

# The Spectroscopic Detection of Drugs of Abuse in Fingerprints after Development with Powders and Recovery with Adhesive Lifters

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## **Abstract**

The application of powders to fingerprints has long been established as an effective and reliable method for developing latent fingerprints. Fingerprints developed *in situ* at a crime scene routinely undergo lifting with specialist tapes and are then stored in evidence bags to allow secure transit and also to preserve the chain of evidence. In a previous study we have shown that exogenous material within a fingerprint can be detected using Raman spectroscopy following development with powders and lifting with adhesive tapes. Other reports have detailed the use of Raman spectroscopy to the detection of drugs of abuse in latent fingerprints including cyanoacrylate-fumed fingerprints. This study involves the application of Raman spectroscopy for the analysis of drugs of abuse in latent fingerprints for fingerprints that had been treated with powders and also subsequently lifted with adhesive tapes. Samples of seized ecstasy, cocaine, ketamine and amphetamine were supplied by East Sussex Police and by the TICTAC unit at St Georges Hospital Tooting. Contaminated fingerprints were deposited on clean glass slides. The application of aluminium or iron based powders to contaminated fingerprints did not interfere with the Raman spectra obtained for the contaminants. Contaminated fingerprints developed with powders and then lifted with

lifting tapes were also examined. The combination of these two techniques did not interfere with the successful analysis. The lifting process was repeated using hinge lifters. As the hinge lifters exhibited strong Raman bands the spectroscopic analysis was more complex and an increase in the number of exposures to the detector allowed for improved clarification. Spectral subtraction was performed to remove peaks due to the hinge lifters using OMNIC software. Raman spectra of developed and lifted fingerprints recorded through evidence bags were obtained and it was found that the detection process was not compromised. Although the application of powders did not interfere with the detection process the time taken to locate the contaminant was increased due to the physical presence of more material within the fingerprint.

*Keywords:* Raman spectroscopy, fingerprints, fingerprint development, fingerprint lifting, drugs of abuse.

## **Introduction**

In a previous study we have demonstrated the ability to use Raman spectroscopy to characterise exogenous material present in latent fingerprints following development with powders and recovery with adhesive lifters [1].

Another report has described the application of Raman spectroscopy to the detection of drugs of abuse and other exogenous substances present in latent fingerprints resulting from an individual depositing a contaminated fingerprint [2]. Significantly this non-destructive technique [1] has the potential to provide evidence concerning materials that the individual had handled [3], while the individual can be identified by traditional fingerprint methods. This technique has also been applied successfully to cyanoacrylate-fumed fingerprints [4 and 5]. It is of interest to establish whether drugs

of abuse can be detected if a latent fingerprint has undergone a variety of other manipulations either singularly or in combination. For instance dusted with powder before being lifted with tape or a hinge lifter and subsequently stored in an evidence bag. The detection through evidence bags is of importance as this would allow evidence to be examined without removal thus reducing the possibility of contamination and also preserving the chain of evidence. This has been reported previously on bulk samples [6]. The materials used in this investigation were seized samples of ecstasy (3,4-methylenedioxy-N-methylamphetamine - MDMA), cocaine, ketamine and amphetamine with pure samples used as references. The use of seized '*street*' samples is important to this study as it reflects the typical samples that would be encountered in forensic casework.

The seized samples of drugs are by their definition not pure drug samples. Work carried out at St Georges Hospital using GC-MS has indicated that caffeine is a common adulterant especially in samples of amphetamine. Lidocaine and phenacetin were found in samples of cocaine powder and caffeine was found in some of the samples of MDMA. Other common cutting agents found in street samples include substances such as paracetamol, citric acid, glucose, lactose and other sugars [7].

The application of powders to latent fingerprints is a simple, common and long established method for their development [8]. The range of powders available for this purpose is extensive with the most commonly used powders consisting of aluminium milled flake, or various grades of graphite. These powders are applied using glass fibre brushes specially constructed to minimise potential damage to the detail of the latent fingerprint [9].

A second group of powders used for fingerprint development are magnetic powders which are based on metals or their oxides that are ferromagnetic. Application of these

powders is via a magnetic applicator. The advantage of such powders is that there is no contact between the applicator and the fingerprint thus reducing the chance of damage being sustained to the fingerprint detail.

There are a wide range of different types of tapes designed for lifting powdered fingerprints from a range of surfaces. The principle of the process is essentially the same regardless of the tape involved. A short length of tape is pressed down onto the fingerprint with care to ensure no air bubbles are present. The tape is then removed slowly and transferred to a backing sheet. Hinge lifters consist of a low tack clear adhesive film lifter (with protective cover) attached to a transparent, black or white backing sheet.

Portable Raman spectrometers are commercially available for the detection of bulk samples from crime scenes and their potential in the field has been reviewed by Harvey *et.al.* [10]. However the research described below involves the use of a Raman microscope to focus on trace samples of material within latent fingerprints. Such instruments are not portable therefore it is not practicable to examine latent fingerprints by this method *in situ*. In addition to this fingerprints on large items, for instance a car, could not be examined without undergoing lifting with tape as such an item would not physically fit under the microscope.

## **Experimental**

Pure samples of MDMA, cocaine, ketamine and amphetamine were obtained from Sigma-Aldrich Company Ltd, Poole, United Kingdom and were used as received.

Samples of seized ecstasy, cocaine, ketamine and amphetamine were supplied by East Sussex Police and by the TICTAC unit at St Georges Hospital Tooting. The TICTAC samples were received as powders as the ecstasy tablets had been ground into

powders as part of another project they had been involved in. These samples were used as received. The samples from East Sussex Police were in the form of tablets and were ground into powders to facilitate this study.

A reference Raman spectrum was obtained for comparison purposes from a small sample of powder or powdered tablet that was placed on a clean glass slide.

Doped fingerprints were prepared by placing between 3 and 8 mg of powder or powdered tablet on a clean glass slide and then pressing a clean thumb, previously washed with soap and water and then dried, onto the powder. Excess powder was then removed with gentle brushing using another finger and a fingerprint deposited on a glass slide. This method was chosen to simulate the handling of bulk samples of drugs or regular handling over a period of time. The resulting fingerprints were examined under the Raman microscope and spectra were obtained from small crystals of the substance observed within the deposited latent fingerprint. Typical particles examined ranged in size from approximately 10 $\mu$ m to 40 $\mu$ m in diameter. This initial study involved the examination of 70 fingerprints from a single donor with Raman spectra being obtained both prior to and subsequent to development.

Development of fingerprints with powders (Volcano from Sirchie Laboratories Inc. and K9 Magneta Flake from CSI Ltd.) and lifting with tapes (Sirchie Laboratories Inc.) and hinge lifters (CSI Ltd.) was performed by standard methods as described in the introduction. Evidence bags were obtained from CSI Ltd.

All Raman spectra were obtained using a Raman microscope, Olympus BX40, with a Uniphase (model 1145) helium-neon laser operating at a wavelength of 632.8nm with a fixed output of 35mW. The laser power at the sample is approximately 4mW and a 50X objective lens was used. The Jobin-Yvon 640 spectrometer incorporates a liquid-nitrogen cooled charge coupled device (CCD) detection array. Raman spectra were

obtained for twenty 5 second exposures to the CCD detector over the range 3250-300cm<sup>-1</sup>, which had been previously determined as the region that contained the Raman bands of interest for these samples. Any variation to this exposure time is indicated where appropriate. The spectrometer was calibrated by reference to a silicon wafer Raman band at 520cm<sup>-1</sup>. Spectra were exported to OMNIC version 7.3 or Origin version 7.0 spectral manipulation packages for processing and presentation.

## **Results and Discussion**

The samples obtained from the TICTAC unit had undergone previous characterisation as part of another research project in addition to this the samples of ecstasy had been quantified. The samples obtained from East Sussex Police were from batches of seized drugs from police raids that had undergone forensic evaluation to determine the identity of the substance seized.

Initially reference samples for the pure samples were obtained from a small sample of the powder placed on a glass slide. A Raman spectrum was obtained in the same manner for all of the samples of seized drugs. This allowed problems with fluorescence to be identified before proceeding onto using the samples in contaminated fingerprints. Six samples were identified as exhibiting fluorescence that was not diminished by photobleaching and these samples were not included in the study.

As the pure samples were not fluorescent the source was attributed to the presence of one or more of the additional excipients present in the sized samples. Such excipients can be added to bulk out the drug for example glucose. They may be impurities that arise from the crude manufacturing process or they may be added to mimic the effects of the drug for example ephedrine present in amphetamine samples. The Raman

spectrometer used in the analysis has a single laser wavelength however if an alternative wavelength of laser had been available, for example a near infra-red laser, then this may have overcome the problem with fluorescence observed in these samples.

The presence of other excipients in the siezed samples caused a lengthening of the detection process as some of the particles found were not the drug of interest. This meant that on some occasions a number of different particles had to be located before a spectrum of the drug could be obtained.

Fig. 1 shows the Raman spectra obtained from samples of the pure drugs obtained from samples of the powder placed on clean glass slides. This clearly demonstrates that the Raman spectrum distinguishes between all of the drugs analysed. Previously it has been shown that Raman can be used to distinguish between a range of chemically similar substances including between different isomers of the same drug [11, 12 and 13].

In Fig. 2 the results obtained from fingerprints contaminated with MDMA are presented. Fig. 2 (a) shows the spectrum obtained from pure MDMA powder as a reference sample. When a fingerprint contaminated with a seized MDMA was examined under the microscope small crystals were revealed. The spectrum of one of these crystals (Fig. 2 (b)) clearly indicates that the particle is MDMA.

Next the fingerprint was developed with Magneta Flake. K9 Magneta Flake is a magnetic powder that consists of iron powder milled and flaked to optimise particle size and then coated with amino acids of a specific molecular weight. The Magneta Flake exhibits a broad weak-medium Raman band at  $660\text{ cm}^{-1}$ . Fig. 2 (c) demonstrates that the detection of MDMA is not compromised by the applied powder. The weak

band at  $660\text{ cm}^{-1}$  from the powder is obscured by the presence of stronger bands in the MDMA spectrum.

The developed fingerprint was then lifted using a hinge lifter. The hinge lifter exhibits a number of peaks in particular there are strong peaks at  $1725$  and  $1615\text{cm}^{-1}$ . The spectrum obtained from the lifted fingerprint, after spectral subtraction, is shown in Fig. 2 (d) the number of exposures to the detector was increased to 50 for improved clarification. The spectrum exhibited strong peaks from the hinge lifter therefore spectral subtraction was performed using OMNIC spectral subtraction program. Fig. 2 (d) shows that the hinge lifter has not prevented detection of the MDMA. Note that small peaks at  $1725$  and  $1615\text{cm}^{-1}$  remain after the subtraction process and are due to residual bands arising from the hinge lifter.

The process was then repeated with samples of cocaine. In Fig 3 (a) the spectrum of pure cocaine powder is shown for reference. The spectrum from a fingerprint contaminated with seized cocaine is shown in Fig 3 (b). It is clear that the spectrum obtained is a match for pure cocaine. The fingerprint was then developed with Magneta Flake and a spectrum obtained from a crystal within the fingerprint and this can be seen in Fig 3 (c). As before the application of the Magneta Flake did not impair the successful detection of the cocaine. Finally the contaminated fingerprint was lifted using a hinge lifter and a Raman spectrum obtained. Fig 3 (d) shows the result of the spectrum after spectral subtraction had been performed as before. The strong bands associated with the hinge lifter are overlapped by very strong bands present in the spectrum of cocaine.

A reference spectrum for pure ketamine is shown in Fig 4 (a). A contaminated fingerprint using a seized sample was produced as described previously and the spectrum obtained, Fig 4 (b), clearly shows it is the same as the pure sample. Once



again application of Magneta Flake did not interfere with the detection process and this is shown in Fig 4 (c).

The fingerprint was then lifted using Sirchie lifting tape which was transferred to a clear backing sheet. Clear backing sheets were used rather than white backing sheets as previous studies had shown white sheets to be fluorescent [1]. The Raman spectrum of blank Sirchie tape exhibited only very weak broad bands at 1725, 1450 and 1040 $\text{cm}^{-1}$ . The Raman spectrum obtained from the lifted fingerprint is shown in Fig. 4 (d) and again detection of the contaminant is not compromised.

Fig. 5 (a) shows the reference spectrum for pure amphetamine. A fingerprint contaminated with a seized sample of amphetamine was examined and a Raman spectrum obtained, Fig. 5 (b), which matched the spectrum of the pure sample.

The fingerprint was then developed using Volcano latent fingerprint powder which is an aluminium based powder that is applied via a standard application brush. The powder only exhibits one weak band at 1050 $\text{cm}^{-1}$ . The Raman spectrum in Fig 5 (c) was obtained from the developed print. The application of aluminium powder has not prevented a Raman spectrum from being obtained and this matches that of the pure amphetamine. There is a band at 1710 $\text{cm}^{-1}$  that is attributed to one of the other excipients present in the seized sample. The band at 1050 $\text{cm}^{-1}$  from the aluminium powder is obscured by very strong bands seen in the amphetamine spectrum at the corresponding wavenumber.

Finally the fingerprint was lifted with a hinge lifter and re-examined. The number of exposures to the detector was increased to 50 for improved clarification and spectral subtraction was performed as before. Fig. 5 (d) shows that the lifting process has not hindered the detection of the amphetamine.

Fig. 6 (b) shows a Raman spectrum, after spectral subtraction, of a fingerprint contaminated with seized ketamine which has then been developed with Magneta Flake, lifted with a hinge lifter and then placed in an evidence bag. A reference sample of the pure drug is given in Fig. 6 (a). In Fig. 7 (b) the Raman spectrum, after spectral subtraction, of a fingerprint contaminated with seized amphetamine, developed with Magneta Flake, lifted with Sirchie tape and placed in an evidence bag is indicated. Again a reference sample (Fig. 7 (a)) is given for comparison purposes. The spectra in figs. 6 and 7 (b) both underwent spectral subtraction using the OMNIC software package. The results show that the evidence bag did not interfere with the spectrum obtained in any way.

Spectra were initially compared by overlaying in Origin or OMNIC then following this they were compared to a library using OMNIC software. The library uses an algorithm that depends on computing a correlation coefficient that relates an unknown spectrum to each entry in the library. The entries are then ranked in descending order based upon the magnitude of the coefficient. The entries having the largest coefficient are reported as the spectra having the most similar to that of the unknown compound. The value of the coefficient has a minimum value of zero and a maximum of 100. A value of zero implies that there is no relationship between the unknown spectrum and any of the library spectra. Conversely a value of 100 would indicate that the unknown spectrum is identical to or the negative of the matched library spectrum [14]. All the spectra presented gave a minimum percentage match of 85%.

## **Conclusions**

The application of powders to develop contaminated latent fingerprints did not prevent the identification of the drug present from the Raman spectrum obtained. The application of the powder did result in an increase in the time taken to locate particles

of the contaminant due to the physical presence of more material within the fingerprint. Typically there was a four to five fold increase in the analysis time. However, once located the Raman spectra obtained allowed the successful identification of the contaminant.

Contaminated fingerprints developed with powder and then lifted with tapes showed again that successful detection was still possible. There were some complications encountered with interference from strong Raman bands associated with the hinge lifters used. These problems can be overcome by the use of lifters with no strong Raman bands to interfere with detection. Alternatively spectral subtraction of Raman bands associated with tapes used in the lifting process can be performed. This was applied with success in this study using the OMNIC software program.

Raman spectra obtained from powdered and lifted fingerprints within evidence bags were also obtained and again successful identification of the contaminant was made. This is of particular importance as it means that items do not have to be removed from evidence bags to be examined thus reducing potential for contamination and also importantly the chain of evidence remains preserved.

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## Figure legends

### Figure 1

Raman spectra obtained from

- (a) pure ketamine powder
- (b) pure MDMA powder
- (c) pure cocaine powder
- (d) pure amphetamine powder

### Figure 2

Raman spectra obtained from

- (a) pure MDMA powder
- (b) fingerprint contaminated with seized sample of MDMA
- (c) fingerprint contaminated with seized sample of MDMA developed with Magneta flake
- (d) fingerprint contaminated with seized sample of MDMA developed with Magneta flake and lifted with hinge lifter (after spectral subtraction)

### Figure 3

Raman spectra obtained from

- (a) pure cocaine powder
- (b) fingerprint contaminated with seized sample of cocaine
- (c) fingerprint contaminated with seized sample of cocaine developed with Magneta flake
- (d) fingerprint contaminated with seized sample of cocaine developed with Magneta flake and lifted with hinge lifter (after spectral subtraction)

### Figure 4

Raman spectra obtained from

- (a) pure ketamine powder
- (b) fingerprint contaminated with seized sample of ketamine
- (c) fingerprint contaminated with seized sample of ketamine developed with Volcano powder
- (d) fingerprint contaminated with seized sample of ketamine developed with Volcano powder and lifted with hinge lifter

### Figure 5

Raman spectra obtained from

- (a) pure amphetamine powder
- (b) fingerprint contaminated with seized sample of amphetamine
- (c) fingerprint contaminated with seized sample of amphetamine developed with Volcano powder
- (d) fingerprint contaminated with seized sample of amphetamine developed with Volcano powder and lifted with hinge lifter (after spectral subtraction)

Figure 6

Raman spectra obtained from

(a) pure ketamine powder

(b) fingerprint contaminated with seized sample of ketamine developed with Magneta Flake, lifted with hinge lifter and placed in evidence bag (after spectral subtraction)

Figure 7

Raman spectra obtained from

(a) pure amphetamine powder

(b) fingerprint contaminated with seized sample of amphetamine developed with Magneta Flake, lifted with Sirchie tape and placed in evidence bag (after spectral subtraction)