DISCRIMINATION OF FOOD WRAPPERS USING ATR-FTIR SPECTROSCOPY AND CHEMOMETRICS

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DISCRIMINATION OF FOOD WRAPPERS USING ATR-FTIR SPECTROSCOPY AND CHEMOMETRICS

by

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Thesis submitted in partial fulfilment of the requirements for the degree of Bachelor of Science in Forensic Science

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CERTIFICATE

This is to certify that the dissertation entitled Discrimination of Food Wrappers using ATR-FTIR Spectroscopy and Chemometrics is the bona fide record of research work done by Leia Susannah Binti Hairunnizam during the period from October 2024 to February 2025 under my supervision. I have read this dissertation, and that in my opinion, it conforms to acceptable standards of scholarly presentation and is fully adequate, in scope and quality, as a dissertation to be submitted in partial fulfilment for the degree of Bachelor of Science in Forensic Science.

Supervisor,

……………………………………….

(Assoc. Prof. Dr. Nik Fakhuruddin Nik Hassan)

Date: 9/2/2025

DECLARATION

I hereby declare that this dissertation is the result of my own investigations, except otherwise stated and duly acknowledged. I also declare that it has not been previously or concurrently submitted as a whole for any other degrees at Universiti Sains Malaysia or other institutions. I grant Universiti Sains Malaysia the right to use the dissertation for teaching, research, and promotional purposes.

……………………………………

(Leia Susannah Binti Hairunnizam)

Date: 9/2/2025

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LIST OF ABBREVIATIONS

ANN	Artificial Neural Networks
ATR-FTIR	Attenuated Total Reflectance-Fourier Transform Infrared
CA	Cluster Analysis
CVA	Canonical Variate Analysis
DA	Discriminate Analysis
DIF	Differential Interference Contrast
DNA	Deoxyribonucleic Acid
EA	Elemental Analysis
EP	Ethylene-Propylene
EVA	Ethylene Vinyl Acetate
EVOH	Ethylene Vinyl Alcohol
GC	Gas Chromatography
HDPE	High-Density Polyethylene
HSI	Hyper-spectral Imaging
ICA	Independent Components Analysis
IR	Infrared
IRMS	Isotope Ratio Mass Spectrometry
LDA	Linear Discriminant Analysis
LDPE	Low-Density Polyethylene
LIBS	Laser-Induced Breakdown Spectroscopy
LIFS	Laser-Induced Fluorescence Spectroscopy
LLDPE	Linear Low-Density Polyethylene
MANOVA	Multivariate Analysis of Variance

LIST OF ABBREVIATIONS

MIR	Mid-Infrared
MS	Mass Spectrometry
NIR	Near-Infrared
OPLS	Orthogonal Partial Least Squares
PA	Polyamide
PC	Polycarbonate
PCA	Principal Component Analysis
PCs	Principal Components
PE	Polyethylene
PET	Polyethylene terephthalate
PLS	Partial Least Squares
PP	Polypropylene
PS	Polystyrene
PVC	Polyvinyl Chloride
PVDC	Polyvinylidene Chloride
RSD	Relative Standard Deviation
SIMCA	Soft Independent Modelling of Class Analogy
UV	Ultraviolet
2D	2-Dimensional
3D	3-Dimensional

DISKRIMINASI PEMBALUT MAKANAN MENGGUNAKAN SPEKTROSKOPI ATR-FTIR DAN KEMOMETRIK

ABSTRAK

Pembungkus makanan sering ditemui dalam kehidupan seharian dan di tempat kejadian jenayah tetapi sering diabaikan sebagai bahan bukti jejak. Ciri fizikal dan komposisi kimianya boleh memberikan maklumat penting dalam penyiasatan forensik. Namun, potensi pembungkus makanan dalam aplikasi forensik masih kurang diterokai. Oleh itu, kajian ini telah menilai penggunaan spektroskopi Inframerah Transformasi Fourier dengan Jumlah Pemantulan Terlemah (ATR-FTIR) yang digabungkan dengan analisis kemometrik untuk membezakan pembalut makanan daripada 15 jenama berbeza merangkumi tiga kategori: makanan ringan, coklat, dan gula-gula. Spektroskopi ATR-FTIR membolehkan analisis kimia yang pantas dan tidak merosakkan tetapi mendedahkan bahawa banyak pembalut mempunyai komposisi polimer yang serupa dalam kategori yang sama, menjadikan pembezaan lebih mencabar. Analisis Komponen Utama (PCA) sahaja juga tidak mencukupi kerana pengelompokan lebih bergantung pada jenis polimer. Gabungan PCA dengan Analisis Diskriminan Linear (PCA-LDA) meningkatkan ketepatan klasifikasi, mencapai kadar klasifikasi betul sebanyak 93.3% dan 98.5% bagi lapisan luar dan dalam pembungkus, masing-masing. Ujian buta selanjutnya mengesahkan kebolehpercayaan model, dengan semua sampel tidak diketahui diklasifikasikan dengan betul. Penemuan ini menunjukkan potensi spektroskopi ATR-FTIR dan kemometrik sebagai alat forensik yang berkesan dalam pengecaman jenama pembungkus makanan. Oleh itu, kaedah ini dapat digunakan sebagai bukti sokongan dalam penyiasatan forensik.

DISCRIMINATION OF FOOD WRAPPERS USING ATR-FTIR SPECTROSCOPY AND CHEMOMETRICS

ABSTRACT

Food wrappers are frequently encountered in daily life and at crime scenes but are often overlooked as trace evidence. Their chemical composition and physical characteristics can provide crucial information in forensic investigations. Nonetheless, the potential evidentiary value of food wrappers in forensic applications remains unexplored. Hence, this study evaluated the use of Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) spectroscopy combined with chemometrics analysis to discriminate food wrappers from 15 different brands across three categories: junk food, chocolates, and candy. ATR-FTIR spectroscopy enabled rapid and non-destructive chemical analysis but revealed that many wrappers had similar polymer compositions within the same category, making differentiation challenging. Principal Component Analysis (PCA) alone was also insufficient for effective brand discrimination, as clustering primarily followed polymer type. Integration of PCA with Linear Discriminant Analysis (PCA-LDA) significantly improved classification accuracy, achieving 93.3% and 98.5% correct classification rates for the outer and inner wrapper layers, respectively. A blind test further validated the model's reliability where all unknown samples were correctly classified. These findings highlighted the potential of ATR-FTIR spectroscopy combined with chemometrics as a powerful forensic tool for distinguishing food wrappers. By enabling the discrimination between specific brands, this method demonstrated the evidential value of food wrappers, supporting its use as corroborative trace evidence in forensic investigations.

CHAPTER 1

INTRODUCTION

1.1 Background of the Study

Food wrappers play a crucial role in modern packaging by acting as protective barriers that help preserve the freshness, quality, and safety of food products. These wrappers are composed of various plastic polymers and often feature multiple layers and additives designed to enhance properties such as moisture resistance, flexibility, and durability (Pilevar *et al.*, 2019). They exhibit distinct physical and chemical characteristics due to the diversity in polymer types, colours, and additives used. This uniqueness presents an opportunity in forensic investigations, where food wrappers can serve as crucial trace evidence.

In forensic science, the ability to distinguish between seemingly similar materials is essential for linking evidence to specific sources. Traditional methods for analysing physical trace evidence, such as visual comparison and physical measurements, can be subjective and may lack the precision necessary for reliable discrimination. As noted by Lawless and Heyman (1999), discrimination tests are conducted to determine whether two samples are perceptibly different. However, human perception alone may fail to detect chemical differences in similar materials. Consequently, objective analytical techniques like Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy have emerged as powerful non-destructive tools for material identification and discrimination. This technique is a non-destructive method that identifies materials by measuring their infrared absorption to provide detailed insights into the chemical structure of materials through characteristic molecular vibrations.

Despite its advantages, ATR-FTIR spectroscopy may not always provide sufficient discrimination when analysing samples with similar spectral appearances. To enhance its discriminatory power, combining ATR-FTIR with chemometric techniques has proven effective. Chemometrics applies statistical and mathematical tools to interpret complex spectral data, allowing for the identification of subtle differences within large datasets. Techniques like Principal Component Analysis (PCA) and Linear Discriminant Analysis (LDA) are commonly employed to reduce dimensionality, visualise data, and classify samples based on their chemical signatures. Previous studies have successfully utilised ATR-FTIR spectroscopy combined with chemometrics for analysing various polymeric materials, including cling films, electrical tape, and plastic trash bags (Nimi *et al*., 2022; Sharma *et al*., 2019; Telford *et al*., 2016).

While significant advancements have been made in the forensic analysis of plastics and polymers, the application of ATR-FTIR spectroscopy combined with chemometrics specifically for food wrapper discrimination remains underexplored. This research aims to fill this gap by developing a reliable method for discriminating food wrappers. By utilising ATR-FTIR spectroscopy alongside chemometric techniques, this study seeks to establish a scientifically validated approach for identifying unique characteristics of food wrappers that could serve as corroborative trace evidence in forensic investigations.

1.2 Problem Statement

Plastics are extensively used in daily life, making them a common type of trace evidence encountered at crime scenes. Various plastic items, including bags, wraps, pouches, and containers, may be unintentionally left behind by suspects. Among these, food wrappers are often overlooked despite their potential forensic value. Food wrappers are so common in everyday life that they are frequently disregarded as evidence. Torn pieces of wrappers may be accidentally left at a crime scene by a suspect who consumed food there, yet such evidence is often left unexamined. In certain cases, such as those involving drug-spiked food that appears professionally packaged, forensic analysis tends to focus on the food rather than the wrapper. However, when a wrapper lacks branding, it may serve as critical evidence, especially if it can be compared to unbranded wrappers found in a suspect's possession (Jain *et al*., 2024).

Although food wrappers are frequently encountered at crime scenes, research on their evidentiary value and the development of standardised forensic methods for their analysis remains absent. Current studies on food wrappers, such as those conducted by Meng *et al*. (2023) and Zimmermann *et al*. (2021), primarily focuses on enhancing their performance and ensuring food safety, such as improving barrier properties or monitoring chemical migration. Limited attention has been given toward the forensic potential of food wrappers. Due to the lack of prior research on the forensic analysis of food wrappers, their potential as probative and corroborative trace evidence has not been fully realised. Thus, this study aims to bridge this gap by enhancing the evidential value of food wrappers in forensic investigation.

1.3 Research Objectives

1.3.1 General Objective

The objective of this study was to study the significance and evidentiary value of food wrappers as trace evidence in forensic investigations using ATR-FTIR spectroscopy and chemometrics.

1.3.2 Specific Objectives

1) To characterise the chemical composition of various types and brands of food wrappers.
2) To discriminate various types and brands of food wrappers.
3) To establish the potential of food wrappers as trace evidence for forensic intelligence purposes.

1.4 Significance of the Study

Almost every item found at a crime scene, from DNA and fingerprints to fibres and other trace materials, can play a crucial role in solving a criminal case. Even something as seemingly insignificant as a food wrapper could potentially incriminate or exonerate a suspect. Despite this, forensic research on food wrappers remains limited. Hence, this study aimed to address the current gap in forensic studies related to food wrappers and simultaneously highlight overlooked trace evidence in forensic investigations.

The goal was to demonstrate that food wrappers can be discriminated based on their unique compositions and can serve as corroborative evidence alongside other forensic materials. This study also intended to establish ATR-FTIR spectroscopy combined with chemometrics as a reliable, accurate, objective, and non-destructive method for analysing food wrappers and other complex polymeric materials. In the long run, these techniques could significantly enhance the ability of forensic laboratories and law enforcement agencies to link packaging materials to suspects and crime scenes with greater accuracy.

By exploring the potential of food wrappers to serve as a new forensic tool, this research sought to highlight how food wrappers can play a vital role in forensic investigations. Food wrappers recovered from a crime scene can be compared with those found in a suspect's possession, providing means to establish connections between the suspect and the scene. It may also help to narrow down a pool of suspects.

Ultimately, this research aimed to improve forensic investigations by introducing a new form of trace evidence. With validated techniques and scientifically sound methods, food wrappers could become a valuable resource in modern forensic science, supporting justice by offering robust and reliable links between evidence, suspects, and crime scenes.

CHAPTER 2

LITERATURE REVIEW

2.1 Food Wrappers: An Overview

2.1.1 Definition of Food Wrappers

A food wrapper is typically defined as a thin plastic film used to seal food items, ensuring they remain fresh and free from contamination. Commonly, this term evokes images of clear, flexible plastic wraps such as saran wrap, cling wrap, or cling film. However, for some, the term may also suggest coloured wrappers with printed texts and images, often classified as "food packaging" rather than simple "food wrappers." Despite this distinction, both terms are frequently used interchangeably when referring to the latter.

Food wrappers or food packaging refer to materials used to enclose, cover, contain, or store food products until they are ready for consumption. These materials act as barriers between the food and external elements. In Malaysia, the Food Act 1983 (Act 281) defines a food package as any item or method used to case, cover, enclose, contain, place, or pack food, in any manner. It also includes various containers such as baskets, pails, trays, or receptacles, whether they are open or closed. Wani *et al*. (2014) further simplified this by defining food packaging as the enclosure of food products in materials such as pouches, bags, boxes, trays, cans, bottles, or other packaging forms.

2.1.2 Functions of Food Wrappers

Food wrappers are essential for preserving the quality and safety of food during storage, transportation, and sale. In today's global trade environment, food products are often shipped over vast distances from producers to consumers. As such, effective food packaging must endure the challenges associated with shipping, handling, and prolonged storage; any compromise in packaging can pose significant hazards that threaten food safety (Onyeaka & Nwabor, 2022). Therefore, food wrappers are primarily designed to protect food from mechanical damage, harmful light exposure, and gases that can trigger undesirable reactions, while also preventing contamination from spoilage microorganisms or toxic substances (Cheng *et al*., 2022).

Beyond their protective role, food wrappers serve several other functions as outlined by Aggarwal and Langowski (2020), which they categorised as PC3: Protection, Containment, Communication, and Convenience. Protection involves safeguarding the product from microbial spoilage and degradation due to environmental factors such as heat, light, or moisture. This is crucial for maintaining the food's safety and quality attributes like flavour, colour, and aroma, which are elements that significantly influence consumer satisfaction. Containment ensures that the product is securely held to prevent spillage or damage during transport.

Communication provides essential information such as ingredients, nutritional facts, preparation instructions, branding, pricing, shelf life, and storage conditions. This information aids consumers in making informed purchasing decisions. Lastly, convenience focuses on user-friendly features such as easy opening and reclosability, which enhance practical handling and storage of food products. Furthermore, Onyeaka and Fwabor (2022) emphasised that the visual appeal of a wrapper plays a crucial role in attracting customers and influencing their purchasing choices in competitive markets. Attractive wrapper designs are more likely to encourage purchases over generic alternatives by instilling confidence in consumers regarding the product's quality.

2.1.3 Early Food Wrapper Materials

Food packaging is not a modern innovation but dates back to prehistoric times. Yusli *et al*. (2023) noted that early nomadic humans gathered food only when they needed to consume it. However, with the advent of agriculture, the need for food storage arose. At that time, materials such as leaves, tree stems, shells, woven grasses, hollowed logs, animal skins, and animal organs were used to store food (Priyadarshi *et al*., 2024). Eventually, humans began shaping pottery, paper, and glass into containers for food storage.

As time progressed, food storage methods evolved into formal food packaging. This is because the Industrial Revolution in the mid-18th century introduced new manufacturing processes and materials, including metal cans and paperboard. Metal cans were initially designed for snuff but were later adapted to store food for military rations, as they allowed for easier heat processing to extend shelf life compared to fragile glass bottles with cork stoppers. Paperboard was mainly used for bags, wrapping paper, or folding cartons. Though, its biggest drawback was its tendency to absorb water and moisture, limiting its use for certain food products (Tajeddin & Arabkhedri, 2020). Plastics including cellulose nitrate, styrene, and vinyl chloride were also discovered in the 1800s, but were not employed in food packaging until the 20th century.

After World War II, significant advancements were made in plastic materials as there was an increasing focus on food quality. Manufacturers were pushed to develop more durable and resistant packaging capable of withstanding long-distance transportation from factories to retail stores and later to customers' homes (Tajeddin & Arabkhedri, 2020). Soon after, many plastic materials developed for war applications found their way into the food packaging industry. This led polyethylene to become one of the first plastics to be widely used for food packaging (Risch, 2009). Today, packaging technology continues to advance, with a wide variety of plastic polymers being used as food wrappers, reflecting ongoing innovations in packaging technology.

2.1.4 The Shift to Synthetic Polymers

Macena *et al.* (2021) noted that materials such as paper, glass, and metals like aluminium, are still used in food packaging nowadays. However, plastics are by far the most widely utilised and preferred materials for food packaging applications due to their affordability, lightweight nature, mechanical strength, and water resistance (Priyadarshi *et al.,* 2024). Plastics, which are synthetic materials composed of long chains of repeating molecular units known as polymers, are primarily derived from petroleum-based sources.

For decades, petrochemical-derived plastics have been the dominant choice for packaging due to their abundant availability, desirable aesthetics, and superior barrier properties against oxygen and aroma compounds (Jabeen *et al*., 2015). Additionally, plastics are highly valued by manufacturers for their versatility in shaping. They can be easily moulded into various forms through processes such as blowing, extrusion, coextrusion, casting, and lamination. This flexibility allows for the packaging of a wide range of products, including those with unconventional shapes that do not fit into standard containers (Tajeddin & Arabkhedri, 2020).

Ncube *et al*. (2020) reported that the primary plastic polymers used in food wrappers include polyethylene (PE), polypropylene (PP), polyethylene terephthalate (PET), polyvinyl chloride (PVC), and polystyrene (PS). Polyethylene is further classified into two types: low-density polyethylene (LDPE) and high-density polyethylene (HDPE). HDPE is a linear form of PE with minimal branching, while

LDPE has significant branching with both short and long side chains, which prevents tight packing of the polymer chains, as shown in **Figure 2.1**. This structural difference makes HDPE stronger and stiffer, making it suitable for rigid applications such as milk, juice, and water bottles. On the other hand, LDPE is more flexible and transparent, making it ideal for film applications, particularly where heat sealing is required. Common applications include bread bags and frozen food packaging (Marsh & Bugusu, 2007).

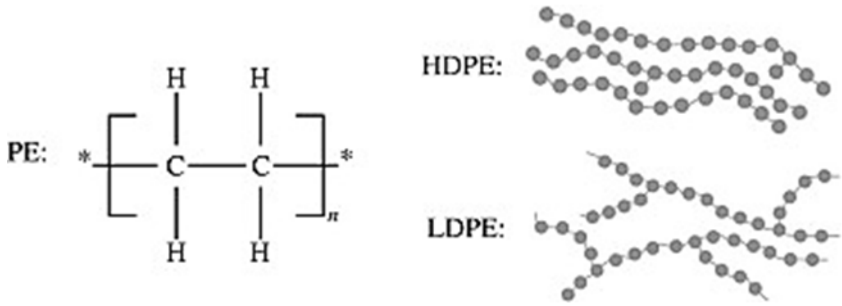

Figure 2.1: Structure of PE, HDPE, LDPE (Baxter *et al.*, 2020)

PP is structurally similar to PE, with the key difference being the presence of a methyl group attached to every other carbon atom in its backbone chain, as seen in **Figure 2.2**. This modification gives PP a higher melting point (160 °C), making it well-suited for applications that require thermal resistance. PP is commonly used in hot-fill packaging, microwavable containers, yogurt tubs, and margarine containers (Marsh & Bugusu, 2007).

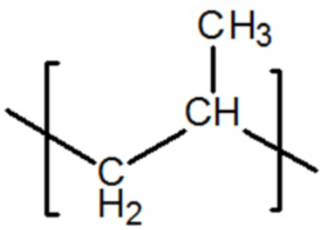

Figure 2.2: Molecular structure of PP (Frizzo *et al.*, 2020)

PET has a molecular structure made up of repeating units of terephthalic acid and ethylene glycol, which are joined by ester bonds to form a strong linear polyester, as illustrated in **Figure 2.3**. PET is lightweight, colourless, and available in both transparent (amorphous) and translucent (semi-crystalline) forms. Its optical clarity and lightweight nature make it ideal for beverage bottles, where consumers can see the product inside. Additionally, PET's stability across a wide temperature range (-60 to 220 °C) allows it to be used in specialty packaging such as boil-in-bag and oven-safe products (Nistico, 2020; Raheem, 2012).

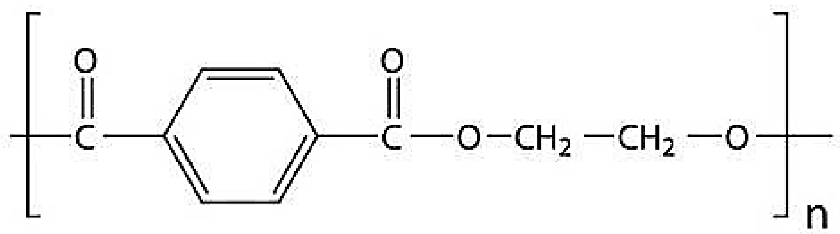

Figure 2.3: Molecular structure of PET (Balamurugan & Rafi, 2021)

Structurally, PVC is similar to PP but differs by substituting the methyl group with a chlorine atom, like in **Figure 2.4**. PVC is predominantly used in medical and non-food applications. However, it is also used in food packaging, particularly for bottles and flexible films. PVC sheets are commonly thermoformed into blister packs for products such as meat and single-dose pharmaceuticals due to their ease of moulding and durability (Marsh & Bugusu, 2007).

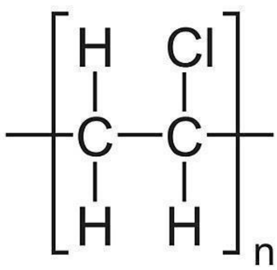

Figure 2.4: Molecular structure of PVC (Mohamed *et al*., 2016)

PS also shares structural similarities with PP and PVC but features a phenyl group attached to the main carbon backbone, as shown in **Figure 2.5**, instead of a methyl or chlorine group. The low cost, low density, low moisture absorption, ease of moulding, and durability of PS make it an attractive choice for food packaging. Its versatility allows it to be used in various applications, such as hot beverage cups, egg cartons, meat trays, and take-home food containers (Pilevar *et al*., 2019).

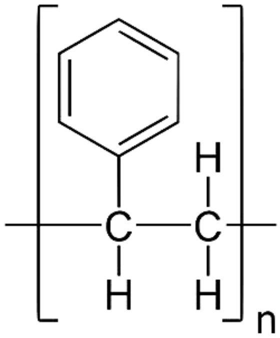

Figure 2.5: Molecular structure of PS (Kik *et al*., 2020)

2.1.5 Multilayer and Composite Wrappers

Plastic wrappers are produced either from single polymers or as multilayered plastics, which are combinations of different polymer types forming multiple plastic layers (Pilevar *et al.*, 2019). More often, multilayered plastic wrappers are preferred because combining various polymers imparts distinct, desirable properties suited to the specific requirements of different food products. In addition to commonly used plastic polymers like PE, PET, PP, and PVC, other less common polymers such as polyamides (PA), polycarbonates (PC), polyvinylidene chloride (PVDC), ethylene vinyl acetate (EVA), and ethylene vinyl alcohols (EVOH) are also incorporated to achieve enhanced functionality.

Multilayered plastic wrappers can be described as a single structure comprising two or more materials with distinct properties, where each layer serves a specific function to improve the overall performance of the wrapper. According to Butler & Morris (2016), these multilayered wrappers typically consist of 3 to 7 layers, though some have even more. Generally, polymers with high oxygen barrier properties form the inner layer, while polymers with better water vapour resistance and mechanical strength are used for the outer layer (Fabra *et al*., 2014).

For example, PE is commonly used as an outer layer due to its toughness and excellent moisture barrier properties. Meanwhile, PA is often incorporated as inner layers or intermediate layers because of their superior oxygen, oil, grease, and aroma barrier properties. Additionally, non-plastic materials like paper and aluminium are sometimes added to enhance the rigidity or stiffness of the wrapper (Bauer *et al*., 2021). **Figure 2.6** illustrates examples of multilayered food wrappers, and **Table 2.1** provides a summary of the functions, materials, and typical layer configurations of these wrappers.

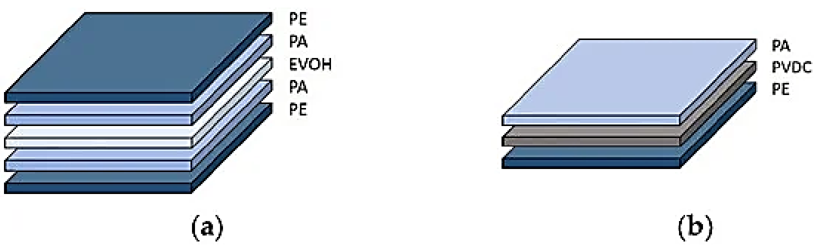

Figure 2.6: Examples of multilayered food wrappers (Bauer *et al*., 2021)

Table 2.1: Layer configuration, functions, and commonly used materials for multilayer food packaging (Schmidt *et al.*, 2022)

Layer	Function	Material
Seal layer (innermost layer facing food)	Heat sealability, inert against filling goods	PE, PP, PA, PET, EVA, ionomers
Barrier layer	Moisture resistance	PE (LDPE, HDPE), PP, EVA, ionomers, PVDC, PET
	Oil/grease resistance	PET, HDPE, PA, ionomers, EVOH, PVDC
	Oxygen resistance	EVOH, PA, PET, PVDC, PA, aluminium, SiOx or Al_2O_3 coatings
	Aroma/flavour resistance	PET, PA, EVOH, PVDC
	Light resistance	Aluminium, TiO_2-filled polymers
Tie layer	Acts as an adhesive, combines two chemically incompatible materials	Polyurethanes, acid/anhydride grafted polyolefins
Structural layer	Toughness	PE, PET
	Puncture resistance	HDPE, PA
	Stiffness	PP, PET, HDPE, LDPE, PA, EVA, ionomers, EVOH
Outer layer	Provides printing surface and mechanical performance	PE, PET
Coating (outermost layer facing environment)	Optional thin film to protect the printed material	Any specialised polymer

2.1.6 Additives in Food Wrappers

In both single polymer and multilayered plastics, additives are commonly incorporated to enhance their physical and chemical properties. These additives improve attributes such as resistance to oxidation and light exposure, impact resistance, hardness adjustment, surface tension control, cost reduction, and flame resistance (Kato & Conte-Junior, 2021). Examples of such additives include fillers, plasticisers, flame retardants, colourants, heat stabilisers, UV stabilisers, antioxidants, and many others.

Fillers are commonly added to reduce production costs while improving the material's stiffness and strength. Plasticisers increase flexibility and reduce brittleness, making the plastic more adaptable for tight wrapping applications. Flame retardants are used to improve fire resistance by slowing down or preventing combustion. Colourants provide aesthetic appeal and help differentiate products through vibrant designs. Heat stabilisers protect the packaging from thermal degradation during processing and use. UV stabilisers shield the plastic from harmful ultraviolet rays that can cause damage to the plastic. Lastly, antioxidants prevent oxidation, which can cause polymer degradation and discoloration over time.

Akoueson *et al.* (2023) highlighted that the type and concentration of additives used in plastic packaging are highly product-specific, depending on the intended performance characteristics. For instance, increasing the amount of plasticiser in a polymer enhances flexibility and softness, making it ideal for packaging fresh produce, baked goods, or other products requiring tight wrapping without tearing. Conversely, products like dry pasta or cereal, which do not require soft packaging, benefit from plastics with lower plasticiser content. This results in a stiffer, more rigid material that offers better structural integrity, ensuring the packaging holds its shape during handling, storage, and transportation.

2.2 Trace Evidence and Its Evidentiary Value

Trace evidence, a crucial component of forensic science, refers to small but measurable materials transferred during the commission of a crime. These materials can be found at crime scenes, on suspects, or on victims, and include fibres, hair, paint, glass, soil, and other minute substances (Mistek *et al*., 2019). Despite their microscopic size, trace evidence holds great forensic value as they can provide insights into what occurred, the source of the material, and how it may have been transferred (Trejos *et al*., 2020).

Landron (2019) describes trace evidence as "silent witnesses" because of its ability to link victims, suspects, witnesses, and even wildlife to a crime scene or objects used in criminal activities. When properly analysed, it can establish critical connections that support or contradict investigative theories. For instance, fibres found on a victim's clothing could originate from a suspect's garment, thus helping to demonstrate the possible contact between them. Similarly, glass fragments on a suspect's clothes may be matched to shattered glass at the crime scene.

The importance of trace evidence in forensic investigations is founded on Locard's Exchange Principle, developed by Edmund Locard in the early 20th century. Locard, director of the first crime laboratory in Lyon, France, proposed that when two objects come into contact, they will exchange materials (Turvey & Baltazar, 2023). This principle, often summarised as "every contact leaves a trace," forms the basis of forensic investigations.

While trace evidence may not always be uniquely identifying unless a physical fit is obtained, it can still provide significant evidentiary support. These materials can corroborate witness testimony, support or refute alibis, and offer critical clues about the sequence of events (Trejos *et al*., 2020). Therefore, trace evidence plays a pivotal role in reconstructing crimes and helping to establish connections between individuals, objects, and locations involved in criminal activities.

2.2.1 Food Wrappers as Trace Evidence

Several studies have examined plastics as trace evidence, but plastic food wrappers, specifically, remain largely unexamined in this context. Trejos *et al.* (2020) recognised a range of materials as trace evidence, including plastics, though they did not specify the types of plastic products. Conversely, Weimer *et al.* (2020) listed specific examples of plastics as evidence, including zip ties, automotive lenses, and sandwich or trash bags. Similarly, Lee (2023) highlighted plastics as forensic evidence but limited the discussion to those found in vehicle accidents, such as fragments from headlamps, dashboards, and bumpers. Schwartz (2024) discussed the forensic value of plastic trash bags, noting that it is often possible to identify the manufacturer and compare bags to known sources using forensic techniques.

Even LDPE trash bags can be analysed and distinguished from one brand to another (Schwartz, 2024). Given that food wrappers are usually multilayered, contain various additives, feature different colours, and incorporate diverse plastic polymers, they may also have forensic value and be capable of discrimination. However, based on the available literature, no studies have specifically examined the use of food wrappers as trace or physical evidence. Most existing research on plastic food wrappers pertains to the food packaging industry. For instance, Gupta, *et al.* (2024) and Pack *et al.* (2021) explored the migration of chemical compounds from wrappers into food and evaluated potential health risks.

Other studies focused on improving packaging materials or environmental concerns. Pavlenko *et al.* (2024) investigated how nanofillers enhance the properties of food packaging materials. Research by Ghasemlou *et al.* (2024) and Perera et al. (2023) examined bioplastic alternatives to conventional plastics. Studies such as those by Bauer *et al*. (2021) and Ncube *et al.* (2020) evaluated the environmental impact of plastic wrappers, proposing biodegradable and recyclable alternatives. Baskaran and Sathiavelu (2020) investigated the degradation of multilayered food packages and assessed their potential environmental impact. Despite the broad research on food packaging, none directly addresses the forensic potential of plastic food wrappers, highlighting a significant gap in forensic science.

2.3 Analytical Techniques for Plastic Polymer Discrimination

2.3.1 Non-Forensic Applications

Plastic food wrappers are typically composed of polymers such as PE, PP, and PET, which are also commonly found in other plastic products. Although numerous studies have investigated the discrimination of various plastic products, most have been conducted in non-forensic contexts, focusing on areas like recycling and environmental impact. These studies have employed a range of analytical techniques, such as gas chromatography, near and mid-infrared spectroscopy, and laser-induced breakdown spectroscopy, many of which could be adapted for the analysis of plastic food wrappers. For instance, Penalver *et al.* (2022) utilised gas chromatography (GC) to discriminate between virgin and recycled PET bottles based on their volatile profiles. They succeeded in differentiating the two due to specific aldehydes and benzene derivatives found only in recycled PET samples. However, due to the destructive nature of GC, as well as the need for sample incubation to obtain headspace gas, its application in large-scale plastic discrimination may be impractical and time-consuming.

Given the limitations of GC, many researchers have turned to non-destructive and rapid spectroscopy techniques for plastic analysis. Penalver *et al.* (2022) demonstrated that Raman spectroscopy, combined with chemometric models such as principal component analysis (PCA), orthogonal partial least squares discriminant analysis (OPLS-DA), and partial least squares (PLS) regression, was effective in distinguishing recycled PET from virgin PET. With minimal sample preparation required, Raman spectroscopy proved to be a rapid and non-destructive alternative to GC. Biasio *et al.* (2010) explored using Fourier transform infrared (FTIR) spectroscopy in the near-infrared (NIR) region, combined with unspecified chemometric models, to differentiate PE and PP polymers for recycling purposes. Their hyperspectral imaging system successfully discriminated not only between PE and PP but also between subclasses like LDPE and HDPE by correlating spectral features with material melting points.

Kassouf *et al*. (2014) achieved similar results using mid-infrared (MIR) spectroscopy and independent components analysis (ICA) to differentiate between PET, PE, PP, PS, PLA, and subclasses of PE. Their MIR-ICA approach yielded 100% discrimination accuracy, making it a reliable tool for plastic waste separation. Other studies have employed attenuated total reflection FTIR (ATR-FTIR) in the mid-IR region for plastic analysis, emphasising its advantages such as minimal sample preparation, ease of use, rapid analysis, and closeness to the industrial conditions of hyper-spectral imaging (HSI) cameras used in sorting facilities (Jung *et al*., 2018; Signoret *et al*., 2019). These studies demonstrated that ATR-FTIR could accurately discriminate between various plastics, including complex samples like polymer blends and degraded plastics.

Recent advancements have focused on both laser-induced breakdown spectroscopy (LIBS) and laser-induced fluorescence (LIF) spectroscopy for distinguishing different plastics. LIBS provides elemental analysis by detecting and quantifying elements in a sample, offering advantages such as rapid analysis, single-shot multi-elemental detection, minimal sample preparation, and standoff detection capability (Junjuri *et al*., 2019). Studies have shown that LIBS, when combined with chemometric models like principal component analysis (PCA) and partial least squares discriminant analysis (PLS-DA), can achieve classification accuracies above 93% for various post-consumer plastics (Abdulmajid *et al.,* 2023; Junjuri *et al*., 2019). Similarly, Bonifazi *et al.* (2024) demonstrated that LIF spectroscopy, combined with PLS-DA, can effectively identify black-coloured plastics, which are often undetectable by NIR-based sorting systems due to their low reflectance.

2.3.2 Forensic Applications

While research specifically targeting the forensic discrimination of food wrappers is limited, numerous studies have examined plastic polymer-based products that share similar chemical compositions with food packaging. These studies provide valuable methodologies that can be adapted for the forensic analysis of food wrappers, facilitating the identification of polymer types and distinguishing chemical components. A notable technique in plastic polymer discrimination involves X-ray diffraction and microscopy methods. Hashimoto *et al.* (2007) employed both X-ray diffraction and optical microscopy techniques, such as differential interference contrast (DIC) and phase contrast microscopy, to differentiate between non-coloured transparent polyethylene (PE) bags commonly used for drug packaging. Their findings indicated that X-ray diffraction effectively classified the PE bags based on its crystalline phase, while optical microscopy allowed for easy discrimination of plastic films due to their morphological differences.

In addition to these methods, infrared spectroscopy with an attenuated total reflectance (ATR) prism was also explored. Hashimoto *et al.* (2007) noted that infrared spectroscopy, particularly when combined with classification software, proved to be the most discriminative method among those tested. However, in the absence of such software or when relying on visual assessments of spectra overlays, optical microscopy emerged as the best discriminator due to the distinct morphologies produced by different manufacturing processes of PE plastics. Building on the concept of process-induced morphological differences, Koh *et al.* (2019) further investigated plastic drinking straws associated with drug paraphernalia and illicit drug packaging through comparison microscopy. They found that while comparing dimensions and polarised patterns provided low discrimination, the examination of manufacturing marks using a comparison microscope yielded a 95% discrimination rate.

Despite the effectiveness of microscopic techniques, they can yield subjective results, highlighting the need for more objective alternatives like spectrometry and spectroscopy. Idoine *et al.* (2005) utilised elemental analysis/isotope ratio mass spectrometry (EA/IRMS) to classify cling films from heroin packages according to their seizure groups. They discovered that a multivariate comparison of carbon, hydrogen, and oxygen isotope ratios could distinguish most samples effectively. Although EA-IRMS offers rapid analysis with minimal sample requirements, it necessitates careful attention to protocols and calibration for accuracy, making it sensitive to operational errors (Grassineau, 2006). Furthermore, as a destructive technique, it requires non-destructive methods to be employed first if multiple analyses are intended.

The adoption of non-destructive analytical techniques is crucial in forensic investigations due to the nature of evidence presented. ATR-FTIR spectroscopy has gained prominence in this area because it is rapid, easy to perform, non-destructive, and requires only small sample quantities with minimal preparation. This technique coupled with chemometrics has been successfully applied for the discrimination of various plastic-based polymers such as cling films, plastic bags, electrical tape backings, and nylon fibres (Enlow *et al.,* 2005; Hashimoto *et al*., 2007; Nimi *et al*., 2022; Sharma *et al*., 2019; Telford *et al*., 2016). Recent advancements have also utilised ATR-FTIR spectroscopy to analyse polymer traces from 3D-printed firearms, demonstrating its ability to link polymer traces to source materials. This was attributed to the high inter-variability observed, resulting from differences in polymer types and pigments used (Falaradeau *et al*., 2024). Despite its established utility in various forensic contexts, no published studies to date have explored the discrimination of plastic food wrappers using ATR-FTIR spectroscopy and chemometrics, highlighting a potential research gap.

2.4 Attenuated Total Reflectance-Fourier Transform Infrared (ATR-FTIR) Spectroscopy

Attenuated Total Reflectance Fourier Transform Infrared (ATR-FTIR) spectroscopy is a widely utilised analytical technique for identifying materials by examining their molecular vibrations. Molecular vibrations refer to the movement of bonds between atoms within a molecule, including stretching and bending motions, which vary based on the specific functional groups present. ATR-FTIR spectroscopy measures these vibrations to identify functional groups and obtain detailed information about the chemical structure of a sample. This technique operates by utilising total internal reflection, where an infrared (IR) beam is directed at a high-refractive index crystal, such as diamond, zinc selenide, or germanium, at an appropriate angle (Kaur *et al*., 2021). **Figure 2.7** illustrates the principle of total internal reflection in ATR-FTIR spectroscopy. The directed IR beam reflects at the interface between the crystal and the sample, forming an evanescent wave that penetrates a few micrometres into the sample, enabling interaction with its surface molecules (Bieberle-Hutter *et al*., 2021).

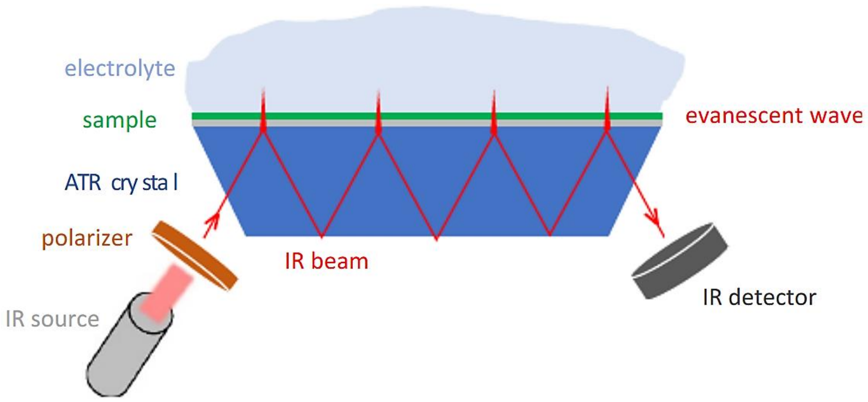

Figure 2.7: General principle of ATR-FTIR spectroscopy (Bieberle-Hutter *et al*., 2021)

In simpler terms, the evanescent wave generated during internal reflection selectively interacts with the sample's molecular bonds, causing absorption of specific IR frequencies corresponding to the sample's vibrational modes. Infrared light spans a broad range of the electromagnetic spectrum, from 10 to 12,800 cm^{-1}, and is divided into near-infrared (NIR: 12,800-4,000 cm^{-1}), mid-infrared (MIR: 4,000–400 cm^{-1}), and far-infrared (FIR: 400–10 cm^{-1}) regions. The mid-infrared region is particularly significant for ATR-FTIR spectroscopy because its frequency range closely matches the natural vibrational frequencies of most molecular bonds, thereby inducing molecular vibrations when absorbed. When the IR frequency matches a bond's natural vibrational frequency, absorption occurs, resulting in measurable changes in the amplitude of vibration (Ojeda & Dittrich, 2012). Most functional groups typically absorb IR frequencies between 3,500 and 1,500 cm^{-1}. **Table 2.2** summarises the bond types and their corresponding frequency ranges. By measuring the absorbed and reflected portions of the IR beam, ATR-FTIR generates a spectrum that represents the sample's molecular composition. The data are processed using Fourier transform algorithms to produce a detailed infrared spectrum.

Table 2.2: Frequency range of functional groups

Bond	Type of Compound	Frequency Range (cm^{-1})
C–H	Alkanes	2850 – 5970
		1340 – 1470
C–H	Alkenes	3010 – 3095
		675 – 995
C–H	Alkynes	3300
C–H	Aromatic rings	3010 – 3100
		690 – 900
O–H	Monomeric Alcohols, Phenols	3590 – 3650
		3200 – 3600
		3500 - 3650
		2500 - 2700
N–H	Amines, Amides	3300 – 3500
C=C	Alkenes	1610 – 1680
C=C	Aromatic rings	1500 – 1600
C≡C	Alkynes	2100 – 2260
C–N	Amines, Amides	1180 – 1360
C≡N	Nitriles	2210 – 2280
C–O	Alcohols, Ethers, Carboxylic Acids, Esters	1050 – 1500
C=O	Aldehydes, Ketones, Carboxylic Acids, Esters	1690 – 1760
NO_2	Nitro compounds	1500 – 1570
		1300 – 1370