Forensic Science International 254 (2015) 185–196

Contents lists available at ScienceDirect

Forensic Science International

journal homepage: www.elsevier.com/locate/forsciint

Fingermark initial composition and aging using Fourier transform infrared microscopy (μ-FTIR)

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ARTICLE INFO

Article history:
Received 30 March 2015
Received in revised form 29 June 2015
Accepted 7 July 2015
Available online 17 July 2015

Keywords:
Fingerprint
Kinetics
Dating
Spearman correlation
PCA
PLSR

ABSTRACT

This study investigated fingermark residues using Fourier transform infrared microscopy (μ-FTIR) in order to obtain fundamental information about the marks' initial composition and aging kinetics. This knowledge would be an asset for fundamental research on fingermarks, such as for dating purposes. Attenuated total reflection (ATR) and single-point reflection modes were tested on fresh fingermarks. ATR proved to be better suited and this mode was subsequently selected for further aging studies. Eccrine and sebaceous material was found in fresh and aged fingermarks and the spectral regions 1000–1850 cm^{-1} and 2700–3600 cm^{-1} were identified as the most informative. The impact of substrates (aluminium and glass slides) and storage conditions (storage in the light and in the dark) on fingermark aging was also studied. Chemometric analyses showed that fingermarks could be grouped according to their age regardless of the substrate when they were stored in an open box kept in an air-conditioned laboratory at around 20 °C next to a window. On the contrary, when fingermarks were stored in the dark, only specimens deposited on the same substrate could be grouped by age. Thus, the substrate appeared to influence aging of fingermarks in the dark. Furthermore, PLS regression analyses were conducted in order to study the possibility of modelling fingermark aging for potential fingermark dating applications. The resulting models showed an overall precision of ±3 days and clearly demonstrated their capability to differentiate older fingermarks (20 and 34 days old) from newer ones (1, 3, 7 and 9 days old) regardless of the substrate and lighting conditions. These results are promising from a fingermark dating perspective. Further research is required to fully validate such models and assess their robustness and limitations in uncontrolled casework conditions.

1. Introduction

Fingermark composition has been studied for decades because of its significance in the development of detection and enhancement techniques. This type of information is also required for research into fingermark aging and dating. Numerous analytical techniques have been used in order to gain more fundamental knowledge about initial fingermark composition. Gas chromatography mass spectrometry (GC/MS) [1–11], advanced mass spectrometry techniques (e.g., laser desorption, electrospray or atmospheric pressure chemical ionisation) [12–19], Raman spectroscopy [20–25] and Fourier transform infrared spectroscopy combined with a microscope (μ-FTIR) [26–47] have been applied in this context. Other studies have also been carried out in order to study the changes occurring in fingermark composition over time. While GC/MS has often been used for this purpose [1–4,7,9,48], the use of advanced mass spectrometry techniques [12,14], liquid chromatography coupled with mass spectrometry (LC/MS) [49] and μ-FTIR [36,41,43,45,46] have also been successful. Further details about these studies are summarised in a number of reviews [50–52].

All the above-mentioned techniques are useful in order to gain knowledge about fingermark composition. However, some of them are time-consuming, expensive and destructive. In fact, most chromatographic techniques (in particular GC/MS and LC/MS) require long sample preparation times and do not allow sample conservation after analysis, as fingermarks have to be extracted from their substrates using solvents. In contrast, spectroscopic techniques are faster to implement, cheaper and non-destructive, allowing the analysis of the same fingermark in its initial state and over time. This can be an asset for research into fingermark aging and dating. While a few studies have reported the use of Raman

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http://dx.doi.org/10.1016/j.forsciint.2015.07.022
0379-0738/

spectroscopy or Raman chemical imaging to analyse fingermark composition and contaminants, μ-FTIR is the most commonly reported spectroscopic technique for fingermark analysis. For fingermark samples, μ-FTIR is generally used in reflection or attenuated total reflection (ATR) modes, coupled with chemical imaging or not. The analysis of fresh fingermarks left on porous and non-porous substrates has been carried out by numerous authors, and better spectral quality has been reported for fingermarks left on metal and glass [26,27,33–37,45,53–55]. Further analyses have revealed that the main spectral features found in the fingermarks of various donors are very similar to each other, and correspond to esters and fatty acids. However, the relative amounts secreted from these two classes of compounds varied significantly between donors [45,55]. Differences in fingermark composition between children and adults were also noted [37,41,43]; residue from children contained far more eccrine volatile compounds (e.g., carboxylic acid salts, amino acids and proteins) than lipid compounds. While one study proposed the development of a regression model allowing the estimation of the age of a person between 4 and 68 years old based on these composition differences [37], other research found no significant age trend for people aged from under 20 years old to more than 50 years old (no precise ages were mentioned) [45]. This study also noted no significant variation in the lipid composition as a function of gender. Numerous studies have also been conducted to determine the ability of FTIR to analyse and identify extrinsic fingermark compounds, such as explosive residue [38–40,42,47], drugs [32,56] and other substances [36,47,56,57]. In the area of fingermark aging, only a few studies have been conducted using μ-FTIR. One study noted an overall decrease in the signal intensity of fingermark spectra over a 9-month period, probably due to evaporation of the fingermark deposit [45]. While this study also reported the greatest loss of lipid material during the first 3 months following deposition, no relevant classification of fingermarks based on age could be obtained using principal component analysis (PCA). Another study compared fingermark aging under ambient and vacuum conditions and observed that exposure to vacuum caused a significant reduction in the lipid composition of fingermarks, with the loss of tetradecanoic and pentadecanoic acid particularly noted [41,46]. The effect of temperature on the aging of fingermark residue (from room temperature to 80 °C) was also studied, and a general decrease in the absorbance of the main bands of lipid components was noted with increasing temperature; this was postulated to be the result of degradation to lower molecular weight compounds with subsequent volatilisation [36]. Two studies focused on children's fingermarks [41,43]. They noted that children's marks were very stable over time because salts were the most abundant compounds in them. Chemometric analyses using hierarchical cluster analysis (HCA) revealed that children's and adults' fingermarks were distinguishable for up to 4 weeks after deposition, based on differences in sebum composition.

All of these studies demonstrated that μ-FTIR has the ability to analyse the composition of fresh and aged fingermarks. Vibrational bands corresponding to eccrine and sebaceous compounds have been identified in fresh fingermarks, while some aging processes have been briefly described in previous studies. However, few studies have actually focused on fingermark aging using μ-FTIR. As a result, it would be particularly interesting to further investigate the capacity of μ-FTIR to gain more fundamental knowledge about fingermark aging processes. Furthermore, since μ-FTIR is a quick and non-destructive analytical technique available to most forensic science laboratories, it could also be an asset in the research and development of fingermark dating methodologies, as its implementation in practical contexts could easily be done at relatively low costs.

The aim of the current work was to use μ-FTIR to study fingermark composition from its initial stage (fresh fingermarks) and over time (up to 1-month-old fingermarks). The effects of two different acquisition modes (reflection and ATR) on the composition and variability of fresh fingermarks were first evaluated. Further, the influence of two substrates (aluminium foils and glass slides) and two different storage conditions (in the light and in the dark) on fingermark aging was investigated. As μ-FTIR data are highly multivariate (hundreds of variables in each spectrum), the technique lends itself to chemometric processing for various sample types [41,57–60]. In addition to visual observation of spectra, principal component analysis (PCA), correlation calculations and partial least squares regression (PLSR) were used in the current work to thoroughly assess the dataset structure. PCA and correlation calculations were used in a first step to assess the variability of fresh and aged fingermarks, to evaluate their similarity and whether they could be grouped by age. Based on these results, PLSR was then conducted in order to study the possibility of modelling infrared spectral data for potential fingermark dating applications.

2. Materials and methods

2.1. Sampling: donor, data sets and deposition protocol

This research was conducted according to a previously published formal framework for fingermark dating [61,62]. This framework considers it impossible to build one aging model that works for all donors' fingermarks because of the large inter-variability of fingermarks from different donors. This framework rather suggests the building of a new aging model for each person. Therefore, in this study, the fingermarks of one single donor were used to study their initial composition and aging. This donor was a Caucasian female aged 27, with a typical diet and wearing no cosmetics. Fingermarks were first deposited on aluminium foil (as available in Australian supermarkets) because of the perfect reflective properties of this surface; these were left to age for 0, 1, 3, 7, 9, 20 and 34 days. Fingermarks were also deposited on glass (Livingstone microscope slide glass Pathology Grade) and left to age for 0, 1, 3, 7 and 9 days. This enabled a comparison of the effects of using different substrates. Two different acquisition modes were tested (reflection and ATR) and fingermarks were stored in two different conditions (in the dark and in the light). For each age, four fingermark specimens were deposited two by two on two different days and six spectra replicates were acquired per specimen, for a total of 24 spectra per age. No more than four fingermarks were deposited per day. Table 1 summarises the acquired datasets.

During fingermark deposition, the following standardised protocol was used:

(1) The donor performed her tasks normally before deposition. The only condition was to avoid hand washing with soap within the last 45 min preceding the deposition.
(2) Both thumbs were gently rubbed on the forehead and the edge of the nose, mimicking a natural movement.
(3) The pressure and time of deposition were controlled. Each fingermark was deposited on a kitchen scale with an approximate pressure of 500 ± 100 g for 15 s.
(4) The donor performed her tasks normally for another 30 min.
(5) A second deposition from each thumb was performed.

After deposition, fingermarks were directly analysed (15–30 min after deposition) and/or stored according to the chosen storage conditions.