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Multiple Contacts of Drug Contaminated Fingermarks and Their Analysis with Raman Microspectroscopy

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Comments

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THE UNIVERSITY OF NEW HAVEN

MULTIPLE CONTACTS OF DRUG CONTAMINATED FINGERMARKS AND THEIR ANALYSIS WITH RAMAN MICROSPECTROSCOPY

A RESEACH PROJECT

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BY

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ABSTRACT

This thesis research aimed to determine if substrate, enhancement technique, and multiple contacts affect the detection and identification of drugs in fingermarks using Raman Spectroscopy. It has the potential to be of great importance in forensic science as fingermarks are one of the most important traces left behind at crime scenes and illicit drugs are a significant criminal justice problem. Thus, being able to associate illicit drugs with a specific fingermark has great potential for forensic science, as it can put the drugs in the hands of a specific individual.

The ridges of fingerprints trap trace amounts of material that result from exchanges between the individual and any surface. When individuals handle illicit drugs, these materials can be transferred and subsequently detected on their hands and fingers, as well as in the fingermarks they leave behind. Understanding the limits of detecting illicit drugs on various substrates and after multiple contacts, as well as after enhancement and collection, can provide valuable information which can be employed in forensic casework where the individuals are suspected of handling illicit substances. In addition to identification purposes, a fingermark could be used for identifying the drug component, thus aiding forensic scientists two-fold.

Previous studies have been conducted on the spectroscopic analysis of drug contaminated fingermarks, however, these projects have only detected the parent drug from a single, secondary transfer. For this research, multiple contacts were taken from 10 participants that planted 15 or 20 successive drug-contaminated fingermarks on a series of 3 different substrates with specific enhancement techniques that are most commonly seen at crime scenes. Benchtop Raman Microspectroscopy and Portable Raman Spectroscopy were employed to assess the number of successive contacts from which drug contaminated marks can be detected and identified from different substrates after enhancement and lifting techniques are performed. Using Benchtop Raman Microspectroscopy cocaine was able to be identified in at least 15 contacts among all

substrates tested. Further, cocaine can persist through multiple contacts even after development of the fingermarks even with variability between individuals. However, contamination of fingermarks was observed from powder brushes that were utilized. Although detection was possible using powder enhancement, it is not advisable due to the possibility of contamination.

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INTRODUCTION

Identifying the source of an unknown substance found at a crime scene has been a common problem in forensic science, as stated by the National Institute Standards and Technology (Saunders, n.d.). In particular, detecting drugs in fingermarks can aid forensic scientists two-fold. In addition to confirming the contents of an unknown substance found, it can then be linked to an individual. However, questions remain about the number of fingermark contacts where drugs are detectable on different substrates.

Knowing this information could have been useful in a Maritime cocaine case that occurred in 2016 (B. Kammrath, personal communication, 10 October 2017). During the proceedings of this trial, the likelihood of the source of cocaine that was identified with Ion Mobility Spectrometry (IMS), located on the steering wheel of the sailboat, was called into question. It was asked whether the cocaine found on the wheel was from the defendants, who were the suspected owners of multiple boxes containing cocaine, or the coast guards, who could have possibly transferred traces of cocaine from their taxi boat after working on a previous case and planted it on to the sailboat. Understanding the amount of contacts that fingermarks can retain drug content and can be detected when left behind, could have aided scientists in providing the source of the cocaine.

Previous research has shown that detecting drugs in fingermarks can be performed by using many different spectroscopic and microscopic techniques. In particular, Raman spectroscopy has been shown to be advantageous for this type of research since it is nondestructive to the sample, requires little to no sample preparation, and has the ability to be transported to the scene of the crime. Factors that can affect the detection of the samples tested

by Raman spectroscopy previously include substrate, enhancement technique, sebaceous oils, fluorescence, and amount of drug present in the friction ridges.

For the current research project, the investigators propose the following question: How does substrate, enhancement technique, and multiple contacts effect the detection of drugs in fingermarks using spectroscopy? This project was conducted by having participants place drug contaminated fingermarks on different substrates, multiple times, to mimic a series of contacts. The latent prints were enhanced and lifted before analysis using Raman Microspectroscopy. Samples from the various substrates will be subjected to either stationary Raman instrument or and a portable version, to test the ability of utilizing this method in the field directly.

In determining the amount of contacts that Raman Spectroscopy can detect drugs in contaminated fingermarks, scientists can then use identification methods to place the drugs in the hands of the suspect.

FINGERMARKS AND RAMAN SPECTROSCOPY

A. Fingerprints and Exchange

Fingerprints are one of the most important traces left behind at crime scenes. This evidence is critical in forensics due to its uniqueness and permanence among individuals. The uniqueness of fingerprints stems from the development process of the friction ridges on the volar pads that occurs about 10 to 16.5 weeks in the gestational period (Wertheim & Maceo, 2002). When these pads come into contact with surfaces, an impression or indentation of these ridges is often left behind. Since the ridge details of fingerprints remain unchanged over the course of a lifetime, they are considered permanent.

There are three types of fingermarks can be left behind: patent, plastic, and latent. Patent prints are those that are visible to the naked eye and often can be seen in blood examined at a crime scene (Bramble & Brennan, 2000). Plastic prints are visible to the eye as well, but leave an indentation based on the soft surface that the skin comes into contact with. However, the most common fingerprint that is left behind at crime scenes are latent prints, or those that are invisible to the naked eye. Enhancement techniques are needed to visualize these prints based on the substrate it is planted on. The impression of the friction ridges left behind in an uncontrolled manner, can also referred to as a fingermark when the trace is recovered (Meuwly, 2014).

The composition of latent prints is determined by the compounds present on the fingertip before the transfer to the surface (Bramble & Brennan, 2000). The residue left behind is comprised of mainly water but also organic as well as inorganic substances. It is determined by the combination of sebaceous, eccrine, and apocrine secretions. Eccrine secretions are located in the palms of the hands solely while sebaceous secretions are from pores all over the body except

from the palms and soles. Apocrine sweat is found in areas such as the axillae, armpit, and genitals.

The exchange of materials involves a two-way transfer of substances and everyday activities that result in the transmission of chemical compounds on to the fingertips (Bramble & Brennan, 2000). As a result, these compounds become trapped in the residue of latent fingermarks and are known as contamination. This evidence can provide great potential for forensic scientists in detecting the compounds as well as an identification of the source can be performed.

In the literature, the term fingermark has been used to describe marks either left in an uncontrolled manner at a crime scene or those simulated to portray the event. Fingerprint refers to a known sample taken from an individual used for comparison and individualization. In this research, the term fingermark was utilized since the depositions were performed to simulate those found at a crime scene.

B. Latent Print Enhancement

Enhancement of fingermarks and the methods utilized are crucial based on the substrate it is found on. Improper enhancement techniques used on fingermarks can inhibit visualization and lead to damaging the mark. Substrates can be classified as porous or nonporous. On porous substrates, the fingerprint residues are usually absorbed however, on nonporous substrates the residues remain (Bramble & Brennan, 2000). Paper and cardboard are considered porous while plastics and metals are considered non-porous (Bramble & Brennan, 2000).

For smooth and non-porous surfaces, powder dusting is the most commonly used procedure (Almog,2000). The particles of the powder bind to the oily components of the deposits. Metallic powders use aluminum flakes with steric acid (Almog,2000). It is applied to

the fingermark by using a brush made of hairs, feather, or fiberglass by twirling or brushing the powder over the print. Other powders such as magnetic powders incorporate iron flakes mixed with copper or aluminum. Using magnetic powders to visualize fingermarks is more advantageous since the wand avoids brushing and destruction of the prints (Almog,2000).

Cyanoacrylate, otherwise known as superglue, is greatly used to visualize fingermarks for plastic bags, aluminum foil, finished and unfinished wood, metal, and rubber. Cyanoacrylate fuming is performed in a tank which evaporates the superglue into a gas and polymerizes when in the presence of the fingermark residues (Almog,2000). Often, dyes and powders are used after the fuming process is completed to further visualize the fingermarks left on these substrates.

Ninhydrin is another technique used to visualize marks left behind on porous substrates such as paper. It reacts with the amino acids present in the residue to produce a colored compound known as Ruhemann's purple (Almog,2000). The substrate is dipped into the solution then dried before placing it in an oven to accelerate the visualization time.

C. Raman Spectroscopy

Raman Spectroscopy has been widely researched and used in the forensic field since can be utilized for a wide range of samples for identification. It is greatly advantageous since it is nondestructive to the samples and can then be used in supplemental testing (Moreno et al., 2004). This is optimal for forensic evidence, especially in testing fingermarks. Once Raman is used to confirm the presence of a particular substance, the same sample can be used to make an identification of the source (Edwards & Day, 2006). Additionally, it is rapid, highly sensitive, and involves little to no sample preparation (Day et al., 2004). One of the disadvantages of Raman is fluorescence which occurs for weak Raman signals with a number of different molecules such as aromatic groups between the 300-700nm range (West & Went, 2010).

However, fluorescence can be avoided by choosing lasers within the ultraviolet or near-infrared range (West & Went, 2010).

Raman Spectroscopy operates by using a single frequency of radiation from a laser to irradiate the sample with a laser. It operates by measuring the scattered light corresponding to the molecular vibrations of the sample (Smith & Dent, 2008). Infrared Spectroscopy differs from Raman as it measures the direct vibrations of the sample dependent on the functional groups due to changes in dipole moments, whereas Raman shows differences in the polarizability of organic molecules (West & Went, 2010). This makes these two instrumentation techniques complementary. Transitions that are weak in Infrared Spectroscopy are strong in Raman Spectroscopy and vice versa. Some instrumentation for Raman has a microscope attached for visualization of the sampling area. This is highly useful especially for materials that have crystalline structures such as drugs in order to locate on a specific component and analyze it. This specific technique is referred to as Raman Microspectroscopy.

Raman Spectroscopy also has a portable form that can be used in the field. It provides a rapid analysis of materials in a handheld device (West & Went, 2010). It is able to identify components of mixtures and allow individuals to see the spectra obtained from a particular sample. However, it has a reduced spectral range over that of a benchtop version of the instrument and allows for slight broadening of the bands (West & Went, 2010). Despite these disadvantages, portable Raman is sufficient for identification of drug samples (West & Went, 2010).

LITERATURE REVIEW

A. Identification of Substances in Fingermarks

Previous research has identified various substances, such as explosives and drugs, using a multitude of analytical techniques. In particular, drugs have been identified by using Raman spectroscopy as early as the 1970s (Willis et al., 1972). Studies have determined the presence of common barbiturates, ecstasy, and phentylamines, as well as other classes of drugs. More recent studies have examined methods of identifying drug components from various substrates.

Microscopic particles of a mixture containing ibuprofen, vitamin C, Sweet 'n Low®, and nondairy creamers were identified by using Fourier Transform Infrared Spectroscopy (FTIR). This study utilized multiple subjects that deposited two fingermarks onto a gold-plated surface. Although the researchers stated that they were able to use the spectral library in order to differentiate the particulates and the corresponding substance, their data shows that the library matches had a hit quality lower than 70. Especially for ibuprofen, the spectral matches for the particulates were found higher than 80% for only 1 or 2 of the particulates. Further, in some of the prints obtained, no particulates were identified. The substances that were identified with greater certainty, such as sweet n low and nondairy creamer proved that this method may be suitable for these substances. However, for those with higher complexity and strong carbon structures such as the ibuprofen, this method did not prove effective and accurate. This is one example, where examination of infrared spectroscopy falls short in identifying particulates.

Studies have also shown the detection of drug crystals planted on currency using Raman microspectroscopy. A mixture of benzocaine and lidocaine as well as a mixture of isoxsuprine and norephredrine were used. However, these mixtures of all four of the drugs resulted in hygroscopic reaction from lidocaine and was removed from other mixtures made (Fredrick et al.,

2004). In examining the white pigmented areas and green pigmented areas, more fluorescence was observed in the white areas and posed many issues for the researchers despite straightforward detection and identification of the crystals on a glass slide (Fredrick et al., 2004). Subtraction techniques were utilized to reduce the fluorescence were effective.

B. Identification of Drugs in Fingermarks

Researchers have analyzed contaminated fingermarks based on identifying drugs in a mixture of substances and understanding how the ridges of the volar pads allow for exchange and handling of materials. Questions concerning drugs of abuse accumulating on an individual's fingers then being deposited in their latent prints was investigated (West & Went, 2010). Identifying these controlled substances allowed for the possibility placing it in the hands of a suspect based on individualizing fingerprinting techniques. This could serve as powerful evidence for forensic scientist. However, the possibility of an innocent transfer must be considered (West & Went, 2010).

One study employed nanoextraction and nanospray ionization mass spectrometry, Raman spectroscopy, and electrospray ionization mass spectrometry for the identification of drugs of abuse in latent print residues. Fingerprint casts were made from silicone and utilized for the impressions. Canola oil was used to mimic gland secretions before the prints were placed on a counter top, glass slide, metal, plastic, or PC board and enhanced with red fluorescent fingerprint powder. Although the casting of the print was sufficient for the experiment conducted, the researchers noted that there were some flaws with the replication of the impression (Clemons, 2013). Nanospray ionization mass spectrometry was used to validate the results from Raman Spectroscopy and showed promise as a confirmation technique for Raman. Although this was

proven to be the best confirmation technique, it was minimally destructive to the sample despite its high sensitivity (Clemons, 2013). Electrospray ionization mass spectrometry was also destructive to the samples as the sebaceous oils were not dissolved in the solvent solution and washing.

Research conducted by Day et al. (2004a) used Raman spectroscopy to detect drugs and non-controlled substances on sebum-rich fingermarks versus those from sweat rich glands. The drug contaminated marks were placed on steel slides for identification by Raman. In detecting these drugs of abuse, the location of the doped particles in the was hindered by other solid particles from the latent fingermark (Day et al., 2004). The difficulty that the researchers encountered could be from not enhancing the contaminated marks on the steel slides before analysis with Raman. The sample quality was lower than the reference data since the doping amount was minimal and interferences were identified with fluorescence from the sebum (Day et al., 2004a). However, techniques such as photobleaching, a technique used to reduce fluorescence by constant irradiation for a long period of time before acquiring the sample, was used in this experiment to lower the fluorescence initially observed from the sebum (Zieba-Palus & Michalska, 2014).

Taking into consideration the issues they had previously had, subsequent research binvestigated fingermarks doped with drugs of abuse and were subjected to cyanoacrylate-fuming on the steel slides to test the effect of enhancement on identification using spectroscopic methods. However, only sweat-rich fingermarks were utilized in this experiment. Photobleaching was also employed in this experiment to reduce fluorescence from the sebum oils and the cyanoacrylate Even with the enhancement technique used, identifying the location of the particles was still difficult. In addition, the spectra gathered, showed great similarity to the

reference spectra obtained. Although the effect of sweat and sebum were investigated, the same substrate was used for both experiments. This could have possibly affected the quality of the spectra collected.

Additionally, studies by West and Went, 2008, mainly analyzed over-the-counter analgesics in fingermarks using powders followed by adhesive lifters. Recently washed fingers were dipped in minute samples of analyte before rubbing the contaminated finger with another to deposit sebum (West & Went, 2008). Once developed with powders and collected with adhesive lifters, examination of the prints was conducted using Raman Microscopy. Although the enhancement process did not interfere with obtaining the spectra, it increased the analysis time in order to determine the location of the drug particle to direct the microscope. The powders were seen to reduce fluorescence from sebaceous fluids (West & Went, 2008). It was also found that hinge lifters exhibited strong bands and made analysis more complex and as a result more exposures were needed as well as spectral subtraction (Moreno et al., 2014) (West & Went, 2008). The researchers also collected spectra from powdered fingerprints that were placed within evidence bags with successful identification of the drug contaminants.

A year later, West and Went repeated the premise of the first experiment with drugs of abuse. However, different powders as well as small particle reagent (SPR) were used in this experiment to visualize the prints. The contaminated fingermarks were deposited and lifted as done before. However, in the analysis of these experiments, many issues were encountered. The red fluorescent powder and small particle reagent showed substantial fluorescence. Therefore, it was determined that this method should be avoided when examining the prints using Raman Spectroscopy. Additionally, the hinge lifters that were used in this experiment also posed issues with fluorescence based on the white background of the lifter.

Although this research introduces aspects of forensic casework by utilizing illicit drugs as the analyte, unlike the initial experiment, both methodologies are not practical for crime scenes since Raman Microscopy is not portable (West & Went, 2008). Also, these experiments only used one donor which does not account for variabilities in sebum between individuals. Furthermore, the researchers describe ways to avoid these issues but did not identify any present solutions for the issues they encountered.

Other studies identified various drugs mixed with different materials to simulate detecting drugs cut with common household powders, to reflect similar cases that occurred. These cutting reagents were very similar to the chemical nature of the drugs of interest. Testing included portable as well as benchtop Raman Spectroscopy to show crime scene applicability. Although fluorescence was observed, to minimize this, principal component analysis (PCA) was employed and showed significant differences between the drugs for identification (Noonan et al., 2009). This study also illustrated that this type of testing can accurately identify these substances using a commercial handheld spectrometer such as a portable Raman instrument. Although successful identifications of the drugs were performed, as stated in the article, the PCA plots in this study showed a minimum correlation with the contamination mixtures. Even though the substances do not have overlapping areas and are distinctly separate, the percentages were shown to be >25% (Noonan et al., 2009).

C. Transfer Evidence

Trace material is often transferred between individuals and different substances from contact. Previous research has been conducted in the hopes of determining the prevalence of these transfers and to establish the mechanisms of these contacts and implications to forensic

protocols. Transfers of materials are affected by three parameters which include the source, the recipient, and the environment (Gassner et al., 2019). A primary transfer occurs when trace materials are deposited onto a person or object. Secondary transfer refers to a sample that is transferred to an object or person indirectly. Transfers occur among many different materials in a forensic context including DNA, gunshot residue, drugs, as well as other trace materials.

In order to visualize how multiple transfers occur, a study utilized UV powder that was placed on one of the participant's hand before being asked to shake the hands of the other participants as well as other tasks. It was determined that the powder transferred to objects with indirect transfers, or those from person-to-object-to-person, as well as direct transfers between individuals (French et al., 2012). Additionally, it was determined that trace particulates readily become secondary transfers as well as additional transfers for up to five hours (French et al., 2012).

In another study, the transfer of gunshot residue (GSR) was observed. In performing three different controlled simulations, multiple contacts including secondary transfer was analyzed. In the first simulation, a handgun was fired and then moved by a nonshooter. The nonshooter that displaced the handguns were tested for the presence of GSR. In the second simulation, a handgun was fired and then the shooter shook a nonshooters hand. The percentage was highly variable and were as high as 94.6% (Gassner et al., 2019). The third simulation entailed the shooter arresting a nonshooter after firing the handgun. Both the shooter and nonshooter were tested for the presence of GSR. Upon testing the nonshooter, in many instances there was more GSR detected on them than the shooter. Additionally, there was an instance where the shooter did not have any GSR present. These observations show the impact of

secondary and multiple transfers. Secondary transfer of GSR is not guaranteed for the shooter since other factors can affect its presence (Gassner et al., 2019).

Understanding multiple contacts can further enhance the ability for forensic scientists to provide more robust evidence where this situation is possible (French et al., 2012). Other scenarios of transfers must be taken into consideration when reconstructing a crime based on this type of evidence. These scenarios should include indirect transfers from unconnected individuals, those deposited by the offender to an innocent individual, as well as those that transfer from the original source to a further transfer (French et al., 2012). These instances can be used when attempting to determine the source of particular traces. Investigating a method that provides determination of a substance found at a scene while also being able to use the evidence for identifying the individual who planted the trace materials, can serve great potential for the forensic field. Previous research indicates the advances in detecting drugs in fingermarks, however no articles have considered multiple transfers and its effect on the detection of drugs. This particular aspect has a wide variety of case applicability and can greatly help forensic scientists put illicit substances in the hands of the suspect. Also, since the newest articles in the field date from 2012, expanding knowledge in this area will give a fresh approach to understanding the prevalence of transferring trace materials in forensics casework.

MATERIALS AND METHODS

Scope of Research

This research aimed to determine if fingermarks that contained cocaine can be detected and identified using benchtop Raman microspectroscopy and portable Raman spectroscopy. Portable Raman spectrometers are available for field use at crime scenes. In Phase I, the methodology was optimized including instrument parameters, amount of multiple contacts, substrate and enhancement processes, and tape lifts. In Phase II, 10 participants were asked to place drug-contaminated fingermarks on 3 particular substrates in a depletion series of up to 20 contacts of a secondary transfer. The fingermarks were then developed and prepared for analysis using both Raman instruments.

Materials

Cocaine hydrochloride was used as the target drug analyte in this research. In the preliminary stages, cocaine was placed on a quartz slide, and used to collect a reference spectrum. The different substrates initially tested included copy paper, duct tape, firearm magazines (donated by the New Haven Police Department), plastic bags, tile, and glass. When participants placed their drug contaminated fingermarks on the substrate, a scale was placed under the substrate to keep the pressure consistent between each mark. The enhancement processes analyzed in this study included: (1) magnetic and fluorescent powders, (2) cyanoacrylate, (3) WetWop, (4) Ninhydrin, and (5) 1,2-indanediole (1,2-IND). Cyanoacrylate processing was performed in a Labconco CApture Fuming Chamber (provided for use in this research by Kenneth Zercie). For applying enhancement powders, a fiberglass brush was used for fluorescent powders and a magnetic applicator was used for magnetic powder development.

Different types of tapes were analyzed in order to determine which was best for lifting the fingermarks with minimal Raman interference: Evident® Tape, Scotch® Brand Magic Tape, Remco® Tape, and Scotch® Brand Packing Tape. All samples were then placed on glass microscope slides to allow for easy navigation of the marks on the stage of the Raman Microspectrometer.

Instrumentation

A Thermo Scientific DXR Raman Microscope equipped with a 780nm laser was utilized for this research. The Raman microscope employs a 10x/0.25 BD objective, for a total magnification of 100x. The following parameters were determined to be optimal for this experimentation: 22mW laser power, 20 seconds for the exposure time, 4 sample exposures, and 50 micrometer pinhole aperature.

A Smiths Detection ACE-ID Portable Raman Spectrometer was utilized to evaluate if field application of drug contaminated marks can be performed in-situ. The ACE-ID has a laser power of 55mW at max, a laser wavelength of 785nm, and the detection time is less than 20 seconds.

Experimental Design Phase I: Optimization of Methodology

Part A: Raman Spectroscopy Procedures

Prior to data collection, a polystyrene standard was analyzed to check the wavelength accuracy of the Raman instrument. The wavenumbers of the polystyrene peaks were compared to those listed in the NIST standard peaks, with a tolerance of +/- 3 wavenumbers.

After a standard spectrum was taken of cocaine, drug-contaminated fingermarks with 10-15 mg were placed on a quartz slide by one participant, in order to optimize settings with minimal interference using Benchtop Raman Microspectroscopy.

Part B: Validation of previous research

A validation of the study "Spectroscopic detection of drugs of abuse in fingerprints after development with powders and recovery with adhesive lifters" was completed (West and Went, 2008). One participant was asked to wipe their finger across their forehead, which is known to contain sebaceous oils, before placing a finger in 10-15 milligrams of cocaine. Then, ten fingermark contacts were completed for each substrate, enhanced with a specific technique and lifted. The following eight (8) substrates and specific enhancement techniques were tested: (1) duct tape with magnetic powder, (2) duct tape with Wet Wop, (3) copy paper with Ninhydrin, (4) copy paper with 1,2-IND, (5) glass with fluorescent powder, (6) plastic bags with cyanoacrylate, (7) tile with magnetic powder, and (8) firearm magazines with cyanoacrylate.

Part C: Tape Lift Optimization

In order to determine which tape would be optimal for Raman Spectroscopy, a study was completed which used Raman microspectroscopy to analyze the following tapes: Evident Tape®, Scotch Brand Magic Tape®, Remco Tape®, and Scotch Brand Packing Tape®. The fingermarks were doped with the 10-15 milligrams of cocaine then the marks were placed on a glass surface and enhanced with fluorescent powder. One participant placed two dirty fingermarks using sebaceous oils in sequence on a glass substrate. The fingermarks were not developed before using the tape to lift. The tape was then placed on top of a microscope slide to

be able to navigate using the Raman Microspectrometer. The tape with the least interference with the Raman spectra of cocaine and substrate was determined and used for the rest of this research.

Phase II: Multiple Contacts Methodology

Phase II used the optimal parameters determined from Phase I. Ten participants were asked to join this study upon signing a consent form that was approved by University of New Haven's Institutional Review Board (IRB) on February 15, 2018 (Appendix page 52-56). The finger used by the participant was randomized for each substrate. However, the pinky finger was excluded to maintain consistency in size of the marks. The participants were asked to follow specific instructions from the researcher.

Table 1: Experimental Substrates, Enhancement Techniques and Methods of Raman Analyses

Substrate	Enhancement Technique	Instrumentation Analysis
Plastic Bags	Cyanoacrylate	Benchtop& Portable
Glass	Fluorescent powder	Benchtop &Portable
Firearm Magazines	Cyanoacrylate	Benchtop

First, the participants were asked to wipe their finger across an area where sebaceous oils were prevalent (i.e. forehead) and place a control sample on the particular substrate. After this, the participants were asked to wipe their finger across an area where sebaceous oils are prevalent again, then were asked to dip their finger in 10-15 milligrams of cocaine before placing the 15-20 consecutive prints on the particular substrates. These fingermark samples were identified as a set of dirty fingermarks. The participants were asked to wash their hands thoroughly to remove

any remnants of cocaine and sebaceous oils. Then the participants were asked to take a clean finger control after drying their hands. After placing the control sample, they were asked to immediately dip their finger in the cocaine sample and place 15-20 fingermarks on the substrate. These fingermark samples were identified as a set of clean marks.

For both the clean and dirty fingermarks, a scale was used to ensure a consistent contact force. A scale was placed underneath each substrate, and participants pressed their finger on the substrate to create the fingermark using a force that equated to between 800-1200g (based on the scale reading).

The fingermarks were then developed using the specific enhancements indicated in Table 1. After development, the substrate containing the fingermark, or a tape lift was taken of the marks and placed on a numbered glass slide for ease of use with the Benchtop Raman Microspectrometer. Each of the marks was tested for the presence of cocaine under the optimal parameters determined from Phase I. The main peaks of cocaine, 1715 cm^{-1}, 1597 cm^{-1}, 1000 cm^{-1}, 869 cm^{-1}, and 785 cm^{-1} (+/- 3 wavenumbers), were used to determine the presence of cocaine in each spectrum.

Samples from plastic bags and glass were used to determine if analysis using Portable Raman Spectroscopy was possible.

Part A: Fingermarks from Plastic Bags enhanced with Cyanoacrylate

Ziploc® plastic sandwich bags were initially cut along the side and bottom in order to allow for extra surface area for sampling. For this substrate each participant placed clean and dirty mark sets in duplicate. The control and doped fingermarks were placed in sequential order and labeled. The plastic bag was placed in a Labconco CApture portable fuming chamber for a

total of 10 minutes: 5 minutes for heating and enhancement and 5 minutes for venting. For each plastic bag, 2 drops of liquid cyanoacrylate were used along with ~5 drops of denatured water. After the samples were developed in the chamber, the fingermarks were placed on top of microscope slides for analysis.

Part B: Tape Lifts of Fingermarks from Glass Enhanced with Fluorescent Powder

The glass utilized for this research was initially cleaned and dried before using. The drug-contaminated fingermarks were placed in order and labeled. Then, using fluorescent powder, the marks were lifted with Scotch Clear Shipping Tape® based on the optimization performed from Phase I. These lifts were then placed on top of microscope slides for spectral analysis. For this substrate, participants placed dirty marks in duplicate.

Part C: Tape Lifts of Fingermarks from Cyanoacrylate Fumed Firearm Magazines

Ten rubberized plastic firearm magazines were donated by the New Haven Police Department. Due to the size of the magazine and witness holes located on the underside, only three sides of the magazine were used for sampling. Additionally, due to the size of the magazine, only a control sample and 15 fingermarks were able to be placed. Based on the number of magazines acquired, only one set of dirty samples from the participants were taken. After sampling the participant, the magazine was placed in the CApture fuming chamber for 10 minutes. Then, the fingermarks were lifted using Scotch Clear Shipping Tape® and placed on top of microscope slides for Raman spectral analysis.

Part D: Portable Raman

A Smiths Detection ACE-ID Portable Raman Spectrometer was employed to determine if field application of drug contaminated marks could be performed in-situ. The amount of times the mark was tested dependent on the relative size of the mark. Smaller marks were analyzed in 3 locations while larger marks were analyzed at up to 10 locations. If there were any areas where the cocaine was visible, analysis of these locations was performed. The Portable Raman was held approximately 5-10 cm away from the mark, as detailed in the instruction manual, and then a spectrum was collected.

RESULTS

Phase I: Optimization of Methodology

Part A: Raman Method Optimization

The main peaks from cocaine hydrochloride were determined using the optimal parameters. Under the Raman Microscope, cocaine was identified by a grey/white crystalline structure (Figure 1). The peaks were: 1715 cm^{-1}, 1597 cm^{-1}, 1000 cm^{-1}, 869 cm^{-1}, and 785 cm^{-1} (+/- 3 wavenumbers).

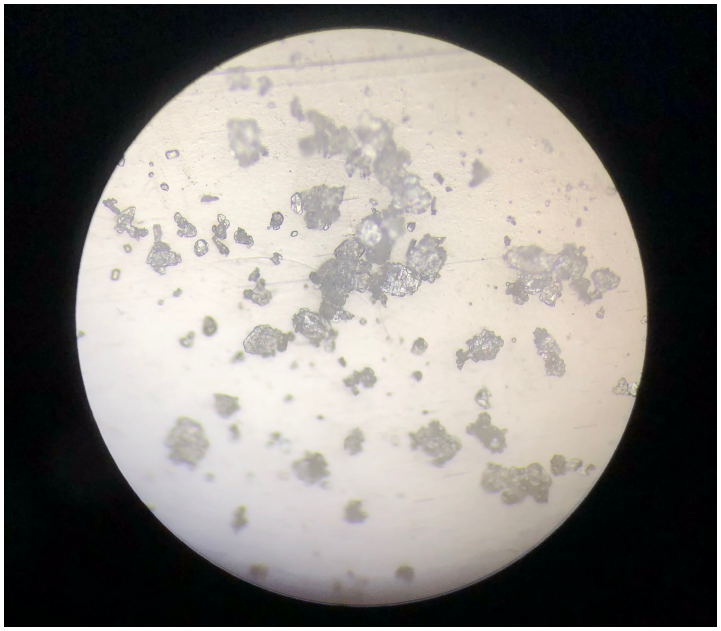

Figure 1: Photomicrograph of cocaine hydrochloride morphology, showing the grey/white crystalline structure observed under the Raman microscope (100X).

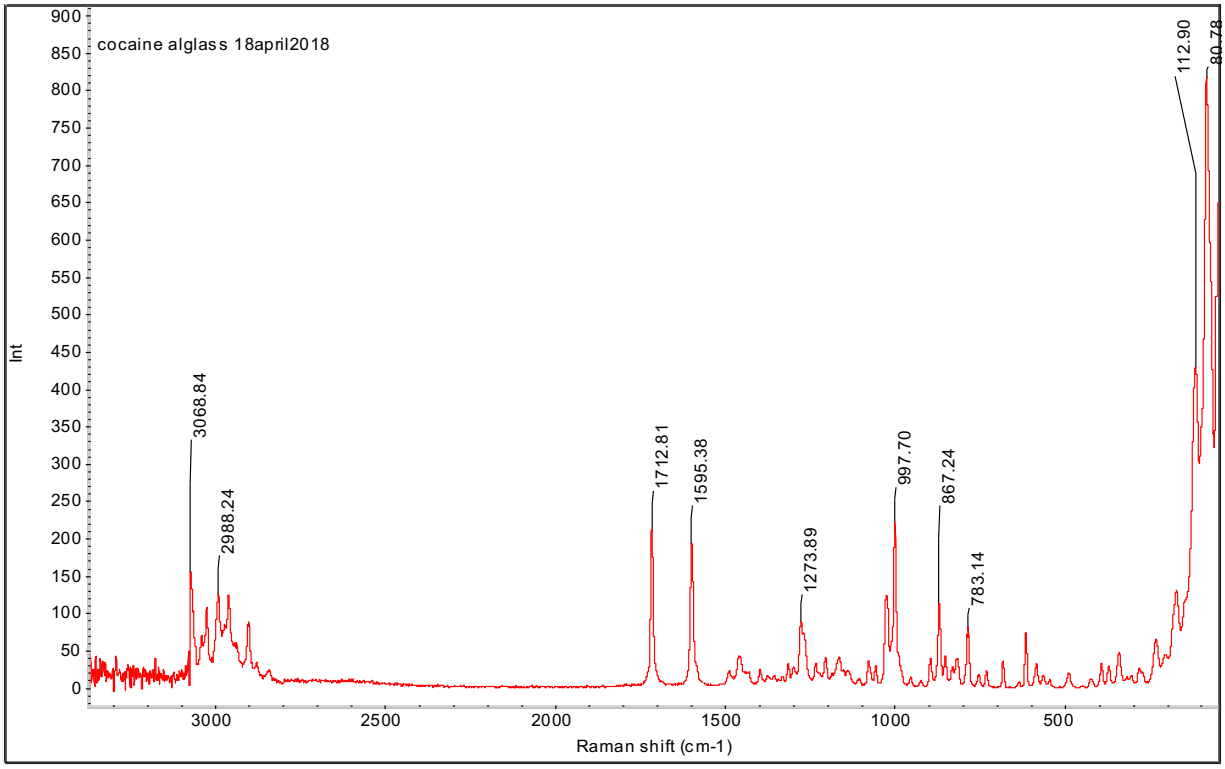

Figure 2: Raman spectrum of Cocaine Hydrochloride

Part B: Validation of previous research

Eight (8) different substrates and enhancement techniques were tested in order to determine which can be used in Phase II of the study.

For duct tape enhanced with cyanoacrylate and magnetic powder, no fingermarks contained visible crystals of cocaine. Also, there was little contrast between the marks and the background, which made it difficult to navigate around the marks when using the Raman Microscope. Although cocaine was identified on the first 3 consecutive marks, the contrast issues became too great to detect the presence of cocaine in subsequent marks. Additionally, it was thought that the magnetic powder overshadowed the cocaine residue present and could not be visualized using the Raman Microscope. Therefore, this substrate and enhancement technique did not move on to Phase II.

Duct tape enhanced with Wet Wop was also considered as a possible technique to be used for this study. However, the aqueous component of the Wet Wop dissolved the cocaine and prevented its detection and identification. Therefore, duct tape enhanced with Wet Wop did not continue on to Phase II.

Copy paper that was enhanced with two different techniques were analyzed with the Raman microscope in order to determine if detection of cocaine was possible. First, drug contaminated marks were placed on copy paper and enhanced with ninhydrin. After enhancement, the dirty marks had visible ridge detail however, no cocaine was able to be detected. The fibrous nature of the paper under the Raman microscope made it difficult to view any crystalline structure from the drug component. To test if the concentration of the cocaine was too small to be detected from the substrate, some of the standard cocaine was placed directly onto a sheet of copy paper then sprayed with ninhydrin. There was no cocaine observed or detected. In addition, since the aerosol ninhydrin standard contained methanol or acetone, this allowed the cocaine to dissolve upon adding the aqueous component. A common substitute for ninhydrin is 1,2-IND. This was also used as an enhancement technique for drug contaminated marks on copy paper. However, by using this technique, the marks had to be viewed using a UV lamp. Since the marks would not be visible under the Raman microscope, this enhancement technique was not suitable for this research. Based on these trials, copy paper enhanced with ninhydrin and 1,2 IND were determined not be practical substrates and techniques for this research or this type of analysis.

Sheets of glass were enhanced with fluorescent powder. The clean fingermarks did not contain visible ridge detail present after development. Since the location of the clean fingermarks was not able to be performed, these marks were not tested and analyzed in Phase II. However,

dirty marks showed great ridge detail and cocaine detection was possible (Figure 3 & 4). Dirty fingermarks on glass that were enhanced with fluorescent powder were examined in Phase II.

Figure 3: Photograph of a developed dirty fingermark lifted from glass. These marks showed great ridge detail and detection of cocaine using these marks was possible.

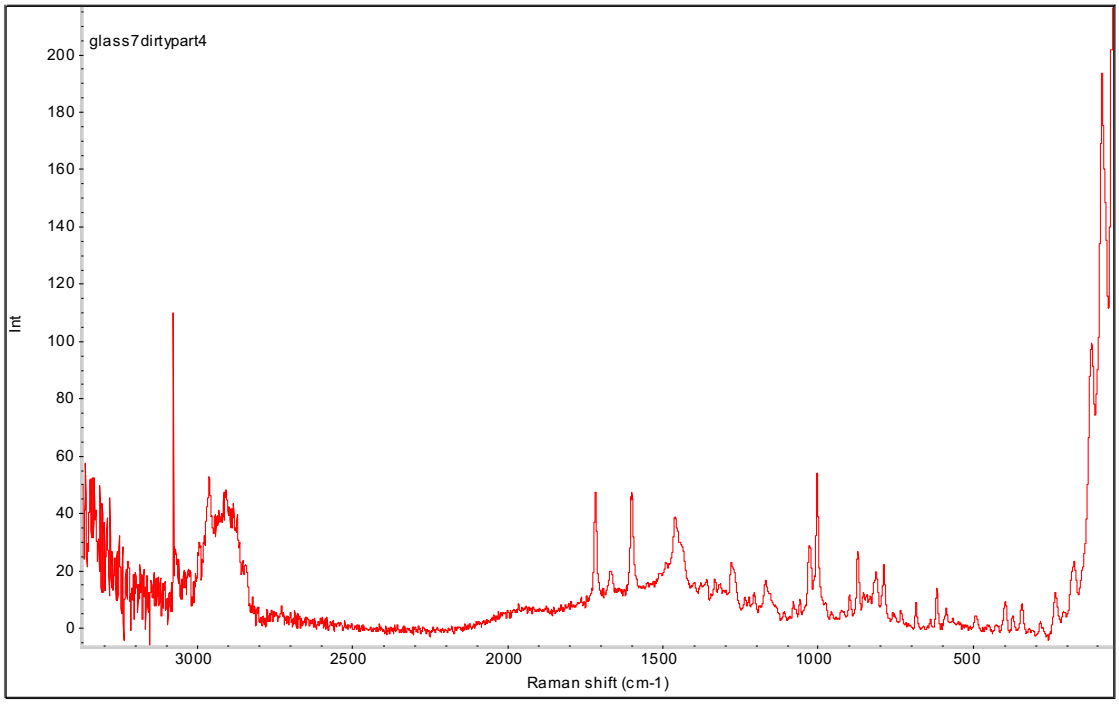

Figure 4: Raman spectrum of a fingermark planted on glass and developed with fluorescent powder.

Ziploc® plastic bags enhanced with cyanoacrylate showed great ridge detail in both clean and dirty fingermarks. Additionally, cocaine detection was possible in these fingermarks (Figure 5 & 6). This technique was examined in Phase II.

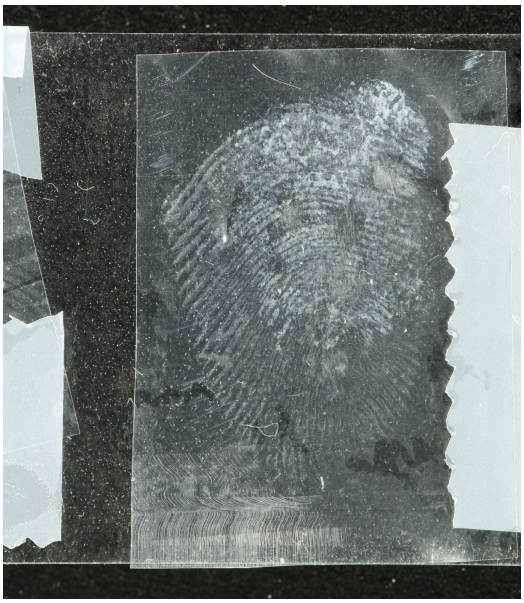

Figure 5: Photograph of a drug contaminated fingermark enhanced with cyanoacrylate on a plastic bag. The ridge detail was very prominent and detection of cocaine within the fingermark was possible.

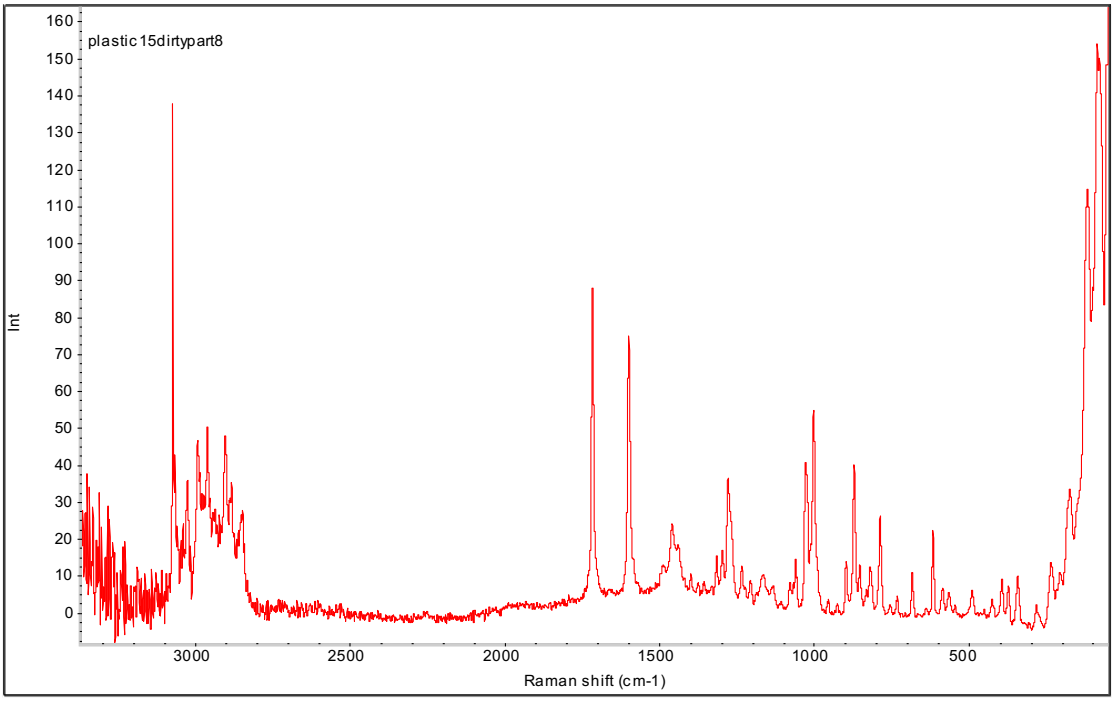

Figure 6: Raman spectrum of a fingermark enhanced with cyanoacrylate on a plastic bag.

Tile enhanced with magnetic powder was tested as well. Ridge detail was visible for both clean and dirty fingermarks. Further, cocaine detection was possible in these fingermarks (Figure 8). Although analysis on tile was able to be performed, it was not continued in Phase II due to timing. A photomicrograph of the cocaine found within tile samples was observed in Figure 7.

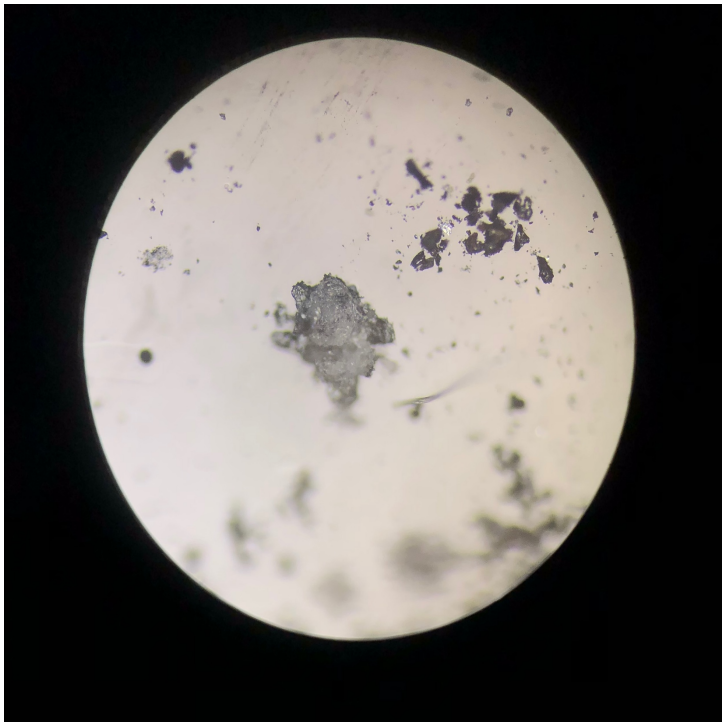

Figure 7: Photomicrograph of a drug contaminated fingermark on tile that was enhanced with magnetic powder and lifted. The lift was analyzed by Raman Microanalysis

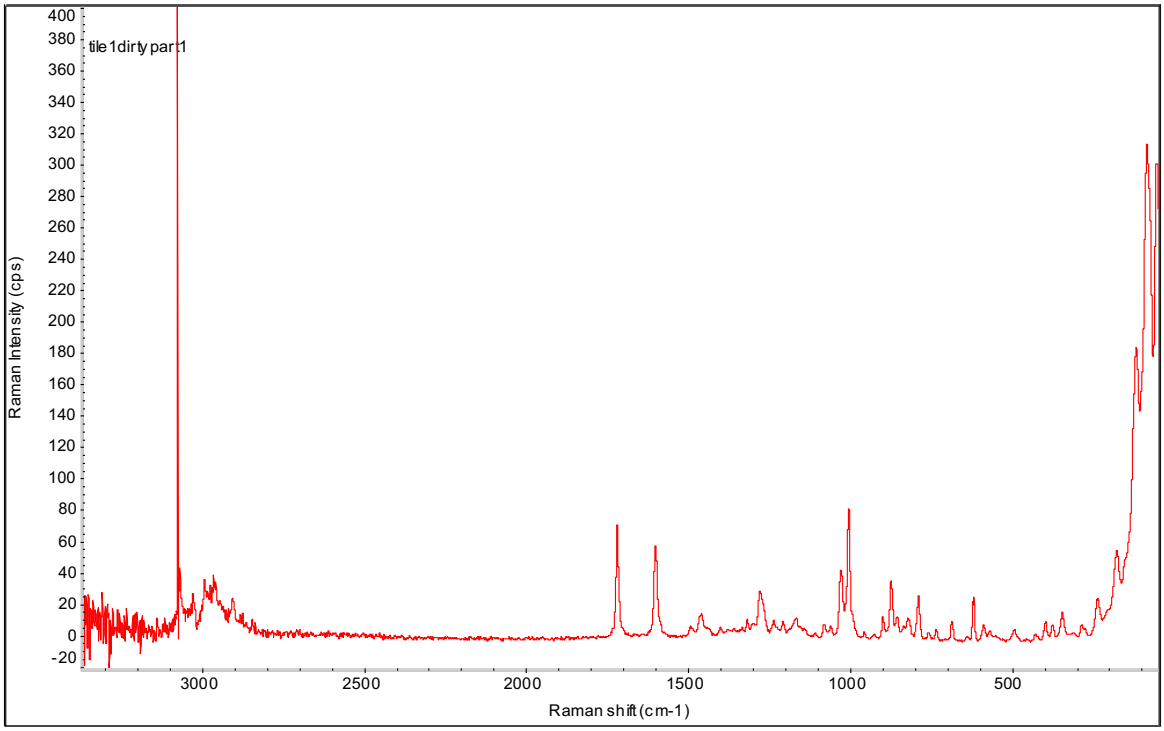

Figure 8: Raman spectrum of Fingermark from Tile

Firearm magazines enhanced with cyanoacrylate were also tested. Ridge detail was visible for few dirty fingermarks however, for subsequent marks no ridge detail was visible. Despite no ridge detail being present, the sebaceous oil residue of the marks was visible and cocaine residue was sometimes located within the oils. Therefore, the location and detection of cocaine was possible (Figure 9 &10). This technique was examined in Phase II.

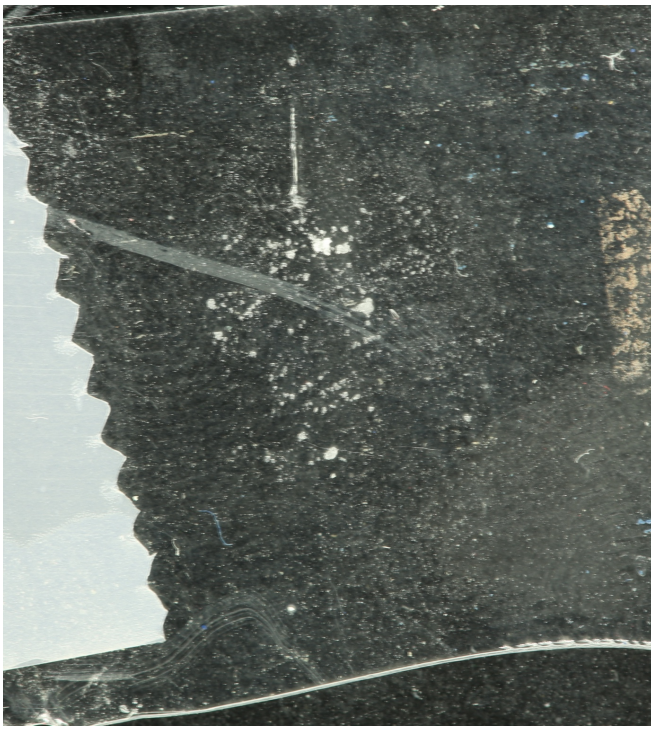

Figure 9: Photograph of a fingermark tape lifted from a firearm magazine. Even though little ridge detail is present, the sebaceous oils and cocaine residue was still visible.

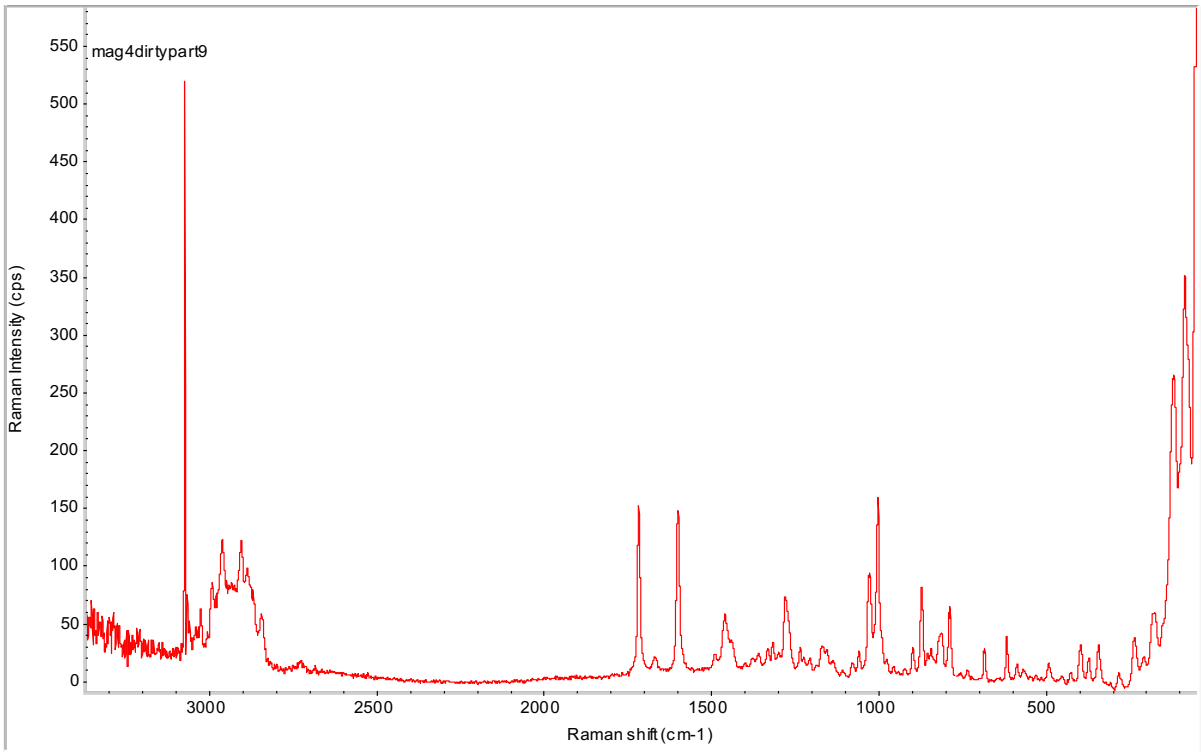

Figure 10: Raman spectrum of Fingermark from Firearm Magazine

Part C: Tape Lift Optimization

In order to determine which tape would be best for lifting the fingermarks from a substrate and provide the least interference with Raman analysis, 4 different tapes were used. The following tapes were analyzed: Evident® Tape, Scotch® Brand Magic Tape, Remco® Tape, and Scotch® Brand Packing Tape. Both a control fingermark and a drug contaminated fingermark were lifted using each of the tapes and subsequently analyzed using the Benchtop Raman. The control samples taken from each were free of contamination. The spectrum from the marks were overlayed with the standard of cocaine spectrum to determine if there was any interference between the lift and detecting cocaine. For the Evident® Tape and Scotch® Brand Magic Tape, interference was observed in identifying the presence of cocaine and was not used for Phase II of this research. For the Remco® Tape no interference was observed however, after more testing, ease of application was limited. Therefore, Remco® Tape was not used for this research. For Scotch® Brand Packing Tape, no interference was observed. Additionally, there was ease of application, thus it was determined to be best for lifting the fingermarks as well as identifying and detecting the presence of cocaine. Scotch® Brand Packing Tape was used for lifting fingermarks and analyzing them using Raman Spectroscopy for this research.

Phase II: Multiple Contacts Methodology

Based on the results from Phase I, the following three (3) substrates and enhancement techniques continued on to Phase II: (1) Plastic bags enhanced with cyanoacrylate (clean and dirty marks), (2) glass with florescent powder and lifted with Scotch® Brand Packing Tape

(dirty marks), and (3) firearm magazines enhanced with cyanoacrylate and lifted with Scotch® Brand Packing Tape (dirty marks).

Part A: Fingermarks from Plastic Bags enhanced with Cyanoacrylate

Under the Raman Microscope, a grey/white crystalline structure was observed in the drug-contaminated samples after being enhanced with cyanoacrylate. Often, the crystals were in clumps and those large enough were also cloudy when viewed under the microscope which resulted in intense Raman spectra. Other samples showed more iridescent, white and were sometimes clear with a grey outline. Both of these aspects are visualized in the photomicrograph shown in Figure 11. The corresponding spectrum of the clump is presented in Figure 12.

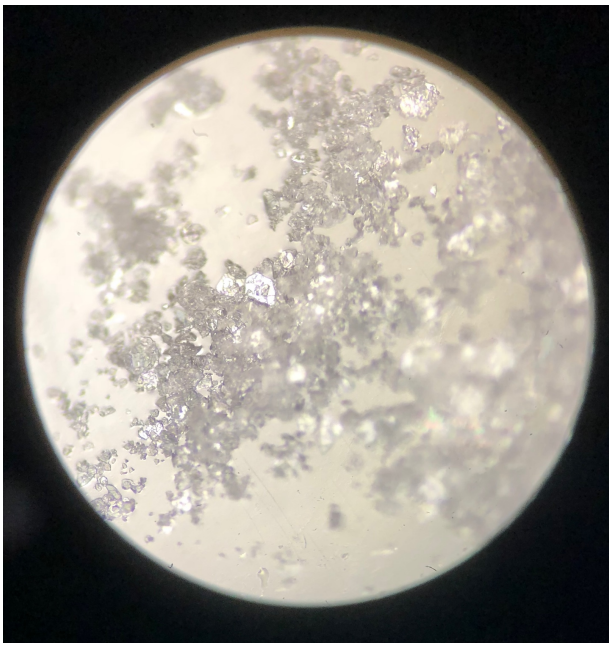

Figure 11: Photomicrograph of the observed crystal clumps of cocaine identified from a drug contaminated fingermark sample. When the cross hairs were placed on these areas resulted in intense Raman spectra

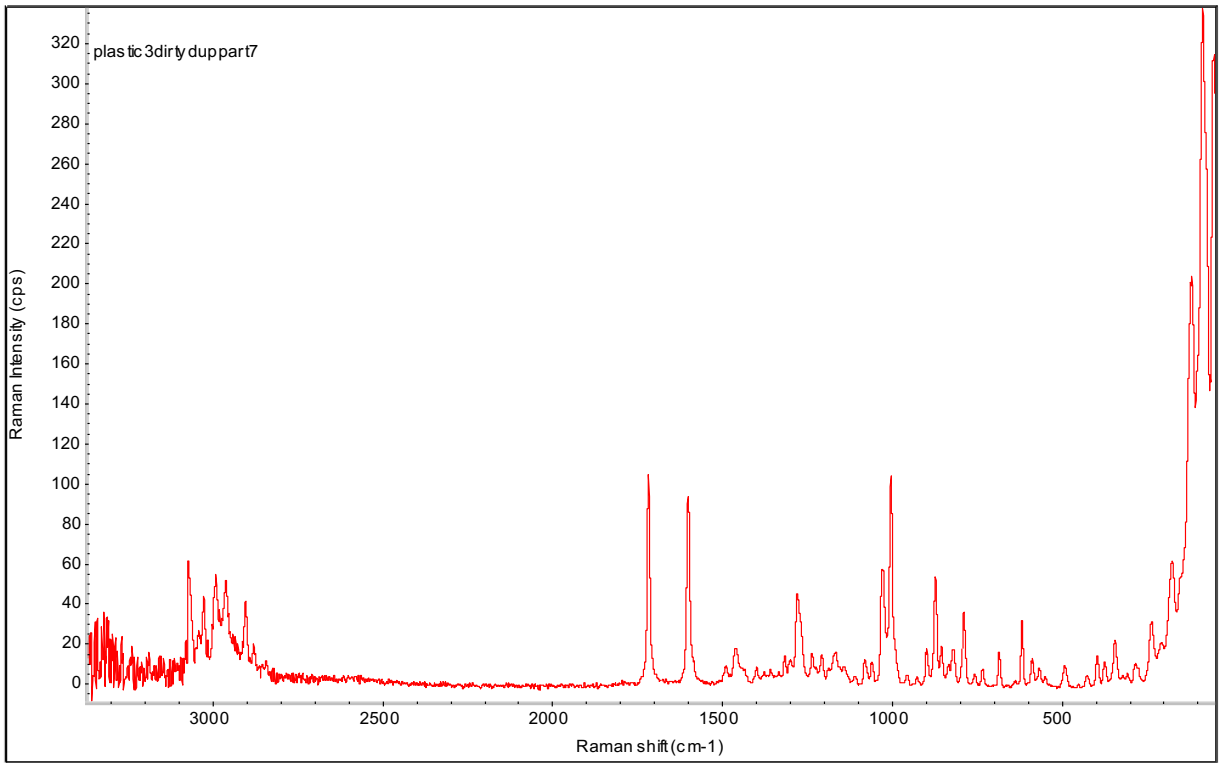

Figure 12: Spectrum of Cocaine Crystal Clump

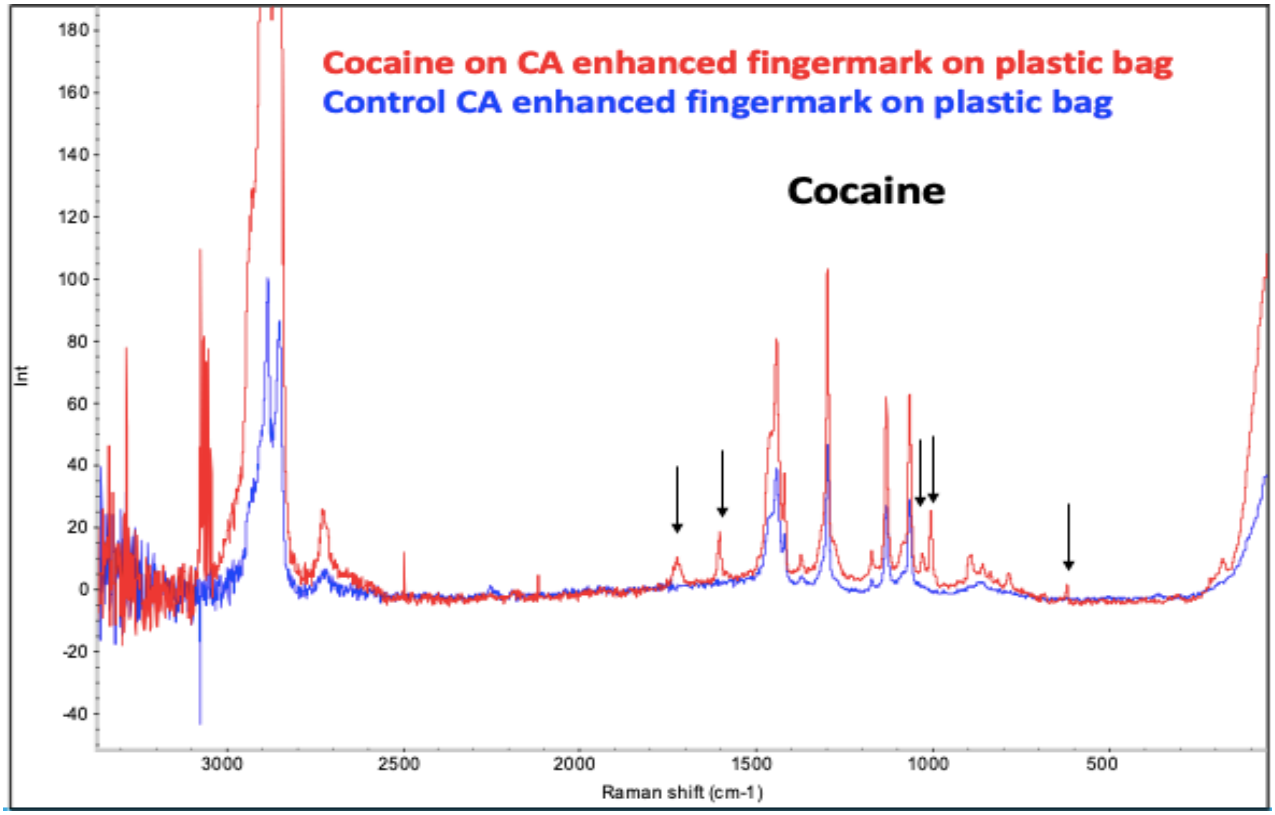

Figure 13 Raman spectra Overlay: Control and Cocaine Fingermarks on Plastic Bags

Cocaine was identified on most of the contacts present on the plastic bags after enhancement with cyanoacrylate. In many of the initial contacts the crystalline structure of cocaine was visible through the microscope's optics. If marks were slightly over processed, this often hindered the visible and spectral cocaine detection under Raman. Additionally, some marks had bubbles of the cyanoacrylate after development. However, other locations of the mark were utilized for the detection of cocaine present. Figure 13 shows an overlay of the Raman spectra of the control fingermark from the plastic bag after development (blue) in comparison to the sample fingermark containing cocaine taken for the substrate (red). The main peaks of cocaine are indicated by the arrows in Figure 13. The significant peaks from the substrate were 1063 cm^{-1}, 1130 cm^{-1}, 1295 cm^{-1}, and 1439 cm^{-1}. The drug contaminated marks taken from the enhanced plastic bags often contained both the control peaks and those from the cocaine, without overlap. This allowed for rapid analysis and identification of the presence of cocaine within each sample.

Figure 14 is a histogram of the results for clean drug-contaminated fingermarks that were placed on plastic bags and enhanced with cyanoacrylate. Each column represents 20 fingermarks at each contact (x-axis). For the clean fingermarks, cocaine was identified in all 20 contacts for 15 out of the 20 sets (each participant performed duplicate sets of the clean marks). For the first 10 contacts, 95-100% of the prints identified and detected the presence of cocaine. Additionally, cocaine was identified in at least 85% of the fingermarks across all 20 contacts. One participant had 37.5% of the fingermarks identified for the presence of cocaine over the two sets of clean fingermarks.

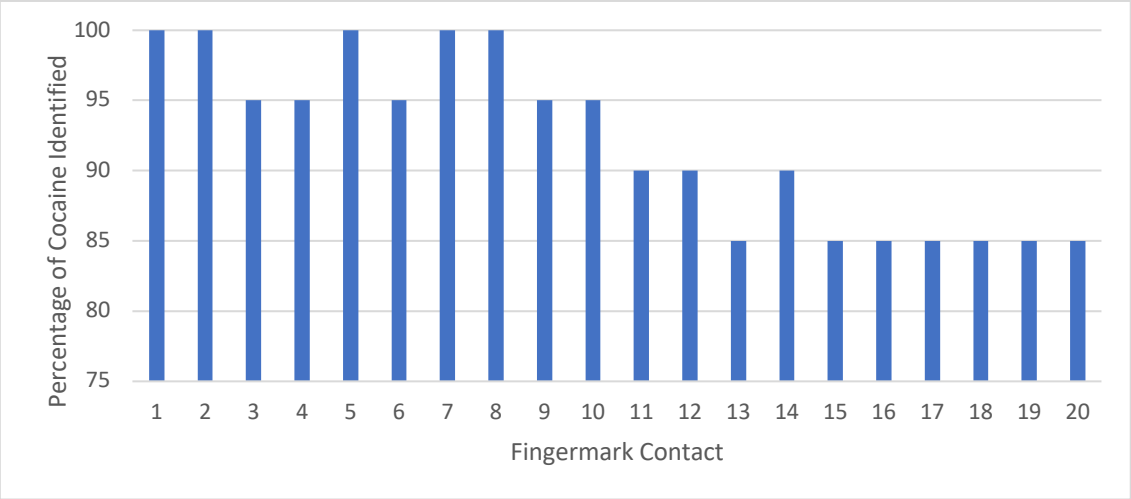

Figure 14 Percent Cocaine Identified: Plastic Bag Clean Fingermarks

Figure 15 represents the results for dirty drug-contaminated fingermarks that were placed on plastic bags and enhanced with cyanoacrylate. Each column represents 20 fingermarks at each contact (x-axis). For dirty fingermarks, cocaine was identified in all 20 contacts for 8 out of the 10 participants. For the first 5 contacts, 95-100% of the marks identified and detected the presence of cocaine. Further, cocaine was identified in at least 85% of the fingermarks for all 20 contacts. With increasing contacts, the dirty marks showed consistent identification and detection of the cocaine.

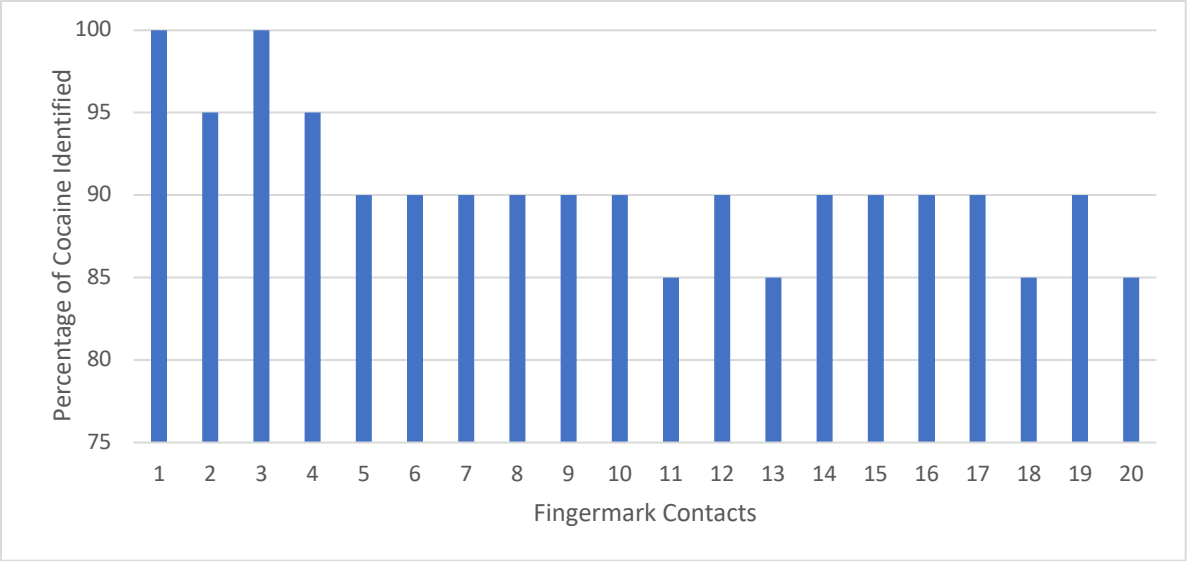

Figure 15 Percent Cocaine Identified: Plastic Bag Dirty Fingermarks

Part B: Tape Lifts of Fingermarks from Glass Enhanced with Fluorescent Powder

Under the Raman Microscope, the cocaine present in the samples was observed by the grey/white crystalline clumps and some showed a slight iridescent nature (Figure 16). These crystals were rarely found without some remnant of the fluorescent powder present or in close proximity. Cocaine was sometimes found underneath clumps of the fluorescent powder as well. In these cases, the cocaine was able to be seen as the crystalline structure showed through certain areas of the powder.

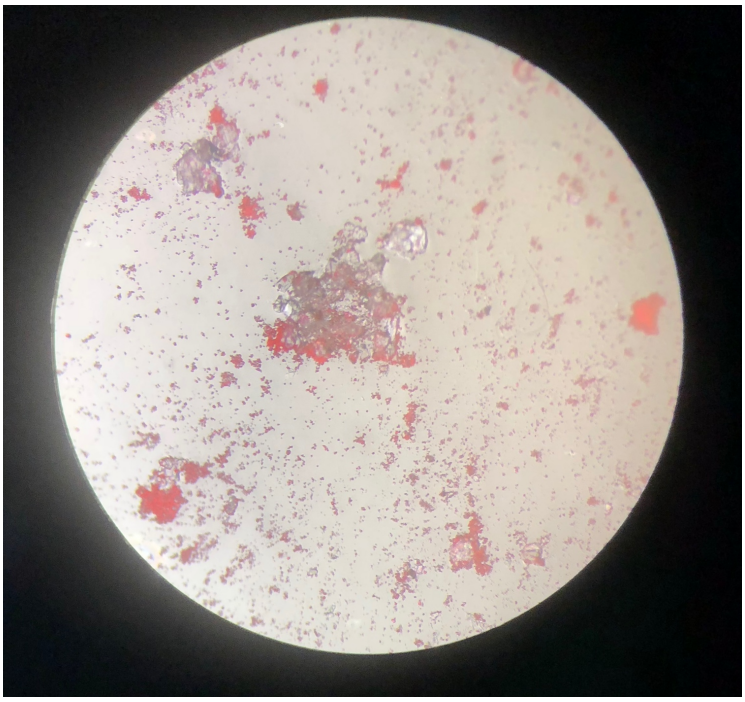

Figure 16: Photomicrograph of the observed iridescent nature of cocaine crystals found surrounded by the fluorescent fingerprint powder.

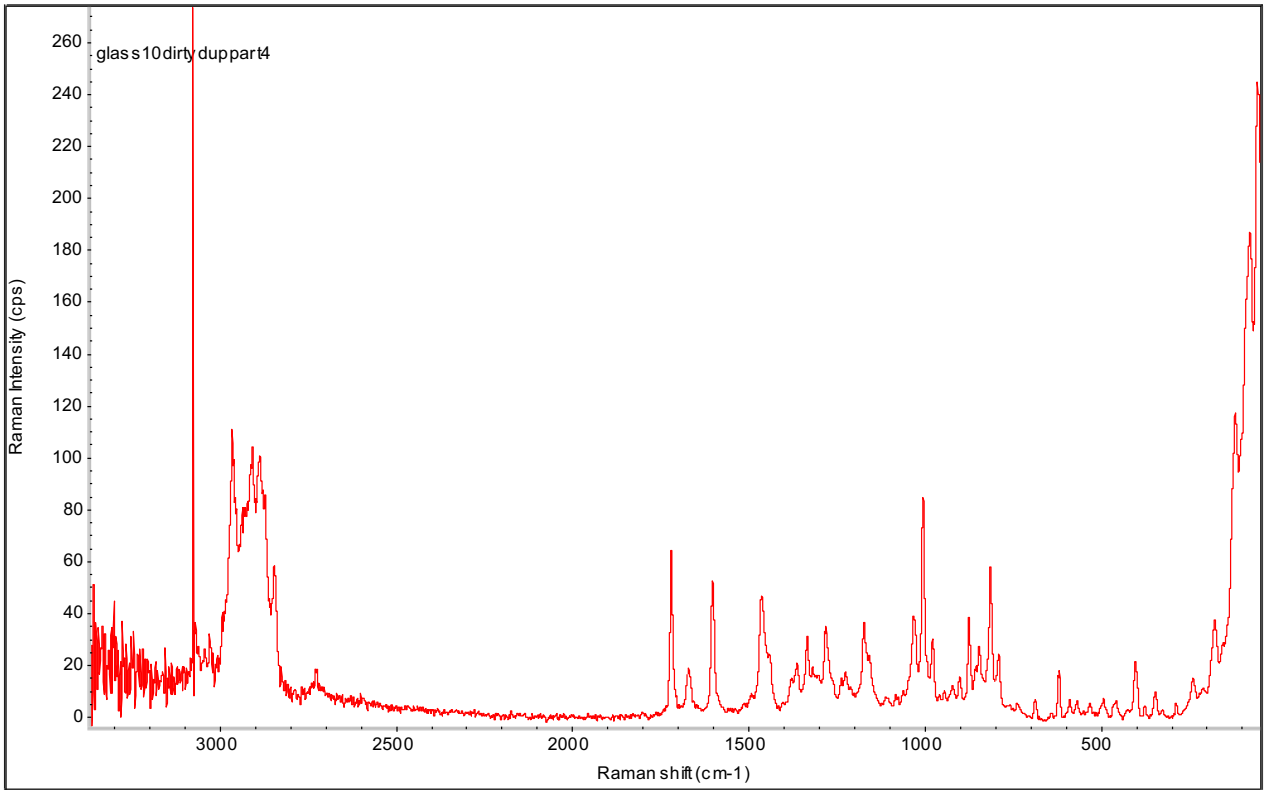

Figure 17: Raman spectrum of Iridescent Cocaine Crystals with Fluorescent Powder

The cloudier in appearance the crystalline structure was, the higher Raman intensity. The cloudy appearance was sought after and yielded the cleanest and most intense spectra. For many of the first initial contacts, cocaine was visible macroscopically and could be differentiated under the microscope light for multiple marks. However, in samples where the cocaine deposit was not visible, the crystalline structure of cocaine was visualized and detected in navigating the mark using Raman Microspectroscopy.

Only dirty drug-contaminated marks with this substrate were taken from participants due to the lack of ridge detail. Figure 18 shows an overlay of the Raman spectra of the control sample (no cocaine) from the tape lift after development in comparison to a drug contaminated fingermark taken for the substrate. The main peaks of cocaine are indicated by the black arrows. In comparison with the controls taken from the participants before introducing cocaine, Raman

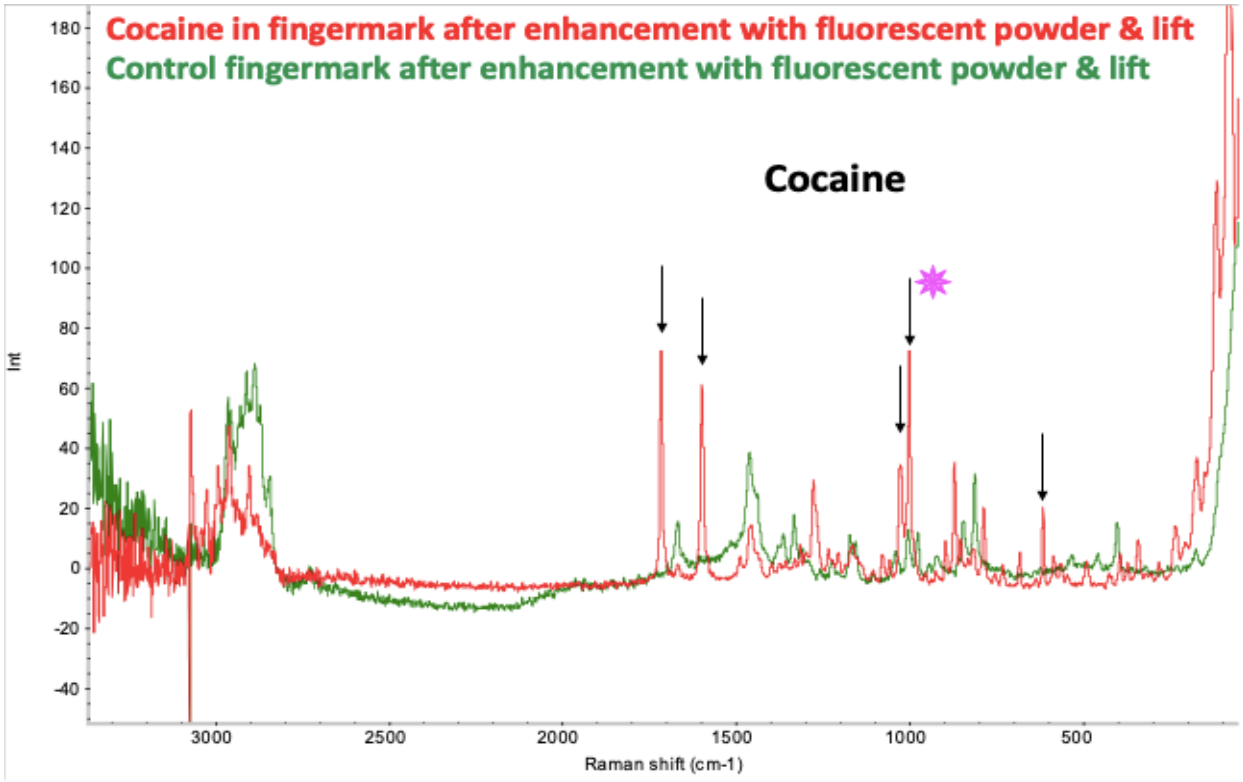

Figure 18: Raman spectra Overlay: Control and Cocaine Fingermarks Tape Lifts from Glass

peaks at ~999 cm^{-1} from the fluorescent powder overshadowed the Raman peak for cocaine at this location (indicated by the asterisk in Figure 18). The other main cocaine peaks at 1715 cm^{-1},1597 cm^{-1} were used to determine the presence of cocaine in these samples, since they usually are the most intense in the spectrum, despite the interference. The peaks at 869 cm^{-1} and 785 cm were also checked to support the identification of cocaine. All peaks needed to have a signal-to-noise ratio greater than 3 to be considered for identification.

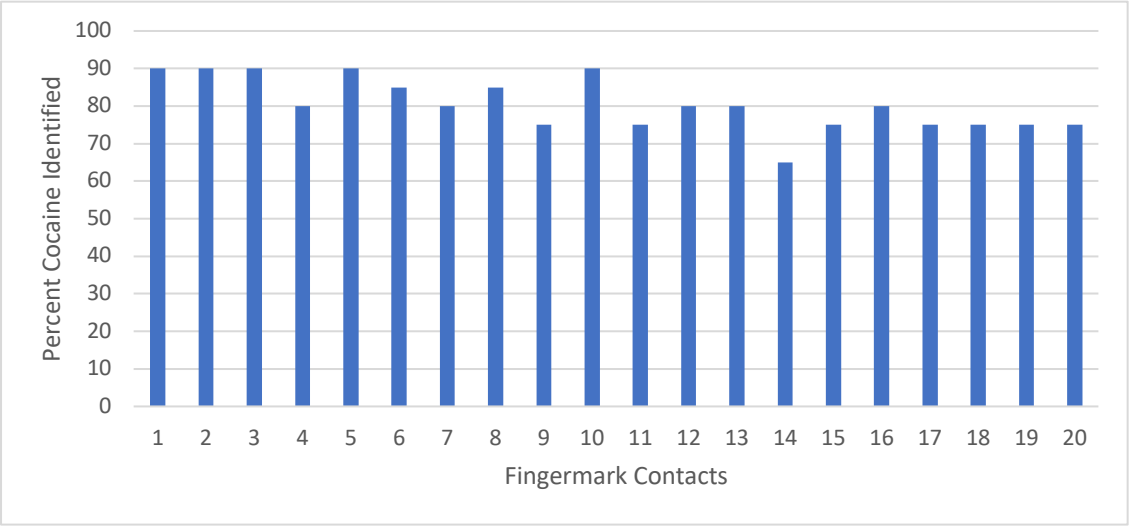

Figure 19 Percent Cocaine Identified: Lifts from Glass Dirty Marks

Contamination of the control fingermarks for participant 3 was identified during the Raman spectral analysis. For these samples, the participant was retested. Additionally, a small contamination study was conducted and identified that the fiberglass brush was moving the cocaine particles to other fingermarks in the dusting process. This has meaningful implications, and which are discussed later in this thesis.

The results of the identification and detection of cocaine from the tape liftings from drug-contaminated fingermarks planted on glass and enhanced with fluorescent powder are shown in Figure 19. Each column represents 20 fingermarks at each contact (x-axis). One participant had no cocaine detected across all fingermarks to the substrate. Cocaine was identified in at least

65% of the fingermarks. However, this technique showed greater variability and more susceptible to contamination than the other substrates tested.

Part C: Tape Lifts of Fingermarks from Cyanoacrylate Fumed Firearm Magazines

Under the Raman Microscope, the cocaine present in the fingermarks on the cyanoacrylate fumed firearm magazines was observed by the grey/white crystalline clumps and some showed a slight iridescent nature (Figure 20). For the first few contacts for most of the participants, the cocaine was visible and found from a substantial cluster. However, for many of the marks only the sebaceous oils were found on the magazine even after the development process. These marks were not enhanced further using powders due to contamination issues faced with the analysis of fingermarks lifted from glass.

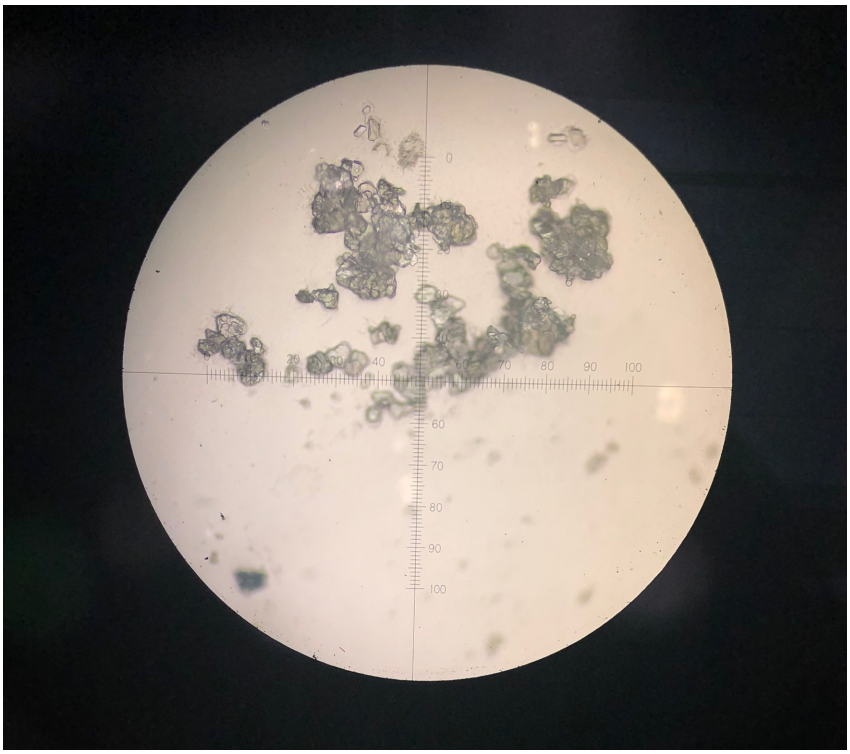

Figure 20: Photomicrograph of clumps of iridescent of cocaine observed under the Raman Microscope for tape lifts from firearm magazines

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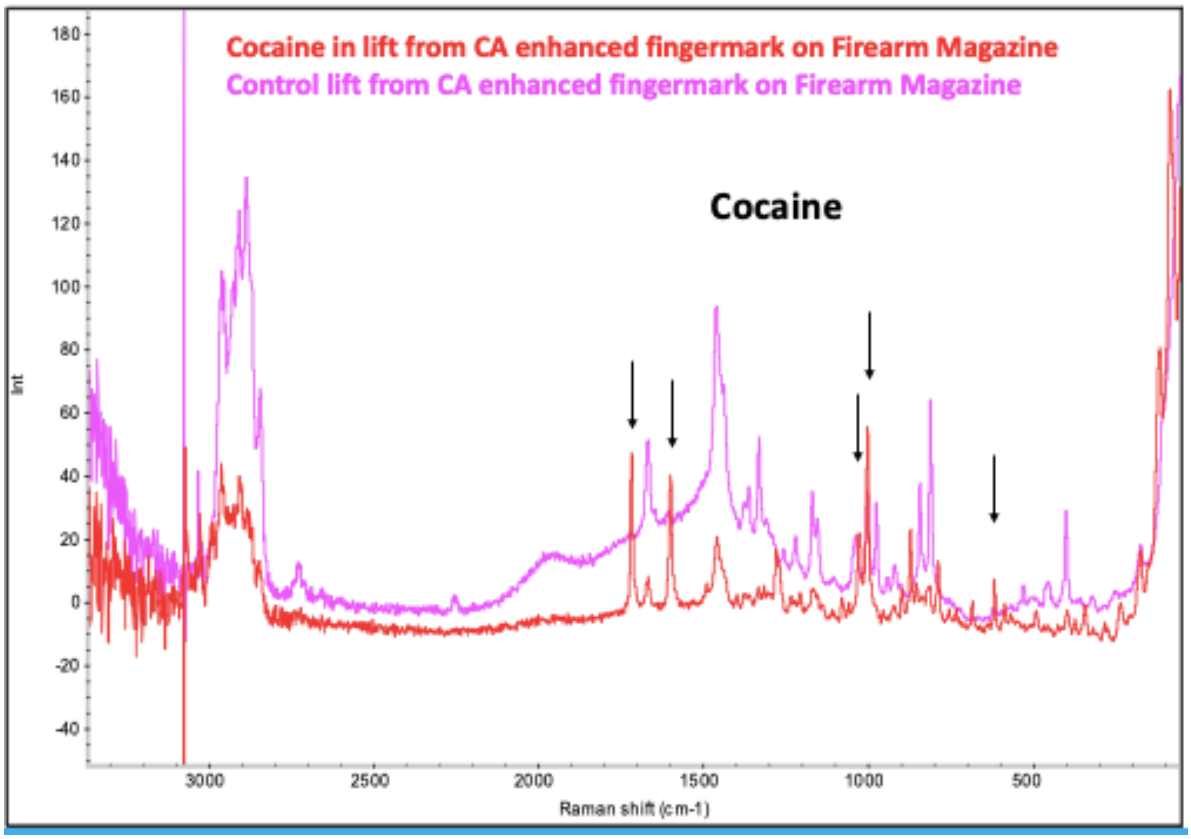

Figure 21: Raman spectra Overlay: Control and Cocaine Fingermarks of Lifts from Firearm Magazine

Figure 21 shows an overlay of the Raman spectra of the control sample (no cocaine) from the tape lift after development in comparison to the fingermark taken from the firearm magazine. The main peaks of cocaine are indicated by the black arrows. In comparison with the controls taken from the participants, Raman peaks at ~999 cm^{-1} overshadowed the Raman peak for cocaine at this location (Figure 21). The other reference cocaine peaks were then used to determine the presence of cocaine in these samples. All peaks needed to have a signal-to-noise ratio greater than 3 to be considered for identification.

For the tape lifts of the drug-contaminated fingermarks recovered from firearm magazines, cocaine was identified in all 15 contacts for 3 out of the 10 participants. Additionally,

cocaine was identified in at least 40% of the fingermarks for all 15 each contact (Figure 22). It can be seen that the 7th contact had the smallest percentage of positive cocaine identifications (40% of the samples), which is notably less than those for the last measured contacts (e.g. 14 and 15).

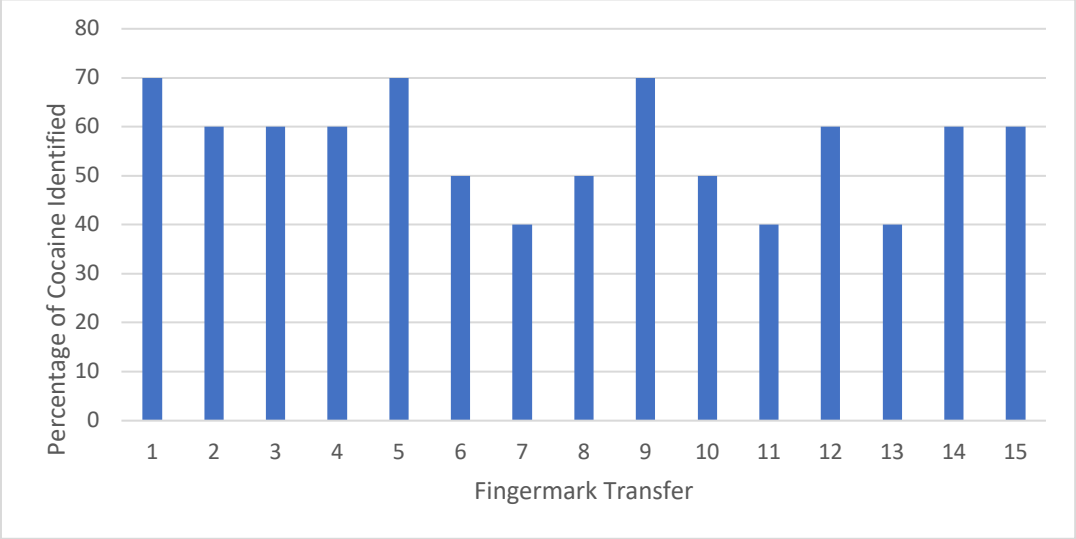

Figure 22 Percent Cocaine Identified: Lifts from Firearm Magazines Dirty Fingermarks

Part D: Portable Raman Spectroscopy

The ACE-ID portable Raman spectrometer is capable of identifying cocaine in the field (Figure 23). However, using the ACE-ID ortable Raman spectrometer, no cocaine was detected within the fingermarks when tested from the plastic bag and glass samples.

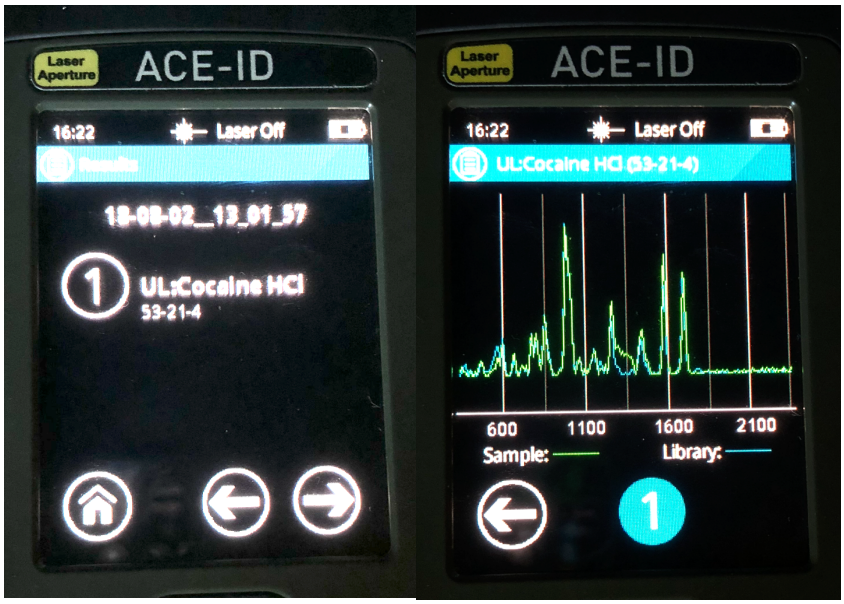

Figure 23: The expected resulting display and spectrum of Cocaine hydrochloride. This result was obtained only by holding a vial containing cocaine hydrochloride to the Portable Raman for analysis. All other samples tested did not detect and identify the presence of cocaine

However, other compounds present within the marks were identified from the instrument's on-board spectral library. For the dirty drug-contaminated fingermarks on a glass substrate, the following materials were identified in spectral library searches:

Magnesium Hydroxide, Toluene 2,4,diisocyanate, Gabapentin, JWH-073, 081,018,015, Sodium Dichromate Dihydrate, mescaline NBOMe HCl, Toilet Bowl Cleaner, 2-methylnapthalene, Acrylic Polymer, Clenbuterol, Pentaerythritol, 2-C-C(Phenetylaine), MAM-2201, MDMA HCL, Chloroquine Diphosphate Salt, Chloroacetone, N-N Dimethylhydrazine, Sodium Dichromate, Sorbitol Hexantirate, Hexanal.

For the dirty drug-contaminated fingermarks on a plastic substrate, the following materials were identified in spectral library searches:

Safrole, 2-methylpentane, magnesium hydroxide, JWH-073, 015, 018, 019, 007, 081, Tributyl phosphate, Gabapentin, N-N;dimethylhydrazine, acrylic polymer, Toluene 2,4,diisocyanate, hexanes, chloroamphetamines, MDMA HCL, caffeine, 5-MethoxyDALT, 2C-C(phenethylamine), chlorpicrin, Pentaerythritol, AB-PINACA, Naphyron 1-Napthyl isomer, 2-propanol, N-dimethyl hydrazine, Griseofulvin, Dihydrosafrole, mescaline NBOMe HCl, MEDA, MAM-2201, 2C-C(Phenethylamine)

For the clean drug-contaminated fingermarks on a plastic substrate, the following materials were identified in spectral library searches:

Acrylic Polymer, 2-propanol, Hexanes, Chloroamphetamine, Clenbuterol, psilocybin, JWH-015, Magnesium Hydroxide, quinine base, Fox 12(GUDN), Toluene 2,4,diisocyanate, Chloroquine Diphosphate Salt

Portable Raman analysis was not continued for the remaining substrates, specifically the fingermarks from the firearm magazine, due to the failure to identify cocaine using this instrument for the glass and plastic bag samples, which was contrary to results from the benchtop Raman microspectrometer.

DISCUSSION AND CONCLUSIONS

A. Fingermarks from Plastic Bags enhanced with Cyanoacrylate

Drug-contaminated fingermarks that were placed on plastic bags and enhanced with cyanoacrylate showed the most consistent results for clean and dirty marks than the other substrates analyzed. For both clean and dirty marks 85% of all marks were identified. For 15 out of the 20 clean mark sets, participants had detectable cocaine within all of the fingermarks up until contacts 20. Dirty marks also showed consistent results as well. The high percentage of cocaine identified even at the last contacts suggests that detection can be made beyond the 20^{th} contact, however, further research would be needed to test this hypothesis. Additionally, the development process employed did not induce contamination between the marks since the oils from the individual fingermark allows for the polymerization from the vaporized cyanoacrylate. This processing also showed the least interference between the control and cocaine doped fingermarks allowing for detection of cocaine using the 5 main peaks in its spectrum.

After development was completed using the chamber, many of the fingermarks showed some bubbling on the ridges. These areas were magnified when viewed under the Raman Microscope, and made detection in some spots difficult. However, in some cases cocaine was able to be detected in testing those areas. It was determined that the bubbles were caused by the high temperature of the fuming chamber. The normal temperature set by the chamber was 176.7°C (350°F) which is above the melting point of cocaine (98°C). Therefore, the bubbles observed were a combination of the melting cocaine and liquid cyanoacrylate.

B. Tape Lifts of Fingermarks from Glass Enhanced with Fluorescent Powder

Dirty drug-contaminated fingermarks were taken from tape lifts from glass. As previously mentioned, clean drug-contaminated fingermarks on glass were not continued from Phase I due to the limited sebaceous oils in these prints which prevented sufficient enhancement of the ridge details using the fluorescent powder. Additionally, when using the fiberglass brush for enhancement with fluorescent powder before lifting, contamination of other marks was observed. The brush moved the cocaine crystals from mark to mark. For some sets, the participants had to resubmit fingermarks since cocaine was identified in the control mark due to the dusting process.

There was notable variability in the ability to detect and identify cocaine in drug-contaminated fingermarks developed with fluorescent powder. For one participant, there was no detectable cocaine present on any of the fingermarks. It is unknown why this participant did not transfer the cocaine to the substrate in any of their fingermarks. One possible explanation is that the collection process was performed under an air-conditioned environment. Previous studies have indicated that these factors can influence the amount of sebaceous oils that can be transferred which could have affected the transfer capability of the cocaine from the fingermarks.

A contamination study was performed due to the reoccurrence of identifying cocaine within control samples for this substrate. Participant 3 was used for this study since many sets taken showed this issue. The participant placed a control and 10 fingermarks using 11mg of cocaine onto the glass substrate. With a new fiberglass brush, the marks were developed and lifted with Scotch® Brand Packing Tape. The control sample taken did not contain any cocaine after analysis using the Raman Microspectrometer. Therefore, it was concluded that the previous brush was in fact moving the drug particulates around to the other samples. The brushes are initially cleaned with soap and water and then allowed to dry for 24 hours. After the elapsed

time, the bristles of the brush are loosened by hitting it against a hard surface and using the twisting technique performed during enhancement. Cleaning the brush between participants seemed to decrease the propensity of contaminating the other marks however, this is not normally done after each use since it can be a tedious and time-consuming drying process.

These samples also showed one overlapping peak (~1000 cm-1) between the spectra of the control samples and the cocaine standard. Despite this, cocaine was able to be identified in the fingermarks by analyzing the other main peaks in the spectra.

Although the detection of cocaine present in fluorescent powder-enhanced fingermarks on glass is possible, it is not advisable due to contamination issues. Brush contamination would be a serious problem if this identification technique were to be utilized in casework.

C. Tape Lifts of Fingermarks from Cyanoacrylate Fumed Firearm Magazines

Only dirty drug-contaminated marks were investigated for this substrate due to the number of firearm magazines obtained. After the development processing, the marks that were found on the substrate were mostly sebaceous oil residues. Many of the fingermark residues also contained observable clumps of cocaine.

Since the fingermarks were subjected to the same development process and parameters as the fingermarks from plastic bags, many of the fingermarks showed the same bubbling under the Raman Microscope. This was caused by the cocaine melting in the high temperature of the fuming chamber combined with the cyanoacrylate polymerized with the drug contaminated area of the fingermark. Similar to that from the plastic bag study, in some instances the bubbles made detection more difficult while in others cocaine was able to be detected in those particular areas.

Fingermarks recovered using this development process and substrate were highly variable between participants. Cocaine was only identified in all 15 contacts for 3 out of the 10 participants. For 2 other participants, no cocaine was identified in any of the contacts.

However, not obtaining sufficient ridge detail from the fingermarks indicates the need for additional enhancement processing after cyanoacrylate fuming. Since contamination issues were observed from using the glass substrate, the firearm magazines were not enhanced with powders. It is possible that white magnetic powder be used to enhance these marks in order to obtain the ridge detail necessary to be using in fingerprint analysis and be used for individualization purposes. Because Raman analysis is non-destructive and does not require contact with the sample, additional enhancement with powder could be done following a spectral examination for illicit drugs. By doing the powder enhancement after Raman microspectroscopy, the brush contamination issue could be avoided.

D. Portable Raman

Experiments were performed with the portable Raman spectrometer to determine if it could be used to identify the presence of cocaine within the fingermarks for the plastic bag and tape lifts from glass samples. However, no cocaine was detected using this instrument. Due to the low concentration of cocaine present within the fingermark ridges, identification of the cocaine within these samples was not possible. This could be due to the large spot size of the portable Raman and reduced sensitivity, when compared to that of a benchtop Raman spectrometer. In the future, as portable technology continues to improve, this may be possible. However, at this time, the detection of drug-contaminated fingermarks is restricted only to laboratory benchtop Raman analyses.

E. Conclusions

Being able to associate illicit drugs with a specific fingermark has great potential because it can literally put the drugs in the hands of a specific individual. Drug contamination present within fingermarks from plastic, glass, and firearm magazines were able to be detected after development using Raman spectroscopy. Identification of cocaine was possible in as many as 20 contacts, and possibly more. Based on these findings, cocaine in fingermarks can persist through multiple contacts even after enhancement techniques are performed. However, there is notable variability in the ability to identify cocaine in multiple contacts of contaminated fingermarks between different individuals and on different substrates.

Of significant interest was the observation that powder brushes were contaminated with the drugs present in one fingermark on glass, and then spread the drug to other fingermarks. Although the detection of cocaine present in these fingermarks is still possible, it is not advisable due to this brush contamination issue. Brush contamination would be a serious problem if this identification technique were to be utilized in casework. Because Raman analysis is non-destructive and does not require contact with the sample, additional enhancement with powder could be done following a spectral examination for illicit drugs. By doing the powder enhancement after Raman microspectroscopy, the brush contamination issue could be avoided.

F. Contributions to Forensic Science

Detection and identification of drug contamination in fingermarks has the potential to be of great importance in forensic science. Using this Raman microspectroscopy, drug-contaminated fingermarks can be identified in at least 15 or 20 multiple contacts, and possibly more, depending on the substrate and method of enhancement. This could be helpful in casework and could have been useful in the previously described Maritime cocaine case. During the trial, it was asked whether the cocaine found on the wheel could have come from the defendants, who

were the suspected owners of multiple boxes containing cocaine, or the coast guard officers, who could have possibly transferred traces of cocaine from their taxi boat after working on a previous case and planted it on to the sailboat. In this case the boat's wheel was swabbed to collect any residues. However, if the cocaine was detected and identified within the ridge details of a fingermark, this evidence could have connected the illicit drugs with the suspects or excluded them from handling the cocaine onboard.

There are several areas of additional research that could be explored on the topic of the detection and identification of multiple contacts of drugs in fingermarks. First, since the substrates researched for this project were mainly non-porous substrates, further investigation of enhancement of latent prints followed by the detection of cocaine should be considered. Other possible techniques could include enhancing copy paper and tile with magnetic powder and sticky side powder for tape lifts. Additionally, future work can be done by expanding this project to more than 20 contacts or testing other drugs in to see if there are similarities in the detection by using this methodology. An important follow-up research project should involve experimentation on drug transfers that occur between multiple participants before planting fingermarks on substrates can also be investigated. Also, investigation into the effect of having drugs that are cut with excipients and how it effects the detection of the drug-contamination would also be of value since many cases involve samples that are not pure. Last, expanding the use of Raman microspectroscopy to the detection and identification of other drugs would widen the application of this research. The expansion of this research into examining the contacts of more types of traces, including other drug contaminations and explosives, has the potential to aid forensic scientists by providing additional understanding of the nature of contacts and persistence of these trace materials and their implications.

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APPENDICES
IRB

B. State the purpose of the research. Include major hypotheses and research design. If the study is part of a larger study, briefly describe that larger study and indicate whether it has received IRB approval from another institution (if so, append the approval to this application). **Please keep in mind that the IRB is composed of individuals from many disciplines and thus the description of your research should be written in terms readily comprehensible by non-experts.**

The purpose of this research is to determine if enhancement techniques, substrates, and cleanliness of fingers has an effect on multiple transfers with drug-contaminated fingerprints. Since previous research has shown that drugs can be detected from the ridges of prints left behind, this project aims to determine the number of successive transfers for which drugs can still be detected. We plan to have participants place their fingers in a minute amount of cocaine before placing prints on particular substrates. Then the prints will be enhanced or visualized based upon which substrate it is planted on. The ridges of the prints will be tested for the presence of cocaine using benchtop and portable Raman Spectroscopy.

C. Describe the source(s) of subjects and the selection criteria. Selection of subjects must be equitable and, in the case of protected populations such as children, prisoners, pregnant women, the mentally disabled, etc. should address their special needs. Attach the text of any advertisement, letter, flier, oral script or brochure used to solicit potential subjects.

For this study, we plan on having 10 participants plant fingerprints on 8 different substrates in duplicates. The selection of the subjects will be either graduate students or professors who wish to participate. Equal selection for specific genders is not necessary for this particular project.

D. Provide a description of the procedures to be followed. Focus the description on the procedures involving the human participants and their data. Append copies of questionnaires and/or interview protocol, or a sufficiently detailed description of the measures to allow the IRB to understand the nature of subjects' involvement.

The participants will be asked to take an initial control for their unclean fingerprint. Then they will be asked to press their finger on about ~30-40 micrograms of cocaine before placing 10 successive prints on the particular substrate. This process will be done for each of their fingers excluding their little fingers for a total of 8 substrates. Then the next day, they will be asked to come back with clean hands and repeat the procedure including a clean control and then placing their fingers in small amounts of cocaine before placing their prints on the substrates. The participants will be asked to wash their hands thoroughly before they leave the premises.

E. Describe any potential harms or benefits to be derived by participants. Include a discussion of the risk/benefit ratio. For approval of any study with more than minimal risk, the benefits must

clearly be shown to outweigh the risk. Describe how the study may expose participants to stress, physical, psychological or interpersonal hazard, including the possibility of pain, injury, disease, discomfort, embarrassment, worry or anxiety. Include any safeguards planned to minimize or mitigate any risks involved.

There are no benefits for agreeing to participate in this study. However, the risks of this experiment are minimal. Placing cocaine on undamaged skin has shown that it is unlikely that anyone can absorb enough of cocaine via this method of absorption to render a positive urine test (Karch, 2008). Previously published studies have performed research with similar methodologies that included using cocaine as well as other illicit drugs such as ketamine and amphetamines. The participants touched these substances and placed the contaminated fingerprints on various substrates (Day et al., 2004; West & Went, 2008). These studies showed that these trace amounts of drug content can be detected on the ridge detail of fingerprints however the current project will determine the number of successive transfers from which the material can still be detected. Further, in a study conducted by Professor Fredrick Smith and student Kevin McGarth in 2011 at the University of New Haven, traces of cocaine were shown to be identified through contact with everyday activities such as handling grocery store shopping carts, using ATM machines, handling money, and fuel pumps (Smith and McGarth, 2011). Due to the minute amount that will be used to contaminate the participants hands, we expect that the risk of handling the cocaine in this fashion is minimal.

F. Describe the specific methods by which confidentiality and anonymity will be protected, include the use of data coding systems, how and where data will be stored and who will have access to it, and what will happen to data after the study has been completed. Note that all studies must conform to the UNH data management plan.

The names of the participants will not be recorded, reported, stored or associated with the submission of their fingerprint. Once these prints are used for analysis they will be properly discarded.

G. If applicable, provide the following: 1) a description of the debriefing procedures to be used in cases where deception has occurred; 2) a statement describing what actions you will take should the research reveal the possibility of a medical or other potentially troubling condition.

If the participants reveal the possibility of a potential medical condition they would be instructed to thoroughly wash their hands with soap and water. If a medical issue still exists they will be referred to the health center in Sheffield Hall. However, since cocaine is not significantly absorbed via the skin or known to cause irritation to the skin, this scenario is not expected to occur.

H. Provide a copy of all the informed consent documents (oral and/or written).

- Include scripts for oral consent and assent forms for research involving minors under the age of .

-When the consent form to be used will be in a language other than English, an English translation must be provided.

The procedures and purpose of the experiment that is outline above will be explained to the participants and further questions will then be discussed. After giving them some time to think it over, if they wish to participate in this study they will be asked to sign a consent form that is provided with this application.

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Informed Consent Form
(University of New Haven)

Title of Project: Multiple Transfers of Drug Contaminated Fingerprints and Their Analysis using Raman Spectroscopy

Principal Investigator: Brooke W. Kammrath, Ph.D
Co-Principal Investigator: Victoria DePrimo

Participant Printed Name: _____

We invite you to participate in the following research study "Multiple Transfers of Drug Contaminated Fingerprints and Their Analysis with Raman Spectroscopy" at the University of New Haven. This project aims to answer the question if substrate, enhancement technique, and multiple transfers affect the detection and identification of drugs in fingerprints using spectroscopic methods. Participation in this study is completely voluntary. We welcome and encourage any questions that you might have in making a decision. If you do so decide that you would like to take part in this study, you must sign this form below.

This research is being conducted to determine the number of multiple transfers containing drug components that can be sufficiently identified using Raman Spectroscopy. This has great implications in forensic science because it will evaluate the ability of the same fingermark to be used to link an individual to a drug material through fingerprint identification methods combined with spectroscopic analysis. This study will require you to make contact with small amounts of cocaine drug particles, after a control sample is taken. Then after rubbing off the excess, you will be asked to place your finger on a given substrate material (e.g. glass, paper, metal) 10 consecutive times with space between each. Following this procedure for each of the substrates, the participant will be asked to wash their hands and repeat the same procedure listed. Further, the participants will be asked to return at their earliest convenience to apply both the unclean and clean prints in the same fashion for duplicates. Although illicit drugs will be used in this experiment, they do not significantly dermally penetrate the skin and should not cause any adverse reactions. However, if you as the participant experience any skin irritation or any other discomfort as a result of participating in this study, please contact the University of New Haven Campus Health Center: 203-932-7079, which is located in the ground floor of Sheffield Hall.

The contaminated fingerprints obtained will have no aspects of individualization attached to them, they will be coded anonymously to be used in presentations, publications, and future projects. Upon request, samples will be removed from the project and destroyed at any time. Once the project is completed, all samples will be destroyed immediately.

Participating in this study is voluntary. In taking part in this study, participants will receive no compensation for donating samples. If you choose to take part, you have the right to decline and stop at any time. Also, if you decide you would not like to participate in this study, there will be no penalty. The Department of Forensic Science at the University of New Haven is funding this study.

In signing below, you agree that you have received this information. Additionally, any questions that you have concerning the project have been answered. You will receive a copy of this signed form to keep as a future reference.

Participant: By signing the consent form below, you indicate that you are voluntarily choosing to be part of this study, and are at least 18 years of age.

_____	_____	_____
Signature of Participant	Date	Printed Name

If you have any questions or concerns regarding this research or your rights as a participant in this study and would like to discuss this with someone other than the researchers, please contact Alexandria Guzman, Chair of the Institutional Review Board at UNH, at 203-479-4562.

Individual Explaining the Research: By signing below, you agree that you have explained the research to the participant along with answering any questions he/she may have had.

_____	_____	_____
Signature of the Researcher	Date	Printed Name

Plastic Bag Enhanced with Cyanoacrylate: Clean Marks
Raw Data

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	Percentage		
Part 1 C1																						
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	100	100	Part 1
Part 1 C2																						
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	100		
Part 2 C1																						
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	100	100	Part 2
Part 2 C2																						
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	100		
Part 3 C1																						
1	1	1	1	1	1	1	1	1	1	1	1		1	1	1	1	1		1	90	95	Part 3
Part 3C2																						
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	100		
Part 4 C1																						
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	100	100	Part 4
Part 4 C2																						
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	100		
Part 5 C1																						
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	100	100	Part 5
Part 5 C2																						
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	100		
Part 6 C1																						
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	100	100	Part6
Part 6 C2																						
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	100		
Part 7 C1																						
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1				1		80	87.5	Part 7
Part 7 C2																						
1	1	1	1	1	1	1	1	1	1	1	1	1	1		1	1	1	1	1	95		
Part 8 C1																						
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	100	100	Part 8
Part 8 C2																						
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	100		
Part 9 C1																						
1	1	1	1	1	1	1	1	1	1											50	37.5	Part 9
Part 9 C2																						
1	1			1		1	1													25		
Part 10 C1																						
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	100	100	Part 10
Part 10 C2																						
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	100		
																					92	Total Percent
Percentage																						
100	100	95	95	100	95	100	100	95	95	90	90	85	90	85	85	85	85	85	85			

Plastic Bags Enhanced with Cyanoacrylate: Dirty Marks
Raw Data

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	Percentage			
Part 1 C1																							
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	100		100	Part 1
Part 1 C2																							
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	100			
Part 2 C1																							
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	100		100	Part 2
Part 2 C2																							
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	100			
Part 3 C1																							
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	100		100	Part 3
Part 3C2																							
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	100			
Part 4 C1																							
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	100		100	Part 4
Part 4 C2																							
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	100			
Part 5 C1																							
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	100		100	Part 5
Part 5 C2																							
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	100			
Part 6 C1																							
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	100		100	Part6
Part 6 C2																							
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	100			
Part 7 C1																							
1		1	1	1	1	1	1	1	1		1		1	1		1	1	1		75		85	Part 7
Part 7 C2																							
1	1	1	1	1	1	1	1	1	1	1	1	1	1		1	1	1	1	1	95			
Part 8 C1																							
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	100		100	Part 8
Part 8 C2																							
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	100			
Part 9 C1																							
1	1	1												1	1			1		30		25	Part 9
Part 9 C2																							
1	1	1	1																	20			
Part 10 C1																							
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1			1	90		95	Part 10
Part 10 C2																							
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	100			
Percentage																						90.5	Total
100	95	100	95	90	90	90	90	90	90	85	90	85	90	90	90	90	85	90	85				

Tape Lifts from Glass Enhanced with Fluorescent Powder: Dirty Marks
Raw Data

	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20			
Part 1 C1																							
	1	1	1	1	1		1	1		1	1	1	1	1	1	1	1		1	1	85	92.5	Part 1
Part 1 C2																							
	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	100		
Part 2 C1																							
	1	1	1	1	1	1	1	1	1	1				1	1	1	1	1	1	1	85	87.5	Part 2
Part 2 C2																							
	1	1	1	1	1	1			1	1	1	1	1	1	1	1	1	1	1	1	90		
Part 3 C1																							
	1	1	1		1	1	1	1	1	1	1	1	1			1	1				70	85	Part 3
Part 3C2																							
	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	100		
Part 4 C1																							
	1	1	1	1	1	1	1	1	1	1	1	1	1			1			1	1	80	72.5	Part 4
Part 4 C2																							
	1	1	1		1	1	1	1	1	1				1	1		1	1			65		
Part 5 C1																							
	1	1	1	1	1	1	1	1	1	1	1	1	1					1			70	80	Part 5
Part 5 C2																							
	1	1	1	1	1	1	1	1		1	1	1	1		1	1	1	1	1	1	90		
																					0		
Part 6 C1																					0		
	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	100		Part6
Part 6 C2																							
	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	100		
																					0		
Part 7 C1																					0		
	1	1	1	1	1	1		1		1	1	1	1	1	1	1	1	1	1	1	90		Part 7
Part 7 C2																					0		
	1	1	1	1	1	1	1	1	1	1		1	1	1	1	1	1	1	1	1	95		
Part 8 C1																							
	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	100	97.5	Part 8
Part 8 C2																							
	1	1	1	1	1	1	1	1	1	1	1	1	1		1	1	1	1	1	1	95		
Part 9 C1																							
	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1		1	1	1	95	97.5	Part 9
Part 9 C2																							
	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	100		
Part 10 C1																							
																					0	0	Part 10
Part 10 C2																					0	0	
																					0	0	
																					0	0	
																					0	0	Total
	90	90	90	80	90	85	80	85	75	90	75	80	80	65	75	80	75	75	75	75			

Tape Lifts from Firearm Magazines Enhanced with Cyanoacrylate
Raw Data

1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	
Part 1 C1															
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	100
Part 2 C1															
1	1	1	1	1				1			1		1	1	60
Part 3 C1															
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	100
Part 4 C1															
1	1	1	1	1	1	1	1	1	1	1	1	1	1	1	100
Part 5 C1															
															0
Part 6 C1															
1	1	1		1	1	1					1		1	1	60
Part 7 C1															
1	1	1	1	1	1		1	1	1	1	1	1	1	1	93.3333333
Part 8 C1															
															0
Part 9 C1															
			1				1	1	1						26.6666667
Part 10 C1															
1				1				1							20
70	60	60	60	70	50	40	50	70	50	40	60	40	60	60	