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Investigation of the History of Fingerprinting, Advancements in the Field, and Development of Potential Methods that Could Improve the Detection of Endogenous And Exogenous Drugs in Latent Prints

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INVESTIGATION OF THE HISTORY OF FINGERPRINTING, ADVANCEMENTS IN THE FIELD, AND DEVELOPMENT OF POTENTIAL METHODS THAT COULD IMPROVE THE DETECTION OF ENDOGENOUS AND EXOGENOUS DRUGS IN LATENT PRINTS

By

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ABSTRACT

When someone thinks of fingerprinting, they are most likely going to picture how a latent print is matched to the fingerprint of a suspect based on ridge pattern analysis. However, there is much more information that can be obtained from a latent print. The work performed in this thesis focuses the detection of exogenous and endogenous drugs in latent prints.

The experiments performed analyzed fingerprints from volunteers that were contaminated with one of three common painkillers: acetaminophen, acetylsalicylic acid (ASA), and ibuprofen. Three different instruments were tested for this purpose: MALDI-MS, ATR-FTIR, and LC-MS. Based on the results gathered, it was determined that both MALDI-MS and LC-MS can accurately detect exogenous drug particles in latent prints. A quantitation study was also carried out using LC-MS which gave the following results: 1.224, 2.632, and 2.201 mg/mL of acetaminophen, 38.886, 35.579, and 40.534 mg/mL of ASA, and 136.054, 13.667, and 150.246 mg/mL of ibuprofen. ATR-FTIR was only able to produce two accurate results after many trials and thus it was concluded that this is not a valid instrument for this application.

Based on current scientific technology and gaps in literature, it was determined that two instruments that should be investigated for the purpose of detecting endogenous drug particles in latent fingerprints include LC-MS/MS and DART-MS. DART-MS shows potential for this application since it is nondestructive, no sample preparation is necessary, and it can detect trace amounts of analyte. LC-MS/MS was chosen because it produces more detailed mass spectra compared to traditional LC-MS.

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LIST OF ABBREVIATIONS

AFIS	Automated Fingerprint Identification Systems
ASA	Acetylsalicylic acid
ATR	Attenuated total reflectance
CHCA	α-cyano-4-hydroxycinnamic acid
CWL	Chromatic white light
DART	Direct analysis in real time
DESI	Desorption electrospray
DHB	2,5-dihydroxybenzoic acid
FBI	Federal Bureau of Investigation
FTIR	Fourier transform infrared spectroscopy
GC	Gas chromatography
IACP	International Association of the Chiefs of Police
IAFIS	Integrated Automated Fingerprint Identification System
IR	Infrared
IRB	Institutional Review Board
LC	Liquid chromatography
MALDI	Matrix assisted laser desorption
MS	Mass Spectrometry
MS/MS	Tandem mass spectrometry
NGI	Next Generation Identification
RDX	Royal demolition explosive
SIMS	Secondary ion mass spectrometry
TFA	Trifluoroacetic acid
TNT	Trinitrotoluene
TOF	Time of flight
UV	Ultraviolet

CHAPTER 1: History of Fingerprinting and Advancements in the Field

1.1 Introduction

Fingerprint evidence has been around since the very early days of forensic investigation, and still remains one of the most important pieces of evidence one can find at a crime scene. There are two main reasons for this: people are constantly touching things everyday leaving behind fingerprints, and no two fingerprints are exactly alike. Even identical twins who possess the exact same DNA will not have the same fingerprint pattern. But exactly how was the valuable, individualistic property of the fingerprint discovered? This history of the fingerprint and the role it plays in individual human identification is not a short, simple, or straightforward story. Many different people independently realized the unique properties of fingerprint ridge patterns at different points in time. It took decades for all of these individual discoveries and realizations to come together as one to give us the standard fingerprint analyzation process that is used today in criminal investigation. Since that time, advancements have been with respect to the latent print beyond just analyzing the ridge pattern in an attempt to determine the identity of the originator. However, it is important to first become familiar with and understand the origins of the fingerprint and how it became one of the most important pieces of evidence that can be found at a crime scene.

1.2 History of Fingerprints and Fingerprinting

Much like the snowflake, fingerprints have been an iconic symbol of individuality due to the fact that no two are the same. This observation has been made multiple times throughout history in various independent scenarios. The earliest documented discovery of the fingerprint and its individual properties dates back to 200 BCE. Chinese records from the Qin Dynasty show that fingerprints were used for identification and as evidence during investigations regarding burglary (1). The first statement that no two fingerprints are alike has been traced back to a book (*Anatomical Copper-plates with Appropriate Explanations*) written in 1788 by German anatomist Johann Christoph Andreas Mayer (2).

Hearing this idea that all fingerprints are unique, individuals in the world of science and criminal investigation began to explore how it could be used to advance the field of criminalistics. Among the first of these individuals was William Herschel. Herschel actually seemed to stumble upon the identification factor of the fingerprint on accident. In 1858, Herschel became a member of the Indian Civil Service and thus resided in India. During his time in India, he often had to make trades or agreements with the local residents. To make the written contracts seem more legitimate, he would require a handprint or fingerprint to be placed on the document, even though he was unaware of the identification powers of the fingerprint at that time (3). After performing this act for some time, Herschel began to realize that the fingerprints could possibly prove the identity of an individual. Though his experimentation on the topic was limited, it was a significant contribution to the advancement of the use of fingerprints for identification. After returning to England, Herschel published an article titled “Skin Furrows of the

Hand" (published in 1880) recapping his first experiences with the fingerprint, and later released a book titled *The Origin of Fingerprinting* (published in 1916) expanding more on the idea of using these prints as personal identifiers (3,4).

The first individual to propose the idea that fingerprints could be used as a method of criminal identification was a Scottish missionary named Henry Faulds. Faulds first encountered pressed fingermarks in 1878 while admiring some ancient pottery (5). Shortly after, in 1880, Faulds became the first person to make a public statement suggesting that fingerprints could be used to solve criminal cases (6.) This was a huge breakthrough in the realm of criminal investigation because, prior to the use of fingerprints, the only seemingly valid method of personal identification was the Bertillon system (also known as anthropometry). Created by Alphonse Bertillon in 1879, the Bertillon system combined measurements of human features to give prisoners a unique profile that could distinguish them from other prisoners (7). The system proved to work in identifying criminals up until the infamous Will West case. In Kansas in 1903, a man by the name of Will West was arrested and had his Bertillon measurements taken. After cross referencing the database of measurements, it was discovered that this man had already been booked under the name of William West. However, it was quickly revealed that this was not the same man since William West was still imprisoned. This was the first time that the Bertillon system obviously failed, but the integrity of the system was questioned long before this case (8).

Since many believed that anthropometry could not be used to accurately distinguish prisoners from one another, people began researching and brainstorming a new method of identification. Due to the close proximity of the invention of the Bertillon

system and the declaration made by Faulds, many people looked deeper into the plausibility of using fingerprints to differentiate between individuals. The technique of fingerprinting developed faster in other countries than it did in the United States. Major strides were made in 1888 by Sir Francis Galton in England when an article of his titled "Personal Identification and Description" was published in *Nature*. In this article, Galton actually studied the fingerprints of William Herschel, specifically from the index and middle fingers of his right hand. Herschel collected his prints in 1860 and 1888 – 28 years apart. Galton closely analyzed the ridge patterns on both sets of fingerprints and found that there are multiple points in the prints that are exactly the same (9). The comparison points used by Galton closely resemble what we would recognize today as classic fingerprint minutiae, including bifurcations, termination/ending ridges, and points/islands (9). This seems to be the first published study of finger impressions over time, and the results of said study suggested that the ridge pattern within the skin of the fingertip remains the same over a long period of time – arguably as long as a lifetime.

Galton made another vital contribution to the history of fingerprinting – the first published classification system. This system divides fingerprints into the three main categories that are still used today: arches, loops, and whorls. Galton described this system in his book titled "Finger Prints" which he published in 1892 (10). This same year that Galton published his book, the first ever criminal fingerprint identification was made. This identification was made in a murder case in Argentina with the help of anthropologist and police official Juan Vucetich. Vucetich was largely inspired by the work of Galton which he expanded upon to create what he considered to be a more advanced fingerprint classification system. This new system was composed of four

categories rather than three: arch, internal loop, external loop, and whorl (11). Using this system, Vucetich began the first fingerprint files which also simultaneously used the Bertillon system.

In June of 1892, inspector Eduardo Alvarez provided Vucetich with bloody finger impressions from the crime scene of a murder of two young boys. Using his own classification system, Vucetich was able to match the prints from the crime scene to Francisca Rojas – the mother of the two boys. This was a shock since Rojas had neck injuries herself and had accused her neighbor, Velasquez, of the murder. After Vucetich made the print identification and presented Rojas with the evidence, she confessed to the murder and explained that she had injured herself and accused the neighbor in an attempt to cover up her actions (12). After this case, Vucetich decided that Bertillon measurements were unnecessary to take and store in the database since it was possible to make an identification using only a fingerprint. Overall, this case was pivotal in the history of fingerprinting since it resulted in the first criminal fingerprint identification ever made, and it proved that better and simpler methods of identification can be used in place of the Bertillon system.

Juan Vucetich was not the only analyst inspired by Galton's work with fingerprints. Edward Henry, chief of police in Bengal, India began implementing the use of fingerprints in criminal records after encountering Galton's publications. In 1893, Henry refined the anthropometric system used in the police departments to include only six Bertillon measurements along with a pressed left thumb print (13). Convinced that a record system based solely off of fingerprints would not only be more efficient but more effective, Henry decided to reach out to Galton to learn more about his classification

system. Galton actually extended an invitation to his laboratory which Henry gladly accepted in 1894. Upon his return back to India, Henry decided that he wanted his system to be based on a formula in order to make criminal identification by fingerprints even more simple and effective than it already was (13). Henry recruited two police officers, Azizul Haque and Chandra Bose, to assist him in his endeavors, and the three dedicated themselves to this project for years before a new system was devised (14).

In 1897, three years after beginning their studies, the trio finally accomplished their goal of developing a new fingerprint classification system. Though this plan was originally set in motion by Edward Henry, the majority of the work was actually conducted by Haque and Bose, and Haque was the one to construct the basis of the new classification system (15). The system Haque created was based on a mathematical formula related to the pattern found on each fingertip – arch, loop, or whorl. The system separates the 10 fingerprints into 5 pairs (each set up as an individual ratio), and specific numbers are assigned to each finger based on the type of print present and which finger it is on. The numerators are then all added together, followed by the denominators, and then 1 is added to each sum (16). This leads to 1,024 'pigeon holes,' or categories, into which an individual can fall under based on their fingerprint ridge patterns (16). This was helpful at the time since all fingerprint cards were stored manually rather than digitally. Despite the fact that Haque devised the system nearly on his own, with only the help of Bose, it became known as "Henry Classification System" (5).

After previously denying Fauld's efforts to implement fingerprinting in 1886, Scotland Yard (London Metropolitan Police) decided to add fingerprinting to their identification system in 1894, which previously only consisted of anthropometry

measurements (5). Their system was initially based on the discoveries of Galton which included overall fingerprint pattern and some pieces of minutiae. However, following the creation and publication of the Henry classification system, England as a whole adopted this as their main fingerprint classification system in 1901 (17).

In 1903, fingerprinting finally had its significant breakthrough in the United States. New York state prison was the first in the US to adopt a fingerprinting system as a means of identifying criminals (18). Shortly after in 1904, R. W. McClaughry, Warden of the Leavenworth Penitentiary, contacted the Attorney General and requested permission and the necessary supplies to take fingerprints of the federal prisoners (19). Permission was granted in November, allowing the creation of the Leavenworth fingerprint collection. The creation of this collection was assisted by an experienced sergeant from Scotland Yard, where fingerprints had been used as a means for identification for the past 10 years (19). The Leavenworth fingerprint repository was later transformed into America's first national fingerprint repository known as the National Bureau of Criminal Identification with the help of the International Association of the Chiefs of Police (IACP) (20). This repository, formed by the IACP, became the main identification bureau for many prisons and police departments.

In 1905, the Department of Justice hoped to create a centralized reference collection of fingerprint cards, and thus created the Bureau of Criminal Identification in Washington, DC (21). Two years later, the collection was moved to Leavenworth Federal Penitentiary in order to save money and resources. Satisfied with the collection they already had going with the IACP, police departments and prisons refused to share their fingerprint archives with the Bureau of Criminal Identification (21). This division

between the two repositories proved to be confusing and unproductive at times, but that did not prevent further advancements from being made in the realm of fingerprinting in the United States.

After many years of using fingerprints to identify criminals in America, fingerprint evidence was finally ruled as admissible in the United States in 1911 (22). On September 19, 1910, Clarence Hitler was shot and murdered by an intruder. Later that night into the next morning, a man by the name of Thomas Jennings was found wandering outside appearing to be visibly injured. Due to his physical state and the time of day, Jennings was stopped and questioned by the police. After giving conflicting statements, the police searched Jennings and found that he was carrying a loaded revolver. He was immediately arrested and taken to the station. There, police discovered that Jennings had recently been arrested, so his fingerprint card was on file. Jennings's fingerprints were compared to four prints lifted from the scene of Hitler's murder, and four different fingerprint experts found the prints to be a match (23). The fingerprint evidence was found admissible in court since fingerprint evidence has been admitted in Great Britain for many years prior to this case (24). In 1911, Jennings was found guilty, and thus *People v. Jennings* became the first criminal trial in the United States that used fingerprints as evidence, and thus established fingerprints as a reliable source of forensic evidence.

Finally, after years of having multiple fingerprint repositories, an Act of Congress led to the establishment of the Identification Division of the Federal Bureau of Investigation (FBI) on July1, 1924. The fingerprint records from both the Bureau of

Criminal Identification led by the Department of Justice, and the National Bureau of Criminal Identification led by the IACP were combined to form the FBI files (25).

Though establishing one central fingerprint repository proved to make the process of identification by fingerprint more efficient, it was still clear to investigators that the process was very cumbersome. All suspected fingerprint matches had to be compared manually with the fingerprint cards on file, which could take up to hours, or even days. It became apparent to the FBI that they needed an automated system for categorizing, searching, and matching fingerprints. On July 28, 1999, the FBI launched the Integrated Automated Fingerprint Identification System (IAFIS) (26). IAFIS was created to integrate all fingerprint records from state and federal law enforcement agencies, all of which had independent Automated Fingerprint Identification Systems (AFIS) (26). IAFIS proved to be a useful invention since it has the ability to automate latent print search capabilities, electronically store fingerprint images, and electronically exchange fingerprint profiles at any given time (26).

Though IAFIS seemed to be the greatest and final breakthrough in the field of fingerprinting, the need for improvement became apparent as the technological world continued to advance. In 2011, the FBI replaced IAFIS with a new system known as the Next Generation Identification (NGI), which they believed would be a more efficient repository of both biometrical and criminal history information (27). NGI has many new and improved capabilities compared to IAFIS including enhanced fingerprint/latent services, a larger search repository for finger and palm prints, rapid search services on individuals of special concern, notification services concerning individuals in positions of trust (teachers, daycare workers), advanced photo system, facial recognition search, and

enhanced services for cold cases (27). By expanding their services beyond just fingerprints, NGI has proven to be a beneficial addition to the world of criminal investigation and identification. Though NGI focuses on more than just fingerprints, it is still considered the world's most extensive collection of fingerprints with more than 149 million criminal and civil fingerprint profiles as of November 2019 (28).

1.3 Predicting Age, Gender, and Ethnicity from a Latent Print

After years of experiencing overwhelming success using fingerprints as a means of criminal identification, researchers began to wonder if latent prints had more to offer to the world of forensics than just personal identification. Could there be more information to glean from the minute, intricate ridge patterns present in each individual fingerprint? What if there is a fingerprint present at a scene, but no suspect leads? Is there a way to use that fingerprint to narrow the scope of the search? Researchers wondered if a ridge pattern could suggest the sex, ethnicity, or even age of the individual who left the print behind. Further questioning led individuals to even look beyond the pattern that is left behind by a fingertip and look into what is actually causing the print to remain on a given surface. Does the composition of this residue vary among individuals in the same way a ridge pattern does? Could this residue also suggest sex, ethnicity, or age of the owner of the print? These questions opened a new door in the world of fingerprinting and led to the publication of countless studies on these topics. Many of these questions have not yet been definitively answered, and thus the research into this topic continues today.

The idea that fingerprints could be analyzed alone to gain information about the individual who left the print was first presented in 1943 by Harold Cummins and Charles Midlo when they published their book titled "Finger Prints, Palms, and Soles: An Introduction to Dermatoglyphics" (29). Cummins and Midlo believed that we were overlooking the potential of fingerprints by simply using them for individual identification. They were convinced that prints vary fundamentally between races and sexes, and therefore a print could be used to predict the individual who left the imprint in cases where there are no suspects. Of their performed experiments, the one with the most compelling results relates to how fingerprints differ between sexes. Through their studies, Cummins and Midlo determined that female fingerprints contain an average of 2.7 ± 0.09 more ridges than male fingerprints (29). This was the first discovery made that could possibly lead to the ability to characterize fingerprints based on gender.

From the time Cummins and Midlo's book was published, a multitude of studies were performed in an effort to support or refute their hypothesis made in regard to how fingerprint ridge density relates to gender. The most compelling and most frequently referenced article relating to this topic surfaced in 1999. This experiment, performed by Mark Acree, examined the fingerprint ridge pattern density in order to determine whether this characteristic could distinctively tell the gender of an individual. Acree, based on Cummins and Midlo's results, hypothesized that women have finer epidermal ridge detail than men, and thus would have a higher ridge density (30). To perform this study, Acree examined 400 randomly selected 10 print cards, 100 being of Caucasian male origin, 100 of African American male origin, 100 of Caucasian female origin, and 100 of African American female origin. A 25 mm^2 box was drawn in the same place of every fingerprint,

and the number of epidermal ridges were counted. The results were averaged, and Acree concluded that a dermal ridge count of 11 ridges/25 mm^2 or less is more likely than not of male origin, while a ridge count of 12 ridges/25 mm^2 or more is more likely of female origin (30). Thus, with this study, Acree was able to prove his own hypothesis while also supporting the previously published results of Cummins and Midlo. Acree's experiment helped re-ignite the fire started by Cummins and Midlo, prompting researchers to look further into fingerprints beyond just using prints to prove the identity of individuals.

Mark Acree's results were expanded upon in 2018 by Mukesh Kumar Thakar, Parveen Kaur, and Tina Sharma in their study titled "Validation Studies on Gender Determination from Fingerprints with Special Emphasis on Ridge Characteristics" (31). This experiment aimed to either support or refute Acree's results using his same experimental procedure, but also using subjects of a different race. By doing this, if their results reflect those of Acree, it would further support that the difference in ridge density is due to gender, regardless of the race of the subject. In the present study, 400 fingerprints were collected from the northern population of India – 200 from male individuals, and 200 from female individuals (31). Using the same analyzation method as Acree, it was determined that the mean ridge density of females is 13.94 ridges/25 mm^2, whereas it is 12.32 ridges/25 mm^2 in males (31). This result supports that of Acree and backs the overall conclusion that females generally have greater fingerprint ridge density compared to males, regardless of race or origin.

Though the scientific studies relating fingerprint ridge density to gender produced comparable results, even more studies were being conducted to determine if gender could be determined from a fingerprint using different aspects of the print. In 2015, a study

performed by Crystal Huynh and others investigated whether the composition of the sweat left behind by a fingertip could be used to determine the gender of the originator (32). In this study titled "Forensic Identification of Gender from Fingerprints," the investigators argue that since sweat contains varying amounts of metabolites produced by the human body, and metabolism acts as a function of gender, the metabolites present in the sweat left behind in a latent fingerprint could thus be used to determine gender (32). Based on previously published studies that amino acid levels in humans can differ based on gender, the investigators decided to narrow the scope of their study and only investigate amino acid content. In a previously reported study, it was concluded that the concentration of each individual amino acid found in sweat is greater in females than in males (33). Based on this, Huynh and others hypothesized that the gender of a fingerprint could be determined from the ultraviolet (UV) radiation absorbance of the fingerprint residue, since amino acids are known to absorb UV radiation (32). Using both mimicked and actual fingerprint samples from both males and females, the absorbance of the sweat residue was measured. Overall, the absorbance of female originated fingerprints was greater than that of males with an absorbance threshold of 0.439 (32). Thus, based on these results, if an unknown fingerprint has an absorbance greater than 0.439, it can be assumed it originated from a female, and if the absorbance is less than 0.439, it can be assumed that the print originated from a male (32).

The bulk of relevant studies into whether gender, race, ethnicity, or age of an individual could be determined from their latent fingerprint alone emerged from 2014 to 2019. In 2014, a study performed by Satyajit Shetage and others aimed to collect and analyze the residue that resides on human skin to determine whether or not this residue

contains information that could suggest one's gender, ethnicity, and age. Knowing that there is a superficial layer of sebum, sweat, debris, and natural moisturizers on the surface of everyone's skin, they hypothesized that the components of this mixture would vary in specific ways based on age, gender, and ethnicity (34). To perform the study, the 'residual skin surface components' of 315 volunteers of varying race, age, and gender was collected on cigarette paper and analyzed by gas chromatography mass spectrometry (GC-MS) (34). They were able to identify 49 different residual skin surface components from the sebum provided by the volunteers; however, it was concluded that there was no significant difference in the quantity of these components based on gender, age, or ethnicity (34). Though this experiment did not reveal any significant results, the authors still believed that there was potential in this area of study and encouraged others to keep investigating this topic.

Another study similar to the one previously discussed was carried out in 2016 by Zhenpeng Zhou and Richard Zare. Since sebaceous secretions are mainly composed of fatty acids and other lipids, the authors of this study decided to analyze the difference between the lipid composition in the sweat left behind by volunteers' fingertips (35). Fingerprint samples from 194 individuals of varying ethnicity, gender, and age were collected and analyzed using desorption electrospray ionization mass spectrometry imaging (DESI-MS) (35). DESI-MS proved to be an optimal instrument to use because it not only provided images of the fingerprint ridge patterns, but also chemical maps of the components of the sebum. In order to determine the age, sex, and ethnicity of unknown fingerprint samples, a set of known samples were first applied to a machine learning algorithm. Once the model was trained using the known standards, the unknown samples

were fed through and the machine predicted the three parameters. The model was able to predict the gender, ethnicity, and age of the originators of the fingerprint samples with 89.2%, 82.4%, and 84.3% accuracy, respectively (35). These results were pivotal in this field of study since relatively accurate results were able to be obtained using a simple experimental method.

Another study conducted by Nichole Fournier and Ann Ross emerged in 2016 which also focused on how fingerprints could be used to differentiate sex and ethnicity. This experiment differs from the other two in the fact that the authors chose to analyze the actual ridge pattern of the fingerprints rather than the components of the residual sebum left behind by a fingertip. Fournier and Ross chose to focus on second level detail which refers to the shape, direction, and orientation of individual ridges – also referred to as minutiae points (36). To conduct the study, 243 nail-to-nail rolls of the right index finger from ten print cards randomly selected from a local database were analyzed for bifurcations, ridge endings, short ridges, dots, and enclosures (36). After performing statistical analyses of the second level detail data, it was determined that the effect of sex on second level detail is insignificant, while the effect of ancestry is significant (36). Much like the previous study, a statistical model was created using known standards. From these standards, it was concluded that African Americans are 5.61 times more likely to have bifurcations than European Americans (36). Based on this, when an unknown print is fed into the model and analyzed for total bifurcations, the model can predict the ancestry of the individual that the print belongs to. However, after continued research with the model, it was determined that there is an error rate of about 42% when predicting the ethnicity of the print originator (36). The authors believe that this study

could be strengthened in the future by investigating whether the minutiae that form are impacted by the location on the fingerprint (near the center, near the edges, etc.). Though this experiment did not produce reliable results, it inadvertently suggests that perhaps it is more beneficial to analyze the sebum left behind by fingerprints rather than the ridge pattern itself in order to gain more information about the person who left the print behind.

During the time in which this area of study began to expand, researchers also decided that it would be helpful to develop a way investigators could determine the age of a fingerprint itself. When fingerprints are found at a crime scene, it could be difficult to determine which ones are relevant to the crime itself. For example, if the crime scene is someone's house, the print could have been placed by anyone who has been in the home at any point in time and could potentially be of no importance to the investigation. Determining the age of the fingerprint would be especially helpful in cases where the fingerprint cannot be immediately connected to an individual based on the ridge pattern. Before the print is carried through any of the previous processes mentioned (or any processes of this sort) to try to determine the possible age, gender, or race of the suspect who left the print, it would be of interest to find out whether or not the print is even connected to the recent crime. If a crime occurred at the scene within the past couple hours, it would be a waste of both time and resources to analyze a print that was deposited days or even weeks prior to the offense. To avoid this issue, researchers have attempted to develop a method to determine how long a latent print has been sitting on a surface.

The first significant proposal regarding this topic was made in 2012 by Ronny Merkel and his research group. Merkel and his team examined fingerprints using a non-

invasive Chromatic White Light (CWL) sensor and captured both 2D-intensity and 3D-topography images through the sensor to determine whether or not these images could be used to estimate the age of a latent print (37). Over 40,000 fingerprint images taken with the CWL sensor and time differences were analyzed based on 17 different features. It was determined that the binary pixel feature was the most representative of the aging of the fingerprint (37). This feature is based on the loss of contrast of a fingerprint when examined via a 2D-intensity image captured by a CWL light sensor (37). The study concluded that 2D fingerprint images captured with the CWL sensor and examined based on the binary pixel feature can be placed into two time classes – [0, 5 hours] and [5, 24 hours] – with 79.29% accuracy (36). Though the authors did not believe that this method alone could reliably predict the age of a latent fingerprint, it still proved to be a compelling method of age determination that could possibly be combined with newer methods in the future to yield more definite results.

By 2015, there was still not an existing process that could be used to accurately estimate the age of a latent fingerprint. Researchers Shin Muramoto and Edward Sisco aimed to change this fact using time-of-flight secondary ion mass spectrometry (TOF-SIMS). The two investigators proposed that the age of a fingerprint could be determined by examining the extent of surface diffusion of biomolecules (specifically palmitic acid) within the print over time (38). Fingerprints from volunteers were collected on silicon sheets and examined for palmitic acid content using TOF-SIMS after 1, 24, 48, 72, and 96 hours (38). They concluded that the content of palmitic acid in latent fingerprints follows a power function over a 96-hour time interval (38). Therefore, based on Muramoto and Sisco's work, the age of a latent print found at a crime scene can be

determined by analyzing the palmitic acid content via TOF-SIMS, as long as the fingerprint was deposited within the past 4 days.

In a recent study performed in 2019, Anna Czech and others examined not only the content of the latent print sebum, but also the friction ridge pattern in order to determine the age of the print. The research team collected fingerprints from 200 volunteers and analyzed the prints under a microscope 5 hours, and 7, 30, 60, and 90 days after they were deposited (39). After comparing images taken through the microscope at these time intervals, the researchers concluded that the width of the friction ridge impressions gradually decreased by 7.3%, 6.7%, and 0.14% between the first four time intervals (39). To their surprise, the width of the ridges actually increased by 3% between the last two time intervals, but this discrepancy was explained by an unforeseen increase in the temperature of the room during the last week of the study, causing any remaining fatty substances to 'melt' and spread out (39). They also found that the amount of sweat and sebum also decreased over time, first becoming evident at the 30-day mark. Between day 7 and 30, the amount of sweat and sebum decreased by 28% and then continued to decrease by 25% and 40% between the last two time intervals (39). Based on these results, it is possible to estimate the age of a fingerprint at a crime scene when compared to other prints found at the scene. When two prints are compared, if one has significantly less sebum and smaller ridge widths, it can be assumed that the prints were deposited at very different times, and thus the print with less sebum and smaller ridges can be ignored.

1.4 Detection of Exogenous Particles in Latent Prints

As the possibilities of what a fingerprint has to offer beyond direct criminal identification started to expand, researchers also began to wonder if a fingerprint could be analyzed to determine information about the suspect that is not necessarily indicative of their appearance. As previously discussed, investigators in the field of fingerprints have been able to successfully develop methods that could help narrow a suspect search based on personal physical aspects such as gender, age, and ethnicity. Other studies relating to the potential information that a latent print holds investigated whether a fingerprint could be used to determine other properties that do not necessarily provide a physical description of the suspect. These studies focused more on the exogenous particles that may be present on a print such as explosives, drugs, cosmetics, or other pieces of trace evidence. Researchers believed that the detection of such particles could help develop a 'lifestyle profile' of the suspect to help refine the search when a suspect is not immediately known, or could make a partial or smeared print that is found at a scene useful since it cannot be used for personal identification.

Trace evidence has been a crucial aspect of criminal investigation since Edmond Locard declared his iconic exchange principle in 1934. Edmond said, "Toute action de l'homme, et a fortiori, l'action violente qu'est un crime, ne peut pas se dérouler sans laisser quelque marque," which translates to "Any action of an individual, and obviously the violent action constituting a crime, cannot occur without leaving a trace" (40). We have seen this idea applied to criminal cases countless times. The paint found on the jacket of a victim of a hit and run being matched to the paint of the suspect's car. A fiber found on a homicide victim being matched to a rug in the suspect's home. Soil found on a

murder victim's clothes being matched to soil found in the treads of the tires of the suspect's vehicle. Since trace evidence has proven to successfully solve a countless amount of criminal cases throughout history, investigators began to wonder if the ideas behind trace investigation could be combined with latent print analysis.

In a study conducted by Nicole Crane and others in 2007, the researchers aimed to develop a method of latent print visualization that would also preserve any trace evidence present (41). Common latent print visualization techniques include powder dusting, cyanoacrylate (superglue) fuming, iodine fuming, silver nitrate soaking, and ninhydrin dipping. All of these techniques involve the latent print being coated with some form of material, thus making it nearly impossible to recover any sort of trace evidence that may be present within the print. Based on this, Crane and her team decided that Fourier transform infrared (FTIR) spectroscopic imaging would be the best method to use in order to both visualize the ridge pattern of the print along with any possible trace evidence (41). To conduct the experiment, volunteer fingerprints were deposited on various surfaces including trash bags, soda cans, tape, paper, cigarette butt paper, dollar bills, and postcards (41). These latent prints were then visualized using FTIR spectroscopic imaging alone. The prints placed on all of these substrates were able to be visualized using this method (41). In addition to collecting a clear image that could be used to evaluate the ridge pattern of the prints, the FTIR image of the fingerprint of the postcard revealed an unknown blue fiber that could not be seen by the naked eye (41). This specific case showed the importance of this method since this fiber would not have been found otherwise. If the fingerprint were developed using any of the common visualization techniques, it is likely that the fiber would have been dusted away or

covered with the developing substrate. The results of this paper proved that using a non-invasive imaging technique, such as FTIR spectroscopic imaging, could be of significant value in criminal cases in order to gather more information from a latent print beyond just the ridge pattern.

Expanding the scope of trace evidence that could be found on a latent print, researchers found it important to develop a method that would be able to detect explosive particles within fingerprints for a few different reasons. First, if a fingerprint is found at a crime scene associated with arson, and it is discovered that the print contains particles of the explosive used during the crime, it helps support the conclusion that the owner of the print most likely committed the crime. Second, if an arson crime is committed and there is only circumstantial evidence pointing to a suspect, that suspect's fingerprint could be collected and analyzed for the same explosive used at the arson scene to help establish a more solid connection of the suspect to the crime. Third, if there are no prime suspects, but a specific explosive could be detected in the latent print, this information could be used to help guide the suspect search based on previous offenders who committed similar crimes with the same explosive.

With these things in mind, Yongyan Mou and Wayne Rabalais began brainstorming ways in which explosive particles could be detected in latent prints. The two aimed to develop a method that would not destroy the fingerprint. This way, if a suspect is determined after the print has been analyzed for explosives, the print could still be used for identification by ridge pattern. In 2008, the duo published their study in which they detected explosive particles in fingerprints using attenuated total reflection Fourier transform infrared spectromicroscopy (ATR-FTIR) (42). In this experiment,

volunteers handled one of three common explosives (trinitrotoluene, trinitrobenzene, or ammonium nitrate), pressed their fingerprint onto a stainless-steel surface, and then the prints were analyzed using ATR-FTIR. The proper explosive was able to be positively identified in each of the analyzed prints (42). They also found that although the instrument does touch the fingerprint during analyzation, the ridge patterns remained undisturbed, and thus the method can accurately be categorized as nondestructive (42).

Another nondestructive method for detecting explosive particles in latent prints was developed in 2014 by Kimberly Kaplan-Sandquist and her research team. In this study, fingerprints that have been in contact with explosives were analyzed for the presence of trinitrotoluene (TNT) and royal demolition explosive (RDX) using matrix assisted laser desorption ionization time of flight mass spectrometry (MALDI-TOF-MS) (43). To prepare the fingerprint samples, first individual solutions of the TNT and RDX were created by dissolving 2500 ng of the explosive in a water and methanol solution, adding enough to dissolve the explosive powders (43). Three different volumes (1, 5, and 10 μL) of the explosive solutions were then deposited onto glass slides and allowed to dry, leaving only solid particles behind (43). Volunteers were then instructed to touch the dried residue and then place their fingerprint on a clean aluminum-coated slide (43). Each volunteer provided a set of 4 latent prints for each of the 3 different concentrations for both explosives. Each set of 4 prints from both explosives was analyzed by MALDI-TOF-MS after the prints were developed using one of four processes: dusting with fingerprint powder, super glue (cyanoacrylate) fuming followed by dusting with fingerprint powder, dusting with fingerprint powder followed by lifting, and spraying with a α-cyano-4-hydroxycinnamic acid (CHCA) MADLI matrix (43). Both explosives

were able to be detected in each of the fingerprints using MALDI-TOF-MS, regardless of the concentration of the explosive or the developing process used (43). It is also important to mention that this was able to be done without destroying the ridge pattern on any of the latent prints. The results of this experiment proved to be pivotal in this area of study since the explosives were able to be detected even after the prints had been developed using three different common crime scene methods. This is important because many prints are not found at a scene until after they have been developed with either a dusting powder, superglue fuming, or being lifted with lifting tape. Since this method can still detect the explosive particles after all three of these development processes, it makes the method much more applicable to real life scenarios and thus is more likely to actually be implemented in crime labs than other methods that do not work after a print has been visually developed.

Following the same mentality and reasoning as to why it could be helpful for crime scene investigators to be able to detect the presence of explosives in a fingerprint, researchers argued that it could also be beneficial to develop a method to detect cosmetic particles in a latent print. Not every crime is arson related, and thus the situations in which methods for detecting explosive particles in latent prints can be used are limited. Are there other exogenous particles that may be present on someone's fingertip that are more universal than explosives? Humans touch so many different things every day, so what should the experiments start with? Though it is difficult to make an overarching statement for all of mankind, it's easy to believe that one thing all people come in contact with multiple times a day is themselves. People are constantly touching their body,

namely, their face. This is what led investigators to decide to limit the scope of their exogenous latent print studies to cosmetics.

Camilla Ricci and Sergei Kazarian decided to investigate the potential of being able to detect cosmetics in latent fingerprints. They followed the assumption that most people touch their face multiple times a day, and thus are likely to have particles present on their fingertips of whatever product they may have applied to their face that day (44). Much like Mou and Rabalais, they wanted to develop a method that would not destroy the ridge pattern of the print, and thus came to the same conclusion that the best method to use is attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) (44). Ricci and Kazarian came to the conclusion that two commercial products that are likely to be on someone's face include face cream and makeup foundation. They split their volunteers into two groups and instructed one group to apply a L'Oréal face cream and the other to apply a Lancôme foundation (44). The volunteers then washed their hands and individually had their fresh prints analyzed on the ATR crystal. Everyone then wiped their fingertip over their forehead and again had their prints individually analyzed on the ATR crystal (44). IR spectra of both the face cream and the foundation were also collected for comparison purposes. After analyzing all of the IR spectra obtained, it was determined that for each sample collected, there were characteristic spectral features of the face cream and foundation present in the respective spectra from contaminated prints that were not present in the spectra of the fresh prints (44).

To further their experiment, Ricci and Kazarian decided to analyze cosmetic products for the body that are potentially used more often than face products. These products included Dove body lotion, Boots body butter, and a serum cream (brand not

listed) (44). Using the same procedure described above, the IR spectra of the volunteers' fresh prints were compared to the IR spectra of the products alone and the corresponding spectra from contaminated prints. Once again, they found that there were characteristic spectral features present in the spectra of the products and the corresponding spectra of contaminated prints that were not present in the spectra from fresh prints (44). These results support the hypothesis that ATR-FTIR could be used to detect the presence of cosmetics in latent fingerprints. This could be beneficial in cases where the ridge pattern cannot be matched to a certain individual and different evidence must be used to suggest that the print originated from a specific suspect. If it could be proven that the suspect uses the cosmetics found in the print, one could argue that the latent print analyzed was deposited by that suspect.

As the field of exogenous particle study within latent prints continued to expand, many investigators hopped on this research trend focusing specifically on drug analysis. Researchers found potential value in being able to detect drug particles in latent prints for the same reasons as to why it would be helpful to be able to detect particles of cosmetics or explosives. In cases where a fingerprint is found but no suspects have been developed, the presence of drug particles could help investigators develop a 'lifestyle profile' of the offender they are looking for which would assist the search process. Also, as discussed with explosives and cosmetics, the ability to be able to detect drug particles on a latent print would make smeared or partial prints useful for investigative purposes. Most of the successful published studies focusing on this topic have used matrix assisted laser desorption/ionization mass spectrometry (MALDI-MS), and the results from just four existing studies using this instrument will be analyzed and discussed.

One of the first experiments examining latent fingerprints containing drug particles using MALDI-MS was performed by Frederick Rowell, Katherine Hudson, and John Seviour in 2009 (45). The study first aimed to determine whether the method would work by analyzing clean fingerprints that were spiked with a codeine standard after deposition, and after analyzing fingerprints that were deposited after the volunteer handled different drugs including codeine, diacetylmorphine, or opium (45). To further the study, 20 fingerprints were placed onto surfaces already spiked with diacetylmorphine, and each print was dusted with a commercial fingerprint visualization powder to determine whether the powders would negatively or positively affect the MALDI-MS results (45). In the portion of the study that focused on codeine spiked fingerprints, half of the prints were only treated with a conventional MALDI matrix, 2,5-dihydroxybenzoic acid (DHB), and the other half of the prints were dusted with a commercial hydrophobic silica powder. Once analyzed by MALDI-MS, it was determined that the codeine was positively identified in each of the spiked prints, regardless of whether the print was dusted or simply sprayed with the DHB MALDI matrix (45). In the portion of the study that analyzed fingerprints deposited by volunteers who had been in contact with drugs, all the prints were dusted with a commercial hydrophobic silica powder, and then half were subsequently lifted using a standard adhesive tape (Cellotape). Once analyzed by MALDI-MS, it was determined that all three drugs were able to be identified, however, the intensity of the peaks on the spectra were weaker for the lifted prints (45). Finally, in the portion of the study where spiked prints were dusted with 20 different commercial powders, the diacetylmorphine could only be detected by MALDI-MS in 4 of the prints (45). The successful powders include two that

contain carbon black, a fine iron powder, and the hydrophobic silica powder that was also used in the first two studies (45). Overall, this experiment yielded a lot of compelling results that show that MALDI-MS can successfully detect exogenous drug particles in latent prints, even if the print has already been dusted by crime scene investigators.

In 2013, Latha Sundar and Frederick Rowell conducted an experiment that also aimed to evaluate the ability of MALDI-MS to detect drug particles in fingerprints that have already been visualized for ridge pattern analysis. In their study, they focused specifically on prints that were developed using cyanoacrylate through a process commonly known as superglue fuming (46), and/or have been dusted with black magnetic fingerprint powder. Volunteers were instructed to handle a mixture of five drugs – aspirin, paracetamol, caffeine, cocaine, and methadone – and then place their fingerprint on a glass slide, or directly onto a MALDI target plate. The latent prints were then treated in one of four ways: cyanoacrylate developed and dusted with the magnetic powder, cyanoacrylate developed and dusted with DHB MALDI matrix, only dusted with the magnetic powder, or only dusted with the DHB MALDI matrix (46). All the fingerprints that were deposited on glass slides were subsequently lifted using fingerprint lifting tape (this was not done for prints placed directly on the MALDI plates), subjected to an acetone vapor treatment, and analyzed using MALDI-MS (45). All prints, regardless of the surface they were deposited on or how they were treated before MALDI-MS produced spectra that confirmed the presence of the 5 drugs (46). The results of this study confirmed those of the prior study discussed showing that dusted prints can be analyzed by MALDI-MS for the presence of drug particles. This experiment

expanded upon the previous one discussed by also showing that this method can be used to detect drug particles in latent prints that have been developed using cyanoacrylate.

The previously discussed study conducted by Kimberly Kaplan-Sandquist and her team which attempted to detect explosive particles in latent prints using MALDI-MS also took a look at exogenous drug particles. Fingerprint samples were prepared using the same method described for the detection of explosive particles (see page 24 for reference), this time using procaine and pseudoephedrine (43). Both drugs were able to be detected in each of the fingerprints using MALDI-TOF-MS, regardless of the concentration of the explosive or the developing process used (43). This study also investigated whether drug particles could be detected in a latent print after brief contact with whole and broken tablets of acetaminophen, aspirin, and ibuprofen. Volunteers were instructed to briefly hold a given whole tablet to mimic the process of normally ingesting a pill, and then place their fingerprint on a glass slide (43). Tablets were then split in half, and the broken surface was dabbed once on the volunteer's fingertip before depositing their print on a glass slide (43). Similar to the first portion of the study, volunteers provided a set of 4 fingerprints for each drug in each of the two forms (whole or broken tablet), and each print in a set was developed using one of the following development processes: dusting with fingerprint powder, super glue (cyanoacrylate) fuming followed by dusting with fingerprint powder, dusting with fingerprint powder followed by lifting, and spraying with a α-cyano-4-hydroxycinnamic acid (CHCA) MADLI matrix (43). The prints were then analyzed by MALDI-TOF-MS, and the results showed that none of the target drugs were able to be detected in any of the samples (43). Overall, the results continued to support the conclusion that MALDI-MS has the power of detecting drug

particles in latent prints when the drugs are in the form of a powder. However, this study also proved that this method has limitations since it cannot detect drug particles in a print after casual contact with whole or broken tablets.

Researcher G. Groeneveld and his team assessed the compatibility of MALDI-MS for latent print drug detection with yet another fingerprint development process in a study conducted in 2015. The team decided to analyze drug contaminated fingerprints that have been developed with either cyanoacrylate fuming, which has been previously studied, or vacuum metal deposition, which has not previously been investigated for this purpose (47). To prepare fingerprint samples, first a 10 μg/mL stock solution of each drug of interest was prepared (47). Next, 50 μL aliquots of each solution were deposited on individual glass slides and allowed to dry until all the solvent was evaporated (47). Volunteers were then instructed to run their fingertip back and forth repeatedly on the drug residue to transfer as much of the drug analyte as possible, and then place their fingerprint on an aluminum sheet (47). Each volunteer contributed two prints that had been contaminated with each of the following drugs: amphetamine, cocaine, THC, and heroin (giving 8 prints total) (47). For each drug, one print was developed using cyanoacrylate fuming, and the other was developed using vacuum metal deposition. All of the latent prints were then analyzed using MALDI-MS. The results show that all of the drugs were able to be positively identified in the fingerprint samples, regardless of how the prints were initially developed (47). However, it is important to note that the prints that were developed using the vacuum metal deposition produced spectra with more intense signals, showing that the chemicals used for the development process actually enhance the performance of MALDI-MS (47). This study proved to be significant since

the results continued to support the conclusion that drug metabolites can be detected in cyanoacrylate developed latent prints, and it also became the first published study to show that it is possible to detect drug particles in latent prints developed using vacuum metal deposition.

As the investigation into if and how exogenous particles could be detected in latent fingerprints continued to evolve, some researchers began to question the practicality of this area of study. How probative is this type of evidence? Researchers became interested in this topic once it was realized that a fingerprint found at a crime scene is useless if the ridge pattern cannot be matched to a suspect, whether it is due to the lack of a suspect, the ridge pattern being smudged, or only recovering a portion of the print. It was hypothesized that there must be other things present in the print that could provide some additional information. This sparked the idea to study exogenous particles within the latent print. Though it has been proven that it can scientifically be done, can it really help investigators when searching for a suspect? Imagine a scenario in which explosive particles are found on a smeared print in which the ridge pattern was not able to be recovered. Once a suspect is generated, how is that information going to help? It is unlikely that the suspect would still have explosives on his or her hands at the point of apprehension. It is also very possible that the explosive is no longer in his or her possession. This scenario reflects the main concern of critics of this particular type of study: longevity.

1.5 Detection of Endogenous Drug Particles in Latent Prints

The previously stated issues constitute what pushed researchers in the direction of endogenous drug studies. All of the previous experiments discussed only examined scenarios in which people came in physical contact with explosives, cosmetics, trace evidence, or drugs. None of the studies reflected scenarios in which particles that were excreted by the originator of the fingerprint were analyzed. Focusing on particles that are present in the sweat that was directly excreted from the fingertip and subsequently left on a surface to create a latent print is arguably more beneficial due to the fact that the particles stemmed from within the perpetrator's body. This is what led researchers to begin investigating if it is possible to detect traces of drugs that have been ingested and subsequently excreted from the body in the form of sweat and deposited on a surface from a fingertip. If this can be done, it would prove to be much more applicable to real world scenarios since drug particles can remain in the body for days, or even weeks. Therefore, if a drug is detected in a smeared or partial print, and a suspect is later developed, that suspect can be tested for that drug to possibly form an association between the suspect, the print, and the crime scene.

One of the first endogenous drug studies on latent fingerprints was performed in 2007 by Richard Leggett and his research team. They aimed to detect nicotine metabolites in latent prints using antibody-functionalized gold nanoparticles (48). The gold nanoparticles were engineered to possess multiple anti-cotinine antibodies on their surface. Cotinine is a metabolite of nicotine, and thus if the nanoparticles are added to the surface of a latent print deposited by a nicotine user, the antibodies on the nanoparticles should interact with the cotinine antigens in the sebum of the print. Fingerprints were

obtained on glass slides from volunteers who admitted to smoking 5-7 cigarettes a day (48). The anti-cotinine nanoparticles were then added to the fingerprints, given time to bind to the cotinine particles in the print, and then the excess nanoparticles were washed away (48). In order to visualize the nanoparticles on the print, a fluorescently tagged secondary antibody fragment (designed to form a conjugate with the nanoparticles) was added to the fingerprint, incubated, and washed to remove any excess (48). After collecting fluorescent images of the prints, it was determined that the nanoparticles successfully bound to the cotinine particles in the latent prints, and thus proved that this method could be used to detect drug metabolites in latent prints (48).

Though the experiment conducted by Leggett and his team yielded viable results, it quickly became clear that this would not be a practical experimental method to use in the crime lab for this purpose. This is mainly because the method is not universal to all the possible drugs that could be detected in a fingerprint. Individual nanoparticles would have to be engineered to contain antibodies against every common drug and drug of abuse. This is not practical in terms of time and resources. This method is also not practical for situations in which investigators are trying to determine what drugs may be present in the print because in order for the antibodies to react with the particles in the print, the investigator must have some prior knowledge as to what drug may be present in order to apply the correct nanoparticles. This completely defeats the purpose of trying to discover what may be present in the print that was not previously known. With these realizations in mind, researchers continued to brainstorm to devise a simpler, more universal method that can be applied to any latent print recovered from a crime scene.

One of the experiments focusing on exogenous drug particles that was previously discussed actually also included a small endogenous drug study. Frederick Rowell and others showed that it is possible to detect exogenous drug particles in latent fingerprints that have been already dusted and/or lifted using MALDI-MS (see page 28 for reference) (45). After finding these results, they decided to use the method they developed to determine whether or not it could also be used to detect drug metabolites that had been excreted from the body in latent prints. The fingerprint of a volunteer who had been taking oral methadone tablets was collected and analyzed by MALDI-MS (45). The resulting spectra showed a peak for both methadone and its major metabolite known as EDDP (45). Though they only acquired the results from one fingerprint, this small experiment showed that there is value in conducting further research into this topic. The fact that the major metabolite of methadone was able to be detected was significant because EDDP can only be formed in vivo, and thus proves ingestion of the drug rather than just casual contact with the drug (45). Such information could prove to be very useful if a case is brought to court.

As researchers began conducting experiments solely dedicated to endogenous drug detection in fingerprints, many of them chose to investigate whether this can be done using liquid chromatography mass spectrometry (LC-MS). In 2014, Ting Zhang and others aimed to discover if methamphetamine and its main metabolite could be detected in the latent prints of abusers using LC-MS (49). The latent print residue from ten drug abusers was collected on cotton swabs. This was done by first having the volunteers deposit their fingerprints on a clean, smooth surface (such as glass or metal), swiping the area where the print was placed with a moistened cotton swab 60 times, and performing

an ultrasonic extraction in methanol (49). The methanol solution was then centrifuged, and the supernatant was analyzed using LC-MS. The results show that both methamphetamine and its major metabolite, amphetamine, were able to be detected in the residue from the fingerprints of all 10 drug abusers, except for 1 print which only showed a peak for methamphetamine (49). The team decided to also analyze fingerprint residue from 10 drug-free volunteers using the same process to act as a blank or negative control (49). As expected, the resulting spectra did not show any peaks for methamphetamine or amphetamine (49).

Another study that was published around the same time as the previous one discussed also evaluated the ability of LC-MS to detect endogenous drug metabolites in latent prints. In this experiment, Kenji Kuwayama and his team chose to analyze a cold medicine that contains a mixture of drugs: ibuprofen, dihydrocodeine, chlorpheniramine, and methylephedrine (50). Volunteers who had not taken any medicines for 2 weeks were administered one dose of S. Tac Eve-Ace, a Japanese cold medicine (50). Their fingerprints were collected on previously wetted filter paper 9 hours, and 1, 2, 3, 4, and 7 days after the medicine was taken (50). The analytes from the fingerprints were analyzed by centrifuging the filter paper in a solution of methanol and water and injecting the supernatant into the LC-MS instrument (50). The results show that dihydrocodeine, chlorpheniramine, methylephedrine, as well as a metabolite of the methylephedrine (ephedrine), were able to be detected in all of the prints collected, except for dihydrocodeine 7 days after drug administration (50). Ibuprofen was not able to be detected in any of the prints collected from the volunteers (50). This could perhaps stem from the amount of ibuprofen present in the medicine in comparison to the other drug

analytes, or it could be that this detection method is not suitable for the detection of ibuprofen – a definite conclusion cannot be drawn after the completion of just one experiment (50).

Both previous LC-MS studies discussed highlight the advantages and disadvantages of using this instrument to identify endogenous drug particles in latent fingerprints. Compared to the gold nanoparticle method, LC-MS is much more practical because it requires less materials, less preparation, less resources, and the process remains the same regardless of the drug being identified. Though this method is more practical than using engineered gold nanoparticles, it is still not very applicable to real life scenarios. This is mainly due to how the samples must be collected. In the second study discussed, fingerprints were collected on wetted filter paper. This is not reflective of how latent prints are found at a crime scene. In the first study, fingerprints were swiped 60 times with a cotton swab in order to analyze the contents of the fingerprint sebum. At the scene, fingerprints are normally developed for visualization, photographed, and lifted with tape. If the fingerprint needs to be destroyed in order to analyze the particles in the print, then investigators only have photographs of the print to use for personal identification. This is not an ideal situation for crime scene investigators. It is preferred to have identifications made from actual lifted prints since it is easier for photographs to be tampered with. Also, if the original print has been collected for further testing and thus destroyed, there is nothing to fall back on in the event that the picture gets inadvertently deleted, or the quality ends up not being high enough to make an identification. After realizing these issues, researchers made the very necessary transition into developing nondestructive methods for analyzing the drug content of latent prints.

In an effort to develop a reliable, nondestructive method for this purpose, Melanie Bailey and her research team decided to investigate three instruments they thought would yield accurate results. In their study, they aimed to detect cocaine and two of its metabolites (benzoylecgonine and methylecgonine) in latent prints using desorption electrospray ionization mass spectrometry (DESI-MS), matrix assisted laser desorption ionization (MALDI-MS), and secondary ion mass spectrometry (SIMS) (51). Fingerprints were collected on glass slides from 5 volunteers who had been attending a drug and alcohol rehabilitation program (51). For DESI and SIMS, no further sample preparation was needed before the prints could be analyzed. For MALDI-MS, the prints only had to be spotted with a α-cyano-4-hydroxycinnamic acid (CHCA) MADLI matrix before being analyzed. Once all of the prints were analyzed, it was determined that MALDI-MS was able to detect benzoylecgonine in all of the tested prints, and DESI was capable of detecting benzoylecgonine and methylecgonine (51). Although SIMS was able to detect a fragmentation ion that is similar to cocaine, benzoylecgonine, and methylecgonine (82 m/z), this could not be considered a positive result since this is also a common fragment found in many other drugs of abuse (51). This experiment made a huge impact in this field of study since it proved the potential of not one, but two different methods that can be used to detect endogenous drug metabolites in latent fingerprints without destroying the print or disturbing the ridge pattern.

This really just scratches the surface of all of the research that has been conducted relating to using fingerprints to determine more personal information about the individual that a ridge pattern cannot provide. Whether it be in an attempt to discover more physical attributes of the suspect, such as age, ethnicity, or gender, or to try to uncover some trace

evidence, such as explosives, cosmetics, or drugs, to help find a suspect of a crime based on their lifestyle or possessions. Though this field of study has been investigated for years producing a countless amount of published studies, this does not mean that there is no more additional research that can be done. Many of the studies analyzed have gaps in the conclusions, are outdated in terms of the technology and instrumentation used, or use methods that are not conducive to current crime scene investigation protocol. While conducting my extensive literature research, I found that the area of study that would benefit most from improvement falls under the idea of analyzing latent fingerprint residue for the potential presence of drugs and their metabolites that have been consumed or handled by the suspect.

CHAPTER 2: DETECTING AND IDENTIFYING EXOGENOUS DRUG PARTICLES IN LATENT PRINTS USING MALDI-MS, ATR-FTIR, AND LC-MS

2.1 Introduction

The majority of published studies focusing on detecting drug particles in latent prints examined exogenous drug particles. This means that the fingerprints analyzed were created to simulate situations in which someone has come in physical contact with a drug and then subsequently deposited their fingerprint on a surface shortly after. Though there are many studies that have been published that gathered viable results, it is important in science to ensure that the results of an experiment are repeatable. For this reason, an exogenous drug study of latent prints was conducted using matrix assisted laser desorption ionization time of flight mass spectrometry (MALDI-TOF-MS) – the most frequently reported method used for this purpose. In order to expand upon the exogenous studies that already exist, latent prints were also analyzed for exogenous drug particles using attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) and liquid chromatography mass spectrometry (LC-MS). The ATR-FTIR method has already been proven to work for exogenous detection of explosive and cosmetic particles in latent prints, so this method was tested to determine if it can also be applied to exogenous drug particles. Similarly, LC-MS has been proven to be able to detect endogenous drug

particles in latent prints, and thus this method was tested to see if it can be applied to exogenous scenarios as well.

2.1.1 MALDI-TOF-MS

Mass spectrometry is an analytical method that is used to determine the identity of a sample, or the identity of multiple components within a sample based on their mass. Mass spectrometry works by ionizing a sample, determining the mass to charge ratio (m/z) of the molecules in the sample, and then determining the identity of the molecules based on the m/z values presented in the produced spectrum (52). MALDI-TOF-MS is a mass spectrometry technique that uses a specific method of ionization and a specific analyzer to determine the identity of a sample. MALDI refers to the ionization technique which employs the use of a laser, and TOF refers to the mass analyzer of the mass spectrometer. MALDI is a soft ionization technique that does not cause major fragmentation of the sample particles being analyzed; it simply charges the molecules by either adding or removing a proton (53). To analyze a sample using MALDI-MS, the sample is first mixed with a crystal forming matrix, spotted on a plate, and allowed to dry to form a crystal (53). The formation of the crystal helps disperse the laser energy – if a crystal does not form, the sample would fragment too much due to the intensity of the laser energy. Once the sample is dry, it is placed into the sample compartment of the instrument where it is blasted with a laser. The laser energy triggers ablation and desorption of the sample and matrix molecules, creating a hot gaseous plume of the molecules. Since the matrix absorbs most of the energy, the matrix molecules will be more readily ionized. In the plume, the analyte molecules are ionized by proton transfer

from the matrix molecules, and then they are accelerated by an electric field towards the mass analyzer.

In this case, the mass analyzer is known as time of flight (TOF). The TOF analyzer is under vacuum and does not contain an external electric field, allowing the ions to drift through the analyzer powered only by the kinetic energy obtained from the laser (54). As the ions travel through the chamber, those with a smaller m/z values travel faster compared to those with greater m/z values. As the ions exit the analyzer, they reach a detector where the m/z is determined. Since this is a soft ionization technique, the molecules should have been ionized by simple proton transfer and therefore have a +1 or -1 charge. The identity of the molecules can then easily be determined from the peak with the largest m/z value since this represents the molecular ion of the analyte and thus will have a value nearly identical to the molar mass of the molecule (should be either +/- 1 due to ionization). The spectrum as a whole can also be referenced against a standard library to determine the identity of the molecule since a molecule's mass spectrum never changes – it is considered to be molecules 'fingerprint'. A general schematic of how MALDI-TOF-MS works is shown below in **Figure 1**.

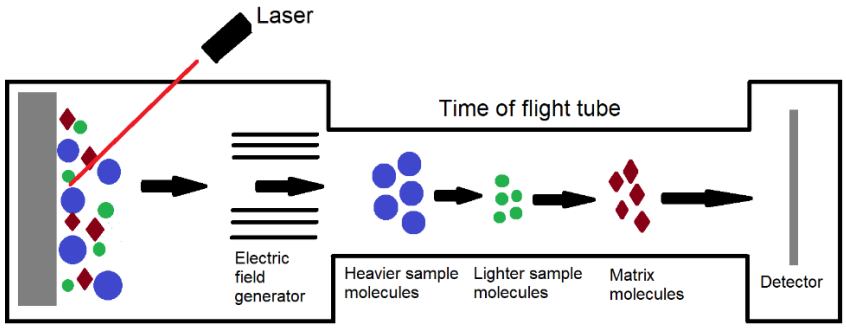

Figure 1: A schematic diagram of a MALDI-TOF-MS system

2.1.2 ATR-FTIR

Infrared spectroscopy is used to determine the identity of a molecule based on its structure. Infrared spectroscopy uses light from the infrared portion of the electromagnetic spectrum to manipulate the vibrational states in a molecule in order to gather specific information about it. When IR radiation is absorbed by a molecule, it transitions from a ground vibrational state to an excited one. In order for a molecule to absorb IR radiation, it must experience a net change in dipole moment, and the energy from the radiation must exactly match the energy difference between the ground and excited states. Each bond in a molecule reacts differently upon absorbance of the infrared energy due to unique vibrational states. Based on this idea, IR spectroscopy makes it possible to determine specific bonds and functional groups within the molecule by measuring the absorbance of the infrared energy as a function of frequency. This is done using a spectrometer.

When a sample is placed in a spectrometer, it is exposed to infrared radiation and subsequently absorbs this radiation. The spectrometer detects the energy and amount of radiation that is being absorbed and uses this information to construct an IR spectrum of the sample. This spectrum is a plot of absorbance or transmittance versus wavenumbers (inverse centimeters) with a range of about 4,000 to 200 wavenumbers. A peak will appear on the spectrum at a specific wavenumber if the sample absorbed the IR radiation at that specific energy value. Each peak represents a specific vibration that was occurring in the molecule as that radiation was absorbed. Every compound has a unique spectrum that is considered its IR ‘fingerprint’. Therefore, if an unknown sample is analyzed with

IR spectroscopy, the peaks present on the IR spectrum can be used to determine the unknown compound.

Fourier Transform Infrared Spectroscopy is a method of infrared spectroscopy that uses a Michelson interferometer; this is the main difference between FTIR and regular, dispersive IR (55). The Michelson interferometer splits the beam of light into two different beams which are directed towards mirrors. After reflecting off the mirrors, the light beams return to the interferometer where it recombines the beams and sends the collective beam towards the sample. Though FTIR splits the radiation beam, it does not split it into separate wavelengths. This allows all wavelengths to interact with the sample at the same time which in turn allows for multiple scans of a sample to be performed in a shorter time. FTIR also uses less mirrors than dispersive IR, allowing more light to reach the detector which leads to better results.

Attenuated Total Reflectance (ATR) is a sampling technique that accompanies FTIR. In ATR, the IR beam is passed through a crystal that has a high refractive index (56). The high refractive index causes the beam to reflect back into the crystal instead of passing through; this is known as total internal reflection. As the beam bounces back and forth within the crystal, energy is absorbed by the sample, which is placed directly onto the ATR crystal. Any radiation that is not absorbed by the sample is reflected and sent to the detector. The detector then produces a spectrum based on the radiation that was absorbed by the sample, and this spectrum can then be used to determine the identity of the components within the sample. A general schematic of how ATR-FTIR works can be seen below in **Figure 2**.

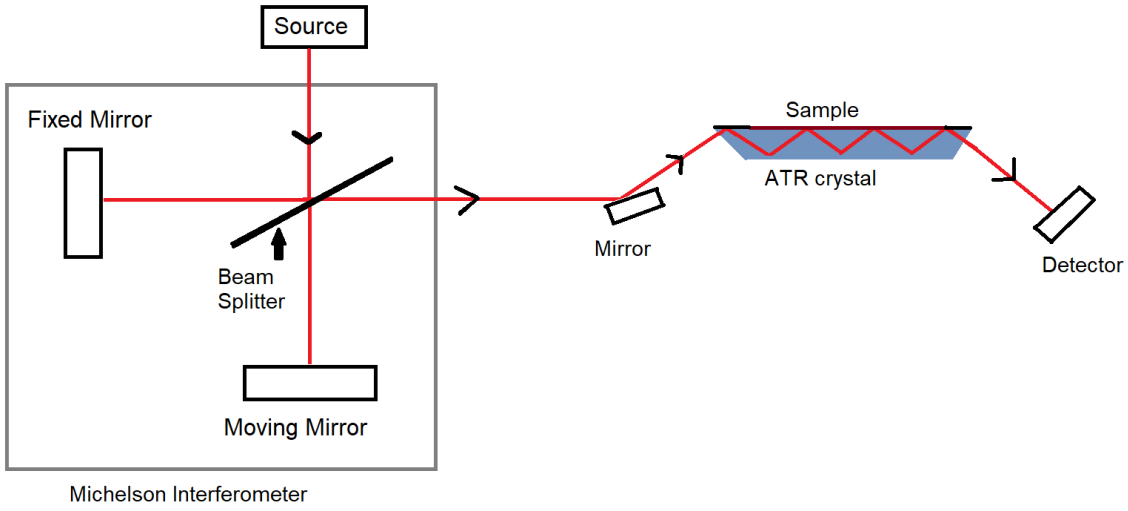

Figure 2: A schematic diagram of an ATR-FTIR system

2.1.3 LC-MS

Liquid chromatography mass spectrometry (LC-MS) pairs two different techniques in one instrument: chromatography and mass spectrometry. As previously discussed in the MALDI-MS section, it is known that mass spectrometry is used for identification of analytes. Chromatography is a scientific technique used to separate the components of a mixture. Separation makes identification of samples by mass spectrometry easier since only one compound will be analyzed at a time. In any chromatographic technique, there is a stationary phase contained in a column, and a mobile phase that travels through the column (57). The mobile phase is a solvent that helps carry the sample through the stationary phase. The stationary phase can be made of a solid, a liquid, or a liquid supported on a solid. As the mobile phase carries the sample through the column, components of the sample will interact with the stationary phase. Different components will interact with the stationary phase for varying amounts of time,

causing the separation of the mixture. Components that have a stronger interaction with the stationary phase will travel more slowly through the column compared to components with a weaker interaction, and thus will elute from the column at a later time (57). When a component reaches the detector, it produces a peak on a plot corresponding with the time of elution and amount of the component that eluted. This plot of time versus relative abundance is known as a chromatogram. The chromatogram and corresponding mass spectra can then be used to determine which components correspond to which peaks. A general schematic of how LC-MS works can be seen below in **Figure 3**.

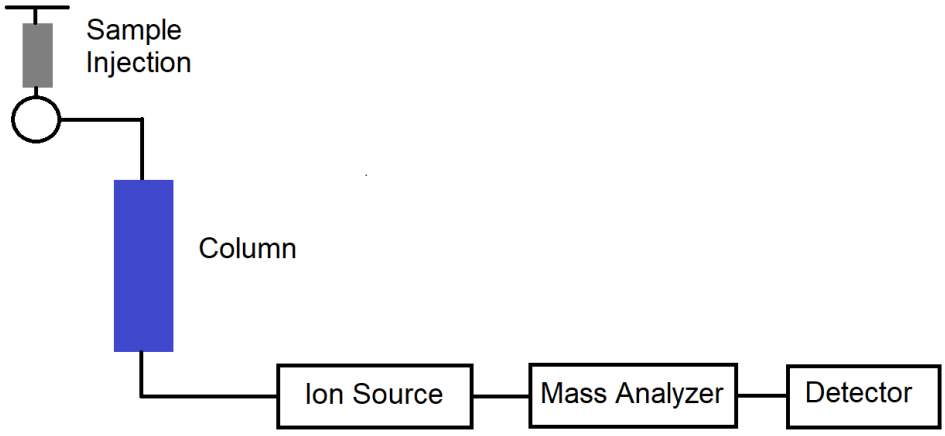

Figure 3: A schematic diagram of an LC-MS system

In liquid chromatography, the sample must be analyzed in the liquid form. In some cases, a solid can be analyzed using liquid chromatography as long as it can be dissolved in a liquid solvent. For this experiment, fingerprint samples were collected and subsequently washed using a solvent to create samples that can be analyzed using LC-MS. The potential benefit of using LC-MS for the detection of exogenous particles in

latent prints is the separation aspect. There are many different components that may be excreted from the body and subsequently deposited on a surface in the form of a fingerprint. Using LC-MS will help separate the target analyte from these components, making the mass spectrum easier to read and ensuring only the analyte of interest is being analyzed.

2.2 Materials and Methods

The selected target drugs used to carry out each of these studies were acetaminophen, ibuprofen, and acetylsalicylic acid (ASA). Generic tablets were purchased over the counter from a drug store in the following dosages: 500 mg acetaminophen, 200 mg ibuprofen, and 325 mg ASA. These common drugs were chosen as the target analytes due to their availability and their frequent use in real life scenarios. Though it could be helpful to be able detect drugs of abuse in latent prints, it may not translate well to actual crime scene investigations since they are not as frequently used as over the counter drugs.

For each of the three methods investigated, the same general sample preparation was used. First, tablets of ASA, ibuprofen, and acetaminophen were individually ground up into a powder using a mortar and pestle. Volunteers were then asked to wash their hands, place their fingertip in the powder of just one of the drugs, and then place their fingertip on the desired surface (fingerprint lifting tape or quartz glass slide, depending on the instrument used). Beyond the general sample preparation, there were unique steps

that had to be taken for each instrument before the samples could be properly analyzed. These steps are discussed in the following sub-sections.

This experiment was approved by the Institutional Review Board (IRB), all volunteer participation was voluntary, and the identity of all of the volunteers remained anonymous throughout the duration of the experiments.

2.2.1 MALDI-TOF-MS

For this portion of the study, volunteer fingerprints were collected on fingerprint lifting tape. Each subject provided three fingerprints, each individually contaminated with either acetaminophen, ibuprofen, or ASA. To prepare the samples for analysis by MALDI-TOF-MS, the pieces of fingerprint tape were individually dissolved in 10 mL of methanol. An aliquot of the solution was then spotted onto a MALDI plate and allowed to dry before being sprayed with a MALDI matrix. The matrix consisted of either α-cyano-4-hydroxycinnamic acid (CHCA) or 2,5-dihydroxybenzoic acid (DHB) (two common MALDI matrices) that has been dissolved in a 50:50 methanol/water solution with 0.1% trifluoroacetic acid (TFA). Once the matrix was allowed to dry, the samples were analyzed by MALDI-TOF-MS. Samples were first prepared using the MALDI matrix containing DHB rather than CHCA because literature shows that DHB results tend to have a higher intensity and accuracy in terms of analyte detection (58,59). For each of the samples analyzed, there were specific instrument parameters used based on the drug analyte present in the print. For samples containing acetaminophen, the instrument was set to positive ion mode and the sample was electrosprayed at a voltage of 2800 with a

flow rate of 1 µL/min. For samples containing ibuprofen, the instrument was set to negative ion mode and the sample was electrosprayed at a voltage of 2500 with a flow rate of 1 µL/min. Finally, for samples containing ASA, the instrument was set to negative ion mode and the sample was electrosprayed at a voltage of 2400 with a flow rate of 1 µL/min. Each resulting mass spectrum was the sum of 5 laser shots that were taken from random spots on the MALDI target plate. The specific instrument used for this experiment was a Voyager DE PRO MALDI-TOF-MS.

2.2.2 ATR-FTIR

For this portion of the study, volunteer fingerprints were collected on quartz glass slides. Quartz glass slides were used as opposed to fingerprint lifting tape because quartz does not absorb IR radiation and thus will not interfere with the results. Each subject provided three fingerprints, each individually contaminated with either acetaminophen, ibuprofen, or ASA. No additional sample preparation was needed before the samples could be analyzed by ATR-FTIR. For each sample, the quartz glass slide was simply placed on the ATR platform. The ATR-FTIR performed 48 scans of each sample from 4000 to 400 cm^{-1} with a fixed spectral resolution of 4 cm^{-1}. The specific instrument used for this experiment was a Bruker IFS-66 FTIR spectrometer with an ATR attachment.

2.2.3 LC-MS

For this portion of the study, volunteer fingerprints were collected on fingerprint lifting tape. Each subject provided three fingerprints, each individually contaminated with

either acetaminophen, ibuprofen, or ASA. To prepare the samples for analysis, the pieces of fingerprint tape were individually dissolved in 10 mL of methanol. LC-MS vials were prepared containing a 100 µL aliquot of each individual sample. The sample vials were then analyzed by LC-MS. The mobile phase used was acetonitrile, the stationary phase used was a C_{18} column, and the samples were analyzed using isocratic elution. The LC parameters consisted of an injection volume of 1 µL, an oven temperature of 50 ºC, and a column temperature of 250 º

LC-MS was also used to perform a quantitative study. To do this, a calibration curve was constructed for each curve which was then used to determine the concentration of the respective drug present in subject latent print samples. First, standard solutions of acetaminophen, ibuprofen, and acetylsalicylic acid were created in the following concentrations: 1, 5, 10, 25, 50, 100, 150, 200, and 250 mg/mL. A 100 µl aliquot of each of these standard solutions was then transferred to an LC-MS vial and analyzed on the instrument using an isocratic elution. Next, the area under the curve for the analyte peak in each chromatogram was determined and recorded. Finally, a calibration curve for each drug was constructed by plotting the area under the curve versus concentration, and a line of best fit was applied to the data points. Volunteers then provided three more latent print samples on fingerprint lifting tape, each individually containing acetaminophen, ASA, or ibuprofen. Once again, each sample was washed with 10 mL of methanol. A 100 µL aliquot from each sample was transferred to an LC-MS vial and analyzed on the instrument using an isocratic elution. The specific instrument used for the LC-MS studies was a LC-MS 6120 Single Quad Agilent.

2.3 Results and Discussion

2.3.1 MALDI-TOF-MS

Using DHB as the matrix, acetaminophen and ibuprofen were able to be detected (**Figures 4 & 5**). However, ASA was not able to be detected in any of the samples analyzed. It was concluded that perhaps ASA is not compatible with the DHB matrix that was used to prepare the samples. Based on this idea, new samples containing ASA were produced using CHCA as the matrix. Changing the matrix proved to solve this issue since the ASA was able to be detected in the new samples (**Figure 6**). In the resulting spectra for each sample analyzed, the top spectrum corresponds to the background and matrix, and the bottom spectrum shows the fingerprint sample obtained from a volunteer. In each sample spectrum, the peak that originates from the target analyte is denoted with a star, and the peak that originates from the matrix is denoted by an arrow. Based on the molecular masses of the three drugs, the peaks appear as expected. The molecular masses of acetaminophen, ASA, and ibuprofen are 151, 180, and 206 g/mol, respectively. In the provided results, the analyte peak appears at 152.44 m/z for acetaminophen, 181.94 m/z for ASA, and 206.34 m/z for ibuprofen. Through comparison with the matrix/background spectra, it can be concluded that each of these peaks represents the respective drug being present in the latent print analyzed since the peaks do not show up in the spectra of the matrix/background alone. The results provided by the remaining volunteers produced similar spectra. All samples analyzed contained the correct corresponding analyte peak.

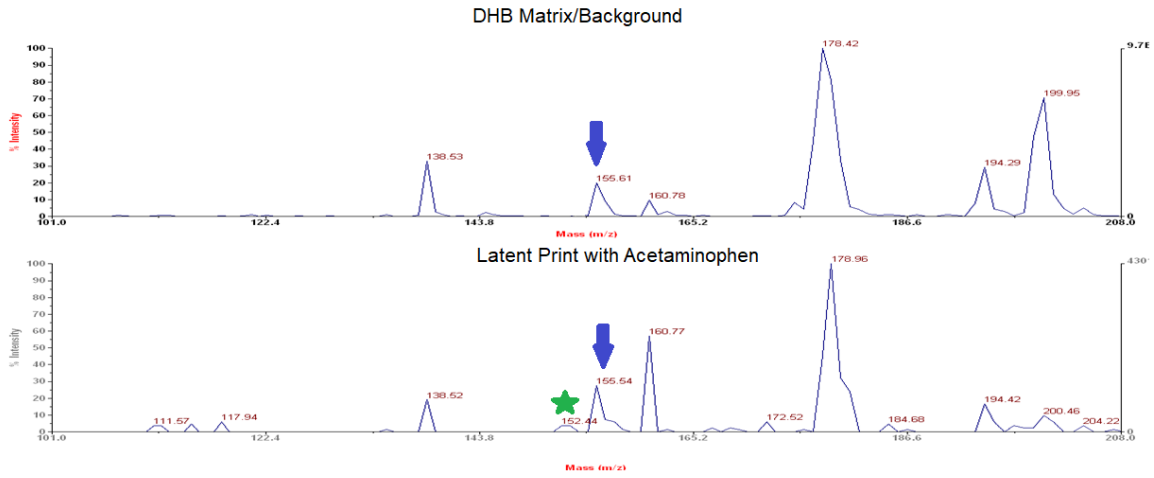

Figure 4: MALDI-TOF-MS results of DHB matrix alone (top) and a latent print containing exogenous acetaminophen (bottom)

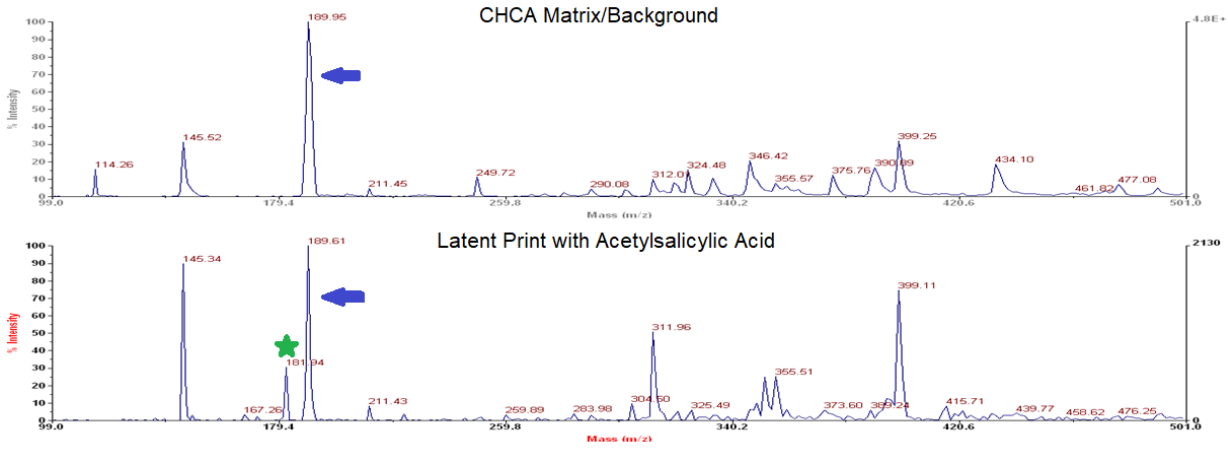

Figure 5: MALDI-TOF-MS results of CHCA matrix alone (top) and a latent print containing exogenous acetylsalicylic acid (bottom)

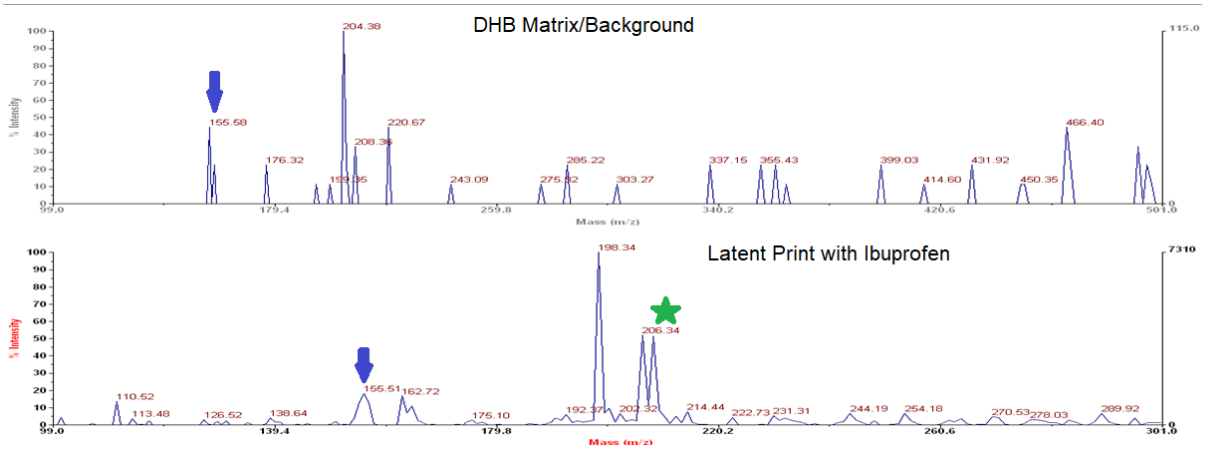

Figure 6: MALDI-TOF-MS results of DHB matrix alone (top) and a latent print containing exogenous ibuprofen (bottom)

The results of this experiment reflect the results obtained in the previously discussed studies that also evaluated the use of MALDI-MS for the detection of exogenous drug particles in latent prints. Therefore, based on the results collected, as well as previously published results, it can be concluded that MALDI-TOF-MS is a viable method for the detection of exogenous drug particles in latent fingerprints.

2.3.2 ATR-FTIR

This study was conducted multiple times, and each time viable results were not collected. The spectra produced were either unreadable due to the intensity of the background noise, or the target analytes were not able to be detected. On the fourth trial, a clear spectrum was obtained from the latent print samples containing ASA and acetaminophen. Below, **Figure 7** shows the spectra obtained from ASA only, and **Figure 8** shows the spectra obtained from the ASA contaminated print. In both figures, the

wavenumber of peaks characteristic of ASA, based on what has been previously published in literature, have been circled in green (60). There are 13 total peaks that are common among the two spectra presented and the spectra of previously published results for ASA. This is sufficient to conclude that ATR-FTIR was able to be used to correctly identify the target analyte for this sample. Similarly, **Figure 9** and **Figure 10** show the obtained spectra of acetaminophen alone, and the acetaminophen contaminated print. Again, the wavenumber of peaks characteristic of acetaminophen, based on what has been previously published in literature, have been circled in green (61). There are 13 total peaks that are common among the two spectra presented and the spectra of previously published results for acetaminophen. Thus, this is enough information to conclude that ATR-FTIR was able to correctly identify the target analyte for this sample as well.

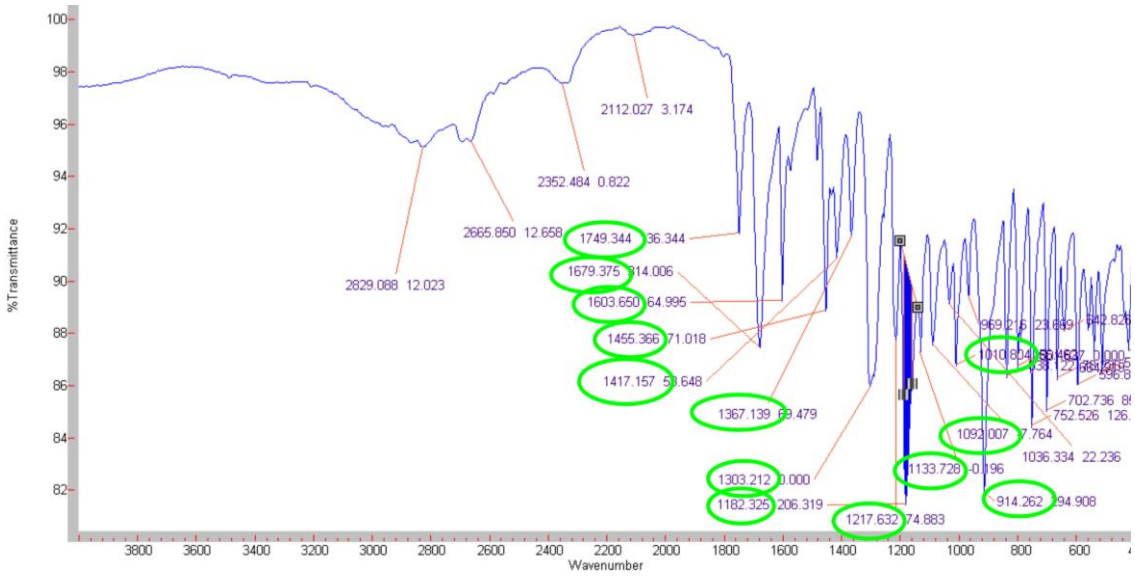

Figure 7: ATR-FTIR results of acetylsalicylic acid

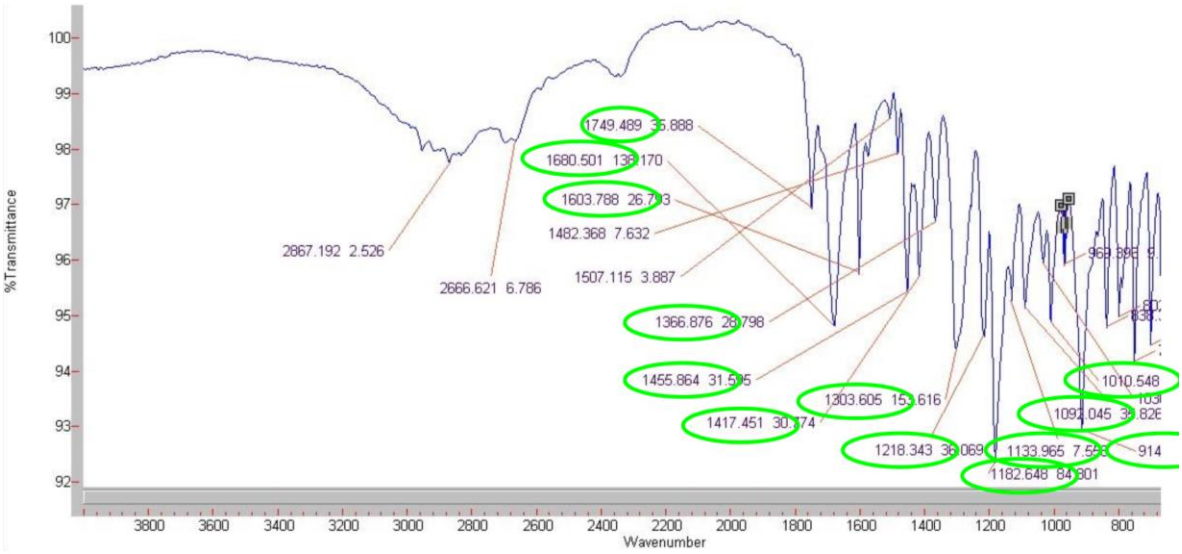

Figure 8: ATR-FTIR results of a latent print containing exogenous acetylsalicylic acid

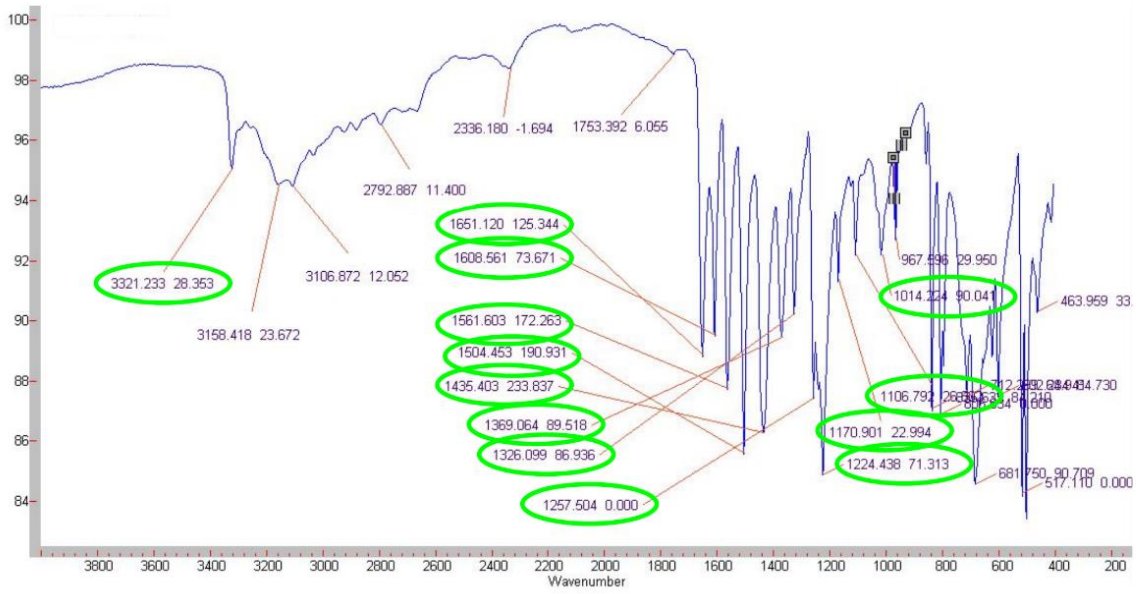

Figure 9: ATR-FTIR results of acetaminophen

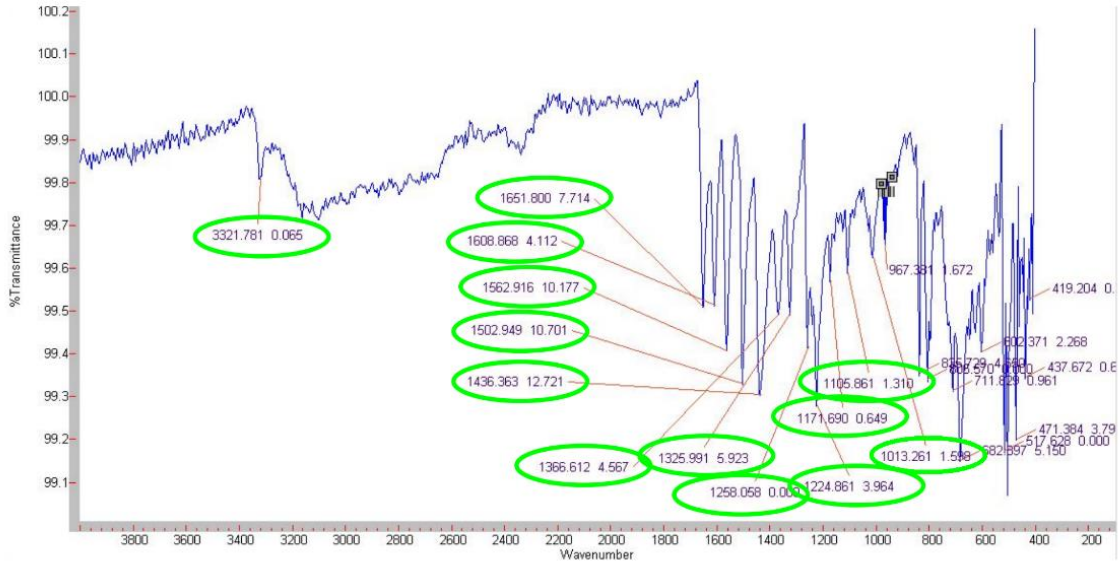

Figure 10: ATR-FTIR results of a latent print containing exogenous acetaminophen

Since only two of the volunteer samples analyzed by ATR-FTIR yielded accurate results, it was concluded that ATR-FTIR is not a reliable method for the detection of exogenous drug particles in latent prints. For the two samples that produced a clear spectrum, it is likely that the volunteer used more pressure when placing their finger in the ASA powder, thus depositing a print that was more saturated compared to the rest. Though this led to clear, accurate results, this is not representative of most real-life scenarios. It is unlikely for a perpetrator to have an abundance of drug powder on their fingertips while committing a crime. Since it is not likely that a fingerprint would be found under optimal conditions at most crime scenes, it was concluded that ATR-FTIR is not a suitable method for the detection of exogenous drugs in latent prints.

Unlike the MALDI-MS results from the previous experiment discussed, the ATR-FTIR results obtained do not match the results from previously published studies that also

used this method. The two experiments that were previously discussed used ATR-FTIR to detect exogenous particles of explosives and cosmetics in latent prints, both of which were successful. This could be due to the amount of analyte present in the prints, or the substrate the prints were placed on. For the explosive experiment, prints were placed onto a stainless-steel surface; for the cosmetic experiment, prints were placed directly onto the ATR crystal. Though both of these sample collection methods were able to produce accurate results, they are not reflective of everyday scenarios. Obviously, there is no way for a latent print found at a crime scene to be directly placed on the ATR crystal. Though stainless steel is a common surface, it is not as common as glass, plastic, or paint. All of these surfaces would absorb IR radiation and thus would not be able to be suitable for ATR-FTIR analysis. Overall, though ATR-FTIR can be used to detect exogenous particles in latent prints in some scenarios, the study conducted shows that it will only give viable results under optimal conditions. Optimal ATR-FTIR analysis conditions would require the print to be deposited on a surface that does not absorb IR radiation and the print containing a high concentration of the target analyte.

2.3.3 LC-MS

First, the results from the initial qualitative study will be discussed. In each of the contaminated latent print samples, the resulting mass spectra show that the correct target analyte was able to be detected by LC-MS (**Figures 11-13**). When cross referenced with the built-in spectral library, the correct drug was able to be identified for each sample.

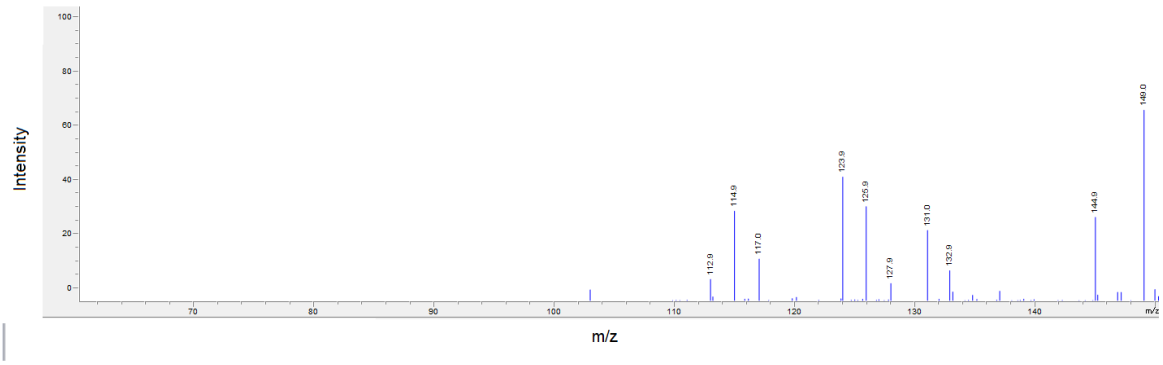

Figure 11: LC-MS results of a latent print containing exogenous acetaminophen

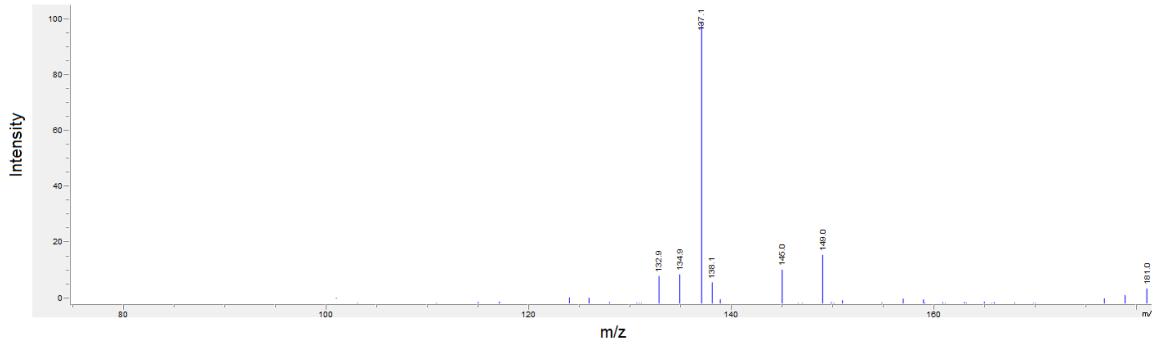

Figure 12: LC-MS results of a latent print containing exogenous acetylsalicylic acid

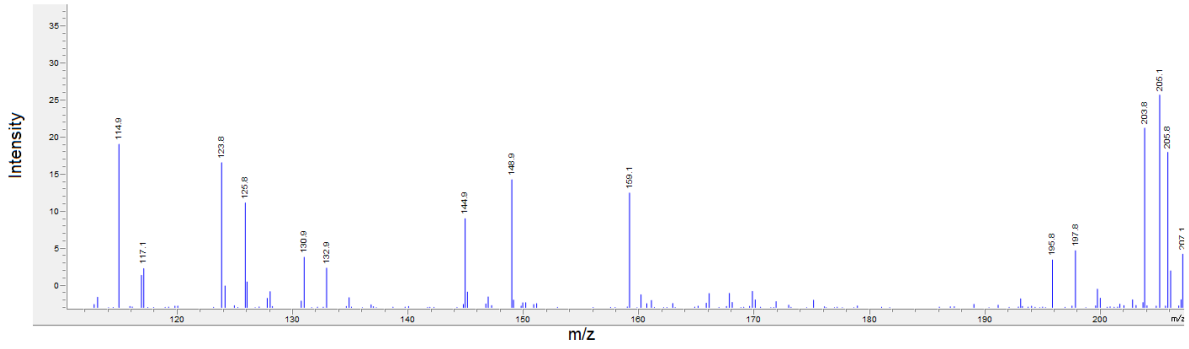

Figure 13: LC-MS results of a latent print containing exogenous ibuprofen

Next, the results for the quantitative portion of the study will be discussed. Before the drug concentration in each of the latent print samples could be determined, calibration curves for each drug had to be constructed. Below, **Figure 14, Figure 15**, and **Figure 16** show the calibration curves for acetaminophen, acetylsalicylic acid, and ibuprofen respectively.

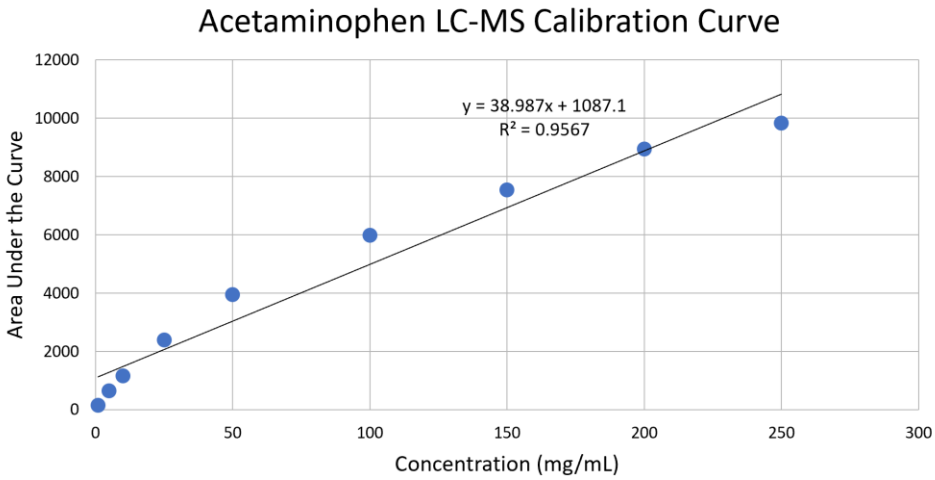

Figure 14: Acetaminophen LC-MS calibration curve

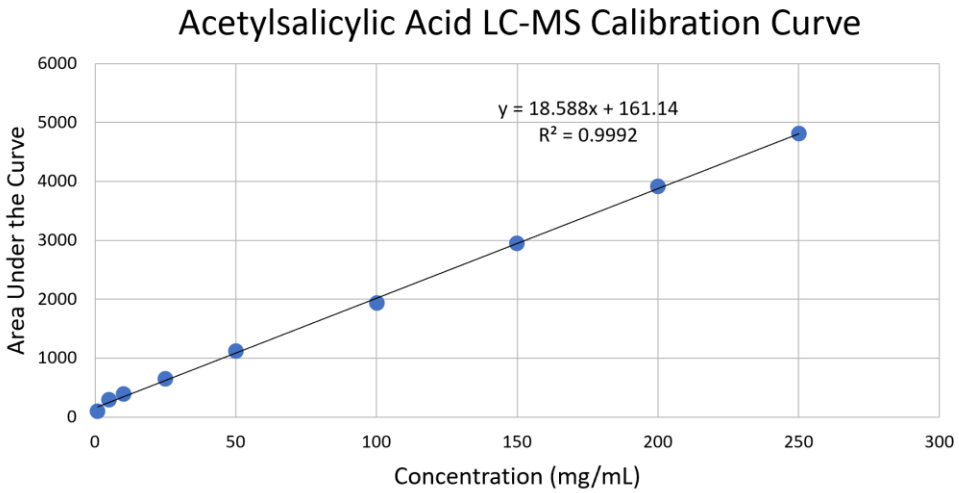

Figure 15: Acetylsalicylic acid LC-MS calibration curve

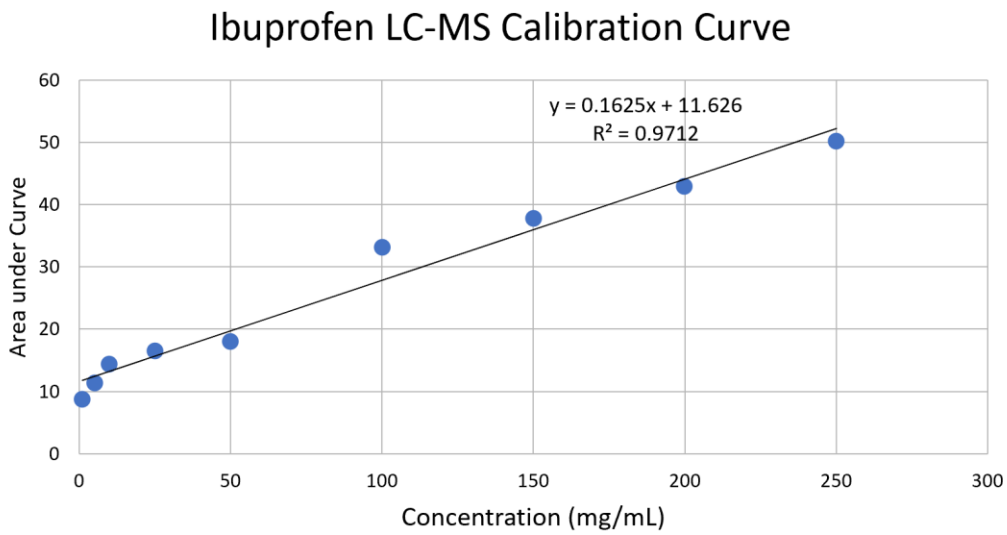

Figure 16: Ibuprofen LC-MS calibration Curve

By analyzing the mass spectra from the latent print samples, it was confirmed that the correct analyte was identified in each sample. Next, the area under the curve for the analyte peak in each chromatogram was determined and recorded. These values, along with the equation for the line of best fit from the calibration curve of the corresponding drug, were used to determine the concentration of drug present in each latent print sample. To do this, the value for the area of the curve was plugged in as the y-value in the equation for the line of best fit for the respective drug, and the equation was then solved for the x-value. This value gives the calculated concentration of drug analyte present in the latent print sample in mg/mL. The results for each drug in order of volunteer (volunteer 1, volunteer 2, then volunteer 3) are as follows: 1.224, 2.632, and 2.201 mg/mL of acetaminophen, 38.886, 35.579, and 40.534 mg/mL of acetylsalicylic acid, and

136.054, 13.667, and 150.246 mg/mL of ibuprofen. These results are summarized below in **Table 1**.

Drug Concentration of Volunteer Latent Print Samples (mg/mL)

	Acetaminophen	Acetylsalicylic Acid	Ibuprofen
Volunteer 1	1.224	38.886	136.054
Volunteer 2	2.632	35.579	13.667
Volunteer 3	2.201	40.534	150.248

Table 1: Calculated drug concentration (in mg/mL) of latent print samples analyzed by LC-MS

The previously discussed published studies relating to LC-MS analyzed endogenous drug particles in latent prints rather than exogenous particles. The results of this study performed show that LC-MS can accurately detect exogenous drug particles in latent prints, thus building upon the results of previously published experiments. This is pivotal because the combined results from all of the studies show that this one instrument can be used for multiple applications in respect to latent print analyzation. So, when a latent print cannot be used for personal identification and must be analyzed for other forms of evidence, LC-MS can safely be used to determine whether or not there are endogenous or exogenous drug particles present. Limiting the amount of tests the print is run through reduces the time and resources needed for analysis, both of which are very valuable in a crime laboratory.

This experiment not only showed that exogenous drug particles can be detected using LC-MS, but the concentration can also be quantified. By calculating the drug concentration in each print, it was easier to determine the range that this instrument has for this purpose. The lowest drug concentration detected was 1.224 mg/mL, and the highest concentration detected was 150.248. This shows that LC-MS has a greater potential for detecting exogenous drug particles in latent prints compared to other instruments (such as ATR-FTIR) since it is not as limited by the drug concentration present in the print. In the future, this experiment should be repeated, asking volunteers to use less pressure when dipping their fingerprints in the drug powder in order to decrease the drug concentration in the latent print. The same procedure and quantitation process should be used to determine if LC-MS is still capable of detecting and quantifying the drug analyte when the concentration is significantly decreased.

2.4 Conclusions

Though not every method tested produced viable results, overall, the experiments conducted confirm that it is possible to detect exogenous drug particles in latent prints. The majority of published studies used MALDI-MS to investigate this idea and were able to obtain accurate results. These results were confirmed by the present MALDI-TOF-MS study conducted. Research shows that ATR-FTIR has been used to positively identify explosive and cosmetic particles in latent prints. However, when this method was used in an attempt to identify exogenous drug particles, only one of three drugs were detected successfully. After analyzing the published study further, it is likely that positive results were only able to be obtained under specific controlled laboratory conditions. This

showed that although it is possible to get positive results using ATR-FTIR, it may not be the most reliable method to use when applied to scenarios with real crime scene evidence. Finally, LC-MS was investigated to determine if it could be used to detect exogenous drug particles in latent prints. Based on the results of this study, it was concluded that this method can be used for this specific purpose. Literature has already shown that LC-MS can be used to detect endogenous drug particles in latent prints. When combined with the results obtained from the present experiment, it was concluded that this one technique can be used to detect both endogenous and exogenous drug particles in latent prints. This reduces the number of tests a latent print needs to be subjected to in a crime scene laboratory, which saves time and resources. In addition to detecting the correct drug analyte, LC-MS was able to quantify the concentration of drug present in the print. This helped show that the range of the instrument is greater compared to other instruments such as ATR-FTIR. In the future, LC-MS should be investigated further to determine the limit of quantitation of the instrument.

CHAPTER 3: PROPOSED METHODS FOR ENDOGENOUS DRUG IDENTIFICATION IN LATENT PRINTS

3.1 Introduction

Now that it has been confirmed that it is possible to detect exogenous drug particles in latent fingerprints, it's time to focus on endogenous drug studies. Endogenous drug identification differs from exogenous due to the fact that with endogenous studies, you are searching for particles that have been ingested and subsequently excreted by the subject. This means that there will be a significant decrease in concentration compared to exogenous studies. Also, the original drugs may be metabolized by the body resulting in different target analytes. Published studies focusing on this topic have shown that it is possible to detect endogenous drug particles in latent prints using desorption electrospray ionization mass spectrometry (DESI-MS), matrix assisted laser desorption ionization (MALDI-MS), and liquid chromatography mass spectrometry (LC-MS). Secondary ion mass spectrometry (SIMS) was also investigated, but this method was not able to accurately detect the target analytes.

Based on the studies that have already been published, current knowledge about scientific instruments, and the resources and instruments available, it was determined that the instruments that show the most potential for the detection of endogenous drug

particles in latent prints and should therefore be investigated include liquid chromatography tandem mass spectrometry (LC-MS/MS) and direct analysis in real time mass spectrometry (DART-MS). The following sections will 1) describe how the instruments work, 2) discuss how they will be used to detect endogenous drug particles in latent fingerprints, and 3) analyze the advantages and disadvantages of each instrument being used for this specific application.

3.2 Experimental Method

Before the instruments are described, the general experimental process for how these studies would have been carried out will be explained. The first step entails finding suitable volunteers for the study. To avoid having to ask volunteers to consume any drugs, people who take daily oral prescriptions will be sought out. Volunteers would then be asked to place their fingerprint on multiple different surfaces that could potentially be found at a crime scene. This could include paper, glass, metal, wood, etc. The identity of the originator of the fingerprint would remain anonymous, and upon the completion of the study, any remaining latent prints would be destroyed in order to protect the identity of the volunteers. All volunteer participation would be voluntary and in accordance with the Institutional Review Board (IRB). Standards of the drugs that the volunteers consume daily will be obtained and analyzed with each instrument, and the limit of detection and limit of quantitation will be determined on each instrument.

To prepare samples for LC-MS/MS, the prints would be dissolved in 10 mL of methanol and added to individual sample vials. The samples would then be analyzed

using LC-MS/MS with a proper column and mobile phase depending on the polarity of the drugs being analyzed. DART-MS requires no sample preparation, so volunteer fingerprints will simply be collected and analyzed.

3.3 LC-MS/MS

Liquid chromatography tandem mass spectrometry (LC-MS/MS) is nearly identical to traditional LC-MS previously discussed when analyzing exogenous drug particles. The main difference is that this method uses a combination of two or more mass analyzers (62). After the components of the sample are separated by the chromatography column, they are sent to the first mass analyzer to be ionized and identified. In LC-MS, this would be the completion of the analyzation process. However, in LC-MS/MS, this first mass analyzer is programmed to target ions of one particular mass to charge ratio (m/z) and let them pass through to the next mass analyzer. All other particles of a different m/z are unable to pass through to this next step. The molecules then enter the next portion of the instrument which causes further fragmentation. These fragments then travel to a second mass analyzer where only ions of the correct m/z are selected for. These molecules then make their way to the detector where the m/z of each is measured and recorded. The final mass spectrum produced will only show signals that stem from the fragments of the specific molecule that was targeted in the first mass spectrometer. This mass spectrum is much more representative of the molecule analyzed than a spectrum that would have been produced by the traditional LC-MS method.

Tandem mass spectrometry is particularly useful when working with a class of compounds in which many of them share the same general structure. This is true of many drug classes, such as amphetamines. Amphetamines all have the same general structure with added functional groups to set them apart from one another. Therefore, the mass spectra of amphetamines will all have similar m/z peaks in common which could make it difficult to tell one amphetamine from another when looking at their mass spectra. This is where tandem mass spectrometry could be helpful since further fragmentation has the potential to produce vastly different mass spectra for two compounds that initially had very similar mass spectra after only one round of fragmentation.

The instrument that would have been used to carry out this experiment is known as a triple quadrupole since the analyte molecules will make their way through three different quadrupoles in the instrument before being detected. A quadrupole contains four conducting rods that run parallel to one another in a rectangular formation. Opposing rods are electrically connected to one another, and a radiofrequency voltage along with a direct current voltage are applied to each pair of rods. The two sets of rods have opposite polarity, causing an oscillating electric field to be generated in the space between the four rods. This electric field has the ability to filter out ions of a certain mass to charge ratio, and all other ions will become unstable and eventually crash into the rods, never reaching the detector. The applied voltage can be changed in order to select for ions with different m/z values. In a triple quad instrument, three sets of these four rods are placed in tandem to one another. The first quadrupole is a mass analyzer that filters out ions of a certain m/z allowing them to continue to travel through the instrument. The second quadrupole is a collision cell that causes the ions to bump into and interact with each other, causing

further fragmentation. These fragments then make their way to the last quadrupole which is also a mass analyzer. Here, the ions of a desired m/z are filtered out and sent to the detector. The end result is a clear mass spectrum that only contains m/z values from the fragments of interest. A general schematic of an LC-MS/MS instrument with a triple quadrupole analyzer can be seen below in **Figure 17**.

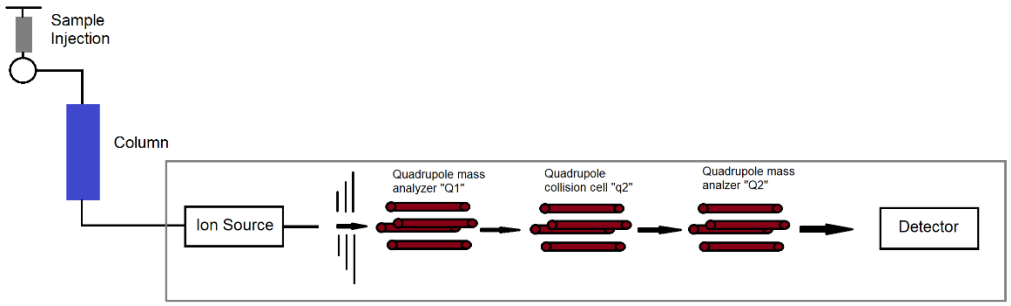

Figure 17: A schematic diagram of a triple quadrupole LC-MS/MS system

This instrument was selected for the detection of endogenous drug particles in latent fingerprints due to its ability to create a detailed mass spectrum of one specific compound in a sample. Since the samples being analyzed are latent prints, there are going to be many more compounds present in the print than just possible drug analytes. Fingerprint sebum contains many byproducts of human metabolism including lipids, amino acids, salts, and much more. This could make it difficult to detect one specific compound within the fingerprint. This problem is solved by the first step of LC-MS/MS: chromatography. As previously discussed, chromatography is a separation technique, and thus helps separate potential drug analytes from the other components that may be present in the fingerprint sebum. Now that the target analyte is separated, it must now be

identified – this is where the mass spectrometry comes into play. Though traditional mass spectrometry with only one mass analyzer could potentially identify the unknown drug analyte correctly, there is also a high possibility that the drug is falsely identified. As mentioned earlier, many drugs of the same class have the same general structure and thus produce similar fragmentation patterns when analyzed by mass spectrometry. This could lead to the wrong drug being identified. Tandem mass spectrometry has the ability to select an ions of a particular m/z value and continue to cause fragmentation, then once again pass these fragments through a mass analyzer before they make their way to the detector. This produces a more detailed mass spectrum that could provide more information to help make a positive drug identification.

Though LC-MS/MS shows potential for this specific application, there is also one major disadvantage. Since this is liquid chromatography, the sample must be in liquid form. The latent print must be dissolved in a liquid solvent in order to create a sample that can be properly analyzed. This is not ideal for crime scene investigation since evidence should be preserved. If a latent print from a crime scene was analyzed for endogenous drug particles using this method, there would no longer be a print that could be used in the future in the event that a comparison must be made using the ridge pattern of the print. However, if this method is tested and proves to produce accurate results, there may be cases where it is more beneficial to destroy the print in order to detect possible endogenous drug particles. This may include cases that have no suspect leads, or cases where multiple identical prints have been left.

3.4 DART-MS

Direct analysis in real time mass spectrometry (DART-MS) uses an ambient, plasma-based ionization source (63). An inert gas (He or N_2) is pumped into a discharge chamber that contains a cathode and an anode. An electrical potential of several kilovolts is applied to the electrodes, initiating a glow discharge that produces ions, electrons, and long lived electronically and vibrationally excited species known as metastables. The gas then flows through multiple electrodes that are biased to remove ions from the gas stream, leaving only metastables. Before the metastables exit the ionization source, they are heated and get further excited. When the metastables exit the ionization source, they interact with the sample in the open air, causing the sample molecules to become ionized. The sample ions are then sent to the mass spectrometer where the sample molecules are detected and a mass spectrum is produced. The fragmentation pattern of the mass spectrum is then used to determine the identity of the unknown components. A general schematic of a DART ionization source can be seen below in **Figure 18**.

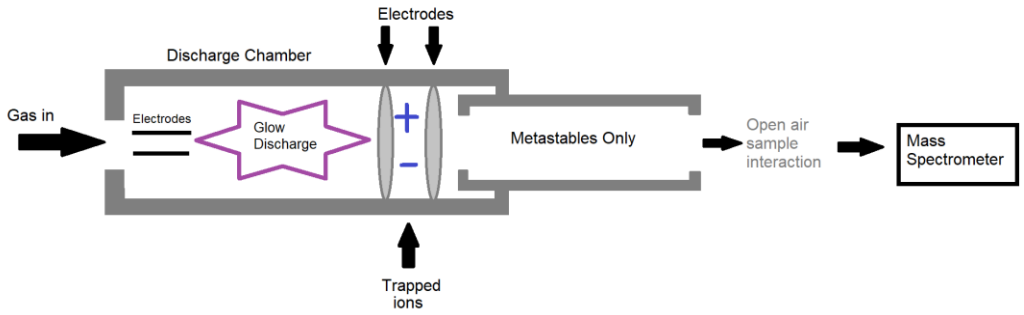

Figure 18: A schematic diagram of a DART ionization source

DART-MS is an instrument of interest for this purpose for many different reasons. First, it is nondestructive and therefore a latent print can be analyzed for endogenous drug particles without damaging the ridge pattern. Second, there is no sample preparation needed. This is advantageous in the forensic field due to how precious time is. Crime laboratories are often backlogged and cannot analyze evidence from cases until weeks or months after the crime has taken place. Because of this, investigators are always looking for new and improved analyzation methods that can save time. With DART-MS needing no sample preparation, samples can be analyzed in a matter of minutes which can potentially shorten the overall time it takes to process evidence for cases. Finally, DART-MS has shown the ability to detect trace amounts of analyte from a small sample. This is important because the amount of sweat deposited by a fingerprint is very small, and thus any endogenous drug particles present would be minute. Since DART-MS can detect trace levels of analytes, it is likely that it would have the ability to detect drug particles that may be present in the sweat that constitutes a latent print.

Though this instrument shows great potential for this area of study, there is one main disadvantage for this particular application. DART-MS is not a common instrument found in a crime laboratory. Resources, in terms of both money and supplies, are often limited for crime laboratories as it is, so it is unlikely for this instrument to make its way into laboratories even if it proves to give accurate results for this purpose. However, research shows that DART-MS is being studied for multiple other forensic applications, including for analysis of writing inks, explosives, and trace evidence from 3D-printed firearms (64, 65, 66). If the use of DART-MS for forensic purposes continues to increase, the likelihood of DART-MS becoming a common instrument among crime laboratories

could also increase. This would then make the process of detecting endogenous drug particles using DART-MS a much more practical method for crime laboratories. This does not seem to be a practical method for most forensic laboratories at the present time.

3.5 Conclusion

Both a destructive and non-destructive method for the detection of endogenous drug particles in latent prints have been proposed. Though liquid chromatography tandem mass spectrometry must destroy the latent print in order for it to be analyzed, this method still shows potential due to its ability to produce very detailed mass spectra. A present issue in the forensic world is that many drugs are so chemically similar that they cannot be distinguished from one another using traditional mass spectrometry. Tandem mass spectrometry is known to produce more detailed mass spectra due to its ability to focus on one molecule of a specific mass to charge ratio and the use of multiple mass analyzers to cause more fragmentation of the molecule. Based on this, it is possible that LC-MS/MS would be able to correctly identify endogenous drug particles in latent prints with a higher accuracy compared to traditional LC-MS. If this method proves to produce highly accurate results, its use could be justified in cases in which there are no suspect leads and more information is needed to identify a suspect, even if it means destroying the ridge pattern of the latent print.

Direct analysis in real time mass spectrometry seems to be the most promising method for the detection of endogenous drug particles in latent prints since it is nondestructive, requires no sample preparation, and can detect trace amounts of analyte

from very small samples. However, the fact that most crime laboratories do not have a DART-MS instrument or the money to buy one means that this method is not applicable to real life evidence analysis. Research shows that DART-MS is currently being investigated for its ability to analyze other pieces of forensic evidence including 3D printed guns, ink, and explosives. If the amount of published studies using DART-MS for forensic purposes continues to increase, it is possible that DART-MS could become a staple instrument in crime laboratories. In this case, it would be well worth it to investigate using this instrument for the detection of endogenous drug particles in latent prints.

Overall, history has shown that fingerprint studies are always advancing. The potential evidence contained in a fingerprint expands alongside the ever growing world of technology. As new scientific methods are developed, it is important to continue to revisit fingerprint evidence and investigate whether or not these new methods can be used to glean new information from latent prints. Just because the personal identification factor of fingerprints is such a reliable piece of forensic evidence does not mean that the potential other applications of prints should be overlooked. One day, with the discovery of the best scientific method for the purpose, it is possible that the analysis of latent prints for trace evidence could become one of the most important forensic analyzation processes.

LIST OF REFERENCES

1. Xiang-Xin, Z, and L Chun-Ge. “The Historical Application of Hand Prints in Chinese Litigation.” Journal of Forensic Identification, vol. 38, no. 6, 1988, pp. 277–284.
2. Barnes-Svarney, Patricia L., and Thomas E. Svarney. The Handy Forensic Science Answer Book: Reading Clues at the Crime Scene, Crime Lab, and in Court. Visible Ink Press, 2019.
3. Herschel, W. J. “Skin Furrows of the Hand.” Nature, vol. 23, no. 578, 25 Nov. 1880, pp. 76–76., doi:10.1038/023076b0.
4. Herschel, William J. The Origin of Finger-Printing. Humphrey Milford, 1916, https://archive.org/details/originoffingerpr00hersrich/page/n3/mode/2up.
5. Beavan, Colin. Fingerprints: The Origins of Crime Detection and the Murder Case That Launched Forensic Science. Hyperion, 2001.
6. Faulds, Henry. “On the Skin-Furrows of the Hand.” Nature, vol. 22, no. 574, 1880, pp. 605–605., doi:10.1038/022605a0.
7. Bertillon, Alphonse. "The Bertillon System of Identification." Forum (1886-1930), 05, 1891, pp. 330. ProQuest, http://umiss.idm.oclc.org/login?url=https://search-proquest-com.umiss.idm.oclc.org/docview/90988679?accountid=14588.
8. Farebrother, Richard, and Julian Champkin. “Alphonse Bertillon and the Measure of Man: More Expert than Sherlock Holmes.” Significance, vol. 11, no. 2, 2 May 2014, pp. 36–39., doi:10.1111/j.1740-9713.2014.00739.x.

9. Galton, Francis. “Personal Identification and Description.” Nature, vol. 38, no. 973, 1888, pp. 173–177., doi:10.1038/038173b0.
10. Galton, Francis. *Finger Prints*. Macmillan and Co., 1892.
11. “Visible Proofs: Forensic Views of the Body: Galleries: Cases: Juan Vucetich and the Origins of Forensic Fingerprinting.” U.S. National Library of Medicine, National Institutes of Health, 5 June 2014, www.nlm.nih.gov/exhibition/visibleproofs/galleries/cases/vucetich.html.
12. Teitelbaum, Jeff. “The First Criminal Conviction Based on Fingerprint Evidence: Argentina, 1892.” Forensic Science Review, vol. 30, no. 1, Jan. 2018, p. 16. Gale Academic OneFile, https://go.gale.com/ps/anonymous?id=GALE|A526068266&sid=googleScholar&v=2.1&it=r&linkaccess=abs&issn=10427201&p=AONE&sw=w.
13. Thompson, Timothy James Upton., and Sue M. Black. Forensic Human Identification: An Introduction. Taylor & Francis, 2007.
14. Dhillon, Manpreet Singh. “Pre-History of DNA ‘Fingerprinting’ in India.” Research Journal of Humanities and Social Sciences, vol. 10, no. 3, 30 Sept. 2019, p. 882., doi:10.5958/2321-5828.2019.00145.1.
15. Sodhi, G. S., and Jasjeet Kaur. “The Forgotten Indian Pioneers of Fingerprint Science: Fallout of Colonialism.” Indian Journal of History of Science, vol. 53, no. 4, Jan. 2018, doi:10.16943/ijhs/2018/v53i4/49543.
16. Henry, E. R. Classification and Uses of Finger Prints. Nabu Public Domain Reprints, 2012.
17. Lambourne, Gerald. The Fingerprint Story. Harrap, 1984.

18. Lofland, Lee. Police Procedure & Investigation: A Guide for Writers. Writers Digest Books, 2007.
19. Hoover, J. Edgar. “Criminal Identification.” The American Journal of Police Science, vol. 2, no. 1, 1931, pp. 8–19., doi:10.2307/1147300.
20. McElreath, David H., et al. Introduction to Law Enforcement. CRC Press, 2013.
21. Pike, John. “History.” Federal Bureau of Investigation, 18 June 2003, fas.org/irp/agency/doj/fbi/fbi_hist.htm.
22. Cole, Simon A. “Grandfathering Evidence: Fingerprint Admissibility Rulings from *Jennings to Llera Plaza and Back Again*.” American Criminal Law Review, vol. 41, no. 3, 2004, pp. 1189–1276.
23. Acree, Mark A. “People v. Jennings: A Significant Case for Fingerprint Science in America.” Journal of Forensic Identification, vol. 65, no. 4, July 2015, pp. 600–602.
24. People v. Jennings, 252 Ill. 534, 96 N.E. 1077, 1911 Ill. LEXIS 2024 (Supreme Court of Illinois December 21, 1911.). advance-lexis-com.umiss.idm.oclc.org/api/document?collection=cases&id=urn:contentItem:3RRM-3CM0-003F-02SY-00000-00&context=1516831.
25. “Fingerprint Identification.” National Institute of Justice. PDF File, https://www.ncjrs.gov/pdffiles1/Digitization/78671NCJRS.pdf
26. “Privacy Impact Assessment for the Fingerprint Identification Records System (FIRS) Integrated Automated Fingerprint Identification System (IAFIS) Outsourcing for Noncriminal Justice Purposes - Channeling.” FBI, 10 June 2016,

www.fbi.gov/services/information-management/foipa/privacy-impact-assessments/iafis.

27. “Next Generation Identification (NGI).” FBI, FBI, 6 May 2016, www.fbi.gov/services/cjis/fingerprints-and-other-biometrics/ngi.
28. “NGI Monthly Fact Sheet.” FBI, FBI, 2 June 2016, www.fbi.gov/file-repository/ngi-monthly-fact-sheet/view.
29. Cummins, Harold, and Charles Midlo. Finger Prints, Palms, and Soles: an Introduction to Dermatoglyphics. Research Pub. Co., 1976.
30. Acree, Mark A. “Is There a Gender Difference in Fingerprint Ridge Density?” Forensic Science International, vol. 102, no. 1, 1999, pp. 35–44., doi:10.1016/s0379-0738(99)00037-7.
31. Thakar, Mukesh Kumar, et al. “Validation Studies on Gender Determination from Fingerprints with Special Emphasis on Ridge Characteristics.” Egyptian Journal of Forensic Sciences, vol. 8, no. 20, 2018, pp. 1–7., doi:10.1186/s41935-018-0049-7.
32. Huynh, Crystal, et al. “Forensic Identification of Gender from Fingerprints.” Analytical Chemistry, vol. 87, no. 22, 2015, pp. 11531–11536., doi:10.1021/acs.analchem.5b03323.
33. Mark, Harker, and Clive R. Harding. “Amino Acid Composition, Including Key Derivatives of Eccrine Sweat: Potential Biomarkers of Certain Atopic Skin Conditions.” International Journal of Cosmetic Science, vol. 35, no. 2, Apr. 2013, pp. 163–168. EBSCOhost, doi:10.1111/ics.12019.

34. Shetage, Satyajit S., et al. “Effect of Ethnicity, Gender and Age on the Amount and Composition of Residual Skin Surface Components Derived from Sebum, Sweat and Epidermal Lipids.” Skin Research and Technology, vol. 20, no. 1, 2013, pp. 97–107., doi:10.1111/srt.12091.

35. Zhou, Zhenpeng, and Richard N. Zare. “Personal Information from Latent Fingerprints Using Desorption Electrospray Ionization Mass Spectrometry and Machine Learning.” Analytical Chemistry, vol. 89, no. 2, May 2017, pp. 1369–1372., doi:10.1021/acs.analchem.6b04498.

36. Fournier, Nichole A., and Ann H. Ross. “Sex, Ancestral, and Pattern Type Variation of Fingerprint Minutiae: A Forensic Perspective on Anthropological Dermatoglyphics.” American Journal of Physical Anthropology, vol. 160, no. 4, 23 Sept. 2015, pp. 625–632., doi:10.1002/ajpa.22869.

37. Merkel, Ronny, et al. “On Non-Invasive 2D and 3D Chromatic White Light Image Sensors for Age Determination of Latent Fingerprints.” Forensic Science International, vol. 222, no. 1-3, 2012, pp. 52–70., doi:10.1016/j.forsciint.2012.05.001.

38. Muramoto, Shin, and Edward Sisco. “Strategies for Potential Age Dating of Fingerprints through the Diffusion of Sebum Molecules on a Nonporous Surface Analyzed Using Time-of-Flight Secondary Ion Mass Spectrometry.” Analytical Chemistry, vol. 87, no. 16, 17 July 2015, pp. 8035–8038., doi:10.1021/acs.analchem.5b02018.

39. Czech, Anna, et al. “Changes in Fingerprints Depending on Physiological Factors.” Journal of Forensic Sciences, vol. 64, no. 3, 21 Oct. 2018, pp. 711–716., doi:10.1111/1556-4029.13937.
40. Vachet, Pierre, and Edmond Locard. La Psychologie Du Vice. La Police Et Les Méthodes Scientifiques. Bernard Grasset, 1934.
41. Crane, Nicole J., et al. “Infrared Spectroscopic Imaging for Noninvasive Detection of Latent Fingerprints.” Journal of Forensic Sciences, vol. 52, no. 1, 2007, pp. 48–53., doi:10.1111/j.1556-4029.2006.00330.x.
42. Mou, Yongyan, and J. Wayne Rabalais. “Detection and Identification of Explosive Particles in Fingerprints Using Attenuated Total Reflection-Fourier Transform Infrared Spectromicroscopy.” Journal of Forensic Sciences, vol. 54, no. 4, 2009, pp. 846–850., doi:10.1111/j.1556-4029.2009.01060.x.
43. Kaplan-Sandquist, Kimberly, et al. “Chemical Analysis of Pharmaceuticals and Explosives in Fingermarks Using Matrix-Assisted Laser Desorption Ionization/Time-of-Flight Mass Spectrometry.” Forensic Science International, vol. 235, 2014, pp. 68–77., doi:10.1016/j.forsciint.2013.11.016.
44. Ricci, Camilla, and Sergei G. Kazarian. “Collection and Detection of Latent Fingermarks Contaminated with Cosmetics on Nonporous and Porous Surfaces.” Surface and Interface Analysis, vol. 42, no. 5, 11 Aug. 2009, pp. 386–392., doi:10.1002/sia.3098.
45. Rowell, Frederick, et al. “Detection of Drugs and Their Metabolites in Dusted Latent Fingermarks by Mass Spectrometry.” The Analyst, vol. 134, no. 4, 8 Jan. 2009, pp. 701–707., doi:10.1039/b813957c.

46. Sundar, Latha, and Frederick Rowell. “Detection of Drugs in Lifted Cyanoacrylate-Developed Latent Fingermarks Using Two Laser Desorption/Ionisation Mass Spectrometric Methods.” The Analyst, vol. 139, no. 3, 2014, pp. 633–642., doi:10.1039/c3an00969f.
47. Groeneveld, G., et al. “Detection and Mapping of Illicit Drugs and Their Metabolites in Fingermarks by MALDI MS and Compatibility with Forensic Techniques.” Scientific Reports, vol. 5, no. 1, 29 June 2015, pp. 1–13., doi:10.1038/srep11716.
48. Leggett, Richard, et al. “‘Intelligent’ Fingerprinting: Simultaneous Identification of Drug Metabolites and Individuals by Using Antibody-Functionalized Nanoparticles.” Angewandte Chemie International Edition, vol. 46, no. 22, 2007, pp. 4100–4103., doi:10.1002/anie.200700217.
49. Zhang, Ting, et al. “Detection of Methamphetamine and Its Main Metabolite in Fingermarks by Liquid Chromatography–Mass Spectrometry.” Forensic Science International, vol. 248, 23 Dec. 2014, pp. 10–14., doi:10.1016/j.forsciint.2014.12.013.
50. Kuwayama, Kenji, et al. “Time-Course Measurements of Drugs and Metabolites Transferred from Fingertips after Drug Administration: Usefulness of Fingerprints for Drug Testing.” Forensic Toxicology, vol. 32, no. 2, 22 May 2014, pp. 235–242., doi:10.1007/s11419-014-0228-7.
51. Bailey, Melanie J., et al. “Rapid Detection of Cocaine, Benzoylecgonine and Methylecgonine in Fingerprints Using Surface Mass Spectrometry.” The Analyst, vol. 140, no. 18, 2015, pp. 6254–6259., doi:10.1039/c5an00112a.

52. “About Mass Spec.” American Society for Mass Spectrometry, www.asms.org/about-mass-spectrometry.
53. Cramer, Rainer. “MALDI MS.” Proteomics Methods in Molecular Biology, 26 May 2009, pp. 85–103., doi:10.1007/978-1-60761-157-8_5.
54. “Time-of-Flight Fundamentals.” Washington University School of Medicine, msr.dom.wustl.edu/time-of-flight-fundamentals/.
55. Bates, J. “Fourier Transform Infrared Spectroscopy.” Science, vol. 191, no. 4222, 9 Jan. 1976, pp. 31–37., doi:10.1126/science.1246596.
56. Schuttlefield, Jennifer D., and Vicki H. Grassian. “ATR–FTIR Spectroscopy in the Undergraduate Chemistry Laboratory. Part I: Fundamentals and Examples.” Journal of Chemical Education, vol. 85, no. 2, 2 Feb. 2008, pp. 279–281., doi:10.1021/ed085p279.
57. Budde, William L., et al. “Liquid Chromatography-Mass Spectrometry: An Emerging Technology for Nonvolatile Compounds.” Journal - American Water Works Association, vol. 82, no. 9, Sept. 1990, pp. 60–65., doi:10.1002/j.1551-8833.1990.tb07021.x.
58. Zhu, Zhangpei, et al. “The Improved Performance of MALDI-TOF MS on the Analysis of Herbal Saponins by Using DHB-GO Composite Matrix.” Journal of Mass Spectrometry, vol. 54, no. 8, 4 July 2019, pp. 684–692., doi:10.1002/jms.4385.
59. Hazama, Hisanao, et al. “Comparison of Mass Spectra of Peptides in Different Matrices Using Matrix-Assisted Laser Desorption/Ionization and a Multi-Turn Time-of-Flight Mass Spectrometer, MULTUM-IMG.” Rapid Communications in

Mass Spectrometry, vol. 22, no. 10, May 2008, pp. 1461–1466., doi:10.1002/rcm.3531.

60. Gipson, Kyle, et al. “Infrared Spectroscopic Characterization of Photoluminescent Polymer Nanocomposites.” Journal of Spectroscopy, vol. 2015, 3 Aug. 2015, pp. 1–9., doi:10.1155/2015/489162.
61. Maswadeh, Hamzah. “Lyoequivalency, Dissolution Kinetics and Drug – Excipient Compatibility of Some Commercially Available Acetaminophen Tablets.” Journal of Pharmacy Research, vol. 11, no. 1, 9 Jan. 2017, pp. 57–63.
62. Mclafferty, F. “Tandem Mass Spectrometry.” Science, vol. 214, no. 4518, 16 Oct. 1981, pp. 280–287., doi:10.1126/science.7280693.
63. Cody, Robert B., et al. “Versatile New Ion Source for the Analysis of Materials in Open Air under Ambient Conditions.” Analytical Chemistry, vol. 77, no. 8, 15 Apr. 2005, pp. 2297–2302., doi:10.1021/ac050162j.
64. Drury, Nicholas, et al. “A Comparison between DART-MS and DSA-MS in the Forensic Analysis of Writing Inks.” Forensic Science International, vol. 289, 24 May 2018, pp. 27–32., doi:10.1016/j.forsciint.2018.05.009.
65. Pavlovich, Matthew J., et al. “Direct Analysis in Real Time-Mass Spectrometry (DART-MS) in Forensic and Security Applications.” Mass Spectrometry Reviews, vol. 37, no. 2, 6 June 2016, pp. 171–187., doi:10.1002/mas.21509.
66. Black, Oscar. “Physical and Chemical Trace Evidence from 3D-Printed Firearms, and Use of a Quadcopter for Targeted Sampling of Gaseous Mercury in the Atmosphere.” 2019. The University of Mississippi, PhD dissertation