Monitoring compositional changes during storage of the lipid fraction of fingermark residues deposited on paper

Abstract

Characterising the changes in fingermark composition as a function of time is of great value for improving fingermark detection capabilities by understanding the processes and circumstances under which target compounds become degraded. In this study, gas chromatography-mass spectrometry was used to monitor relative changes in the lipids from latent fingermarks over 28 days. Principal component analysis of the relative composition of 15 lipids in fingermarks showed that fingermark age was a significant contributor to the variability observed in the data, but that inter-donor variability was also significant. This was attributed principally to changes in the relative amounts of squalene, which rapidly decreased in the fingermarks. It was also observed, however, that most fingermarks exhibited relatively small changes in composition during the first seven days, followed by more rapid changes up to 28 days. Significant inter-donor variation of both initial fingermark composition and the rates and nature of loss processes was observed, which was reflected in the relative projection of samples from different donors. Finally, samples stored with no exposure to light or airflow for 28 days were projected significantly closer to the samples analysed on the day of deposition than those exposed to light, due to the reduced photodegradation rate of squalene.

Keywords: Latent fingermarks, Lipids, Degradation, Gas chromatography–mass spectrometry, Principal component analysis

1. Introduction

In recent years, there have been several investigations into the changes in latent fingermark composition that occur as a function of time. The stated aims have included the development of a means to estimate the age of a fingermark for the purposes of criminal investigations [1-6], as well as obtaining a better understanding of the processes of fingermark degradation that affect their detection [1, 7], and the identification of compounds which remain stable over time (or are stable degradation products) as potential targets for fingermark development [1, 8-10].

The lipid fraction comprises the more durable portion of latent fingermark residue (compared to the water-soluble eccrine components), due to its hydrophobic and non-volatile nature. It is also highly subject to compositional changes, and so it is this fraction of latent fingermarks which has been studied most extensively in regards to changes in composition over time [4, 7, 9, 11-15]. Due to the inherent variability of fingermark samples, a timeframe of the loss processes of the lipids has proved difficult to characterise in detail; so far only broad trends have been identified [7, 9].

A recent study has explored the compositional variability of the lipid fraction of recently deposited latent fingermarks [16]. It is recognised that this initial composition is not necessarily representative of what is encountered in criminal investigations, as items may not be examined for latent fingermarks until several days to weeks after deposition [17, 18]. Latent fingermark composition begins to alter very soon after deposition, as evidenced by the quality of developed fingermarks of increasing age [1, 7, 11, 19, 20]. The lipid fraction of fingermark residue is considered to consist of two broad categories of ‘fragile’ (fatty acids and triglycerides) and more stable ‘robust’ components (thought to include large, insoluble proteins and lipoproteins) [21]. Physical developer, the most routinely used method for detecting fingermarks on wetted paper substrates, is thought to target a mixture of compounds, including the ‘robust fraction’, hence its ability to detect fingermarks that are several months old. Conversely, detection treatments that target the ‘fragile fraction’, such as the lipophilic dyes Oil red O and Nile red, perform comparatively poorly on fingermarks more than a few weeks old due to the

more short-lived nature of these compounds [22, 23]. Storage conditions, microbial activity, and the application of development reagents are all thought to impact upon the rate and types of changes that may occur [1-3, 7, 24, 25]. Environmental factors, including light exposure, substrate type, temperature, humidity, airflow and immersion in water, are known to play a significant role in the degradation rate; however, little is understood about their specific impact upon fingermark chemistry [3, 4, 8, 12, 13, 19, 26-29]. The initial composition of a latent fingermark also has great influence on its longevity [4, 7, 19].

Gas chromatography-mass spectrometry (GC-MS) has been utilised in several investigations into the degradation of fingermark lipids as a function of time and environment [4, 7, 9, 25]. A crucial aspect missing from these studies is frequent and consistent monitoring of compositional changes, to establish whether or not degradation rates are uniform under constant environmental conditions, and how degradation processes may vary between donors. Mong *et al*. analysed samples from all donors at infrequent intervals of 0, 10, 30 and 60 days after deposition (or 0 and 30 days in the case of children's samples) [9], while Archer *et al*. analysed samples at smaller time intervals of 1 – 12 days over 33 days, but samples from only up to three of the five donors were analysed at any one time [7]. The required more comprehensive and frequent analyses will generate large multivariate datasets that may give rise to issues in interpretation. Multivariate statistics can assist in extracting the maximum amount of information from such datasets, by enabling the exploration of patterns and trends in compositional changes over time in an objective and simplified manner [30].

This paper details an explorative investigation into the application of a previously described gas chromatography-mass spectrometry method in conjunction with multivariate statistics to examine the chemical changes undergone by latent fingermark lipids as a function of time [16]. Principal component analysis (PCA) was performed on this data to assess the effects of inter-donor variation and storage conditions on the types and rates of degradation processes, and therefore the projection of samples within a three-dimensional scores plot. This approach enables the determination of which compounds contribute the most variation over time, and hence are most likely to affect the detection of older fingermarks.

2. Materials and methods

2.1 Chemicals

Tetradecanoic acid (Aldrich, USA), hexadecanoic acid (Fluka Analytical), hexadec-9-enoic acid (Sigma–Aldrich, USA), octadecanoic acid (Aldrich, USA), squalene (Sigma–Aldrich, USA), cholesterol (BDH, UK), tetradecyl hexadecanoate (Nu-Chek Prep, Inc, USA), tetradecyl hexadecanoate (Nu-Chek Prep, Inc, USA), hexadecyl hexadecanoate (Nu-Chek Prep, Inc, USA), hexadecyl hexadecenoate (Nu-Chek Prep, Inc, USA), octadecenyl tetradecanoate (Nu-Chek Prep, Inc, USA), USA), octadecyl tetradecanoate (Nu-Chek Prep, Inc, USA), octadecyl hexadecenoate (Nu-Chek Prep, Inc, USA), hexadecyl octadecenoate (Nu-Chek Prep, Inc, USA), octadecyl hexadecanoate (Nu-Chek Prep, Inc, USA) and dichloromethane (Macron Chemicals, USA) were used as received. A set of standard solutions of the free fatty acids, squalene, cholesterol and wax esters were prepared as individual solutions in dichloromethane at 50 ppm. All standard solutions were stored at −20 °C before and after analysis to prevent degradation and solvent evaporation.

2.2 Sample collection and storage

Latent fingermark samples were collected from 8 donors on filter paper circles (25 mm qualitative filter paper, Grade 1; Whatman, UK). The donors were selected based on the chromatograms of fingermark samples provided in previous investigations [16], and also for the relatively small differences in age. A variety of strong and weak lipid donors were chosen, as well as some known to use cosmetic products regularly. A summary of the characteristics of the donor population is presented in Table 1.

Table 1: Summary of donor information

Sex	**Male (*n*)**	**Female (*n*)**
	4	4
Age (years)	**20 – 29 (*n*)**	**30 – 39 (*n*)**
	6	2
Recent skin product use (<12 hours)	**Yes (*n*)**	**No (*n*)**
	7	1
Total	**8**	

Donors were instructed to briefly rub the tips of their middle three fingers of each hand on their forehead or nose, and then press the fingertips of one hand gently to a filter paper circle for approximately ten seconds, followed by the immediate deposition of fingermarks from the other hand. Fourteen sets of sample replicates were collected in triplicate from each donor, during 3 sampling times over a period of 5 h, to provide a total of 336 fingermarks. A maximum of 5 sets of samples were collected at each sampling time, with a period of at least 1 h in between sampling times, to allow sebum to re-accumulate on the skin surface. Information regarding donor activity and handled substances was collected at each sampling time.

One set of samples from each donor was analysed by GC–MS on the day of collection (within 2 h of deposition) to obtain profiles of initial fingermark composition. Twelve sets from each donor were placed in uncapped 20 mL glass vials (Gerresheimer, Germany), with all replicate samples in each set stored in the same vial. Sample vials were placed in a tray and stored on a shelf in an office environment at room temperature (21–23 °C) with exposure to light and airflow for up to 28 days. An open vial containing clean filter papers was stored with the samples to provide analytical blanks for each analysis time. The final sample set from each donor were stored in glass vials that were completely wrapped and sealed in aluminium foil, and stored in a cardboard box adjacent to the open-topped vials. These samples were stored alongside the samples in open vials for 28 days.

2.3 Sample preparation

From the samples stored in open glass vials, one randomly selected sample set from each donor was analysed 2, 5, 7, 9, 12, 14, 16, 19, 21, 23, 26 and 28 days after deposition. The samples stored in foil-wrapped vials were analysed 28 days after sample collection. Extraction of fingermark residue from the filter papers was performed as described by Frick et al. [16]. Analytical blanks consisting of the stored, clean filter papers were prepared and analysed with each set of samples. Chromatograms from 329 samples were used in the PCA dataset due to there being no detectable amounts of target lipids in several samples from donor CB050 (all samples analysed 16 and 28 days after deposition, and one sample stored in a foil-wrapped vial).

2.4 Gas chromatography-mass spectrometry

Chromatographic analysis was performed using a Hewlett–Packard 6890N series GC interfaced with an Agilent 5975 inert mass selective detector as described by Frick et al. [16].

2.5 Data analysis

The data was pre-processed using Chemstation Data Analysis (Agilent Technologies, USA) by background subtraction of all chromatograms, followed by manual integration of 15 selected peaks in the total ion chromatograms (tetradecanoic acid, pentadecanoic acid, hexadecenoic acid, hexadecanoic acid, octadecanoic acid, squalene, C28:0 wax esters, C30:1 wax esters, C30:0 wax esters, cholesterol, C32:1 wax esters, C32:0 wax esters, C34:1 wax esters and C34:0 wax esters), which were identified as described by Frick *et al*. [16]. Replicates from each donor were treated as individual samples in the data matrix. Peak areas were normalised to the sum and autoscaled using Microsoft Excel. Principal component analysis (PCA) of the data was performed using the Unscrambler® X 10.4 software (CAMO Software AS, Oslo, Norway).

3. Theory

Difficulties in interpreting the volume of data generated by this study (329 chromatograms) can be overcome through the application of multivariate statistical methods, or chemometrics [31-33]. One of the most widely used such methods is principal component analysis (PCA) [34]. PCA simplifies large, multivariate datasets, such as chromatographic data, in an objective and reproducible manner [34-37]. This is achieved by reducing data dimensionality through the transformation of multiple variables from the original datasets into a reduced number of new, orthogonal variables known as principal components (PCs) [34, 36, 38-40]. The first PC explains the largest percentage of variance within the original dataset, and each subsequent PC describes a decreasing value of the remainder [35, 37, 38, 41]. Generally, only the first few PCs need to be examined to account for the vast majority of the variance within the original dataset. These PCs may then be used to construct a scores plot: a 2- or 3-dimensional visualisation of patterns and relationships within the dataset that may not be discernible by examination of the original variables [33, 37-39, 42]. Further interpretation of the data is achieved through comparison of the scores plot with the loadings plot, which indicates the variable(s) in the original dataset which have the greatest influence on each PC [39, 43-45]. PCA is often used in exploratory data analysis and in the construction of predictive models in conjunction with linear discriminant analysis (LDA) [40-42].

4. Calculation

4.1 Constant-sum normalisation

Chromatograms were normalised to the sum of all integrated peak areas ($\sum A_i$) to overcome variation in the amounts of residue deposited by donors due to differences in fingermark size or deposition technique, as well as instrument response:

$$Normalised\ peak\ area = \frac{A}{\sum_{i=1}^{n} A_i}$$

Donors often do not reproducibly deposit an impression of the entire fingermark pattern, which may contribute to reproducibility issues. Normalisation to the sum was compared to normalisation to the square root of the sum of squares, which can further reduce the influence of this variability on the PCA models. The scores plots showed no significant differences in projection. As such, the former method was used.

4.2 Autoscaling

Autoscaling was performed on all normalised peak areas in order to reduce the influence of the most abundant and variable compounds (i.e. squalene, hexadecanoic acid and hexadecenoic acid) on the dataset:

$$Autoscaled\ peak\ area = \frac{(x - \bar{x})}{S_x}$$

Here, x represents the normalised area of each peak in a sample, and $\bar{x}$ and S_x the corresponding mean and standard deviation across the dataset, respectively.

4.3 Euclidean distance

Distance plots were constructed from the datasets of each donor using the scores from the first two PCs as x, y coordinates for each sample. The centroid (i.e. the mean coordinates) of the day 0 replicates was used as the point of origin for each distance plot ($\bar{x}, \bar{y}$), and the distances between each of the samples and the centroid were calculated using the formula:

$$Distance = \sqrt{(x - \bar{x})^2 + (y - \bar{y})^2}$$

Distance plots were constructed using the average distance for samples from each day of analysis, with error bars showing the range.

5. Results and discussion

Major compositional changes with increasing sample age were found to be common to all donors with regards to the relative abundance of the 15 compounds of interest during the 28 day period. The most obvious change was the marked reduction in peak height of squalene, such that hexadecenoic acid and hexadecanoic acid became the predominant compounds (Figure 1). The precise timing and the extent of this change appeared to be dependent on the initial composition of the fingermark; samples collected from donors with a naturally low fatty acid to squalene ratio exhibited this change sooner than those from donors with a much higher ratio.

The rapid reduction of squalene is consistent with observations made by Archer *et al*. [7], with the exception that squalene was still detected in samples from 7 of the 8 donors after 28 days, whereas Archer *et al*. reported that squalene could not be detected in any samples stored under constant light after 20 days. The experimental conditions used by Archer *et al*. utilised constant, direct illumination to contrast with the effects of storage in complete darkness, whereas in this study, samples were stored under fluorescent office lights set to switch off when the office was unoccupied, thereby providing a more typical diurnal exposure. Samples were stored in an office environment rather than a laboratory to mimic the conditions on which fingermarks on documents or other paper substrates might commonly be stored, and to prevent contamination from reagents [9]. This difference in illumination conditions may account for the differences in squalene degradation, given that squalene undergoes photo-oxidative degradation [46].

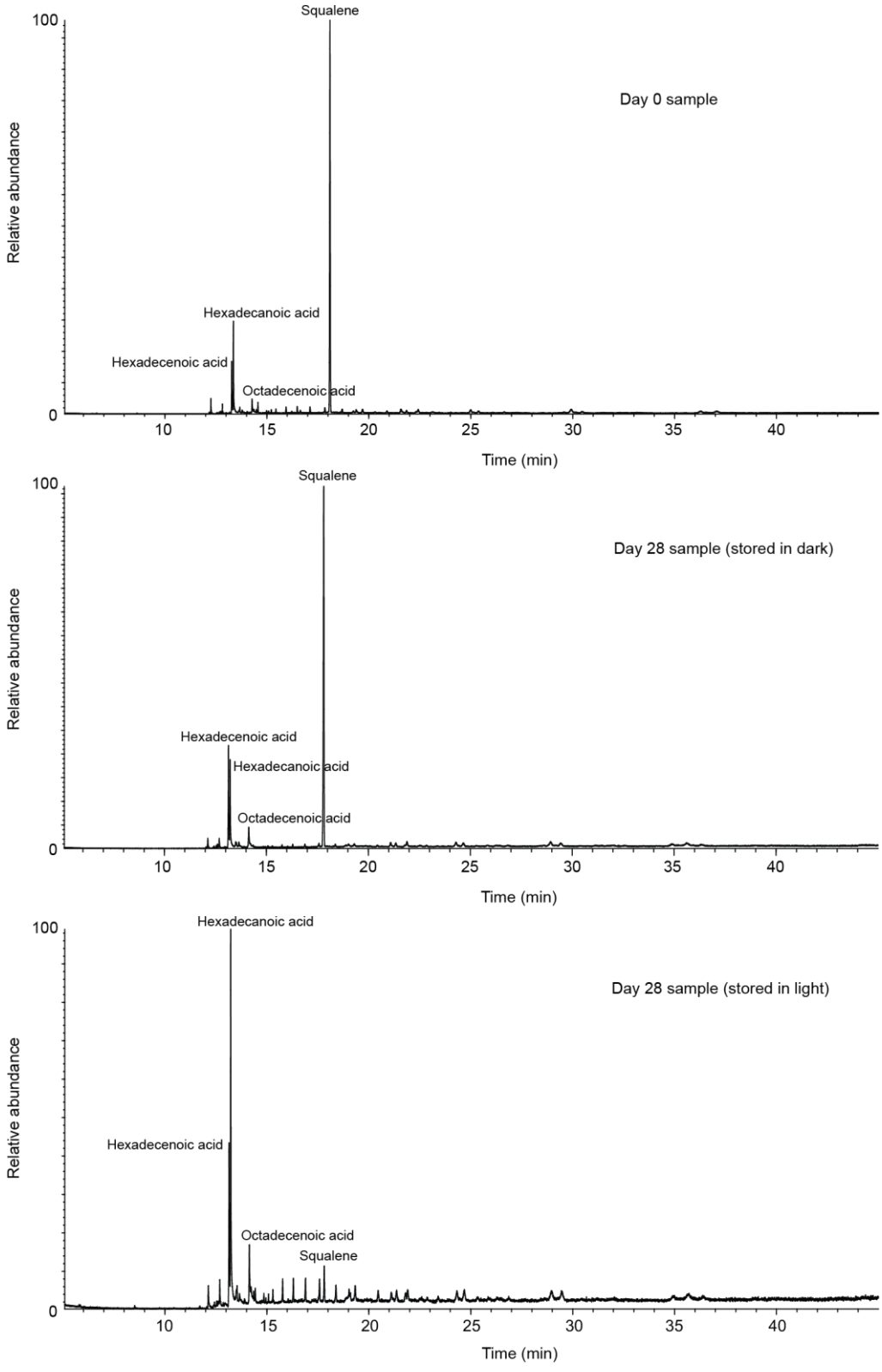


Figure 1: Total ion chromatograms representing changes in relative abundances of compounds detected in fingermarks from a single donor

The relative peak areas of the free fatty acids themselves were highly variable, with a general trend towards an overall increase at the end of the 28 days. The proportion of the peak areas of the

saturated wax esters to their monounsaturated counterparts appeared to increase. It is unclear from only a visual inspection of the chromatograms as to whether these represent actual compositional changes related to the age of the fingermark [9]. As repeated analyses of a sample over the 28 days was not possible, due to the destructive nature of the extraction and GC-MS method, it must be assumed that all samples from each donor have an identical initial composition as the sample collection strategy was designed to minimise intra-donor variation. However it must be borne in mind that variation may still be present. Numerous studies have shown that latent fingermarks can exhibit significant intra-donor variation, which impacts upon reproducibility. GC-MS studies into the ageing of latent fingermarks, particularly for age estimation, that utilise absolute quantification methods are frequently complicated by difficulties in obtaining reproducible, homogenous samples for comparative purposes [7, 9, 25, 47].

PCA of the total dataset (329 chromatograms) revealed that 83.04 % of the variance within the dataset was accounted for by the first 5 PCs (Figure 2). The scores plot constructed from the first 3 PCs (Figure 3) revealed that significant changes in composition occurred over the 28 days of the investigation. PCA of the normalised and autoscaled data was compared against PCA following normalisation to the sum only, which revealed that 99.23% of the variance within the dataset was accounted for by the first 5 PCs. While the cumulative variance of the autoscaled data was lower than that of the data processed using only normalisation, it was found that autoscaling prior to PCA enabled subtle trends in the dataset to become more apparent, as the influence of squalene, hexadecanoic acid and hexadecenoic acid were reduced.

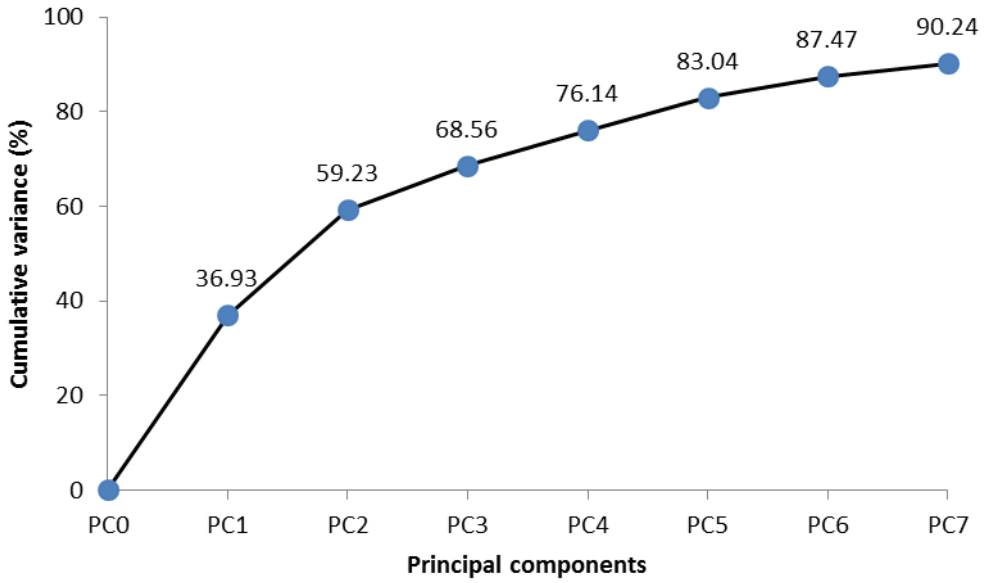


Figure 2: Scree plot depicting the variance the dataset accounted for by each PC

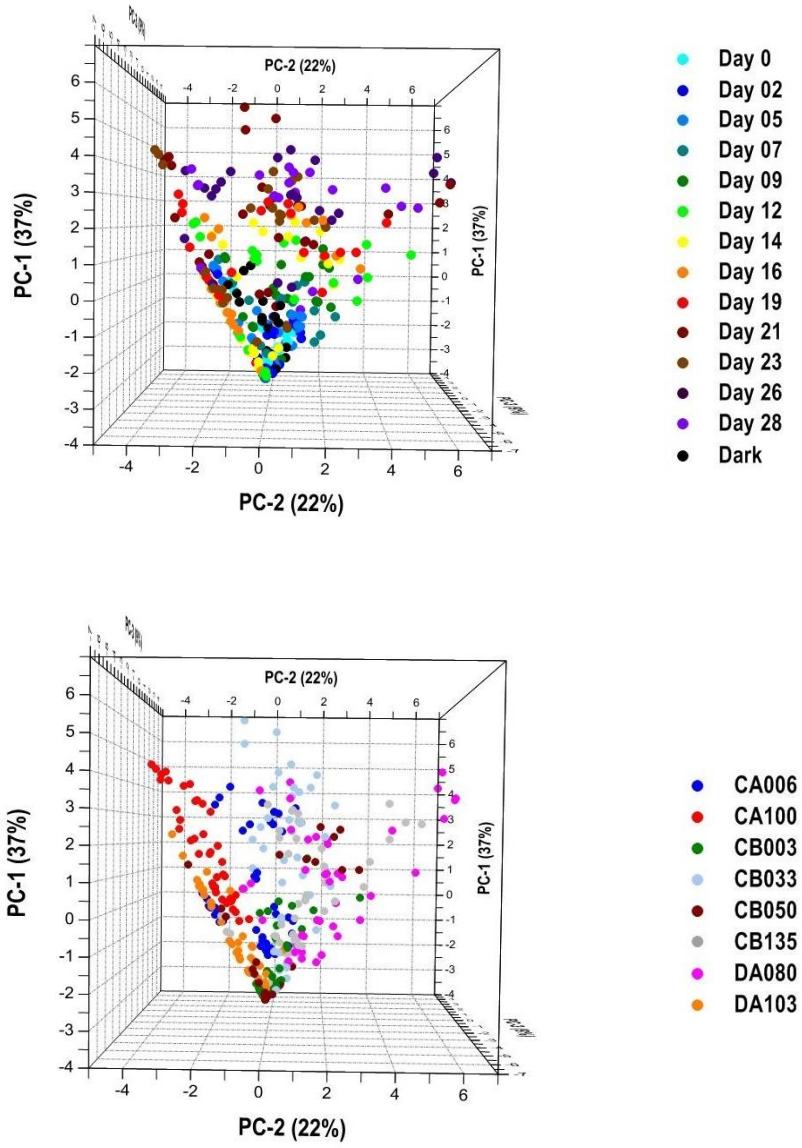


Figure 3: 3-dimensional scores plot generated from the first 3 PCs, demonstrating the distribution of fingermarks of increasing age collected from 8 donors. Samples are colourised by sample age in days (top) and individual donors (bottom)

Samples from all 8 donors were projected primarily along PC1, with scores increasing with sample age. The 'starting point' of this scatter (i.e. lowest scoring samples on PC1) was different for each donor, which is likely due to inter-donor compositional differences. Over the 28 day period, samples from each of the 8 donors also became scattered in different directions along the second and third PCs. With increased sample age, replicate samples were projected further away from each other, indicating that disparities between replicates became exacerbated by degradation processes.

The factor loadings for the first 3 PCs (Figure 4) were utilised to identify the compounds that contributed most to the variance within the dataset. The loadings plot for PC1 revealed significant negative correlation to squalene, as well as positive correlation to the free fatty acids and the wax esters of ≥30 carbon units. Hence, more recently deposited samples, which contained relatively large amounts of squalene and relatively small amounts of the fatty acids and wax esters, were assigned

negative scores on PC1, while older samples had increasingly positive scores as squalene concentration decreased.

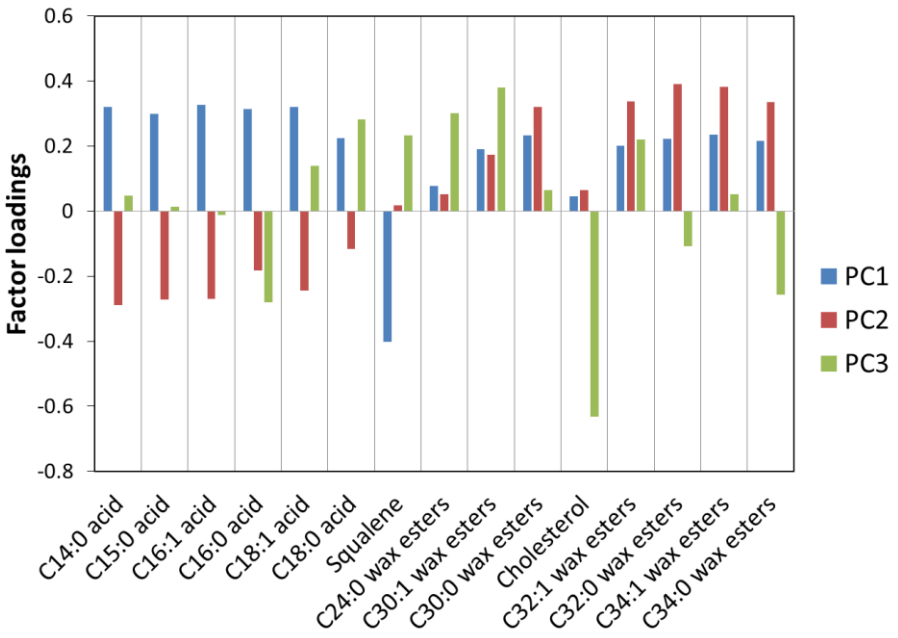


Figure 4: Factor loadings plots for the first 3 PCs

The relative amounts of squalene, fatty acids and wax esters are reflective of compositional changes in samples of increasing age, as well as inter-donor variation, as evidenced by the projection of the day 0 samples. Consequently, the total dataset comprising all 8 donors is not well suited to estimating fingermark age. The loadings plot for PC2 revealed significant negative correlation to the free fatty acids, and significant positive correlation to several of the wax esters. Examination of the scores plot, in comparison with the appearance of the chromatograms, indicates that sample projection along PC2 is influenced by a combination of sample age and inter-donor compositional differences related to the relative proportions of the more volatile components. For example, day 0 samples from donors CA100 and DA080 contained relatively high levels of free fatty acids and wax esters, respectively, compared to other donors. The loss of squalene accounts for the increasingly large difference in scores assigned to samples from the two donors over time, as this would increase the relative amounts of the other components. The loadings plot for PC3 revealed significant positive correlation to octadecanoic acid, squalene, and the C24:0 and C30:1 wax esters, some negative correlation to hexadecanoic acid and C34:0 wax esters, and a significant negative correlation to cholesterol. Due to the differences in projection of older samples between donors, it is unclear from examination of the scores plot as to whether sample distribution along the third PC is due to sample age, inter-donor variation or a combination of the two. Samples from most donors obtained scores of approximately 0 along this PC, while older samples from two female donors, CB050 and CB135 attained increasingly negative scores, indicating a larger proportion of cholesterol. The factor loadings of this PC may be influenced by exogenous contaminants in the form of cosmetic or other skin products.

The changes in sebaceous lipid composition over time has a marked impact on the ability to assign latent fingermarks to a particular individual or specific characteristics such as age or biological sex. With increasing age, samples from the total dataset are increasingly scattered, rather than forming separate groups. While the points for some donor's fingermarks may follow a clear linear trend primarily along PC1, such as donor CA100, those from others, such as donor CB135, are more scattered. The inconsistency of fingermark degradation poses enormous difficulties in establishing a

method of estimating fingermark age, but does demonstrate that lipid degradation can be expected to significantly affect any kind of classification model.

5.2 Effect of storage conditions on degradation rate

Storage conditions had a significant impact upon squalene loss mechanisms, as samples stored in foil-wrapped vials for 28 days did not exhibit the dramatic decrease of this compound seen in the samples stored in open vials for the same length of time (Figure 1). Samples that had been stored in foil-wrapped vials for the duration of the investigation were generally projected very close to the day 0 samples for each donor in the PCA scores plot (Figure 3). This observation is consistent with previous reports that the decrease in squalene concentration in latent fingermarks is accelerated by exposure to light, compared to those stored in dark conditions [1, 7]. That these samples were not projected separately from the day 0 samples along the second or third PCs further indicates that these PCs reflect inter-donor variation rather than degradation processes involving free fatty acids, cholesterol or wax esters. Due to time and practicality constraints, additional samples were not collected to further investigate the effects of sample storage conditions on sample projection throughout the 28 day period.

Difficulties in the detection of older fingermarks have often been linked to environmental conditions, as well as fingermark age. Whether or not a latent fingermark was recently deposited has been inferred from the quality of ridge development with powdering methods [6, 12], but this is a highly unreliable method as high quality fingermarks up to 6 months old may be detected in such a manner [12, 48]. It is shown here that the environment that a fingermark has been exposed to, including factors such as exposure to light, has a significant effect on the rate of degradation of certain compounds, which may account for some of these inconsistencies. The effects of other factors such as temperature and humidity have been speculated upon, but not as thoroughly investigated [7]. The effect of temperature is an important factor that needs to be explored further, particularly considering the substantial effect that higher temperatures have on the detection of children's fingermarks [29, 30]. Additionally, substrate type has been shown to have a marked effect on fingermark longevity, with faster degradation on nonporous substrates than porous ones [4].

5.3 Inter-donor variation

As discussed above, the disparate projection of samples from the 8 donors caused by inter- and intra-donor variation, as well as sample age, creates difficulties in interpreting the dataset in its entirety. The extent to which samples from each donor are projected along PC1 in the scores plot generated from the total dataset indicates that the rate of change in fingermark composition over the 28 day period is also subject to inter-donor variation. Subsequently, samples from each donor were treated as individual datasets to better enable examination of compositional changes as a function of time and storage conditions, independent of inter-donor variables.

When PCA was performed on samples from a single donor, the first two PCs accounted for 52–95% of the variance within each dataset. Data for one donor (CA006) is provided here as an example of the results discussed in this section. The scores plots constructed from the first 2 PCs (Figure 5), were broadly similar to the scores plot generated from the total dataset. Samples were projected primarily along the first PC, with older samples again attaining increasing scores. When fingermark degradation was examined on a per donor basis, other compositional changes became more evident. Examination of the scores plots revealed that samples from several donors appeared to exhibit a 'stable period'. This period lasted approximately 7 days for most donors, with only small changes in the chromatograms. However, this stable period was as short as 2 days and as long as 14 days for some

donors. This indicates that the extent and rate of lipid loss varies between individuals, which is in part a reflection of the initial composition. Other groups in the scores plots were formed by samples ranging from 21–28 days old from some donors, and additional clusters of samples of intermediate age were also observed. Samples that had been stored in foil-wrapped vials were generally projected close to samples analysed within up to a few days following deposition.

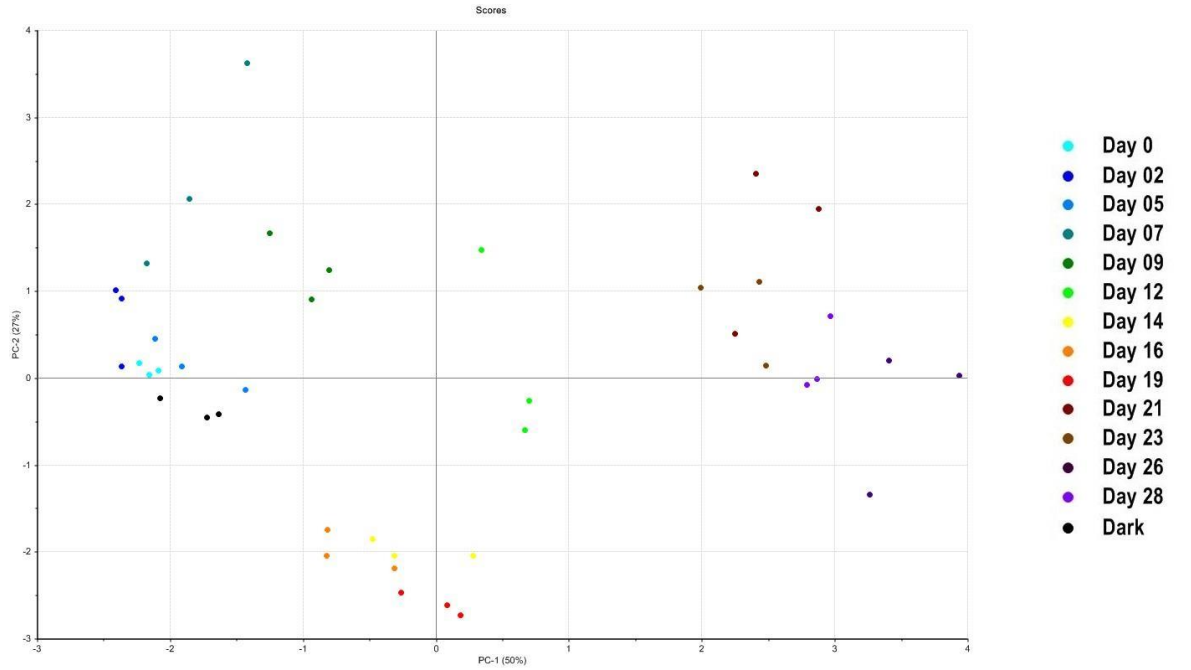
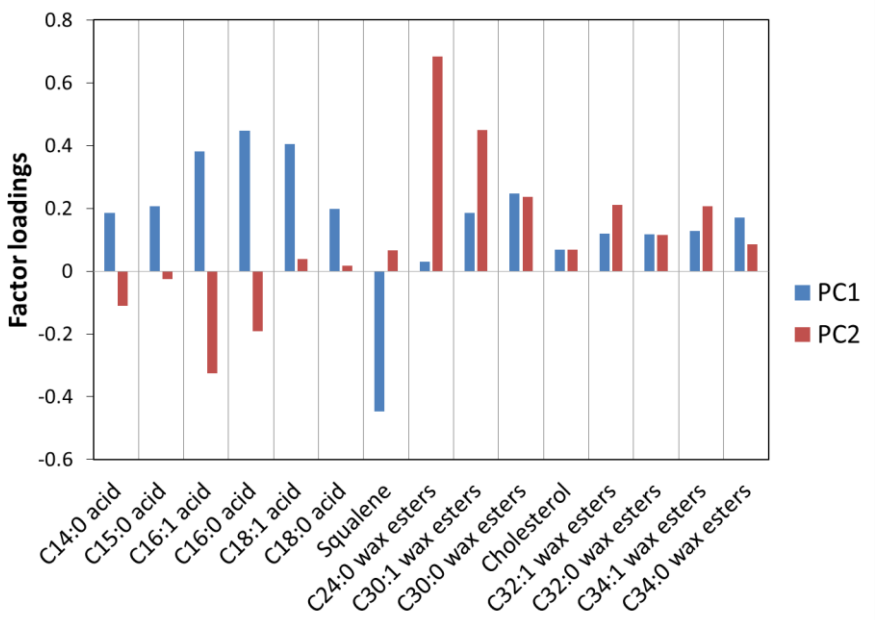


Figure 5: 2-dimensional scores plot generated from the first 2 PCs, demonstrating the distribution of fingermarks of increasing age of samples from donor CA006

The factor loadings for the first 2 PCs from the PCA analysis of samples from single donors were utilised to identify the key compounds contributing to the variance within each dataset (Figure 6). For all but one donor, the loadings plots for PC1 revealed significant negative correlation to squalene and positive correlation to several of the fatty acids and wax esters, emphasising the influence of squalene loss as a predominant degradation process over the 28 days of this study. The loadings plots for the second PC revealed different chemical changes between donors, mainly fluctuations in the relative amounts of free fatty acids and wax esters, with some influence from squalene and cholesterol in certain donors. In some donors, there appeared to be a relative increase in wax esters, in conjunction with increases and/or decreases in several fatty acids, particularly hexadecanoic and octadecanoic acids, over the 28 days. For four donors, there was no significant variation or clear trend in sample distribution along this PC. Archer et al. observed that the amounts of long chain fatty acids first decreased, and then increased in ageing fingermarks, and concluded that this may be indicative of two competing mechanisms of degradation, one acting on the fatty acids themselves, and another acting on wax esters or triglycerides [7]. It should be noted that wax esters and triglycerides were not detected using the methodology employed by Archer *et al*., making it difficult to be certain about the source of the fatty acids [7]. Conversely, Weyermann *et al*. reported no significant changes in fatty acid concentrations over 30 days [4]; however, these samples were stored in complete darkness.



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343 **Figure 6:** Factor loadings for the first 2 PCs of samples from donor CA006

344 The rate and nature of fingermark degradation, as well as differences in rate between donors, were
345 further investigated using Euclidean distance plots. Fingermarks from all donors that were stored in
346 the light followed a general trend of increased distance from the centroid (the mean coordinates of
347 the day 0 replicates) with time, which for 5 of the donors appeared to be linear (Figure 7). The samples
348 from the other three donors produced more exponential distance plots. It is unclear, based on these
349 data, as to why the nature of the rate of compositional change varied as such amongst the 8 donors.
350 The samples stored in the dark for 28 days were plotted a significantly closer distance to the centroid
351 than those stored in the light for the same period of time. In some donors this distance was virtually
352 indistinguishable from the day 0 samples, while in others there was a greater difference, but still much
353 closer to the centroid than the samples stored in light.

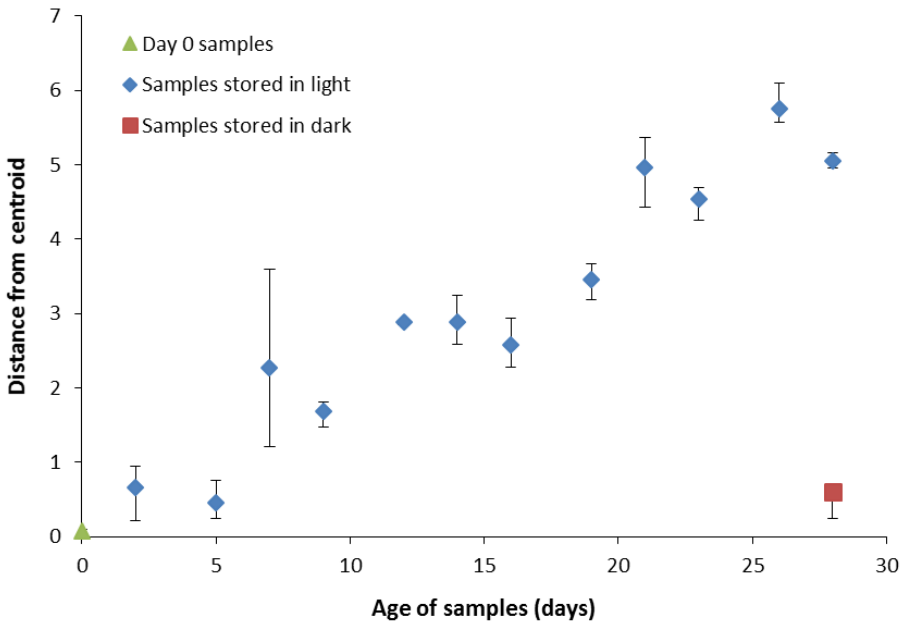

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Figure 7: Distance plot constructed from scores of first two PCs, depicting rate of total compositional change over time of samples from donor CA006

The impact of intra-and inter-donor variation is such that a ubiquitous timeline for latent fingermark degradation processes is difficult to establish. For example, compositional differences between donors may also have some impact on whether squalene can still be detected in a fingermark after a significant period of time [7, 9]. Girod *et al*. proposed that due to the significant variability in fingermark composition, and its resultant effect on degradation rates and processes, that individual-specific regression curves should be constructed as required to estimate fingermark age [25]. However, this approach is impractical in an operational context. Firstly, an identifiable fingermark needs to be obtained, so that the corresponding individual may be located and be present to provide fingermark samples in order to construct a degradation model [25]. Secondly, as demonstrated here and in numerous other studies, storage conditions can have a marked effect on degradation rate; therefore, a lack of knowledge regarding the environment in which a fingermark has been stored will complicate the comparison of the questioned fingermark to a degradation curve. Given the impact that intra-donor variation may have on degradation, even if the above factors can be accounted for, age estimation of latent fingermarks may still be prone to large uncertainties [7].

The main implication of these results is that the rates and types of changes in fingermark composition with age are influenced by numerous variables. Further studies are required to account for additional environmental factors to explore the impact of storage conditions on compositional variation. Exposure to varying degrees of light, temperature, humidity, immersion in water, airflow, microbial action, and presence of contaminants are only some of the factors which can affect lipid degradation. Such studies would assist in providing detailed information regarding fingermark degradation processes and possible new target compounds in degradation products.

6. Conclusions

The number of lipid species present in latent fingermarks presents a great challenge not only to research into compositional variation between individuals, but also regarding their degradation as a function of time and environment. Difficulties in obtaining reproducible samples from individual donors further complicated the distribution of older samples within scores plots. Although work to fully explore the potential of utilising fingermark composition for development of classification systems for donor traits, individualisation or fingermark age could be envisaged, such efforts would be complicated by the uncontrollable variables influencing fingermark composition. A preliminary comparison into the effects of storage conditions emphasises that storage conditions can have significant effects on the rate of degradation. While only a limited number of environmental conditions were explored, this reinforces that there are many challenges facing the development of detection methods that can be applied successfully to older fingermarks.

This study further bolsters the potential of analytical methods such as GC–MS to provide an accurate account of chemical changes associated with fingermark degradation over time. While the rapid decrease in the relative concentration of squalene when exposed to light and airflow presents a potential method for monitoring fingermark age, it also makes this compound unsuitable as a target for fingermark detection. Other components such as free fatty acids and wax esters may be better suited due to their persistence in samples up to 28 days old, regardless of light exposure. Longer-term investigations are required to establish the relative degradation rates of these compounds, in order to narrow the selection of candidate targets based on their durability. Similar studies targeted towards a larger range of constituents, such as non-volatile di- and triglycerides, as well as degradation products, will enable a more detailed understanding of the processes that affect fingermark detection.

Such information will greatly assist in the development of novel methods for the detection of older fingermarks.

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