The author(s) shown below used Federal funds provided by the U.S. Department of Justice and prepared the following final report:

Document Title:	**Raman Spectroscopy with Multi-component Searching for Complex Clandestine Laboratory Sample Analysis (I), Raman Spectroscopy as a Rapid, Non-destructive Screening Test for Methamphetamine in Clandestine Laboratory Liquids (II), and Raman Spectroscopy for Enhanced Synthetic Cathinone Analysis (III)**
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Document No.:	**248557**
Date Received:	**January 2015**
Award Number:	**2010-DN-BX-K178**

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Raman Spectroscopy with Multi-component Searching for Complex Clandestine Laboratory Sample Analysis (I), Raman Spectroscopy as a Rapid, Non-destructive Screening Test for Methamphetamine in Clandestine Laboratory Liquids (II), and Raman Spectroscopy for Enhanced Synthetic Cathinone Analysis (III)

NIJ Grand Award: 2010-DN-BX-K178

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ABSTRACT

Three aspects of raman spectroscopy were explored relative to clandestine laboratory and synthetic cathinone analysis in the forensic controlled substance laboratory.

The use of raman spectroscopy and a spectral deconvolution software was examined to determine whether the software was capable of identifying the dissolved components of clandestine laboratory liquid samples. Mock laboratory samples as well as true forensic case samples were analyzed by raman spectroscopy and the deconvolution software. Unfortunately, the raman signal from the dissolving solvent was too strong and masked the dissolved components signal too much for the software to be able to reliably identify any dissolved components.

Raman spectroscopy was examined as a possible rapid, safe, and non-destructive screening technique for clandestine laboratory liquids. It was discovered that while the bulk of the raman signal is masked by a dissolving solvent, methamphetamine exhibits a strong raman band at approximately 1003 cm^{-1} that can be seen even when dissolved in typical clandestine laboratory solvents like ethanol and diethyl ether. This raman band is discernible down to approximately 4% methamphetamine (w/v) and combined with the ability of raman spectroscopy to analyze samples through container, represents a useful screening technique for multiple liquids submitted in a clandestine laboratory that improves not only efficiency but the safety profile of the analysis.

The use of raman spectroscopy as an analytical technique to more effectively discern very similar structural isomers of synthetic cathinones was investigated. Preliminary data shows potential for this analysis; however, the instrumentation available was not sufficient to overcome fluorescence interference that occurs with many of the cathinone compounds. A raman spectrometer with a 780 nm laser operating at a significantly higher power than what was available or, ideally, a raman spectrometer with a 1064 nm laser is much better suited for this analysis and represents strong future research potential.

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EXECUTIVE SUMMARY

In recent years, Raman spectroscopy has increased in use in the forensic laboratory, particular in the trace chemistry and drug chemistry disciplines. In drug chemistry Raman spectroscopy provides a useful analytical tool due to its rapid and non-destructive nature. The ability to sample through-container provides an efficient analytical mechanism particularly for bulk samples.

This study examined the use of Raman spectroscopy in three aspects of drug chemistry analysis: the use of raman spectroscopy with a deconvolution software to identify clandestine laboratory liquid components, the use of raman spectroscopy as a rapid, nondestructive screening test for methamphetamine in clandestine laboratory liquid samples, and the use of raman spectroscopy as a enhanced technique for the isomeric determination of synthetic cathinones.

I. Multi-component searching in complex clandestine laboratory mixture samples
Clandestine laboratory liquid samples present a unique problem to the forensic drug chemist. They require above average sample preparation time, they often contain noxious substances, and in many cases samples are indiscriminately collected and sent to the laboratory with not preliminary determination of what the sample contains. Recent advances in raman spectroscopy hardware and software afford a possible mechanism to enhance the overall efficiency of the sample analysis through the use of spectral deconvolution algorithms.

In the late 2000's Thermo Scientific developed the Omnic Specta software which included a "multicomponent" searching module. This module was supposed to be able to deconstruct a composite raman spectrum and return a report of the component compound spectra that would combine to afford the composite one. In this way, the multicomponent searching software was reported to be able to identify mixtures without a separation step like gas or liquid chromatography.

In this study two mock clandestine laboratories were performed using the two most common illicit methamphetamine manufacturing methods and samples were collected during the procedures. More than 30 samples were collected and analyzed via raman spectroscopy. The spectral deconvolution software was used to attempt to identify the dissolved components of the liquids, particularly methamphetamine.

Ultimately the software was unable to reliably identify the dissolved components of a solution. In practice, the contribution of the dissolving solvent was too significant a contributor to the composite spectrum and almost completely masked any dissolved components' spectra. To that end, the multicomponent searching could not identify the minor contributors.

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Surfaced enhanced raman spectroscopy (SERS) was also investigated to determine whether gold colloid suspensions were able to increase the intensities of the dissolved components enough to yield better search results. For this part of the experiment, solutions of methamphetamine in ethanol and diethyl ether were prepared at concentrations ranging from 0.5% to 10% (w/v). Four different gold colloid solutions in water (4 different size colloids) were added to the prepared methamphetamine solutions. While there was an increase in signal intensity of the dissolved components, particularly at the higher concentrations with the larger colloid sizes, the multicomponent search results were not enhanced sufficiently for reliable identification.

Lastly, true forensic case samples were analyzed both neat and with the SERS solutions to ensure that the preparation techniques were not the cause of the software failure. The results of the raman analysis of these samples were compared to the forensic analysis by GCMS. The results of the analysis were similar to the mock clandestine laboratories and prepared solutions – the software was unable to reliably identify the components of the solution.

The results of this study do not have an immediate impact on justice policy or laboratory analysis, however future research should be performed to attempt to optimize the SERS technique.

II. Rapid, non-destructive screening test for methamphetamine in clandestine lab samples

The industrial chemicals and illicit nature of clandestine methamphetamine laboratories result in frequent submissions of noxious liquids to the forensic drug chemistry laboratory. Additionally, experience at our laboratory has shown than many times liquids are submitted indiscriminately and can contain anything from pure solvents, to precursor materials, to in-process reactions, and final product solutions. To that end, a rapid screening test for clandestine liquids that could be performed through-container would enhance both the safety profile of the analysis and the efficiency of identifying relevant samples for further workup. Raman spectroscopy fills that need.

Previous experiments by our group showed that most of the raman spectrum of a solid substance is overwhelmed by the dissolving solvent in a solution. In some instances, however, very intense raman bands in the spectrum of the dissolved substance can be observed. To test this for methamphetamine, solutions were made at varying concentrations of methamphetamine in ethanol, diethyl ether, and Coleman fuel (concentrations = 0.5%, 1.0%, 2.0%, 4.0%, 6.0%, 8.0%, and 10% w/v). Each of the solutions was analyzed by raman spectroscopy to determine whether any artifacts of the methamphetamine spectra could be observed.

We found that the most intense raman band in the methamphetamine spectrum (1003 cm^{-1}) was observable in each of the solvent systems at 4.0% w/v and above. The band increases in

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intensity in linear fashion with concentration. It was hypothesized that this band could serve as a screening test for the presence of methamphetamine in clandestine laboratory liquids.

To test the hypothesis, several true forensic case sample solutions were analyzed through-container by raman spectroscopy and the results of the preliminary indication by observation of the 1003 cm^{-1} band was compared against the results of forensic analysis by GCMS. In almost all instances, solutions that indicated methamphetamine by observation of the 1003 cm^{-1} band were later confirmed to contain methamphetamine by GCMS.

The results of these experiments could have an immediate impact on a forensic drug laboratory. While the product of this study is simply a screening test, it can improve a laboratory's efficiency by identifying probative samples without any prior sample preparation and it could enhance laboratory safety by allowing chemists to screen samples for methamphetamine without having to open the containers and possibly inhale noxious fumes unnecessarily. Further studies can be performed on this same region of the raman spectrum to determine whether pseudoephedrine exhibits a band at an identical location and whether the band produced by pseudoephedrine can be discriminated from the one produced by methamphetamine.

III. Enhanced analysis of novel synthetic cathinones

Recent years have seen a dramatic increase in various synthetic cathinones submitted to the forensic drug chemistry laboratory. Illicit manufacturers are currently engaged in a cat-and-mouse game with legal authorities. As a state or local government regulates certain cathinones as controlled substances, manufacturers are synthesizing derivatives or making slight structural modifications to the compounds. The result is literally hundreds of synthetic cathinone isomers and derivatives with very minor structural changes. These minor structural differences, in some instances, create difficulties for the forensic drug laboratory as some instrumentation is able to identify the parent compound, but not the particular isomer (e.g.- a methyl substitution at the ortho, meta, or para position on a phenyl ring). Raman spectroscopy, with its very defined, narrow bands and greater sensitivity to alkyl modifications could present an enhanced analytical tool for use in synthetic cathinone cases over traditional GCMS techniques.

Sixty-three synthetic cathinone compounds were acquired from Cayman Chemical company and analyzed on a Thermo Scientific SmartRaman DXR spectrometer with a 780 nm excitation laser and the spectra were compared to determine whether band patterns could be observed among isomers that were sufficient for discrimination of the distinct isomer. Unfortunately, we found that in many instances (68% of the samples), the spectra exhibited a fluorescence interference that either moderately or completely obscured the spectrum and prevented a more rigorous analysis. The compounds were categorized into groups based on similar structural substituents, however only one group (2-, 3-, and 4-methoxymethcathinone) gave useful spectra without any fluorescence for all compounds. In many instances, a full comparison was not possible. Futher

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work is necessary to better examine the spectra of these compounds, however a preliminary indication was observable in several samples that bands appearing at approximately 1600 cm^{-1} may discriminate regioisomers based on whether the same substitution is made at the 2-, 3-, or 4-phenyl position.

The samples were later analyzed on a different instrument provided by the Defense Forensic Science Center in Forest Park, Georgia that is equipped with an excitation laser operating at 1064 nm. The spectra produced by this instrument were far superior than those obtained by the instrument with the 780 nm excitation laser.

Preliminary data suggests that there are regions in the raman spectrum that may assist in the distinction of positional isomers of synthetic cathinones. While there is no implication at this time for policy or practice improvements, future research should focus on the use of 780 nm lasers operating at a higher power (based on literature research) or excitation lasers operating at 1064 nm.

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INTRODUCTION

Statement of the problem

The analysis of clandestine laboratory liquid samples presents several challenges to the forensic drug laboratory, from efficiency issues to safety concerns. Similarly, there are analytical challenges present in the novel synthetic cathinones that have erupted onto the illicit drug in recent years. Raman spectroscopy offers distinct analytical advantages to assist with these unique challenges.

I. Multi-component searching in complex clandestine laboratory mixture samples
The analysis of clandestine laboratory liquids in the forensic drug chemistry laboratory is often more complex than other routine analyses, such as powders, tablet, and plant materials. In particular, clandestine laboratory cases often have many more exhibits submitted for analysis. Additionally, often times many of those submitted exhibits are nearly colorless liquids, with little contextual information available to make preliminary decisions about their contents. Liquid samples in clandestine laboratories can represent a broad range of steps in the process of methamphetamine manufacture from pure starting materials, to simple solvents, to the final methamphetamine product dissolved in a solvent prior to precipitation. In this way, samples range from completely non-probative, to dangerous, to harmful to delicate (and expensive) analytical equipment, to extremely valuable evidence. Lastly, clandestine laboratory liquids can range from single component, to complex mid-reaction mixtures containing unreacted starting materials, intermediates, and final product.

Instrument manufacturers began describing the ability of deconvolution software to deconstruct composite raman spectra of mixtures in the late 2000's. The ability of a raman instrument with spectral deconvolution software to deconstruct complex clandestine laboratory liquid mixtures into their component raman spectra would be a significant advancement and highly useful to the forensic drug laboratory.

II. Rapid, non-destructive screening test for methamphetamine in clandestine lab samples
From a safety perspective, clandestine laboratory liquids are inherently hazardous. Routine clandestine laboratory submissions include strong acids, strong bases, strong ammonia vapors, and unreacted lithium metal. Raman spectroscopy affords a safety benefit over traditional analytical techniques in that it can analyze samples through-container. The development of a through-container presumptive analysis of clandestine laboratory liquids for the presence of methamphetamine could reduce the exposure of a forensic drug chemist to caustic and noxious chemicals by identifying probative samples for further analysis. Efficiency gains could also be realized by reducing the liquid sample workup required for traditional GCMS analysis on samples that do not screen positive for methamphetamine.

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III. Enhanced analysis of novel synthetic cathinones

In recent years, novel synthetic cathinones have exploded onto the illicit drug market. In an effort to evade drug laws, multiple cathinone derivatives and isomers of derivatives were formulated to barely escape the chemical definitions contained in most drug laws. The legal community responded by adding the new substances to controlled lists, however frequently the compounds were just slightly modified and the new derivative or isomer again escaped legal control. This "cat-and-mouse game" persists today.

The constant influx of new synthetic cathinones presents a problem to forensic drug chemistry laboratories. Until the last couple years, mass spectral reference spectra for many of these compounds were difficult to find as many mass spectral libraries did not contain the bulk of new synthetic cathinones. Additionally, the constant changing nature of the compounds was difficult to track. Lastly, use of the most common analytical technique in the forensic drug laboratory, mass spectrometry, became challenging as it cannot differentiate between positional isomers as well as was desired.

Raman spectroscopy offers a unique advantage to the analysis of synthetic cathinones as it is expected to better differentiate very similar isomers and derivatives. Raman spectroscopy is an optical technique that eliminates the structural challenges of mass spectrometry in this area, and is expected to afford a benefit over traditional fourier transform infrared spectroscopy, as raman bands are typically narrower and more discrete than FTIR bands and the sensitivity of raman to alkyl differences between compounds should be better than FTIR.

Literature citations and review

I. Multi-component searching in complex clandestine laboratory mixture samples

Raman spectroscopy has seen advances in recent years that make it far more accessible and useful in forensic drug chemistry laboratories than before.[1] In particular, the development of spectral deconvolution software shows promise in overcoming prior difficulties in optical spectroscopies that would otherwise require relatively pure samples, which is a rarity in forensic casework.[2,3,4,5]

An additional resource to explore when analyzing liquid mixtures that may contain low concentrations of the target analyte is the potential for using Surface Enhanced Raman Spectroscopy (SERS). Surface enhanced Raman Spectroscopy uses a gold colloid either affixed to a slide or in a liquid suspension to enhance the raman signal of dissolved organic compounds. Several studies have shown a several-fold increase in Raman signal from dissolved compounds when using SERS.[6,7]

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II. Rapid, non-destructive screening test for methamphetamine in clandestine lab samples
Raman spectroscopy has developed into a tool that can increase laboratory throughput and efficiency and has seen measurable increases in the forensic laboratory equipment inventory.[1] Several papers describe the value of Raman spectroscopy with regard to its non-destructive ability to analyze samples through-container.[1,2,8,9] Additionally, several published articles have examined the ability of Raman spectroscopy to serve as a screening tool based on characteristic raman bands present in a mixture sample. These bands can be used as discrete markers for the presumptive presence of a particular substance, and general have a fairly linear relationship between intensity and sample concentration.[10,11,12,13]

III. Enhanced analysis of novel synthetic cathinones
Based on the recent increased use of Raman spectroscopy in the forensic laboratory, the basic characterization studies of novel synthetic cathinones (a.k.a. "bath salts") have already begun to include Raman studies and spectra in addition to the more typical characterizations with mass spectroscopy, infrared spectroscopy, and nuclear magnetic resonance spectroscopy.[14,15] To that end, studies have just begun publishing Raman data. It is expected that a more thorough examination of a wide variety of synthetic cathinones via Raman spectroscopy may help differentiate the fine differences between similar structural isomers of the various bath salts products on the market.[16]

Statement of hypothesis or rationale for the research

I. Multi-component searching in complex clandestine laboratory mixture samples
The analysis of clandestine laboratory liquid mixtures by Raman spectroscopy will enable a forensic drug chemistry laboratory to more efficiently and safely analyze complex and potential hazardous samples. It is hypothesized that multiple liquids will be able to be screened through-container and the components of the mixtures identified by the spectral deconvolution software. This will enable the chemist to make more efficient decisions on which samples to select for further time-consuming chemical workup and make more effective decisions on which samples contain pertinent compounds to the manufacture of methamphetamine and which are simple solvents or non-probative samples.

II. Rapid, non-destructive screening test for methamphetamine in clandestine lab samples
The use of Raman spectroscopy is expected to increase efficiency and safety in the screening of clandestine laboratory liquid samples that contain methamphetamine. Using characteristic bands in the Raman spectrum of methamphetamine, it is hypothesized that a rapid, non-destructive, through-container screening test can be developed that will eliminate the need for a forensic drug chemist to open multiple unnecessary containers that may contain caustic and noxious substances. The efficiency and safety profile of this analysis will be improved.

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III. Enhanced analysis of novel synthetic cathinones

Novel synthetic cathinones present a unique challenge in that they are often very similar in structure. This leads to difficult mass spectral differentiation. It is hypothesized that Raman spectroscopy will better discriminate between positional isomers due to its enhanced sensitivity to alkyl rearrangements compared to mass spectroscopy and infrared spectroscopy. The distinction between positional rearrangements in the alkyl chain and on the phenyl ring of cathinones is expected to be more efficiently resolved using raman spectroscopy.

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METHODS

I. Multi-component searching in complex clandestine laboratory mixture samples

A. Obtaining clandestine laboratory samples

During the summer of 2011, two demonstration clandestine laboratories were set up at the Kentucky State Police Central Forensic Laboratory. In a controlled environment, methamphetamine was produced using the red phosphorus/iodine method and the birch reduction method. Samples were obtained of all starting materials, including solvents, at 30 minute intervals during the Red P/iodine production process and at 10 minute intervals for the Birch reduction process. Lastly, samples were taken of the finished product. In all, more than 30 samples were obtained for analysis by raman spectroscopy. Each sample was analyzed through-container by the raman spectrometer at two different collection settings in an attempt to obtain the optimal balance between number of exposures and exposure time.

B. Materials

In an effort to simulate illicit methamphetamine manufacture in as much of an authentic manner as possible, lab-grade chemicals were not used if reasonable common goods were available. Precursor and solvent materials such as coleman fuel, 100% ethanol, Red Devil Lye, drain cleaner (containing sulphuric acid), and lithium batteries were purchased from a local hardware store. Pseudoephedrine tablets were obtained from the Kentucky State Police Drug Enforcement Section. It was necessary to obtain red phosphorus and anhydrous ammonia from Fisher Scientific. In order to ensure safety, laboratory grade glassware was used including round bottom flasks, heating mantles, Tygon tubing, and a reflux condenser, all obtained from VWR.

C. Raman spectrometer collection parameters

Raman spectra were collected on a Thermo Scientific DXR SmartRaman spectrometer with a 780nm near-IR laser operating at 10mW power using Thermo Scientific Omnic Software Version 8.2.387. A 400 lines/mm grating was used and the spectrograph aperture was set at a 50 μm slit. Data was collected over a range of 100-3410 cm^{-1}. The software's rastering feature was turned on and configured to collect and average the spectra for each sample over a 5 mm x 5 mm sample area to achieve a more homogeneous sample spectrum without the need for rotating the sample containers. Two collection settings were used for each sample. Setting 1 included a collection of ten exposures at five seconds per exposure. Setting 2 included a collection of twenty exposures at ten seconds per exposure. The exposures were averaged, internally, by the Omnic software to produce a final composite spectrum.

D. Surface Enhanced Raman Spectroscopy (SERS)

Four different gold colloid suspensions were purchased from Thermo Scientific (gold colloid sizes of 30, 50, 70, and 90 nm in water). Five different clandestine laboratory liquid samples were prepared for SERS analysis by combining 2 mL of sample with 2 mL of each of the gold

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colloid suspensions for a total of 20 solutions. Each solution was analyzed via the same raman collection parameters as the original samples (Setting 1 and Setting 2).

II. Rapid, non-destructive screening test for methamphetamine in clandestine lab samples

A. General

Samples of methamphetamine dissolved in solvents relevant to clandestine laboratories were prepared at specific concentrations. These samples were then analyzed by raman spectroscopy through-container and the resulting spectra studied to identify any characteristic, concentration-dependent peaks from the methamphetamine spectra that appear in the composite methamphetamine-solvent raman spectra.

B. Solution Preparation

Methamphetamine in ethanol—

Ethanolic methamphetamine HCl solutions were prepared by dissolving 10.00 grams of methamphetamine HCl (Lot #051M1142V, 100%, Sigma-Aldrich, St. Louis, MO) in 100 mL of ethanol (Lot #03J14QA, AAPER Alcohol & Chemical Company, Brookfield, CT) to achieve a 10% w/v solution. This solution was serially diluted with ethanol to achieve solutions of 8%, 6%, 4%, 2%, 1%, and 0.5% w/v. Each solution was placed into a 21 mm x 70 mm (O.D. x height) colorless, borosilicate glass vial (Lot #6-1-2, VWR, Radnor, PA). The vials were placed on their side in the spectrometer collection compartment and the solutions were analyzed through-container (the sides of the vials are thinner and more uniform in thickness than the bottom and yield better spectra based on previous experiments).

Methamphetamine in diethyl ether—

An aqueous sodium hydroxide solution was prepared by dissolving 2.68 grams of NaOH (Lot #984565, Fisher Scientific, Pittsburgh, PA) with 100 mL of deionized water (house supply). To the aqueous sodium hydroxide solution was added 12.44 grams of methamphetamine HCl (Lot #051M1142V, 100%, Sigma-Aldrich, St. Louis, MO), with stirring, at which time methamphetamine base formed as an oil layer on top of the aqueous layer. Quickly, to avoid evaporative loss, the solution was extracted with two 50 mL portions of diethyl ether (Lot #113125, Fisher Scientific, Pittsburgh, PA). The two diethyl ether portions were combined to afford a 10% w/v solution of methamphetamine base in diethyl ether. This solution was serially diluted with additional diethyl ether to achieve solutions of 8%, 6%, 4%, 2%, 1%, and 0.5% w/v. Each solution was then analyzed through the containing glass vial as in the ethanol solutions.

Methamphetamine in Coleman Fuel—

Coleman® Premium Blend Fuel (Lot #CR08A02072, Coleman®, Wichita, KS, later referred to as "Coleman fuel" or "C.F.") was purchased at a local retail store. Methamphetamine base was prepared as described in the diethyl ether solutions. Instead of extraction with diethyl ether, the methamphetamine base / aqueous sodium hydroxide bi-layered solution was extracted with two 50 mL portions of Coleman fuel. The two Coleman fuel portions were combined to afford a 10% w/v solution of methamphetamine base in Coleman fuel. This solution was serially diluted with additional Coleman fuel to achieve

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solutions of 8%, 6%, 4%, 2%, 1%, and 0.5% w/v. Each solution was then analyzed through the containing glass vial as in the ethanol and diethyl ether solutions.

C. Raman spectrometer collection parameters

Raman spectra were collected on a Thermo Scientific DXR SmartRaman spectrometer with a 780nm near-IR laser operating at 10mW power using Thermo Scientific Omnic Software Version 8.2.387. A 400 lines/mm grating was used and the spectrograph aperture was set at a 50 μm slit. Data was collected over a range of 100-3410 cm^{-1}. The software's rastering feature was turned on and configured to collect and average the spectra for each sample over a 5 mm x 5 mm sample area to achieve a more homogeneous sample spectrum without the need for rotating the sample containers. For each sample, a total of five exposures were collected at five seconds per exposure. The exposures were averaged, internally, by the Omnic software to produce a final composite spectrum.

III. Enhanced analysis of novel synthetic cathinones

A. Obtaining cathinone standards

Sixty-three synthetic cannabinoid standards were obtained from Cayman Chemical Company to analyze via raman spectroscopy (listed in Appendix A). Twenty milligrams of each standard was obtained. Each standard was analyzed by Raman spectroscopy at the Kentucky State Police Central Forensic Laboratory and later analyzed at the Defense Forensic Science Center in Forest Park, Georgia.

At the Kentucky State Police laboratory, 5-10 milligrams of sample was placed on a 35mm glass bottom culture dish (MatTek Corp, part no.: P35G-0-10-C). These dishes have a No. 0 glass coverslip on the bottom that is transparent in the raman frequency range.

At the Defense Forensic Science Center, 5-10 milligrams of sample was placed in a glass GCMS insert vial (Thermo Scientific polyspring inserts, 300µLm, part no.: 60180-734), and the vial was placed in a custom-built sample holder that held the vial in the path of the laser.

B. Raman spectrometer collection parameters

Kentucky State Police raman spectrometer—

Raman spectra were collected on a Thermo Scientific DXR SmartRaman spectrometer with a 780nm near-IR laser operating at 20mW power using Thermo Scientific Omnic Software Version 8.2.387. A 400 lines/mm grating was used and the spectrograph aperture was set at a 50 μm slit. Data was collected over a range of 100-3410 cm^{-1}. The software's rastering feature was turned on and configured to collect and average the spectra for each sample over a 5 mm x 5 mm sample area to achieve a more homogeneous sample spectrum without the need for rotating the sample containers. For each sample, a total of fifty exposures were collected at five seconds per exposure. The exposures were averaged, internally, by the Omnic software to produce a final composite spectrum.

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Defense Forensic Science Center raman spectrometer—
Raman spectra were collected on a Thermo Nicolet 6700 NXR FT-Raman spectrometer with a 1064 nm Nd:$YV0_4$ operating at 2.5 W using Thermo Scientific Omnic Software. For each sample, 32 scans were collected at 2 seconds per scan. The scans were averaged, internally, by the Omnic software to produce a final composite spectrum.

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RESULTS

Statement of the Results

I. Multi-component searching in complex clandestine laboratory mixture samples
The multi-component searching software did not yield very reliable data for complex mixtures. Over the course of the experiment, multiple instrument collection parameters were explored, as well as spectral enhancement techniques like surface enhanced raman spectroscopy (SERS). Ultimately, the spectral deconvolution software was not able to reliably and repeatedly identify multiple components of the mixtures. In nearly all instances, the solvent was easily identified as the key contributor to the spectrum. In a few instances, the software was able to roughly identify that either pseudoephedrine or methamphetamine may be present. Beyond a few instances, however, the search results were not correct and ultimately did not provide any useful information.

II. Rapid, non-destructive screening test for methamphetamine in clandestine lab samples
During the attempts to use the spectral deconvolution software on liquid samples containing methamphetamine, one phenomenon was observed that was useful. When true clandestine laboratory samples obtained from the demonstration labs were found to be problematic, we began studying simplified solutions that contained only one solvent and methamphetamine dissolved at increasing concentrations. The strongest Raman band in the methamphetamine spectrum occurs at approximately 1003 cm^{-1}. It was observed during these experiments, that even in dilute samples where the majority of the methamphetamine spectrum was obscured by the strong solvent spectrum, the 1003 cm^{-1} band could usually be seen at concentrations exceeding 4-6% w/v. From those observations, a screening test was developed for methamphetamine in clandestine laboratory liquids. It was determined that in common solvents to clandestine laboratories such as ethanol, diethyl ether, and even industrial mixtures like Coleman Fuel, the appearance of a Raman band at 1003 cm-1 could serve as a presumptive indication of methamphetamine and serve to help chemists screen multiple samples for further workup and definitive analysis.

III. Enhanced analysis of novel synthetic cathinones
The analysis of sixty-four synthetic cathinones did not provide the intricate regioisomeric determinations that was anticipated (it was hoped that Raman could distinguish ortho, meta, and para substitutions, or various geometric isomers), largely based on significant fluorescence interference that was encountered with many samples. The raman spectrometer available at the Kentucky State Police forensic laboratories was simply not suitable for this analysis. In further reading and collaborations with the Defense Forensic Science Center, it was further determined that in order to overcome the significant fluorescence encountered with the cathinones, either a

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1064 cm^{-1} laser is necessary (compared to our 780nm one) or a laser of considerable higher power (e.g.- 200mW versus 20mW) must be used.

The samples collected at the Kentucky State Police laboratories afforded only twenty-eight usable raman spectra out of sixty-four, however a collaboration with the Defense Forensic Science Center in Forest Park, Georgia allowed us to confirm that the 1064 cm^{-1} will acquire usable spectra. To that end, other researchers should be encouraged that further work in the area should focus on the use of the 1064 cm^{-1} systems or microscope systems with high power lasers such as the one used in the *R. Christie et al* paper.[16]

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CONCLUSIONS

Discussion of Findings

I. Multi-component searching in complex clandestine laboratory mixture samples
Tables 1 and 2 show the deconvolution software's multicomponent search results for several of the samples taken during the demonstration clandestine laboratories. It can be seen that the software can typically identify the main component of the mixture easily, in these instances the major solvent used in the reactions. The software was unable, however, to identify the minor components. The software was more successful on solid samples rather than liquids. In Table 2, the search results for ground pseudoephedrine tablets are shown. The software successfully identified pseudoephedrine and lactose and components of the tablets. It appears that for liquid samples the raman spectra of the dissolved components are sufficiently overwhelmed by the solvent spectra that the software is unable to successfully discern the identities of the components. The individual search results for each sample in Tables 1 and 2 are shown in Figures 1 – 13.

More than 10 true forensic case samples were also analyzed by the instrument deconvolution software in order to ensure the demonstration lab results were consistent with real samples. The results were compared with the laboratory's Gas Chromatography-Mass Spectrometry results. Unfortunately the results were similar to those of the demonstration labs, with the software being unable to discern the compounds present other than the major solvent. Figures 14 and 15 show the multicomponent search results of two representative examples. The results of the forensic analysis of the samples shown in figures 14 and 15 showed that both samples were found to contain methamphetamine.

In order to examine whether Surface Enhanced Raman Spectroscopy (SERS) could afford better spectra, sample solutions were prepared of methamphetamine in ethanol ranging in concentration from 0.5% w/v to 10% w/v. The results of the 10% methamphetamine in ethanol solution with the 4 different SERS solutions are given in Figure 16. It does appear that the SERS solutions do afford an increase in signal of the methamphetamine component. In Figure 16 the signal appears most increased with the 71 nm colloid. For the bulk of the samples examined, though, the 87 nm colloid showed the largest signal increased. Figures 17 and 18 show the difference between the multicomponent search results in the neat 10% ethanolic methamphetamine spectrum and the same solution with addition of the 87 nm SERS solution. While the SERS search results don't indicate methamphetamine, they do indicate the presence of ephedrine, which has a very similar raman spectrum (though the quality score of the match is 4.87 out of 100). The SERS solutions were then tested on true forensic case samples, which were found to contain methamphetamine in the original forensic analyses. The result of one representative sample is show in Figures 19 and 20. Figure 19 shows that the multicomponent search on the neat case sample did not yield

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any useful information about the components of the solution other than the bulk solvent present. In figure 20, the addition of the 87 nm colloid solution did yield search results that included pseudoephedrine, but oddly omitted the solvent as a component which was the primary contributor to the spectrum. These results were consistent for the majority of forensic samples analyzed. While more promising than the search results of neat solutions, the multicomponent searching with the SERS solutions still fell short of expectations.

II. Rapid, non-destructive screening test for methamphetamine in clandestine lab samples

Ethanol, diethyl ether, and Coleman fuel were chosen as solvents due to their frequent use in illicit clandestine laboratories. Figure 21 shows the comparison of raman spectra between the three selected solvents and methamphetamine and shows the strong band exhibited in the methamphetamine spectrum at 1003 cm^{-1}. A literature indicates that this band corresponds to the aromatic carbon vibrations in a mono-substituted benzene structure, though the exact assignment does appear to be debated.[17] Because the 1003 cm^{-1} peak in the methamphetamine spectrum is both the most prominent peak and is also notably absent in any of the solvent spectra, this peak was chosen to investigate as a potential marker for the presence of methamphetamine in solution. Figures 22-24 show methamphetamine dissolved in each solvent at 7 concentrations: 0.5%, 1.0%, 2.0%, 4.0%, 6.0%, 8.0%, and 10% (w/v) and these same spectra are displayed in Figures 25-27 with an expanded view at 400-1800 cm^{-1} to better observe the peak of interest. From these spectra, it can be seen that the 1003 cm^{-1} becomes vaguely discernible at approximately 2.0%, but is more readily apparent at 4.0% and above.

One of the more interesting ways to observe the solutions is presented for each solvent in Figures 28-30. Figures 28-30 show the various concentrations in each solvent system presented in an overlay format and with the spectra further expanded to show only the 940-1070 cm^{-1} range. In this format, the diagnostic 1003 cm^{-1} is clearly observed to increase in abundance with increased concentration in an approximate linear fashion. For each set of data, the neat solvent spectrum was also added to present an absolute baseline at 1003 cm^{-1}.

Based on the observations of near linear intensity increases of the 1003 cm^{-1} band in Figures 28-30, a rough plot was created of the intensity of the band versus concentration. This plot is shown in Figure 31. It must be acknowledged that the concentration due to the small band intensities at lower concentrations, a manual integration was necessary to obtain some of the data. While the authors attempted to rigorously assign the baseline consistently, the data must be considered an estimate only. Nevertheless, after the data was plotted in Microsoft Excel, a trendline calculated, and correlation coefficient observed, the data strongly supports a linear increase in band intensity based on increasing concentration. The correlation coefficients were 0.9975, 0.9985, and 0.9973 for methamphetamine in ethanol, Coleman fuel, and ether respectively.

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Lastly, several true forensic case samples were analyzed for the presence of the 1003 cm^{-1} raman band and those results compared to the results of forensic analysis via gas chromatography-mass spectrometry. In nearly every sample that tested positive for methamphetamine by GC-MS, the 1003 cm^{-1} raman band was also observable. Five representative case samples are presented in Figures 32 and 33.

III. Enhanced analysis of novel synthetic cathinones

Table 3 shows all sixty-three cathinones that were analyzed in this study. A generalized cathinone structure is provided and the particular substituted functional groups are shown with their relative positions on the molecule. Lastly, an indication is given whether the raman spectrum obtained from the 785nm laser showed no fluorescence, moderate fluorescence, or high fluorescence (indicated by "yes"). Twenty-eight of the sixty-three cathinones (44%) showed strong fluorescence in the raman signal at 785 nm rendering the spectrum so obscured that no useful data was available. Fifteen of the cathinones (24%) had spectra that showed moderate fluorescence, meaning the spectrum had some potentially useful information but was incomplete for rigorous analysis. Finally, 20 cathinones (32%) had no fluorescence in the raman spectrum with the 785 nm laser system and provided complete spectra with useful data.

Table 3 also breaks down the set of cathinone compounds into similar structural categories in an attempt to obtain group-based data for particular substitutions. Unfortunately, while 32% of the cathinones provided complete raman spectra, only one set of "group" data was complete, which significantly limited the conclusions that could be drawn. Figure 34 illustrates this difficulty. Figure 34 shows the raman spectra of one group of cathinones – combinations of a single methyl or ethyl substituent on both the amine nitrogen and the phenyl ring. Of the twelve combinations, five gave good spectra, 4 were considered to have a high level of fluorescence interference and 3 were considered to have a moderate level of fluorescence interference. Further complicating the matter is the fact that the fluorescence does not initially appear predictable based on structure. There is no complete series of any combination in the twelve shown in Figure 34. In some series, substitutions at the 4-phenyl position have fluorescence; in others, substitutions at the 2-position have fluorescence. This also seems to occur independent of whether the substitutions are methyl or ethyl functional groups.

Fortunately, there are some preliminary observations that are observable and ripe for further research. Figures 35-38 show the spectra of this group sorted by phenyl position (e.g.-all the combinations of 2-phenyl substitutions). While every series has at least one spectrum that suffers from fluorescence interferences, some vague trends emerge. One interesting phenomenon is the change in band(s) at 1600 cm^{-1} based on the location of the phenyl substituent. There are two discrete bands centered around 1600 cm^{-1} for all of the 2-phenyl substitutions in Figure 35. In Figure 36, there is less separation between the two bands, and in fact, for 3 of the spectra the lower frequency band appears as more of a shoulder to the more

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intense band. Lastly, in Figure 37, while two of the spectra don't provide any useful data, two spectra show the complete unification of these two bands, resulting in only 1 discrete band at approximately 1600 cm^{-1}. This phenomenon appears to be confirmed in Figure 38, which shows the 2-, 3-, and 4-methoxymethcathinone regioisomers. Further work to obtain better spectra with less fluorescence interference may provide better insight into these spectral changes based on functional group positional substitution.

Lastly, Figure 39 shows the difference between analysis of 3 representative synthetic cathinones using the raman system with a 780 nm laser and a raman system with a 1064 nm laser. On the 785 nm laser system none of the 3 regioisomers provided any useful data whatsoever. Fluorescence interference completely obscures the raman spectrum of each compound. On the 1064 nm laser system, however, the spectra are well defined and there is no sign of fluorescence. Figure 39 illustrates the need for further investigation in this area using the 1064 nm laser raman system.

Tables

I. Multi-component searching in complex clandestine laboratory mixture samples

Table 1 – Red Phosphorus/Iodine Method – Deconvolution Software *Calculated* Components

Sample Source	**Component #1**	**Component #2**	**Component #3**	**Component #4**
Tablet Extract with EtOH	Denatured alcohol	Benzphetamine	Pseudoephedrine	Glutethimide
Rxn solution @ 0 hours	Denatured alcohol	Iodine	Glutethimide	Acetylsalicylic acid
Rxn solution @ 1 hour	Denatured alcohol	Glutethimide	Acetylsalicylic acid	Hydromorphone
Rxn solution @ 2 hours	Denatured alcohol	Iodine	Glutethimide	Doxepin
Rxn solution @ 3 hours	Denatured alcohol	Glutethimide	Acetylsalicylic acid	Ethinamate
Final solution aqueous layer	Denatured alcohol	Starting fluid (ethyl ether)	Testosterone decanoate	Mephobarbital
Final solution ether layer	Starting fluid (ethyl ether)	Denatured alcohol	Methyl sulfone	Methamphetamine
Final product	Desipramine	Diphenhydramine	Methamphetamine	4-bromo-2,5-dimethoxy-amphteamine

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Table 2 – Birch Reduction Method – Deconvolution Software *Calculated* Components

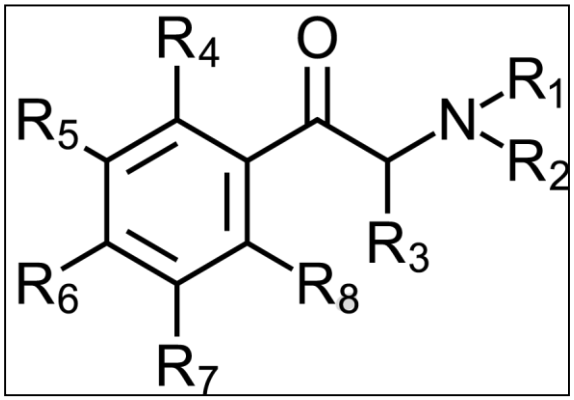
Sample Source	Component #1	Component #2	Component #3	Component #4
Ground pseudoephedrine tablets	Pseudoephedrine	Lactose	Oxazepam	Fentanyl
Rxn solution @ 0 minutes	Mephobarbital	Amitriptyline	Medazepam	Morphine sulfate
Rxn solution @ 10 minutes	Pemoline	Triazolam	Desipramine	Acetylsalicylic acid
Rxn solution @ 20 minutes (after quenching rxn)	Methenolone	19-nortestosterone	Methylenedioxy-ethylamphetamine	Butorphanol
Final solution ether layer	Starting fluid (ethyl ether)	Denatured alcohol	Methyl sulfone	Phenacetin

II. Rapid, non-destructive screening test for methamphetamine in clandestine lab samples

-None-

III. Enhanced analysis of novel synthetic cathinones

Table 3 – Cathinones analyzed by structural category and results of interfering fluorescence



Name	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8	Inhibiting Fluorescence
Methyl/Ethyl regioisomers combination substitutions									
2-methylmethcathinone	H	Me	Me	Me	H	H	H	H	Yes
3-methylmethcathinone	H	Me	Me	H	Me	H	H	H	Moderate
4-methylmethcathinone	H	Me	Me	H	H	Me	H	H	No

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2-methylethcathinone	H	Et	Me	Me	H	H	H	H	No
3-methylethcathinone	H	Et	Me	H	Me	H	H	H	Yes
4-methylethcathinone	H	Et	Me	H	H	Me	H	H	Moderate
2-ethylmethcathinone	H	Me	Me	Et	H	H	H	H	No
3-ethylmethcathinone	H	Me	Me	H	Et	H	H	H	Moderate
4-ethylmethcathinone	H	Me	Me	H	H	Et	H	H	Yes
2-ethylethcathinone	H	Et	Me	Et	H	H	H	H	No
3-ethylethcathinone	H	Et	Me	H	Et	H	H	H	No
4-ethylethcathinone	H	Et	Me	H	H	Et	H	H	Yes
Alkyl Substitutions									
ethcathinone	H	Et	Me	H	H	H	H	H	Moderate
N-ethylbuphedrone	H	Et	Et	H	H	H	H	H	Yes
Buphedrone	H	Me	Et	H	H	H	H	H	No
Pentedrone	H	Me	Pr	H	H	H	H	H	Moderate
4-methylbuphedrone	H	Me	Et	H	H	Me	H	H	Yes
4-methyl-α-ethylaminobutiophenone	H	Et	Et	H	H	Me	H	H	No
Nor-mephedrone	H	H	Me	H	H	Me	H	H	Moderate
2,3-dimethylmethcathinone	H	Me	Me	Me	Me	H	H	H	Moderate
3,4-dimethylmethcathinone	H	Me	Me	H	Me	Me	H	H	Yes
3,4-dimethylethcathinone	H	Et	Me	H	Me	Me	H	H	Moderate
Ring Methoxy substitutions									
2-methoxymethcathinone	H	Me	Me	MeO	H	H	H	H	No
3-methoxymethcathinone	H	Me	Me	H	MeO	H	H	H	No
4-methoxymethcathinone	H	Me	Me	H	H	MeO	H	H	No
Ring Fluoro substitutions									
2-fluoromethcathinone	H	Me	Me	F	H	H	H	H	Yes
3-fluoromethcathinone	H	Me	Me	H	F	H	H	H	No

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4-fluoromethcathinone	H	Me	Me	H	H	F	H	H	No
2-fluoroethcathinone	H	Et	Me	F	H	H	H	H	Yes
3-fluoroethcathinone	H	Et	Me	H	F	H	H	H	Moderate
4-fluoroethcathinone	H	Et	Me	H	H	F	H	H	Yes
N-dialkyl substitutions									
Diethylcathinone	Et	Et	Me	H	H	H	H	H	Yes
N,N-methylcathinone	Me	Me	Me	H	H	H	H	H	No
4-ethyl-N,N-dimethylcathinone	Me	Me	Me	H	H	Et	H	H	No
4-methoxy-N,N-dimethylcathinone	Me	Me	Me	H	H	MeO	H	H	Moderate
4-methyl-N-methylbuphedrone	Me	Me	Et	H	H	Me	H	H	No
N-ethyl-N-methylcathinone	Me	Et	Et	H	H	H	H	H	Yes
Ring methylenedioxy substitutions									
2,3-methylenedioxymethcathinone	H	Me	Me	Methylenedioxy		H	H	H	No
methylone	H	Me	Me	H	Methylenedioxy		H	H	No
butylone	H	Me	Et	H	Methylenedioxy		H	H	No
2,3-pentylone isomer	H	Me	Pr	Methylenedioxy		H	H	H	Moderate
pentylone	H	Me	Pr	H	Methylenedioxy		H	H	Yes
bk-MDEA	H	Et	Me	H	Methylenedioxy		H	H	Yes
eutylone	H	Et	Et	H	Methylenedioxy		H	H	Yes
bk-MDDMA	Me	Me	Me	H	Methylenedioxy		H	H	Moderate
bk-DMBDB	Me	Me	Et	H	Methylenedioxy		H	H	No
N-pyrrolidine substitutions									
α-pyrrolidinopropiophenone	Pyrrolidine		Me	H	H	H	H	H	Yes
α-pyrrolidinobutiophenone	Pyrrolidine		Et	H	H	H	H	H	Yes

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α-pyrrolidinopentiophenone	Pyrrolidine	Pr	H	H	H	H	H	Yes
2-methyl-α-pyrrolidinopropiophenone	Pyrrolidine	Me	Me	H	H	H	H	Yes
3-methyl-α-pyrrolidinopropiophenone	Pyrrolidine	Me	H	Me	H	H	H	Yes
4-methyl-α-pyrrolidinopropiophenone	Pyrrolidine	Me	H	H	Me	H	H	Yes
2-methyl-α-pyrrolidinobutiophenone	Pyrrolidine	Et	Me	H	H	H	H	Yes
3-methyl-α-pyrrolidinobutiophenone	Pyrrolidine	Et	H	Me	H	H	H	Yes
4-methyl-α-pyrrolidinobutiophenone	Pyrrolidine	Et	H	H	Me	H	H	Yes
Pyrovalerone	Pyrrolidine	Pr	H	H	Me	H	H	Moderate
4-methyl-α-pyrrolidinohexanophenone	Pyrrolidine	Bu	H	H	Me	H	H	Yes
4-methoxy-α-pyrrolidinopropiophenone	Pyrrolidine	Me	H	H	MeO	H	H	Yes
Combination ring and N-cyclic substitutions								
2,3-methylenedioxypyrovalerone	Pyrrolidine	Pr	methylenedioxy		H	H	H	Moderate
3,4-methylenedioxy-α-pyrrolidinopropiophenone	Pyrrolidine	Me	H	methylenedioxy		H	H	No
3,4-methylenedioxy-α-pyrrolidinobutiophenone	Pyrrolidine	Et	H	methylenedioxy		H	H	Moderate
Naphyrone (1-naphthyl isomer)	Pyrrolidine	Pr	Phenyl		H	H	H	Yes
Naphyrone	Pyrrolidine	Pr	H	Phenyl		H	H	Yes
*Where: **Me** = methyl, **Et** = ethyl, and **Pr** = propyl, **Bu** = butyl, **MeO** = methoxy*								

Figures

I. Multi-component searching in complex clandestine laboratory mixture samples

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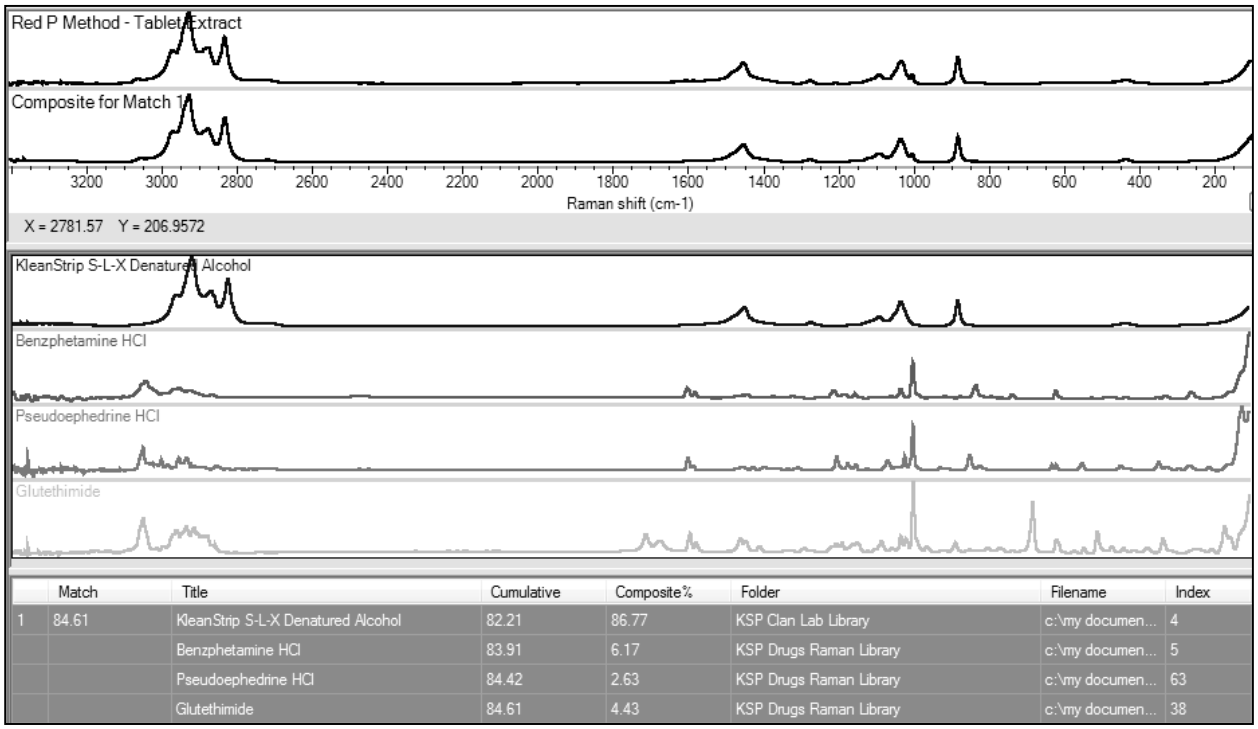
Figure 1 – Multicomponent search – Red P/Iodine method – Tablet Extract (with EtOH)



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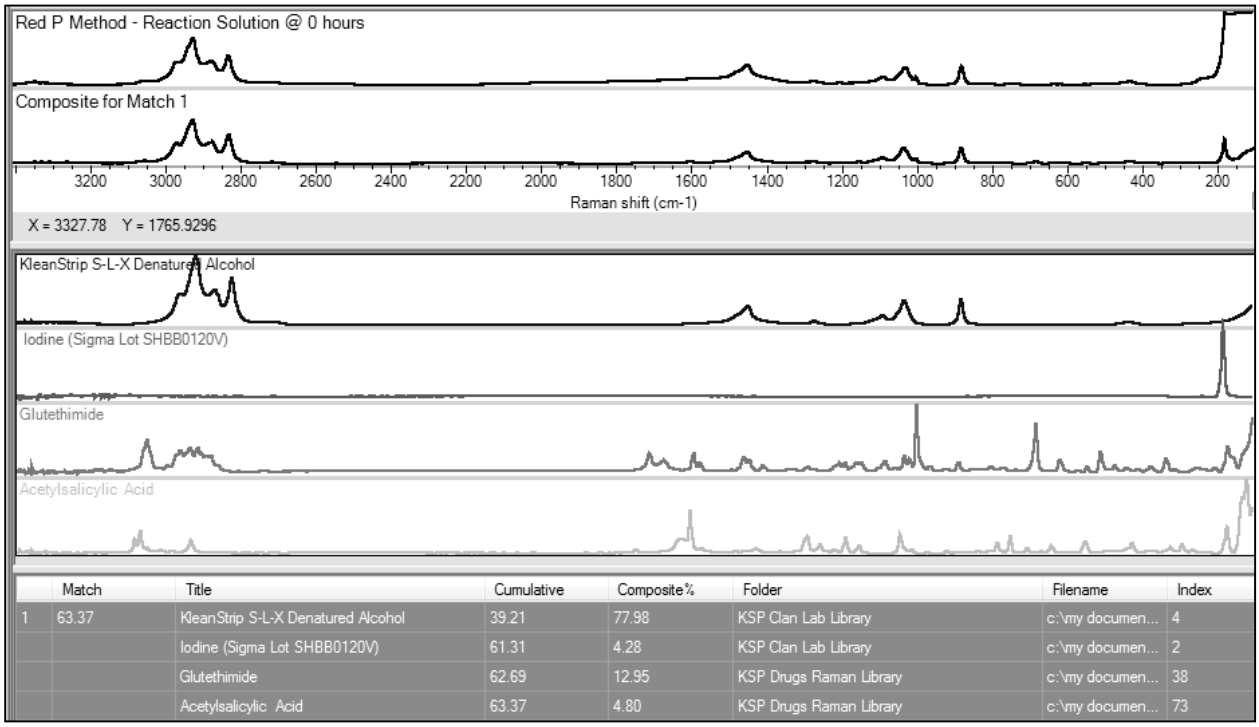
1	84.61	KleanStrip S-L-X Denatured Alcohol	82.21	86.77	KSP Clan Lab Library	c:\my documen...	4
		Benzphetamine HCl	83.91	6.17	KSP Drugs Raman Library	c:\my documen...	5
		Pseudoephedrine HCl	84.42	2.63	KSP Drugs Raman Library	c:\my documen...	63
		Glutethimide	84.61	4.43	KSP Drugs Raman Library	c:\my documen...	38

Figure 2 – Multicomponent search – Red P/Iodine method – Reaction solution @ 0 hours(initial)



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1	63.37	KleanStrip S-L-X Denatured Alcohol	39.21	77.98	KSP Clan Lab Library	c:\my documen...	4
		Iodine (Sigma Lot SHBB0120V)	61.31	4.28	KSP Clan Lab Library	c:\my documen...	2
		Glutethimide	62.69	12.95	KSP Drugs Raman Library	c:\my documen...	38
		Acetylsalicylic Acid	63.37	4.80	KSP Drugs Raman Library	c:\my documen...	73

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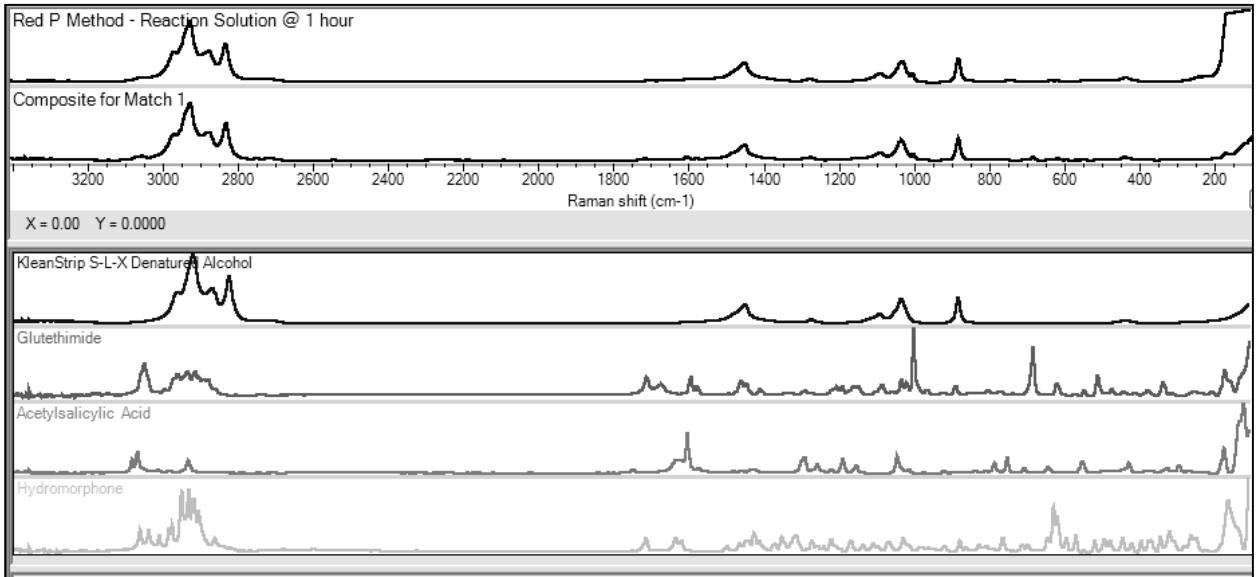
Figure 3 - Multicomponent search – Red P/Iodine method – Reaction solution @ 1 hour



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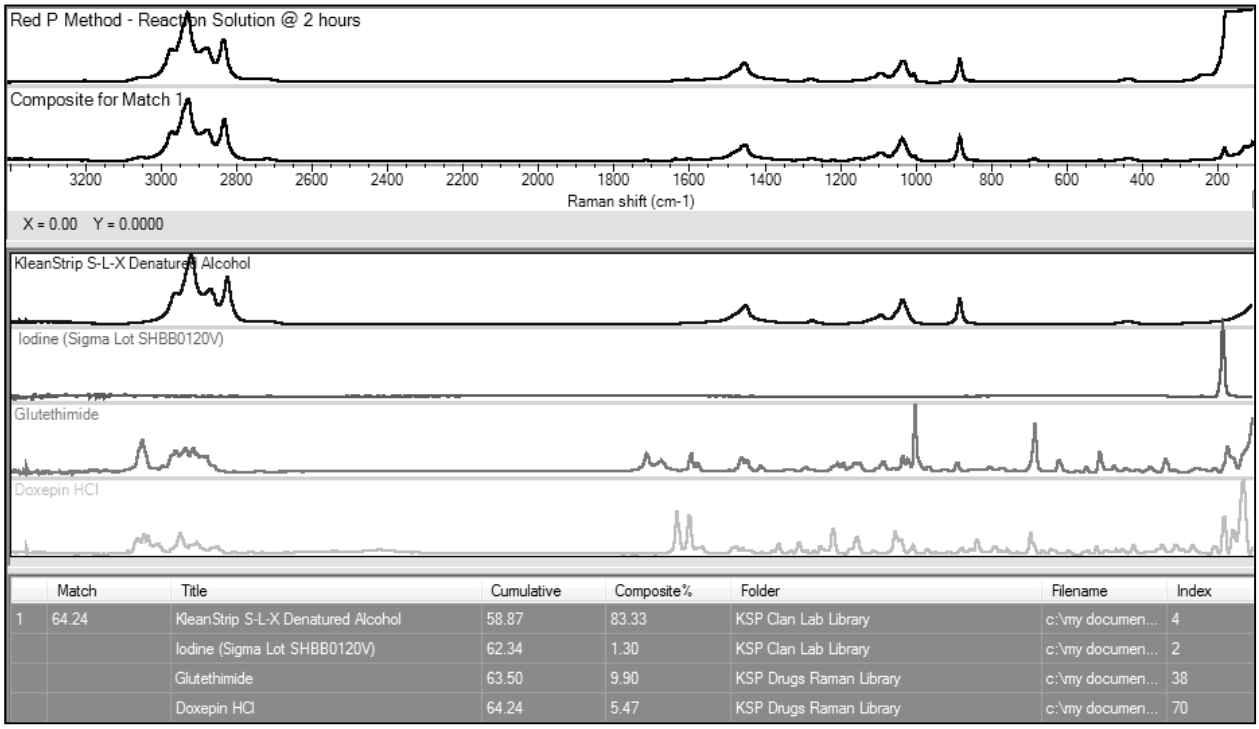
1	62.73	KleanStrip S-L-X Denatured Alcohol	58.80	74.75	KSP Clan Lab Library	c:\my documen...	4
		Glutethimide	61.43	13.75	KSP Drugs Raman Library	c:\my documen...	38
		Acetylsalicylic Acid	62.15	4.24	KSP Drugs Raman Library	c:\my documen...	73
		Hydromorphone	62.73	7.27	KSP Drugs Raman Library	c:\my documen...	18

Figure 4 – Multicomponent search – Red P/Iodine method – Reaction solution @ 2 hours



	Match	Title	Cumulative	Composite%	Folder	Filename	Index
1	64.24	KleanStrip S-L-X Denatured Alcohol	58.87	83.33	KSP Clan Lab Library	c:\my documen...	4
		Iodine (Sigma Lot SHBB0120V)	62.34	1.30	KSP Clan Lab Library	c:\my documen...	2
		Glutethimide	63.50	9.90	KSP Drugs Raman Library	c:\my documen...	38
		Doxepin HCl	64.24	5.47	KSP Drugs Raman Library	c:\my documen...	70

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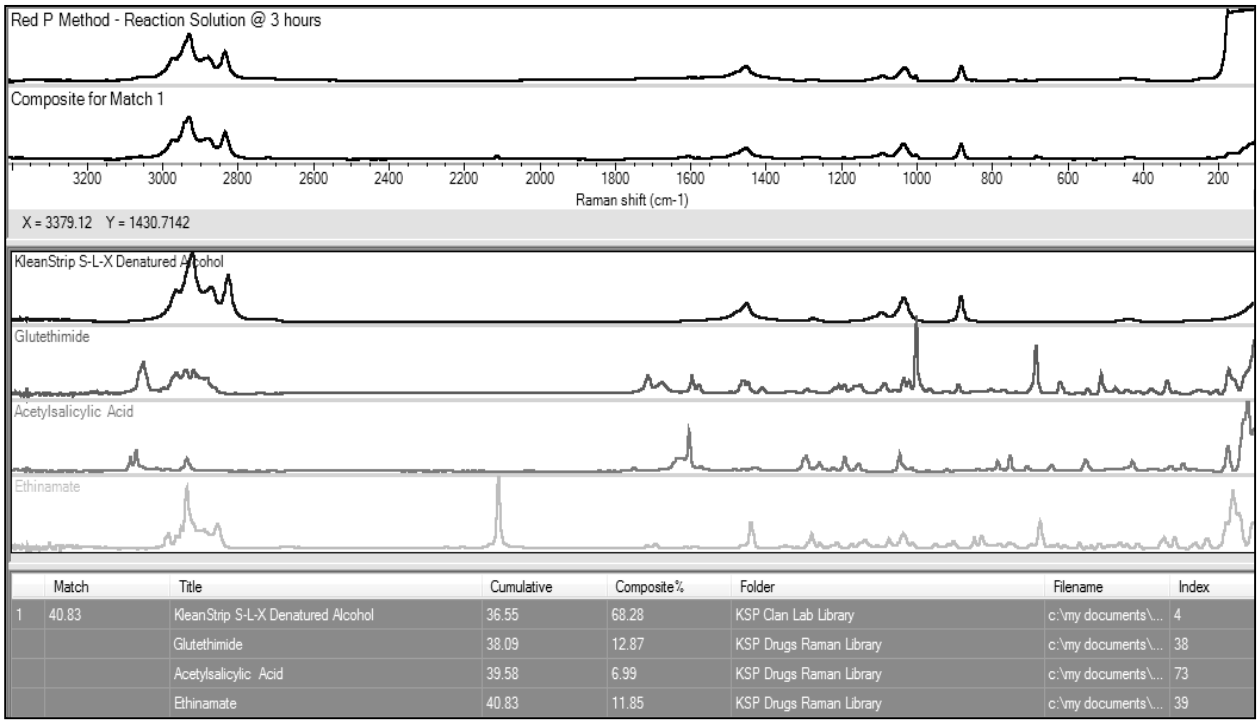
Figure 5 – Multicomponent search – Red P/Iodine method – Reaction solution @ 3 hours



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1	40.83	KleanStrip S-L-X Denatured Alcohol	36.55	68.28	KSP Clan Lab Library	c:\my documents\...	4
		Glutethimide	38.09	12.87	KSP Drugs Raman Library	c:\my documents\...	38
		Acetylsalicylic Acid	39.58	6.99	KSP Drugs Raman Library	c:\my documents\...	73
		Ethinamate	40.83	11.85	KSP Drugs Raman Library	c:\my documents\...	39

Figure 6 – Multicomponent search – Red P/Iodine method –Final solution aqueous layer*

* Author's Note: While the reaction layers analyzed in a few instances are referred to as the "aqueous layer", it should be noted that water has no Raman bands in the studied frequencies. Spectral bands from the "aqueous layer" samples are the result of dissolved organic solids or solvents.

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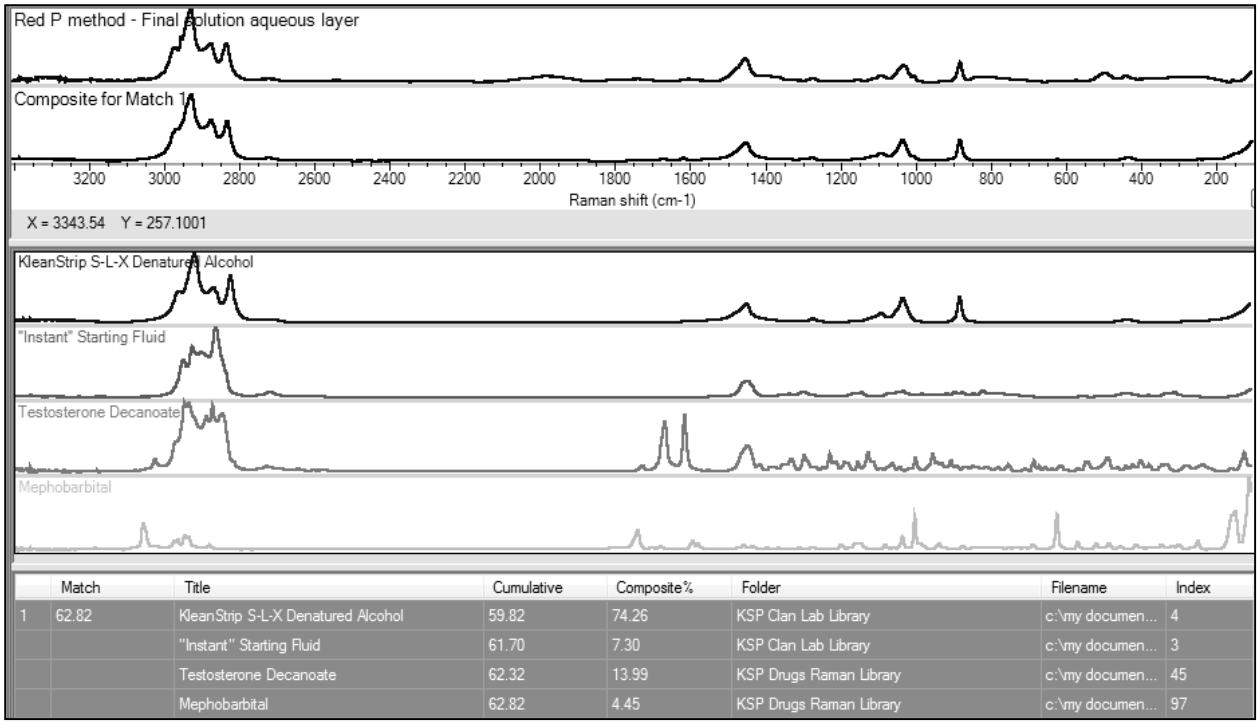

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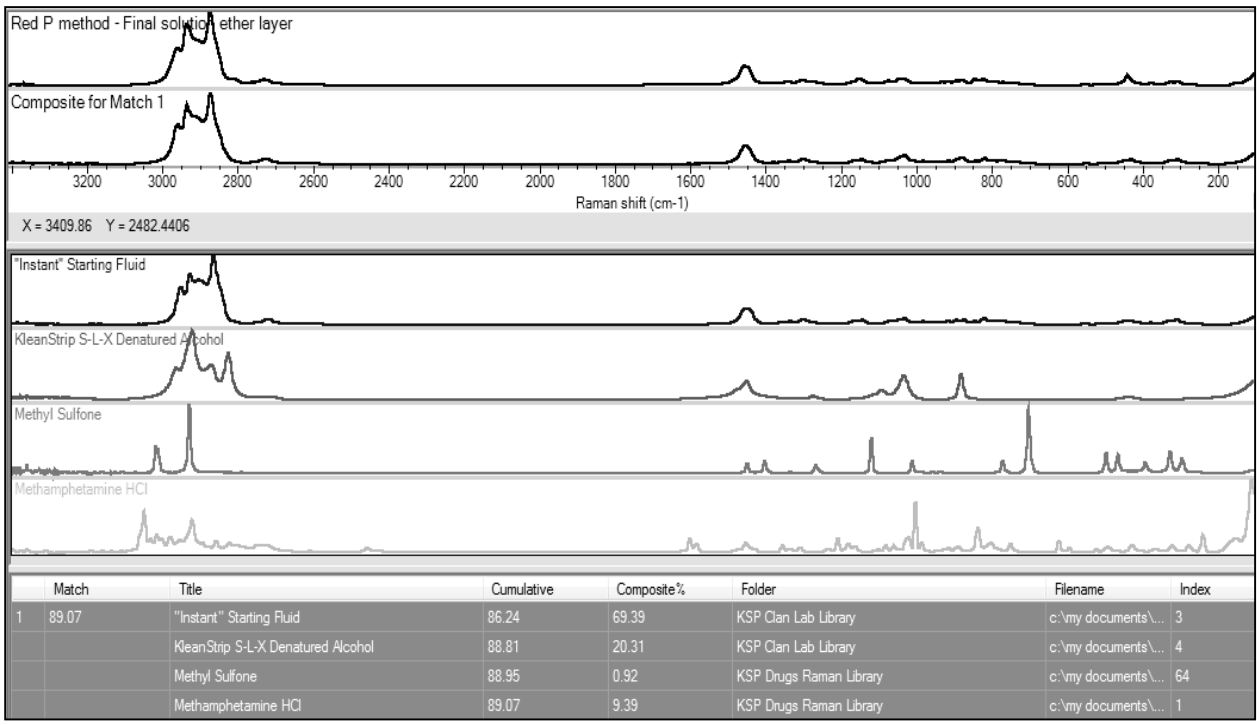
1	62.82	KleanStrip S-L-X Denatured Alcohol	59.82	74.26	KSP Clan Lab Library	c:\my documen...	4
		"Instant" Starting Fluid	61.70	7.30	KSP Clan Lab Library	c:\my documen...	3
		Testosterone Decanoate	62.32	13.99	KSP Drugs Raman Library	c:\my documen...	45
		Mephobarbital	62.82	4.45	KSP Drugs Raman Library	c:\my documen...	97

Figure 7 – Multicomponent search – Red P/Iodine method – Final solution ether layer



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1	89.07	"Instant" Starting Fluid	86.24	69.39	KSP Clan Lab Library	c:\my documents\...	3
		KleanStrip S-L-X Denatured Alcohol	88.81	20.31	KSP Clan Lab Library	c:\my documents\...	4
		Methyl Sulfone	88.95	0.92	KSP Drugs Raman Library	c:\my documents\...	64
		Methamphetamine HCl	89.07	9.39	KSP Drugs Raman Library	c:\my documents\...	1

Figure 8 – Multicomponent search – Red P/Iodine method – Final product

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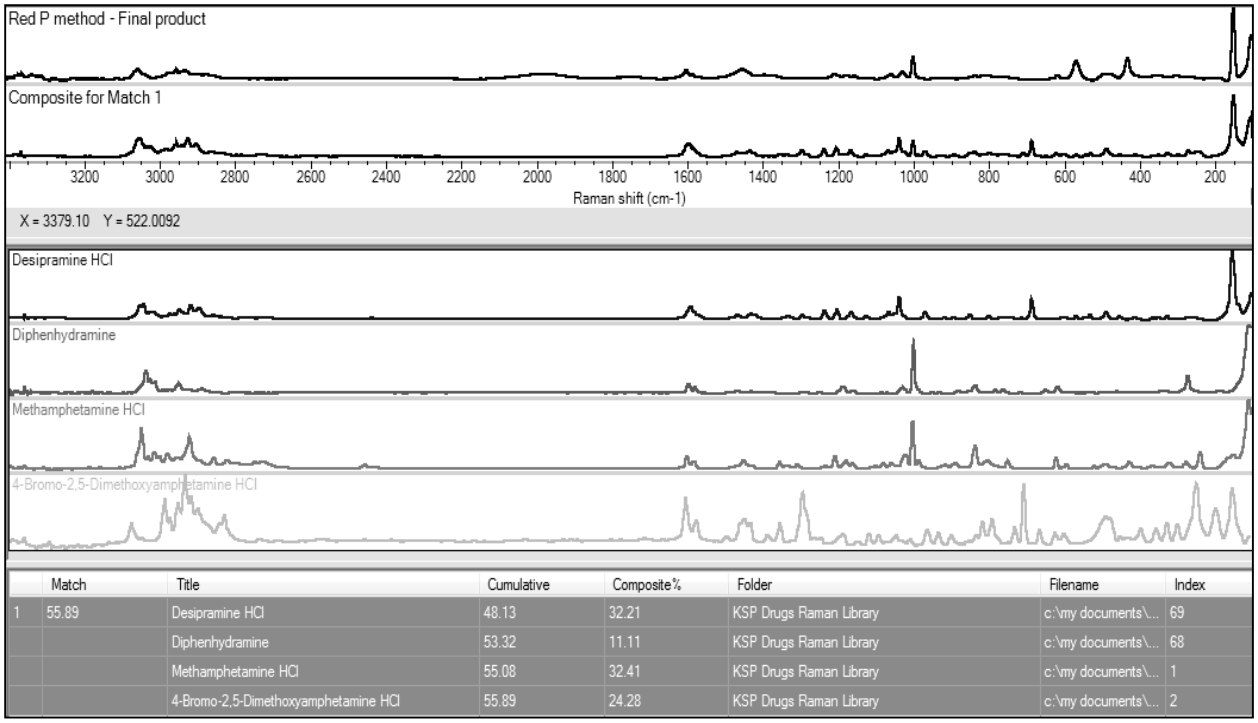
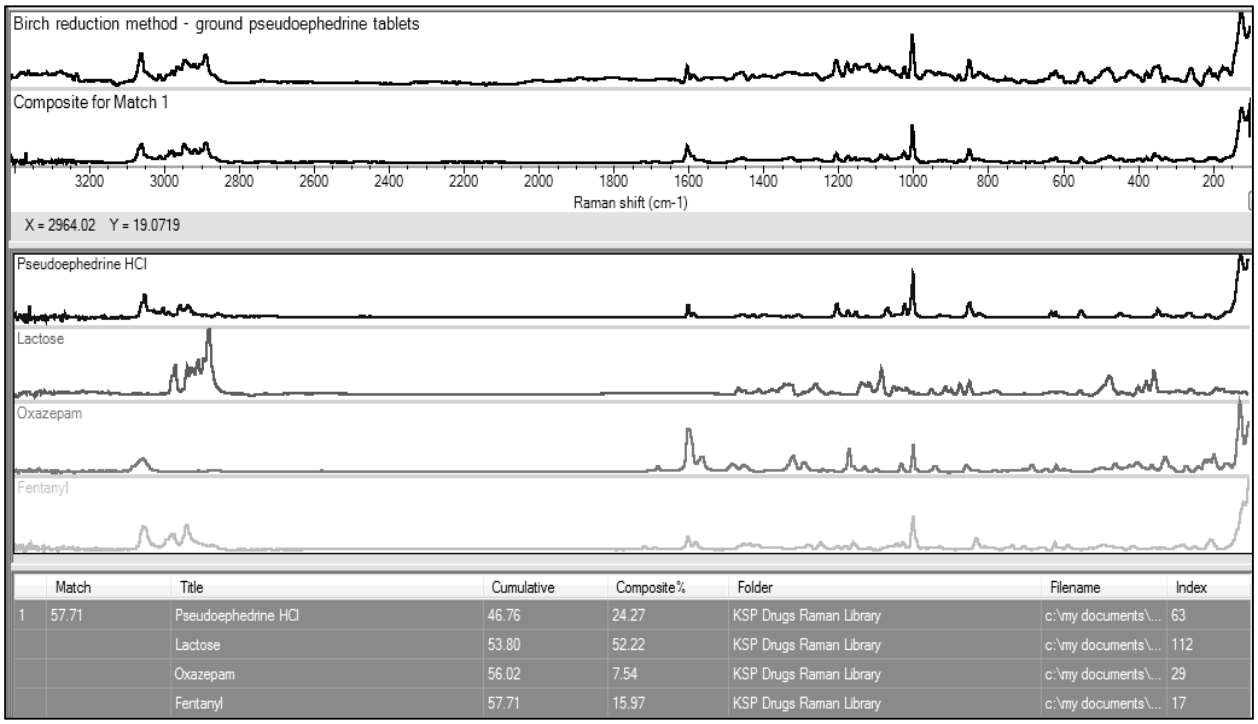


	Match	Title	Cumulative	Composite%	Folder	Filename	Index
1	55.89	Desipramine HCl	48.13	32.21	KSP Drugs Raman Library	c:\my documents\...	69
		Diphenhydramine	53.32	11.11	KSP Drugs Raman Library	c:\my documents\...	68
		Methamphetamine HCl	55.08	32.41	KSP Drugs Raman Library	c:\my documents\...	1
		4-Bromo-2,5-Dimethoxyamphetamine HCl	55.89	24.28	KSP Drugs Raman Library	c:\my documents\...	2

Figure 9 – Multicomponent search – Birch reduction method – Ground pseudoephedrine tablets



	Match	Title	Cumulative	Composite%	Folder	Filename	Index
1	57.71	Pseudoephedrine HCl	46.76	24.27	KSP Drugs Raman Library	c:\my documents\...	63
		Lactose	53.80	52.22	KSP Drugs Raman Library	c:\my documents\...	112
		Oxazepam	56.02	7.54	KSP Drugs Raman Library	c:\my documents\...	29
		Fentanyl	57.71	15.97	KSP Drugs Raman Library	c:\my documents\...	17

Figure 10 – Multicomponent search – Birch reduction method – Reaction solution @ 0 minutes

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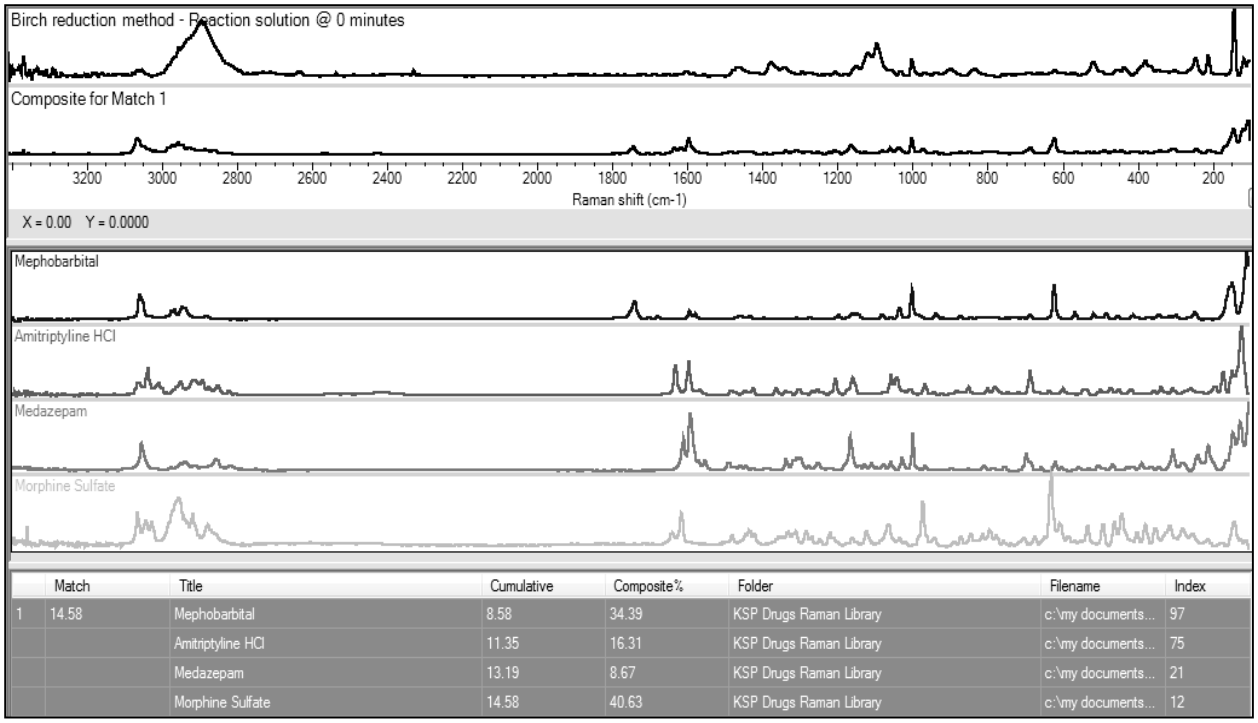
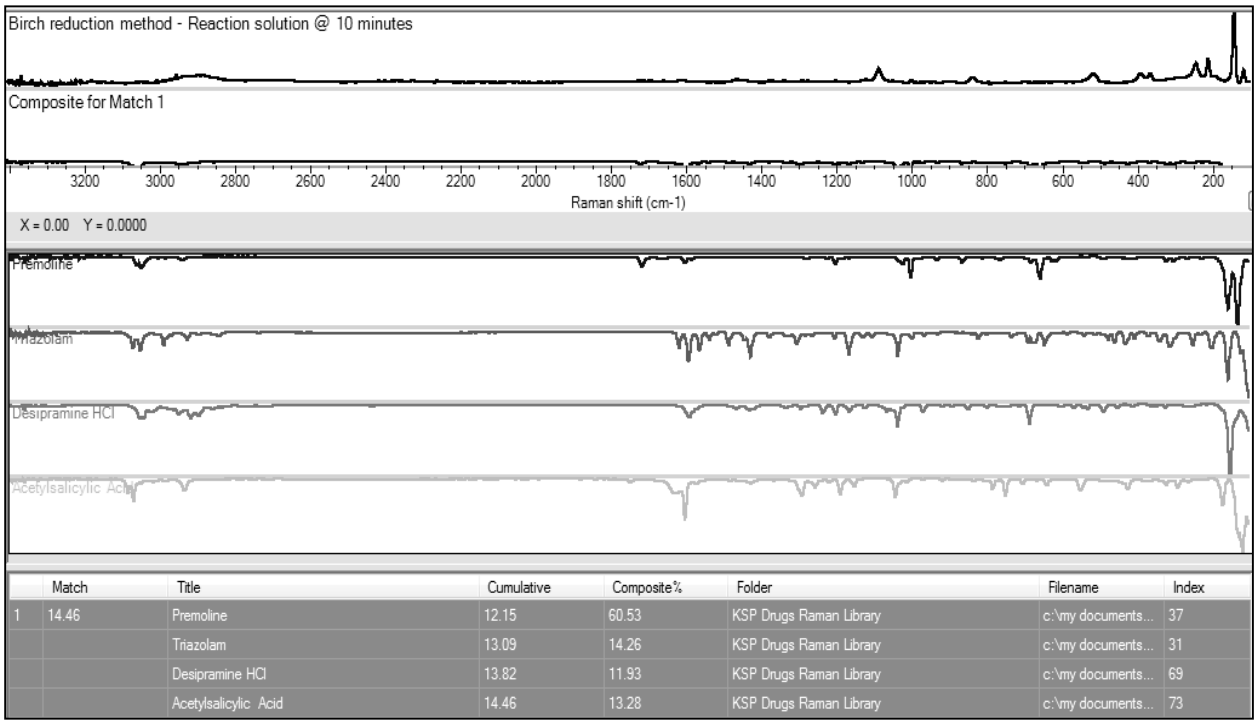


	Match	Title	Cumulative	Composite%	Folder	Filename	Index
1	14.58	Mephobarbital	8.58	34.39	KSP Drugs Raman Library	c:\my documents...	97
		Amitriptyline HCl	11.35	16.31	KSP Drugs Raman Library	c:\my documents...	75
		Medazepam	13.19	8.67	KSP Drugs Raman Library	c:\my documents...	21
		Morphine Sulfate	14.58	40.63	KSP Drugs Raman Library	c:\my documents...	12

Figure 11 – Multicomponent search – Birch reduction method – Reaction solution @ 10 minutes



	Match	Title	Cumulative	Composite%	Folder	Filename	Index
1	14.46	Premoline	12.15	60.53	KSP Drugs Raman Library	c:\my documents...	37
		Triazolam	13.09	14.26	KSP Drugs Raman Library	c:\my documents...	31
		Desipramine HCl	13.82	11.93	KSP Drugs Raman Library	c:\my documents...	69
		Acetylsalicylic Acid	14.46	13.28	KSP Drugs Raman Library	c:\my documents...	73

Figure 12 – Multicomponent search – Birch reduction method – Reaction solution @ 20 minutes

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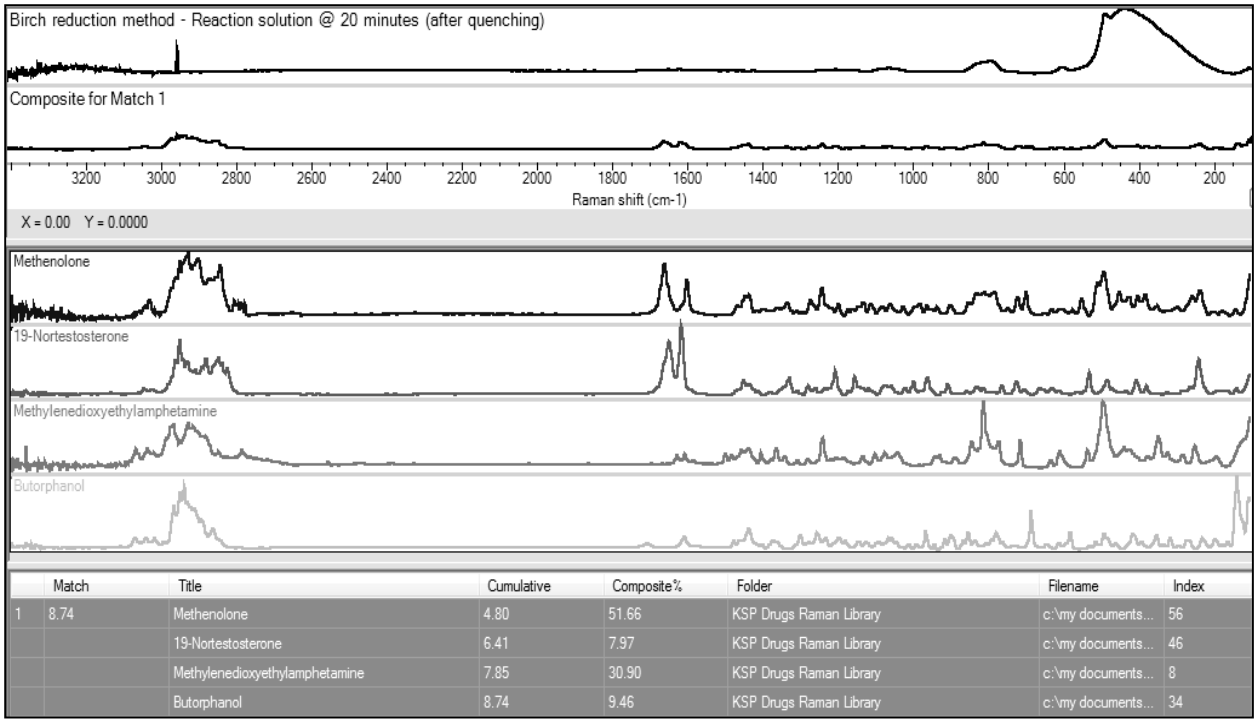
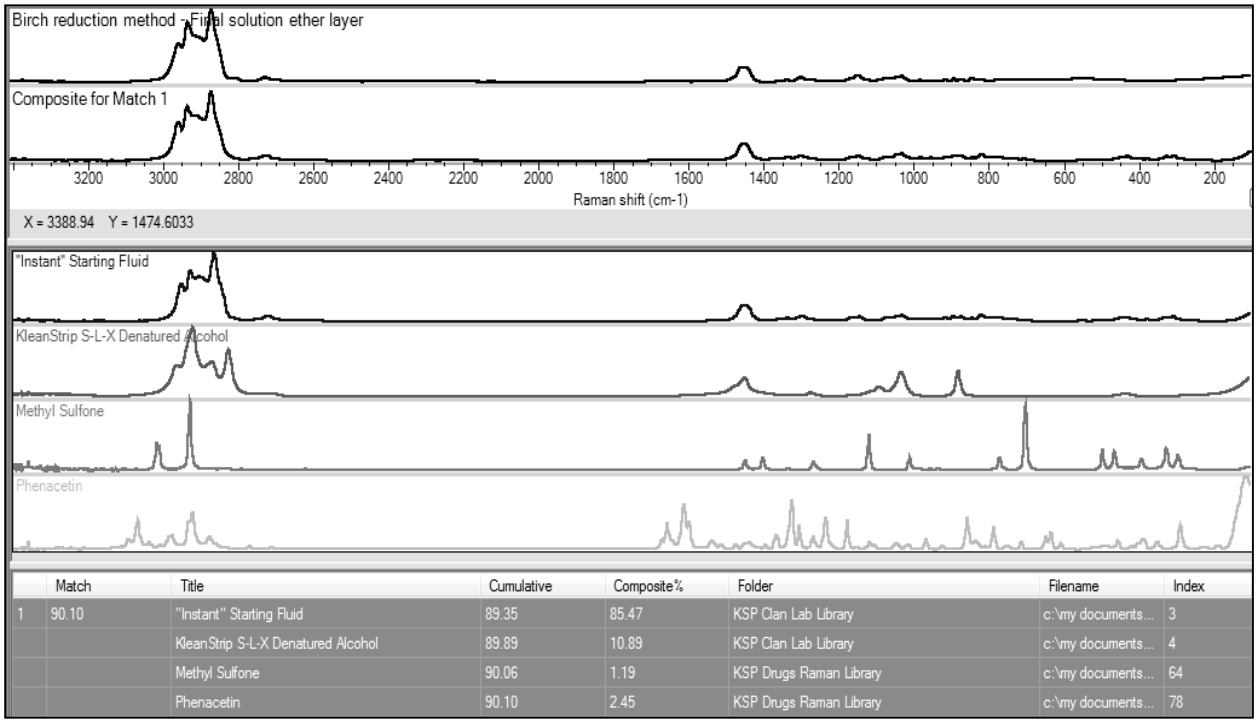


	Match	Title	Cumulative	Composite%	Folder	Filename	Index
1	8.74	Methenolone	4.80	51.66	KSP Drugs Raman Library	c:\my documents...	56
		19-Nortestosterone	6.41	7.97	KSP Drugs Raman Library	c:\my documents...	46
		Methylenedioxyethylamphetamine	7.85	30.90	KSP Drugs Raman Library	c:\my documents...	8
		Butorphanol	8.74	9.46	KSP Drugs Raman Library	c:\my documents...	34

Figure 13 – Multicomponent search – Birch reduction method – Final solution ether layer



	Match	Title	Cumulative	Composite%	Folder	Filename	Index
1	90.10	"Instant" Starting Fluid	89.35	85.47	KSP Clan Lab Library	c:\my documents...	3
		KleanStrip S-L-X Denatured Alcohol	89.89	10.89	KSP Clan Lab Library	c:\my documents...	4
		Methyl Sulfone	90.06	1.19	KSP Drugs Raman Library	c:\my documents...	64
		Phenacetin	90.10	2.45	KSP Drugs Raman Library	c:\my documents...	78

Figure 14 – Multicomponent Search – Case Sample #1

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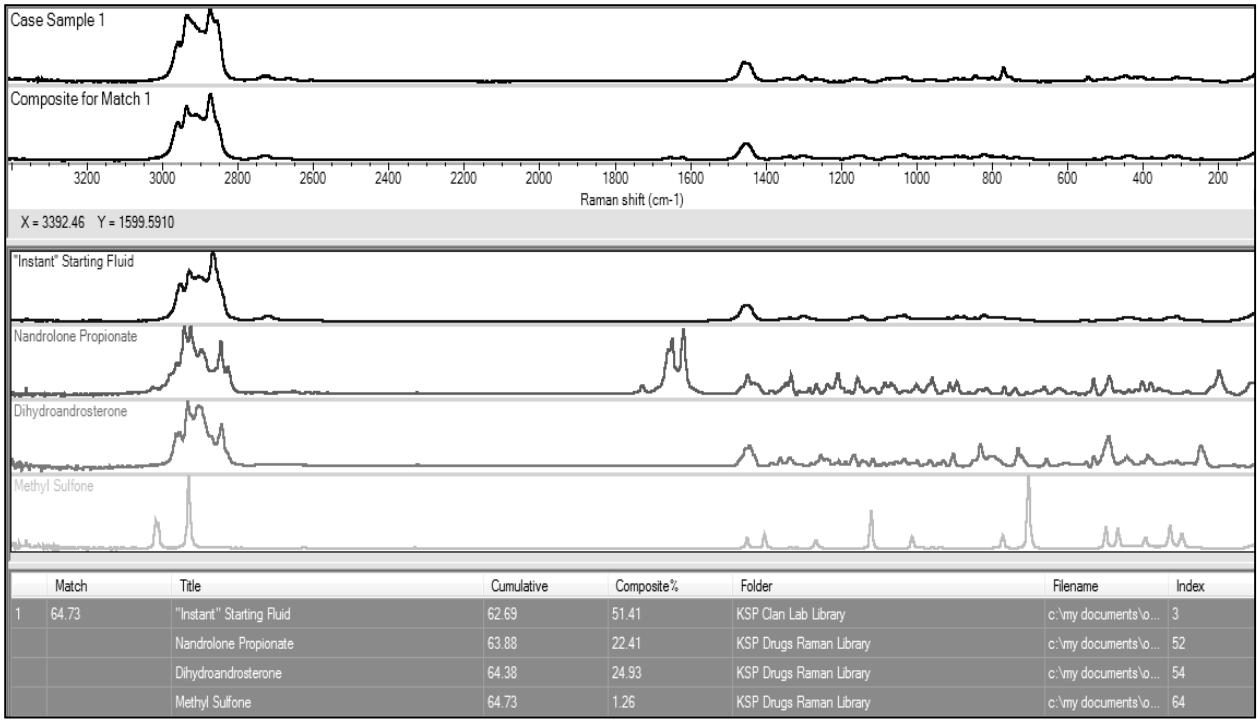
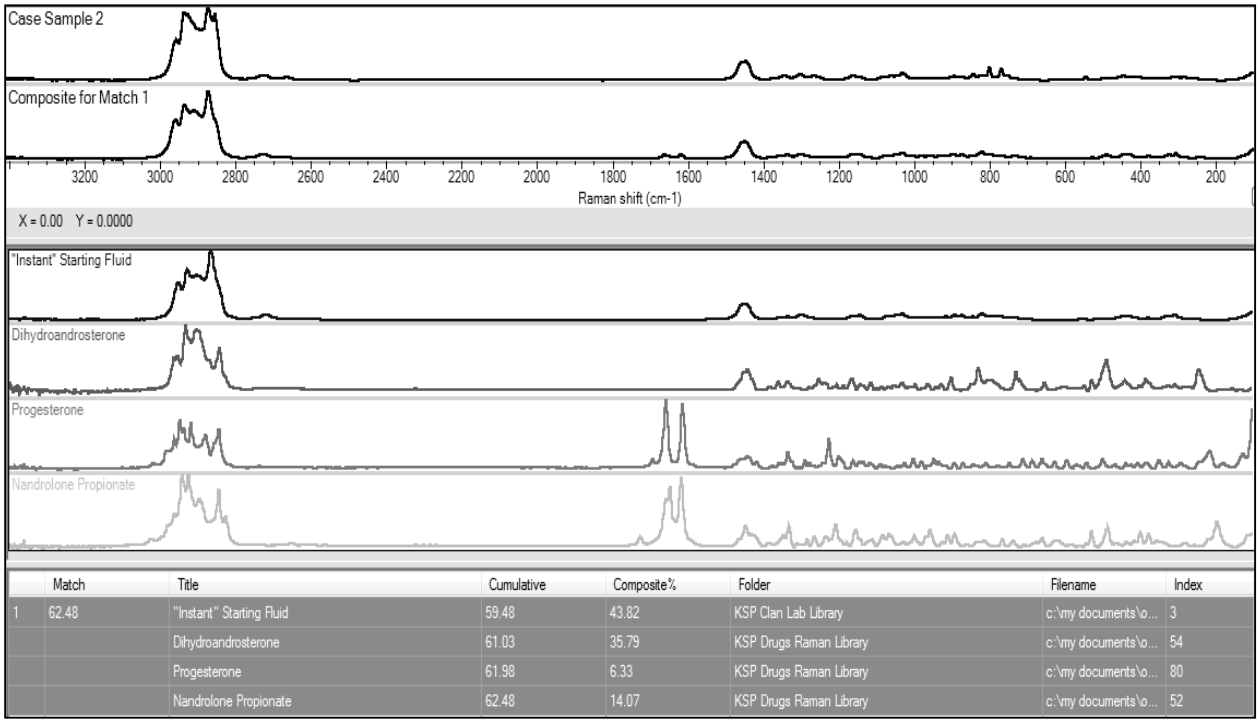


	Match	Title	Cumulative	Composite%	Folder	Filename	Index
1	64.73	"Instant" Starting Fluid	62.69	51.41	KSP Clan Lab Library	c:\my documents\o...	3
		Nandrolone Propionate	63.88	22.41	KSP Drugs Raman Library	c:\my documents\o...	52
		Dihydroandrosterone	64.38	24.93	KSP Drugs Raman Library	c:\my documents\o...	54
		Methyl Sulfone	64.73	1.26	KSP Drugs Raman Library	c:\my documents\o...	64

Figure 15 –Multicomponent Search – Case Sample #2



	Match	Title	Cumulative	Composite%	Folder	Filename	Index
1	62.48	"Instant" Starting Fluid	59.48	43.82	KSP Clan Lab Library	c:\my documents\o...	3
		Dihydroandrosterone	61.03	35.79	KSP Drugs Raman Library	c:\my documents\o...	54
		Progesterone	61.98	6.33	KSP Drugs Raman Library	c:\my documents\o...	80
		Nandrolone Propionate	62.48	14.07	KSP Drugs Raman Library	c:\my documents\o...	52

Figure 16 – 10% methamphetamine solution with 4 gold colloid SERS preparations

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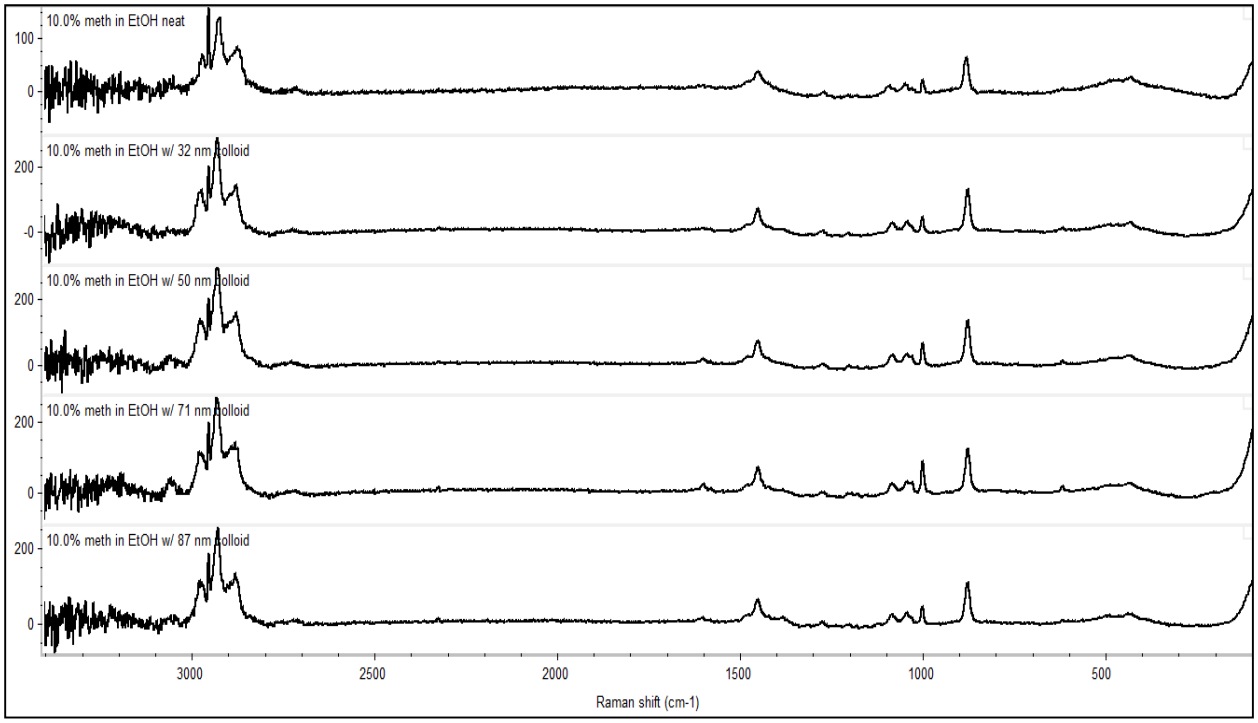

Figure 17 – Multicomponent Search – 10% methamphetamine solution neat

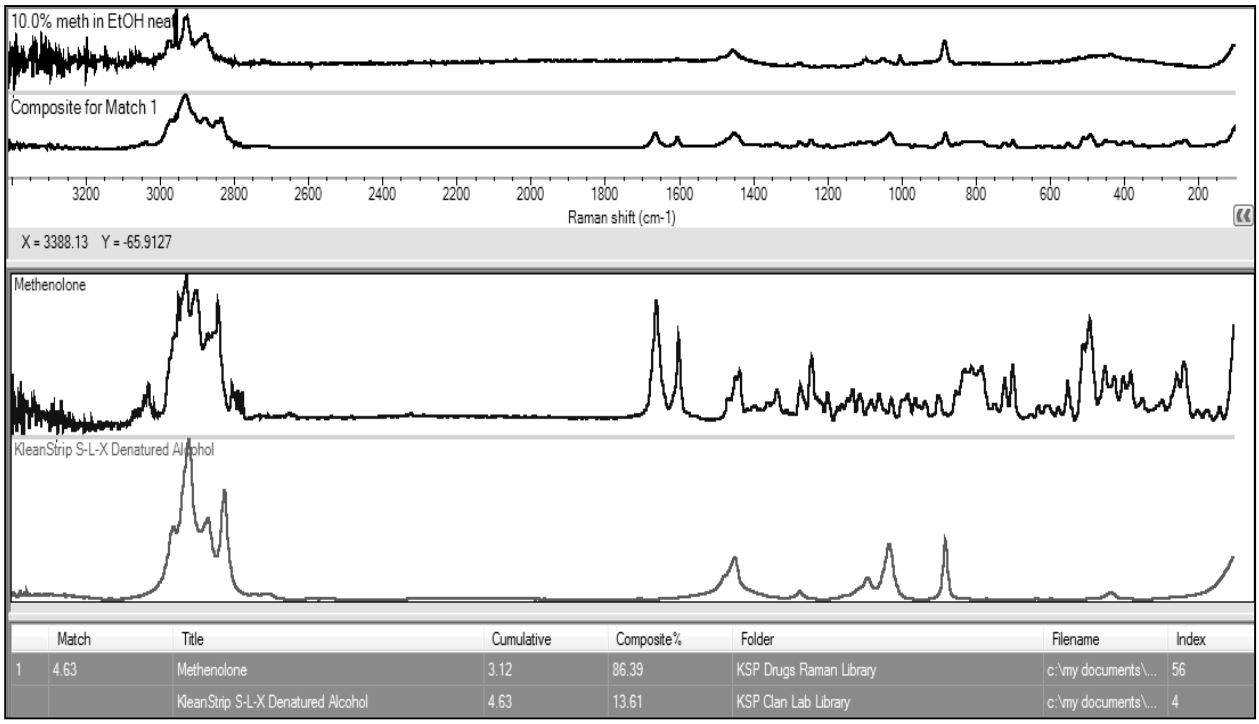

Figure 18 – Multicomponent Search – 10% methamphetamine solution with 87 nm gold colloid

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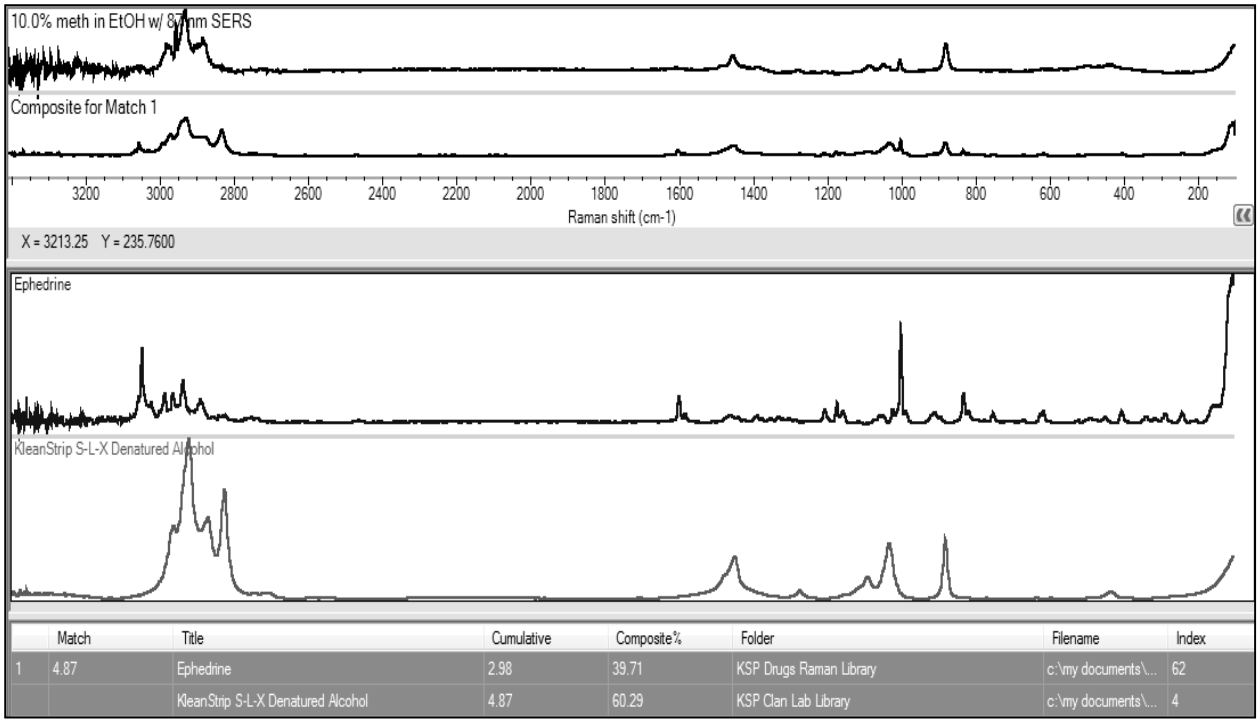

Figure 19 – Multicomponent Search – Forensic Case Sample neat

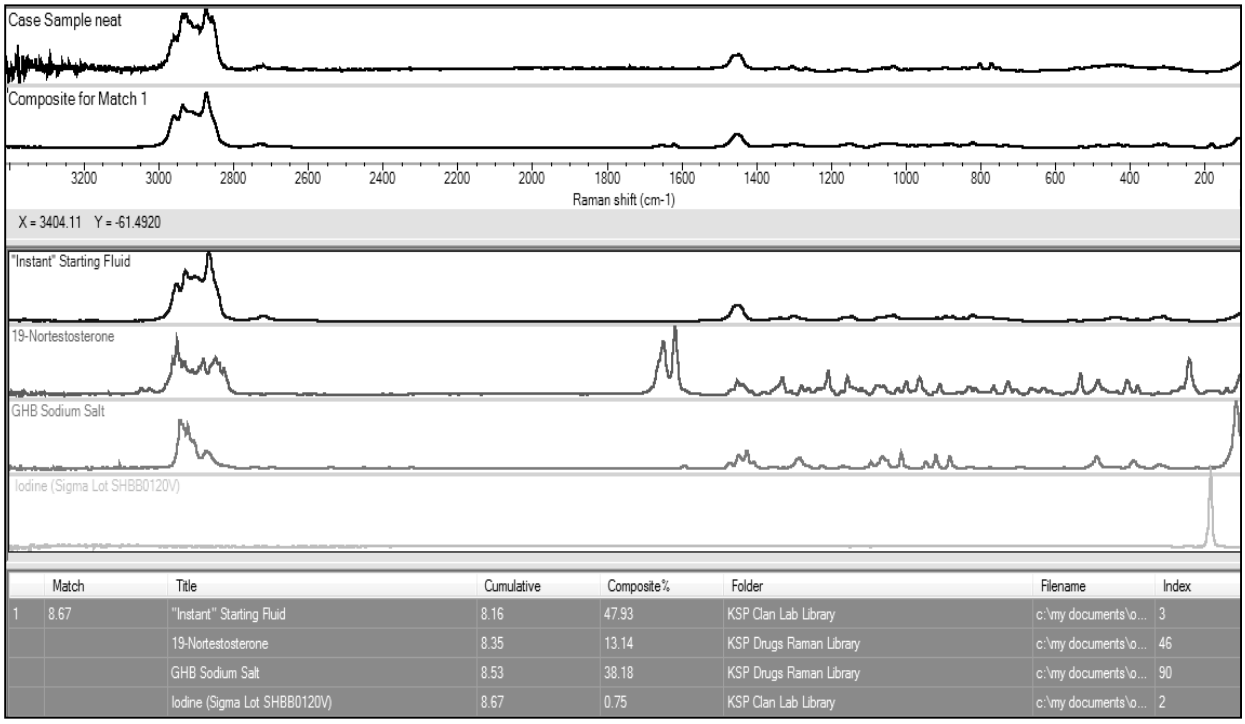

Figure 20 – Multicomponent Search – Forensic Case Sample with 87 nm gold colloid

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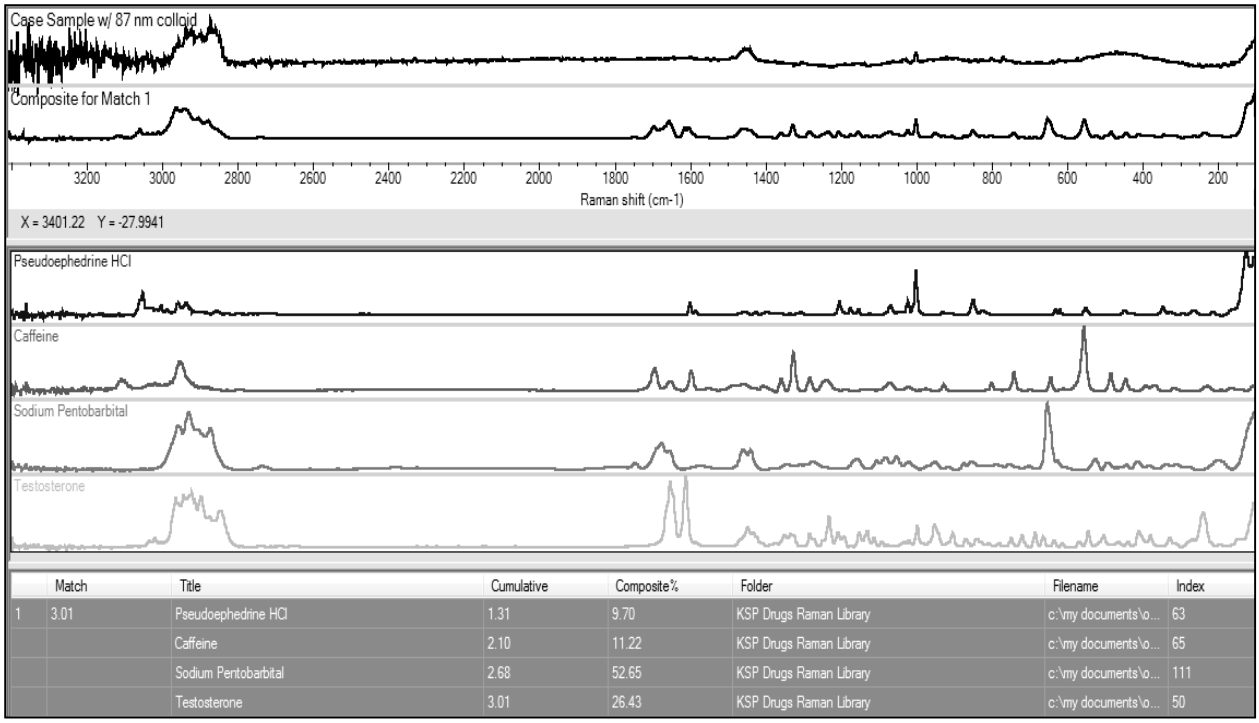

	Match	Title	Cumulative	Composite%	Folder	Filename	Index
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		Caffeine	2.10	11.22	KSP Drugs Raman Library	c:\my documents\o...	65
		Sodium Pentobarbital	2.68	52.65	KSP Drugs Raman Library	c:\my documents\o...	111
		Testosterone	3.01	26.43	KSP Drugs Raman Library	c:\my documents\o...	50

II. Rapid, non-destructive screening test for methamphetamine in clandestine lab samples[†18]

Figure 21 – Comparison of ethanol, diethyl ether, Coleman fuel, and methamphetamine raman spectra

[†] Author's Note: All spectra are from the cited published work. Copyright assigned to the American Academy of Forensic Science, Journal of Forensic Sciences, Blackwell Publishing per publishing requirement.

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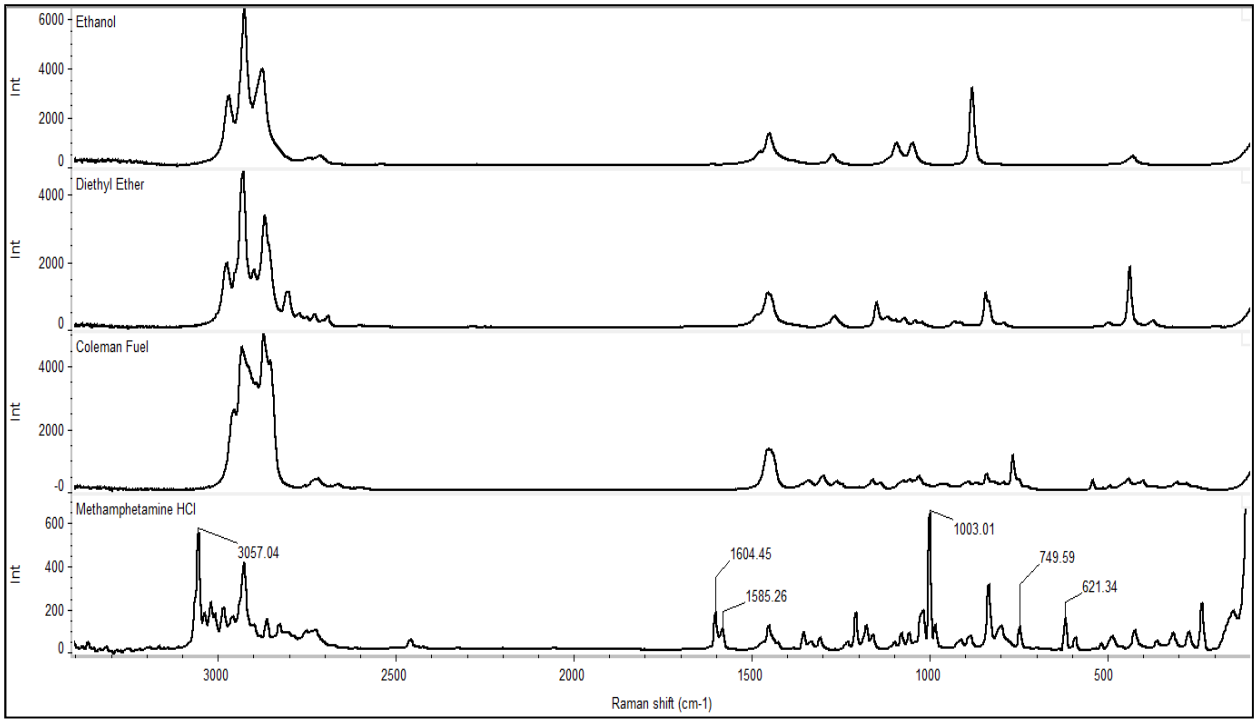

Figure 22 – Methamphetamine in ethanol solutions (full scale)

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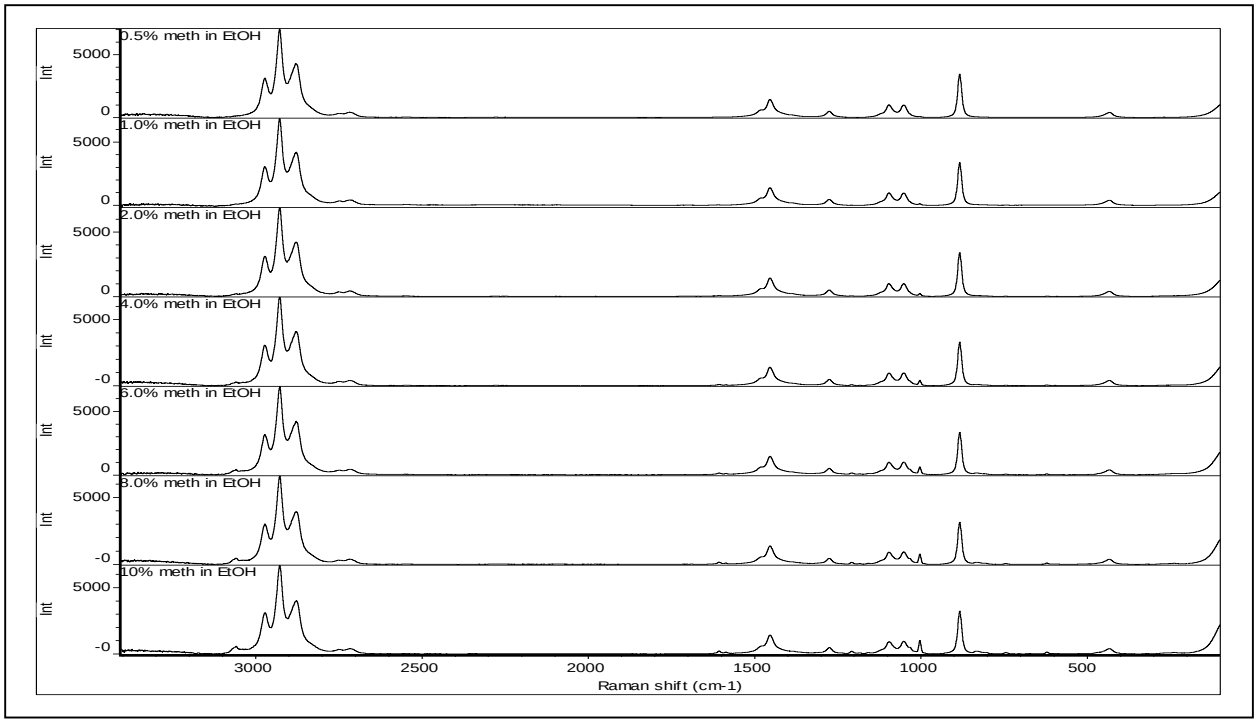

Figure 23 – Methamphetamine in diethyl ether solutions (full scale)

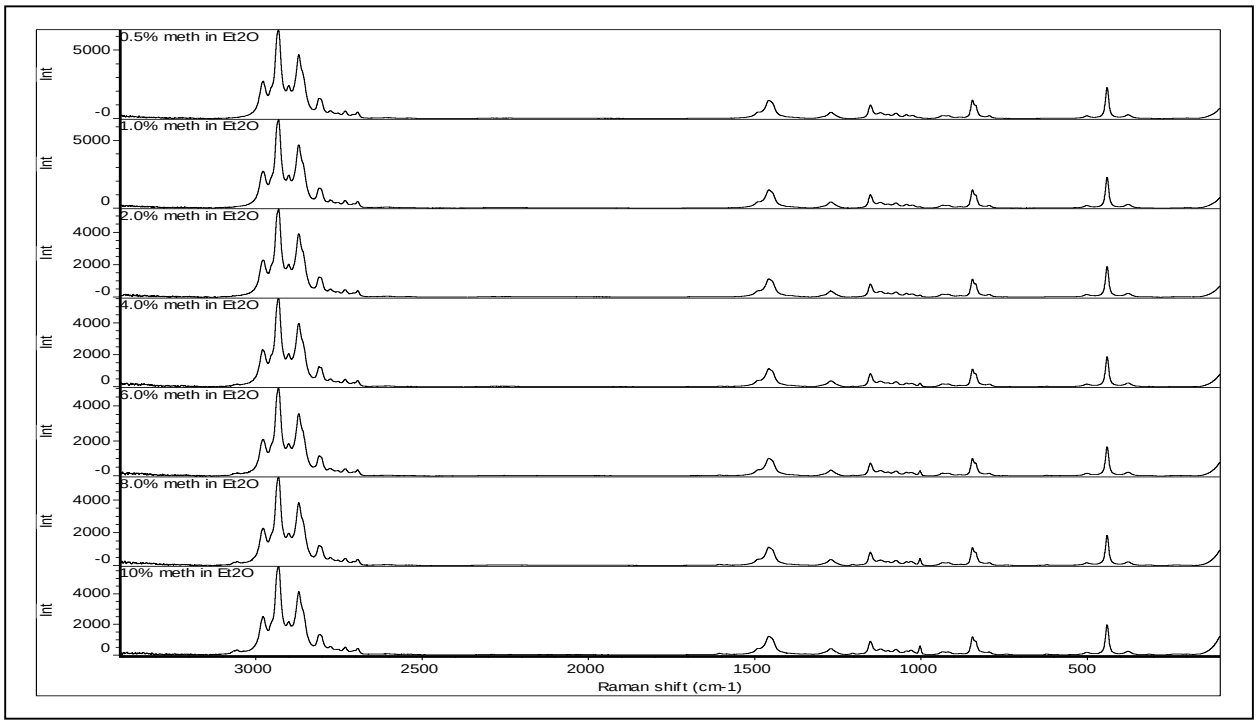

Figure 24 – Methamphetamine in Coleman fuel solutions (full scale)

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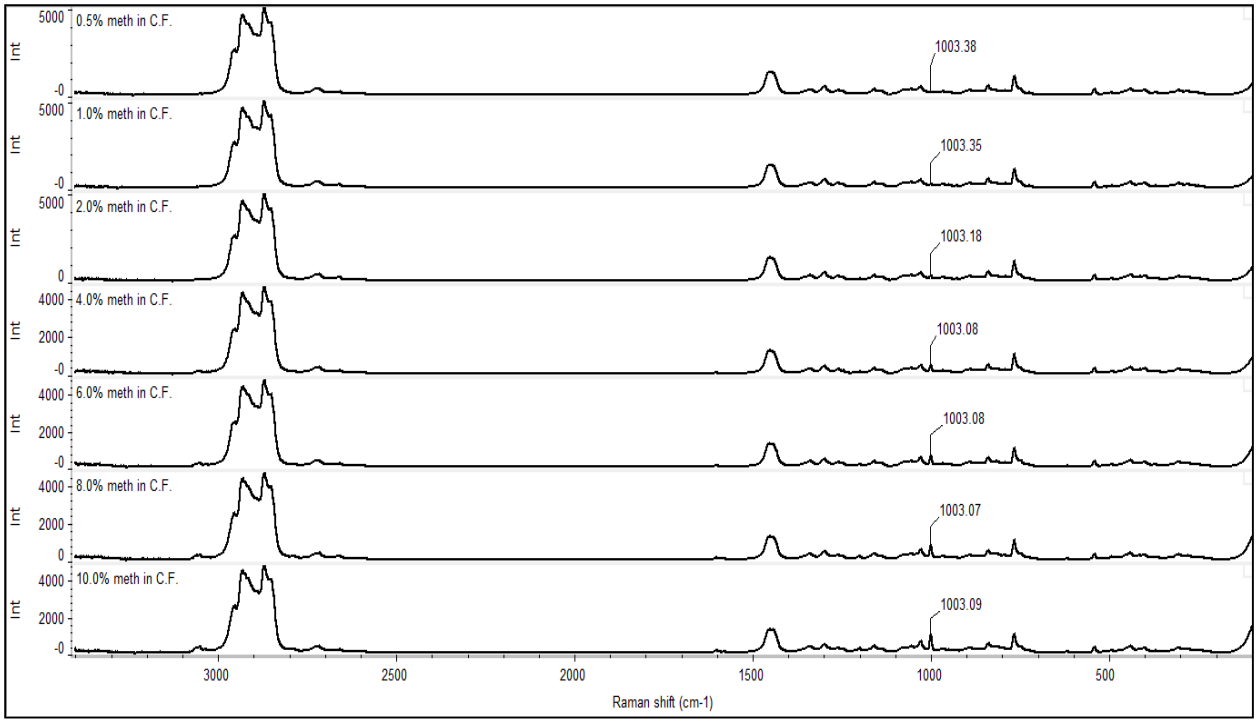

Figure 25 – Methamphetamine in ethanol solutions (400-1800 cm^{-1})

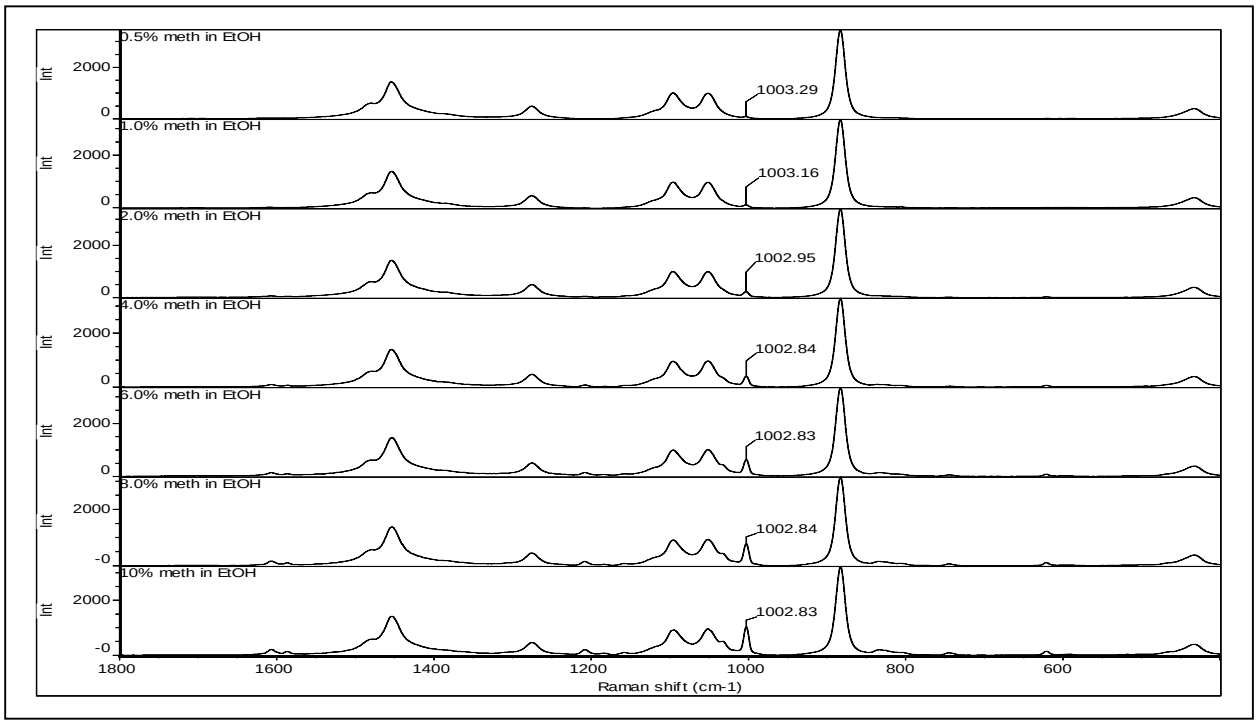

Figure 26 – Methamphetamine in diethyl ether solutions (400-1800 cm^{-1})

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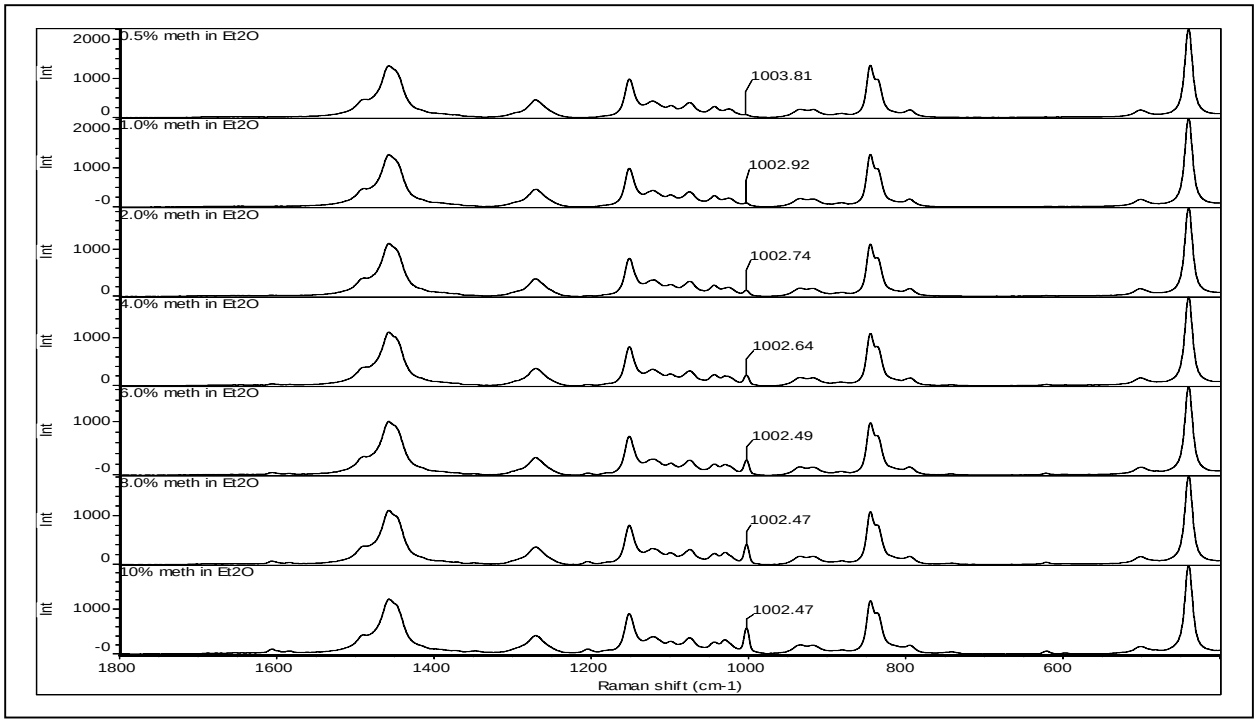

Figure 27 – Methamphetamine in Coleman fuel solutions (400-1800 cm^{-1})

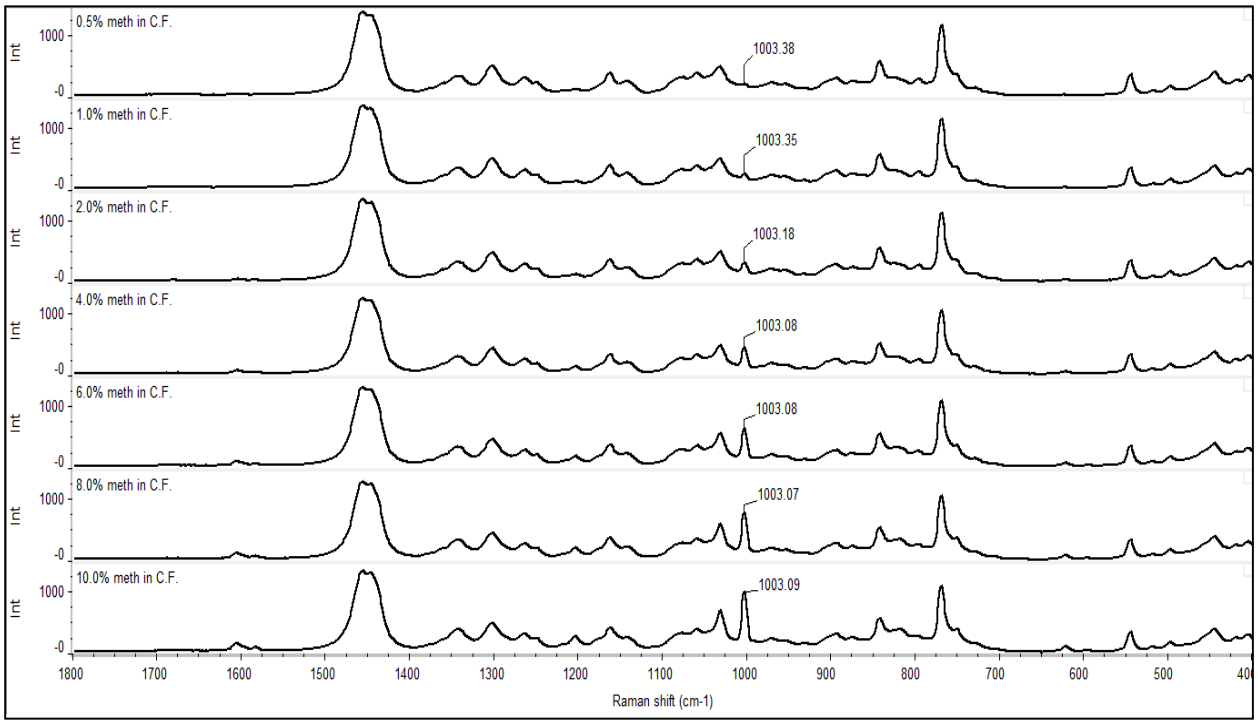

Figure 28 – Methamphetamine in ethanol solutions overlay (940-1080 cm^{-1})

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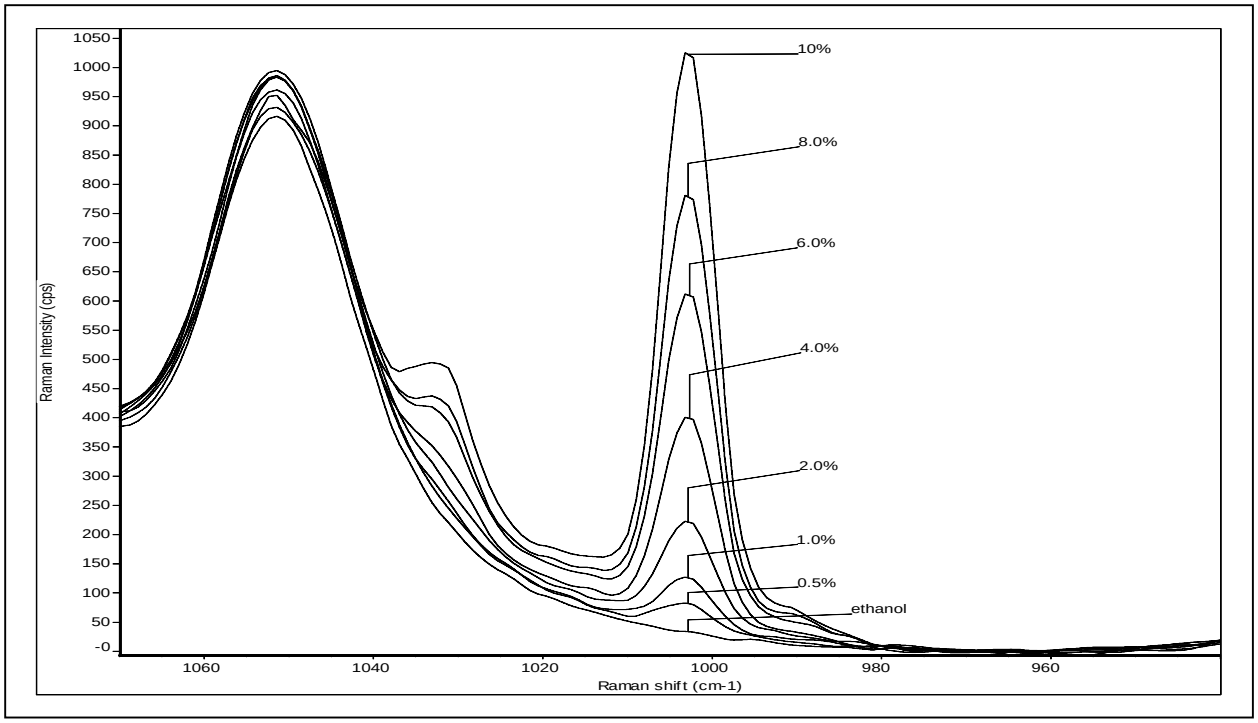

Figure 29 – Methamphetamine in diethyl ether solutions overlay (940-1080 cm^{-1})

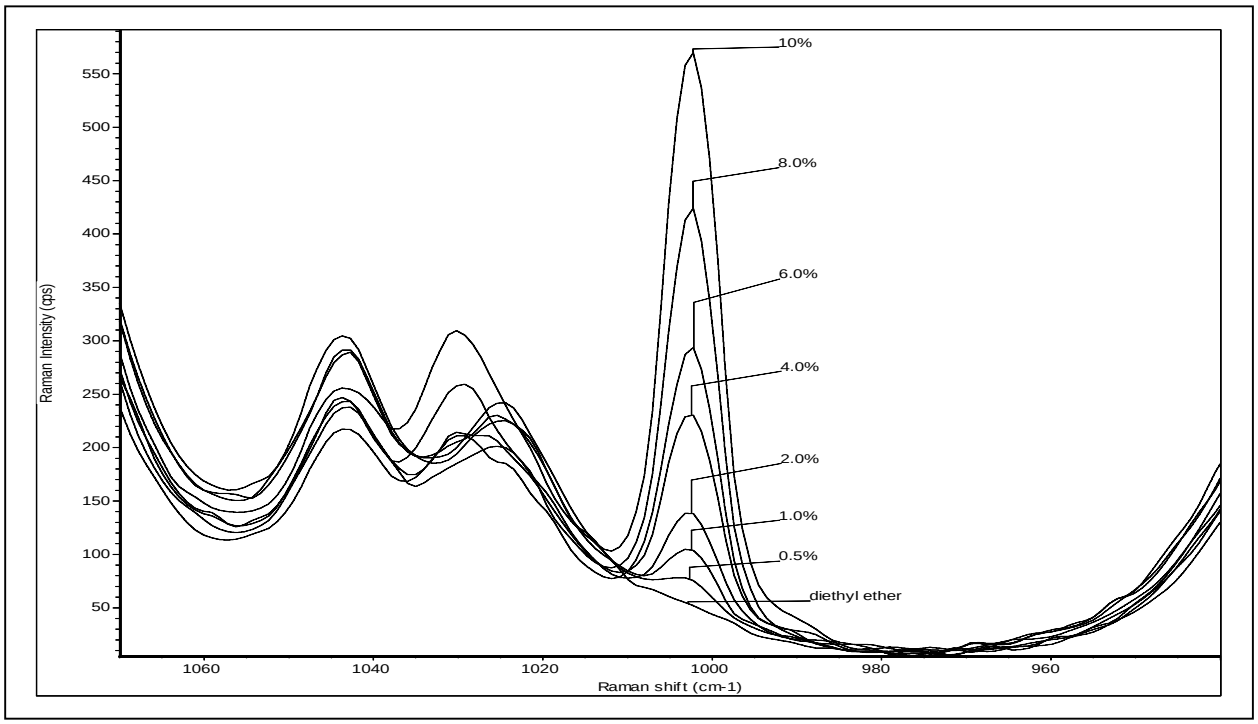

Figure 30 – Methamphetamine in Coleman fuel solutions overlay (940-1080 cm^{-1})

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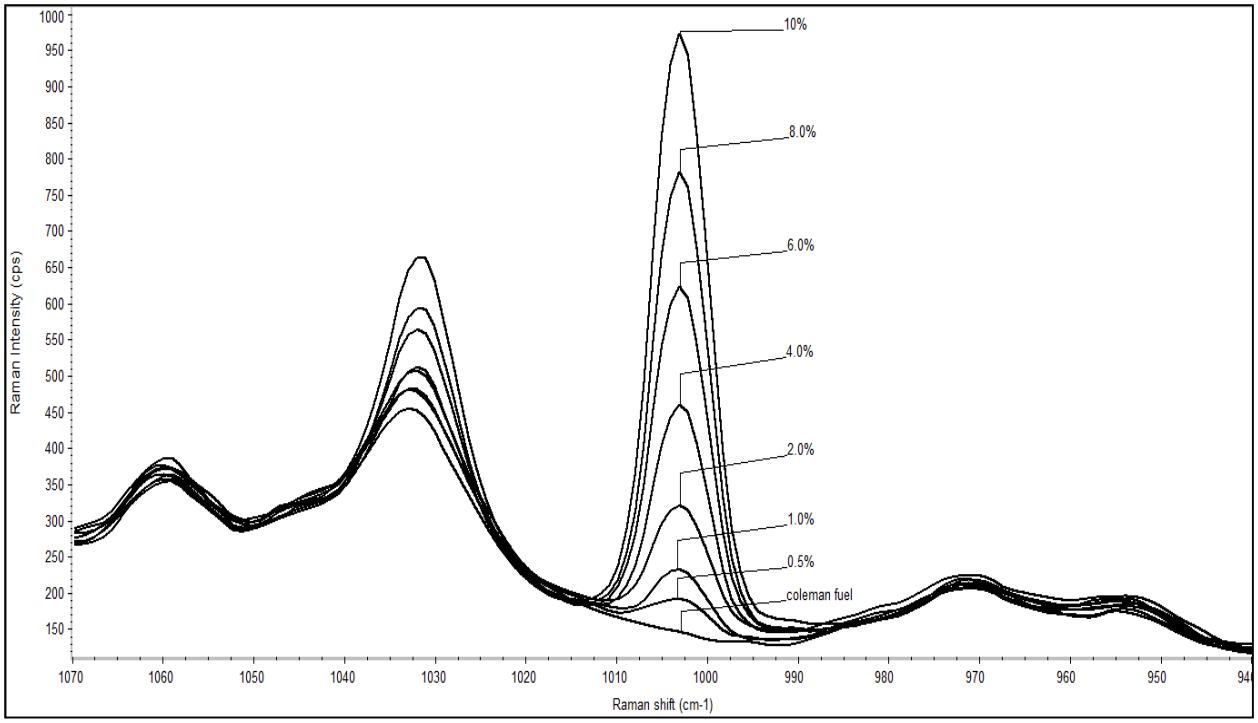

Figure 31 – Plot of diagnostic peak response versus solution concentration

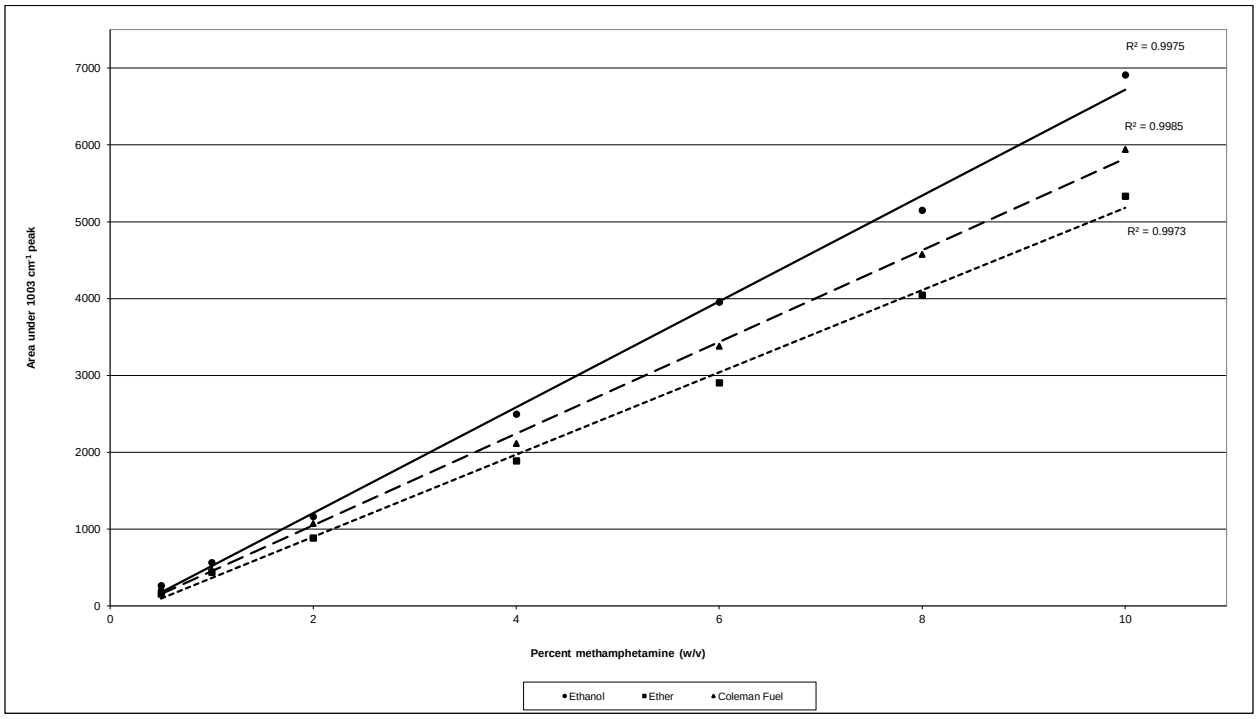

Figure 32 – Analysis of five case samples (full scale)

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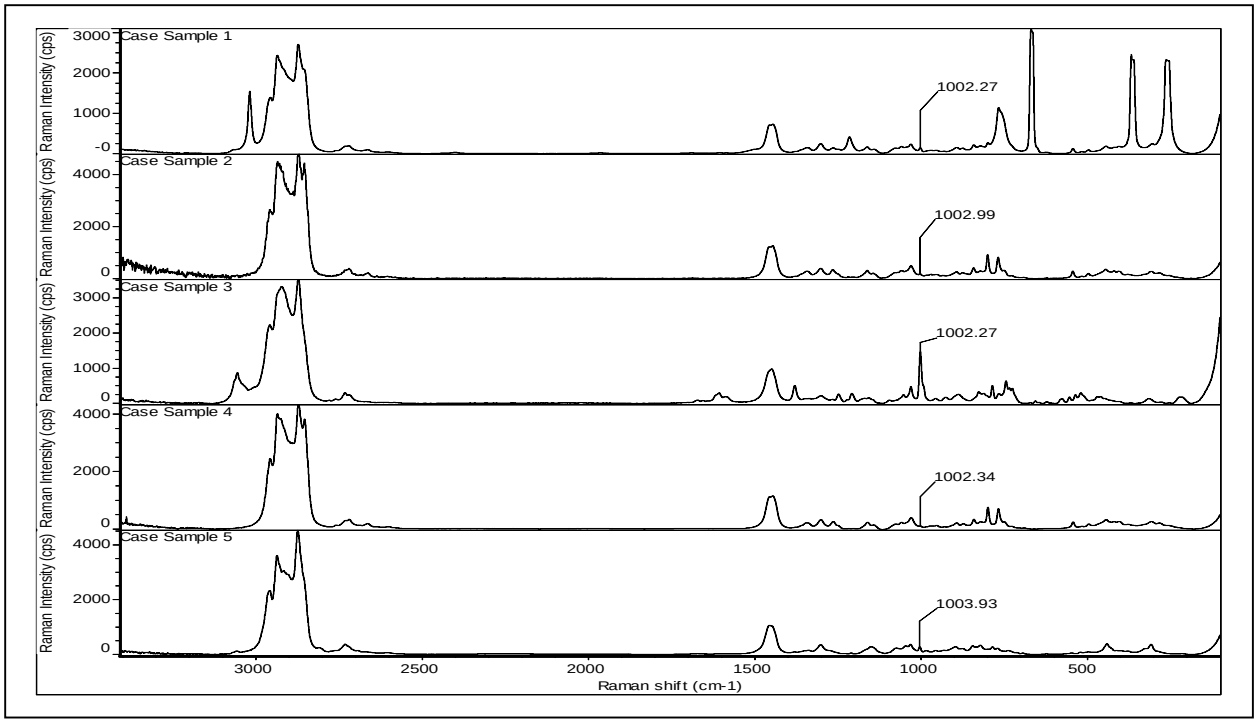
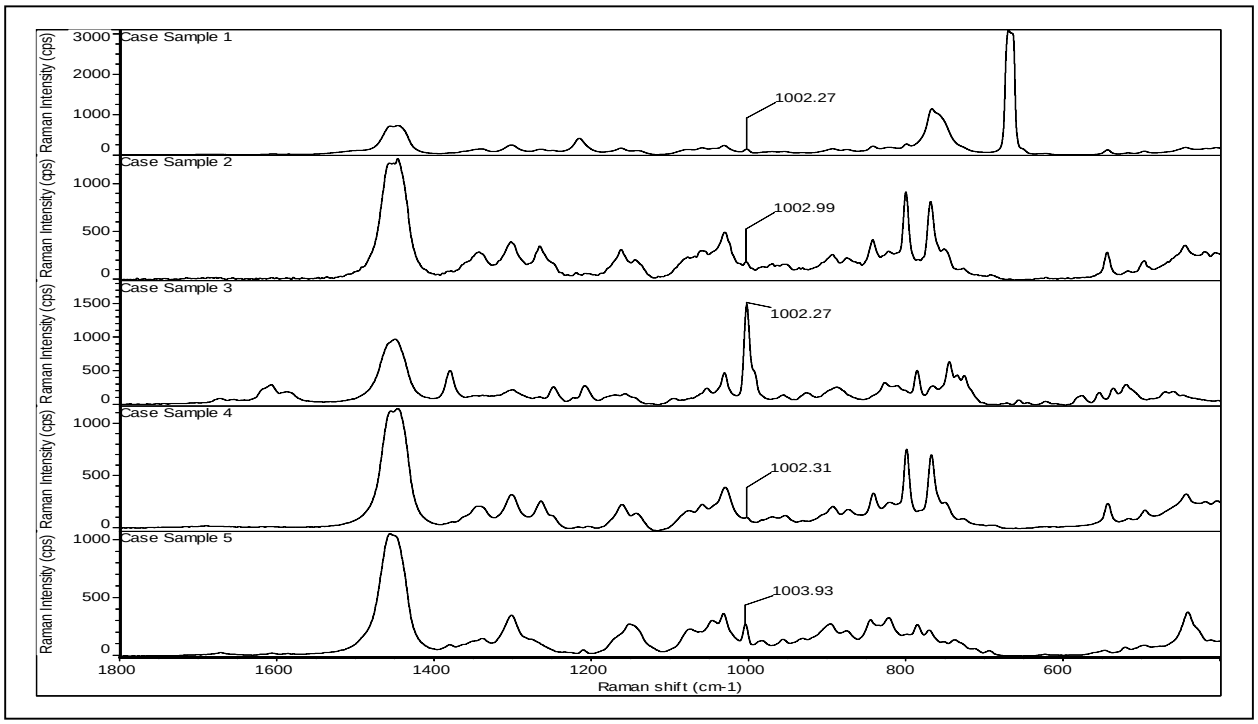


Figure 33 – Analysis of five case samples (400-1800 cm^{-1})



III. Enhanced analysis of novel synthetic cathinones

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Figure 34 – Twelve selected synthetic cathinone isomers (methyl and ethyl substitutions, all 3 benzyl ring substitutions)

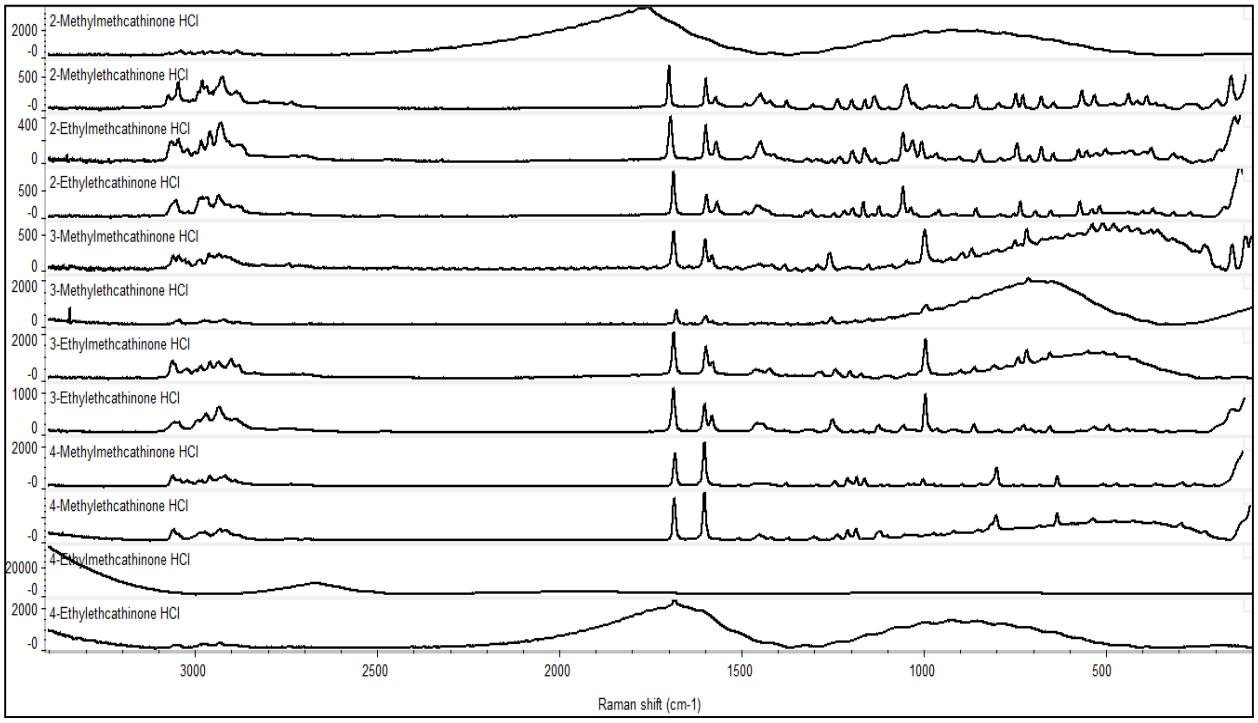

Figure 35– Synthetic cathinones: methyl and ethyl substitutions at the 2-phenyl position

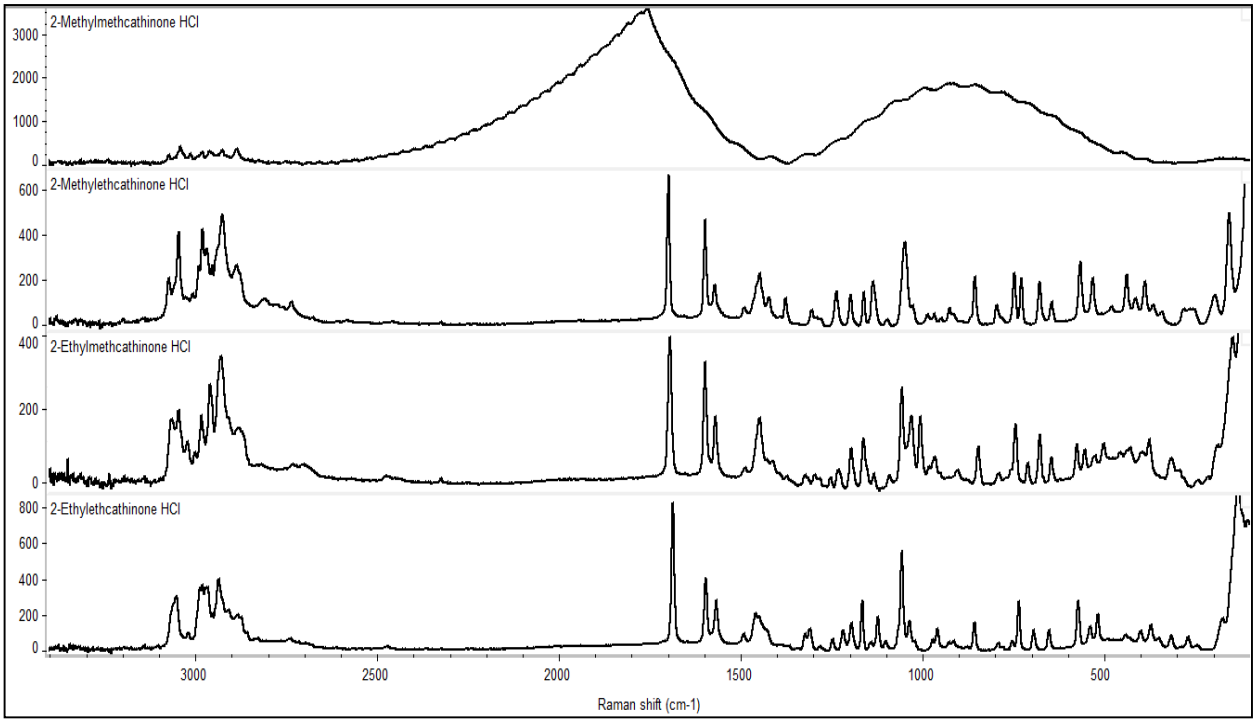

Figure 36 – Synthetic cathinones: methyl and ethyl substitutions at the 3-phenyl position

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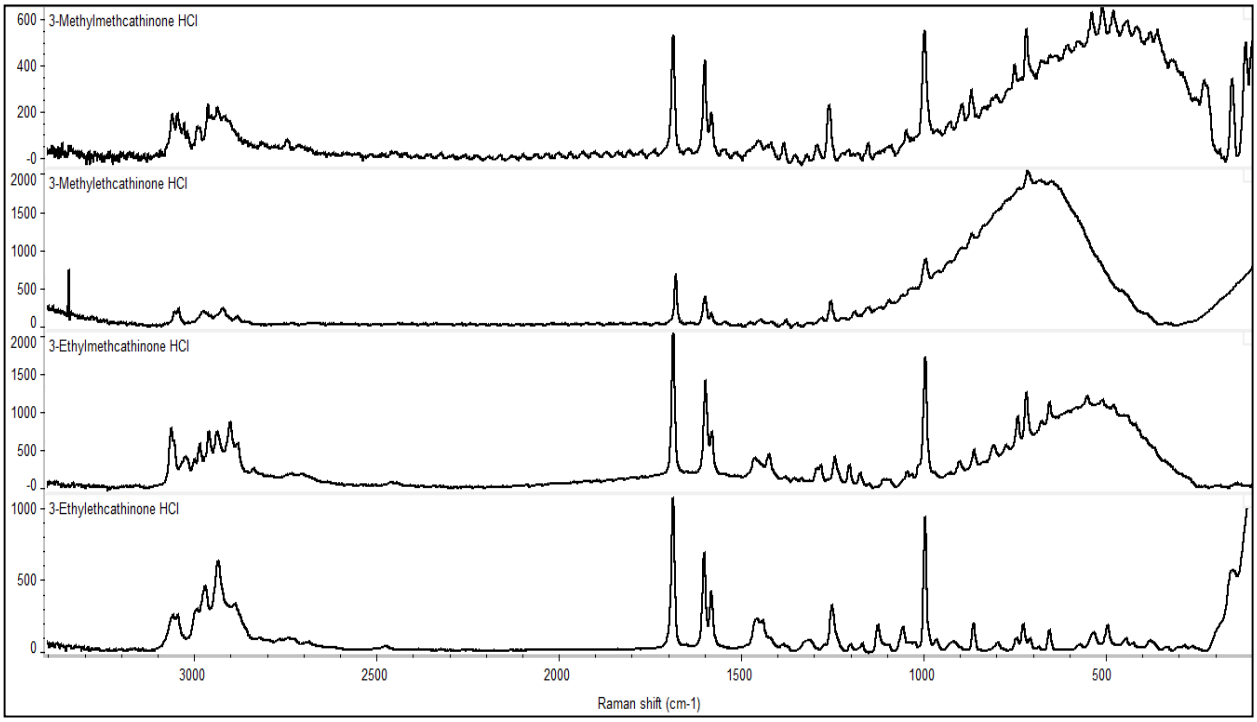

Figure 37 – Synthetic cathinones: methyl and ethyl substitutions at the 4-phenyl position

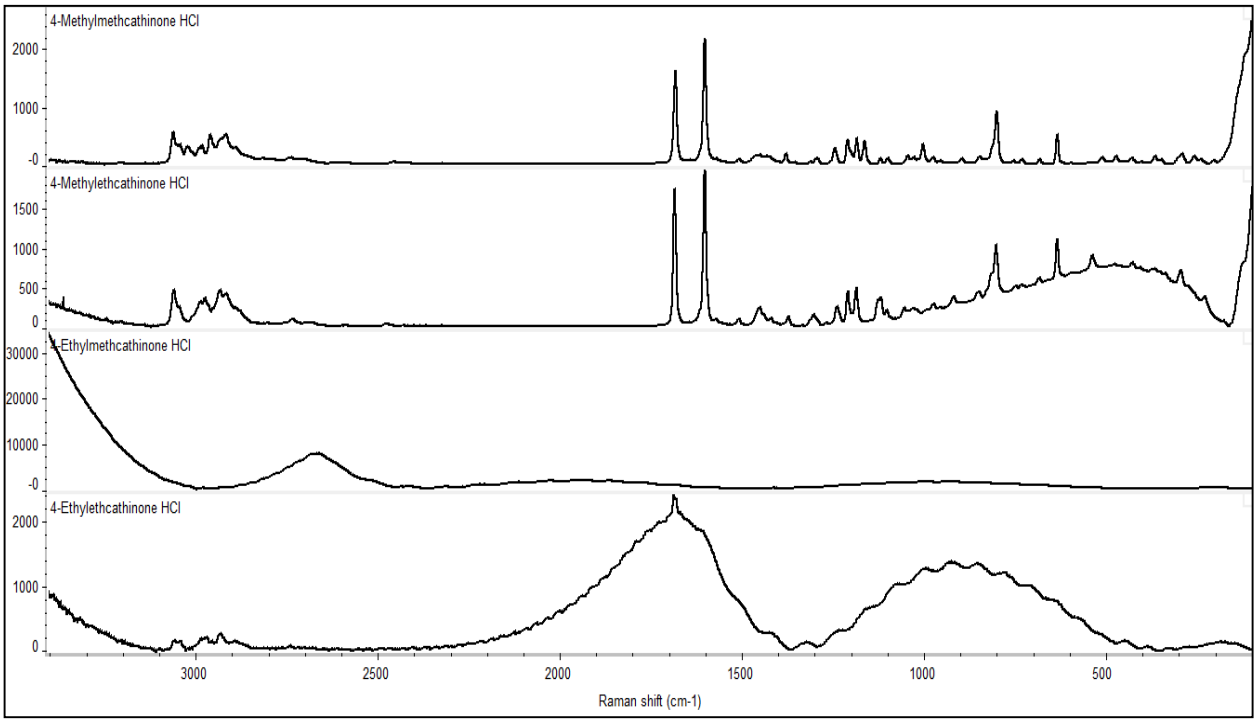

Figure 38 – Synthetic cathinone regioisomers: 2-, 3-, and 4-phenyl methoxymethcathinones

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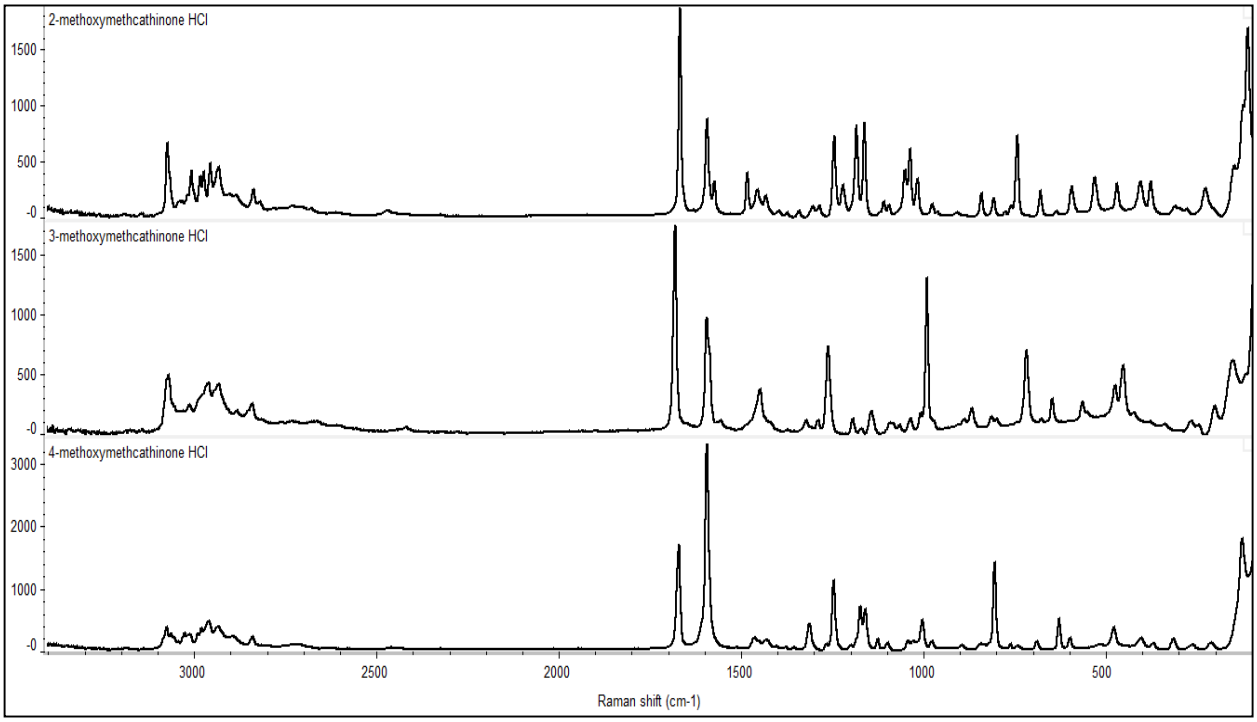
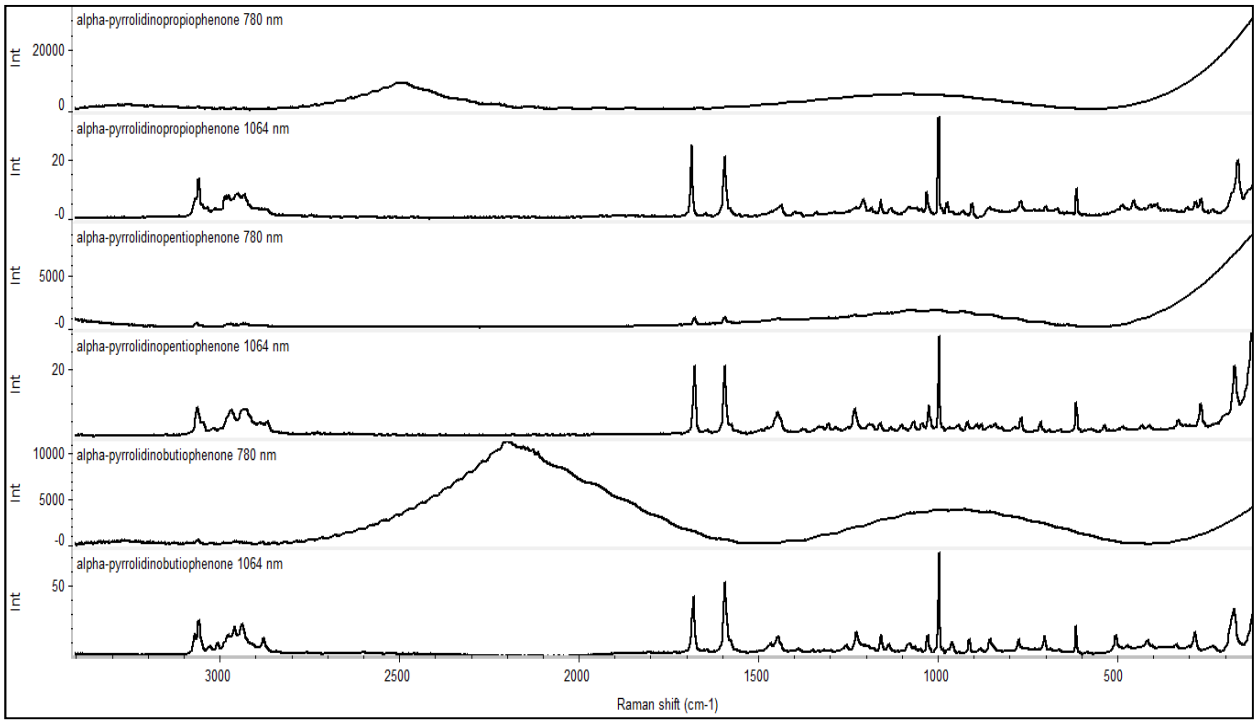


Figure 39 – Comparison of 3 synthetic cathinones analyzed by 780 nm laser and 1064 nm laser



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Implications for Policy and Practice

I. Multi-component searching in complex clandestine laboratory mixture samples
Based on our experiments, there is little implication for the multi-component searching software as it applies to clandestine laboratory liquid samples. The solvent spectrum is too strong relative to the spectra of the dissolved components to provide reliable and useful information about the minor contributors to the composite spectrum. Surfaced Enhanced Raman Spectroscopy (SERS) shows some promise in its ability to enhance the dissolved component signal, but still did not provide enough strengthening of the signal to afford reliable search results.

II. Rapid, non-destructive screening test for methamphetamine in clandestine lab samples
The use of raman spectroscopy as a simple, rapid, non-destructive screening test shows promise for use in forensic laboratories. By analyzing samples through-container, chemists are not subjected to harmful vapors. The screening of multiple liquid submissions for the most probative sample can reduce sample preparation time, save on materials, reagents, and consumables, and generally increase the efficiency of testing clandestine laboratory cases by rapidly identifying liquids that may contain methamphetamine before further workup.

III. Enhanced analysis of novel synthetic cathinones
Based on our experiments, there is a reasonable chance that discrimination between regioisomers and structural isomers can be accomplished via raman spectroscopy. In a few regions of the raman spectrum, there is preliminary evidence that predicable band pattern changes occur as a result of specific substitutional rearrangements, particularly regioisomer positions on the phenyl ring. From a practice standpoint, our experiments show that the best analysis of drug samples with structures that may induce fluorescence is either a 780 nm laser with high power (200mW)[16], or a 1064 nm laser. The 1064 nm laser dramatically improved the raman spectra obtained from the panel of cathinones in this experiment over the 780 nm laser.

Implications for Further Research

I. Multi-component searching in complex clandestine laboratory mixture samples
Further research can be done using Surfaced Enhanced Raman Spectroscopy to potentially identify an optimal enhancement technique for dissolved components in liquids. It is yet to be seen whether the multicomponent searching software can readily discern these dissolved constituents; however, the use of SERS techniques likely represents the most probable path forward if this identification is possible.

II. Rapid, non-destructive screening test for methamphetamine in clandestine lab samples
Further research is possible on the discrimination of pseudoephedrine and methamphetamine at the 1003 cm^{-1} raman band. Our experiments showed that the strongest raman band for

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methamphetamine appears at approximately 1003 cm^{-1}. This band is discernible in solution and can be used as a marker for the presence of methamphetamine. In other experiments, we have also observed that pseudoephedrine has a similar raman band. This, alone, does not negate the usefulness of raman as a screening technique for methamphetamine in solution, since both methamphetamine and pseudoephedrine are pertinent substances to clandestine laboratory cases. Further research can be conducted, however, to determine whether these substances can be discriminated in solution, which would further enhance the screening technique.

III. Enhanced analysis of novel synthetic cathinones

There is significant further research that can be done in this area. By identifying the most useful laser wavelength and/or power, panels of structural isomers can be analyzed in the future for predictable and discriminating raman band features. While the scope and timeline of this grant project is finished, there is a large amount of further work that can be done in the future on this issue.

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DISSEMINATION OF RESEARCH FINDINGS

I. Multi-component searching in complex clandestine laboratory mixture samples
-None-

II. Rapid, non-destructive screening test for methamphetamine in clandestine lab samples

1. Triplett JS, Hatfield JA, Kaeff TL, Ramsey CR, Robinson SD, Standifer AF Raman spectroscopy as a simple, rapid, nondestructive screening test for methamphetamine in clandestine laboratory liquids. J Forensic Sci 2013;58(6):1607-14.

III. Enhanced analysis of novel synthetic cathinones
-None-

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SUPPLEMENTARY MATERIAL

Appendix A – Synthetic Cathinones from Cayman Chemical Company

Compound Name	Cayman Item #	Cayman Lot #
Butylone HCl	10393	0435106-31
3,4-methylenedioxy-α-pyrrolidinobutiophenone HCl	10437	0435471-14
3,4-methylenedioxy-α-pyrrolidinopropiophenone HCl	10439	0436978-16
α-pyrrolidinopropiophenone HCl	10445	0430867-35
4-methyl-α-pyrrolidinopropiophenone HCl	10446	0439938-10
4-methyl-α-pyrrolidinohexanophenone HCl	10448	0439898-8
4-methoxy-α-pyrrolidinopropiophenone tosylate	10449	0431252-26
Naphyrone HCl	10517	0434404-29
Methedrone HCl	10529	0431543-53
3-fluoromethcathinone HCl	10730	0432765-8
4-methylmethcathinone HCl	10801	0429260-39
Pyrovalerone HCl	10836	0427897-30
4-fluoromethcathinone HCl	10859	0428646-50
methylone HCl	10986	0430267-68
Pentedrone HCl	11011	0442629-14
4-ethylethcathinone HCl	11197	0433939-23
3-ethylethcathinone HCl	11198	0440268-7
2-ethylethcathinone HCl	11199	0440080-8
4-ethyl-N,N-dimethylcathinone HCl	11207	0434033-14
2-methylethcathinone HCl	11221	0436091-25
3-methylethcathinone HCl	11222	0435404-30
2-methylmethcathinone HCl	11223	0437035-18
3-methylmethcathinone HCl	11224	0435099-24
2,3-dimethylmethcathinone HCl	11225	0439131-14
3,4-dimethylethcathinone HCl	11228	0434936-16
2-fluoroethcathinone HCl	11229	0434902-17
3-fluoroethcathinone HCl	11230	0435340-14
4-fluoromethcathinone HCl	11231	0434486-15
Ethcathinone HCl	11241	0434415-30
Buphedrone HCl	11283	0440681-16
Diethylcathinone HCl	11333	0435860-15
2,3-Pentylone isomer HCl	11463	0442119-3
2-methyl-α-pyrrolidinopropiophenone HCl	11484	0438731-18
3-methyl-α-pyrrolidinopropiophenone HCl	11485	0439653-13
4-methylbuphedrone HCl	11486	0438555-20
4-methyl-α-ethylaminobutiophenone HCl	11489	0438613-6
Isopentedrone HCl	11563	0437252-12

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N-ethyl-N-methylcathinone HCl	11604	0439194-8
N-ethylbuphedrone HCl	11665	0438716-19
4-methoxy-N,N-dimethylcathinone HCl	11666	0438581-9
4-methyl-N-methylbuphedrone HCl	11667	0438612-9
Pentylone HCl	9000746	0437646-29
Nor-mephedrone HCl	9000940	0439309-5
2,3-methylenedioxypyrovalerone HCl	9001051	0435485-10
4-methylethcathinone HCl	9001069	0430408-60
4-ethylmethcathinone HCl	9001078	0431443-40
2-ethylmethcathinone HCl	9001081	0439299-9
3-ethylmethcathinone HCl	9001082	0439825-12
α-pyrrolidinopentiophenone HCl	9001083	0437630-44
3,4-dimethylmethcathinone HCl	9001098	0437447-23
Eutylone HCl	9001103	0433752-29
bk-MDEA HCl	9001123	0439296-5
bk-MDDMA HCl	9001124	0432923-34
bk-DMBDB HCl	9001125	043563-2
2,3-methylenedioxymethcathinone HCl	9001133	0441601-10
2-fluoromethcathinone HCl	9001135	0433177-33
N,N-dimethylcathinone HCl	9001144	0438825-4
4-fluoroisocathinone HCl	9001146	0442691-4
3-methoxymethcathinone HCl	9001187	0435064-18
2-methyl-α-pyrrolidinobutiophenone HCl	9001188	0435101-17
3-methyl-α-pyrrolidinobutiophenone HCl	9001189	0435102-7
4-methyl-α-pyrrolidinobutiophenone HCl	9001190	0435103-21
α-pyrrolidinobutiophenone HCl	9001195	0435009-26

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