The Spectroscopic Detection of Exogenous Material 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. The powders adhere to the ridge pattern of the fingerprint only, thus allowing the image to be visualised. Fingerprints developed *in situ* at a crime scene routinely undergo lifting with specialist tapes to facilitate subsequent laboratory analysis. As with all recovered evidence these samples would be stored in evidence bags to allow secure transit from the scene to the laboratory and also to preserve the chain of evidence. In this paper the application of Raman spectroscopy for the analysis of exogenous material in latent fingerprints is reported for contaminated fingerprints that had been treated with powders and also subsequently lifted with adhesive tapes. A selection of over the counter (OTC) analgesics were used as samples for the analysis and 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. In most cases background fluorescence attributed to the sebaceous content of the latent fingerprint was reduced by the application of the powder thus reducing spectral interference. 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 of exogenous contaminants by Raman spectroscopy. 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. Raman spectra of developed and lifted fingerprints recorded through evidence bags were obtained and it was found that the detection process was not compromised in any way. 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. The presence of interfering Raman bands from lifting tapes is another potential complication. This however could be removed by spectral subtraction or by the choice of lifting tapes that have only weak Raman bands.

Keywords: Raman spectroscopy, fingerprints, fingerprint development, fingerprint lifting, exogenous material, analgesics.

Introduction

A recent 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 [1]. Significantly this non-destructive technique has the potential to provide evidence concerning materials that the individual had handled, while the individual can be identified by traditional fingerprint methods. This technique has also been applied successfully to cyanoacrylate-fumed fingerprints [2]. It is of interest to establish whether exogenous

substances can be detected if a latent fingerprint has undergone a variety of other manipulations either singularly or in combination. For instance dusted with powder or chemically enhanced, for example with small particle reagent (SPR), 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 [3]. The materials used in this initial investigation were a range of OTC analgesics.

The application of powders to latent fingerprints is a simple, common and long established method for their development [4]. 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.

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.* [5]. 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

Tesco co-codamol tablets, containing a mixture of paracetamol and codeine and manufactured by Wallis Laboratory Ltd were used as received. Veganin tablets, Codis 500 soluble tablets, Anadin Original tablets, Solpadine Plus tablets and Nurofen Plus tablets were also all used as received. In addition to these samples gamma-hydroxybutyric acid (GHB) synthesised within the School of Physical Sciences was also analysed. 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 35 mg of 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 10μm to 30μm in diameter. This initial study involved the examination of 100 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. SPR and 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 three 10 second exposures to the CCD detector over the range 1800-300cm^{-1}, 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^{-1}. Spectra were exported to Galactic Peaksolve or Origin spectral manipulation packages for processing and presentation.

Results and Discussion

These studies involved a number of OTC analgesics as samples. The samples investigated included Tesco Co-codamol tablets, Veganin tablets, Codis 500 soluble tablets, Anadin Original tablets, Solpadine Plus tablets and Nurofen Plus tablets. Similar results were obtained from the various samples and will be discussed in detail for the co-codamol tablets. The tablets contain paracetamol (500 mg), codeine phosphate (8 mg), maize and potato starch, povidone, stearic acid, talc, magnesium stearate, methyl-p-hydroxy benzoate, ethyl-p-hydroxy benzoate and propyl-p-hydroxy benzoate. The Raman spectrum of a powdered tablet figure 1(a) is not surprisingly dominated by absorptions due to paracetamol [6]. Examination of a fingerprint contaminated with co-codamol under the Raman microscope revealed small crystals of substance whose spectrum figure 1(d) is clearly that of co-codamol. The spectrum shows background fluorescence which is presumably due to sebum present in the fingerprint. Figure 2 shows the spectrum obtained from an uncontaminated fingerprint deposited on a clean glass slide no Raman bands are observed merely a moderately fluorescent background which corresponds with the fluorescence observed in figures 3 (b) and 3(c).

The effect on the detection of the co-codamol powder by a variety of fingerprint powders was then investigated. Volcano latent fingerprint powder is an aluminium based powder that is applied via a standard application brush. The powder only exhibits one Raman band in the region 1800-300 cm^{-1} at 1050 cm^{-1}. Application of the powder to a co-codamol doped fingerprint resulted in a decrease in spectral intensity and the exposure time was increased from 10 to 40 seconds. The spectrum figure 1(b) is clearly still that of co-codamol with only the addition of a small peak at 1050 cm^{-1} due to the powder. Moreover, the application of the powder has significantly reduced

the background fluorescence. In order to ensure that the fluorescence had not been reduced by a photobleaching effect from increased laser exposure further doped fingerprints were examined. Raman spectra were obtained from three 10 second exposures followed by three 40 second exposures following which the fingerprint was developed using aluminium powder and a final spectrum was recorded for three 40 second exposures. As indicated in figure 3(c) the small increase in exposure time was not sufficient to reduce fluorescence by photobleaching however application of the aluminium powder as shown in figure 3(a) has resulted in a significant reduction of the background fluorescence. The aluminium powder is designed to adhere to the sebaceous content of fingerprints which is the likely source of fluorescence and hence the powder is blocking out this potential source of spectral interference.

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 cm^{-1}. Figure 1(c) demonstrates than the detection of co-codamol is not compromised by the applied powder. Again here a reduction in background fluorescence is observed with explanation as given before.

Experiments were performed with red fluorescent magnetic powder, but not surprisingly these interfered significantly with the Raman spectra and should be avoided in this type of investigation. Negative results were also obtained when the appearance of the latent fingerprints was enhanced with SPR which consists of a very fine suspension of molybdenum disulphide in a detergent solution. The SPR is supplied as a pump spray that is sprayed onto the fingerprint after which the excess is removed by simply rinsing with water. It is therefore suggested that the developing of

fingerprints with chemical solutions should not be performed if subsequent Raman analysis may be required.

Problems were also observed when investigating fingerprints contaminated with GHB. Figures 4(a) and 4(b) demonstrate that it can be detected in fingerprints if they are recovered quickly, but the hygroscopic nature of GHB means that it becomes difficult to detect using this method after a short period of time.

The next stage of the investigation involved doped fingerprints that had been developed using the powder methods described previously and then lifted with tape or hinge lifters. Raman spectra were obtained for blank samples of each of the lifting tapes. It was found that the Sirchie lifting tape exhibits only very weak broad bands at 1725cm^{-1}, 1450cm^{-1} and 1040cm^{-1}. However the hinge lifter had a more complex Raman spectrum showing a number of bands within the region of interest for co-codamol in particular two very strong bands at 1725cm^{-1} and 1615cm^{-1}. The spectra obtained from both lifting tapes are shown in figure 6.

Fingerprints doped with co-codamol and developed with Magneta Flake were initially lifted with Sirchie lifting tape and transferred to a clear backing sheet. For comparison purposes Raman spectra were obtained both prior and subsequent to the application of the powder and finally after the lifting process had been completed. Previous investigations had shown that the Magneta Flake did not interfere with the detection process and figure 5(d) demonstrates that the combination of this with the lifting of the fingerprint has also not compromised this detection.

This process was then repeated using a hinge lifter and the results obtained are shown in figure 5(b). Due to the strong bands associated with the hinge lifter the number of exposures to the detector was increased to 100 to ensure that all the weaker (relative to the hinge lifter) Raman bands associated with co-codamol could be observed. As

the hinge lifter has Raman bands that overlap with some of those of co-codamol the detection process here is less straightforward. However clear differences between the two spectra are evident and these differences are consistent with the spectrum of co-codamol. In order to confirm the spectra of co-codamol and the hinge lifter combined a small sample of co-codamol was lifted from a clean glass slide and a spectrum obtained. The results showed that the spectrum is identical to that obtained from the doped fingerprint and exhibits the same clear differences with the blank hinge lifter. Spectra were compared by overlaying in either Origin or Peaksolve however it is anticipated that in practical applications that automated software would be applied in order to obtain a percentage match with a reference library.

Fingerprints treated with Magneta Flake lifted with Sirchie tape and transferred to white backing sheets were also examined. However it was found that background interference from fluorescence attributed to the white backing sheet prevented successful detection.

These initial observations indicate that the choice of lifting tape applied could have potential implications for the unambiguous identification of exogenous material within a latent fingerprint where Raman bands due to lifting tapes overlap significantly with the material present in the fingerprint. Therefore if this type of investigation is to be performed the choice of tape to be used could be influenced by previous knowledge of its Raman spectrum. This would enable a choice of tape either with only weak Raman bands or with no Raman bands at all. Tapes having a number of strong Raman bands could then be avoided if subsequent Raman analysis is to be undertaken.

A fingerprint doped with co-codamol, treated with Magneta Flake and lifted with a hinge lifter was placed inside an evidence bag and a spectrum obtained figure 5(c) this

was compared to that of the spectrum taken without the evidence bag. The evidence bag did not interfere with the spectrum obtained in any way.

Conclusions

The application of powders to develop contaminated latent fingerprints did not prevent the identification of the contaminant from the Raman spectrum obtained. The application of powder also had the advantage of reducing spectral interference from background fluorescence attributed to the sebaceous content of latent fingerprints. 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 firstly with problems attributed to fluorescence from backing sheets that lifted prints were attached to and secondly with interference from strong Raman bands associated with the hinge lifters used. These problems can be overcome by the use of backing sheets with no fluorescence or the use of lifters with no strong Raman bands to interfere with detection. Spectral subtraction of Raman bands associated with tapes used in the lifting process is another method that could be employed to remove interfering bands.

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.

This small initial study indicates that this technique shows promise for further development. Studies on pure samples of narcotics have been performed by Day *et.al.* [1,2] and further studies underway at the University of Kent are extending this work to samples of seized drugs, for example cocaine, ecstasy, amphetamine and ketamine, in order to reflect samples that would be encountered in forensic casework.

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Figure legends

Figure1 Raman spectra obtained from

(a) co-codamol powder

(b) co-codamol doped fingerprint developed with Volcano powder

(c) co-codamol doped fingerprint developed with Magneta Flake

(d) co-codamol doped fingerprint

Figure 2

Raman spectrum of uncontaminated fingerprint

Figure 3 Raman spectra obtained from

(a) co-codamol doped fingerprint developed with Volcano powder (three 40 second exposures)

(b) co-codamol doped fingerprint (three 10 second exposures)

(c) co-codamol doped fingerprint (three 40 second exposures)

Figure 4 Raman spectra obtained from

(a) GHB crystal

(b) GHB doped fingerprint approximately 30 mins after deposition

Figure 5 Raman spectra obtained from

(a) co-codamol powder

(b) co-codamol doped fingerprint developed with Magneta Flake and lifted with a hinge lifter

(c) co-codamol doped fingerprint developed with Magneta Flake and lifted with a hinge lifter obtained from within an evidence bag

(d) co-codamol doped fingerprint developed with Magneta Flake and lifted with Sirchie Tape

Figure 6 Raman spectra obtained from

(a) blank hinge lifter

(b) blank Sirchie tape