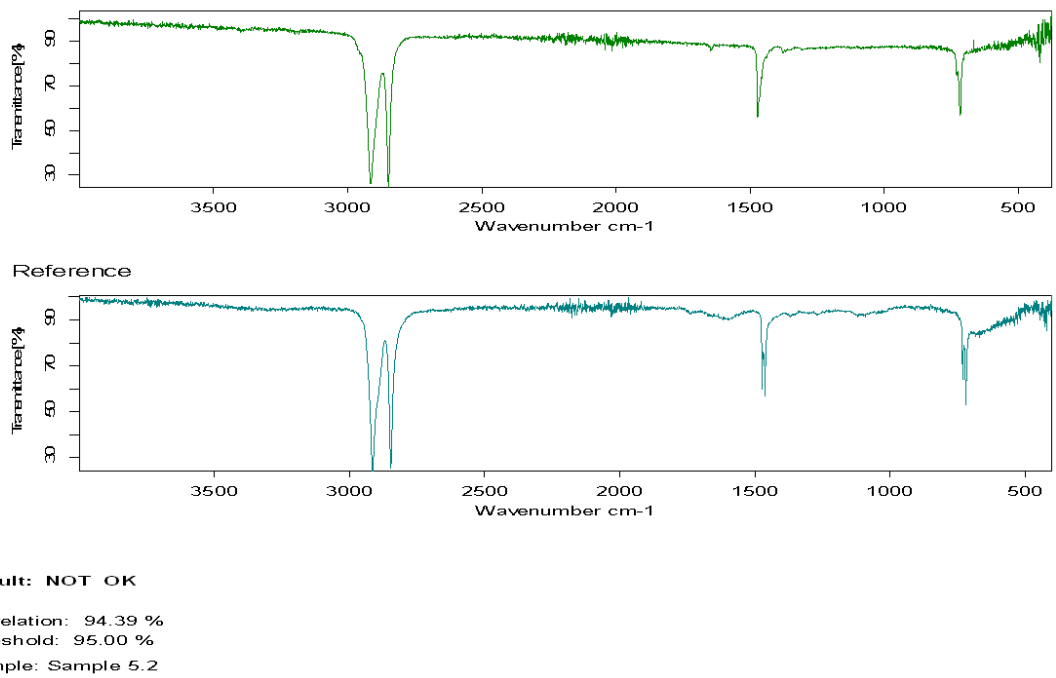
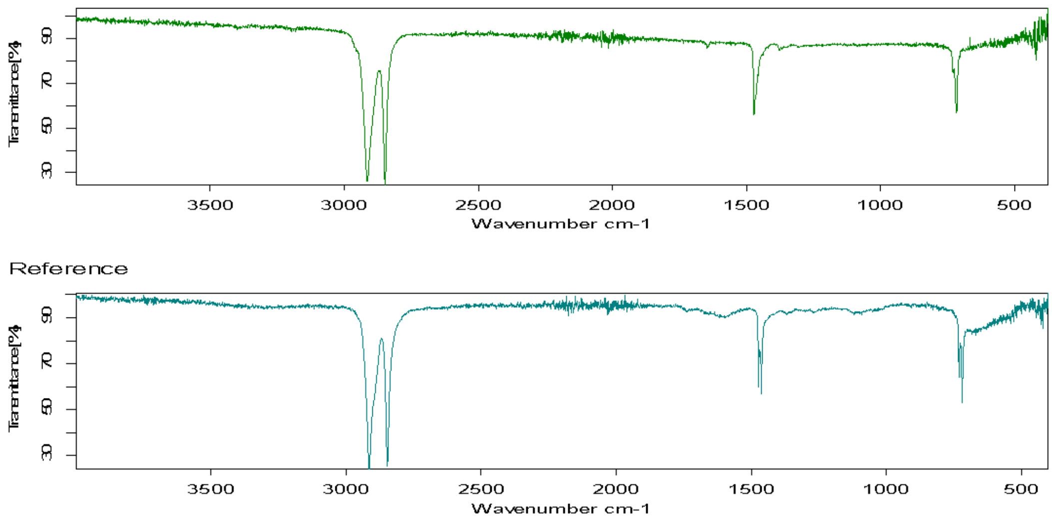


Figure AP. 44 FTIR QCM of LDPE 1 between 1300-1550cm^{-1}

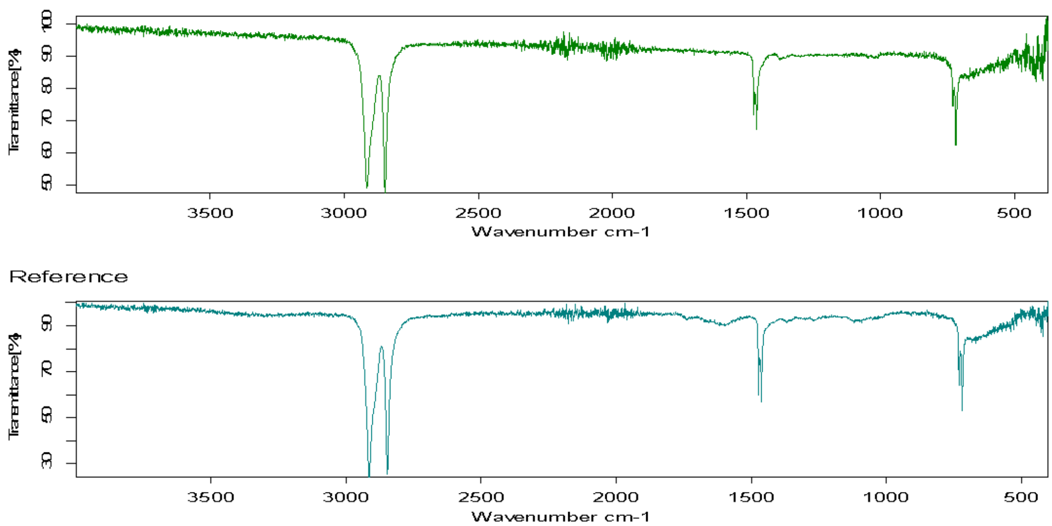


Result: OK

Correlation: 99.07 %
Threshold: 95.00 %

Sample: Sample 5.2

Figure AP. 45 FTIR QCM of LDPE 1 between 2800-3000cm^{-1}

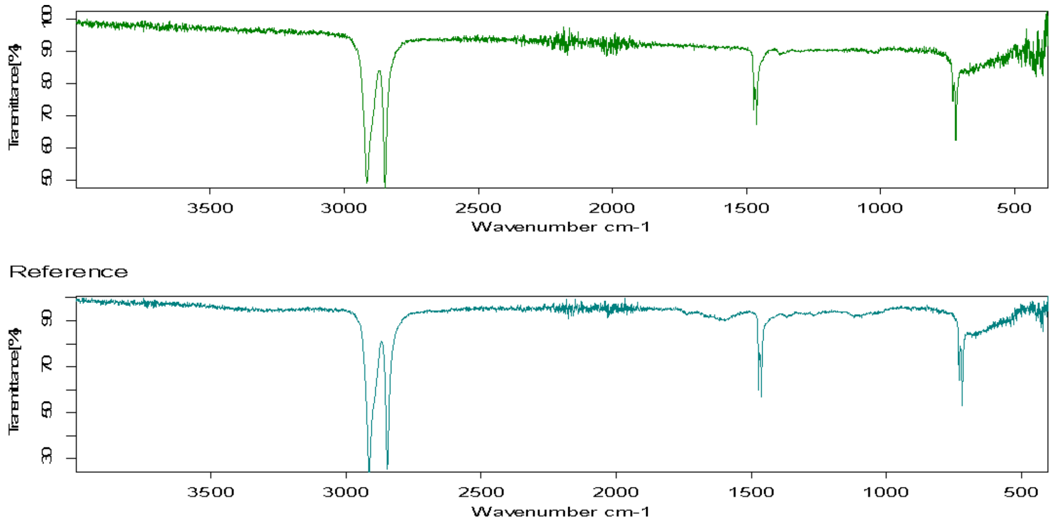


Result: OK

Correlation: 98.98 %
Threshold: 95.00 %

Sample: Sample 24.0

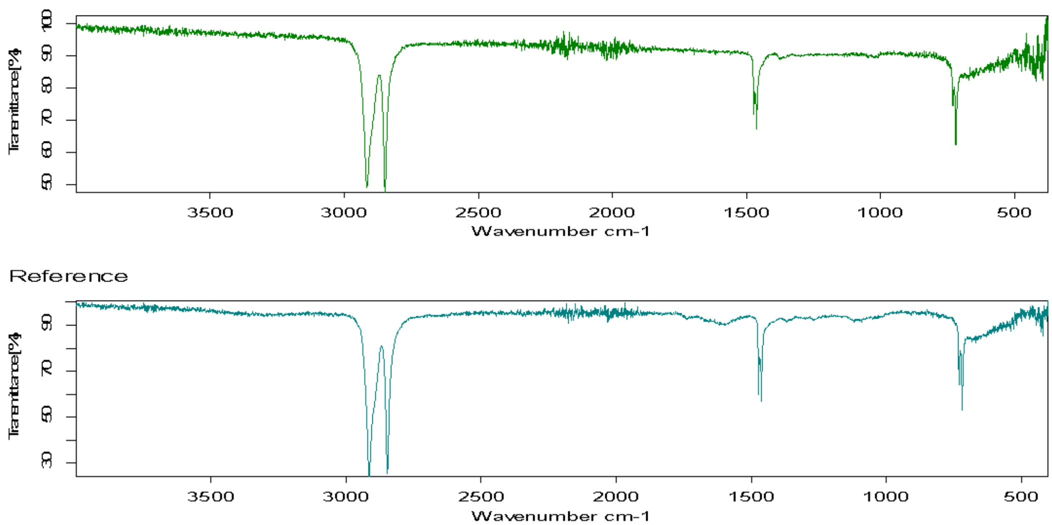
Figure AP. 46 FTIR QCM of LDPE 2 between 700-900cm^{-1}



Result: OK

Correlation: 98.65 %
Threshold: 95.00 %
Sample: Sample 24.0

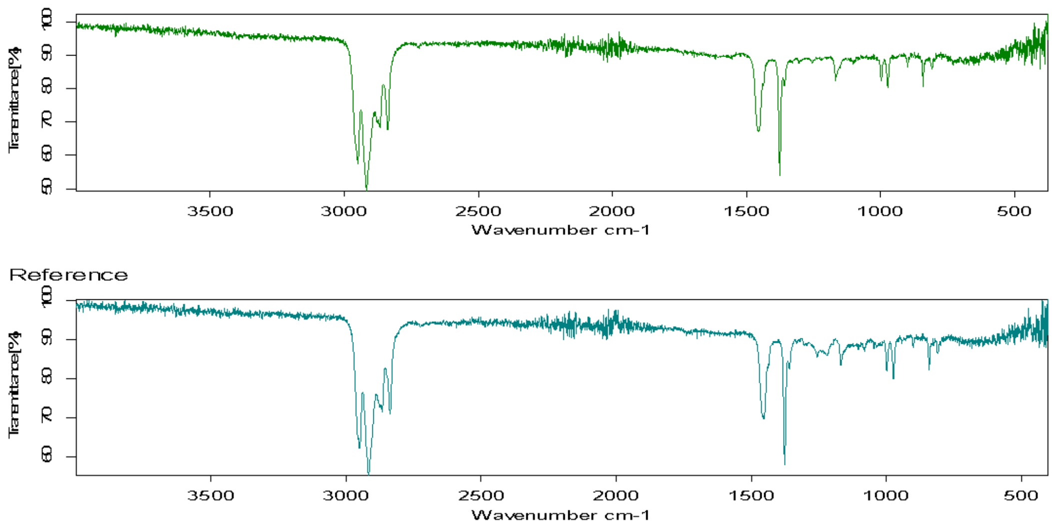
Figure AP. 47 FTIR QCM of LDPE 2 between 1300-1550cm^{-1}



Result: OK

Correlation: 99.73 %
Threshold: 95.00 %
Sample: Sample 24.0

Figure AP. 48 FTIR QCM of LDPE 2 between 2800-3000cm^{-1}

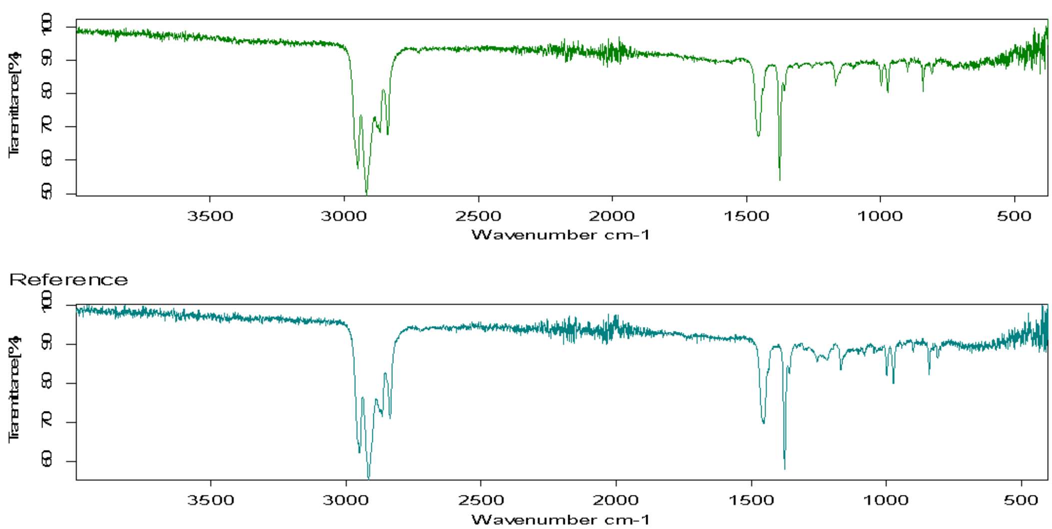


Result: NOT OK

Correlation: 87.89 %
Threshold: 95.00 %

Sample: Sample 8.2

Figure AP. 49 FTIR QCM of PP 2 between 700-900cm^{-1}



Result: OK

Correlation: 99.86 %
Threshold: 95.00 %

Sample: Sample 8.2

Figure AP. 50 FTIR QCM of PP 2 between 1300-1550cm^{-1}

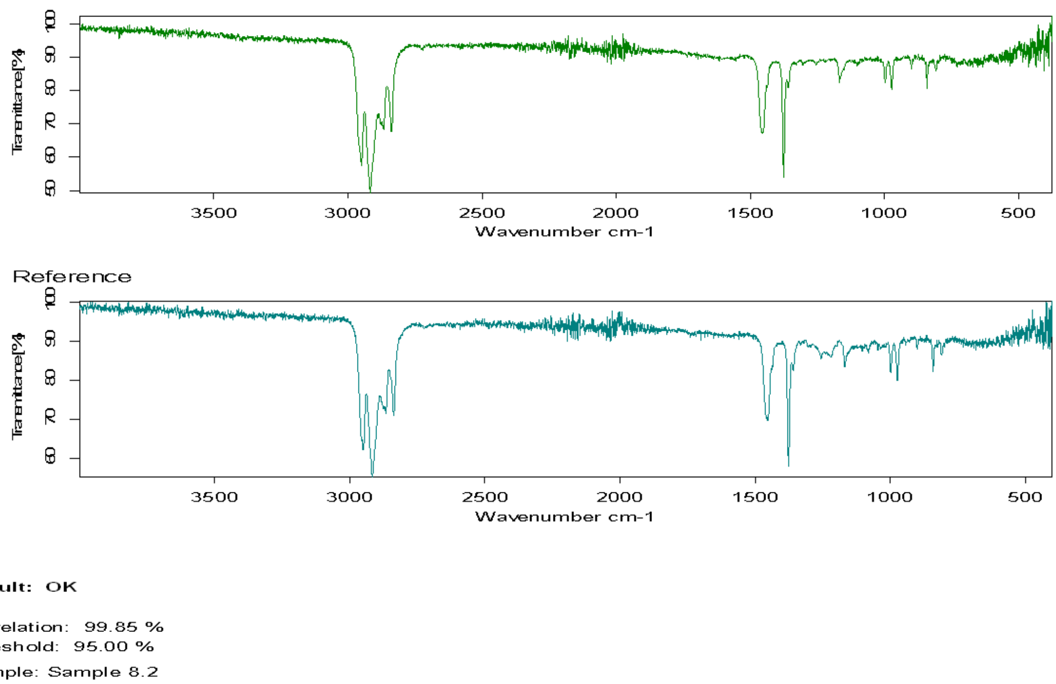


Figure AP. 51 FTIR QCM of PP 2 between 2800-3000cm^{-1}

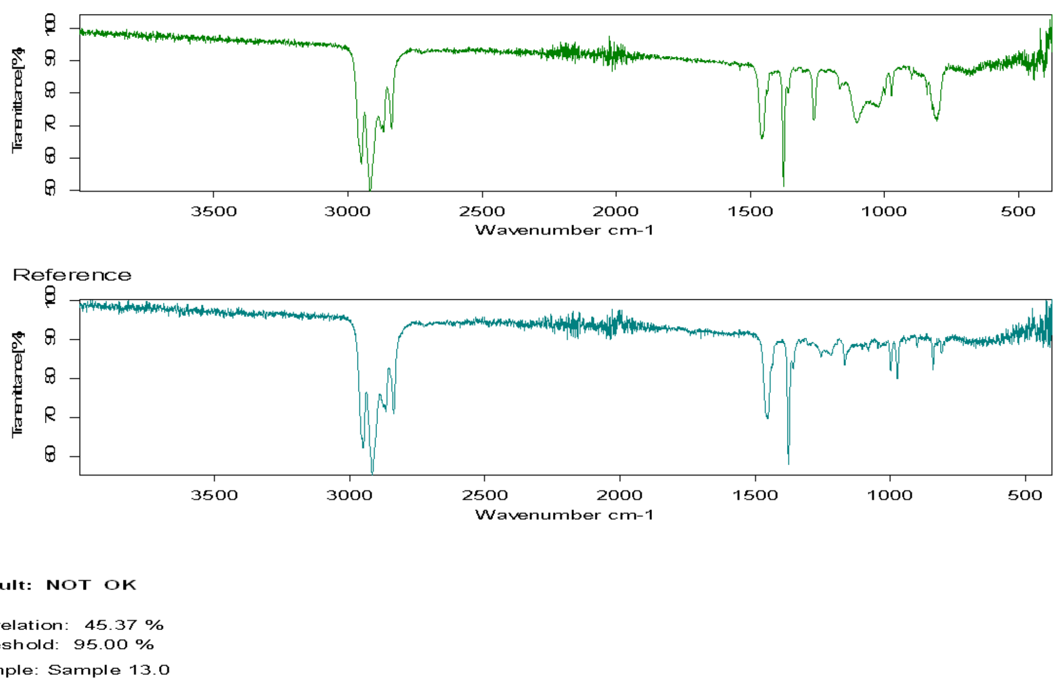
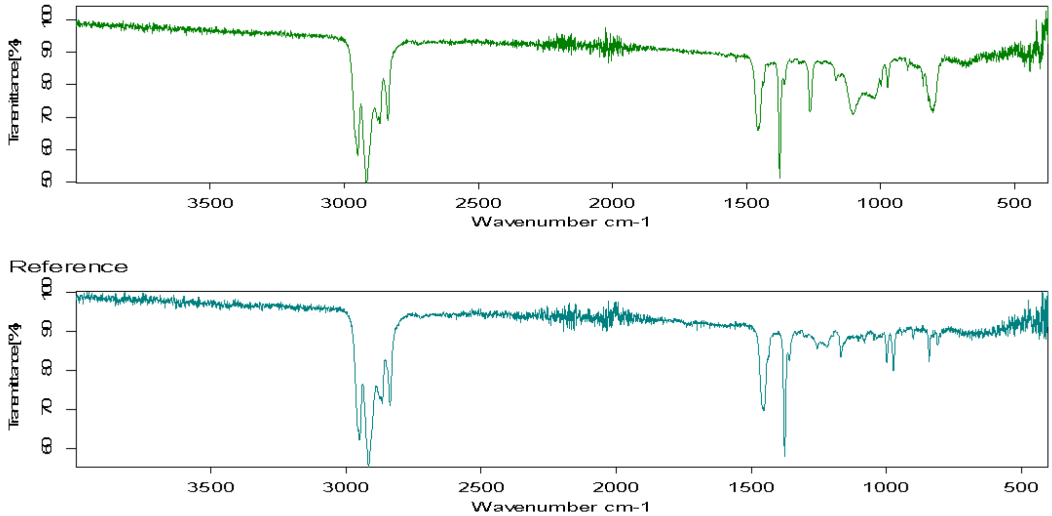


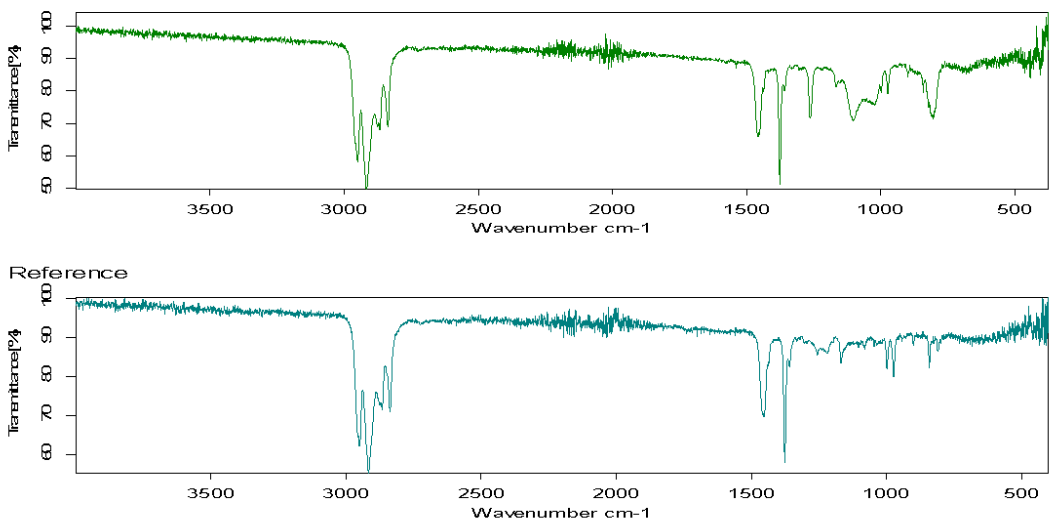
Figure AP. 52 FTIR QCM of PP 3 between 700-900cm^{-1}



Result: OK

Correlation: 99.64 %
Threshold: 95.00 %
Sample: Sample 13.0

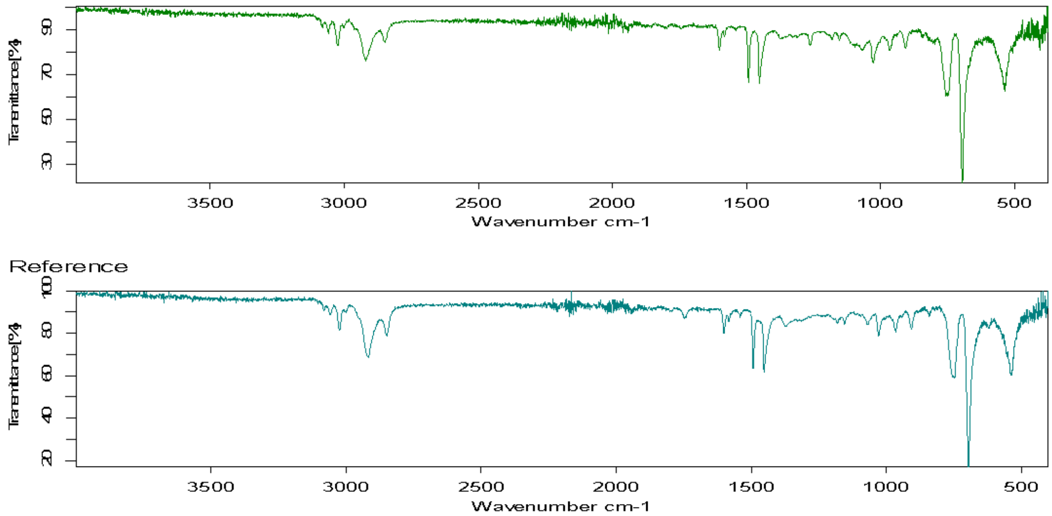
Figure AP. 53 FTIR QCM of PP 3 between 1300-1550cm^{-1}



Result: OK

Correlation: 99.75 %
Threshold: 95.00 %
Sample: Sample 13.0

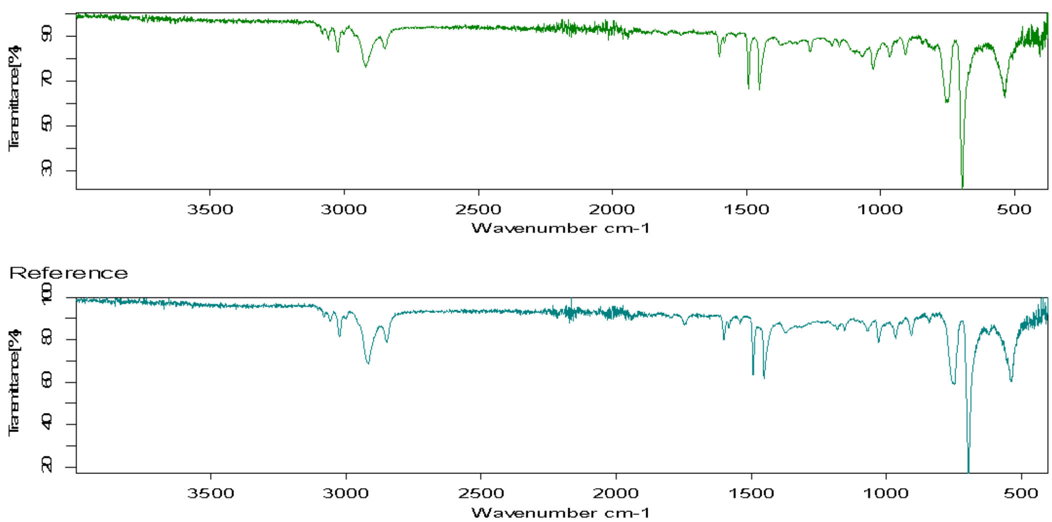
Figure AP. 54 FTIR QCM of PP 3 between 2800-3000cm^{-1}



Result: OK

Correlation: 98.23 %
Threshold: 95.00 %
Sample: Sample 42.0

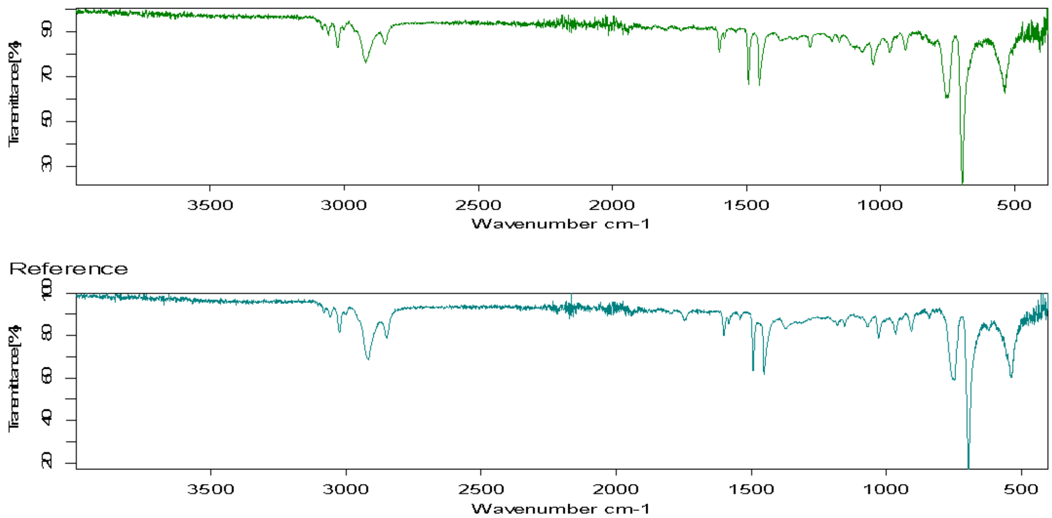
Figure AP. 55 FTIR QCM of PS 2 between 700-900cm^{-1}



Result: OK

Correlation: 99.01 %
Threshold: 95.00 %
Sample: Sample 42.0

Figure AP. 56 FTIR QCM of PS 2 between 1300-1550cm^{-1}



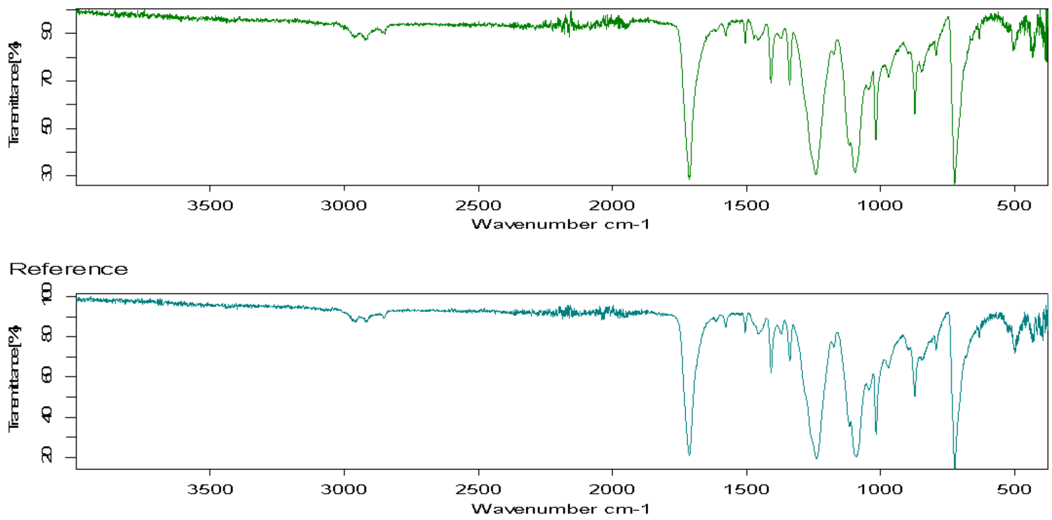
Result: OK

Correlation: 99.39 %
Threshold: 95.00 %

Sample: Sample 42.0

Figure AP. 57 FTIR QCM of PS 2 between 2800-3000cm^{-1}

Comparisons at 1300-1550cm^{-1}

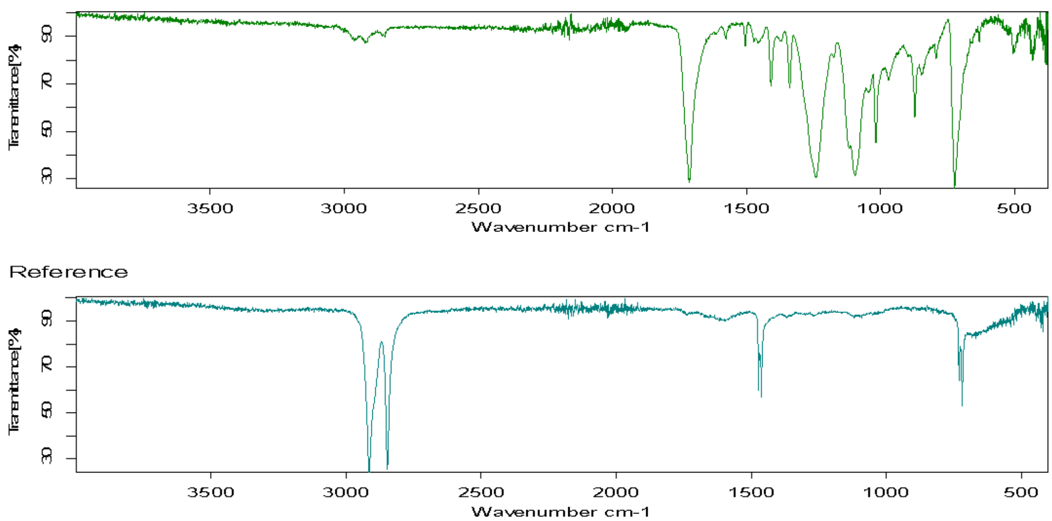


Result: OK

Correlation: 97.58 %
Threshold: 95.00 %

Sample: Sample 30.2
Compared with Reference: Sample 1.0

Figure AP. 58 FTIR QCM of PET 2 between 1300-1550cm^{-1} for PET 1 reference

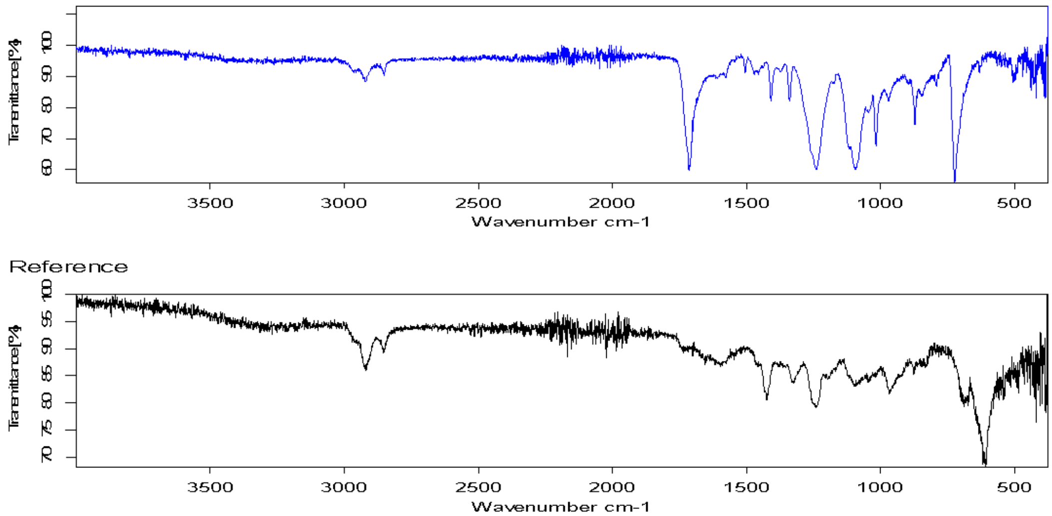


Result: NOT OK

Correlation: 2.09 %
Threshold: 95.00 %

Sample: Sample 30.2
Compared with Reference: Sample 2 compare.0

Figure AP. 59 FTIR QCM of PET 2 between 1300-1550cm^{-1} for HDPE 1 reference

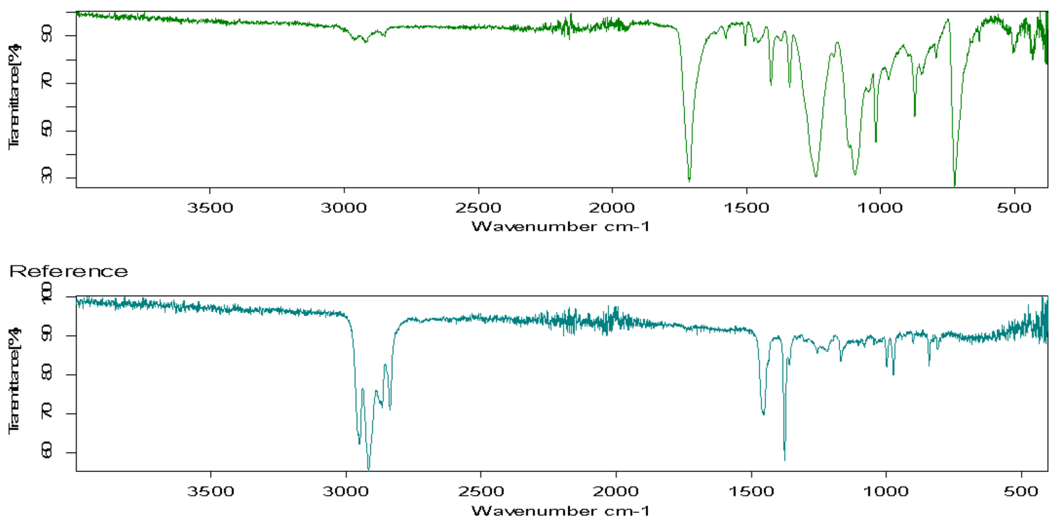


Result: NOT OK

Correlation: 36.33 %
Threshold: 95.00 %

Sample: Sample 30.3
Compared with Reference: Sample 53 PVC.0

Figure AP. 60 FTIR QCM of PET 2 between 1300-1550cm^{-1} for PVC 1 reference



Result: NOT OK

Correlation: 5.45 %
Threshold: 95.00 %

Sample: Sample 30.2
Compared with Reference: Sample 3.0

Figure AP. 61 FTIR QCM of PET 2 between 1300-1550cm^{-1} for PP 1 reference

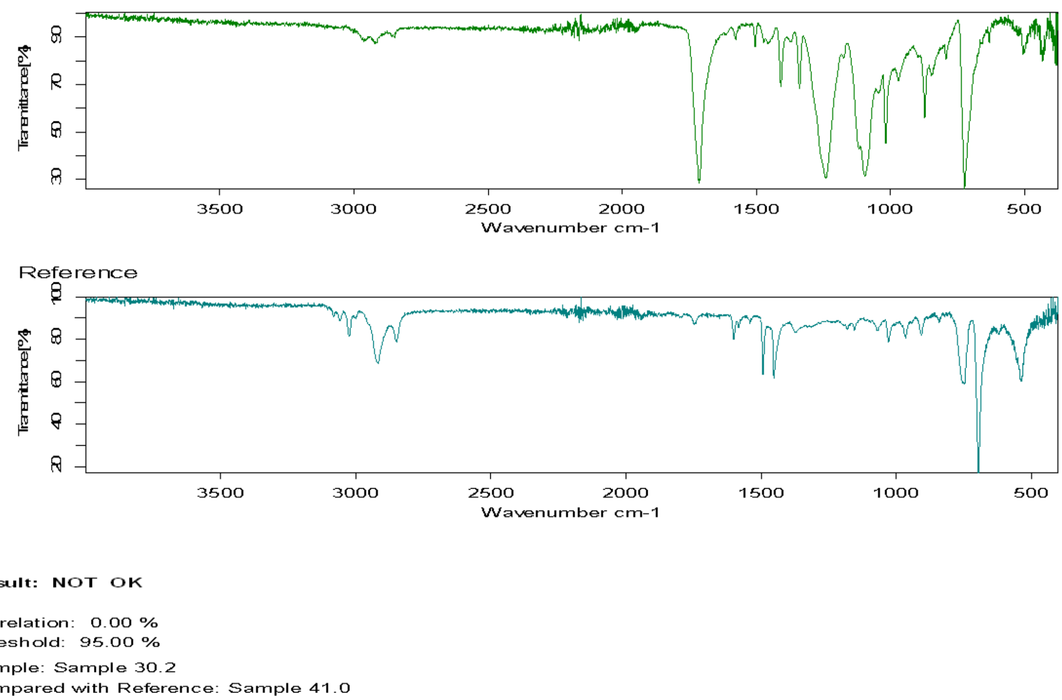


Figure AP. 62 FTIR QCM of PET 2 between 1300-1550cm^{-1} for PS 1 reference

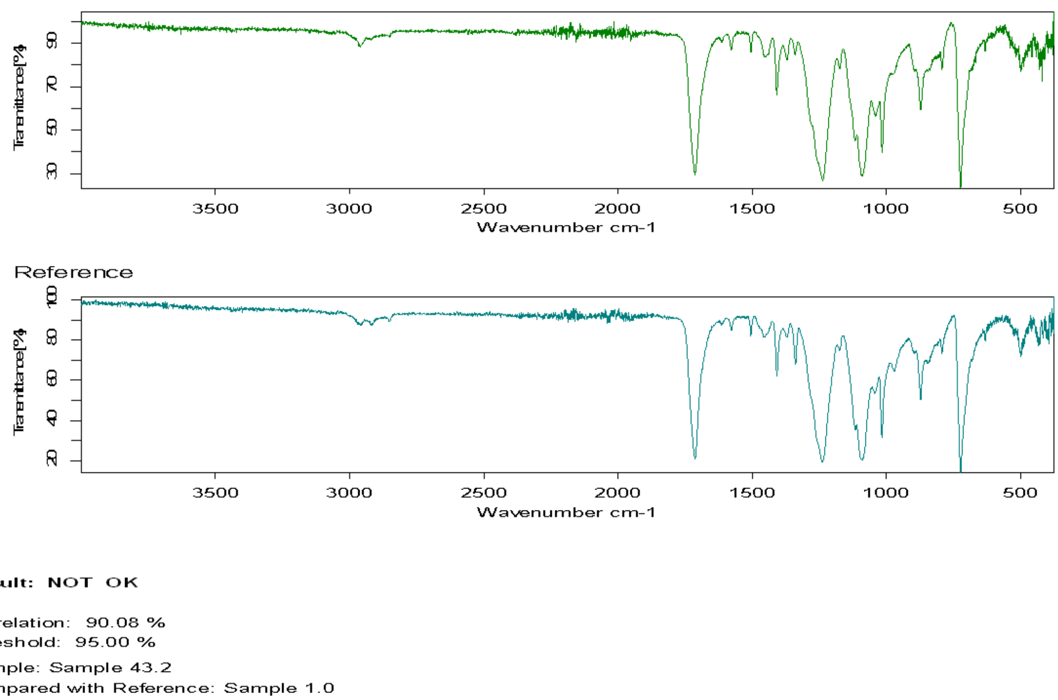
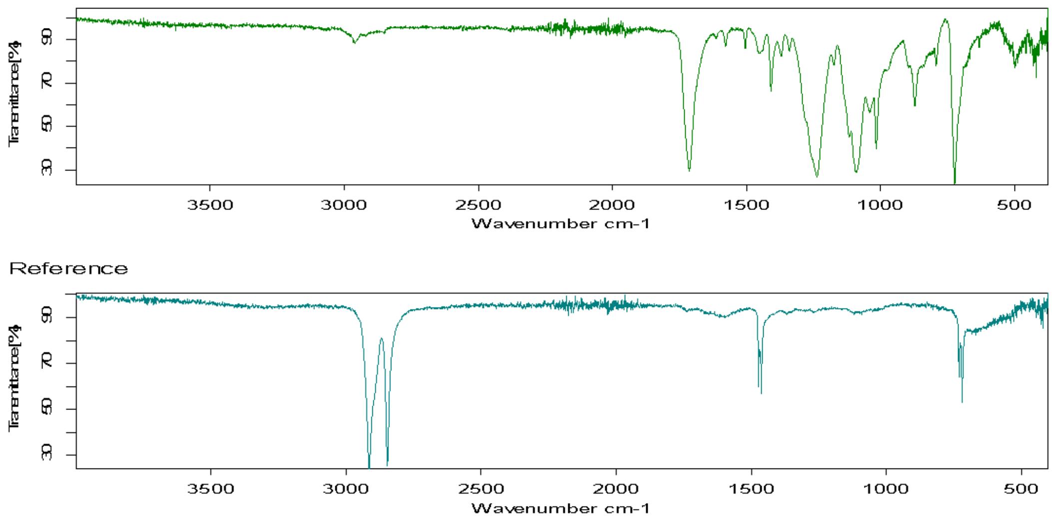


Figure AP. 63 FTIR QCM of PET 3 between 1300-1550cm^{-1} for PET 1 reference

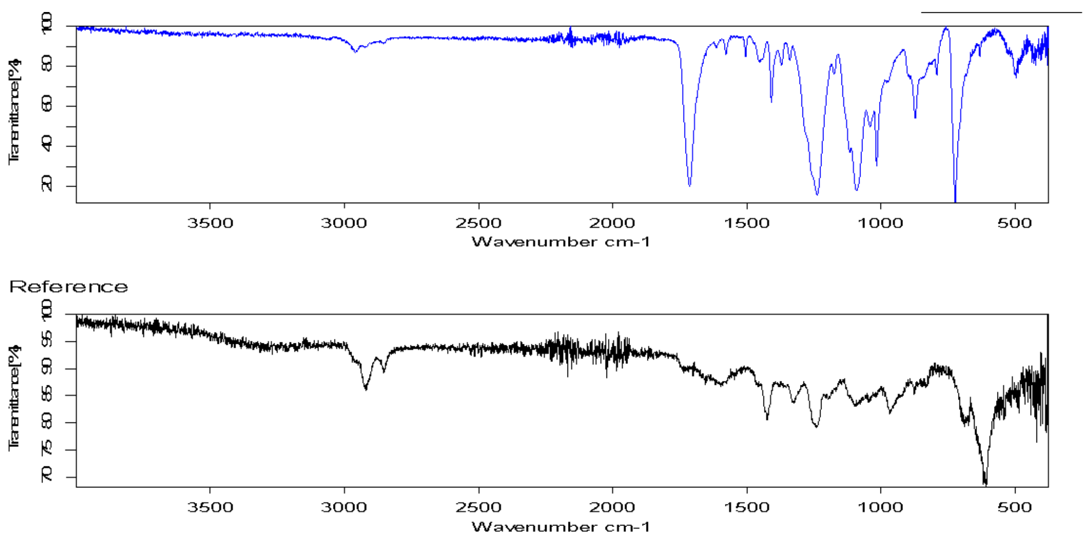


Result: NOT OK

Correlation: 0.53 %
Threshold: 95.00 %

Sample: Sample 43.2
Compared with Reference: Sample 2 compare.0

Figure AP. 64 FTIR QCM of PET 3 between 1300-1550cm^{-1} for HDPE 1 reference

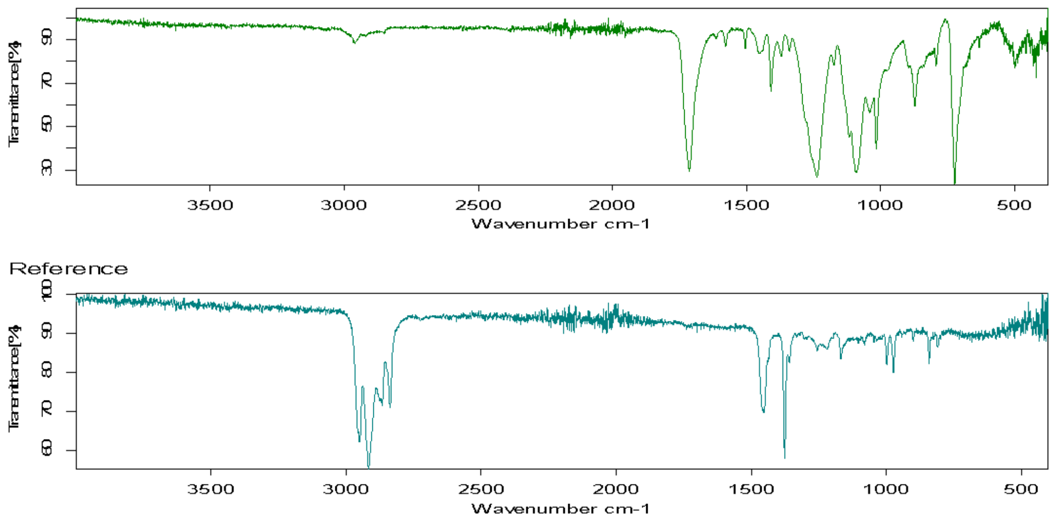


Result: NOT OK

Correlation: 38.40 %
Threshold: 95.00 %

Sample: Sample 43.3
Compared with Reference: Sample 53 PVC.0

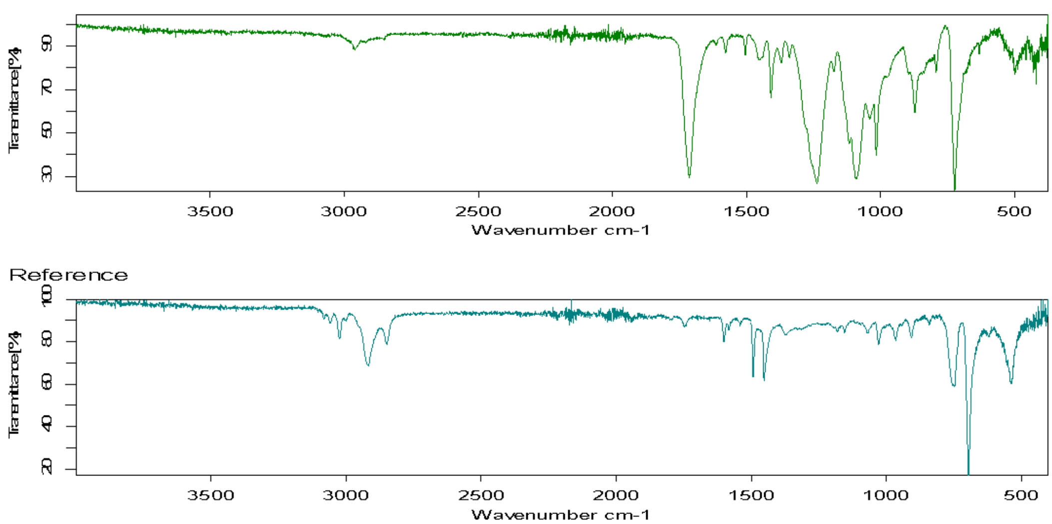
Figure AP. 65 FTIR QCM of PET 3 between 1300-1550cm^{-1} for PVC 1 reference



Result: NOT OK

Correlation: 23.84 %
Threshold: 95.00 %
Sample: Sample 43.2
Compared with Reference: Sample 3.0

Figure AP. 66 FTIR QCM of PET 3 between 1300-1550cm^{-1} for PP 1 reference



Result: NOT OK

Correlation: 9.77 %
Threshold: 95.00 %
Sample: Sample 43.2
Compared with Reference: Sample 41.0

Figure AP. 67 FTIR QCM of PET 3 between 1300-1550cm^{-1} for PS 1 reference

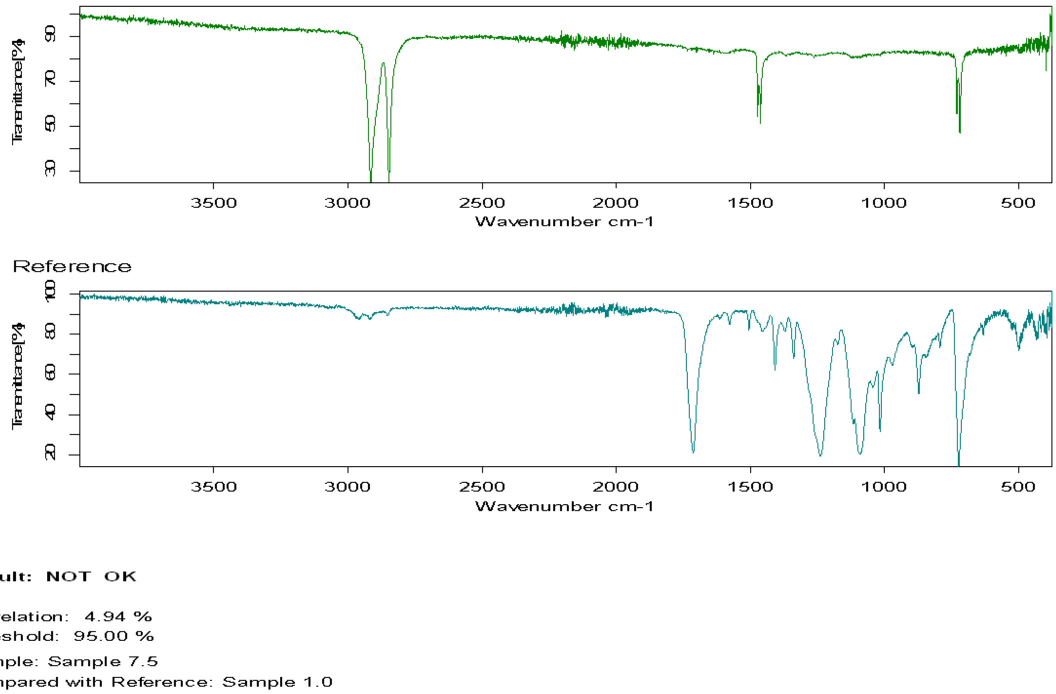


Figure AP. 68 FTIR QCM of HDPE 2 between 1300-1550cm^{-1} for PET 1 reference

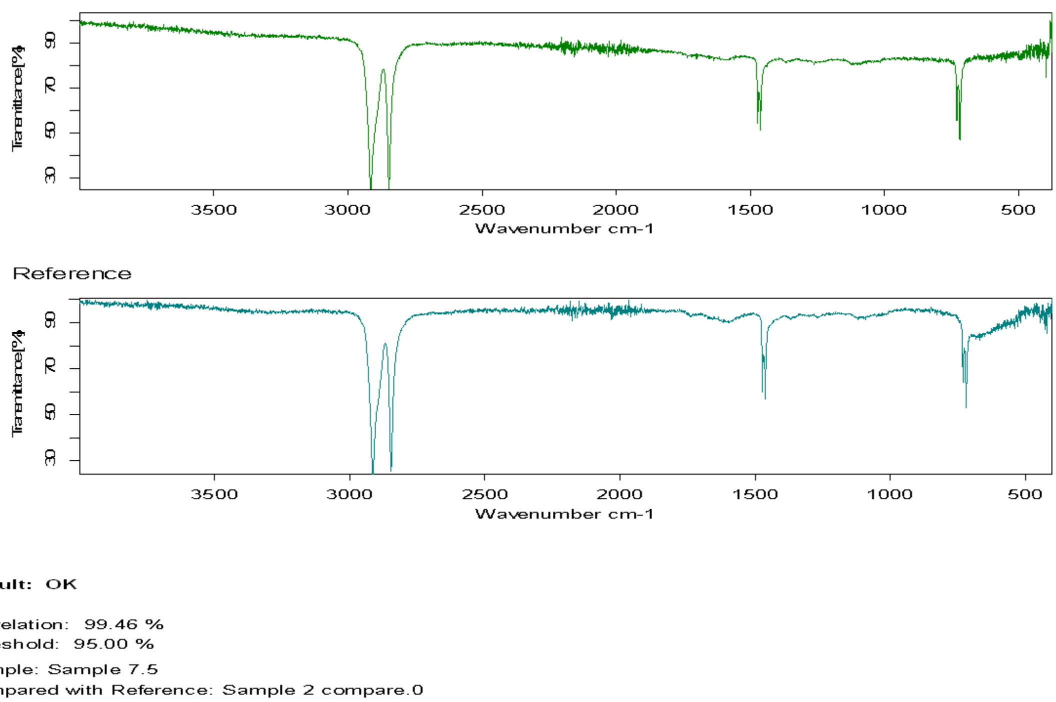
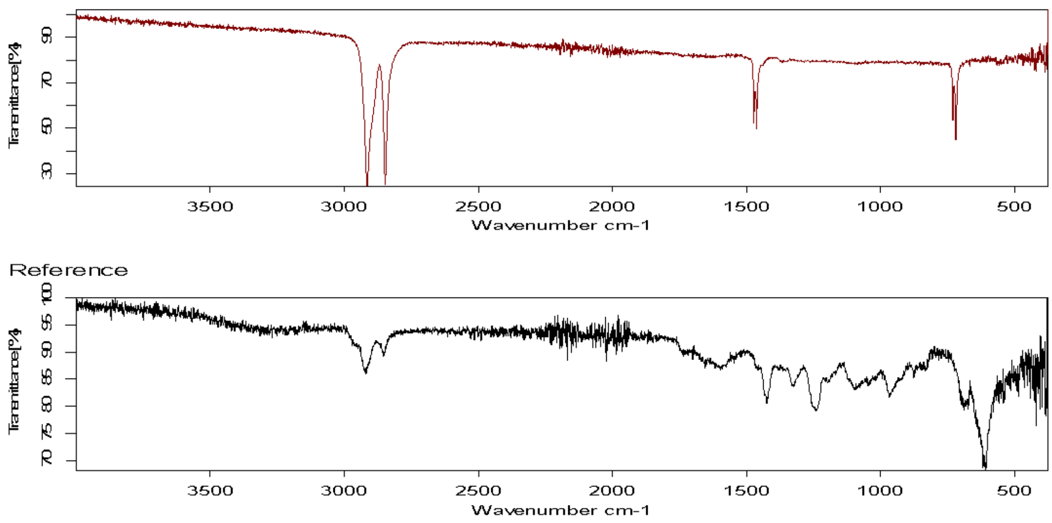


Figure AP. 69 FTIR QCM of HDPE 2 between 1300-1550cm^{-1} for HDPE 1 reference

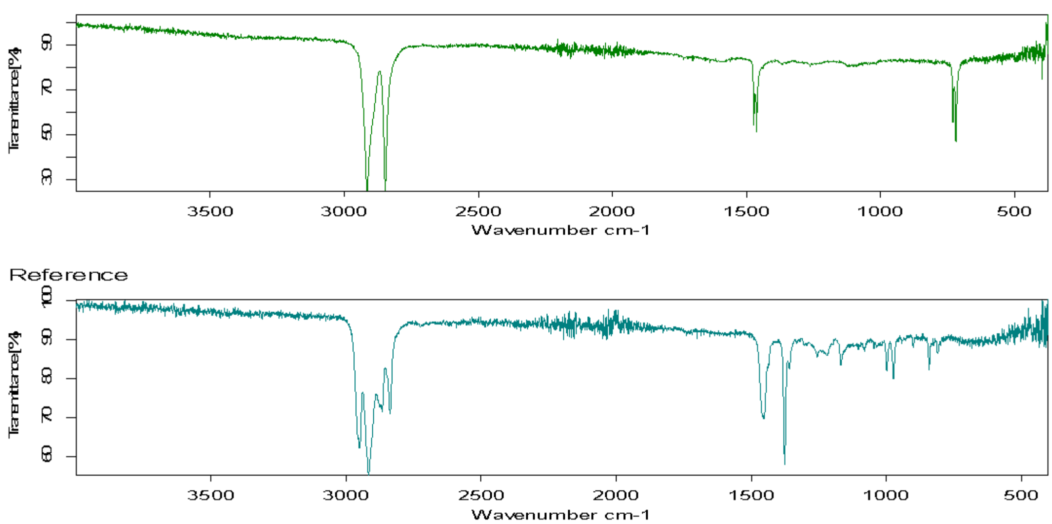


Result: NOT OK

Correlation: 0.00 %
Threshold: 95.00 %

Sample: Sample 7.7
Compared with Reference: Sample 53 PVC.0

Figure AP. 70 FTIR QCM of HDPE 2 between 1300-1550cm^{-1} for PVC 1 reference

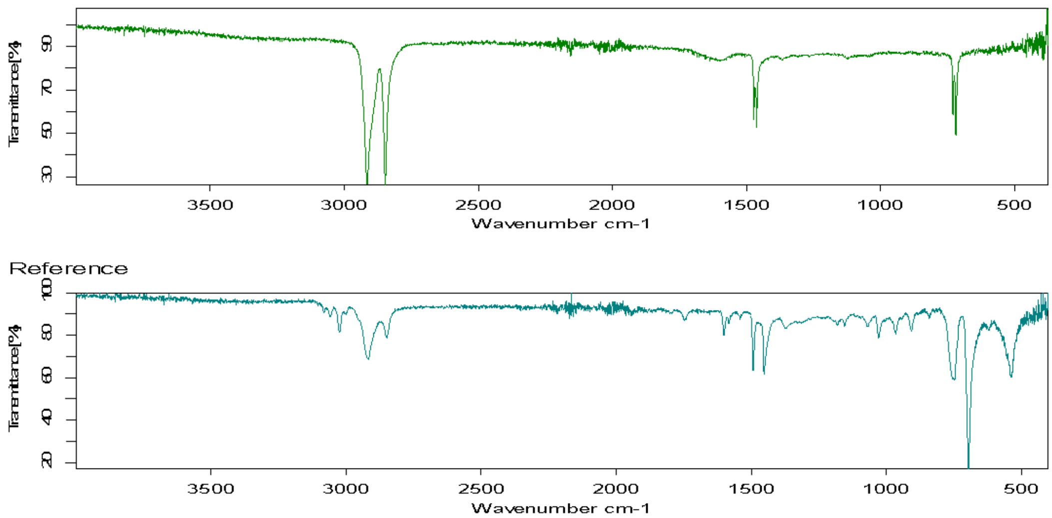


Result: NOT OK

Correlation: 47.96 %
Threshold: 95.00 %

Sample: Sample 7.5
Compared with Reference: Sample 3.0

Figure AP. 71 FTIR QCM of HDPE 2 between 1300-1550cm^{-1} for PP 1 reference

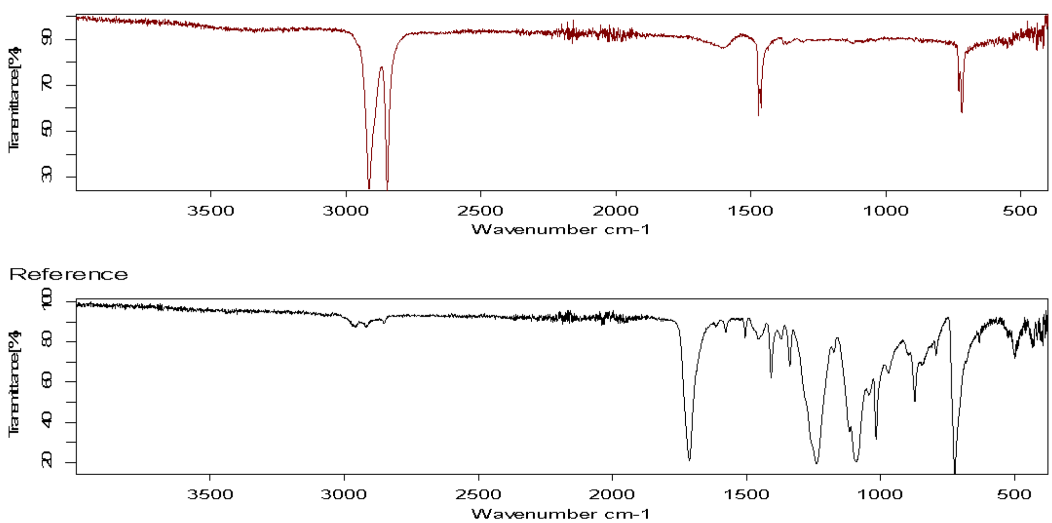


Result: NOT OK

Correlation: 16.97 %
Threshold: 95.00 %

Sample: Sample 7.6
Compared with Reference: Sample 41.0

Figure AP. 72 FTIR QCM of HDPE 2 between 1300-1550cm^{-1} for PS 1 reference

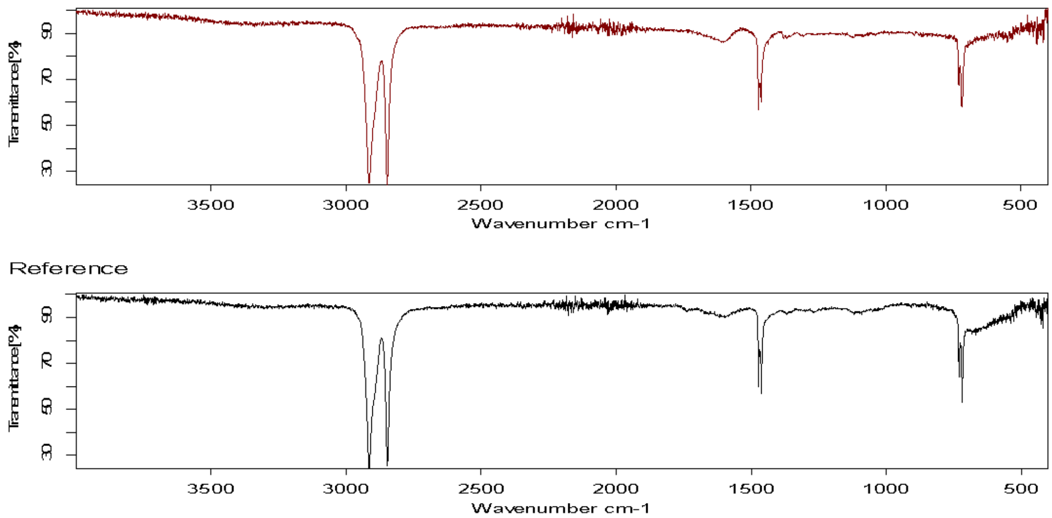


Result: NOT OK

Correlation: 2.57 %
Threshold: 95.00 %

Sample: Sample 20.3
Compared with Reference: Sample 1.0

Figure AP. 73 FTIR QCM of HDPE 3 between 1300-1550cm^{-1} for PET 1 reference

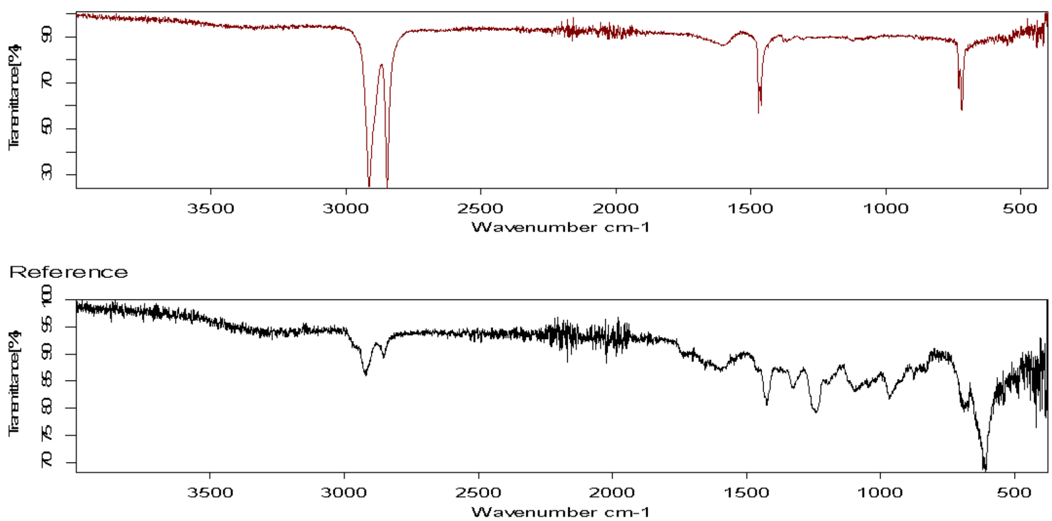


Result: OK

Correlation: 97.62 %
Threshold: 95.00 %

Sample: Sample 20.3
Compared with Reference: Sample 2 compare.0

Figure AP. 74 FTIR QCM of HDPE 3 between 1300-1550cm^{-1} for HDPE 1 reference

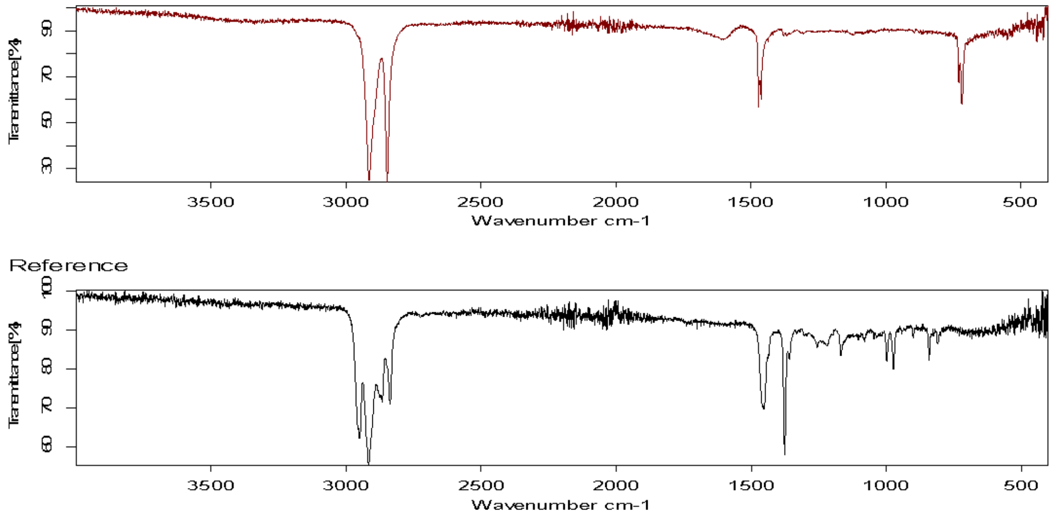


Result: NOT OK

Correlation: 0.00 %
Threshold: 95.00 %

Sample: Sample 20.3
Compared with Reference: Sample 53 PVC.0

Figure AP. 75 FTIR QCM of HDPE 3 between 1300-1550cm^{-1} for PVC 1 reference

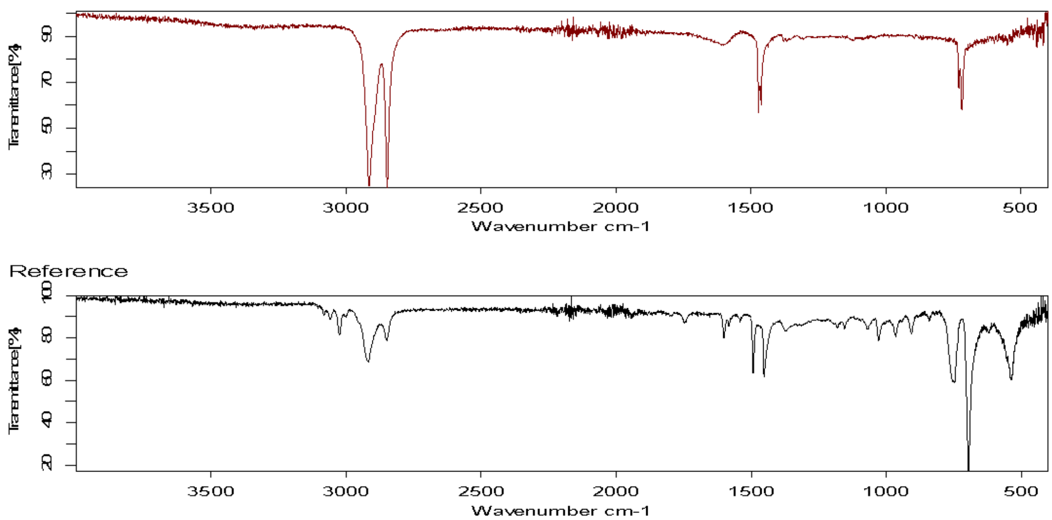


Result: NOT OK

Correlation: 50.01 %
Threshold: 95.00 %

Sample: Sample 20.3
Compared with Reference: Sample 3.0

Figure AP. 76 FTIR QCM of HDPE 3 between 1300-1550cm^{-1} for PP 1 reference

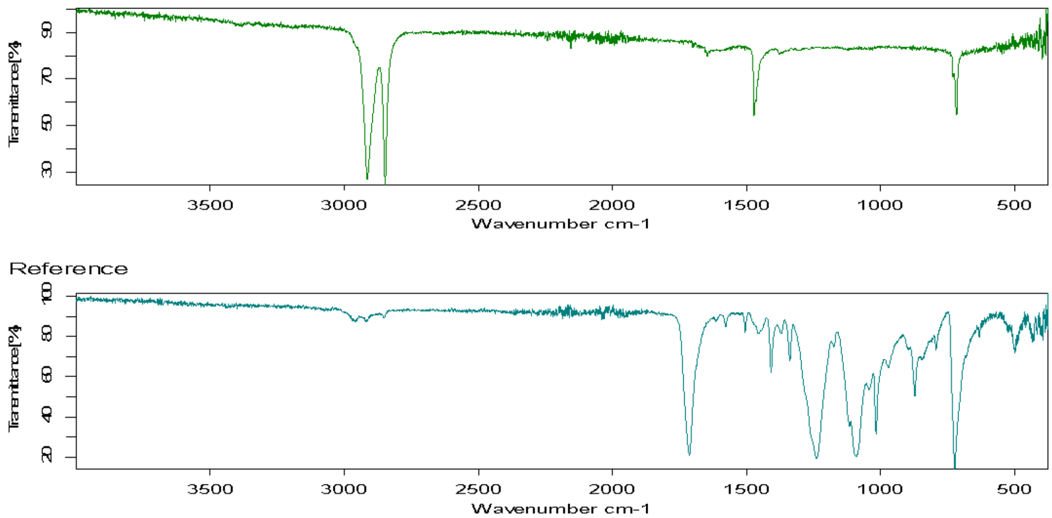


Result: NOT OK

Correlation: 23.05 %
Threshold: 95.00 %

Sample: Sample 20.3
Compared with Reference: Sample 41.0

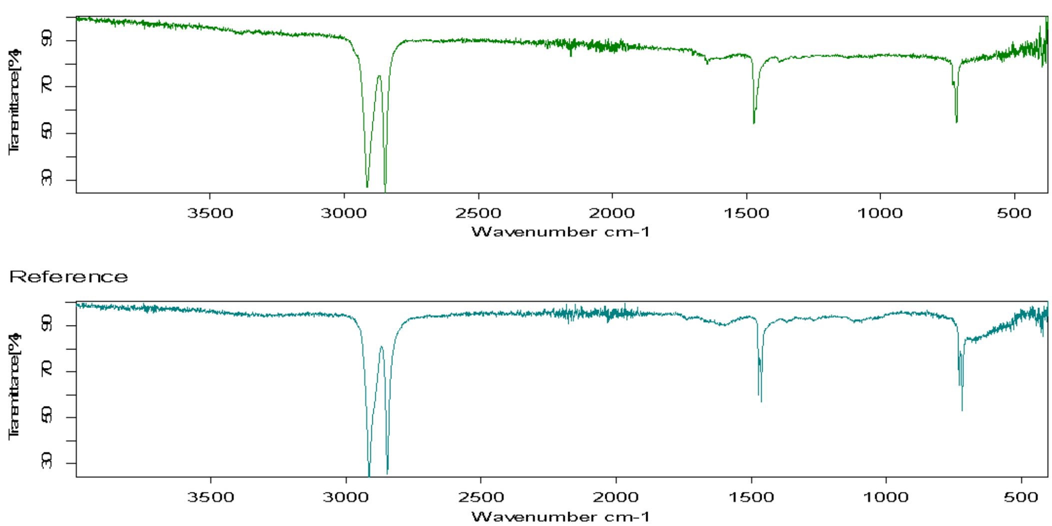
Figure AP. 77 FTIR QCM of HDPE 3 between 1300-1550cm^{-1} for PS 1 reference



Result: NOT OK

Correlation: 2.08 %
Threshold: 95.00 %
Sample: Sample 5.3
Compared with Reference: Sample 1.0

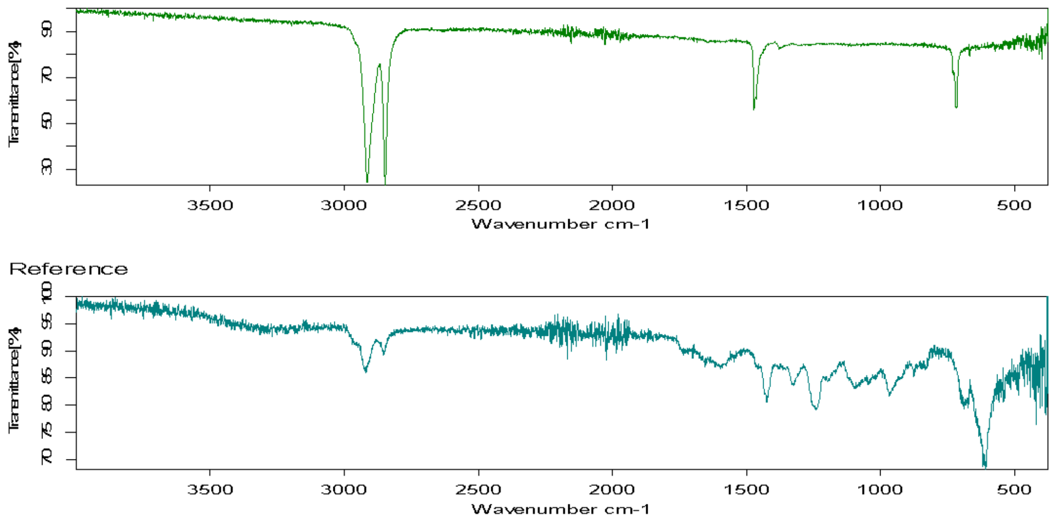
Figure AP. 78 FTIR QCM of LDPE 1 between 1300-1550cm^{-1} for PET 1 reference



Result: OK

Correlation: 95.03 %
Threshold: 95.00 %
Sample: Sample 5.3
Compared with Reference: Sample 2 compare.0

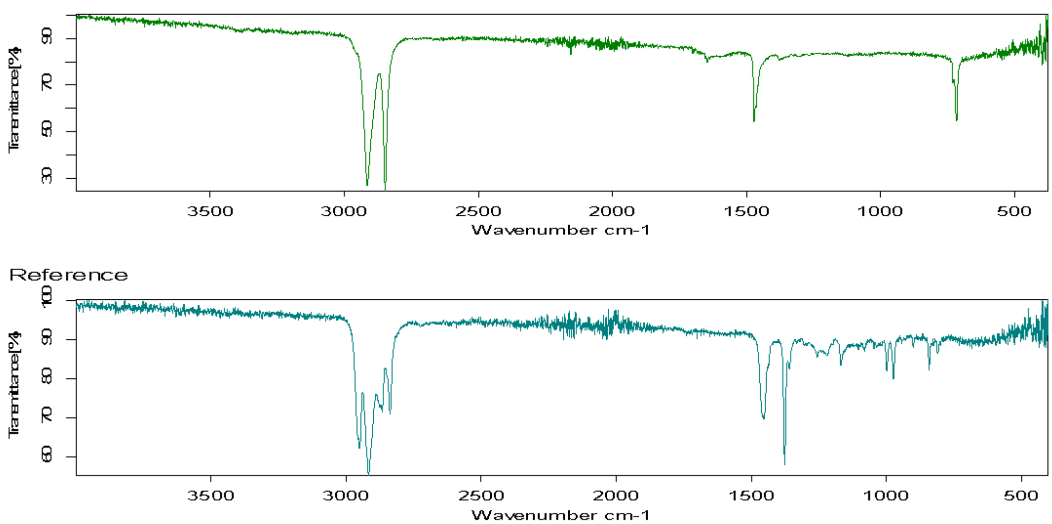
Figure AP. 79 FTIR QCM of LDPE 1 between 1300-1550cm^{-1} for HDPE 1 reference



Result: NOT OK

Correlation: 0.00 %
Threshold: 95.00 %
Sample: Sample 5.1
Compared with Reference: Sample 53 PVC.0

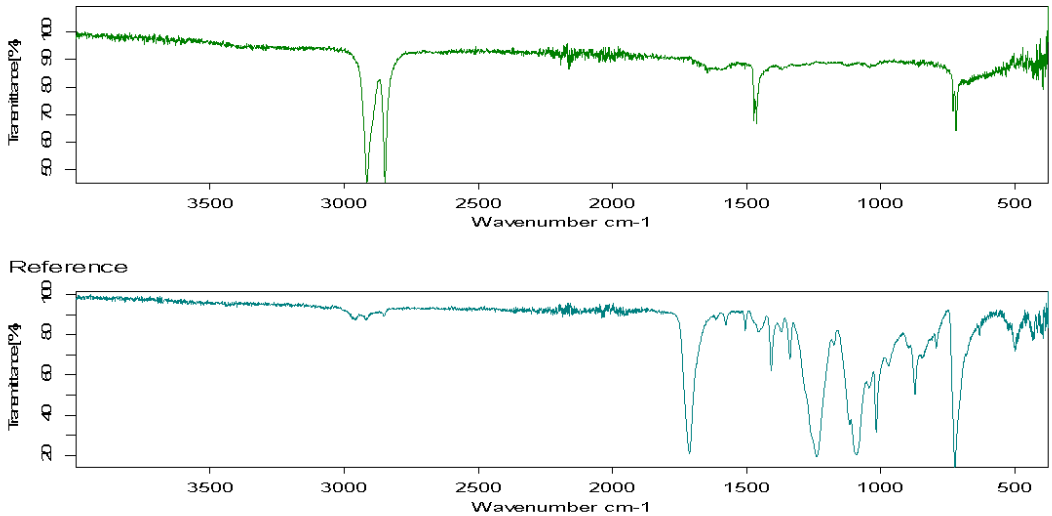
Figure AP. 80 FTIR QCM of LDPE 1 between 1300-1550cm^{-1} for PVC 1 reference



Result: NOT OK

Correlation: 50.72 %
Threshold: 95.00 %
Sample: Sample 5.3
Compared with Reference: Sample 3.0

Figure AP. 81 FTIR QCM of LDPE 1 between 1300-1550cm^{-1} for PP 1 reference

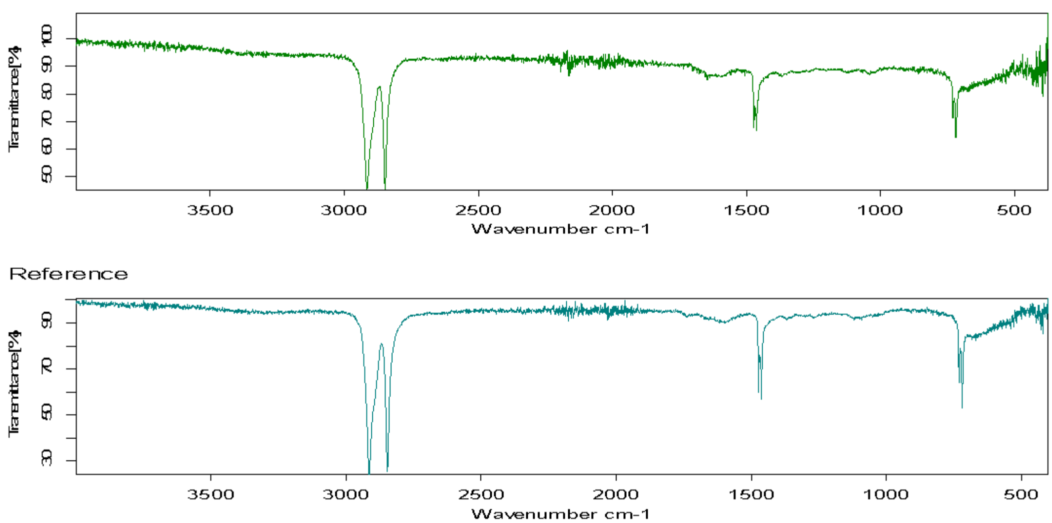


Result: NOT OK

Correlation: 2.28 %
Threshold: 95.00 %

Sample: Sample 24.1
Compared with Reference: Sample 1.0

Figure AP. 82 FTIR QCM of LDPE 2 between 1300-1550cm^{-1} for PET 1 reference

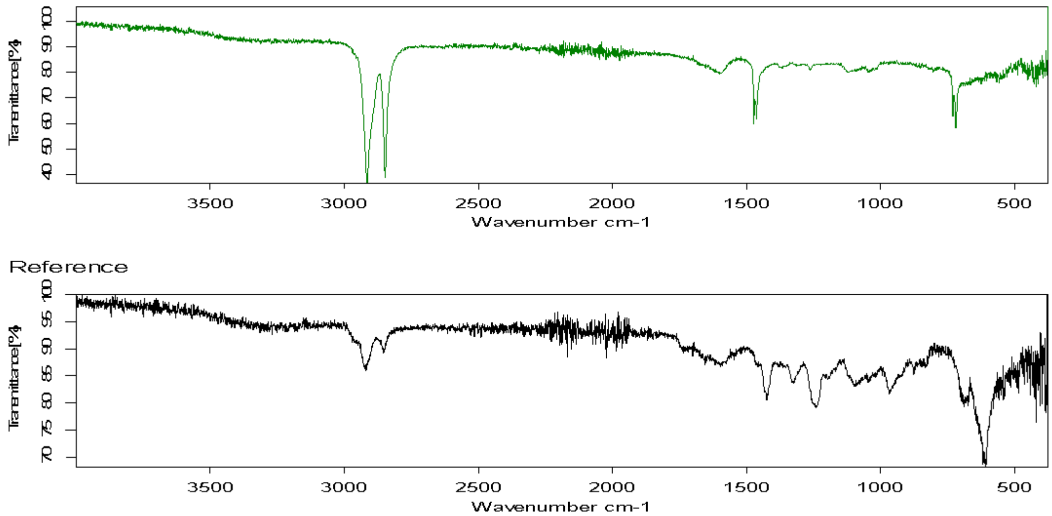


Result: OK

Correlation: 98.77 %
Threshold: 95.00 %

Sample: Sample 24.1
Compared with Reference: Sample 2 compare.0

Figure AP. 83 FTIR QCM of LDPE 2 between 1300-1550cm^{-1} for HDPE 1 reference

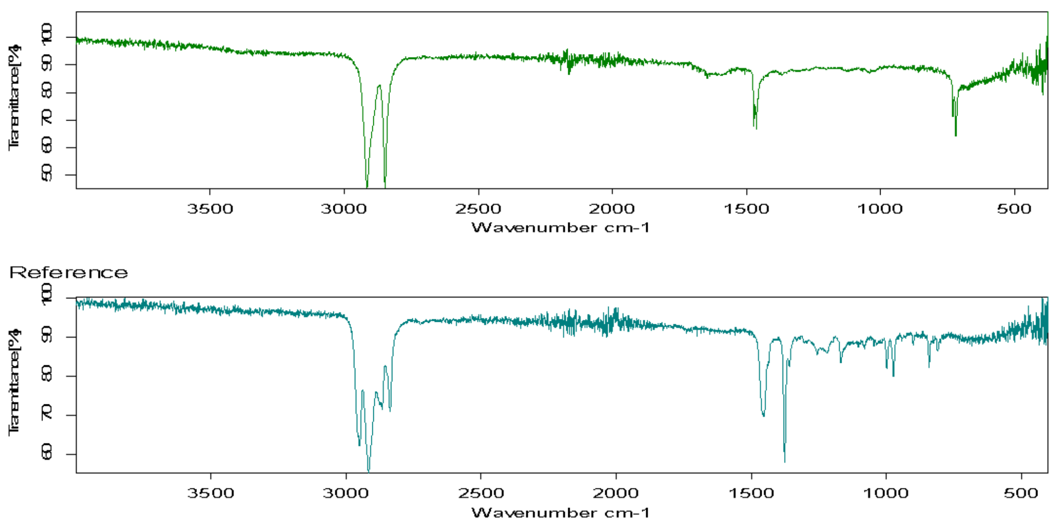


Result: NOT OK

Correlation: 5.56 %
Threshold: 95.00 %

Sample: Sample 24.4
Compared with Reference: Sample 53 PVC.0

Figure AP. 84 FTIR QCM of LDPE 2 between 1300-1550cm^{-1} for PVC 1 reference

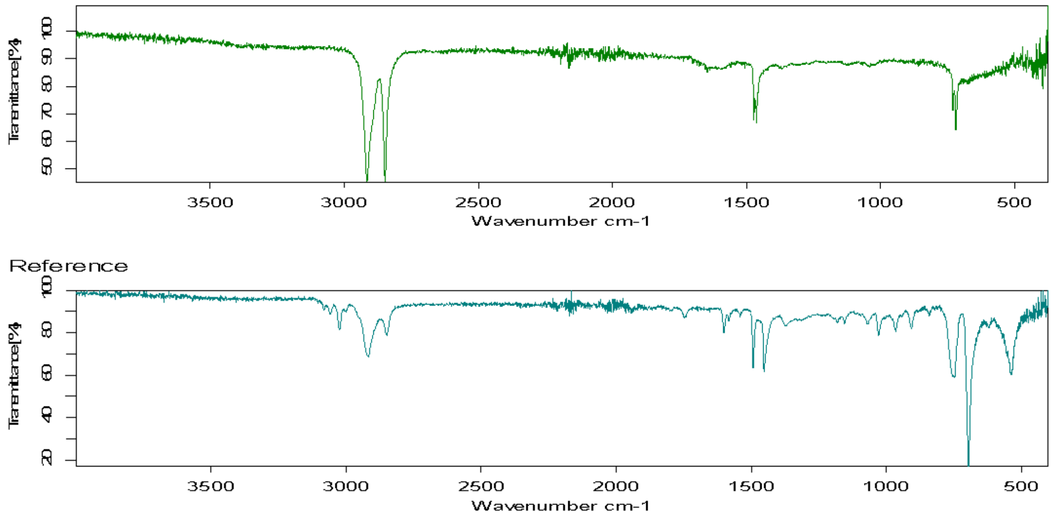


Result: NOT OK

Correlation: 52.83 %
Threshold: 95.00 %

Sample: Sample 24.1
Compared with Reference: Sample 3.0

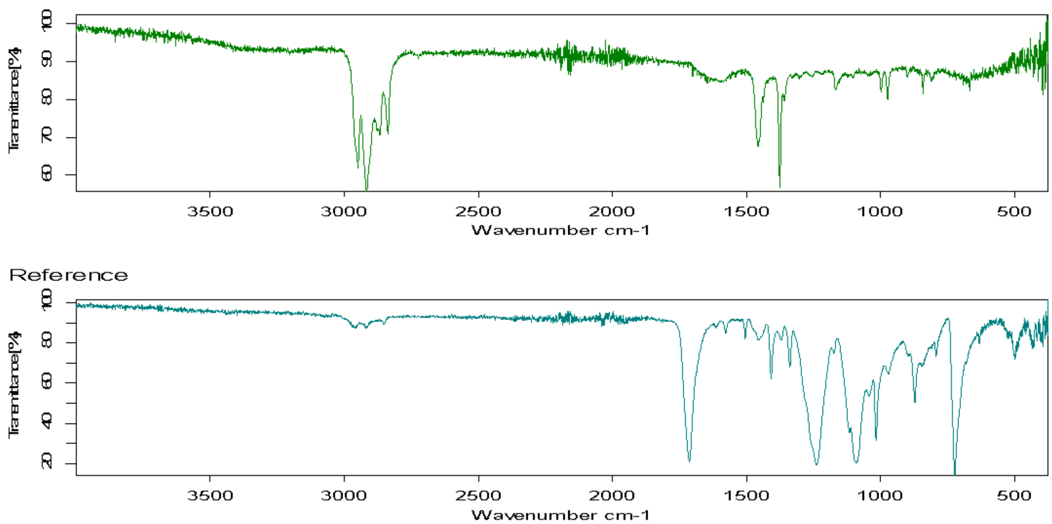
Figure AP. 85 FTIR QCM of LDPE 2 between 1300-1550cm^{-1} for PP 1 reference



Result: NOT OK

Correlation: 23.24 %
Threshold: 95.00 %
Sample: Sample 24.1
Compared with Reference: Sample 41.0

Figure AP. 86 FTIR QCM of LDPE 2 between 1300-1550cm^{-1} for PS 1 reference



Result: NOT OK

Correlation: 9.93 %
Threshold: 95.00 %
Sample: Sample 8.3
Compared with Reference: Sample 1.0

Figure AP. 87 FTIR QCM of PP 2 between 1300-1550cm^{-1} for PET 1 reference

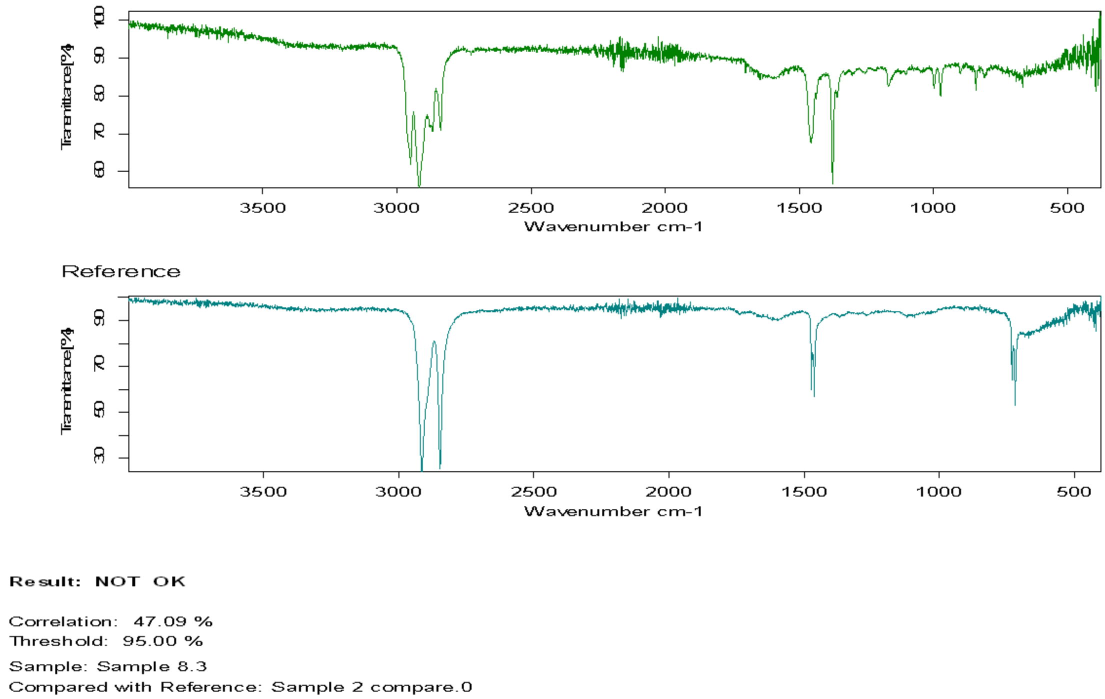


Figure AP. 88 FTIR QCM of PP 2 between 1300-1550cm^{-1} for HDPE 1 reference

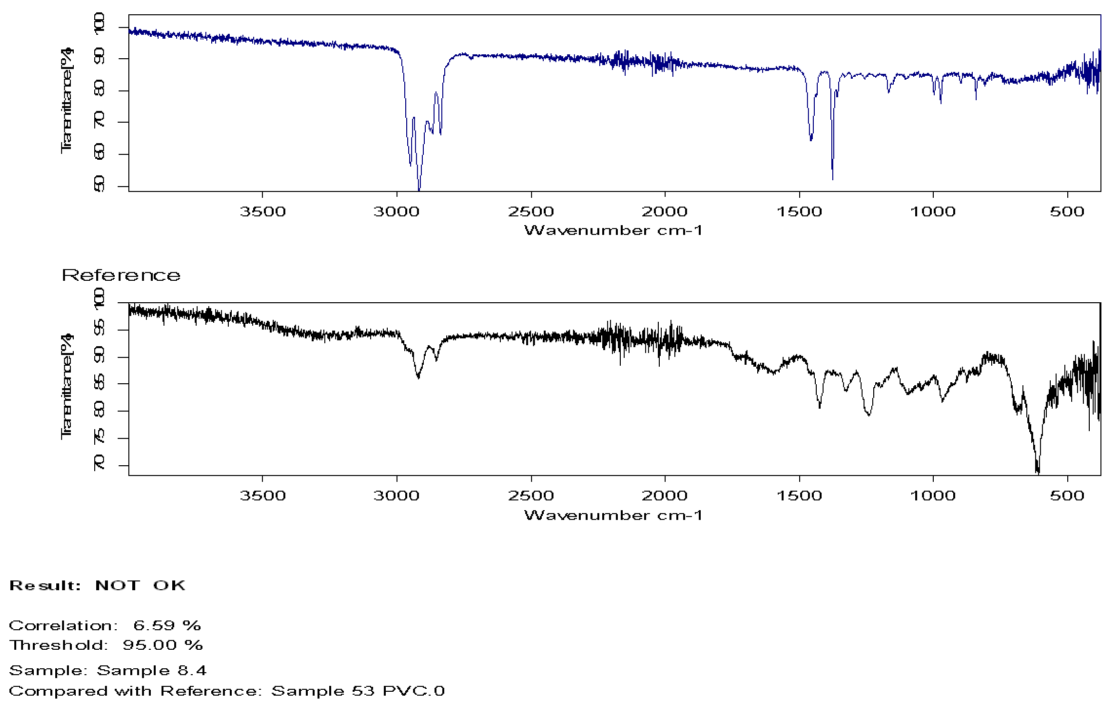
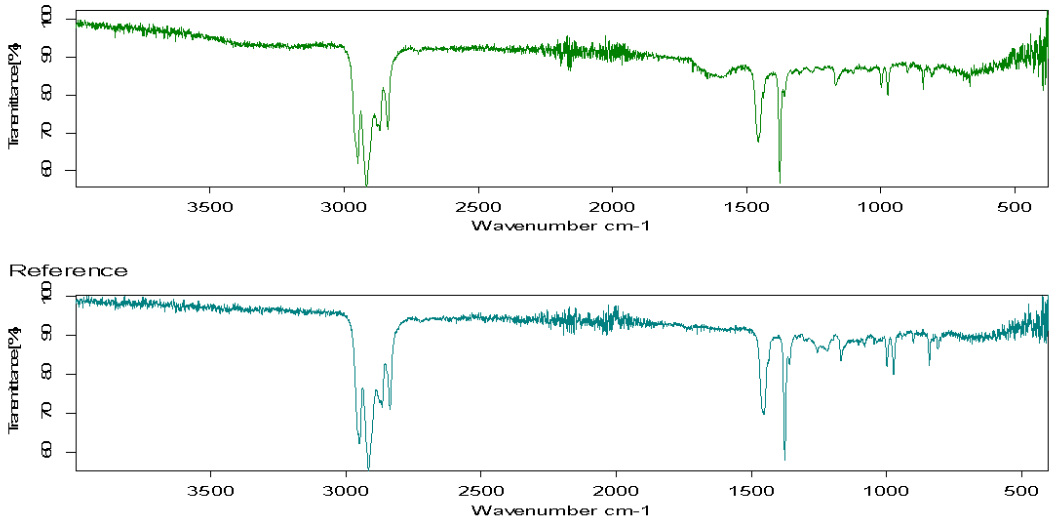


Figure AP. 89 FTIR QCM of PP 2 between 1300-1550cm^{-1} for PVC 1 reference

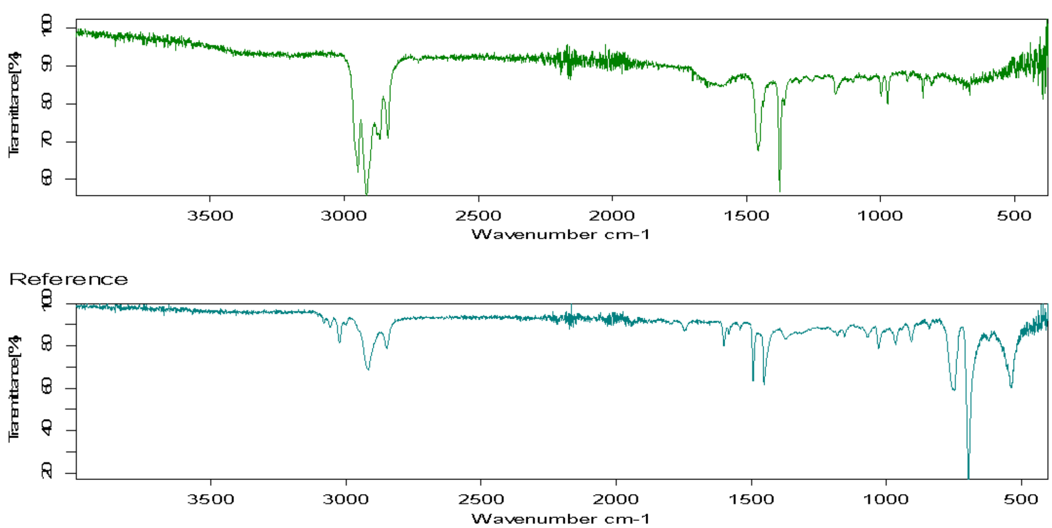


Result: OK

Correlation: 99.63 %
Threshold: 95.00 %

Sample: Sample 8.3
Compared with Reference: Sample 3.0

Figure AP. 90 FTIR QCM of PP 2 between 1300-1550cm^{-1} for PP 1 reference

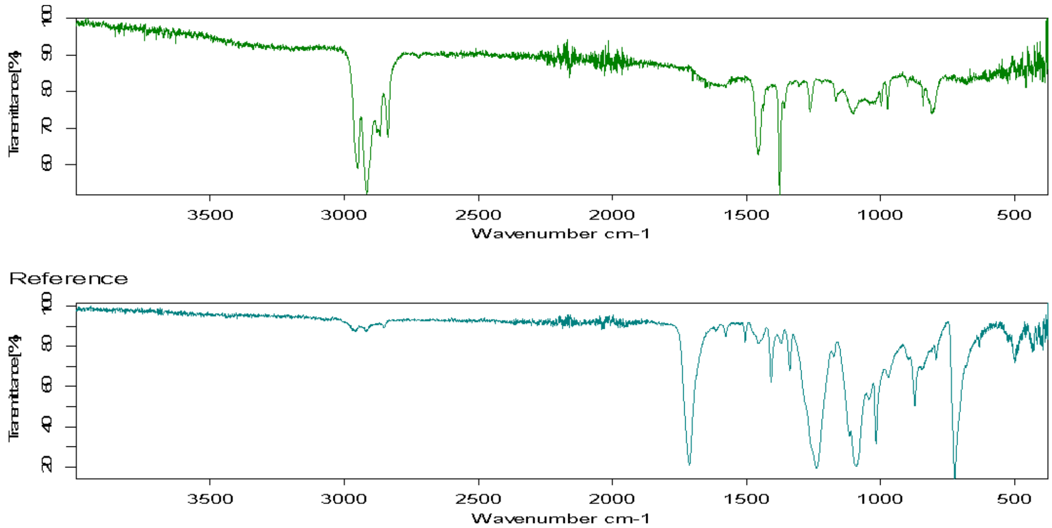


Result: NOT OK

Correlation: 45.20 %
Threshold: 95.00 %

Sample: Sample 8.3
Compared with Reference: Sample 41.0

Figure AP. 91 FTIR QCM of PP 2 between 1300-1550cm^{-1} for PS 1 reference

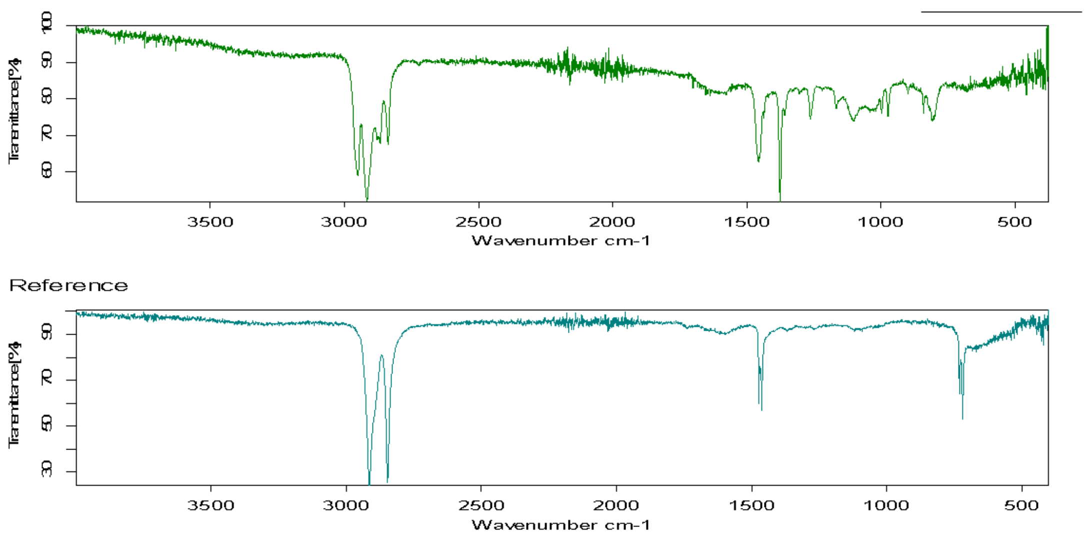


Result: NOT OK

Correlation: 11.02 %
Threshold: 95.00 %

Sample: Sample 13.2
Compared with Reference: Sample 1.0

Figure AP. 92 FTIR QCM of PP 3 between 1300-1550cm^{-1} for PET 1 reference

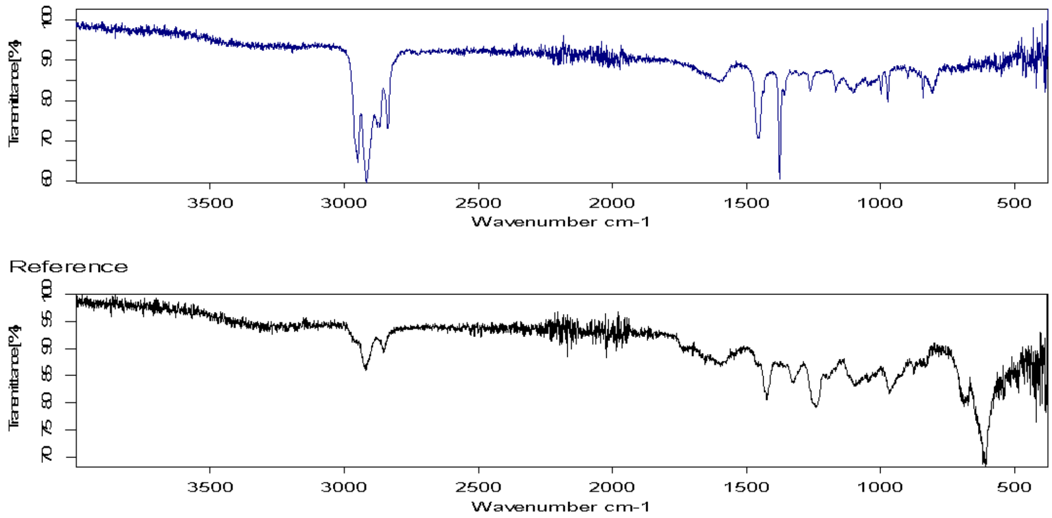


Result: NOT OK

Correlation: 47.28 %
Threshold: 95.00 %

Sample: Sample 13.2
Compared with Reference: Sample 2 compare.0

Figure AP. 93 FTIR QCM of PP 3 between 1300-1550cm^{-1} for HDPE 1 reference

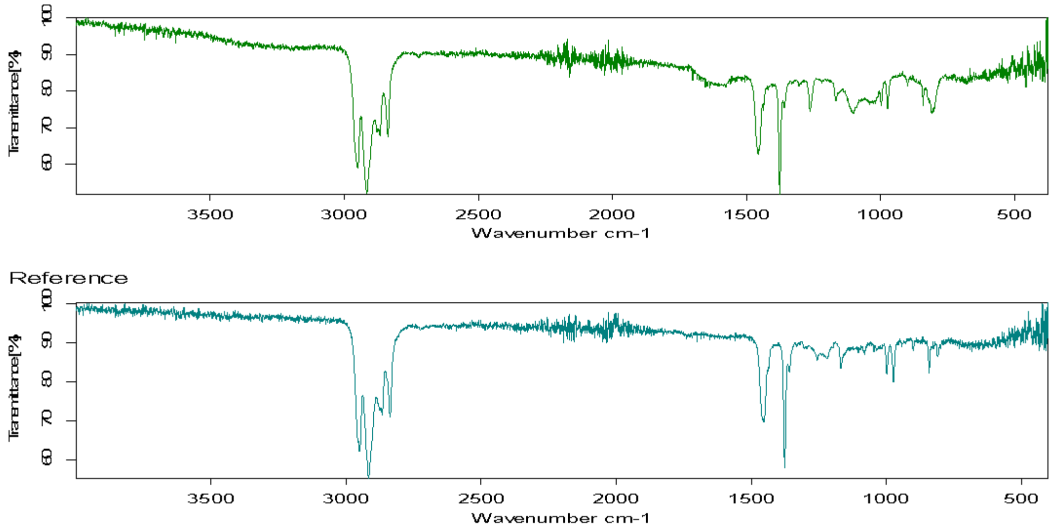


Result: NOT OK

Correlation: 9.44 %
Threshold: 95.00 %

Sample: Sample 13.3
Compared with Reference: Sample 53 PVC.0

Figure AP. 94 FTIR QCM of PP 3 between 1300-1550cm^{-1} for PVC 1 reference

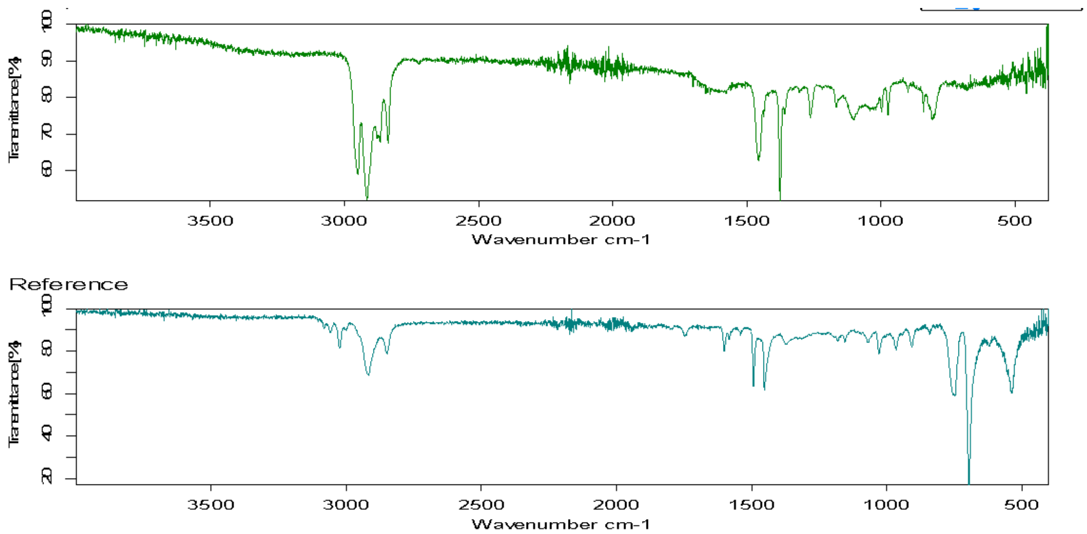


Result: OK

Correlation: 99.67 %
Threshold: 95.00 %

Sample: Sample 13.2
Compared with Reference: Sample 3.0

Figure AP. 95 FTIR QCM of PP 3 between 1300-1550cm^{-1} for PP 1 reference

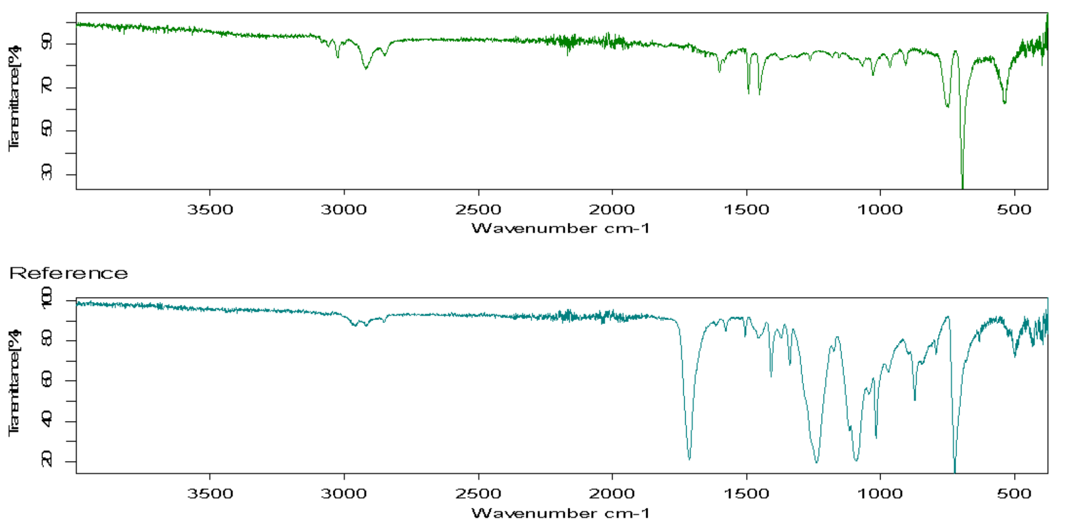


Result: NOT OK

Correlation: 45.27 %
Threshold: 95.00 %

Sample: Sample 13.2
Compared with Reference: Sample 41.0

Figure AP. 96 FTIR QCM of PP 3 between 1300-1550cm^{-1} for PS 1 reference

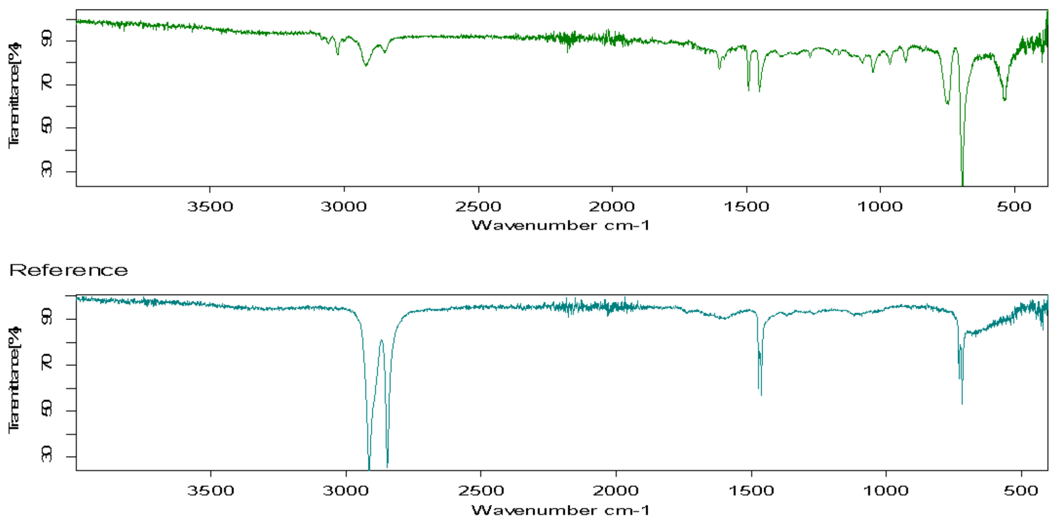


Result: NOT OK

Correlation: 0.00 %
Threshold: 95.00 %

Sample: Sample 42.1
Compared with Reference: Sample 1.0

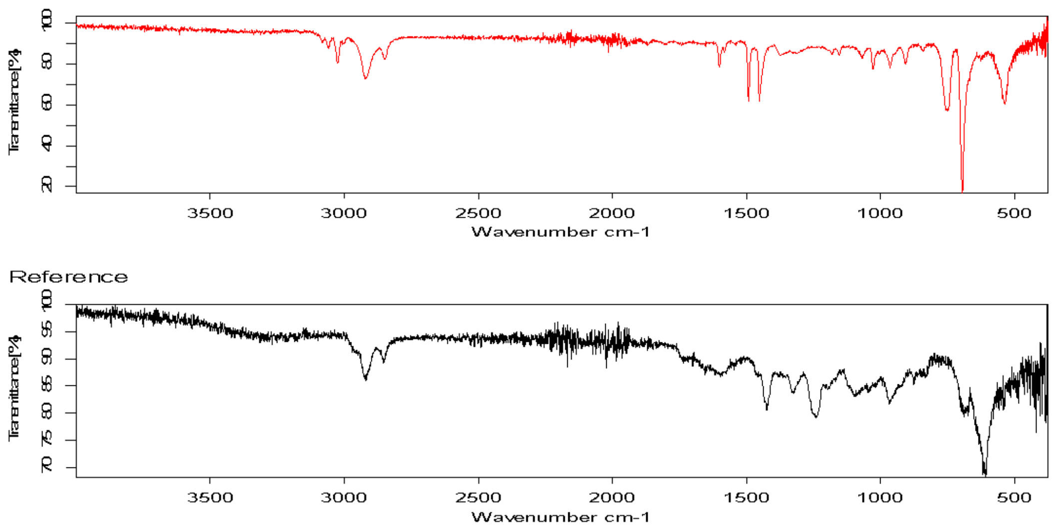
Figure AP. 97 FTIR QCM of PS 2 between 1300-1550cm^{-1} for PET 1 reference



Result: NOT OK

Correlation: 7.89 %
Threshold: 95.00 %
Sample: Sample 42.1
Compared with Reference: Sample 2 compare.0

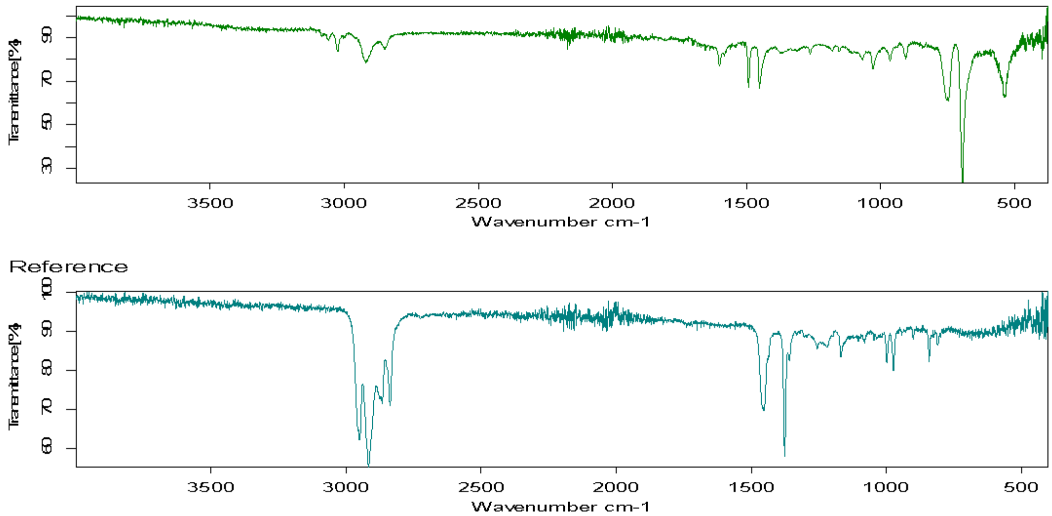
Figure AP. 98 FTIR QCM of PS 2 between 1300-1550cm^{-1} for HDPE 1 reference



Result: NOT OK

Correlation: 5.12 %
Threshold: 95.00 %
Sample: Sample 42.3
Compared with Reference: Sample 53 PVC.0

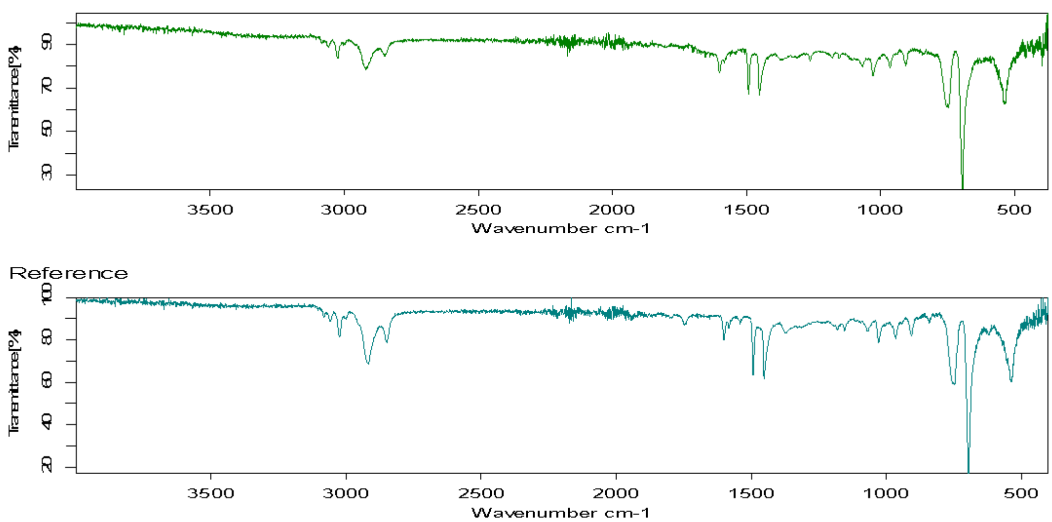
Figure AP. 99 FTIR QCM of PS 2 between 1300-1550cm^{-1} for PVC 1 reference



Result: NOT OK

Correlation: 41.89 %
Threshold: 95.00 %
Sample: Sample 42.1
Compared with Reference: Sample 3.0

Figure AP. 100 FTIR QCM of PS 2 between 1300-1550cm^{-1} for PP 1 reference



Result: OK

Correlation: 99.06 %
Threshold: 95.00 %
Sample: Sample 42.1
Compared with Reference: Sample 41.0

Figure AP. 101 FTIR QCM of PS 2 between 1300-1550cm^{-1} for PS 1 reference

Resolution Tests

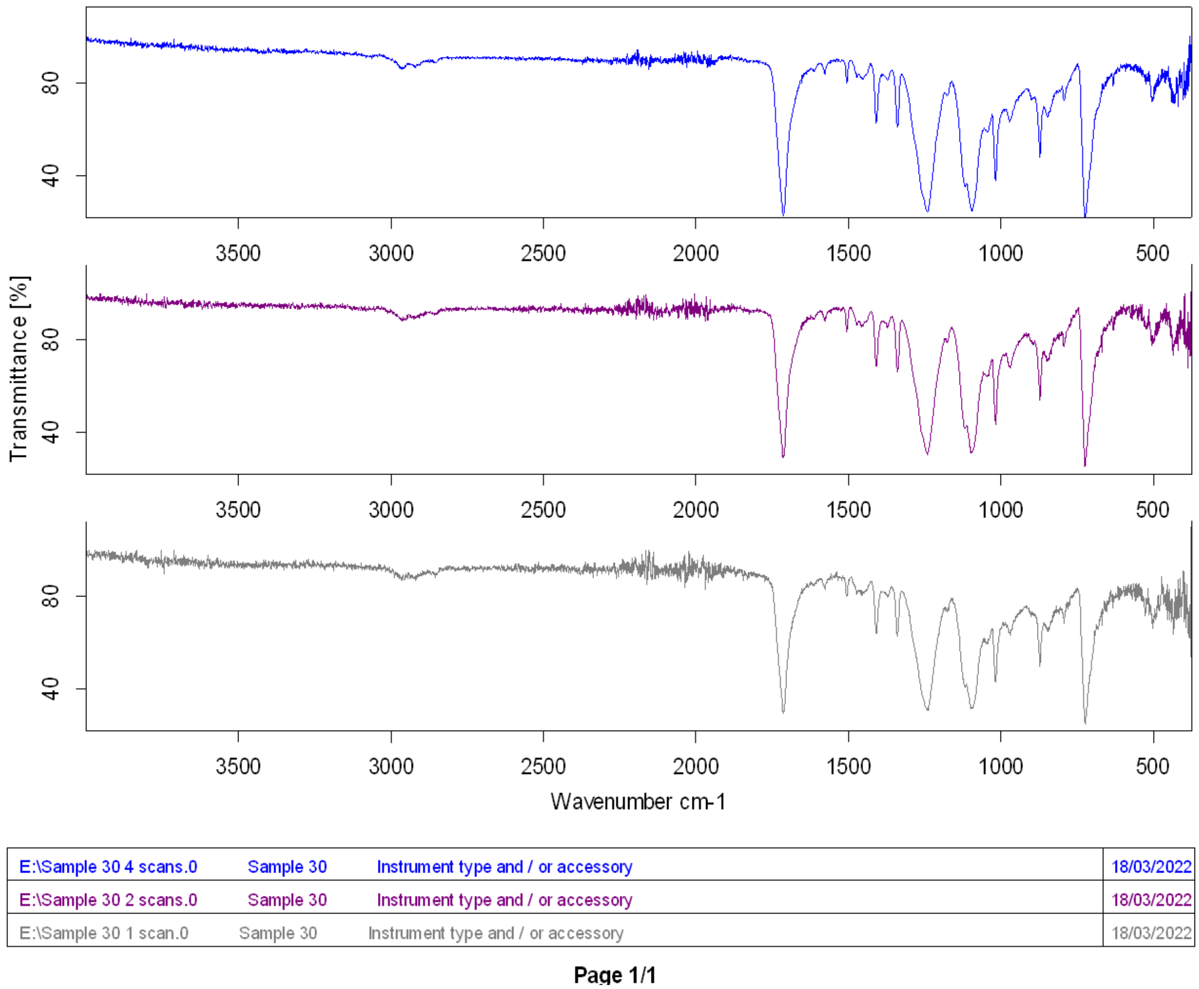
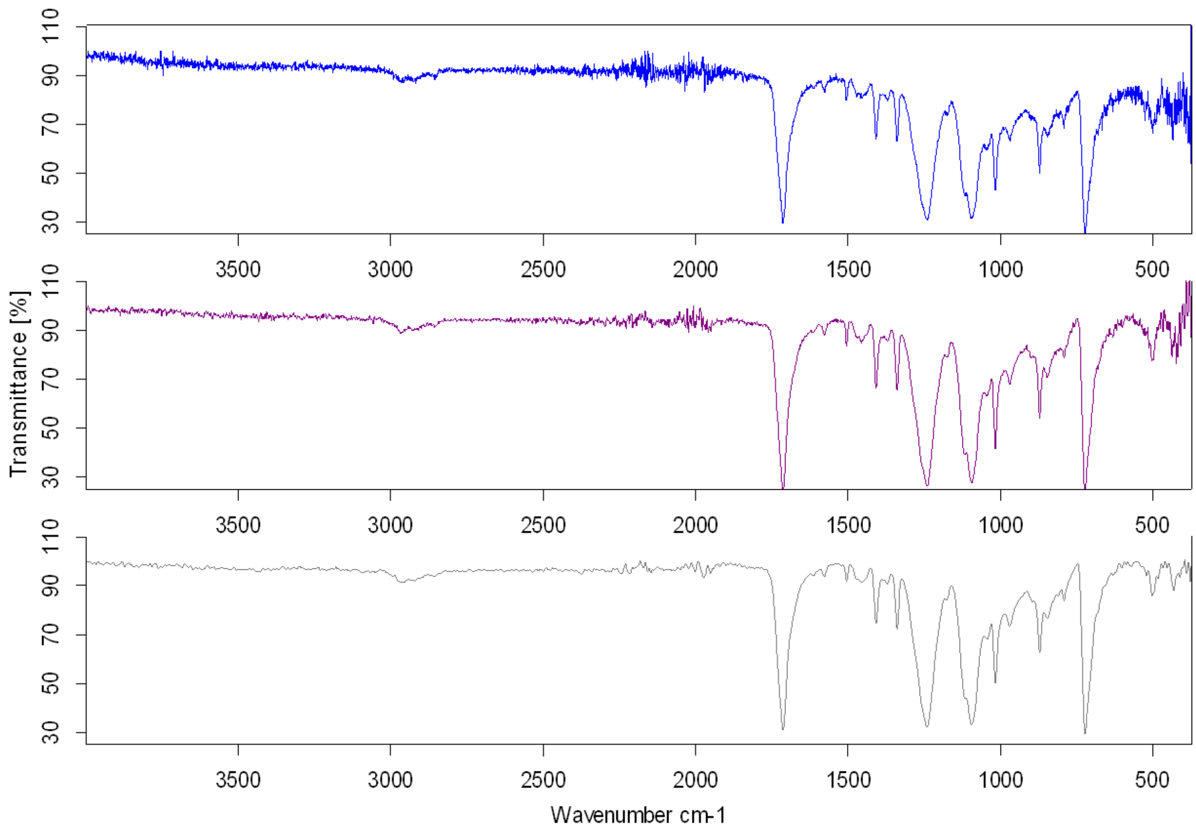


Figure AP. 102 FTIR of PET 2 with 4 scans, 2 scans, and 1 scan



E:\Sample 30 1 scan.0	Sample 30	Instrument type and / or accessory	18/03/2022
E:\Sample 30 1 scan 2cm-1.0	Sample 30	Instrument type and / or accessory	18/03/2022
E:\Sample 30 1scan 5cm-1.0	Sample 30	Instrument type and / or accessory	18/03/2022

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Figure AP. 103 FTIR of PET 2 with 0.9cm^{-1}, 2cm^{-1}, 5cm^{-1} resolution with 1 scan

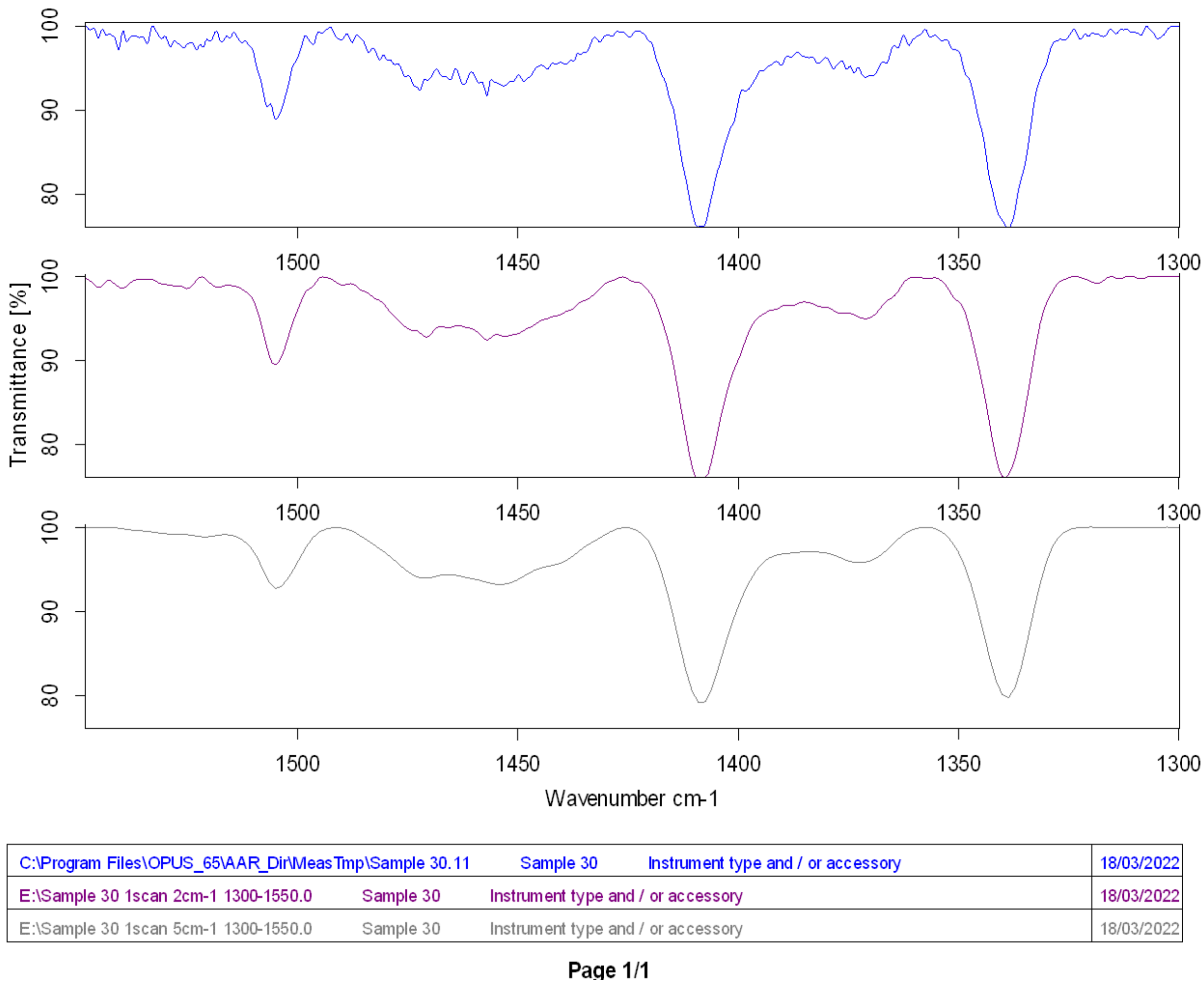


Figure AP. 104 FTIR of PET 2 with 0.9cm^{-1}, 2cm^{-1}, 5cm^{-1} resolution with 1 scan between 1300-1550cm^{-1}

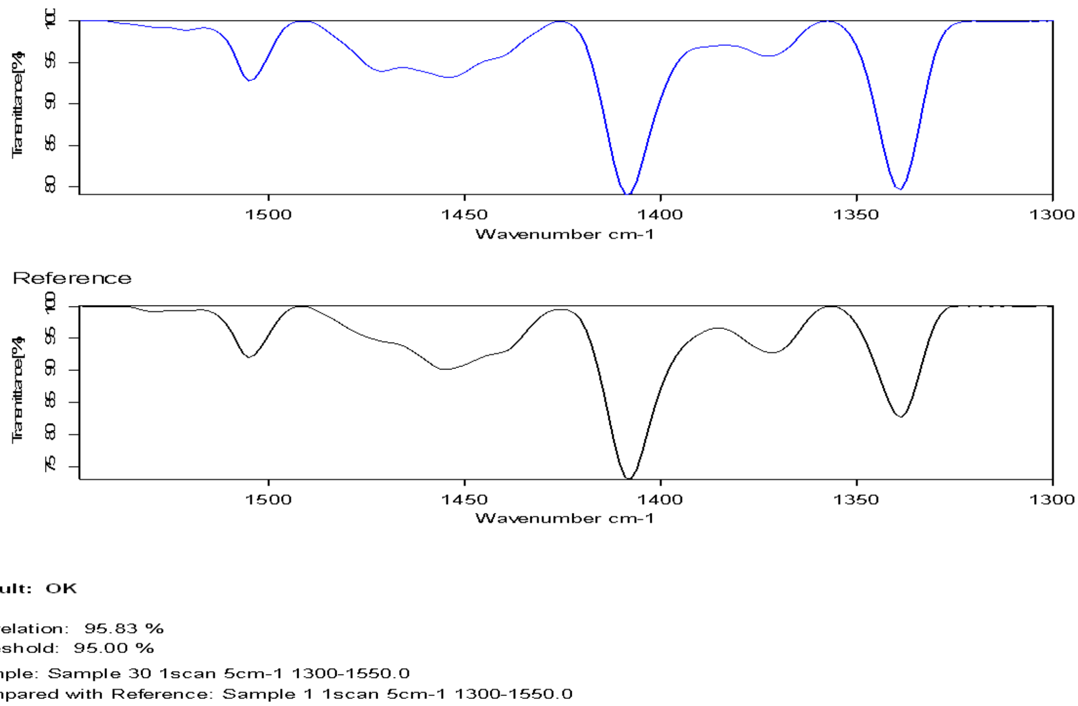


Figure AP. 105 FTIR QCM of PET 2 5cm^{-1} resolution with 1 scan, between 1300-1550cm^{-1}

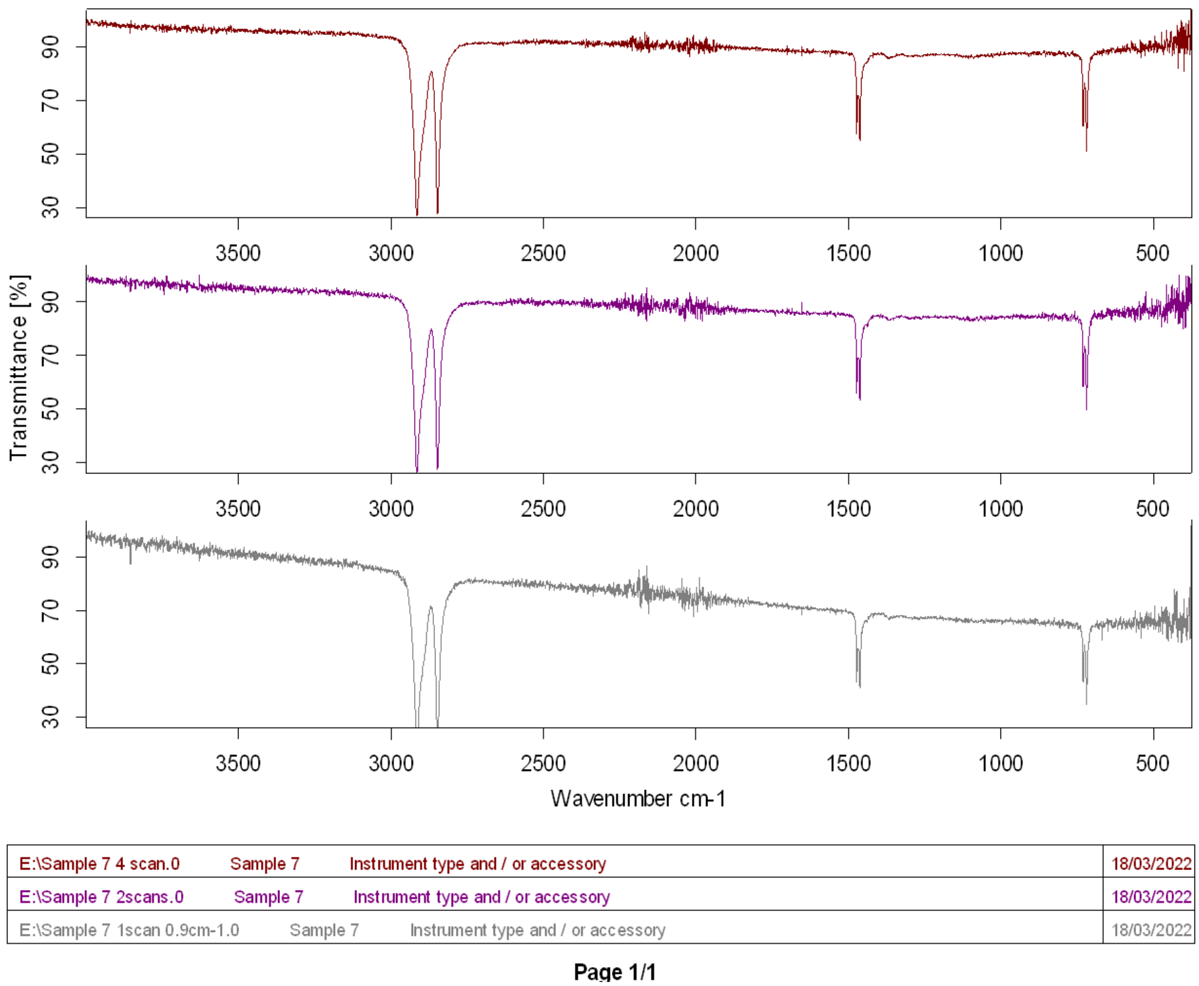


Figure AP. 106 FTIR of HDPE 2 with 4 scans, 2 scans, and 1 scan

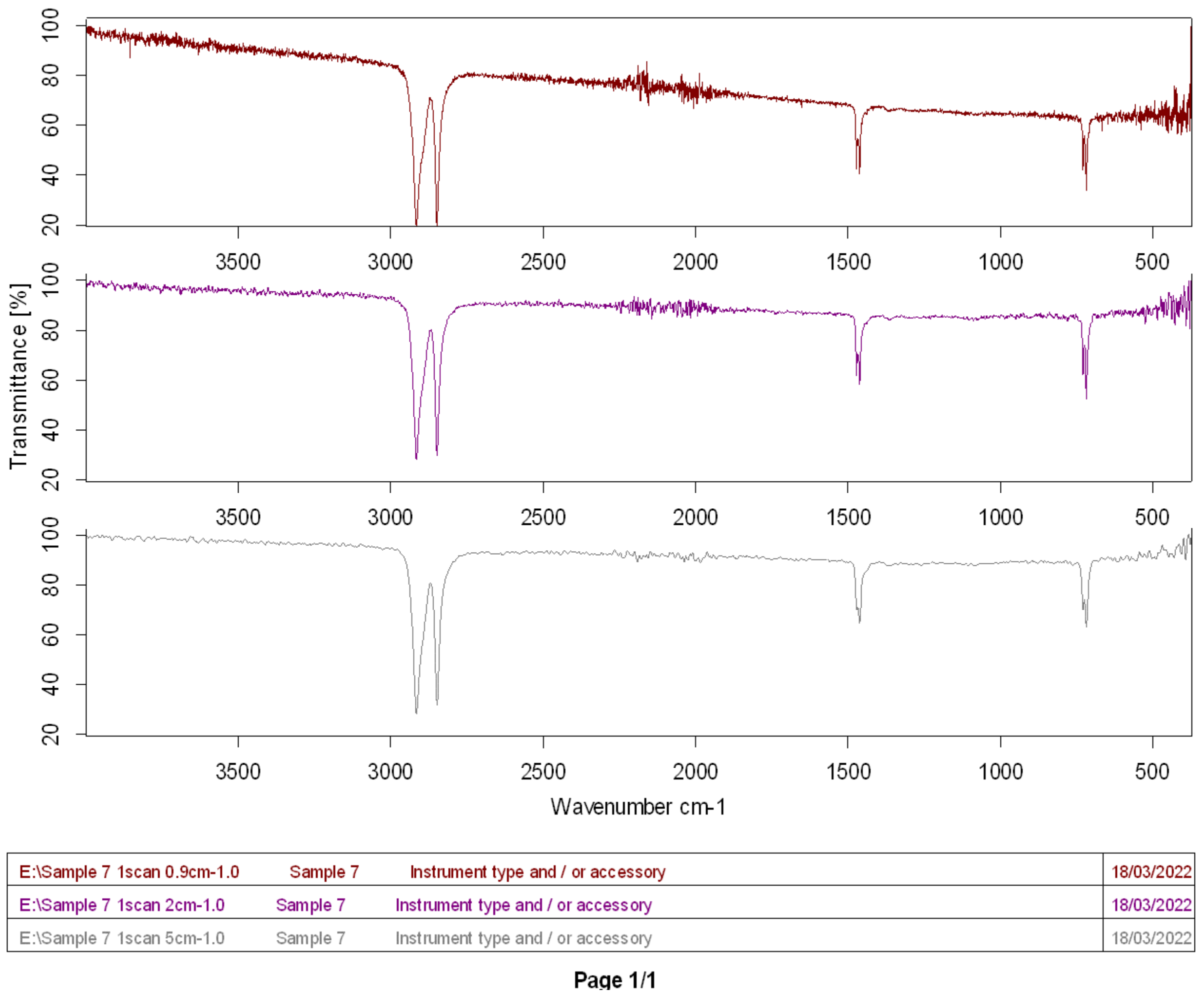
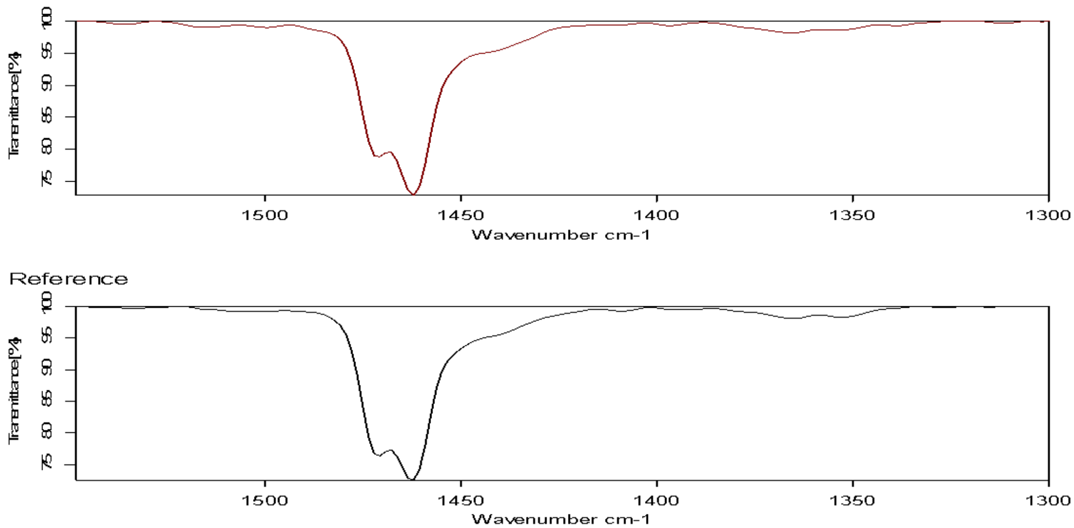


Figure AP. 107 FTIR of HDPE 2 with $0.9cm^{-1}$, $2cm^{-1}$, $5cm^{-1}$ resolution with 1 scan

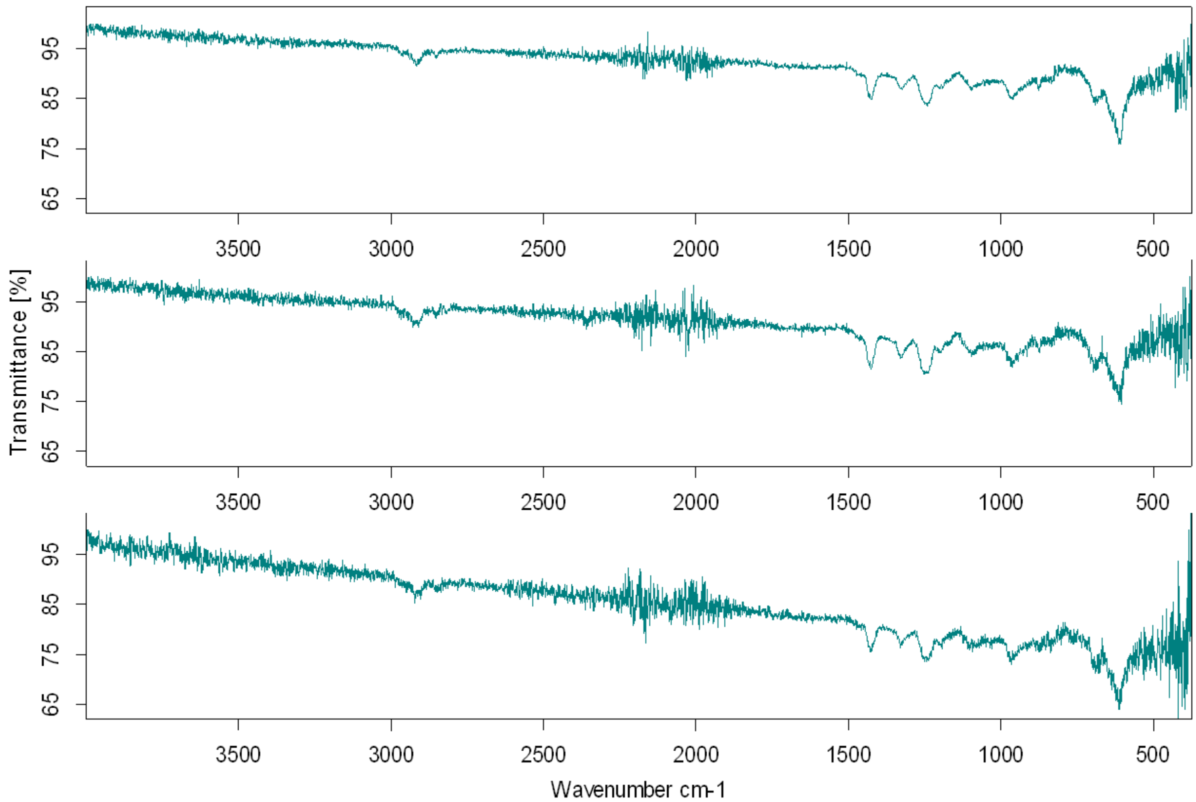


Result: OK

Correlation: 99.81 %
Threshold: 95.00 %

Sample: Sample 7 1scan 5cm-1 1300-1550.0
Compared with Reference: Sample 2 1scan 5cm-1 1300-1550.0

Figure AP. 108 FTIR QCM of HDPE 2 5cm^{-1} resolution with 1 scan, between 1300-1550cm^{-1}



E:\Sample 53 4scans 0.9cm-1.1	Sample 53	Instrument type and / or accessory	14/03/2022
E:\Sample 53 2scans 0.9cm-1.0	Sample 53	Instrument type and / or accessory	14/03/2022
E:\Sample 53 1scan 0.9cm-1.0	Sample 53	Instrument type and / or accessory	14/03/2022

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Figure AP. 109 FTIR of PVC 1 with 4 scans, 2 scans, and 1 scan

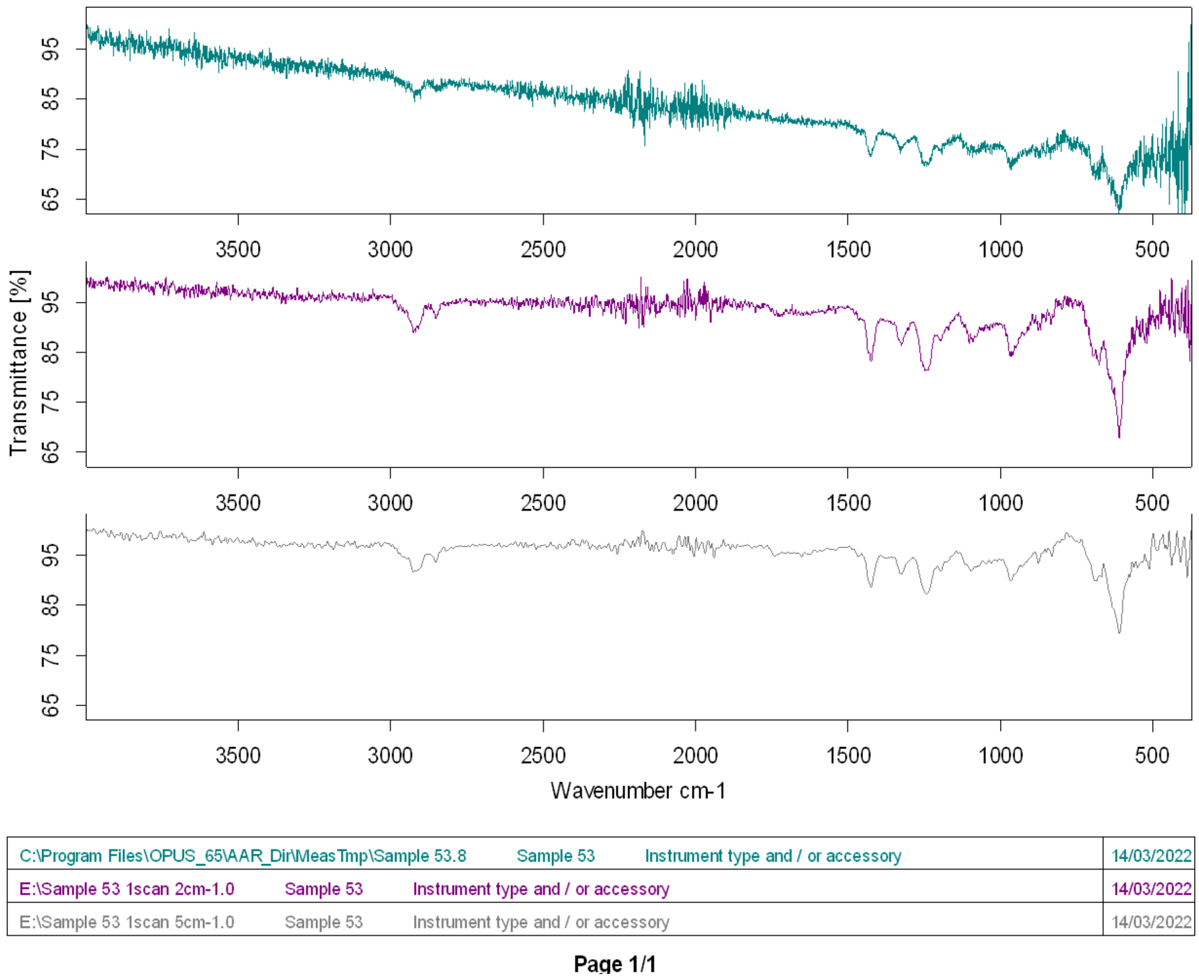
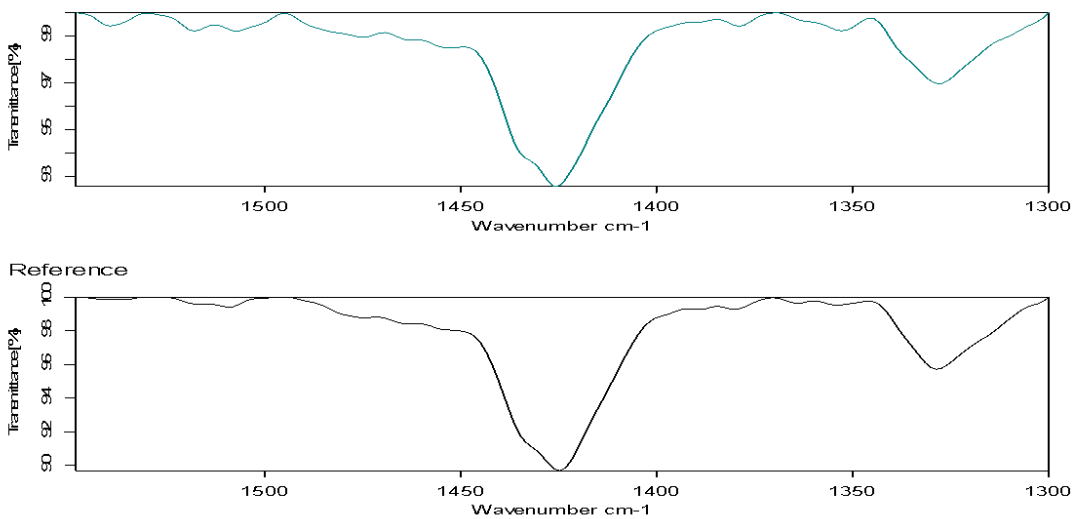


Figure AP. 110 FTIR of PVC 1 with 0.9cm^{-1}, 2cm^{-1}, 5cm^{-1} resolution with 1 scan



Result: OK

Correlation: 99.59 %
Threshold: 95.00 %

Sample: Sample 53 1scan 5cm-1 1300-1550.0
Compared with Reference: Sample 53 1scan 5cm-1 1300-1550 2.0

Figure AP. 111 FTIR QCM of PVC 1 5cm^{-1} resolution with 1 scan, between 1300-1550cm^{-1}

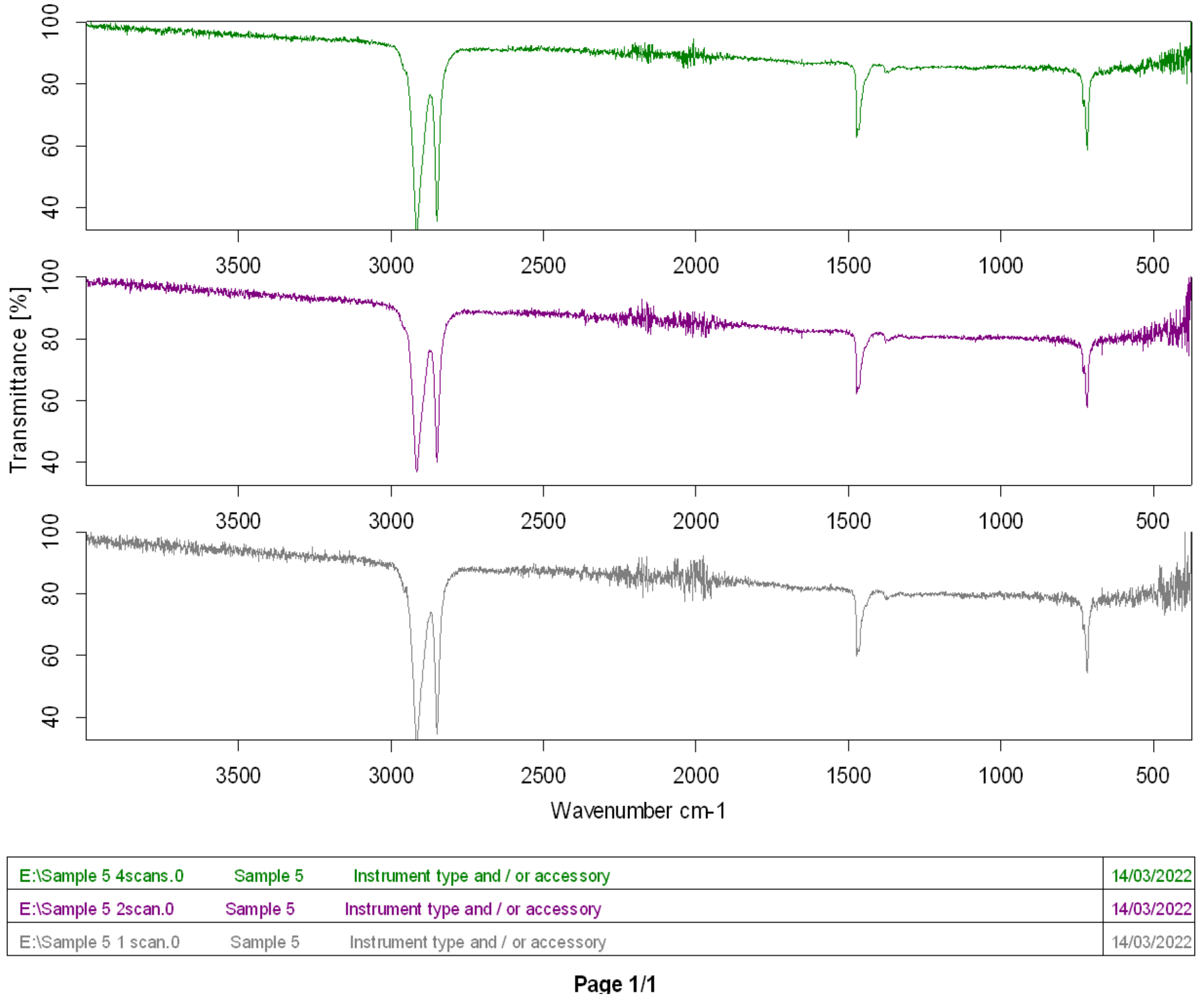


Figure AP. 112 FTIR of LDPE 1 with 4 scans, 2 scans, and 1 scan

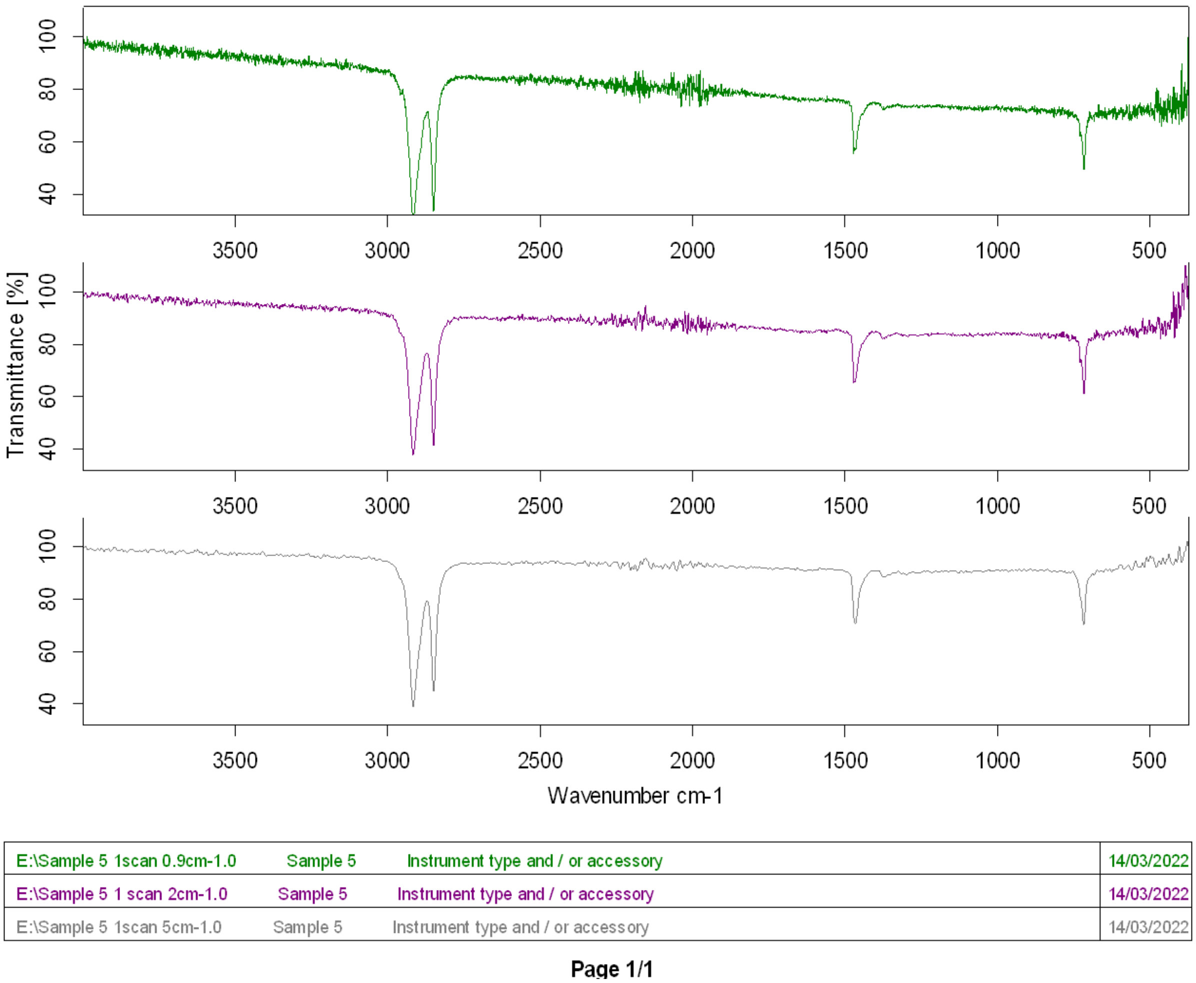


Figure AP. 113 FTIR of LDPE 1 with 0.9cm^{-1}, 2cm^{-1}, 5cm^{-1} resolution with 1 scan

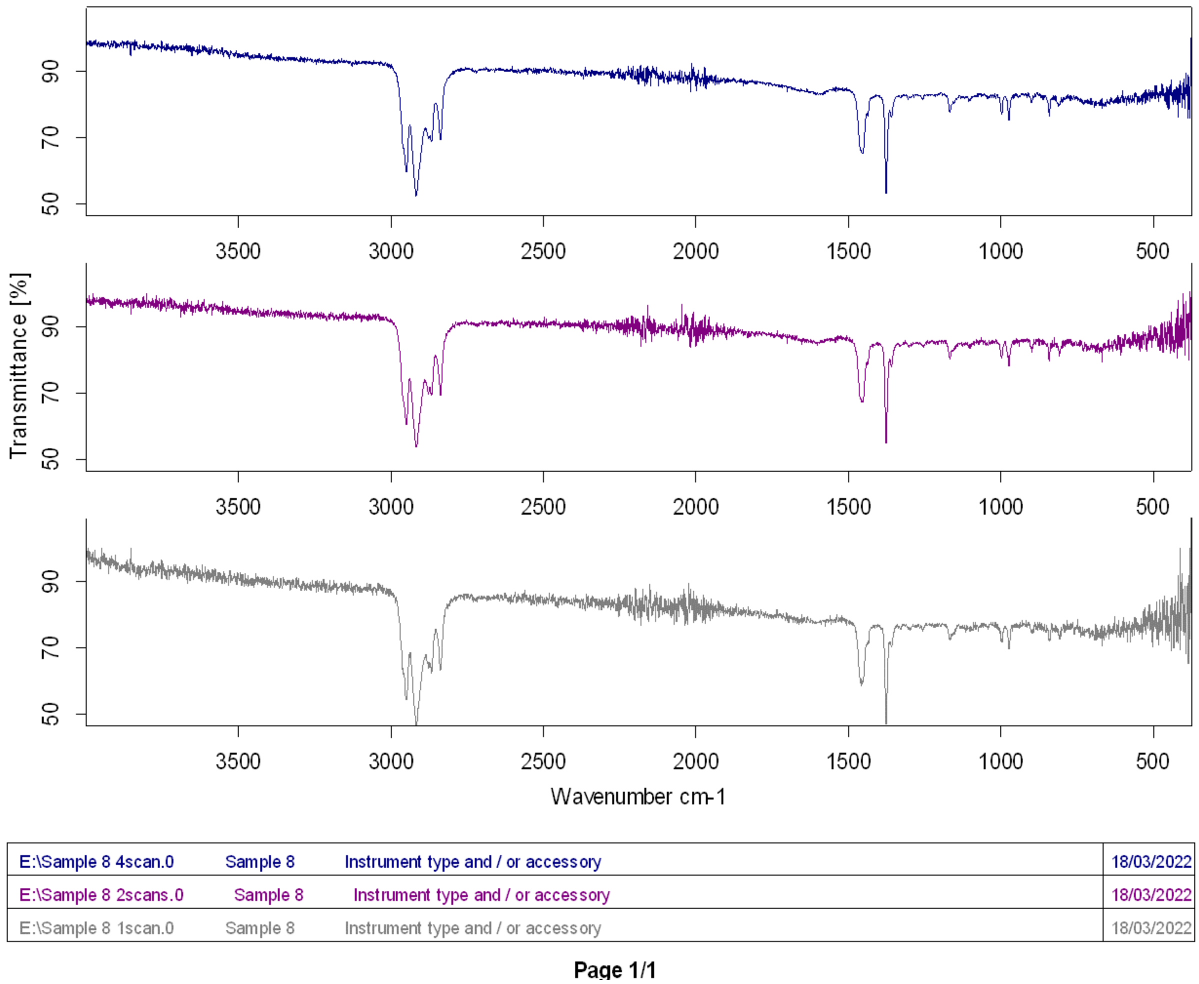


Figure AP. 114 FTIR of PP 2 with 4 scans, 2 scans, and 1 scan

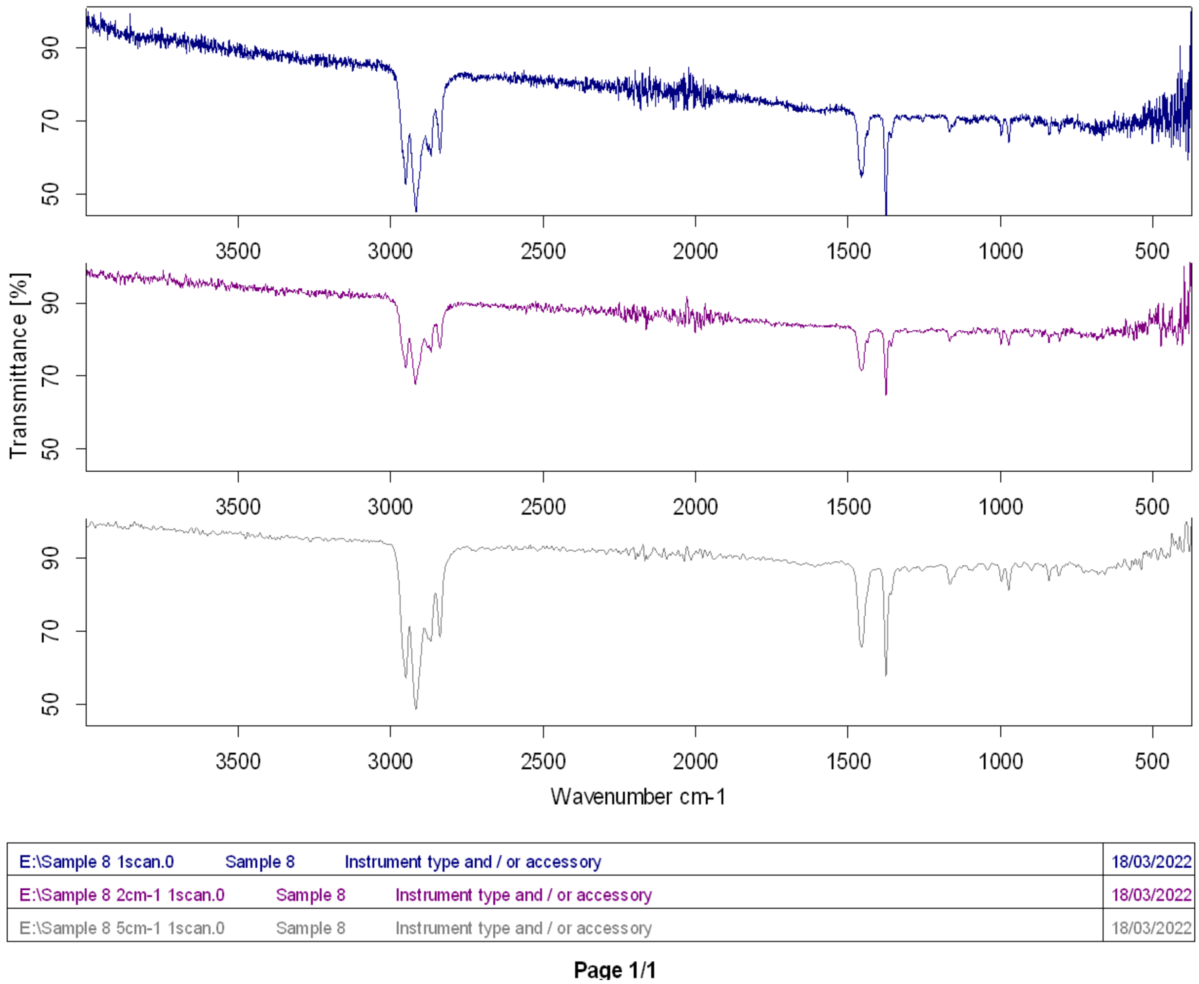
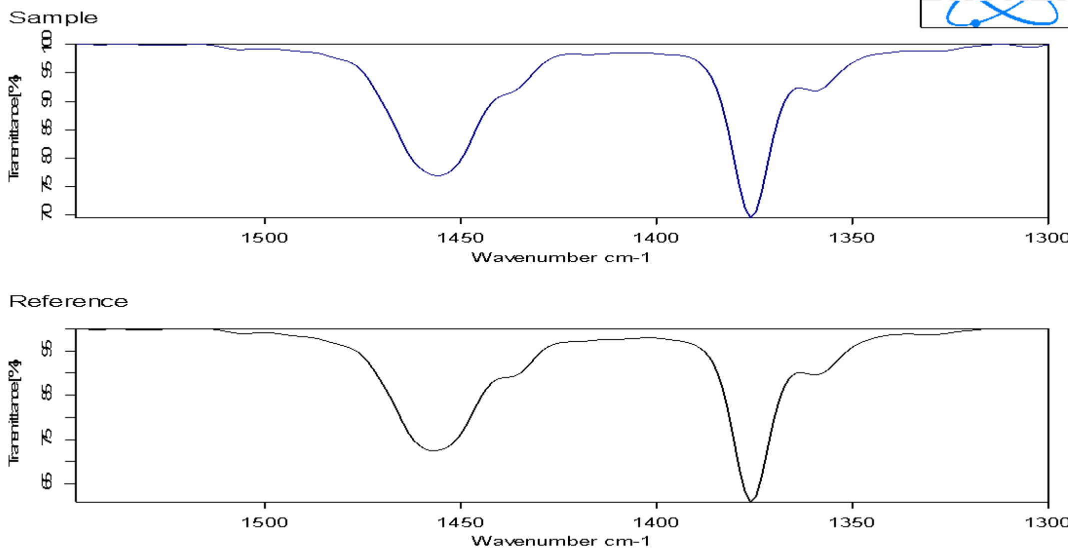


Figure AP. 115 FTIR of PP 2 with $0.9cm^{-1}$, $2cm^{-1}$, $5cm^{-1}$ resolution with 1 scan

Spectra Comparison



Result: OK

Correlation: 99.86 %
Threshold: 95.00 %

Sample: Sample 8 5cm-1 1scan 1300-1550.0
Compared with Reference: Sample 3 5cm-1 1scan 1300-1550.0

Method file: S3 1scan 5cm-1 1300-1550.qcm (2022/03/18 15:00:54 (GMT-3))
Operator: jmvanleeuwen
Date and time (measurement): 18/03/2022 10:57:12.640 (GMT-4)
Comment:

____________________________ ____________________________

Signature (Operator) Signature (Release)

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Figure AP. 116 FTIR QCM of PP 2 5cm^{-1} resolution with 1 scan, between 1300-1550cm^{-1}

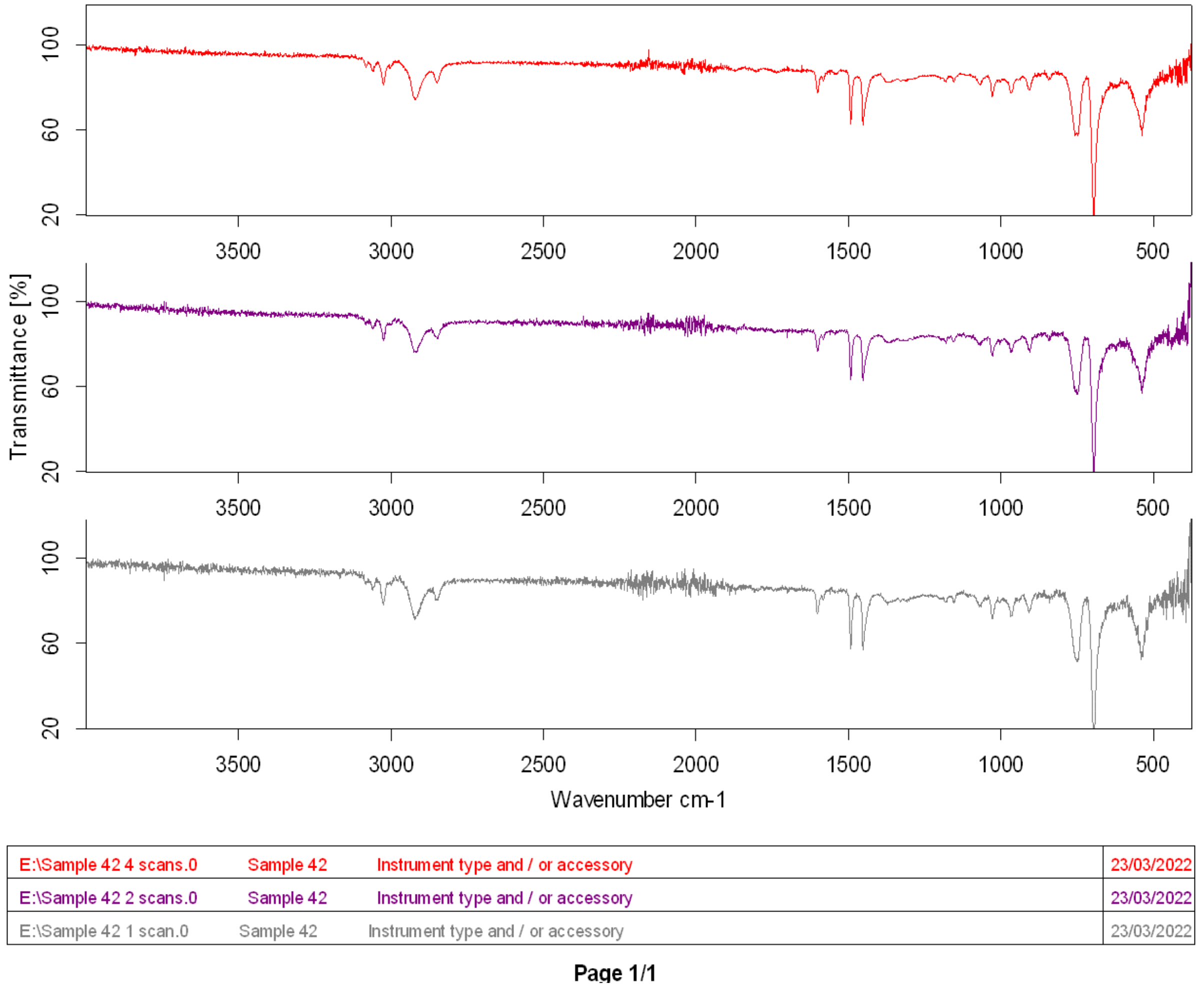


Figure AP. 117 FTIR of PS 2 with 4 scans, 2 scans, and 1 scan

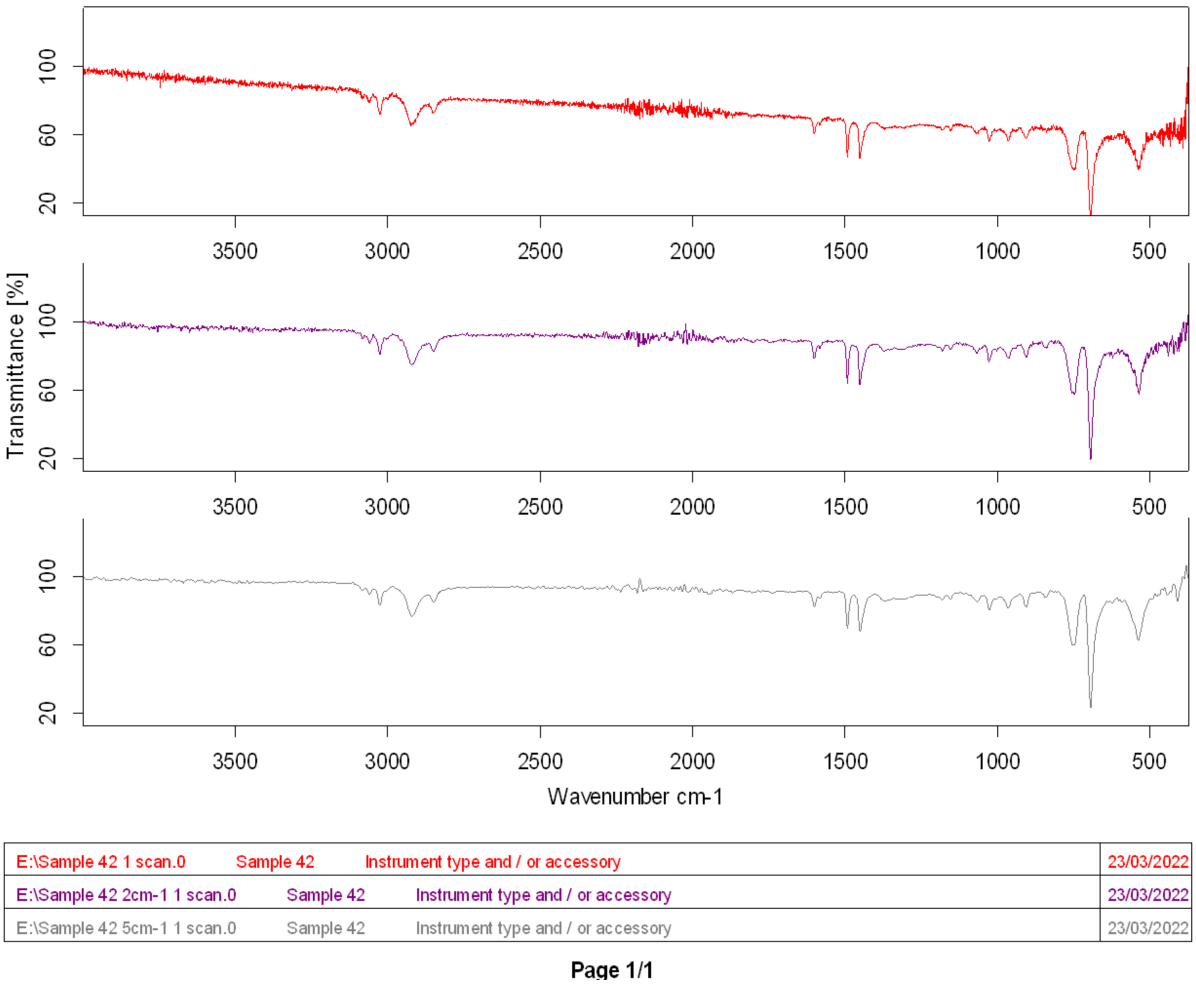
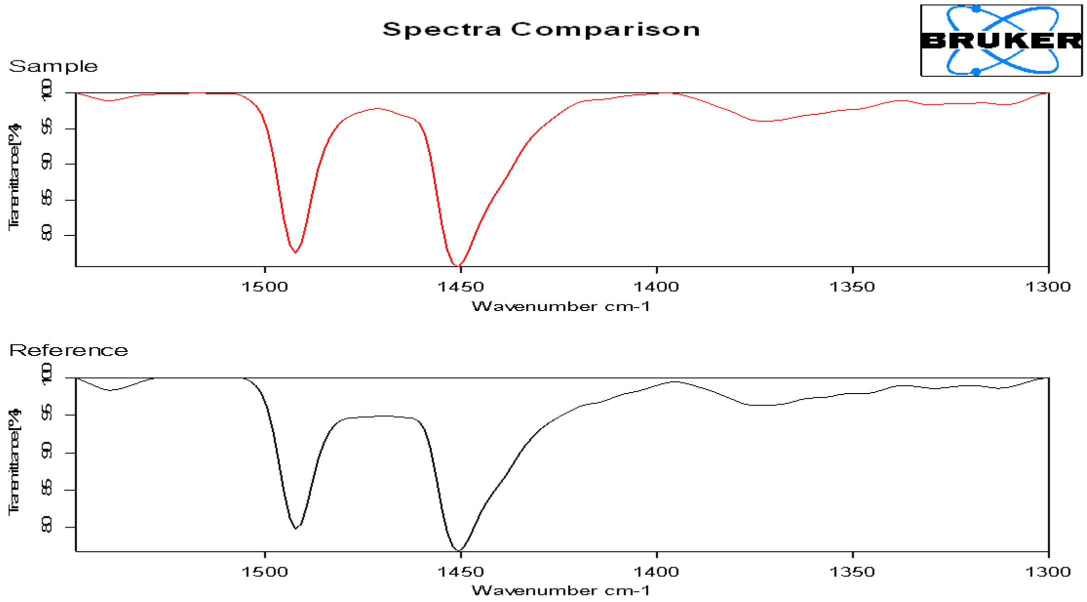


Figure AP. 118 FTIR of PS 2 with 0.9cm^{-1}, 2cm^{-1}, 5cm^{-1} resolution with 1 scan



Result: OK

Correlation: 98.18 %
Threshold: 95.00 %

Sample: Sample 42 5cm-1 1 scan 1300-1550.0
Compared with Reference: Sample 41 5cm-1 1 scan 1300-1550.0

Method file: S41 1scan 5cm-1 1300-1550.qcm (2022/03/23 19:07:12 (GMT-3))
Operator: jmvanleeuwen
Date and time (measurement): 23/03/2022 15:03:19.230 (GMT-4)
Comment:

__________________________ Signature (Operator)

__________________________ Signature (Release)

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Figure AP. 119 FTIR QCM of PP 2 5cm^{-1} resolution with 1 scan, between 1300-1550cm^{-1}

Appendix C – Raman Spectra

Initial Spectra

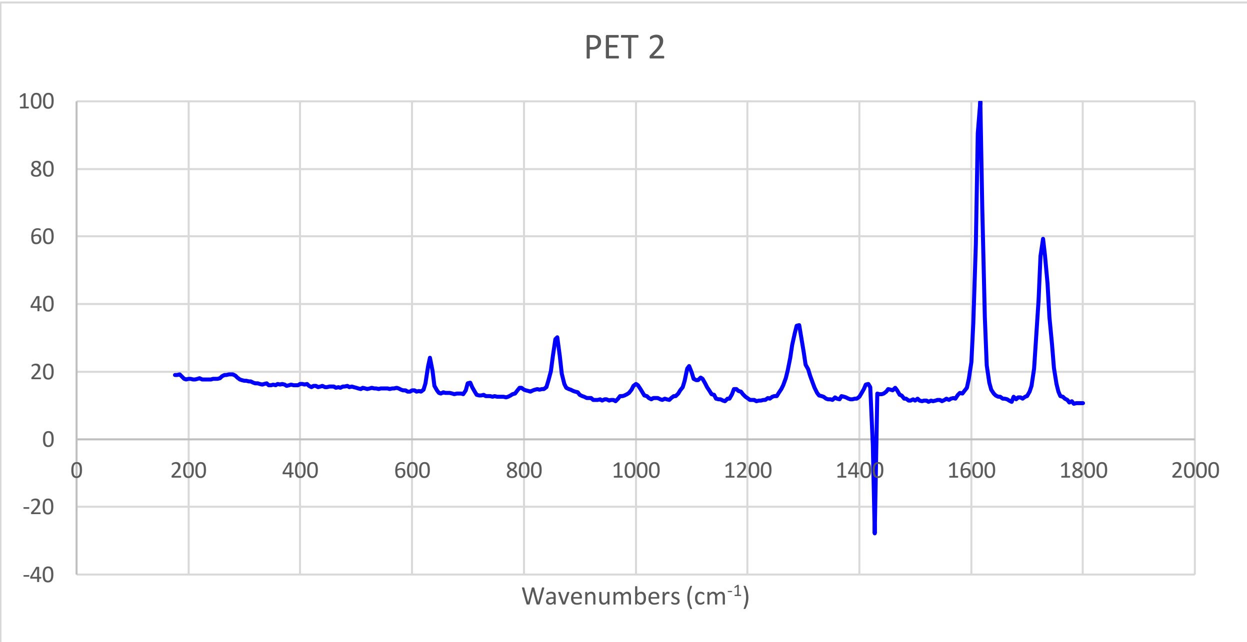

Figure AP. 120 Raman spectrum of PET 2

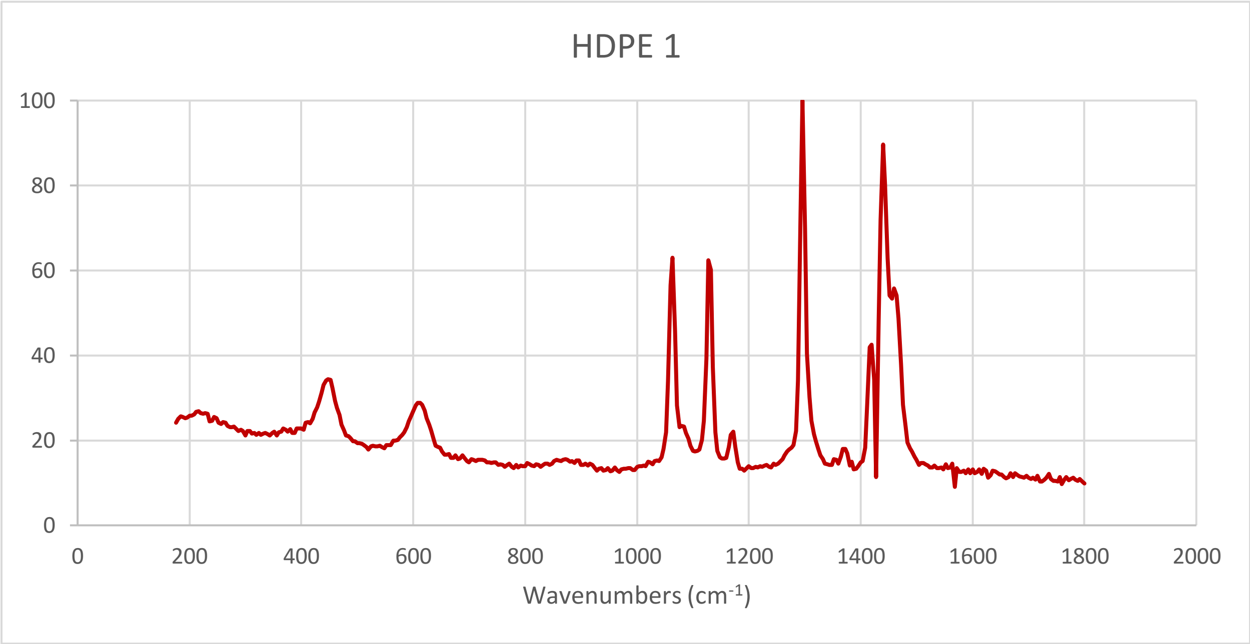

Figure AP. 121 Raman spectrum of HDPE 1

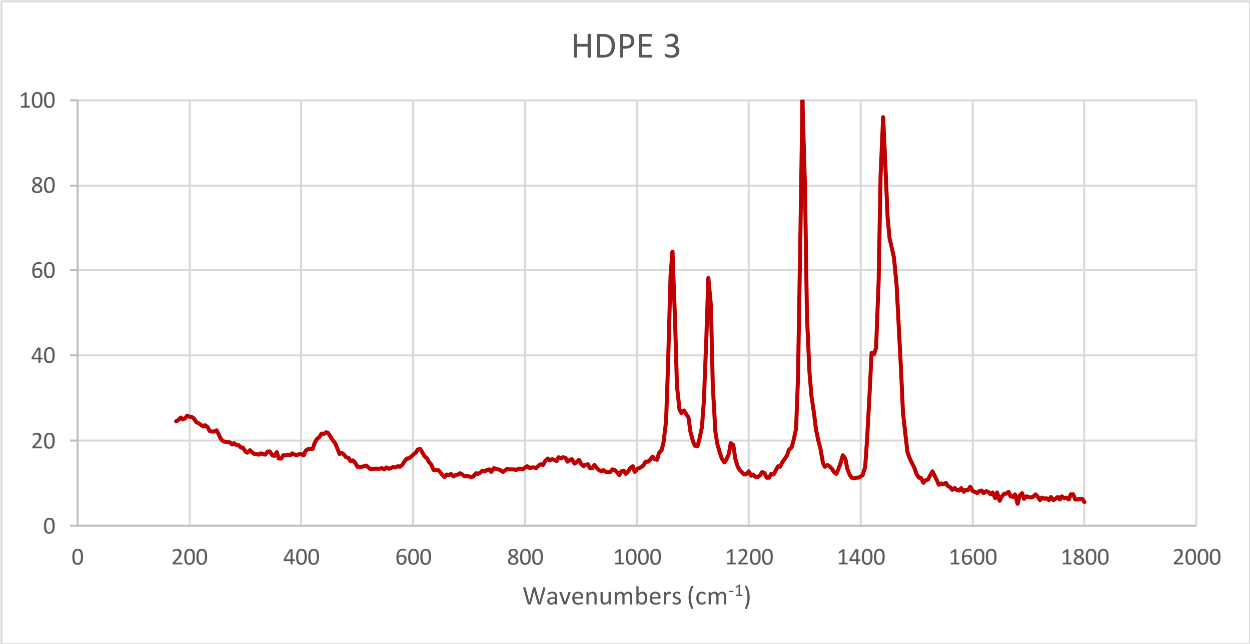

Figure AP. 122 Raman spectrum of HDPE 3

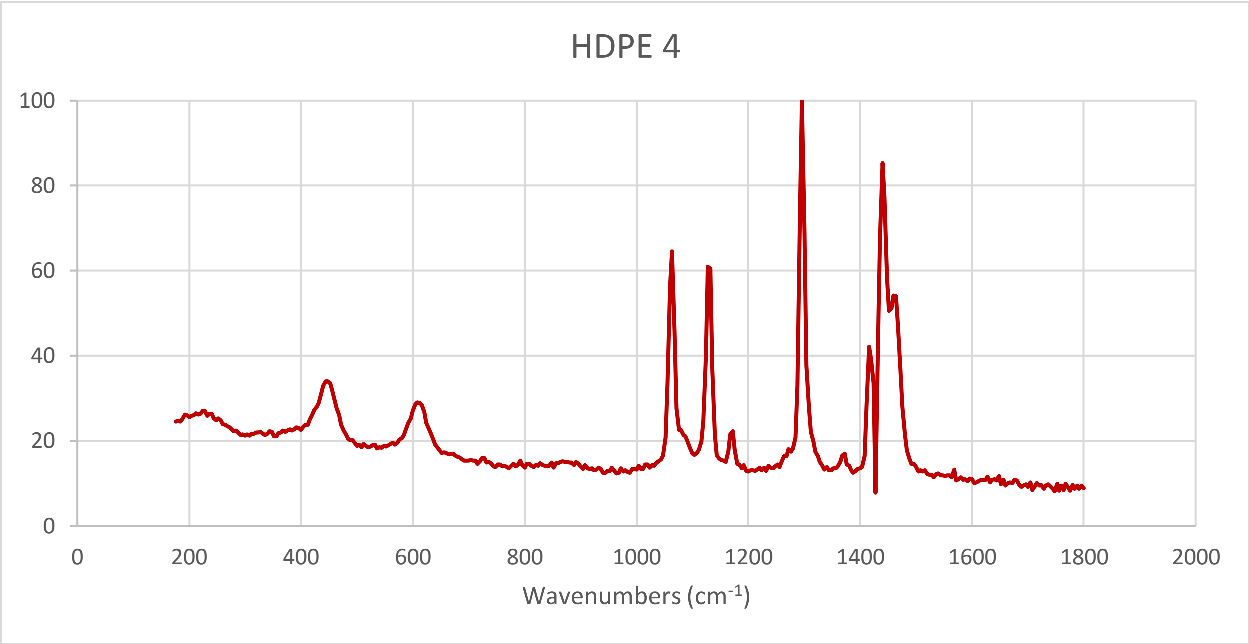

Figure AP. 123 Raman spectrum of HDPE 3

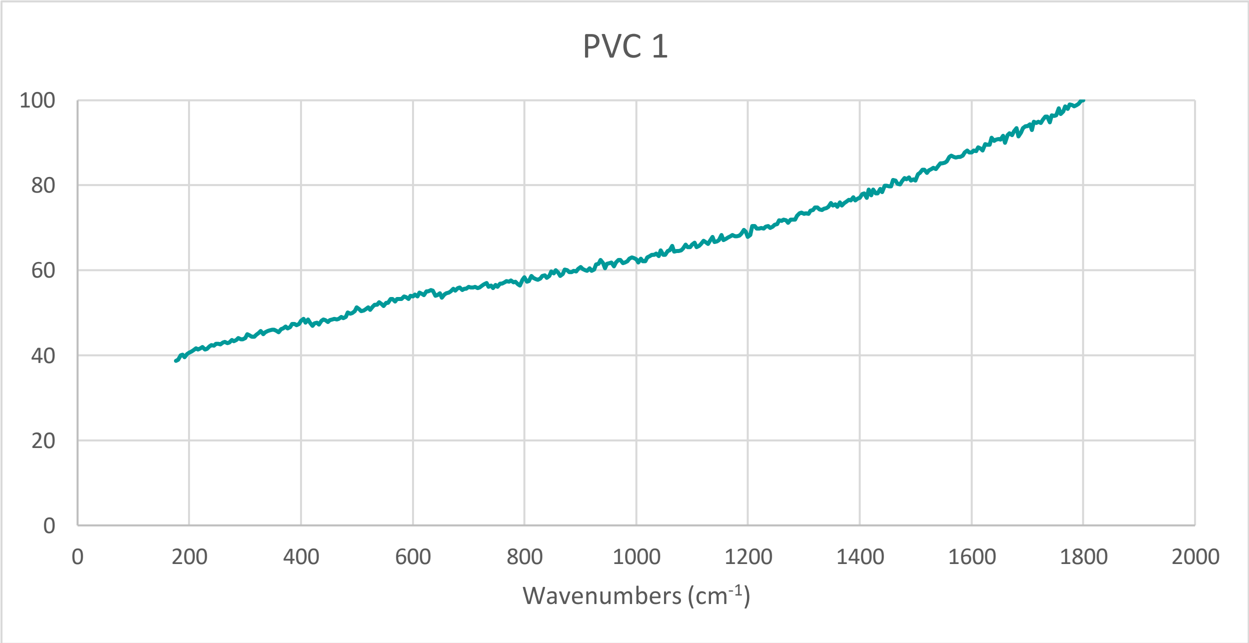

Figure AP. 124 Raman spectrum of PVC 1

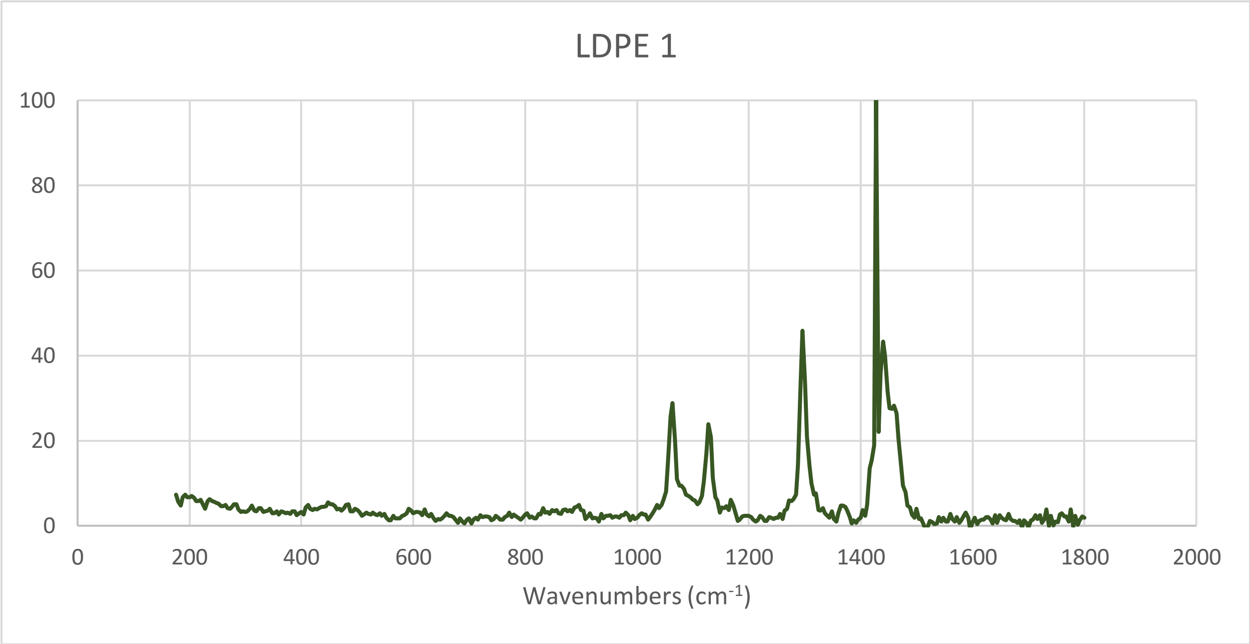

Figure AP. 125 Raman spectrum of LDPE 1

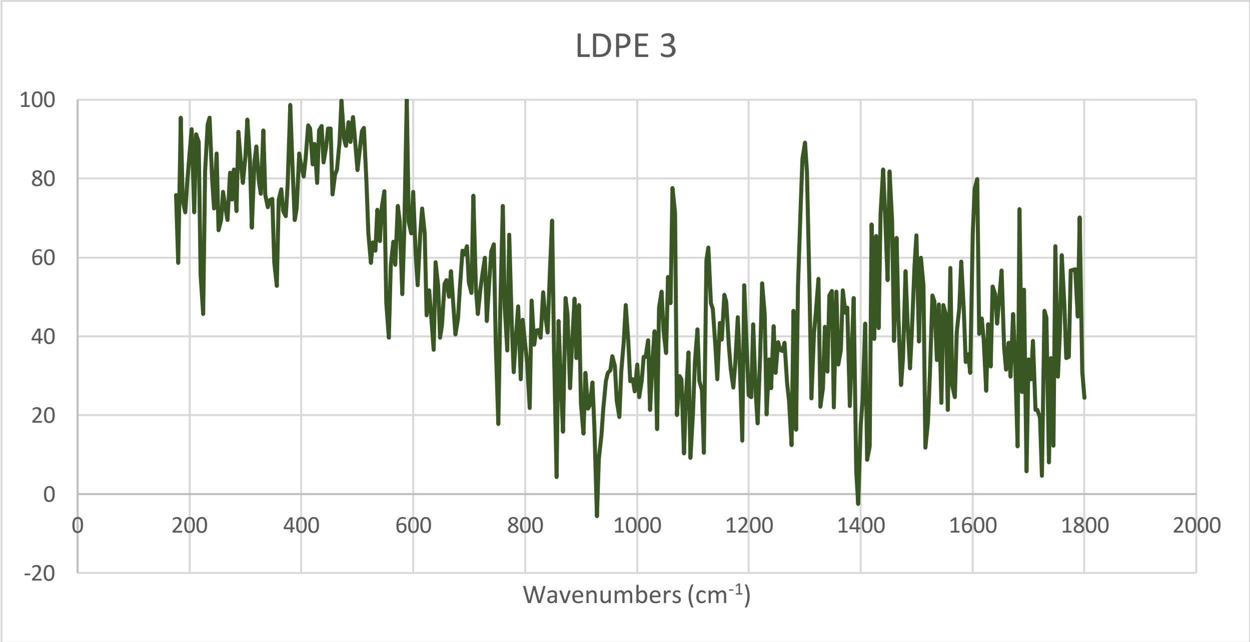

Figure AP. 126 Raman spectrum of LDPE 3

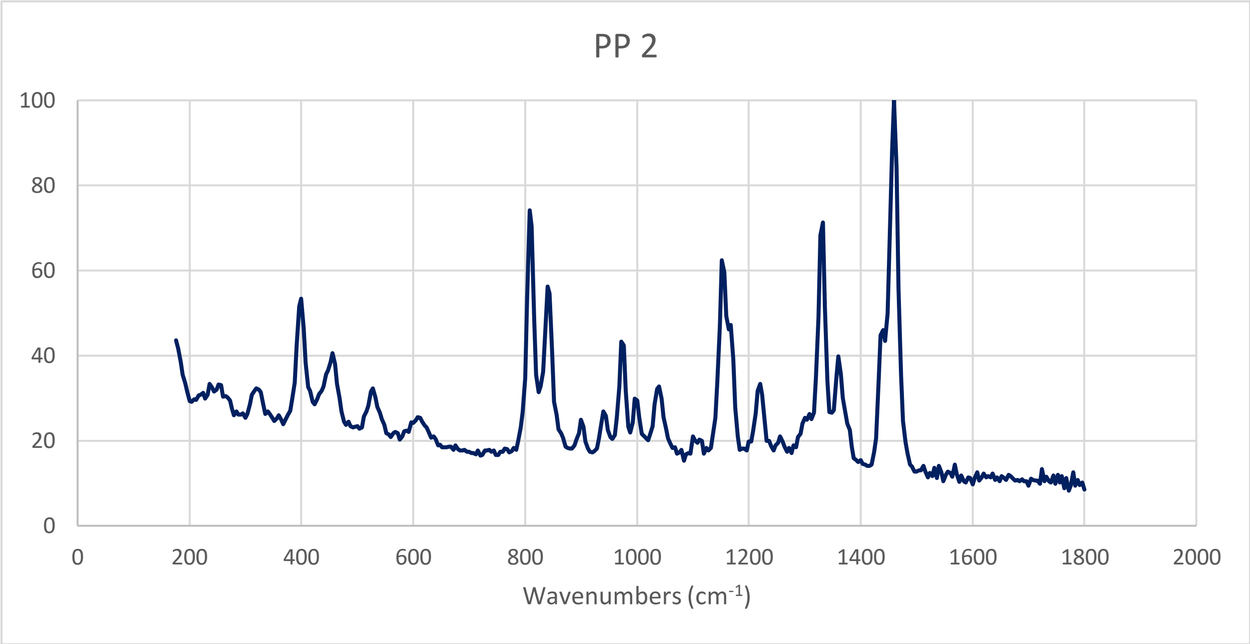

Figure AP. 127 Raman spectrum of PP 2

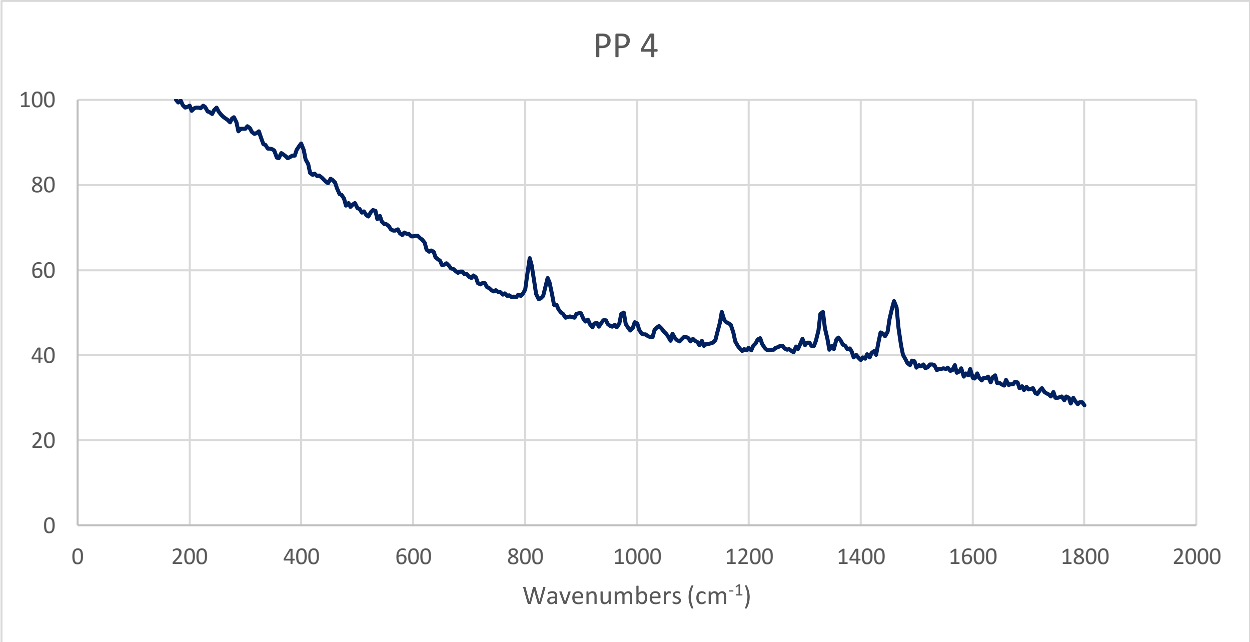

Figure AP. 128 Raman spectrum of PP 4

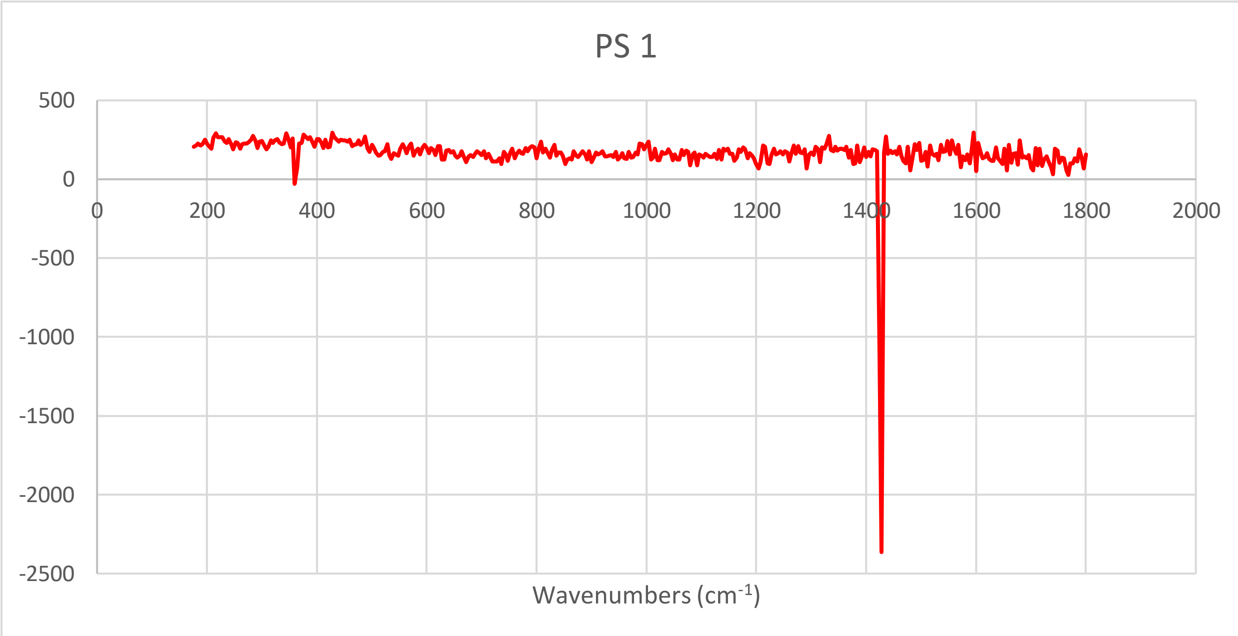

Figure AP. 129 Raman spectrum of PS 1

Colour Comparison

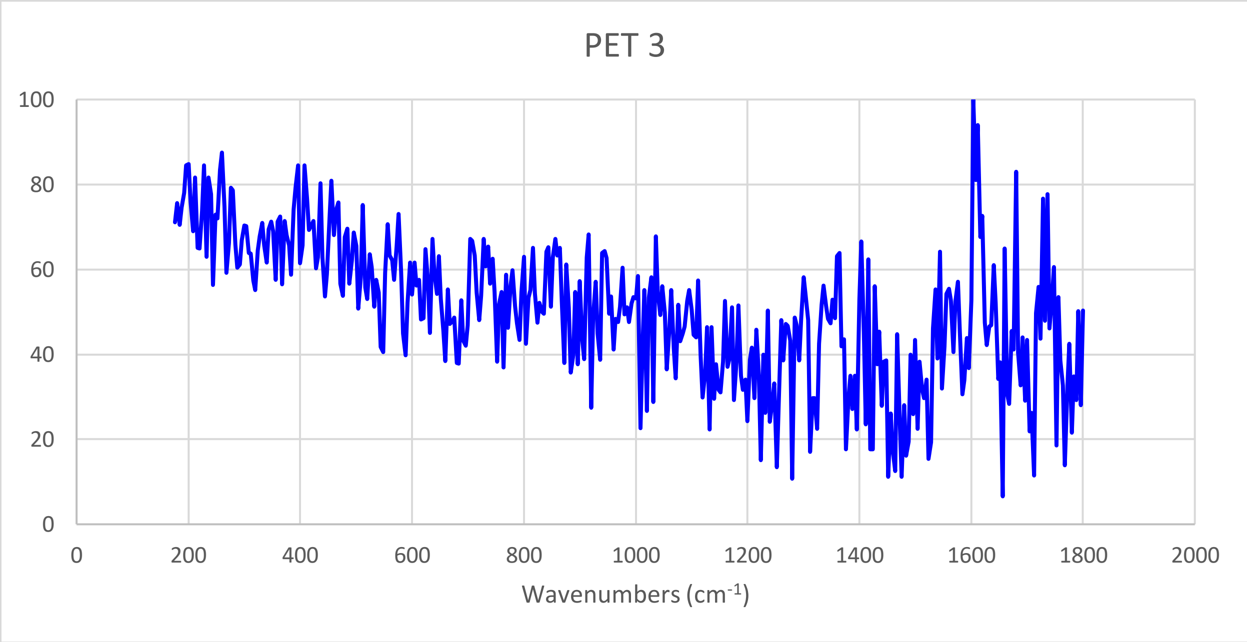

Figure AP. 130 Raman spectrum of PET 3

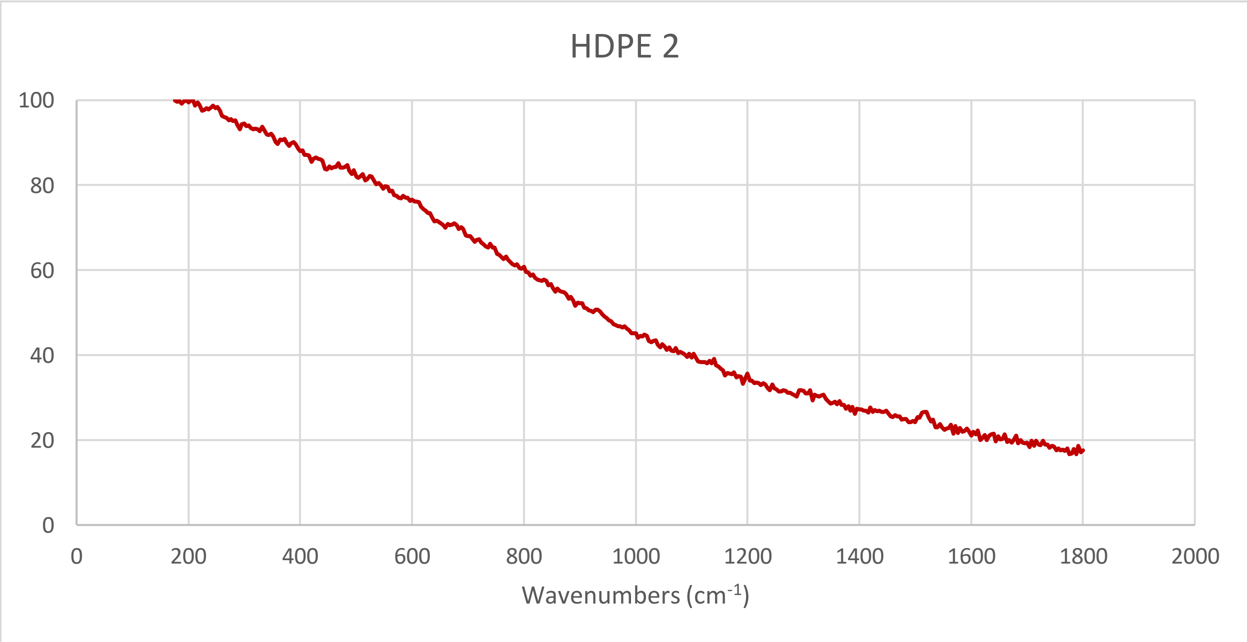

Figure AP. 131 Raman spectrum of HDPE 2

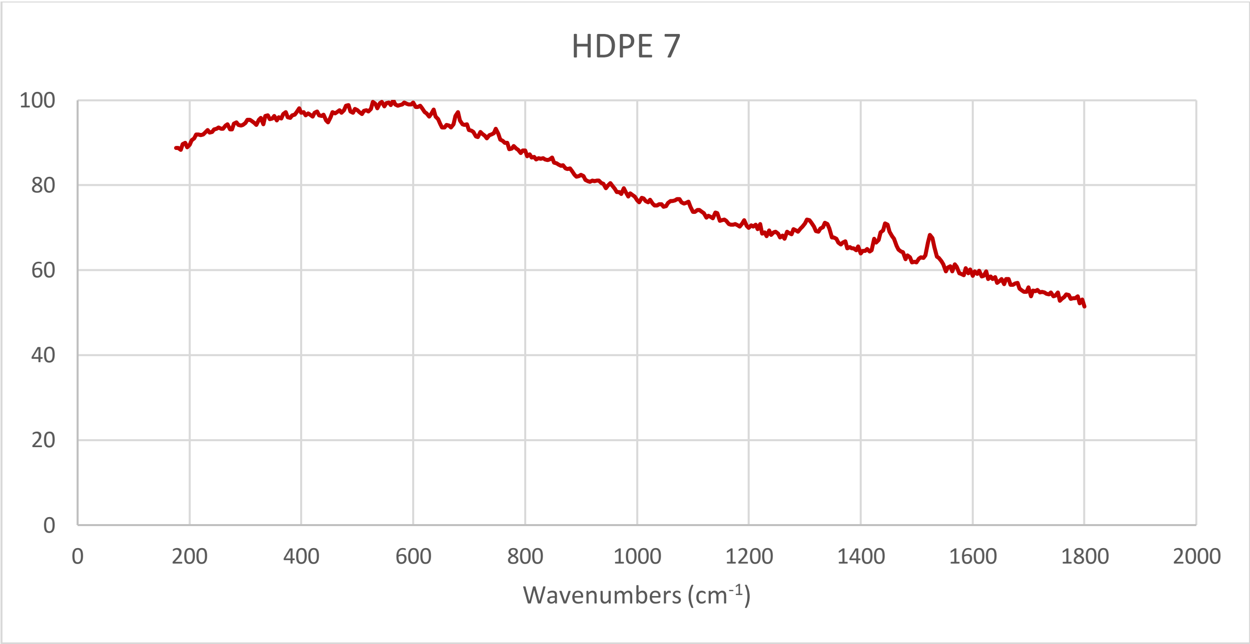

Figure AP. 132 Raman spectrum of HDPE 7

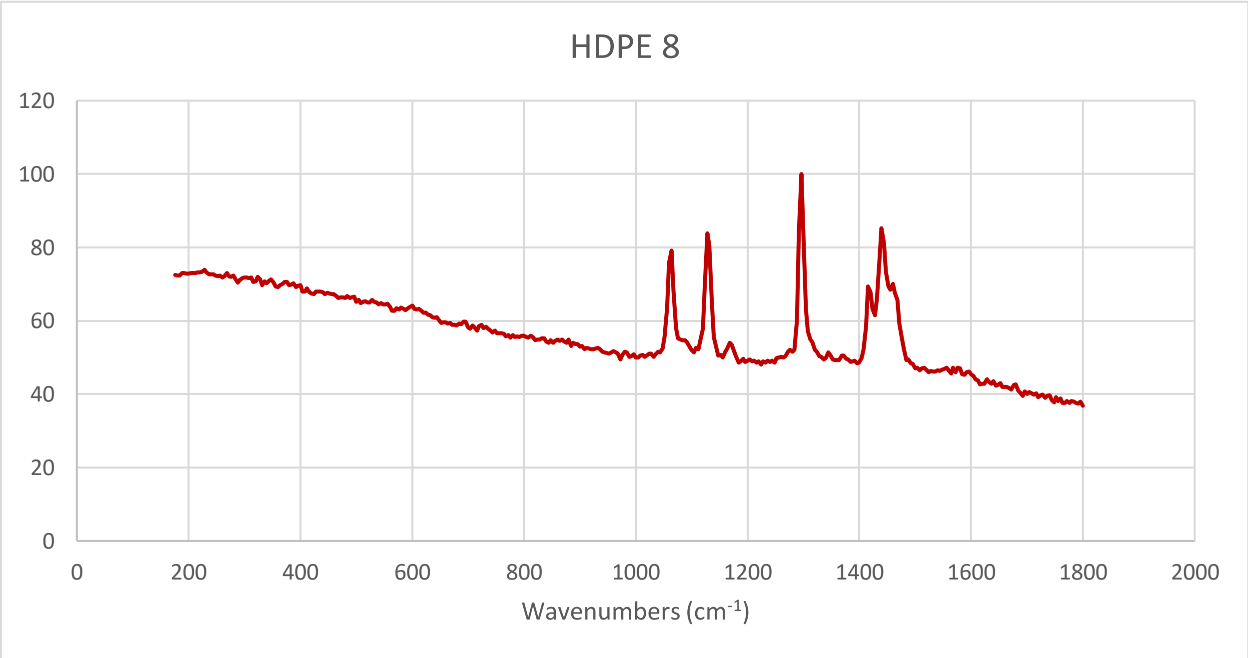

Figure AP. 133 Raman spectrum of HDPE 8

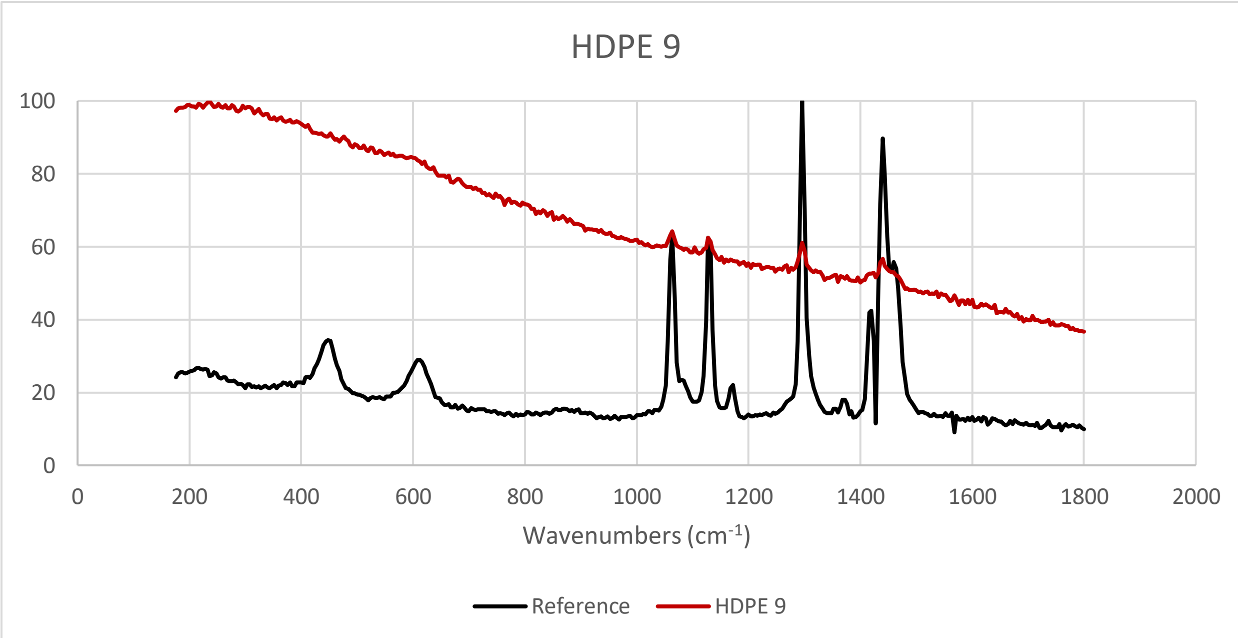

Figure AP. 134 Raman spectrum of HDPE 9

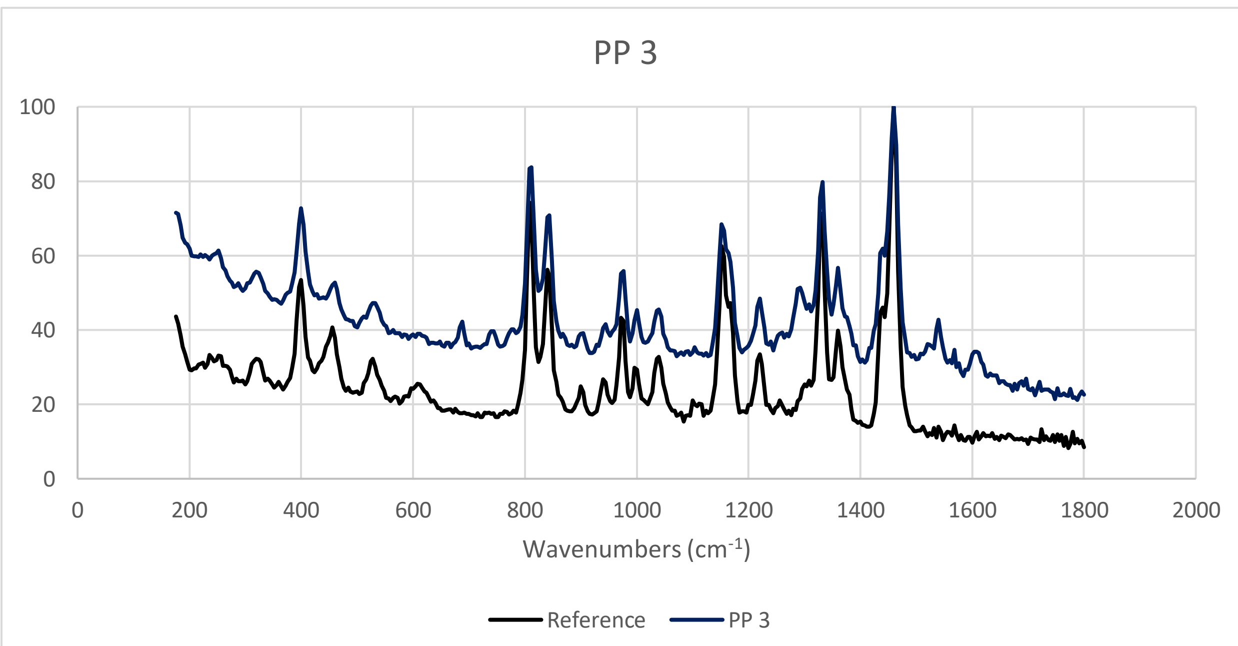

Figure AP. 135 Raman spectrum of PP 3

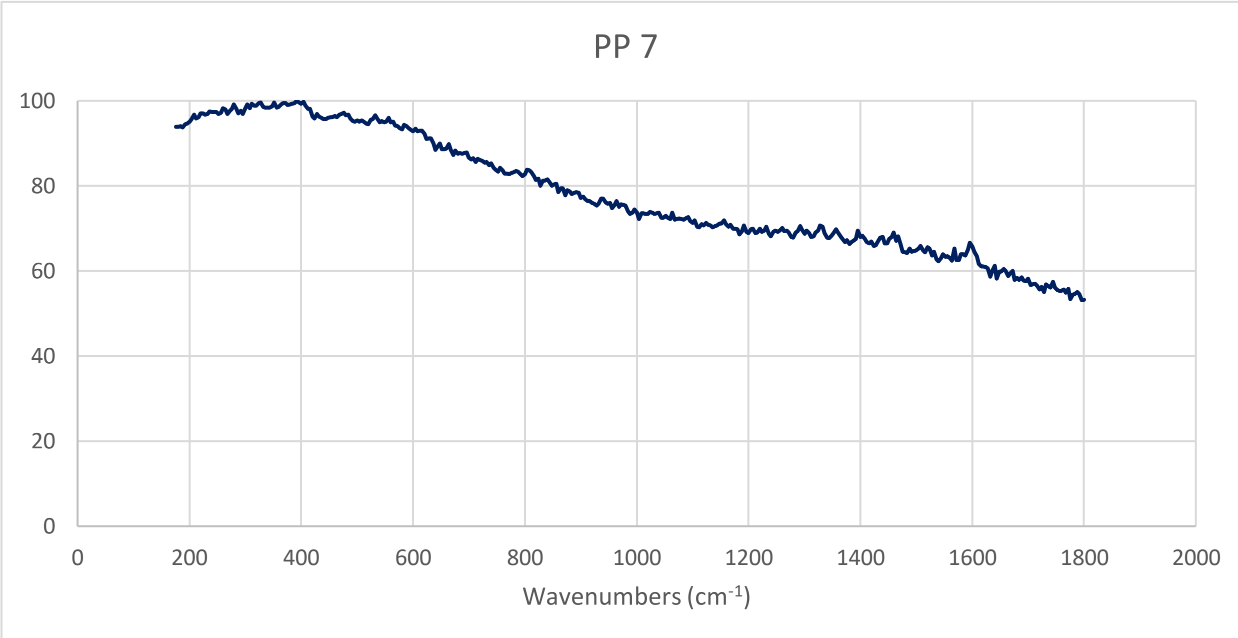

Figure AP. 136 Raman spectrum of PP 7

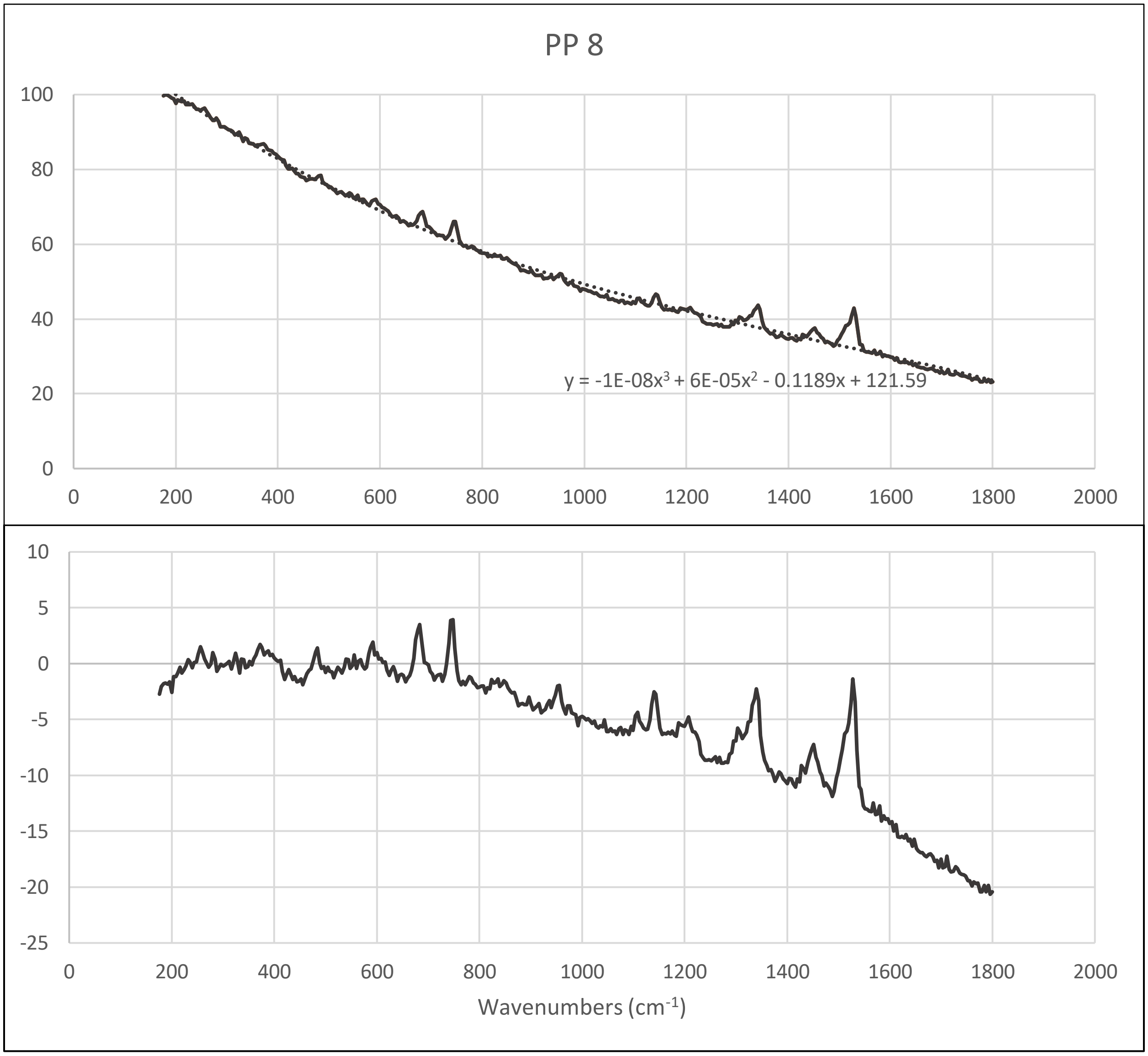

Figure AP. 138 Raman spectrum of PP 8

Clear Comparison

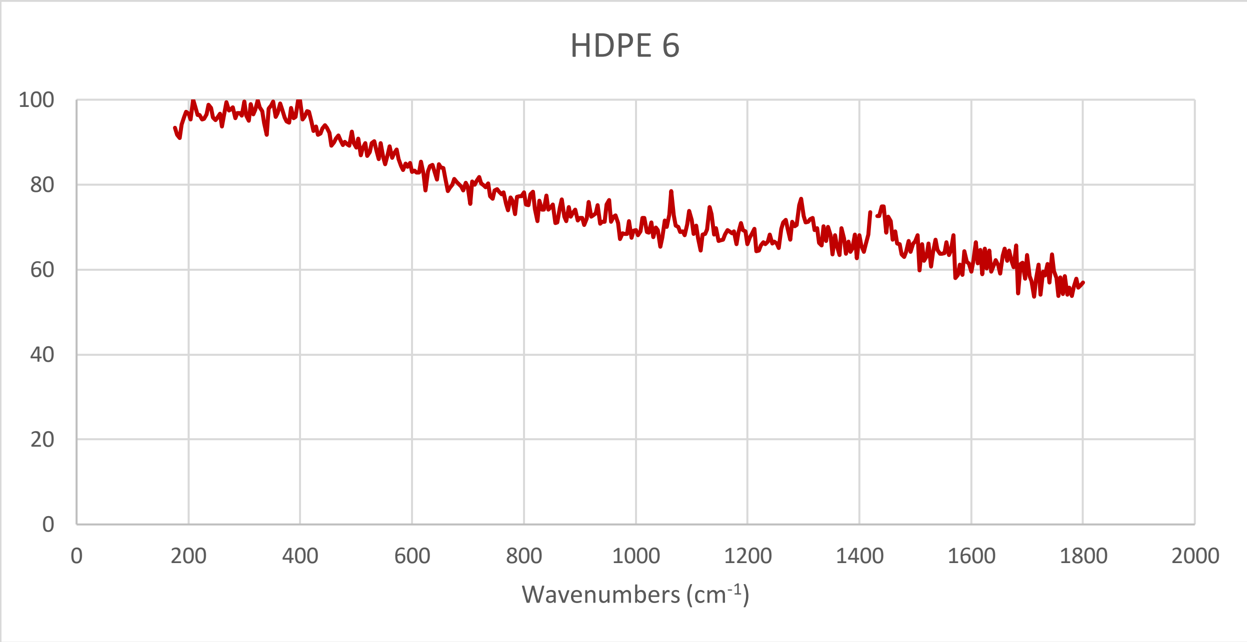

Figure AP. 139 Raman spectrum of HDPE 6

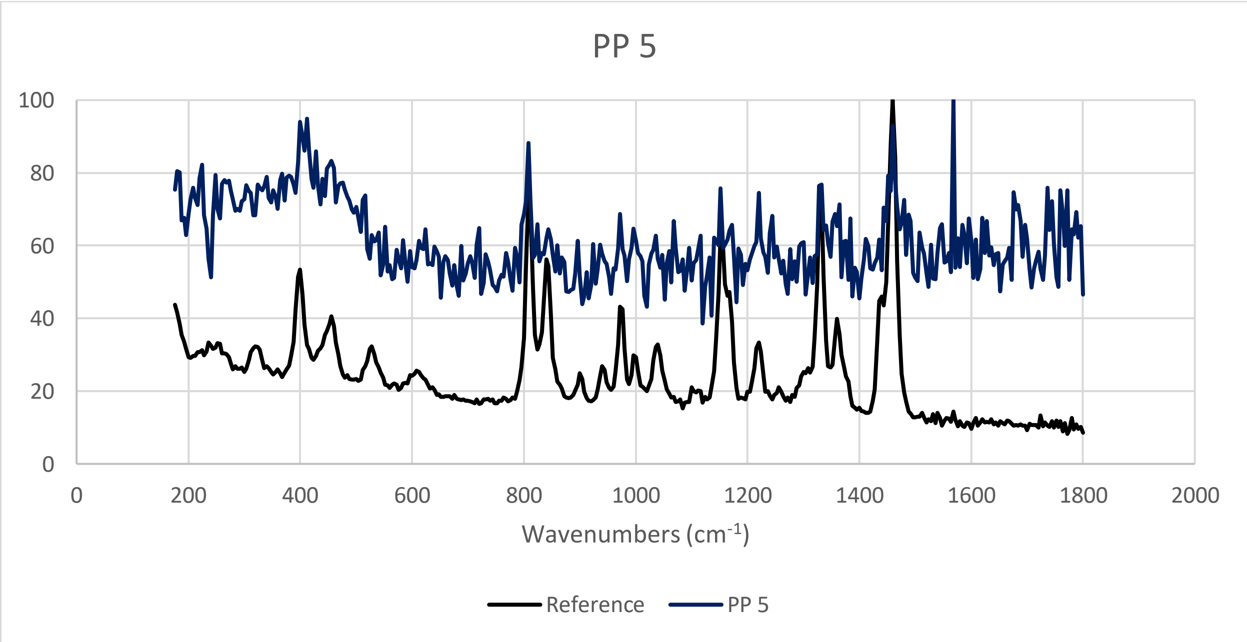

Figure AP. 140 Raman spectrum of PP 5

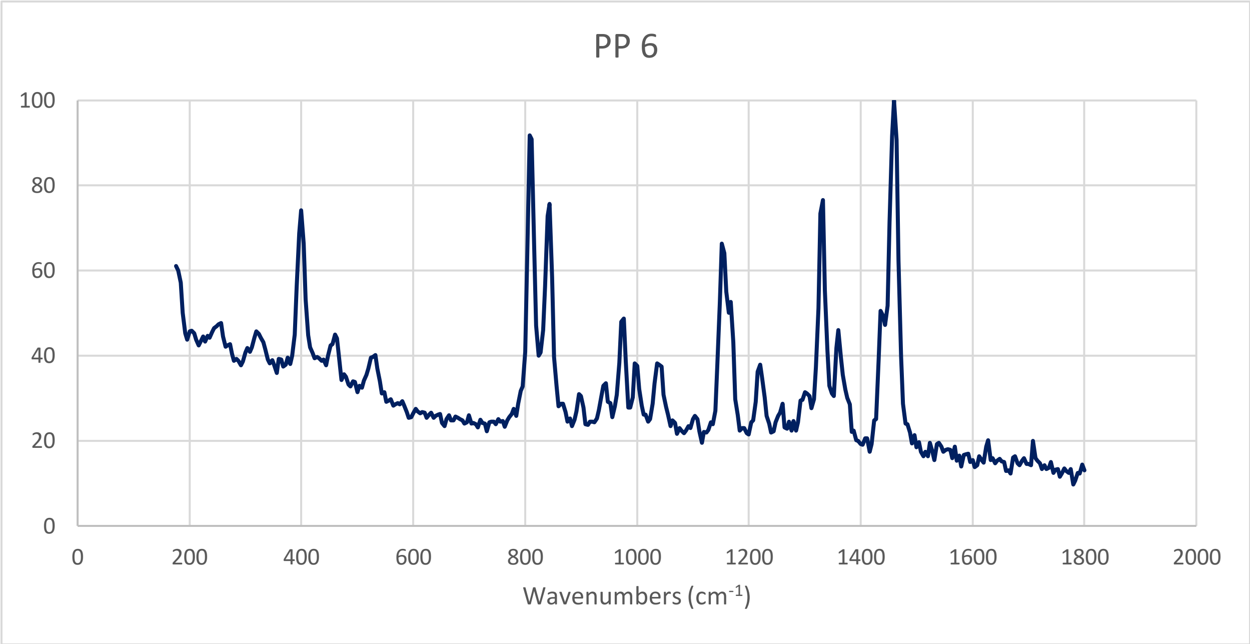

Figure AP. 141 Raman spectrum of PP 6

Label Comparison

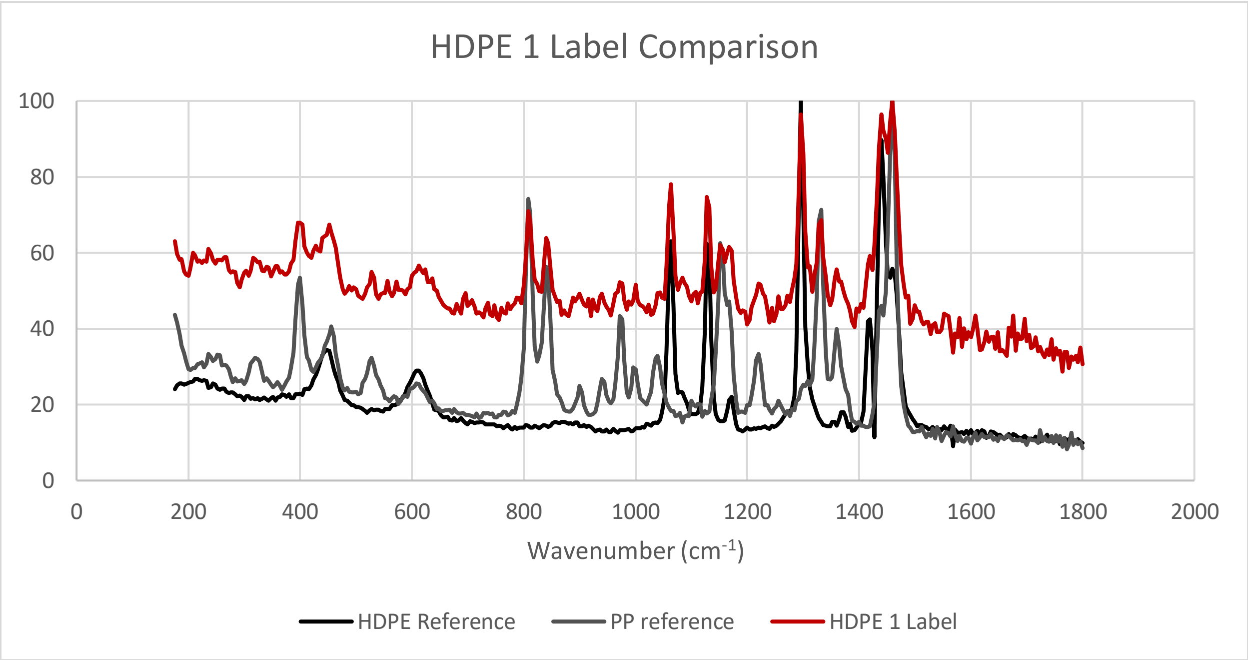

Figure AP. 142 Raman spectrum label comparison of HDPE 1 with HDPE and PP references

Figure AP. 143 Raman spectrum label comparison of HDPE 3 white and green sides

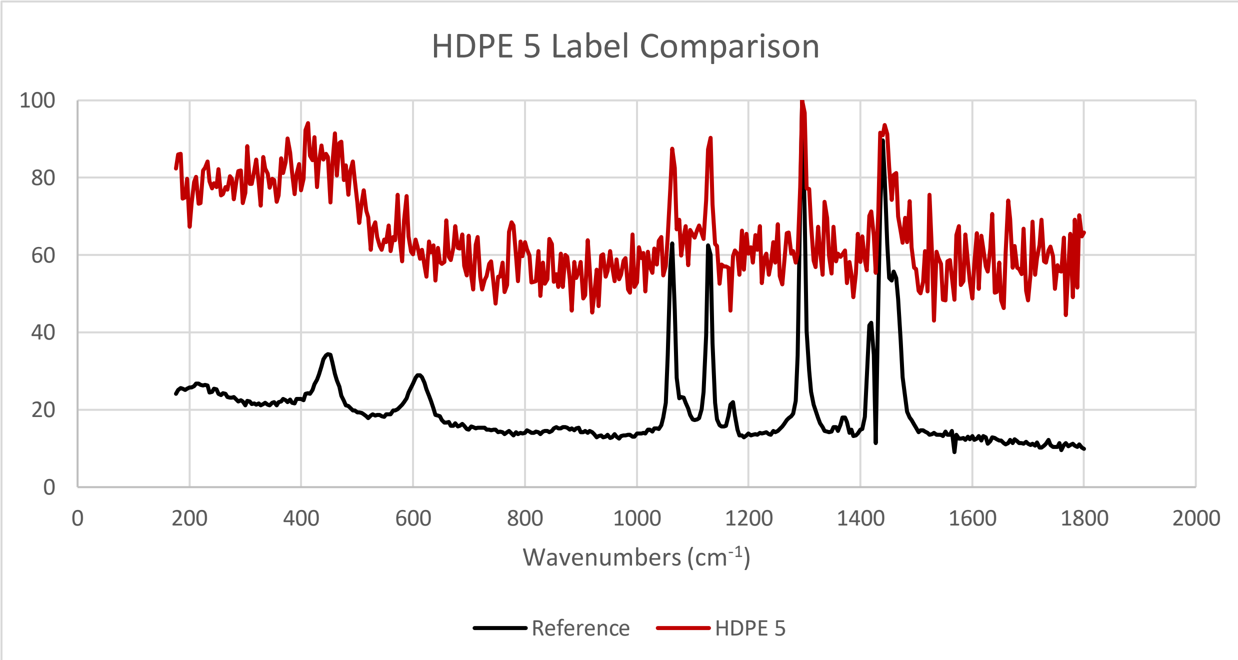

Figure AP. 144 Raman spectrum label comparison of HDPE 5 with HDPE reference