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A study of the intermolecular interactions of lipid components from analogue fingerprint residues

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ABSTRACT

A compositionally simplified analogue of a latent fingermark was created by combining single representatives of each major component of a natural fingermark. Further modified analogues were also produced each having one component removed. The aim of this study was to investigate the intermolecular interactions that occurred within these analogue samples using Fourier Transform Infrared (FT-IR) Microspectroscopy. FT-IR microspectroscopy showed that the absence of squalene and cholesterol significantly restricted the interactions between the other organic constituents within the analogue samples. Investigating the intermolecular interactions of organic compounds within a simplified analogue solution could indicate corresponding interactions that occur within natural fingermarks. These potential interactions could go on to be the target of further investigation of latent fingermark chemistry, and ultimately contribute to a better understanding of the aging processes and degradation mechanisms that take place post-deposition.

1. Introduction

The dynamic nature of fingermark chemistry post-deposition is a complex process, yet of great interest to the forensic community. Numerous studies have examined the aging of fingermarks, the oxidation mechanisms that take place, both short and long term [1,2], and the resulting end products [2–5], [8], [9–12]. However, an in-depth understanding of fingermark degradation processes remains limited. Various studies have investigated the breakdown of key components within a fingermark such as squalene [1–3], [9,13], fatty acids [2–5,7], cholesterol [4], [9–11], [14] and amino acids [15,16], although very little research has studied the intermolecular interactions between these constituents and their impact on each other. Ultimately, a better understanding of these intermolecular interactions within a fingermark will allow for improved modelling of the fingermark aging process.

Cholesterol and its oxidation products have a significant effect on the decomposition of triglycerides and fatty acids [10], indicating that lipid stability is influenced by these intermolecular interactions within latent fingermarks. Auto-oxidation, oxidation in the absence of enzymatic catalysis, of cholesterol by free radicals and hydroperoxides to form oxysterols is an established degradation mechanism [10], although evidence of these oxidation products are yet to be found in latent fingermarks. It has also been shown that the decomposition of cholesterol can be accelerated by both triglycerides and fatty acids [11,17,18]. This suggests a form of positive feedback wherein cholesterol affects the decomposition of triglycerides resulting in a mixture of saturated and unsaturated fatty acids [6]. This increase in fatty acid concentration could then increase the rate of decomposition of cholesterol.

Squalene is an unsaturated steroid precursor that has received a great deal of attention in previous studies of fingermark degradation mechanisms and the aging of fingermarks [1–3], [9,13]. In latent fingermarks squalene degrades rapidly over time through direct oxidation and photo-oxidation mechanisms. Measurable reductions in concentration can be demonstrated within 24 h following deposition and it is almost undetectable after a week [1]. Although this degradation is dependent on light conditions as squalene can still be detected in fingermarks up to 33 days after deposition when stored in the dark [3]. During degradation various intermediary and complete oxidation products have previously been identified [1,2]. Of particular note is the formation of various hydroperoxides as squalene decomposes through direct oxidation. These hydroperoxides then undergo thermolysis with homolytic scission of the peroxide bond, yielding hydroxyl radicals [18]. Both hydroperoxides and free radicals, such as hydroxyl radicals produced from squalene degradation, would then impact cholesterol breakdown and impact the degradation of triglycerides and fatty acids.

This investigation utilized Fourier transform infrared (FT-IR) microspectroscopy, is a recognised tool for forensic research applications. Previous studies using IR techniques have successfully identified the key components of latent fingermarks [19–25]. FT-IR is ideally suited to

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the analysis of latent prints due to its non-destructive nature and specificity in identifying functional groups in organic compounds. Of particular relevance to this study FT-IR spectroscopy lends itself to studying the intermolecular interactions within fingermarks as a major contributor to IR band width is the strength of intermolecular interactions. Broader peaks being a function of stronger intermolecular interactions over a wider range and therefore a large number of energy states.

The antisymmetric and symmetric C—H stretch of the CH_2 groups at 3000–2850 cm^{-1} within a fingermark are not truly decoupled due to the slight variation in chemical environment of the differing species present. Intermolecular forces such as hydrogen bonding, dipole/dipole interactions, and London Dispersive Forces all combine to increase organic molecular interactions [26–32]. These interactions will dictate the rate of reaction and therefore the molecular decomposition in the presence of (in particular) long chain unsaturated species. These intermolecular interactions affect the range of vibrational modes of the C—H stretch region of CH_2 groups, increasing variations in bond distance and changing the spring constant [31–35]. The more intermolecular interactions occurring the broader the antisymmetric and symmetric vibrational modes and the coupling effect visible on the spectrum (Fig. 1). Fewer intermolecular interactions perturb the range of vibrational modes of the C—H stretch mode at 3000–2850 cm^{-1}, minimising the coupling effect of the antisymmetric and symmetric C—H peaks, and producing two distinct peaks at 3000–2850 cm^{-1}.

The aim of this study was to generate a simplified chemical analogue of a fingermark, comprised of a single representative of the major components, in order to better understand the interactions between these compounds. Studying these intermolecular interactions could ultimately enable a better understanding of their effect on the aging of fingermarks post-deposition. Once an acceptable analogue was developed and the IR spectra compared to that of sebaceous-loaded fingermarks, further analogues were developed, each with one component removed, and IR spectra were then obtained. This allowed assessment of how this removed component affected the interactions of the others.

Replicates of latent fingermarks have previously been developed for both research and commercial purposes [5,36,37] to provide a 'standardised' deposition model, and with more complexity than the analogue samples developed for this study. The objective of this study however was not to create a complete replicate of a latent fingermark, but to deliberately develop a much simplified composition that allowed for fundamental analysis of any critical intermolecular interactions that may occur. More complex replicates involving hundreds of compounds would have made analysis of specific intermolecular interactions near impossible, or at least far less conclusive. Another reason why such a simplified composition was used in this study was because, as stated previously [37], synthetic solutions can behave differently to natural fingermarks, and the more complex the solution the more potential there is for inconclusive variability in the results. A primary use for replicate solutions is for identifying effective fingerprint development reagents. The International Fingerprint Research Group (IFRG) have stated that replicates are useful for fundamental research and initial study of molecular interactions, but are not appropriate for optimisation or validation trials [36], and have warned caution about using (particularly) synthetic lipid solutions for direct evaluation with natural latent fingermarks, although this was specifically regarding fingerprint development reagents [38].

It is evident therefore that a degree of caution must be employed when using a simplified analogue solution to study the chemical interactions within fingermarks, and certainly no direct comparisons between the two can be made. This study therefore aimed to provide a general indication of the intermolecular interactions that *may* occur within latent fingermarks, and thus present a target for further work to look for these potential interactions in latent fingermarks and their impact on fingerprint degradation.

2. Experimental

2.1. Sample preparation

2.1.1. Analogue 'fingermark' preparation

The composition of the analogue solution was based on the principal compounds observed during previous studies of latent fingermarks [2,5,19,37,39,40]. Where there was significant variation in the literature regarding the concentration of a component, an average of all available data was used.

Sebaceous and organic eccrine secretions were selected for the analogue. The sebaceous secretions comprised a sterol, sterol precursor, a fatty acid, mixed triglycerides (100 mg triacetin, tributyrin, tricaproin, tricaprylin, tricaprin, all equal amounts by weight), and a wax ester. The eccrine secretions were composed from an amino acid and lactic acid. For simplicity, the most abundant compound within each family (i.e. amino acid, fatty acid, wax ester) was selected to represent the compounds within that family. For example, serine, being the most abundant amino acid [41–43] was selected to represent all amino acids, and palmitic acid, the most abundant fatty acid, represented all fatty acids [2,3] (Unsaturated fatty acids, although more likely to have an impact on intermolecular interactions due to a targetable functional

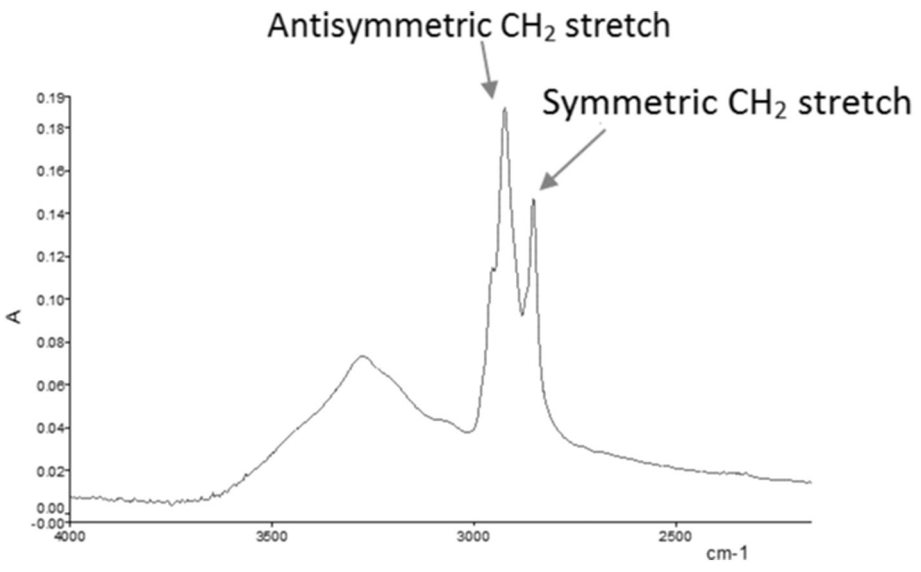

Fig. 1. Coupling effect of the antisymmetric and symmetric C—H stretch of CH_2 group.