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Presumptive Field Testing Using Portable Raman Spectroscopy

Research and Development on Instrumental Analysis for Forensic Science

**Award Number 2010-DN-BX-K201
Final Technical Report**

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Abstract

The Las Vegas Metropolitan Police Department (LVMPD) currently utilizes commercially prepared chemical color test kits that officers use to presumptively identify cocaine, methamphetamine, and marijuana in the field. Over the past few years, false positive results have been discovered due to subjectivity of color interpretation and tedious procedures. Recognizing the need to find a more reliable method for presumptive field testing, the LVMPD Forensic Laboratory began investigating the use of Raman spectroscopy. The laboratory used National Institute of Justice funds to research and enhance existing Raman field technology to provide presumptive analysis of controlled substances. Part of the research focused on evaluating the performance of the ReporteR device, manufactured by SciAps, Inc. (previously DeltaNu, Inc.). Research was successful for analyzing methamphetamine and cocaine through the implementation of improvements designed to enhance the ReporteR device. The laboratory also investigated the advantages of algorithm-based fluorescent baseline correction technology by integrating a Raman microscope into the research design. To examine the specificity of the handheld device and validate its accuracy, the laboratory also used the microscope to compare results generated by the ReporteR.

Casework evidence samples were analyzed in three distinct phases, comparing the ReporteR to the current chemical-based field test kits. The first phase of testing consisted of solely laboratory-based evaluation of the ReporteR. In the next two phases, narcotics detectives were recruited to perform tests on substances encountered in the field. From the onset of testing until after the enhanced ReporteR was evaluated, methamphetamine field testing accuracy increased 19.4%. Cocaine field testing accuracy increased 26.6% after enhancements. The reliability of the ReporteR was investigated through random re-testing of samples and results were consistent in approximately 87% of instances. Correlation settings and library content were studied and it was found that proper regulation of these factors can decrease erroneous results.

Alleviating fluorescence issues of commonly encountered drugs is important to the future of Raman-based field testing. Unlike other techniques, the advantage of algorithm-based fluorescence baseline correction technology is that it could be translated to a portable system. During the third phase, the laboratory used the Raman microscope to determine if a specific patented algorithm would aid in the identification of fluorescing substances (e.g. ecstasy tablets, black tar heroin, and marijuana). Repeatable spectra indicating the presence of cannabinoids in

marijuana plant material were collected using the Bruker Senterra Raman microscope. Testing ecstasy evidence revealed that substances can be identified, regardless of color and binding agents. A few synthetic drug analog reference materials were also evaluated. The compounds did produce spectra, however, in some instances; fluorescence caused hindrances in which the baseline correction technology was essential. Typically, testing black tar heroin directly is not feasible with Raman technology. In an attempt to remedy this, one technique involved the use of graphene to quench the fluorescence. The ReporteR device revealed possible indications of heroin peaks with the addition of graphene. An evaluation of cocaine/diluent mixtures using the Raman microscope demonstrated that baseline correction is valuable to the differentiation of mixture components.

By testing the handheld devices in the lab, in the field, and by utilizing a Raman microscope, the LVMPD Forensic Laboratory has determined that portable Raman technology is an effective and reliable tool to presumptively identify methamphetamine and cocaine in the field. The laboratory has also identified which characteristics of portable Raman technology need enhancement in order to be implemented in a presumptive field testing program. Enhancing and implementing a new method of presumptive field testing will benefit law enforcement, forensic laboratories, and the court system by increasing safety, decreasing costs and time, decreasing the incidence of false positive results, and expediting the judiciary process.

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Executive Summary

In order to develop a new field testing program and enhance current Raman-based field technology, casework evidence samples were analyzed in three distinct phases, comparing the ReporteR to the current chemical-based field test kits. The first phase of testing consisted of solely laboratory-based evaluation of the ReporteR on suspected methamphetamine and cocaine samples. In the next two phases, narcotics detectives were recruited to perform tests on substances encountered in the field. During the third phase, the laboratory used a Bruker Senterra Raman microscope to determine if the patented convex function ‘f’ (also known as concave rubber band correction) algorithm would aid in the identification of fluorescing substances (e.g. ecstasy tablets, black tar heroin, and marijuana) and clarify spectra exhibiting a high background. A few synthetic drug analog reference materials were also evaluated using the Raman microscope. Enhancements were made to ReporteR based on the testing performed and were evaluated in the field and laboratory.

- Before enhancements, methamphetamine field testing accuracy was 77.9%.
- After enhancements, methamphetamine field testing accuracy was 100%.
- Before enhancements, cocaine field testing accuracy was 73.4%.
- After enhancements, cocaine field testing accuracy was 100%.
- The reliability of the ReporteR was investigated through random re-testing of samples and results were consistent in approximately 87% of instances.
- Correlation settings and library content were studied and it was found that proper regulation of these factors can decrease erroneous results.
- Repeatable spectra indicating the presence of cannabinoids in marijuana plant material were collected using the Raman microscope and patented baseline correction.
- Testing ecstasy evidence revealed that substances can be identified, regardless of color and binding agents using the Raman microscope and patented baseline correction.
- Spectra was collected for synthetic drug analogs, however, in some samples where high background caused hindrances, the baseline correction technology was essential.
- An evaluation of cocaine/diluent mixtures using the Raman microscope demonstrated that fluorescence baseline correction is valuable to the differentiation of mixture components.

- Testing black tar heroin directly is not feasible with current Raman technology, regardless of baseline correction.

Enhancing and implementing a new method of presumptive field testing will benefit police officers, law enforcement field workers, forensic laboratories, and the court system. These benefits include safety, cost saving, time saving, and expedition of the judiciary process. A new method of field testing will enhance the ability of the law enforcement community to identify, analyze and interpret controlled substance evidence using a robust tool that gives immediate and defensible preliminary results for frequently encountered controlled substances. This scientific evaluation and justification for the court system is of utmost importance. The handheld device can give an officer the results he needs to present in court, but the court must first understand that it is a valid and reliable tool in preliminary identification of controlled substances. This will be accomplished by presenting extensive research to support such a proposal.

Preliminary field testing was implemented by the Las Vegas Metropolitan Police Department in order to combat the rapidly increasing caseloads due to the proliferation of drug use across the population. This program provides the police department with a method to presumptively identify controlled substances in the field and present those findings in court, in lieu of laboratory analysis. The presumptive field testing program has been beneficial for many years, but the discovery of non-controlled substances yielding false positive chemical field test results for methamphetamine and cocaine prompted the LVMPD Forensic Laboratory to research a superior field testing system for police officers to preliminarily identify controlled substances. With over 34,000 items of evidence being field tested each year, the elimination of the field testing program would overwhelm the laboratory and compromise due process.

In 2009, the LVMPD spent \$42,293 for color test field kits in order to presumptively identify methamphetamine, cocaine, and marijuana. The yearly expenditure of maintaining a Raman handheld unit is far less than the purchase of the color test field kits, with the one-time cost of a handheld unit being approximately \$20,000. Besides subjectivity, the current chemical field testing method has other important drawbacks that further elevate the need for a new field testing method. The premade kits contain hazardous chemicals and require the police officers to directly handle the evidence and measure required testing amounts, which has possible safety and contamination considerations.

Since 2008, the LVMPD Forensic Laboratory has been working with SciAps, Inc. (previously DeltaNu, Inc.), the manufacturer of a handheld Raman spectrometer, to devise a new preliminary field test for methamphetamine. The forensic laboratory's research has shown the portable Raman method has several benefits over the existing field test. These include increased specificity, objectivity, non-destructive sampling, elimination of direct handling of drugs and hazardous chemicals, decreased human error, digital recording of results, and decreased cost to the department on a long term basis.

The obvious shortcoming to using any type of Raman spectrometer is the interference of fluorescence. Fluorescence encountered during Raman analysis is inherent to many substances and many of these compounds are routinely submitted to the LVMPD laboratory. It was of particular interest to assess whether algorithm-based fluorescence baseline correction technology would assist in the analysis of such drug evidence.

It is understood that current portable Raman technology may not be able to directly measure marijuana, ecstasy, or black tar heroin, as powerful fluorescence rejection tools are not normally applied or available with portable testing systems. A Raman microscope with an automated or semi-automated fluorescence correction option was essential in this research process to determine if this specific fluorescence baseline correction technology will aid in the identification of cocaine mixtures, black tar heroin, ecstasy, and marijuana.

For methamphetamine and cocaine studies, a parallel study of the spectra collected by the handheld device versus the Raman microscope provided the data necessary to identify specific spectral variances that are unique to the substances being tested. This is intended to encourage manufacturers of portable Raman technology to further enhance devices that include immediate automatic baseline correction. Six portable ReporteR devices (manufactured by DeltaNu, Inc. / SciAps, Inc.), chemical color test field kits (manufactured by ODV), and a Bruker Senterra Raman microscope were purchased for use throughout the research. During the studies, LVMPD lab-created libraries were loaded onto the handheld devices and tested by both the field officers and in the laboratory. To decrease the incidence of erroneous results, test the specificity and selectivity of the handheld unit, and to simplify the testing procedure, each sample was tested no more than three times with a ReporteR through 2 mil polyethylene (the most commonly seen) plastic bags. In the first phase of methamphetamine and cocaine testing, adjudicated and current casework evidence samples were analyzed solely by the laboratory with the ReporteR and

chemical field test kits. In the second phase of methamphetamine and cocaine testing, prior to receiving the microscope, analysis was completed on recently seized case samples tested in the field and in the laboratory using the ReporteR, and chemical field test kits. Narcotics detectives from varied assignments (LVMPD Narcotics, an outside jurisdiction, an interdiction team, and a federal task force) were trained on the use of the ReporteR and testing procedures. The detectives performed tests with the ReporteRs on white to off-white, powdery, and chunky substances encountered in the course of duty. The third phase of methamphetamine and cocaine testing included the incorporation of the Raman microscope. Each evidence sample tested during this period was subjected to field testing with chemical field test kits and a ReporteR, and laboratory testing with a ReporteR, chemical field test kits (cocaine only), and the Raman microscope. All samples tested throughout the research project were confirmed via analysis with gas chromatography/mass spectrometry (GC/MS). A side by side comparison of selected methamphetamine and cocaine spectra collected during the research was performed using the OPUS software (Bruker, Inc.).

In the first phase of laboratory methamphetamine testing, the ReporteR accuracy rate was 92%. Chemical color field testing of suspected methamphetamine evidence in the lab and in the field resulted in an accuracy rate of 100%. It was determined, after receiving these results, and finding that the prevalence of isopropylbenzylamine had waned, that methamphetamine chemical field test kits would no longer be performed in the remaining laboratory portion of the testing (but would continue in the field) unless a false positive field result was discovered. The second phase of methamphetamine ReporteR field testing revealed an accuracy rate of 77.9%. The lab accuracy rate was 100%. In the third phase of testing, suspected methamphetamine cases were tested in the field using an enhanced ReporteR with an accuracy rate of 100%. The laboratory accuracy rate for testing the same samples with a non-enhanced ReporteR was 96% during this phase.

In the first phase of laboratory cocaine testing, the ReporteR accuracy rate was 73%. Chemical color field testing of suspected cocaine evidence in the lab and in the field also resulted in an accuracy rate of 73%. Due to these results, it was determined that cocaine chemical field tests would continue to be performed in the remaining laboratory portion of the testing. In the second phase of testing, ReporteR results for items suspected to contain cocaine had an accuracy rate of 73.4% for both officer and lab testing. In the third phase of testing, a total of 27 suspected

cocaine cases were tested in the field using an enhanced ReporteR with an accuracy rate of 100%. The laboratory accuracy rate for testing the same samples with a non-enhanced ReporteR was 66% during this phase.

After the first and second phases of methamphetamine and cocaine testing, the LVMPD Forensic Laboratory requested that the manufacturer of the ReporteR (DeltaNu, Inc. / SciAps, Inc.) make specific software and firmware changes to the device to further enhance its usability. The final enhancements included a small portable Bluetooth printer that produces a customizable printout, enhanced software that has an improved signal-to-noise ratio, a newly designed polystyrene standard that prevents an officer from having to switch attachments in order to perform a self-test, a forced self-test in which an administrator can set the length of time allowed between self-tests, a new results display incorporating a number correlation rather than a bar graph, and a stronger magnet that secures the removable sampling attachment to the device. After these enhancements were applied to a ReporteR device and implemented in the field, they were well received by the detectives using the equipment. The enhancements also made the presumptive field testing system more efficient by eliminating the need for forensic scientists to perform scheduled calibration checks. Recording the results was also made more manageable by way of a physical print out. As is evident from both methamphetamine and cocaine ReporteR-based field testing result trends during the third phase of testing, the enhancements also appeared to increase testing accuracy.

To test the reliability of the ReporteR devices, confirmed cocaine and methamphetamine samples previously tested during the first phase of laboratory testing were randomly selected and retested using the ReporteRs. The combined results for methamphetamine and cocaine were consistent in approximately 87% of instances.

Although one false positive (benzoylecgonine) for cocaine had been discovered during laboratory reference material testing, the occurrence of this substance in evidence submissions is rare and encountered under unique circumstances. The benzoylecgonine false positive was discovered during ReporteR result correlation testing. These correlations translate to a bar graph in which intensity determines whether a match or “No match” result is displayed. By varying the level of an acceptable correlation, an administrator can somewhat regulate the number of false negatives, or false positives, that are received. A few false positive mismatches occurred during the third phase of methamphetamine testing (methamphetamine samples resulting in low

correlation cocaine matches), but these were determined to be due to equipment malfunctions and did not reoccur after the equipment was repaired. Preventative measures to deter these types of results from being submitted to preliminary court hearings are two-fold. (1) The correlation level could be set such that a result under a certain correlation could not be used for court purposes, and (2) Require that suspected cocaine samples that were discovered under wet or degraded conditions be submitted directly for laboratory analysis.

An evaluation of cocaine versus commonly accompanying diluents was completed using the Raman microscope. Various spectral interferences were discovered and can explain the notable incidence of false negative results when testing cocaine mixtures with the ReporteR. It was evident that baseline correction capabilities are valuable to the study of the cocaine and diluent mixtures.

Analysis of plant materials using Raman instrumentation has been regarded as difficult or impossible by researchers in the past, however, with recent advances, plant material may be analyzed non-destructively using this technology. Marijuana plant material casework samples from ten different events and two suspected marijuana “wax” samples were tested with the Senterra Raman microscope at 785 nm on aluminum foil slides. Secondary negative plant material samples were also examined using the Raman microscope. No viable spectra (spectra with peaks or features that could be differentiated) were obtained during plant material and tetrahydrocannabinol testing with the ReporteR. Several attempts were made on many samples to determine if there were actual microscopic features of the plant material that yielded viable spectra. Such features were identified. These features are best described as globular, amber colored resinous structures that can be smooth or striated in appearance. Repeatable spectra from marijuana plant material were collected using the Bruker Senterra Raman microscope and spectral attributes in common with cannabinoids were evident, specifically cannabiniol and delta-9-tetrahydrocannabinol. Baseline correction was indispensable when detecting cannabinoids in marijuana. Although the probability of being able to use non-microscope based Raman technology on marijuana samples in the field is unlikely, the idea of detecting tetrahydrocannabinol and cannabiniol in situ using spectroscopy opens the door for another confirmatory forensic drug testing method.

As with marijuana, testing black tar heroin directly is not feasible with Raman-based portable technology. Various methods were investigated using both the microscope and the ReporteR. One technique included the use of in-house created graphene based substrates to quench the

fluorescence of the dark, black-brown substance. The Raman microscope did not produce any viable spectra during the graphene/heroin testing. The graphene testing did not produce any well-defined, detailed spectra with the handheld device, however, possible low intensity peaks in common with a heroin reference material were indicated, but this could not be confirmed.

Ecstasy tablets are also routinely encountered by the LVMPD Forensic Laboratory. Contrary to marijuana and black tar heroin, testing ecstasy tablets directly is possible with Raman-based portable technology, but limited. Ecstasy tablets pose additional problems with Raman testing as they are often mixtures of several different compounds, come in a variety of colors, and could contain multiple binding agents. These may not only cause fluorescence issues, but mixture interferences as well. Limited testing on ecstasy tablets was completed. The testing of such items revealed that spectra of the diluents present in the tablets are more likely to be collected, however if focused on a crystal within the tablet that contains methylenedioxymethamphetamine, it can be detected by the microscope, even on colored tablets. ReporteR testing on selected samples did not collect viable spectra, only a high baseline.

Various synthetic drugs were also tested as the proliferation of these compounds has caused recent concerns. A few designer synthetic drug analog reference materials were evaluated. Viable spectra were obtained; however, it was apparent that the amount of fluorescence or other background interference was dependent on isomeric form. Although it is unlikely that a field testing program will be useful in identifying the emerging synthetic drug analogs (i.e. cathinones, phenethylamines, cannabimimetics) due to their structural attributes and propagation, indications that these drugs may be present can be determined by portable Raman spectroscopy. As the manufacture of new synthetic drugs continues to increase, it is imperative that a method of assisting law enforcement in detecting such substances is available. As these analogous substances come and go from the illicit drug market on a daily basis, the identification of them is daunting. If these drugs can, in the very least, be detected by their base structure in the field using portable Raman spectroscopy, it would aid officers in their duties, even if the results could not be used in court. As the standard chemical color tests cannot differentiate between such compounds, and Raman technology can differentiate isomers, exploring the use of a portable instrumental based testing system is worth the time and consideration.

The use of the baseline correction technology incorporated with the Bruker microscope system was essential in the collection of spectra of compounds that inherently produce fluorescence, namely

marijuana, ecstasy, and synthetic designer drugs. A high baseline was also evident in some methamphetamine and cocaine spectra when tested using the ReporteR, and baseline correction technology was useful in increasing the library matching capabilities of the OPUS software. Automatic baseline correction may not prove valuable against cocaine/caffeine mixtures, but it may help in deconvoluting spectra containing other contaminants. An algorithm based method would also be useful to assist in presumptive Raman analysis of components in cocaine mixtures.

The development and implementation a successful field testing program to replace or, at the very least, reduce the use of chemical field test kits was the ultimate goal of this research. To determine if testing typically difficult samples with the fluorescence correction algorithm is achievable, and to explore the possibilities of applying this technology to a handheld device was also an important portion of the research. Improving handheld Raman technology and exploring the possibilities of alleviating the fluorescence issues of commonly encountered drugs is important to the future of field testing using Raman technology. With the research completed thus far, we have determined what aspects are important to implementing an instrumental based field testing program and which characteristics of portable Raman technology need enhancement in order to increase its user friendly attributes, efficiency, selectivity, and reliability. By testing the handheld devices in the lab, and in the field by narcotics officers, we have collected data in order to implement a reliable field testing method for methamphetamine and cocaine using Raman technology.

I. Introduction

1. Statement of the problem

Preliminary field testing was implemented by the Las Vegas Metropolitan Police Department in order to combat the rapidly increasing caseloads due to a sudden increase in population, bringing along with it a sudden increase in drug use. The field testing program provided the LVMPD with multiple benefits. The laboratory did not have to employ extra scientists in order to handle the increased caseload. The program accelerated the judiciary process by accepting field test results at the preliminary hearing level. As the police officers are required to weigh the evidence prior to preliminary testing, the program assists them in determining which charges to file when booking the evidence.

The presumptive field testing program has been beneficial for many years, but the discovery of a non-controlled substance yielding a positive color test result for methamphetamine in submitted evidence at LVMPD and other laboratories [2, 5] prompted the LVMPD Forensic Laboratory to find a better field test for police officers to preliminarily identify methamphetamine. Laboratory tests have also confirmed that presumptive tests performed in the field revealed false positive results for street samples purported as, but not containing, cocaine. With this information, it is possible that the Clark County, Nevada District Attorney's Office will determine that the current field testing methods are no longer sufficient, in lieu of conclusive laboratory analysis, for preliminary hearings. With over 34,000 items of evidence being field tested each year, the elimination of the field testing program would overwhelm the laboratory and compromise due process.

Law enforcement agencies spend tens of thousands of dollars on chemical-based color test field kits every year. In 2009, LVMPD spent \$42,293 for color test field kits. The yearly expenditure of maintaining a Raman handheld unit is far less than the purchase of the color test field kits, with the one-time cost of a handheld unit being approximately \$20,000. The handheld device may need replacement of its laser after 3 to 5 years, but at an estimated \$2,500, it is a fraction of the yearly cost of color test field kits. This is a major consideration for most policing agencies, especially in the current economic climate. In addition, the training for this technology could be cost effective and easily obtainable by producing online video instruction.

The current chemical field testing method has other important drawbacks that further elevate the need for a new field testing method. The premade kits contain hazardous chemicals and require the police officers to directly handle the evidence and measure out required testing amounts. This

makes for a dangerous, messy, and destructive presumptive test. A Raman device has far fewer safety considerations, can test through plastic packaging, and only takes the press of a button to get immediate results.

Since 2008, the Forensic Laboratory has been working with SciAps, Inc. (previously DeltaNu, Inc.), the manufacturer of a handheld Raman spectrometer, to devise a new preliminary field test for methamphetamine and cocaine. After some trial and error, and with enhancements to the device, the forensic laboratory's research has shown the Raman method to have several benefits over the existing field test. These include increased specificity, objectivity, non-destructive sampling, elimination of direct handling of drugs and hazardous chemicals, decreased human error, digital recording of results, and decreased cost to the department on a long term basis. Although shortcomings will have to be properly examined, the advantages of portable Raman technology over the current chemical preliminary field testing outweigh the disadvantages.

The LVMPD realized that not only would certain enhancements to the portable device for use in the field be necessary, but an actual field testing system would need to be developed. Currently, using the chemical field test kits, an officer must complete a checklist and locate another field test certified officer to witness the test and sign the form as proof that testing was completed. This type of system creates room for human error. Certain enhancements such as adding a portable printer to the device so that an officer can include traceable results with the evidence at the time of booking, is one way to improve functionality and efficiency of a field testing program.

The obvious limitation when using any type of Raman spectrometer is the interference of fluorescence. Fluorescence is inherent in many controlled substances [4, 16, 36]. In Nevada, ecstasy, cocaine, and heroin are frequently encountered controlled substances and are routinely submitted to the LVMPD laboratory for analysis. The predominant type of heroin encountered by Nevada law enforcement is in the form known as "black tar" and is dark black-brown in color. Ecstasy tablets come in all shapes, sizes, and colors. Cocaine is often diluted with substances that cause various spectral interferences [3, 25, 26, 35]. Each of these drug forms can be difficult to analyze using Raman technology due to the fluorescent background and high baselines they can produce. Current and future advances to current technology may help to solve these issues.

Analysis of plant materials using portable Raman technology has previously been regarded as impossible. Fluorescence is an obvious culprit as to why testing would be difficult, but as so many chemicals are present in plant material, a microscope is, at this time, required for analysis to identify

certain areas of a plant that would contain the compound of interest. As marijuana is included in the LVMPD's field testing program, the ability to test it in the field using instrumental based technology rather than field color test kits would be advantageous. With recent advances, researchers have shown that it is possible to analyze plant material using laboratory grade instrumentation [18-24]; however, the collection of spectral data of cannabinoids from marijuana plants has not been thoroughly studied.

Improving handheld Raman technology and exploring the possibilities of alleviating the fluorescence issues of commonly encountered drugs is important to the future of field testing using Raman technology. A field testing program that will replace chemical-based testing methods would not only improve the preliminary testing system and judicial system for Clark County, Nevada, but may also serve as a model benefiting other jurisdictions with budgetary, staffing, and backlog issues.

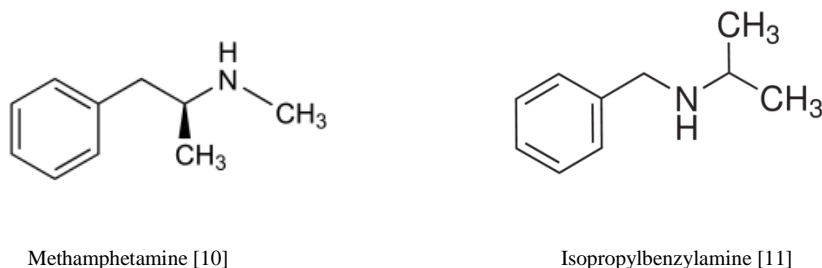
2. Literature Citations and Review

Color tests are useful tools in identifying the presence of a particular molecular moiety in groups of compounds [1]. Opiates like heroin and oxycodone, stimulants like methamphetamine and amphetamine, and hallucinogens like psilocin and lysergic acid diethylamide (LSD) represent groups of related compounds, or those that yield similar color test results [12]. In the early stages of controlled substance analysis, positive color test results were considered definitive and conclusive identification for controlled substances [1]. Color testing, now considered a preliminary "Category C" technique by the Scientific Working Group for the Analysis of Seized Drugs (SWGDRUG), is the principle method of law enforcement presumptive field testing of controlled substances.

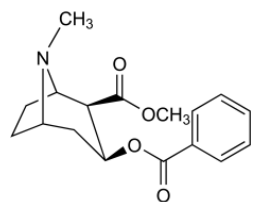
With the explosive, yet fleeting, emergence of the non-controlled substance isopropylbenzylamine into the street market, the non-specific nature of color tests became immediately more pertinent to the LVMPD Forensic Laboratory and the Drug Enforcement Administration (DEA) [2, 5]. The street form of isopropylbenzylamine was a crystalline substance visually similar to crystal methamphetamine. The Marquis field color tests (in this instance the Marquis test indicates the presence of amines) [12] yielded color changes similar to those obtained with methamphetamine and amphetamine [2]. The sodium nitroprusside color test is the second step in the methamphetamine field test, and differentiates between primary and secondary amines (e.g. amphetamine and methamphetamine) [12]. When isopropylbenzylamine was tested using the sodium nitroprusside field test kit, a blue color identical to that of methamphetamine resulted [5]. Instrumental testing confirmed that methamphetamine was not present.

Isopropylbenzylamine and methamphetamine are isomers, meaning they have similar structures (**Figure 1**). It is intuitive that the two substances would give similar color results because they both contain ring structures with secondary amines. The LVMPD Forensic Laboratory's research performed in 2008 showed that a portable Raman device can differentiate between the two extremely similar structures.

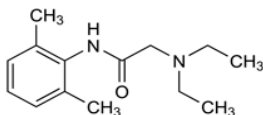
Figure 1. Structures of methamphetamine and isopropylbenzylamine.



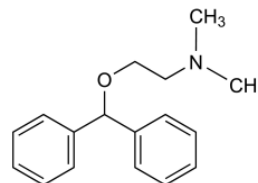
Diphenhydramine, commonly known by the trade name Benadryl, and lidocaine, an anesthetic, have been discovered to give positive results for the Scott's color test when tested by officers in the field. This test is used to presumptively identify cocaine [12], with a two-layer, pink over blue result being positive. There have been appearances of these non-controlled substances in various LVMPD submissions purported to contain cocaine. The suggested partial mechanism of how the first step of the Scott's test works, and how its blue color is developed, is that the cobalt within the reagent coordinates with the nitrogen on the molecule [42]. Even though diphenhydramine, lidocaine, and cocaine each contain a tertiary amine group, they do not share such strong structural similarities like methamphetamine and isopropylbenzylamine. Knowing that structures of cocaine, lidocaine, and diphenhydramine are so different (**Figure 2**), and that they are all capable of reacting with the Scott's test, it is logical to use an instrumental preliminary testing method that differentiates substances based on those structural dissimilarities.

Figure 2. Structures of cocaine, lidocaine, and diphenhydramine.

Cocaine [10]



Lidocaine [10]



Diphenhydramine [10]

Most forensic laboratories utilize mass spectrometry (MS) and Fourier transform infrared (FTIR) spectroscopy as methods of conclusive identification. Both of these technologies identify compounds based on their molecular structure [13]. The results produced are typically unique to one molecule, especially when coupled with gas or liquid chromatography (GC or LC). Unfortunately, both MS and FTIR have limitations that make them less than ideal candidates for conversion to very small, portable field devices.

Many plastics absorb IR light and can cause difficulties with collecting the desired spectrum [37]. Rather than collecting absorbance data, like that of IR spectroscopy, Raman spectroscopy relies on the scattering of light. In Raman processes, a laser excites the bonds in a compound causing changes in molecular vibrational energy which inelastically scatters the light from the laser. When the light is scattered, a new energy response is emitted. It is this response of scattered light that essentially generates the information used to create a spectrum specific to a molecule. [14, 15] Since many illicit drug packages are transparent, Raman spectra can be collected directly through the package making contamination and degradation of the sample unlikely [37]. Like MS and FTIR, Raman spectroscopy has the ability to identify a substance based on molecular structure, but unlike the other instrumentation, it is easily converted into a small handheld system that can test through plastic packaging.

Suspected methamphetamine and cocaine are frequently encountered and tested using three separate presumptive field test kits. Being able to eliminate three color test reagents from the field testing program would aid in cost savings and supply issues. Both drugs have been evaluated using various Raman-based instrumentation [3, 25, 35, 43, 44]. Two similar studies indicated that portable Raman field testing was less than 75% accurate in reporting correct results, which leads to the supposition that improvements are needed. Radtke and Patterson, from the Minnesota Bureau of

Criminal Apprehension (MBCA), completed a validation study on mixtures of methamphetamine and mixtures of cocaine using a handheld Raman device called FirstDefender manufactured by Ahura (now Thermo Scientific). When they tested case samples, 27.6% of their results were found to be incorrect when compared to GC/MS results (these were mostly false negatives). [27] The National Forensic Science Technology Center completed an evaluation of the FirstDefender RM (Thermo Scientific) and found the device to be approximately 61-69% accurate across various sample sets of various substances using the “point-and-shoot” method. The retail price of this Raman device at the time of the latter discussed study was approximately \$50,000. [43] Not only should the accuracy be higher if it is to be implemented in a field testing program, but the system should be more affordable and easily implemented.

Portable Raman devices have a few limitations when compared to the more sophisticated laboratory-grade spectrometers and microscopes [4]. Fluorescence, which can cause a high background that can essentially mask the desired spectrum, is one limitation that has been addressed in sophisticated instrumentation, but has not been remedied in portable equipment [16]. Fluorescence in Raman spectra is often encountered when testing dark colored substances [4, 36] or compounds where fluorescence is inherent [16].

There are concerns posed by the LVMPD Forensic Laboratory and other researchers about diluents and adulterants that are often mixed with illicit substances which may fluoresce under certain light excitations. Fluorescence has been an issue with cocaine hydrochloride mixtures seen in evidence submissions [3, 16]. Three studies reviewed were able to identify cocaine in mixtures quantitatively using bench-top Raman spectrometers [3, 25, 26]. Littleford and colleagues described successful analysis of 75% and 86% pure cocaine; however, they do not believe they would have had as much success using field instrumentation without fluorescence rejection [26]. Ryder has also completed quantitative studies on narcotic mixtures with laboratory-grade Raman equipment. He discussed using the “most intense peaks” in narcotic spectra for “rapid discrimination” of the different classes of drugs examined [25]. Using this information, the portable Raman devices may show promise in detecting cocaine in mixtures with future enhancements, such as automated baseline correction and peak detection [30, 41].

Researchers have had success testing opiates such as codeine, morphine, and hydrocodone, which are known to be poor Raman scatterers [31]. However, this was done using Surface Enhanced Raman Scattering (SERS) which is not beneficial to this research. Although reference material

samples of heroin hydrochloride present viable spectra at 785nm [3, 35], previously documented success of testing black tar heroin using confirmatory Raman spectroscopy in a research setting has not been located. Due to the tar's dark brown-black color and other chemical interferences, the fluorescence is completely overpowering, and sample burning is certain. The TruNarc, a handheld Raman device produced by Thermo Fisher Scientific, has demonstrated success in presumptively testing black tar heroin using a patented sampling system that involves diluting the substance in ethanol and then evaporating the liquid on a metal wafer sampling device [40]. Using graphene as a substrate to quench fluorescence in Raman analysis has also been successful and may be useful for testing a substance such as black tar heroin [45, 46].

Ecstasy tablets pose additional problems with Raman testing as they are often mixtures of several different compounds, come in a variety of colors, and could contain multiple binding agents. These not only cause fluorescence issues, but mixture interferences as well. There are published accounts of using Raman microscopy to "map" ecstasy tablets, but this is both time consuming and not applicable to portable technology [33].

Analysis of plant materials using portable Raman technology and some bench-top instruments has been regarded as difficult or impossible by researchers in the past. Many researchers had to chemically prepare the plant substance in order to test it with Raman instrumentation [23], however, with recent advances, plant material may be analyzed non-destructively [18-24]. Gierlinger and Schwanninger state that their research demonstrated that near infrared Fourier transform (NIR-FT) Raman eliminates fluorescence which makes analysis of green plant material simple [23]. Another set of researchers were able to non-destructively analyze components in a cashew nut without chemically altering the plant material [19].

Although fluorescence interference is encountered in Raman analysis, whether portable or not, it may be combatted utilizing certain specialized fluorescence rejection techniques and technologies which are typically more applicable to laboratory grade instrumentation. The development of SERS alleviated some fluorescence issues in Raman analysis of controlled substances [26, 31], but it involves the use of a Raman microscope and chemicals, which is not applicable to a field test program. Researchers have found that using longer wavelengths and near infrared Raman excitation reduces fluorescence, but this increases the likelihood of sample burning [26, 32, 35, 38], and adds complexity to the instrumentation [38]. Kerr gated Raman spectrometers have proven effective in rejecting fluorescence from street samples of cocaine and cutting agents. This type of analysis

requires special hardware attached to a laboratory based Raman system and high powered lasers which precludes it from being utilized by a portable Raman device [26]. SERDS (shifted-excitation Raman difference spectroscopy) has shown to be useful in the analysis of fluorescing compounds and research has been completed with a focus of translating this technology to a portable system. It requires the implementation of two laser diodes with slightly off-set fixed wavelengths. This technology can be extended to portable Raman spectrometers, but is enabled by coupling an instrument to a separate laser source. [38,39] Chemometric baseline correction methods have been evaluated by various researchers and are typically applied to portable Raman systems due to the capability of these methods to be automated. The Reporter, manufactured by SciAps, Inc. (previously DeltaNu, Inc.), uses a derivative method of baseline correction. Derivative based correction methods have shown to be useful in reducing noise and variations in background features, but are not as beneficial in resolving high baselines [34, 35] as are often seen in fluorescence laden spectra. Polynomial baseline correction has also been used by researchers to correct fluorescence in Raman spectra, but this cannot be applied automatically without first determining the degree of the polynomial needed [30, 35, 34]. This approach is not feasible in a police officer's field testing situation. A viable option which may translate to a portable Raman device is the incorporation of automated fluorescence correction technology. Bruker, Inc. manufactures the Senterra Raman microscope which employs a semi-automated baseline correction method in its OPUS software. This company's technology, known as 'convex function f' baseline correction, utilizes a "rubber band" convex polynomial that fits along the baseline of the spectrum in order to find and subtract the "convex envelope" below the spectrum and correct the baseline. The main advantage to this specific technology is that it is applied as an algorithm and was particularly created to correct baselines caused by fluorescence. [30] A patent was published in January of 2013 by Wright, et al, entitled "Methods of Automated Spectral Peak Detection and Quantification Without User Input" that provides a method of automatically applying baseline correction [41]. This invention lends hope that future technology has the potential of not requiring any manipulation on the user end to correct spectral interferences and therefore may be translated to an officer friendly portable system, unlike other fluorescence rejection techniques and technologies.

3. Rationale for the Research

By testing the handheld devices in the lab, and in the field by narcotics officers, the LVMPD can determine what features about the device need to be enhanced to increase its user friendly

attributes, efficiency, selectivity, and reliability. This also aids in developing a successful field testing and training program. Whether or not the officers will be able to accept and use the technology successfully is evaluated by this study. This portion of the research also compares the accuracy of the portable Raman handheld device versus the currently employed chemical color test field kits. Higher accuracy, in terms of fewer false positives, as compared to the color test kits is expected for the Raman technology due to the fact that the instrumentation should provide results based on the whole molecular structure versus only a functional group on that molecule.

For methamphetamine and cocaine, a parallel study of the spectra collected by the handheld device versus the Raman microscope will provide the data necessary to identify specific spectral variances that are unique to the substances being tested and lead to further enhancement of the portable Raman technology. Not only are the fluorescence correction capabilities valuable to the study of the cocaine mixtures, the confirmatory instrumentation will aid in identifying more specific spectral features to that of cocaine, versus the presumptive, handheld device. The microscope's accuracy and resolution can discern the subtleties that the handheld units may not detect.

It is understood that current portable Raman technology may not be able to directly measure marijuana, ecstasy, or black tar heroin as powerful fluorescence rejection tools are not normally applied or available with portable testing systems. A Raman microscope with an automated or semi-automated fluorescence correction option is essential in this research process to determine if fluorescence correction technology is effective for cocaine mixtures, black tar heroin, ecstasy, and marijuana. If repeatable spectra are collected utilizing the Raman microscope for substances where fluorescence precluded their identification previously, then confirmed against traceable reference materials, the application of this fluorescence correction technology to a portable system in the future is feasible.

Based on the research findings, suggestions were made to the manufacturer that enhanced the current portable technology. The LVMPD Forensic Laboratory ultimately hopes that these studies will help establish case law that may assist other local and state districts to utilize this technology in the field. This scientific evaluation and justification for the court system is of utmost importance. Most police officers do not have the expertise to evaluate spectra and to explain to the trier of fact how the technology works. The handheld device can give an officer the results he needs to present in

court, but the court must first rule that it is a valid and reliable tool in preliminary identification of controlled substances (satisfy the Frye standard).

The development of a successful field testing program that will replace the use of chemical field test kits is the ultimate goal of this research. To determine if testing typically difficult samples with the fluorescence baseline correction algorithm is achievable, and to explore the possibilities of applying this technology to a handheld device is an important portion of the research. The information obtained from the studies completed will aid in creating a definitive, new method of field testing that will enhance the ability of the law enforcement community to presumptively identify controlled substance evidence.

II. Methods

Beginning in 2008, preliminary research had been completed in conjunction with DeltaNu, Inc. (now SciAps, Inc.), the manufacturer of a handheld Raman device called the ReporteR [28]. While working with DeltaNu, Inc., a small number of improvements were made to the firmware and design of the ReporteR. These changes took place prior to the National Institute of Justice award for this project. After applying for this grant, but prior to initiating this study, further enhancements to the ReporteR were completed by the manufacturer, including the addition of a “test number” to be displayed on the screen. The “test number” was intended to facilitate coordination between the evidence case number and the data stored on the device so that a spectrum can be viewed at a later time. It was discovered during data analysis that the test number did not correlate to the data file. This was remedied during the third phase of testing after enhancements had been completed.

After the LVMPD was awarded this grant, six ReporteRs, chemical color test field kits, and a Bruker Senterra Raman microscope were purchased (the Raman microscope was purchased after one year of research was completed). Upon receipt, the ReporteR devices were calibration checked and the color test field kits were quality control checked according to LVMPD Forensic Laboratory procedures, using traceable reference materials. All primary, secondary, non-controlled and controlled reference materials used in the study were provided by LVMPD. The verified reference materials used throughout the study are included in **Table 3**. During analysis, all appropriate blanks and quality control checks were completed in accordance with the laboratory’s requirements and procedures.

A paper checklist for methamphetamine and cocaine was developed for officers so that the required procedure would be followed when performing the Raman handheld test. This ensured that the tests were consistently and correctly performed in the field. The checklist that was developed is shown in **Figure 3**. Throughout the testing process, various LVMPD lab-created libraries were loaded onto the handheld devices and used by both the field officers and in the laboratory. This was done to determine the best combination of reference spectra for the most accurate testing. The reference materials included in the libraries are shown in **Tables 1** and **2**. The ReporteRs were validated by testing known controlled and non-controlled reference materials against the libraries that were created using the accompanying software. In addition, 37 neat negative controls, similar in appearance and/or structure to methamphetamine and cocaine, and negative control mixtures were examined to study the potential of receiving false positive results and to test the specificity and selectivity of the handheld unit by testing each with a ReporteR through plastic bags. They were also tested with color test field kits. Positive controls of confirmed casework samples were also run against the created libraries (**Tables 4.1-4.7**).

Figure 3. Field Checklist.

LAS VEGAS METROPOLITAN POLICE DEPARTMENT PORTABLE RAMAN PRELIMINARY FIELD TEST CHECKLIST AND RESULTS	
Subject Name and ID# _____	Event # _____
Package # / Item # _____	Tester's Name and P # _____
Gross Weight _____ grams	Device # _____
<p>The ReporteR uses a laser. Always point laser port away from yourself and others.</p> <ol style="list-style-type: none"> Only powders, crystalline, and chunky/rocky substances are to be tested (do not test tablets, capsules, liquids, plant material, or dark tar-like substances). If the ReporteR is turned off, turn on the ReporteR's power by pressing the red power symbol button so that "Standby" is shown on the screen. Place evidence item on a light colored solid surface (evidence may remain in bag or package providing that it is transparent plastic). DO NOT TEST ON OR THROUGH GLASS. If the package is not transparent plastic or is unsuitable for testing, a layer of clear plastic may be placed as a barrier between the device and the substance. Ensure that "Standby" is shown on the screen and that the small opening of the red attachment is free of debris. Place the small opening of the red attachment directly on the transparent plastic package or plastic barrier ensuring the substance inside the package is directly underneath the opening (THE LASER IS EMITTED FROM THIS OPENING. USE CARE WHEN IN USE). Press the button with the yellow star symbol so the screen reads "Armed." Press the button again so the screen reads "Acquiring" and wait for a result to appear on the screen. If the screen reads "No Signal" at any time during the testing below, press the green checkmark button underneath "Done" on the screen to view the test #. Record the test # in the box to the right of this step. Press the green checkmark button again to return to "Standby." Move the device to a new spot and repeat this step. Only record "No Signal" test numbers in the box provided. Circle the result shown on the screen: Methamphetamine Cocaine No Match # of bars _____ Press the green checkmark button to view the test number. Enter the test # from the ReporteR's screen _____ (If "No match" go to step 10; if "Methamphetamine" or "Cocaine" go to step 15) Press the green checkmark button and repeat steps 5 & 6 on a different area of the substance through the package: Circle the result shown on the screen: Methamphetamine Cocaine No Match # of bars _____ Press the green checkmark button to view the test number. Enter the test # from the ReporteR's screen _____ (If "No match" go to step 14; if "Methamphetamine" or "Cocaine" go to step 15) Press the green checkmark button and repeat steps 5 & 6 on a different area of the substance through the package: Circle the result shown on the screen: Methamphetamine Cocaine No Match # of bars _____ Press the green checkmark button to view the test number. Enter the test # from the ReporteR's screen _____ (If "No match" go to step 18; if "Methamphetamine" or "Cocaine" go to step 15) Press the green checkmark button. If "No match" is shown on the screen three times, the evidence must be analyzed by the Forensic Laboratory prior to trial. Go to step 20. Test(s) performed by (signature) _____ Date: _____ Time: _____ Witness signature: _____ PS _____ If no further testing is required at this time, turn off the ReporteR by pressing the red power symbol button and make sure the ReporteR is plugged in to make sure the battery stays fully charged. <u>VERSION 4/25/11</u> 	
RESEARCH PURPOSES ONLY	<p>No Signal test #s:</p> <p>_____</p> <p>_____</p> <p>_____</p> <p>_____</p> <p>_____</p> <p>_____</p> <p>_____</p> <p>_____</p> <p>_____</p> <p>_____</p>
<p>Comments: _____</p>	

Two different ways of displaying results were tested on different versions of the ReporteR with the changes implemented by DeltaNu, Inc. (SciAps, Inc.). One version of the results display screen included the listing of the actual library reference material name and the actual correlation value (e.g. “dimethylsulfone 0.69”). The other version included the listing of “methamphetamine,” “cocaine,” or “no match” and a bar value which was set to a certain correlation. See **Figure 4**. The number of bars and corresponding correlation values were concurrently tested while trying to assess the regular incidence of false negative results with cocaine mixtures. Approximately 40% and 50% cocaine/caffeine mixtures (by weight) were used to test different levels of bar correlations with 5 bars being the best match, ranging from 0.60 to 0.85. Negative controls were tested against the 5 level bar correlation which was set to 0.80 to 0.90. For all correlation settings, see **Table 6**.

Figure 4. Photos of display screens.



In the first phase of methamphetamine and cocaine testing, samples were analyzed solely by the laboratory. Each forensic scientist participating in the research created a database describing the evidence and its packaging, the case number, the item number, the inventory number of the ReporteR used, and the results of each test performed. Research testing continued until forensic scientists had tested over 280 white to off-white powders, crystalline substances, and chunky substances from adjudicated and current casework evidence samples with the ReporteR and chemical field tests. This was a side-by-side study of the current field testing method with the proposed field testing method. This study tested the capabilities of the instrumentation and whether or not it is as specific and as sensitive as the chemical field test. When a spectrum was obtained, it was saved electronically and/or as a hardcopy. While testing the casework samples, each forensic scientist performed varied calibration checks on the ReporteR and recorded the

results in their database. This was completed in order to determine the length of a valid calibration and test the reliability of the device. The evidence samples were confirmed by gas chromatography/mass spectrometry (GC/MS) (see parameters included at the end of this section).

In order to test the reliability between devices, items of controlled substance evidence from some of the adjudicated cases mentioned above were retested randomly. Adjudicated cases to be retested were selected at random after initial testing, so a few items were retested by the same forensic scientist.

In the second phase of methamphetamine and cocaine testing, narcotics detectives from varied assignments (LVMPD Narcotics, an outside jurisdiction, an interdiction team, and a federal task force) were trained on the use of the ReporteR, checklists, and procedures. Detectives completed testing on 140 white to off-white powder or crystalline case samples in the field using a ReporteR and chemical field test kits. The detectives completed the corresponding checklists for both chemical and Raman tests. The checklists were included in the evidence package and delivered to the laboratory through LVMPD evidence handling procedures. The data from the handheld devices was stored on a disk inside the units and was periodically collected by the laboratory. After the handheld devices were enhanced to include portable Bluetooth printers, the printouts (**Figure 5**) replaced the Raman checklist and were included with the evidence. All field tested evidence was retested in the laboratory using ReporteRs and confirmatory testing procedures used by the LVMPD (the compounds in the substances were confirmed via GC/MS). It was determined that, as the prevalence of isopropylbenzylamine had waned, and the 100% accuracy of first phase color testing, methamphetamine chemical field test kits would no longer be performed in the remaining laboratory portion of the testing (but would continue in the field) unless a false positive field result was discovered. Cocaine field color test kits would be used both in the field and the lab. Two different sampling attachments were tested to discover whether or not a specific design was more amenable to testing through plastic bags. In preparation for the field testing, the forensic scientists attached a chain to the device to secure the sampling attachment to prevent loss. As manufactured, the attachment fits onto the device and is held by a weak magnet. The attachment was easily removed and had the potential to become separated from the device.

instrument malfunctions. These data files were sent to DeltaNu, Inc. (SciAps, Inc.) for review and it was determined that the issues were due to possible light interference and focusing issues. These problems were addressed by performing routine maintenance on the ReporteR and reverting back to an earlier version of the sampling attachment. These false results may be mitigated by requiring that positive results have correlations over a set number, or by requiring that a non-methamphetamine or a non-cocaine result be submitted to the lab for confirmatory testing.

Methamphetamine

In the first phase of laboratory methamphetamine testing, the ReporteR accuracy rate was 92%. Chemical color field testing of suspected methamphetamine evidence in the lab and in the field resulted in an accuracy rate of 100%. It was determined, after receiving these results, and finding that the prevalence of isopropylbenzylamine had waned, that methamphetamine chemical field test kits would no longer be performed in the remaining laboratory portion of the testing (but would continue in the field) unless a false positive field result was discovered. The second phase of methamphetamine field testing revealed an accuracy rate of 77.9%. The lab accuracy rate was 100%. In the third phase of testing, suspected methamphetamine cases were tested in the field using an enhanced ReporteR with an accuracy rate of 100%. The laboratory accuracy rate for testing the same samples with a non-enhanced ReporteR was 96% during this phase. It is concluded from this trend that the enhanced, upgraded device (after repairs) caused an increase in accuracy for officer field testing for methamphetamine, which may be partly due to ease of use, but is most likely due to an increase in the signal-to-noise ratio. This trend is also evident in the cocaine data.

Upon reviewing spectra of methamphetamine collected in the field using the ReporteR, and in the lab using a ReporteR and a microscope, there was no notable trend in field data versus lab data collected. Microscope collected spectra were obviously more detailed. ReporteR collected spectra were mostly adequate, but varied in quality. In fact, of the spectra examples shown in **Figure 8**, the best spectrum was collected in the field. It is evident that spectra collected may vary based on sampling technique and the quality of signal received by the ReporteR. The ReporteR also shows higher baselines in its spectra compared to the microscope. Lidocaine mismatches were due to the library spectrum of lidocaine as seen in **Figure 8**. Any spectrum collected with a similar baseline may result in a match to lidocaine, which could explain the incidence of lidocaine mismatches for

methamphetamine samples. An automatic baseline correction method added to an enhanced portable Raman device would be beneficial against this hindrance.

Cocaine

A historical review of cocaine chemical field tests performed by officers in the field revealed flaws in the implementation of testing and/or interpretation of results. LVMPD's current chemical field testing program tries to ensure quality by requiring that apparent errors made by officers during testing are recorded, the officers and chain of command are notified, and remedial training may be required. Across the board, most errors are clerical, as is indicated on the checklist that officers are required to complete. Some errors are defined as false positives. Even though the chemical field tests for cocaine are formulated such that very few substances should give a false positive result, if the test is performed incorrectly (overloading) or interpreted incorrectly (blue color appears in the wrong step), an erroneous positive result may be recorded. In such cases where a false positive is suspected or no cocaine is identified in a sample, an identical field test is performed by laboratory personnel. If the results cannot be replicated in the lab, this is considered an error. All errors that are noticed by the Clark County, Nevada District Attorney's Office are sent to the lab as a confirmatory analysis is needed prior to trial. As the Forensic Laboratory only sees a small portion of these field results, the true percentage of errors due to false positives is unknown. Use of a portable Raman field testing program would virtually eliminate such errors, including subjective color interpretation which can lead to false positives, and the checklists would be replaced by a printout reporting the results.

The lower the correlations are set, the more often a positive result is obtained. However, the possibility of receiving false positives increases. When the lowest number of bars was set to 0.30, a benzocaine reference material tested positive for cocaine using the ReporteR. Benzoylecgonine had correlation values as high as 0.71, testing positive for cocaine. The comparison of spectra collected using the Senterra showed the similarities between cocaine HCl, cocaine base and benzoylecgonine, but differences were notable. Cocaine samples mixed with various diluents also often caused results with low correlation values. According to the results shown in **Table 7**, if the minimum correlation value was set above 0.71 (in order to avoid false positive results with benzoylecgonine), ~74% of accurate positive cocaine results from the ReporteR would be eliminated. However, if wet or suspected degraded cocaine samples were not tested during the field testing (to avoid possible

benzoylecgonine samples), and the correlation levels were set above 0.35 (to avoid benzocaine false positives), only ~15% of results would be eliminated from being used for court purposes.

As shown in **Figure 9**, a cocaine sample tested using the Senterra matched to diphenhydramine after performing a library search. However, after baseline correction, the sample then matched to cocaine. This sample was found to contain levamisole and cocaine hydrochloride using GC/MS and FTIR/ATR (Fourier transform infrared/attenuated total reflectance). The baseline correction algorithm utilized by the Raman microscope aided in detection of cocaine for this sample.

The ReporteR does seem to have some advantages when it comes to testing samples in which the pinpoint accuracy of the microscope would be a detriment. In **Figure 9**, cocaine spectra collected on the same substance in two types of packaging is shown. The sample tested through gray, opaque colored plastic yielded a lab ReporteR correlation of 0.85. The spectrum collected on the microscope as shown in the eighth window of the figure, shows the high baseline generated from testing the gray plastic packaging, as the Senterra's laser caused sample burning.

As with methamphetamine, the quality of ReporteR spectra varied (**Figure 9**, windows in the 3, 5, and 7 positions). The results of cocaine testing are far less accurate than the methamphetamine testing. This is likely due to the spot size and amount and assortment of diluents used to cut cocaine. When comparing cocaine to common diluents encountered in the laboratory, there are peaks that are unique to cocaine and may assist in creating a method to increase detection of cocaine in mixtures. Caffeine, in particular, may cause a great amount of interference, especially around the two abundant cocaine peaks at 1598 cm^{-1} and 1715 cm^{-1} . Caffeine also has two peaks in this area at 1600 cm^{-1} and 1699 cm^{-1} . Development of methods to isolate peaks specific to cocaine as compared to caffeine may be necessary.

In the first phase of laboratory cocaine testing, the ReporteR accuracy rate was 73%. Chemical color field testing of suspected cocaine evidence in the lab and in the field also resulted in an accuracy rate of 73%. Due to these results, it was determined that cocaine chemical field tests would continue to be performed in the remaining laboratory portion of the testing. In the second phase of testing, ReporteR results for items suspected to contain cocaine had an accuracy rate of 73.4% for both officer and lab testing. In the third phase of testing, a total of 27 suspected cocaine cases were tested in the field using an enhanced ReporteR with an accuracy rate of 100%. The laboratory accuracy rate for testing the same samples with a non-enhanced ReporteR was 66% during this phase. As indicated from this trend, the enhancements made to the ReporteR

increased testing accuracy for cocaine. It does not appear that the field ReporteR equipment malfunctions affected the device's ability to test cocaine; however, fewer tests were performed on suspected cocaine samples. It is decidedly unknown why cocaine did not seem to be as affected by the malfunctions, but it may be due more to the nature of the methamphetamine data and its interaction with the programming and library matching algorithms.

Although the officer detected cocaine at a 0.41 correlation, lab ReporteR testing indicated that acetaminophen, lidocaine, and cocaine were present in a sample when tested three consecutive times on different spots (first lab ReporteR result: 0.82 acetaminophen, second lab ReporteR result: 0.62 lidocaine, third lab ReporteR result: 0.33 cocaine) (**Figure 9**). The microscope testing was able to detect both acetaminophen and cocaine. Acetaminophen, lidocaine, levamisole, and cocaine were confirmed to be contained in the sample via GC/MS. This supports that a sample may need to be tested multiple times for an accurate positive result, however, three times was determined to be the limit in order to simplify testing procedures and decrease the possibility of errors.

Marijuana

Repeatable spectra from marijuana plant material have been collected using the Bruker Senterra Raman microscope and spectral attributes in common with cannabinoids were evident, specifically cannabidiol and delta-9-tetrahydrocannabinol. Two samples of marijuana, of the ten tested, did not produce any viable spectra from the features found. At this stage, portable Raman field testing of marijuana is not practical due to the necessity of the microscope to locate the resinous structures in which the cannabinoids were detected in situ. However, the use of the baseline correction function of the Raman microscope's software proved effective in reducing the fluorescence background in the spectra and would prove useful if automatically applied in a portable device.

Testing using the ReporteR device included various methods of trying to extract cannabinoids from plant material in preparation for Raman testing. This negates the purpose of trying to stray from the use of hazardous chemicals, and this research was discontinued.

Heroin

Although a few weak repeatable spectra were collected using the ReporteR and graphene, it is evident that more research is needed in order to directly use portable Raman technology for the presumptive analysis of black tar heroin. Indications of a peak at 625 cm^{-1} and the triplet at $869\text{-}908\text{ cm}^{-1}$ are seen in the ReporteR spectra as compared to the reference material analyzed using the microscope. It is the opinion of the researcher, that spectra collected using the TruNarc

sampling system are identifiable, but less than ideal, and the future of using Raman spectroscopy to analyze black tar heroin seems dependent on using some sort of liquid sampling system.

Ecstasy

Contrary to marijuana and black tar heroin, testing ecstasy tablets directly is possible with Raman-based portable technology, but limited. Ecstasy tablets tend to come in all colors and are made with various binding materials, both of which cause fluorescence issues. They also can contain various compounds, not only methylenedioxymethamphetamine, which is the historically typical substance encountered in ecstasy. The concentration of drug can vary widely, and the recent emergence of new synthetic compounds has complicated the issue further, as many of these compounds have been detected in supposed ecstasy tablets. By testing different colors of samples containing various components, it can be concluded that the baseline correction technology is useful in the reduction of fluorescence caused by the colorings and bindings present in the tablets, and aids in identification of spectra.

Synthetics

Although it is unlikely that a field testing program will be useful in identifying the emerging synthetic drug analogs (i.e. cathinones, phenethylamines, cannabimimetics) due to their strong molecular similarities, superfluity, and constant structural manipulation, indications that these drugs may be present can be determined by portable Raman spectroscopy. Testing a few selected reference materials with the Raman microscope determined that isomeric form may be differentiated using this type of instrumentation, and fluorescence interference may be based on the isomer. A few reference materials exhibited high baselines when tested with the ReporteR, but these spectra could be corrected using baseline correction technology.

2. Implications for Policy and Practice

Enhancing and implementing a new method of presumptive field testing will benefit police officers, law enforcement field workers, forensic laboratories, and the court system. These benefits include safety, cost saving, time saving, and expedition of the judiciary process. A new method of field testing will enhance the ability of the law enforcement community to identify, analyze and interpret controlled substance evidence using a robust tool that gives immediate and defensible preliminary results for cocaine and methamphetamine, and other drugs if possible.

Using a portable Raman device will take the subjectivity out of field testing, which will have an impact on exonerations. By completing this research, the laboratory ultimately hopes to

establish case law that may assist other local and state agencies to utilize this technology in the field. This scientific evaluation and justification for the court system is of utmost importance. Because most police officers do not have the expertise to evaluate spectra and to explain to the trier of fact how the technology works, a handheld device such as the ReporteR can give officers the results they need to present in court. In order for this to happen, the court must first be presented with scientific proof to satisfy the Frye standard that a Raman handheld device is a valid and reliable tool for preliminary identification of controlled substances.

This has other implications for judiciary proceedings. Contamination is a common question from defense attorneys when testifying as to the validity of the field color tests. This research has also shown that there are discrepancies between officer and forensic scientist interpretations of chemical field test results. Not only would contamination be less of an issue with the Raman testing procedure, the incidence of the false positive results that occur with chemical field test misinterpretations might be eliminated, and the officers' results in lieu of analysis may be used in preliminary hearings, saving time for both the laboratory and the court.

The following illustrates an example of the difficulties experienced by officers in the field pertaining to the interpretation of colors observed when performing field tests. A submission which had field tested positive for cocaine by an officer was tested as part of our research. The chemical field test and ReporteR tests performed in the laboratory both gave negative results and the GC/MS data concluded the substance contained only lidocaine with no cocaine detected. This discrepancy may be attributed to an officer overloading a sample that contained only lidocaine and inattention to intermediate color changes in the chemical-based field test which led to an incorrect positive result for cocaine.

As indicated by the research, cocaine testing using portable Raman technology may be somewhat limited. The correlation settings on the ReporteR may be set in order to prevent false positive occurrence, but this also hinders the ReporteR's ability to accurately detect the target compound in mixtures. This may slightly increase the number of suspected cocaine submissions to the laboratory, due to more inconclusive results, but it significantly decreases the chance of false positive results.

Law enforcement agencies spend tens of thousands of dollars on color test field kits every year. By switching to a portable Raman-based method for testing cocaine and methamphetamine, over \$30,000 could be saved per year (after initial costs). Cost is a major consideration for most policing agencies, especially in the current economic climate. In addition, the training for this

VI. Dissemination of Research Findings

“Presumptive Raman Portable Field Testing” But Wait, There’s More! Combining Multiple Methods Into an “All-In-One” Option for Evidence Processing and Testing. National Institute of Justice Conference, June 19, 2012, Arlington, VA.

The author was interviewed by Dr. Edward Bartick of Suffolk University in early 2010 in regards to preliminary laboratory testing using the ReporteR which was completed prior to the award of this grant. This information was used by Dr. Edward Bartick in a chapter titled “In Situ Crime Scene Analysis” in a book titled *Infrared and Raman Spectroscopy in Forensic Science*, 1st Edition, edited by Chalmers, Edwards, and Hargreaves, published by John Wiley and Sons, Ltd. in 2012.