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The detection of drugs of abuse in fingerprints using Raman spectroscopy II: cyanoacrylate-fumed fingerprints

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Abstract

This paper describes the application of Raman spectroscopy to the detection of exogenous substances in cyanoacrylate-fumed fingerprints. The scenario considered was that of an individual handling a substance and subsequently depositing a contaminated fingerprint. These fingerprints were enhanced by cyanoacrylate fuming, a process in which a layer of white cyanoacrylate polymer is deposited on the fingerprint material, enabling visual detection. Five drugs of abuse (codeine phosphate, cocaine hydrochloride, amphetamine sulphate, barbital and nitrazepam) and five non-controlled substances of similar appearance, which may be used in the adulteration of drugs of abuse (caffeine, aspirin, paracetamol, starch and talc), were used. The substances studied could be clearly distinguished using their Raman spectra and were all successfully detected in cyanoacrylate-fumed fingerprints. Photobleaching was necessary to reduce the fluorescence background in the spectra of some substances. Raman spectra obtained from the substances in cyanoacrylate-fumed fingerprints were of a similar quality to spectra obtained from the substances under normal sampling conditions, however, interfering Raman bands arising from the cyanoacrylate polymer were present in the spectra. In most cases the only interfering band was the C≡N stretching mode of the polymer, and there were no cases where the interfering bands prevented identification of the substances. If necessary, the interfering bands could be successfully removed by spectral subtraction. The most difficult aspect of the detection of these substances in cyanoacrylate-fumed fingerprints was visually locating the substance in the fingerprint beneath the polymer layer in order to obtain a Raman spectrum.

Keywords: Raman spectroscopy; Controlled substances; Drugs of abuse; Fingerprints; Cyanoacrylate fuming

1. Introduction

In an earlier paper [1] we described the application of Raman spectroscopy to the detection of drugs of abuse and other exogenous substances present in latent fingerprints. This paper extends the research to include the Raman spectroscopic detection of the same exogenous substances in fingerprints which have been enhanced by cyanoacrylate fuming, a technique which is being adopted of the forensic crime scene examination of invisible fingerprints.

Latent fingerprints are invisible and must be enhanced in some way before they can be visually detected. Cyanoacrylate fuming is a technique in which the latent fingerprint is exposed to vapours of cyanoacrylate monomer, a liquid adhesive sold commercially under numerous trade names, including Superglue®. The cyanoacrylate monomer vapour polymerises on the material comprising the latent fingerprint to form a layer of white polymer, which increases the contrast between the fingerprint and the background, thus enhancing its visibility. The polymer layer also protects the fingerprint, preventing it from being smudged.

The chemical composition of latent fingerprints has been discussed in an earlier paper [1]. Briefly, latent fingerprints are predominantly composed of the human skin secretions, sweat and sebum, although they may also contain any other material present on the fingers when the fingerprints was deposited, e.g. cosmetics, food residues and skin cells [2].

The polymerisation of cyanoacrylate monomer at room temperature occurs via an anionic polymerisation mechanism. This is shown in Fig. 1 for ethyl-2-cyanoacrylate [3,4]. Polymerisation on latent fingerprints is generally believed to be initiated by the moisture they contain [5]; hydroxyl groups in water are known initiators of cyanoacrylate polymerisation [4]. It has been suggested that the cyanoacrylate

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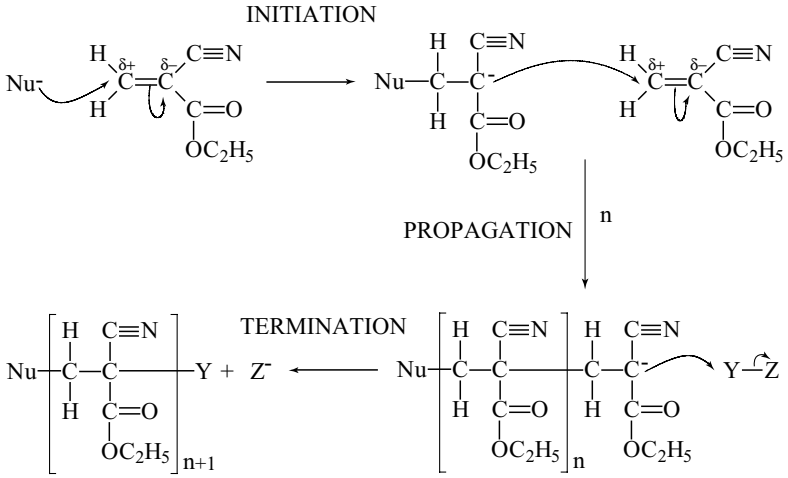

Fig. 1. Anionic polymerisation mechanism of ethyl-2-cyanoacrylate.

monomer also reacts with bases, lipids, fatty acids, amino acids and proteins present in the fingerprint material [6], and a study involving cyanoacrylate fuming of artificial fingerprints has shown that the presence of hygroscopic or highly basic salts increases the amount of cyanoacrylate polymer deposited on a fingerprint [7].

Cyanoacrylate fuming of fingerprints can be accomplished by simply placing the items bearing the latent fingerprints in a sealed chamber with an open vessel of cyanoacrylate monomer for several hours [8]. It is, however, more common for an acceleration technique to be used to speed up the process [6]. Acceleration techniques include circulating the air inside the chamber [6], increasing the surface area of cyanoacrylate monomer [9,10] available for exposure and creating a vacuum inside the chamber [11]. The most common method, however, is heating the cyanoacrylate monomer using either an electric heat source [6,12–14] or via an exothermic reaction on base-treated cotton pads [6,15]. The results of cyanoacrylate fuming are also improved by raising the relative humidity in the chamber to 70–80% during fuming [16]. Several of these techniques are often used in combination, e.g. in a commercially available fuming cabinet.

There are several processes by which drugs of abuse may be deposited in fingerprints. The scenario considered during this research was that of an individual handling a substance and then touching a surface, depositing a contaminated fingerprint. In an earlier paper we reviewed the application of Raman spectroscopy to the analysis of drugs of abuse [1]. Raman spectroscopy has also been applied to the analysis of drugs in polymeric drug delivery systems [17–19]; characteristic bands in the spectra of the drugs could be identified in the spectra of the mixtures by virtue of the differences in the Raman scattering intensities of the drug and polymer, which suggests that the detection of drugs of abuse beneath the polymer layer of a cyanoacrylate-fumed fingerprint is feasible. FT-IR spectroscopy has been used in the examination of cyanoacrylate-fumed fingerprints [20], however, the material of interest was the cyanoacrylate polymer, not the fingerprint beneath. The aim of this research was to determine whether Raman spectroscopy could be used to detect exogenous substances in a fingerprint beneath a layer of cyanoacrylate polymer. Because Raman spectroscopy is a non-destructive technique and requires no sample preparation, the fingerprint remains unchanged by Raman analysis, allowing its subsequent use for the identification of an individual.

2. Experimental

The drugs of abuse used in this research were codeine phosphate, cocaine hydrochloride, amphetamine sulphate, barbital and nitrazepam. Also included in the study were five non-controlled substances; caffeine, aspirin, paracetamol, starch and talc. These substances were selected due to their similar appearance to the controlled substances, which may lead to them being mistaken for drugs of abuse or used as adulterants. The samples were white, crystalline powders, with the exception of starch, which consisted of microscopic spherical granules.

Fingerprints doped with each of these substances were prepared on steel slides, which were cleaned with acetone before use and subsequently handled as little as possible. The hands were washed using ordinary soap and water and dried with a paper towel. Doped fingerprints were prepared by placing some of the drug of abuse or potential adulterant onto a clean surface and touching it with a clean finger in order to contaminate the fingertip with powder. Excess loose powder was brushed away using another finger. The substance was left on the finger for 30 min to allow sweat to accumulate on the fingertip, during this time nothing was touched with the contaminated finger. The contaminated fingertip was then pressed onto a clean steel slide in order to deposit a doped

fingerprint. Latent fingerprints which were not doped with any substance were also prepared. All fingerprints were then enhanced by cyanoacrylate fuming.

Cyanoacrylate fuming of fingerprints was performed in a custom-designed fuming cabinet with a heat source to accelerate monomer vapour production, air circulation and climate control at 30 °C and 80% relative humidity. The slides bearing the latent fingerprints were suspended in the fuming chamber and 0.5 cm^3 commercially available cyanoacrylate adhesive (RS Components Ltd., approximately 98% ethyl-2-cyanoacrylate monomer) was heated to 200 °C. After 30 min, excess cyanoacrylate monomer vapours were extracted from the chamber and the slides were removed.

Raman spectra were obtained from each of these substances to use as "reference" spectra for comparison with the spectra obtained from doped fingerprints. A small amount of each substance was placed on a steel slide and Raman spectra were obtained from individual crystals or granules, or clusters of small crystals. The dimensions of the particles examined were in the range 3–30 μm. Raman spectra were then obtained from polymer-covered single crystals/granules or clusters of small crystals in each of the doped, cyanoacrylate-fumed fingerprints.

All Raman spectra were obtained using a Raman microscope (Renishaw plc.) with 633 nm helium–neon laser excitation. The laser power at the sample was approximately 5 mW. A 50× objective lens was used, giving a laser spot diameter of 2 μm. Spectra were obtained for one 30 sec exposure of the CCD detector in the region 3600–100 cm^{-1} using the extended scanning mode of the instrument. Fluorescent samples were photobleached by exposing the sample to the laser for varying periods of time (10–40 min), depending on the intensity of the fluorescence. The use of photobleaching and the exposure time used is indicated where appropriate.

The spectral subtractions described below were performed using the static subtraction application of GRAMS/32 software (version 5.21, © Galactic Industries Corporation, 1991–1999).

3. Results and discussion

The cyanoacrylate-fumed fingerprints appeared white to the naked eye, although the polymer layer was often discontinuous and the fingerprint pattern appeared as a series of islands of white polymer. When viewed under a microscope, the white areas of the cyanoacrylate-fumed fingerprints appeared dark, and the polymer layer appeared "fibrous" in some areas and "granular" in others.

Solid particles were visible through the polymer layer, even in the cyanoacrylate-fumed non-doped fingerprints. These were assumed to be flakes of skin and other debris, as observed in the latent non-doped fingerprints described earlier [1]. Fig. 2 shows the Raman spectrum obtained from a polymer-covered area of a cyanoacrylate-fumed non-doped fingerprint. The polymer was slightly fluorescent at 633 nm. The spectral bands are tentatively assigned in Table 1.

The cyanoacrylate-fumed doped fingerprints were similar in appearance to the cyanoacrylate-fumed non-doped fingerprints, although they contained a greater number of solid particles due to the presence of the drug or potential adulterant. In the cyanoacrylate-fumed fingerprints it was more difficult to visually distinguish between the particles of dopant and the solid particles present in the fingerprint material, because the polymer layer made the particles indistinct. The particles were, however, easily distinguishable using their Raman spectra. Some dopant particles were not covered by cyanoacrylate polymer, either because they were

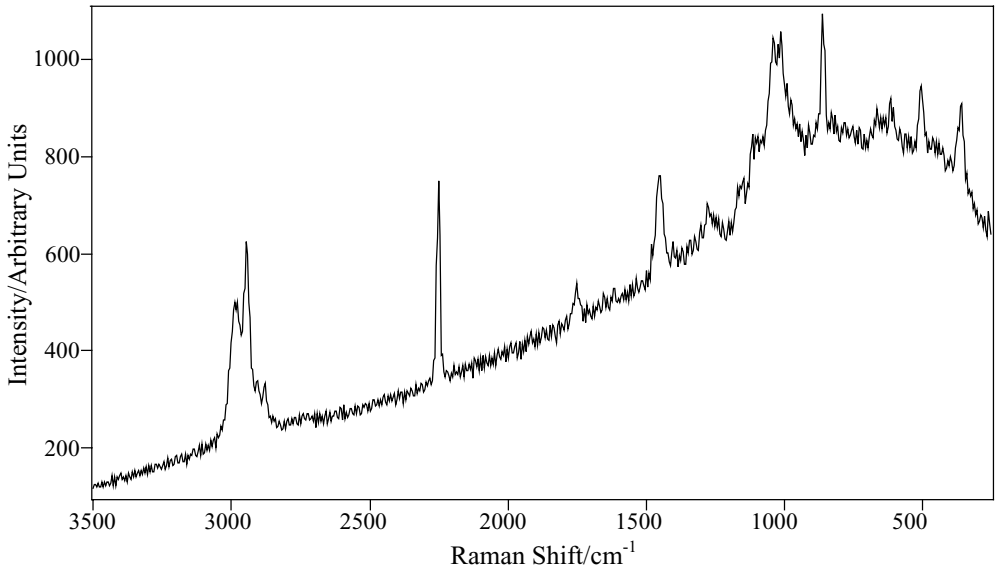

Fig. 2. Raman spectrum obtained from polymer-covered area of a cyanoacrylate-fumed fingerprint (after 10 min photobleaching).

Table 1
Tentative assignment of the Raman spectrum obtained from a polymer-covered area of a cyanoacrylate-fumed non-doped fingerprint (s = strong, m = medium, w = weak, v = very) [21]

Raman shift/cm^{-1} and relative intensity		Assignment
2981	s	C–H stretches
2945	vs	
2902	w	
2877	w	
2249	vs	C≡N stretch
1750	w	C=O stretch
1450	m	CH_3 deformation/CH_2 scissors
1395	vw	C–CH_3 deformation
1273	w	C–O stretch
1159	w	C–C skeleton stretch
1113	w	C–O stretch
1039	m	C–O stretch
1012	m	C–O stretch
859	m	C–C skeleton stretches
663	vw	
611	vw	
502	w	
360	w	

large and protruded through the polymer layer or because they lay between the fingerprint ridges, where no polymer was deposited. In this research, spectra were obtained only from dopant particles which were covered by the polymer layer, which made the visual location of particles for analysis more difficult.

The reference spectra obtained from the drugs of abuse and potential adulterants under normal sampling conditions showed that all of the substances studied could be distinguished from each other using their Raman spectra. The spectra obtained from the substances in cyanoacrylate-fumed fingerprints were, in general, of a similar quality to these reference spectra, and each substance could be identified. The fluorescence background was generally higher in the Raman spectra obtained from the cyanoacrylate-fumed fingerprints as a result of the fluorescence emission from the polymer. There were also slight differences in the relative intensities of some Raman bands between the reference spectra and those obtained from the same substance in cyanoacrylate-fumed doped fingerprints, which were attributed to differences in the orientation of the crystals with respect to the incident laser beam.

The principal difference between the reference spectra and those obtained from the cyanoacrylate-fumed doped fingerprints was the presence of cyanoacrylate polymer bands in the spectra obtained from the fingerprints. The C≡N stretching mode (2249 cm^{-1}) was the most prominent of these interfering bands, present in all spectra obtained from cyanoacrylate-fumed fingerprints, because it occurs in an otherwise unpopulated region of the spectra of the substances. Fig. 3 shows a representative example of the spectra obtained; Fig. 3(a) shows the spectrum of barbital in a cyanoacrylate-fumed fingerprint and Fig. 3(b) shows the spectrum obtained from barbital under normal sampling conditions. Fig. 4(a) and (b) show the corresponding spectra for codeine phosphate.

The relative intensity of the interfering polymer band(s) was dependent on the relative scattering cross-sections of the dopant and the cyanoacrylate polymer, and on the amounts of each in the area examined, i.e. the size of the dopant particle and the thickness of the polymer layer. The cyanoacrylate polymer was a weaker Raman scatterer than the substances studied, therefore there were no cases where the presence of the polymer bands prevented identification of the dopant.

The interfering C≡N stretching mode could easily be identified as arising from the polymer layer by comparison

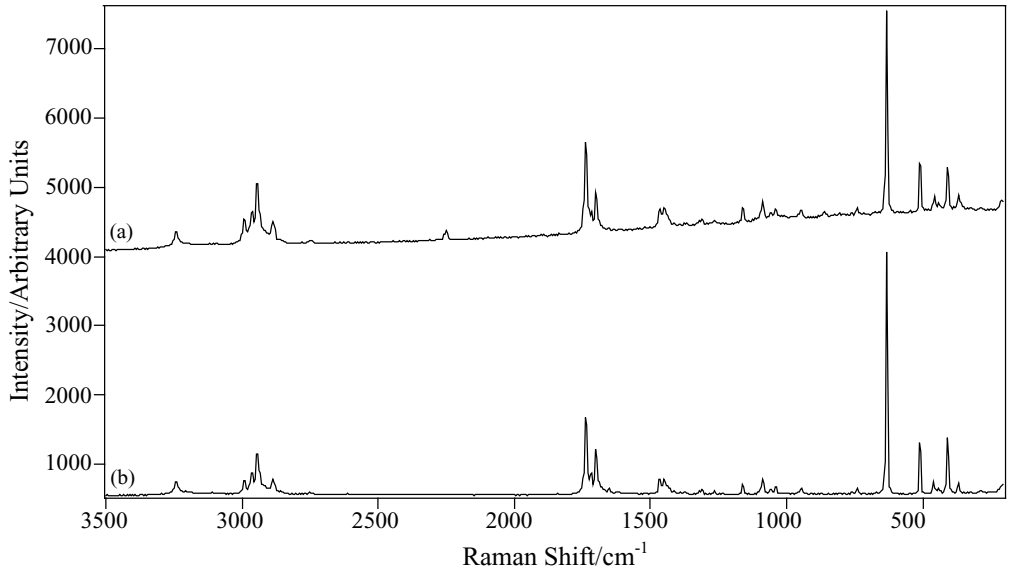

Fig. 3. Raman spectra obtained from (a) crystal in cyanoacrylate-fumed barbital-doped fingerprint and (b) barbital crystal.

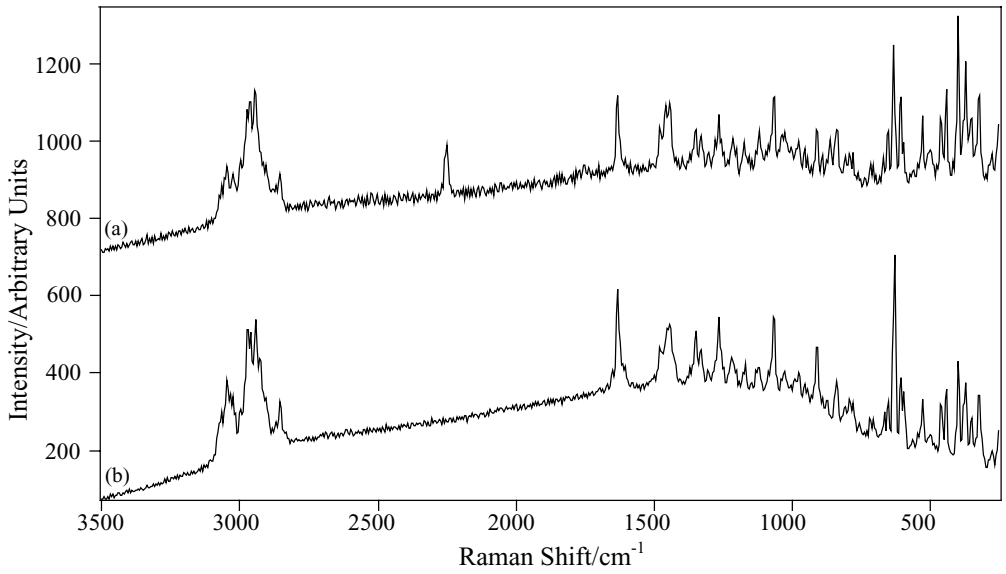

Fig. 4. Raman spectra obtained from (a) crystal in cyanoacrylate-fumed codeine phosphate-doped fingerprint and (b) codeine phosphate crystal (after 30 min photobleaching).

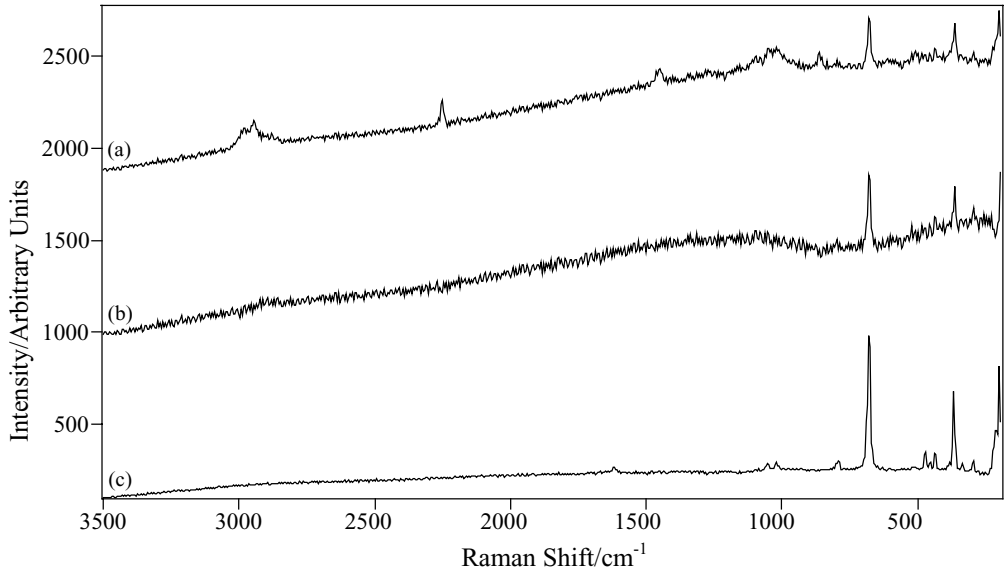

Fig. 5. Raman spectra obtained from (a) crystal in cyanoacrylate-fumed talc-doped fingerprint (after 40 min photobleaching); (b) same spectrum after subtraction of spectrum of cyanoacrylate polymer; and (c) talc crystal (after 15 min photobleaching).

of the spectra with those obtained from cyanoacrylate-fumed non-doped fingerprints. In cases where this was the only interfering band, it could be simply disregarded when using spectra to identify a dopant, and spectral subtraction was not necessary. This was the case for the majority of the substances studied, however, the full cyanoacrylate polymer spectrum was superimposed on the relatively featureless spectrum of talc. In this case, identification was aided by subtracting the spectrum of cyanoacrylate polymer from that of talc in a cyanoacrylate-fumed fingerprint. Fig. 5(a) shows the spectrum of talc in a cyanoacrylate-fumed fingerprint, Fig. 5(b) shows the same spectrum after subtraction of the spectrum of the cyanoacrylate polymer and Fig. 5(c) shows the spectrum of talc for comparison.

4. Conclusions

All of the drugs of abuse and potential adulterants studied were successfully detected in cyanoacrylate-fumed fingerprints using Raman spectroscopy. Spectra obtained from the dopant particles in cyanoacrylate-fumed fingerprints were of a similar quality to the “reference” spectra obtained from the substances under normal sampling conditions,

allowing identification of the dopant in each case. Spectra obtained from cyanoacrylate-fumed fingerprints had higher fluorescence background levels than the reference spectra, and also contained interfering Raman bands attributable to the cyanoacrylate polymer. Neither of these factors prevented the use of the spectra to identify the dopants in the cyanoacrylate-fumed fingerprints, however, it is beneficial to obtain a spectrum of cyanoacrylate polymer in order to determine which spectral bands can be discounted. The cyanoacrylate polymer spectrum can also be subtracted from the spectra of the polymer-covered substances to clarify the spectra.

The main difficulty in the detection of these drugs of abuse and adulterants in cyanoacrylate-fumed fingerprints was the visual location of particles of the dopant within the fingerprint, which was hindered by the presence of solid particles in the latent fingerprint material and masking by the polymer layer. This problem will increase as the amount of drug or adulterant deposited in a fingerprint decreases, although it is theoretically possible to detect a single crystal of the dopants studied in a cyanoacrylate-fumed fingerprint. The location of exogenous substances in cyanoacrylate-fumed fingerprints could potentially be simplified using Raman imaging or mapping.

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