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The Analysis of the Fatty Acid Content of Fingerprint Residues Using Gas Chromatography/Mass Spectrometry

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Thesis submitted
to the Eberly College of Arts and Sciences
at West Virginia University

in partial fulfillment of the requirements for the degree of

Master of Science in
Forensic and Investigative Science

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Abstract

The Analysis of the Fatty Acid Content of Fingerprint Residues Using Gas Chromatography/Mass Spectrometry

Ashley Cochran

One of the recurring issues in the practice of forensic science is human subjectivity, especially within the field of fingerprint examination. Smudged fingerprints at crime scenes that contain little to no ridge detail often cause problems for examiners who, in turn, are unable to make identifications or exclusions in the absence of DNA markers. In recent years, researchers have explored the chemical composition of fingerprint residues to either provide an alternative means for including or excluding potential donors, or to provide investigative leads. Research into the chemical composition of fingerprints has shown that it may be possible to determine sex, age, and race from residues that are left behind when a fingerprint is deposited on a surface. However, it is important to first ensure that residues deposited by one individual remain consistent over a period of time.

In this study, five different types of skin residues (natural, eccrine, face, neck, and groomed fingerprints) were collected from six participants over the course of 56 days to assess both intra- and inter-subject variability of the different sample types. Natural prints consisted of any substances that were on the participant's hands upon arrival at each collection event. Eccrine residues were collected after washing hands with soap and water. Groomed prints were collected after rubbing hands across the subject's own face and neck. The measured variables were the relative quantities of fatty acid methyl esters (FAMES), squalene, and cholesterol in each subject's residues. The fatty acid methyl esters were analyzed using a conventional gas chromatography/mass spectrometry (GC/MS) instrument. Canonical discriminant analysis (CDA) was used to classify the data into known grouping factors to determine if there were sufficient differences between the residues of different samples or subjects to enable classification between groups.

The results show that within an individual, 82% of the original grouped cases were correctly classified and 62% of the cross-validated grouped cases were correctly classified to the correct source of the sample. In other words, there are significant chemical differences between the five types of samples collected from an individual. Natural and eccrine residues generally contained the fewest compounds and in the lowest amounts and were not helpful for discriminating between individuals. Saturated fatty acids such as C16:0 and C18:0 were the most commonly observed compounds in the natural and eccrine residues. Groomed fingerprint residues contained more FAMES than the natural and eccrine residues, although not as many FAMES as the face and neck residues. Using leave-one-out cross validation, classifying subjects using a fixed sample type, like face or neck, provided better than 92% and 77% accuracy, respectively, even when including the intra-subject variability over a 56-day period. The results indicate that residues on surfaces like the face and neck are more highly

discriminating than eccrine secretions, the latter of which are dominant in fingerprint residues. Although freshly groomed fingerprints contain many of the compounds from the face and neck sebaceous secretions, the chemical composition of groomed prints is significantly different from natural fingerprints.

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I. INTRODUCTION

Fingerprint Morphology

Hairs, fibers, glass, drugs, DNA, and fingerprints are all types of evidence that are commonly encountered at crime scenes. Although no two crime scenes will contain the same types of evidence, certain types of evidence, such as fingerprints, are discovered more frequently than others [1]. Ever since the late nineteenth century, fingerprints have provided some of the most important pieces of evidence used in court to link a suspect to the scene of a crime [1].

Fingerprints are impressions that are deposited when friction ridge skin comes into contact with a surface. Both the palms of the hands and the soles of the feet are composed of friction ridge skin. According to the Scientific Working Group on Friction Ridge Study, Analysis and Technology (SWGFAST), friction ridge skin is defined as “a raised portion of the epidermis on the palmar or plantar skin, consisting of one or more connected ridge units” [2].

Fingerprints at Crime Scenes

There are three different types of fingerprints found at crime scenes: latent, patent, and plastic. Latent fingerprints, the most common type of fingerprint found at a scene, are prints that are invisible to the naked eye. Latent prints can be enhanced by different methods including, but not limited to, black powders, cyanoacrylate fuming, and ninhydrin [1]. Patent prints are visible to the naked eye and can be photographed without chemical or physical enhancement. These types of fingerprints are commonly made when an individual transfers a substance such as blood, ink, or dirt that was

previously on his or her hands to a surface. Plastic fingerprints are three dimensional prints that are created when a fingerprint is deposited on any type of pliable surface, such as putty, wax or casting materials [1].

Subjectivity in Fingerprint Examination

When fingerprints are processed, collected, and enhanced, they are analyzed by latent fingerprint examiners and compared to ten-print cards using a process termed ACE-V, discussed below. A ten-print card is an exemplar of a suspect's friction ridge impressions. Latent fingerprints and exemplars—the known prints of an individual—are run through the Automated Fingerprint Identification System (AFIS) Database [2]. This system attempts to mate a latent print found at a crime scene to a known print that has also been entered into the database.

AFIS revolutionized the field of fingerprint identification because it vastly expedited the process of identifying the closest potential matching exemplars, and it reduced the need for paper files that had been previously stored. The first AFIS algorithm was based on a list of minutiae that matched a specific location and orientation [1]. Minutiae are described as events along a ridge path, including bifurcations, ending ridges, and dots, as illustrated in Figure 1 [2]. As the algorithm advanced, the software improved and was able to locate these minutiae in the fingerprint, as well as account for issues such as distortion [1]. Eventually, the AFIS system was placed in law enforcement agencies [1].

Figure 1. Example of a ridge ending, bifurcation, and dot, respectively [3].

After fingerprints are run through the AFIS database, a match score between the most closely correlated prints is generated by the system. The latent fingerprint examiner must then determine whether or not a fingerprint originated from a particular source. In order to assess the details of the print in question, examiners complete the analysis, comparison, evaluation, and verification of the print, or ACE-V, for short. The implementation of the AFIS system throughout the country has greatly improved the efficiency of the latent print department.

The field of fingerprint identification is based on the principle that all fingerprints are inherently unique and persistent, yet this has never been proven [1]. A lack of objectivity in forensic science is an issue that has been repeatedly discussed within the community. In 2009, the National Academy of Sciences (NAS) brought some of the current issues in forensic science to light with the publication “Strengthening Forensic Science in the United States: A Path Forward” [4]. In this report, commonly referred to as the NAS report, the flaws of fingerprint examination, specifically subjectivity, were discussed. The authors mentioned that friction ridge analysis is not necessarily repeatable between examiners because the ACE-V method is not strictly quantitative—analysts must take both qualitative and quantitative measurements into account, making

this an extremely subjective field. Additional research has even shown that “experienced examiners do not necessarily agree with even their own past conclusions when the examination is presented in a different context some time later” [4].

Subjectivity in the field is a major problem that could lead to wrongful convictions when faulty fingerprint evidence is brought into a court of law.

In order to address this issue of subjectivity, there has been some research conducted on the error rates of fingerprint analysis in the past few years. The FBI completed a black box study to determine the accuracy of the examiners in making decisions. In this study, it was determined that of 169 latent print examiners comparing 100 fingerprint pairs, there was a 7.5% false negative rate and a 0.1% false positive rate [5]. There have been a few other studies with similar results, but there are still a lot of questions about the science of fingerprint examination that have been left unanswered [6].

The NAS report often compares the subjective fields such as fingerprint analysis to the more objective methods such as DNA analysis and gas chromatography/mass spectrometry (GC/MS). Both DNA analysis and GC/MS are considered to be the gold standards of their respective fields because they have research to support the documented error rates [4]. The methods used in these fields are based on the scientific method and have research and data to support the conclusions that are reached.

The Future of Fingerprint Analysis

The NAS report suggests that the areas of fingerprint examination, firearms examination, and trace evidence need to become more objective. In the past 20 years,

research has been conducted to try to advance the objectivity of forensic science as a whole, especially in fingerprint examinations.

In recent years, both touch DNA and bacterial genotyping have been used to obtain an individual's profile from fingerprint residues. A few studies have determined that it is possible to obtain a full DNA profile from fingerprint residues, but the success rate of the method depends on the substrate on which the print was deposited and the collection method [7, 8]. For example, Tozzo et al. acquired a DNA profile from only 44 of 80 latent fingerprints deposited on different substrates by collecting them with cotton swabs, but profiles were obtained from 61 of 80 prints when COPAN swabs were used [8]. With both of these collection methods, approximately 30% showed complete genetic profiles. As shown by this data, obtaining touch DNA from latent fingerprints is not always guaranteed. It is important to note that all of these studies were completed under laboratory conditions, so it is possible that the results may differ in practice.

Bacterial genotyping has been investigated as a possible method for fingerprint identification in addition to DNA profiling. All humans have microbes, specifically microflora, on their fingers, which are thought to be specific to the area in which the host resides [9]. Tims et al. studied these microflora and found that they are persistent within some individuals over the course of three weeks [9]. In the future, it is possible that these microflora could be used to help identify an individual, but at this point in time, the technique is not a realistic investigative tool due to the lack of research.

In addition to profiling for the purpose of identification, fingerprint residues have also been found to contain materials that are exogenous to the human body. Recently, a few studies have found that it is possible to detect the metabolites of certain drugs,

such as cocaine, in fingerprint residues [10-12]. This information is very important because the presence of metabolites means that the drug of interest passed through the individual's bloodstream and was not just merely in his or her possession. Advances like these could eventually lead to a non-invasive drug detection method [10].

Determining all of the compounds that could potentially be present in fingerprint residues could be very beneficial to the scientific community as a whole, such as for chemical biomarkers and environmental exposure.

Due to the abundance of fingerprint evidence at crime scenes, as well as the suggestions put forth by the NAS report, researchers have revisited the chemical composition of fingerprint residues as a means to identify an individual [13]. When a fingerprint is deposited on a surface, the residues that are left typically consist of compounds from eccrine, sebaceous, and apocrine glands. Eccrine glands are found only on the palmar and plantar surfaces, and secretions from these glands contain about 99% water. The remaining 1% of eccrine secretions consist of amino acids, sugars, and ions, such as potassium and sodium chloride [1]. However, it is very rare that a fingerprint residue consists of only eccrine secretions because the hands usually come into contact with the face and hair throughout the day. Research has found that individuals tend to touch their face approximately 23 times per hour—this accounts for the sebaceous residues that are found on fingerprint residues [14].

Sebaceous glands are found throughout the body, including, but not limited to, the scalp, face, and nose [1]. These glands help to lubricate the skin and hair and often originate from hair follicles before reaching the surface of the skin. The sebaceous

secretions are primarily composed of lipids such as fatty acids, cholesterol, and wax esters.

Apocrine glands are located in the axillary and pubic areas and their secretions are typically described as milky in appearance and are composed of cholesterol, carbohydrates, proteins, and iron [1]. A combination of secretions from these three glands is usually left behind when a fingerprint is deposited on a surface. Once a fingerprint is deposited at a crime scene, the residues can still be detected days, weeks, or even years later [1]. Table 1 provides a breakdown of the composition of the secretions from the eccrine, sebaceous, and apocrine glands.

Table 1. Composition of Glandular Secretions [1, 15]

Gland	Lipid	Percentage
Eccrine	Water	99%
	Amino acids, chlorides, metal ions, ammonia, lactic acid, lipids (trace amounts)	1%
Sebaceous	Glycerides	33%
	Fatty Acids	30%
	Wax Esters	22%
	Cholesterol Esters	2%
	Cholesterol	2%
	Squalene	10%
Apocrine	Glycerides and Fatty Acids	19.20%
	Wax Esters	3.60%
	Cholesterol Esters	0.09%
	Cholesterol	76.20%
	Squalene	0.20%

Research has determined that it may be possible to identify factors such as sex, race, and age from a fingerprint found at a crime scene [16-18]. The effects of aging on

a latent print and the relative abundances of the compounds within them have been studied as well [19-21]. In the future, information gathered from the chemical composition of fingerprint residues could be used in tandem with fingerprint examination to provide more information about the individual from which the print originated.

Chemical Composition of Fingerprint Residues

Previous research has demonstrated that it may be possible to use the chemical composition of fingerprint residues to narrow down suspects who may have committed a crime—a preliminary analysis of the fingerprint residue could potentially prove useful to investigators [22].

In 1997, Buchanan et al. used gas chromatography/mass spectrometry (GC/MS) to determine whether or not there are any significant differences between the fingerprint composition of adults and children. It was found that children tended to have higher levels of relatively volatile free fatty acids whereas adults had higher concentrations of less volatile long chain esters of fatty acids [13]. The authors concluded that the lipid composition differences explain why the fingerprints of adults tend to stay on surfaces longer than the fingerprints of children.

A follow up study by Antoine et al. was conducted over the course of four weeks using Fourier transform infrared (FTIR) microscopy [19]. Fingerprints from a father and son were collected in the beginning of the study and their prints were easily distinguishable because the lipids clustered differently between them. Although some degradation of the fingerprints occurred, the fingerprints of the adult and child could still be distinguished after four weeks of aging. The degradation was mainly due to the loss

of cholesterol, which had almost completely disappeared within four weeks [19]. These results, when found at a crime scene, could also give investigators clues as to when the fingerprints were deposited. According to the findings by Antoine et al., if cholesterol is not present the day after a crime was committed, the chemical signature of the fingerprint could indicate that it was deposited before the crime in question occurred [19]. However, it is important to note that the sample size used in this study was very small and that the experiment would have to be repeated for statistically significant results.

Other studies have also found compounds in fingerprint residues that degrade over time. Weyermann et al. studied the effect of time on fingerprint samples that were deposited on different substrates (porous, semi-porous, and nonporous) using GC/MS. In this experiment, participants contributed a mixture of eccrine and sebaceous secretions for analysis by rubbing their forehead before depositing a fingerprint on the desired surface [20]. Squalene, an intermediate metabolite in the synthesis of cholesterol (shown in Figure 2), was found to be the largest peak in the resulting chromatograms. After examining the different substrates on which prints were deposited, the concentrations of fingerprint residues were highest on Polyvinylidene fluoride (pvdf) and paper and lower on glass surfaces [20]. However, the authors failed to mention the confidence interval of their measurements.

Figure 2. Chemical structure of squalene.

Squalene could be detected after 30 days on porous surfaces like paper, but not on non-porous surfaces like glass. In other work, the amount of squalene decreases significantly when exposed to light [21]. Within 9 days of storage, squalene was not detected in the prints of some donors, yet when stored in the dark, squalene was still detected after 33 days. However, the observed concentration of squalene was much lower after 33 days in the dark than with fresh prints. Samples were collected on glass fiber filter paper twice a day from 5 participants to ensure that the samples that were obtained were consistent in nature [21]. All samples were analyzed using GC/MS.

Another recent study by Pleik et al. evaluated the degradation of fatty acids in fingerprint residues using GC/MS. They found that Δ^6 -Hexadecenoic acid and Δ^8 -octadecenoic acid, as well as associated degradation products, could be useful in determining the age of a fingerprint left on a surface [23]. This information could ultimately be useful in a forensic investigation to exclude a fingerprint that was not deposited contemporaneous with the predicted time that the crime of interest occurred.

Chemical Imaging, FTIR, and Raman

Other instruments besides GC/MS have also been used to examine the composition of fingerprint residues. Fourier transform infrared spectroscopy-attenuated total reflection (FTIR-ATR) has been used to chemically image the residues—it is possible to view the print and obtain the chemical information about it at the same time [24]. Research has also shown that μ -FTIR can provide analysts with data about the age of latent prints when stored in different conditions for varying lengths of time [25].

Other techniques such as Raman spectroscopy and Surface Enhanced Raman Spectroscopy (SERS) identified the composition of latent fingerprint residues through chemical imaging. [26]. Research has also shown that it may be possible to determine the contribution of eccrine secretions in a print based on the vibrational scatter signals [26].

Sex, Age, and Race Determination

It has been suggested that it may be possible to determine the sex, race, and/or age of an individual based on chemical composition of his or her fingerprint residues. Liquid chromatography/mass spectrometry (LC/MS) has been used to analyze the amino acid contributions of 20 individuals [18]. LC/MS was used in this study because GC/MS can be problematic, especially if the compounds are not properly derivatized. In the study by De Puit et al., fluorenylmethoxycarbonyl chloride-derivatization was used as a protecting group before injecting samples. The authors analyzed the relative amino acid ratios in the samples collected from the participants and found that not all participants contributed the same amino acids. Only two of the ten female donors contributed tryptophan, whereas six of the ten male participants contributed tryptophan. Differences between fingerprint residues have also be found in other studies when looking at the ratios of fatty acids (i.e. certain individuals have contributed cholesterol whereas others have not) [21].

Inconsistencies like these have been attributed to contaminants such as cosmetic products, moisturizers, or even the genetic makeup of the individual [27]. These are important issues that have not been examined in sufficient detail. Research

in these areas may help to explain some of the inconsistencies that have been noted across-the-board.

Another study used laser desorption/ionization time-of-flight mass spectrometry (LDI-TOF-MS) to determine sex from fingerprint residues [28]. Emerson et al. ultimately concluded this is not a suitable method for sex determination because most triacylglycerols (TAGs) present in the residue were unable to show specificity at a 95% or 97.5% confidence interval [28].

Matrix-assisted laser desorption/ionization mass spectrometry (MALDI MS) has also been used to determine the sex of an individual from the residue of a latent fingerprint that has been deposited on a surface. This study by Ferguson et al. found that it is possible to directly detect proteins and peptides in fingerprint residues to determine sex with 85% accuracy when coupled with multivariate modeling [29]. The detection of certain peptides was important in the profile for sex determination: SSL-29 and LEK-45 for males and DCD-1L for females [29].

Natural vs. “Groomed” Prints

The chemical composition of fingerprints varies frequently due to the amount of sebaceous secretions present on the individual’s fingers at the time of deposition. Some studies have only analyzed “groomed” prints, wherein the participants had to run their hands across their foreheads or through the hair before depositing fingerprints on a surface [20, 30, 31]. Other studies have used “natural” prints and asked participants not to wash their hands approximately 1 hour preceding sampling; the authors wanted to simulate the conditions of a suspect at a crime scene [30, 32]. However, it is important

to note that by asking participants not to wash their hands within an hour of sampling, that conditions are not truly representative of what could be found at a crime scene. Moreover, individuals do not always touch their face and hair before touching an object. In order to fully assess the differences in fingerprint residues that could be deposited by one individual, it is necessary that multiple types of samples be collected from one individual.

Variability of Fingerprint Residues

The variability of fingerprint residues over time has been previously studied: this variability may be due to the time since deposition, the diet of an individual, the substrate and conditions to which the fingerprint has been exposed, the sex of the donor, cosmetic products, age, etc. [22, 27, 33]. Due to some of the aforementioned issues, it is important to characterize the variability within an individual's fingerprint residues as well as determine the source of the lipids that are being deposited. Therefore, the purpose of this study was threefold: 1) to determine the variability of fingerprint residues within an individual over the course of several weeks, 2) to assess the relative proportion of endogenous (eccrine/sebaceous) and exogenous sources of lipids, and 3) to provide insight into potential biomarkers in fingerprint residues.

II. METHODS

Sample Collection

All samples were collected in accordance with West Virginia University IRB protocol regulations (protocol # 1605127273). Participants were consented prior to collection, and all information was made anonymous using an alphanumeric code. This study consisted of 6 participants, 3 males and 3 females, all between the ages of 23 and 30. Fingerprint residues were collected multiple times a week for a total of 56 days. (N=20 per sample type for each participant, total n=600.)

Example:

Day 1: 5 sample types x 6 participants = 30 samples/day

30 samples/day x 20 collection days = 600 total samples collected

*note that only 20 days over the course of the 56 days were sample collection days

Five types of samples were collected from each participant at each collection event:

1. *Natural*: consisted of any substances that were on the participant's hands upon arrival at each collection event;
2. *Eccrine*: collected after the participant washed his or her hands using hand soap (Softsoap®) and let hands air-dry;
3. *Face residues*: collected to evaluate the residues present on the face;
4. *Neck residues*: collected to evaluate the residues present on the neck;
5. *Groomed*: collected after the participant rubbed his or her hands across his or her face and neck.

The natural, eccrine, and groomed samples were collected using glass beads (7 mm diameter). After rubbing hands together, each participant was asked to roll 2 glass beads between the thumb, index finger, and middle finger of the right hand for 30 seconds before depositing the beads into a previously labeled glass vial. This procedure was repeated for the aforementioned three samples each day. Face and neck residues were collected using 3/4" x 1" cuts of aluminum foil and were each placed into a glass vial. All beads and foil cuts were handled using tweezers cleaned with methanol and hexane prior to each usage. Finally, participants were asked to complete a questionnaire regarding their activities from earlier in the day.

Sample Preparation

The sample preparation process was performed using three reagents and was adapted from previous research [34]. Reagent 1 consisted of 45 g NaOH, 150 mL methanol, 150 mL distilled water. Reagent 2 consisted of 325 mL of 6.0 N HCl and 275 mL methanol. Reagent 3 consisted of a 1:1 (V:V) mixture of hexane:methyl tert-butyl ether [34].

Saponification was performed by adding 1 mL of reagent 1 to each vial. Samples were capped, vortexed, and heated in a 115° dry bath for 5 minutes. Samples were removed from the bath, vortexed once again, and placed back into the bath for 30 minutes. After samples were cooled, 50 µL of a 190 ppm deuterated C16:0 fatty acid (in methanol) was added as an internal standard. Next, 3 mL of reagent 2 were added and samples were capped, vortexed, and placed into an oven at 90°C for 10 minutes.

Samples were removed from the oven and 1.25 mL of reagent 3 were added. Samples were lightly shaken for 5 minutes. The top layer containing the fatty acid methyl esters (FAMEs) was extracted and placed into a labeled GC vial. Vials were left uncapped and placed into a 90°C oven until the solvent evaporated. Samples were reconstituted with 200 µL hexane for analysis.

Gas Chromatography/Mass Spectrometry

All samples were analyzed using an HP 5977A Agilent Gas Chromatograph/Mass Spectrometer (GC/MS) with a 30 m HP5 column (Agilent). Parameters for the GC/MS were set as follows: the injection volume was 1 µL and the injector temperature was set to 250°C with a 1:20 split ratio. The oven was set at 100°C for 2 minutes, ramped to 280°C at 15°C/min, then held for 6 minutes. The carrier gas was helium with a flow rate of 1 mL/min and the transfer line temperature was set to 280°C. The mass spectrometer had a solvent delay of 2 minutes, and the scan range was m/z 50-550. These particular conditions were selected after performing optimizations for FAME analysis using the aforementioned instrument.

A blank of hexane, an n-alkane ladder, and bead/aluminum foil blanks were run with all samples, and samples were run in a random order. Resulting data was collected, extracted, background subtracted, and analyzed using Excel 2013 for Windows (Microsoft, Redmond, WA, USA) and SPSS 24 for Windows (IBM, Armonk, NY, USA). The internal standard co-eluted with a compound of interest, so a correction was performed to subtract the contribution of the internal standard from the peak area of the co-eluting peak in the TIC. The calibration curve was created using the ratio of

extracted ion m/z 77 (EIC) to the total ion chromatogram (TIC) of the internal standard peak ($n=13$).

III. RESULTS AND DISCUSSION

Major Compounds Observed

A total of 46 unique compounds were observed between the 6 participants over a total of 56 days ($n=600$). Figure 3 is an example TIC of face residues and shows some of the most commonly observed compounds across the 5 different sample types. The identity of the compounds, as well as their prevalence and relative abundances, differed within one individual, between individuals, between sample types, and between days.

Forty-six (46) commonly occurring compounds were tentatively identified in the 5 types of samples, and most of these compounds were fatty acid methyl esters (FAMES). Table 2 shows the average number of compounds identified in the residues recovered from each sample type for each person. Note that the natural and eccrine (post-hand washing) residues are strikingly similar. In general, natural and eccrine residues tend to contain fewer compounds than do residues from the face and neck or those deposited after grooming. After hand washing, hexadecanoic acid, methyl ester and occasionally methyl stearate were typically found, along with the internal standard. The soap was characterized for FAMES and contained low levels of several FAMES. Although C16:0 FAME was found in the soap, C16:0 was present in lower concentration than C13:0. The C13:0 FAMES was below the limit of detection in all of the eccrine residues, so we can be confident that any C16:0 present in any of the eccrine samples must have originated from the participants' hands, not from the soap. The purpose of the hand

soap was to simulate a real situation in which a perpetrator washes his or her hands prior to committal of a crime.

Across all participants, the face residues generally contain the greatest number of compounds out of all sample types. This observation may be due to multiple factors such as cosmetic products, lotions, moisturizers, hair products, and natural oils. Additionally, sebaceous glands are located on the face and neck, which accounts for the increased amount of FAMES that are present.

Figure 3. Chromatogram depicting the most commonly observed compounds in fingerprint residues during the course of this study. **1:** methyl tetradecenoate (branched 14:1 FAME, RT=7.369); **2:** tetradecanoic acid, methyl ester (C14:0 FAME, R=7.642); **3:** pentadecanoic acid, methyl ester (C15:0 FAME, RT=8.366); **4:** co-elution: internal standard (deuterated C16:0 FAME) + hexadecenoic acid, methyl ester (C16:1 FAME, RT=8.907); **5:** hexadecanoic acid, methyl ester (C16:0 FAME, RT=9.057); **6:** octadecenoic acid, methyl ester (C18:1 FAME, RT=10.192); **7:** octadecanoic acid, methyl ester (C18:0 FAME, RT=10.346); **8:** squalene (RT=14.387). Participant 4, day 17, face residues.

Table 2. Average number of chemical residues identified per sample type per participant (n=20 per sample type per participant).

Participant	Natural	Eccrine	Face	Neck	Groomed
1	5	2.1	21	10.7	11.2
2	6.9	4.6	19.3	12.7	11.6
3	3.1	1.6	13.0	8.1	8.4
4	4.3	1.7	11.8	7.8	8
5	4.9	2	12	9.2	6.2
6	3.7	1.8	11.5	8.1	7.3
AVERAGE ± 95% CI	4.6 ± 0.4	2.3 ± 0.3	14.7 ± 1.1	9.4 ± 0.7	8.8 ± 0.7

Deuterated C16:0 free fatty acid was used as an internal standard. After derivatization, the deuterated C16:0 FAME co-eluted with hexadecenoic acid, methyl ester (C16:1 FAME, RT=8.907), as seen in Figure 3 peak #4. The peak contribution of the internal standard in the co-eluting peak in each sample therefore had to be subtracted to provide the peak area for C16:1 FAME. To understand the relationship between the TIC for the internal standard and a fragment ion that is unique for the internal standard, the internal standard was analyzed at different concentrations in the absence of the co-eluting FAME (hexadecenoic acid methyl ester). Figure 4 shows the resulting correlation between the EIC peak area for the deuterated internal standard (using m/z 77) and the TIC peak area for the internal standard. By measuring the EIC peak area at m/z 77 in each sample, this curve could then be used to subtract the TIC contribution of the internal standard and provide the TIC peak area for C16:1 FAME in the sample.

Figure 4. Calibration curve created using the ratio of extracted ion m/z 77 (EIC) to the total ion chromatogram (TIC) of the internal standard peak ($n=13$) when the internal standard was run in the absence of the co-eluting C16:1 FAME.

PCA and CDA were performed with the corrected peak area for C16:1 and without the C16:1 peak to test the effect of this compound on the classification results. The leave-one-out cross-validation CDA classification results were typically no different or superior in the absence of the C16:1 peak, so this peak was left out of all the reported classification models.

Peak Identification

All TIC peaks were identified using the same process. The fragmentation pattern of each unknown was analyzed and compared to tentative NIST library matches. In most cases, the top 10-15 closest matches were all fatty acid methyl esters. To find the most likely identity, we focused on the presence of a molecular ion in both the unknown and the library match, as seen in Figure 5. Dominant peaks at m/z 74 and 87 in the mass spectrum identify the peak as a FAME. Because the methyl ester contains a

carbon that is not a part of the acyl chain, the acyl chain must contain one less carbon than the elemental composition would indicate. In the absence of major fragments at m/z 74 and 87, the same molecular ion could indicate a free fatty acid, which would have all of the carbons in the acyl chain. For example 15:0 FAME and 16:0 FA share the same molecular mass, but only the FAME gives dominant peaks at m/z 74 and 87. Finally, the retention indices of the unknown peak and the library match were compared. Retention indices of the unknown peaks were calculated using AMDIS software (NIST, Gaithersburg, MD) and compared to the retention indices in the NIST database. For example, the retention index (RI) of the unknown below, calculated in AMDIS, was 1825 and one of the entries for the RI for pentadecanoic acid methyl ester in the NIST library database is 1826 (for a similar DB-5 column) [35]. The combination of pattern match and retention time match provided a tentative assignment for all the structures proposed hereafter. Exceptions include seven common FAMES (e.g. C14:0, 16:0, 16:1, 18:0, 18:1), which were confirmed through the analysis of a standard mixture of fatty acid methyl esters run on the same instrument, using the same method.

Figure 5. Example of library tentative library match comparison process. The molecular ion present in both spectra is at m/z 256.

Intra-Subject Variability

Intra-subject variability was assessed during this study to determine whether or not the fingerprint residues deposited by an individual remain consistent between days, weeks, and months. In a forensic context, it is crucial that fingerprint residues remain unchanged so that a crime scene print can be linked to a suspect, especially when weeks have passed between the fingerprint deposition and the exemplar collection. Factors that could potentially influence the deposited fingerprint residues include hormonal changes, health changes, changes in skin biota, contamination from external sources, and touching of the face, neck, or any surfaces containing fatty acids or other substances.

Figure 6 shows the similarities and differences between residues deposited by participant 1 on day 2 and day 11 of this study. The variability between sample types is also visible, meaning that natural fingerprint residues do not necessarily mimic groomed fingerprint residues. Differences between sample types are important from a research perspective if one wishes to replicate crime scene conditions; in other words, asking an individual to “groom” their fingers prior to deposition may not be chemically equivalent to a natural print.

Figure 6. (a-e) Fingerprint residues from participant 1 collected on day 2. (f-j) Fingerprint residues collected from the same participant 9 days later on day 11. Note the major similarities and minor visual differences between the days.

Furthermore, all sebaceous residues (i.e., face, neck, etc.) do not necessarily contain the same compounds or the same ratio of compounds. There are two likely explanations as to why there are differences between natural samples and groomed samples: 1) low concentration; i.e. the compounds may be present on the fingers in the same ratio, but are below the limit of detection, and/or 2) the residues deposited differ based on differences in chemical transfer interactions between an individual's face, neck, and his/her fingertips.

Visually, differences in sample type tend to be quite apparent in Figure 6—these differences are supported in Table 2 by the average number of compounds found in each sample type. For every sample, the relative peak area of each compound was normalized to the total area under the TIC. The fractional peak area of each compound was then used as a variable for multivariate analysis.

Prior to multivariate analysis, ANOVA was performed to assess the variance of data with two different grouping factors: participant and sample type. The fractional peak areas at different retention times were used as the dependent variables. When participant ID was used as the grouping factor, all sample types were grouped together to simulate a real-life scenario when the origin and composition of the residues left behind are unknown. In other words, if a perpetrator has recently rubbed his forehead or washed his hands before leaving a fingerprint at a crime scene, the model used would have to take into account all possible residue contributions from a particular individual. However, this data set failed the homogeneity test, which is a requirement for ANOVA, so results were not included.

The participant data was then separated into different sample types. However, the data set still failed the homogeneity test, so the results were not included. Failure of the homogeneity test implies that residues differ from day to day within an individual in a non-random manner. In this data set, many compounds were close to the threshold value (limit of detection), so they were either absent or present above a certain value. The effect is a bimodal distribution for the low-abundance or low-frequency compounds.

Canonical Discriminant Analysis (CDA) was used, as shown in Figure 7a, to examine the factor of intra-subject variability of participant 1. CDA provided two discriminant functions with eigenvalues greater than 1, which together explained 90.5% of the total variance (4 discriminant functions total to explain 100% of variance). Figure 7 shows a bivariate plot of the first two discriminant functions and establishes that the residues do differ depending on the source (face, neck, etc.). Although some overlap is apparent, the different sample types generally cluster together. It is intriguing, yet not surprising, that the samples collected after washing the hands (eccrine) cluster the closest because these samples typically provided only 1-2 detectable compounds. The groomed samples appear between the eccrine, neck, and face samples, which is to be expected because the groomed samples contain residues from all three sources.

Figure 7b plots the correlation values of each variable with the first two discriminant functions. Correlation values are generated in SPSS via a structure matrix and represent the pooled within-groups correlations between discriminating variables and the canonical discriminant functions. The structure matrix can assist in determining whether or not a specific variable is useful for predicting group membership [36]. The correlation values are calculated using the following equation

$$R = S_{11}^{-1} W_{11} V$$

where R is the correlation value of the discriminating variable and the canonical discriminant function, S_{11}^{-1} is the inverse of the first q rows (number of variables selected) and columns of S , W is the within-sample matrix of sums of squares and cross products, and V is the matrix of eigenvectors [37, 38].

The structure matrix shows that C16:0 FAME (RT=9.057) correlates very strongly with both the eccrine and natural residues. C16:0 FAME correlates the strongest with the eccrine residues because it is usually one of the only, or the only, compound present in the residues after washing the hands. C16:0 FAME is therefore the most abundant compound in natural fingerprint residues, which explains its very strong correlation. The FAMES C14:0, C15:0, C18:1 and squalene (RT= 7.642, 8.366, 10.192, and 14.387, respectively) are all very positively correlated with Function 1 and negatively correlated with Function 2. These compounds are most abundant in the neck sebaceous secretions, but are also present in the face and groomed residues. They are least abundant in the natural and eccrine samples. A few studies have found similar compounds in sebaceous fingerprint residues, and one particular study by Frick et al. also observed that hexadecenoic acid and squalene both contribute to variation in

fingerprint residues [21, 22, 27]. As seen in Figure 7, face residues are more correlated with a branched C14:1 FAME and a branched 15:1 FAME (RT= 7.369 and 7.95, respectively). Although some variability is present between the sample types of one individual, these residues could be useful in a forensic context if the within-group variability of one participant is smaller than the between group variability of the other participants.

Both original classification and leave-one-out cross-validation were performed during the analysis. The original classification model was built using *a priori* information, whereas the performance of the model was assessed using leave-one-out cross-validation. For participant 1, the classification rate for the original grouped cases was 79% and the cross-validation classification rate was 62%. All canonical discriminant functions were used for classification purposes, although only CD1 and CD2 are plotted.

The classification rates were also evaluated for the other 5 participants using CDA. Table 3 summarizes the number of original cases classified correctly and the number classified correctly using leave-one-out cross-validation. In all cases, the original classification rates are higher than the cross-validated rates because of the biased nature of the classification algorithm. Correct classification rates range from 52%-62% for the cross-validated cases. The classification model rarely confused the face samples with any other sample types, but the groomed prints were frequently misclassified as natural or eccrine, and vice versa.

Figure 7. a) Canonical Discriminant Analysis (CDA) showing the ability to classify the sources of residues by sample type for participant 1. Five different sample types were collected over the course of 56 days. Within-sample-type samples tend to cluster together; however, they do not separate completely. $n=120$. b) Structure matrix correlation values. Of the original grouped cases, 79% were correctly classified, and 62% of cross-validated grouped cases were correctly classified.

Table 3. Summary of intra-subject variability classification results.

	Participant					
	1	2	3	4	5	6
Original	79%	84%	76%	80%	76%	66%
Cross-Validated	62%	59%	62%	56%	61%	52%

Inter-Subject Variability

Inter-subject variability is another factor that was assessed in this study. Examples of the variability between participants can be seen in Figure 8. Previous literature has noted the potential to identify individuals based on the chemical composition of fingerprint residues [18, 21, 27, 29]. For identification to be possible, an individual's residues must cluster separately: i.e. the within-person variance must be smaller than the between-persons variance. Figure 9 shows the variability between subjects. Whereas the within-subject samples do seem to cluster, they do not classify based on participant because of the large within-person variance. This result is not ideal from a forensic perspective, but it is promising for a number of reasons.

First, using leave-one-out cross-validation, 53% of the cases were correctly classified. Although the error rate is unacceptably large, this method of classification for an unknown sample would still be three times more effective than guessing (1/6, approximately 17% chance of guessing correctly). Secondly, the result proves that there is a potential for this type of analysis—despite the fact that it will not be possible to positively identify an individual, such chemical analysis is likely to provide exclusions (with caveats regarding possible external contamination).

The data in Figure 9 summarizes all of the data collected during the course of this study. The within-participant variance is larger for all five sample types combined than it would be for one sample type alone due to variability between sample types. Some sample types are more discriminating than others for classification purposes. For example, Figure 10 shows the clustering of the face residues for all 6 participants using CDA.

Although there was no natural clustering of the data with principal component analysis (PCA results not shown), CDA was able to classify the face residues based on participant ID (Figure 10). One hundred percent of the original grouped cases were correctly classified, and 92.5% of the leave-one-out cross-validated grouped cases were correctly classified. The within-face-residue variance in Figure 10 is much smaller than with all the sample types combined (Figure 9), which is a reflection of the large between-person to within-person variance for facial sebaceous secretions.

In Figure 10, participant 3 is separated to a large extent by discriminant function 1, whereas the other subjects are separated more effectively by discriminant function 2. The correlation structure matrix in Figure 10b shows that the peak at 9.384 minutes is at a much higher concentration for participant 3 than the other participants. Visual inspection of the chromatograms for the facial samples for participant 3 shows that this peak is indeed larger than for the other participants. The peak at 9.384 minutes is identified as a branched C17:0 FAME. The structure matrix also shows that participant 5 correlates with the peak at 8.65 minutes, which is assigned as a branched C16:1 FAME. Finally, C15:0 FAME (RT=8.366) correlates more strongly with participant 6 than the other participants.

Figure 8. Example TICs of groomed fingerprint residues from all six participants collected on the same day. Note the visual similarities and differences between participants.

Figure 9. Canonical Discriminant Analysis (CDA). Samples classified by participant ($n=600$). All 5 sample types included per participant. Of the original grouped cases, 59.8% were correctly classified, and 55.7% of cross-validated grouped cases were correctly classified.

Figure 10. a) CDA with face residues classified by participant. b) Structure matrix correlation values. ($n=120$). Of the original grouped cases, 100% were correctly classified, and 92.5% of the cross-validated grouped cases were correctly classified.

Figure 11. a) CDA with neck residues classified by participant. b) Structure matrix correlation values. ($n=120$). Of the original grouped cases, 90.8% were correctly classified, and 76.7% of the cross-validated grouped cases were correctly classified.

Figure 12. a) CDA with groomed residues classified by participant. b) Structure matrix correlation values. ($n=120$). Of the original grouped cases, 85.0% were correctly classified, and 72.5% of the cross-validated grouped cases were correctly classified.

Figure 13. a) CDA with natural residues classified by participant. b) Structure matrix correlation values. ($n=120$). Of the original grouped cases, 59.2% were correctly classified, and 40.0% of the cross-validated grouped cases were correctly classified.

Figure 14. a) CDA with eccrine residues classified by participant. b) Structure matrix correlation values. ($n=120$). Of the original grouped cases, 34.2% were correctly classified, and 30.0% of the cross-validated grouped cases were correctly classified.

Figure 11a shows that there is some clustering for the neck residues. Whereas the classification results were not as accurate as they were for the face residues (76.7% cross-validated cases correctly classified for neck vs. 92.5% for face), different relative concentrations between the neck and face secretions allow the participants to be separated. For example, many of the neck residues contributed by participant 2 seem to be separated by the contribution of a compound at RT=8.797, which is a branched C16:0 FAME. Additionally, participants 2 and 5 contain the largest amount of a branched C16:1 FAME (RT=8.65), as shown by the correlation values in Figure 11b.

The groomed residues (Figure 12) show less discrimination between subjects than the face and neck residues, presumably because of the large within-subject variability in preparing a groomed fingerprint. As discussed before, the groomed fingerprint residues contain different contributions of three different sources, and the relative contribution of each source causes more within-person variance than for other sample types. This large within-subject variance means that participants do not classify quite as well as face and neck residues (72.5% cross-validated cases correctly classified).

Figure 13 shows that C15:0 FAME (RT=8.366) is correlated with the natural residues of participant 2 on certain days, although it is not present on all days, which influences the separation of all of the samples. Because C15:0 FAME is a methyl ester of an odd chain fatty acid, this compound is most likely present due to bacteria present on the individual or due to dairy intake [39]; humans cannot anabolize odd-numbered fatty acids. A few of the eccrine samples contain stearic acid methyl ester (C18:0 FAME, RT=10.346), which helps separate a few samples from participant 1 (Figure 14).

The separation of both the natural and eccrine residues is very poor because of the lack of discriminating compounds among individuals.

Table 4 summarizes the inter-subject variability classification rates using CDA. In this study, face residues were found to be the most discriminating sample type, whereas eccrine residues were found to be almost indistinguishable between participants. The overall inter-subject variability class classification rates appear to be almost an average between the five sample types—face, neck, and groomed residues help to distinguish individuals whereas natural and eccrine residues are less distinguishable. Groomed fingerprints are more unique than natural fingerprints, which is an important fact when considering whether or not to use groomed fingerprints as a source of fingerprint residues in a study.

Table 4. Summary of inter-subject variability classification results.

	Sample Type					
	Face	Neck	Groomed	Natural	Eccrine	Overall
Original	100%	90.8%	85%	59.2%	34.2%	59.8%
Cross-Validated	92.5%	76.7%	72.5%	40.0%	30%	55.7%

Inter-Sample Variability

All data was also classified using CDA by sample type to determine whether or not the between-sample-type variance was significantly larger than the within-sample-type variance, and to see if the differences were consistent enough to enable the prediction of sample type, regardless of the donor. Figure 15 shows a similar result (v-shape) to the same analysis conducted within-person in Figure 7. Figure 15 shows that

the observations seen within-subject in Figure 7 indeed hold true when all the subjects are included. This result indicates that there is a high degree of consistency or similarity for each sample type between individuals. Such correlation is helpful in a forensic setting for helping to determine the type of residue that is left at a crime scene.

Figure 15. Canonical Discriminant Analysis (CDA). All samples classified by sample type ($n=600$). Of the original grouped cases, 61.2% were correctly classified, and 55% of cross-validated grouped cases were correctly classified.

IV. CONCLUSIONS

This study has found that a range of fatty acids is present in the fingerprint residues of individuals. Some of the most commonly observed compounds include C16:0 FAME, C18:0 FAME, and squalene. Additionally, “natural” fingerprint residues contain significantly fewer fatty acid residues than “groomed” fingerprints or face and neck residues. Sebaceous secretions from the neck and face were found to contain higher levels of branched C14:1 and C15:1 FAMES, C14:0 and C15:0 FAMES, and squalene. Intra-subject variability and discrimination are observed when analyzing residues from different sources (i.e. groomed, face, neck, etc.), which means that human skin has significantly different secretions in the face and neck, even though both provide sebaceous secretions. The exception to discrimination is between the natural and eccrine samples. Fingerprint residues between individuals (inter-subject variability) cannot be clearly discriminated because the within-group variance is larger than the between-group variance. Overlap in the residues of different individuals could therefore lead to a potential misclassification in a forensic setting. Ultimately, the variability within an individual’s fingerprint residues leads to an inability to distinguish individuals from each other with a high degree of confidence.

Although natural and groomed residues do contain some chemical similarities with regard to fatty acids, future studies should acknowledge the differences between the types of prints. If an individual has not recently washed his or her hands, the natural and groomed prints may represent each other better; however, if samples are collected recently after hand washing, major differences could be found in the fatty acid content of

the residues. It is the opinion of the researcher that natural and groomed fingerprints are too different from each other to be used interchangeably.

The limit of detection was one of the major limitations of this study, especially for compounds that were close to the threshold value. In the future, lower limits of detection could improve the results because compounds close to threshold would no longer be counted as absent when they are actually present in very low quantities. This improvement could provide a more accurate representation of the composition of fingerprint residues, in turn minimizing the intra-subject variability and maximizing the inter-subject variability.

V. FUTURE WORK

Future studies could be directed toward the variability of amino acids in fingerprint residues, as previous research has shown that there are potential differences in the amino acid ratios between males and females [18]. As the current study has shown, it is important to evaluate the variability of different residue types over a period of time before determining the utility of the residues.

A study by Croxton et al. found that there are no significant differences in the amino acid content between natural and groomed prints; however, the study did not evaluate at the variability of residues over a period of time [30]. It is possible that the differences between natural and groomed residues were statistically insignificant on that particular day but that they differ from day to day. Although the concentration of fatty acids differs between natural and groomed prints, it is possible that the composition of the amino acids present could be useful in the field of forensic science, given that the

amino acid concentrations do not vary from day to day. Ultimately, the present study has found that the assessment of intra-subject variability is crucial before making decisions about the chemical composition of a latent fingerprint from an unknown source.

VI. REFERENCES

1. The Fingerprint Sourcebook. *U.S. Department of Justice*, 2011.
2. Document #19 Standard Terminology of Friction Ridge Examination. *Scientific Working Group on Friction Ridge Analysis, Study and Technology*, 2013.
3. Meuwly, D., Fingerprint, Forensic Evidence of. *Encyclopedia of Biometrics*, 2009.
4. Strengthening Forensic Science in the United States: A Path Forward *Committee on Identifying the Needs of the Forensic Sciences Community, National Research Council* 2009.
5. Ulery, B.T., et al., Accuracy and reliability of forensic latent fingerprint decisions. *Proc Natl Acad Sci U S A*, 2011. **108**(19): p. 7733-8.
6. Tangen, J.M., M.B. Thompson, and D.J. McCarthy, Identifying fingerprint expertise. *Psychol Sci*, 2011. **22**(8): p. 995-7.
7. Daly, D.J., C. Murphy, and S.D. McDermott, The transfer of touch DNA from hands to glass, fabric and wood. *Forensic Sci Int Genet*, 2012. **6**(1): p. 41-6.
8. Tozzo, P., et al., Effect of two different swabs on genetic profiling of enhanced fingerprints. *Forensic Science International: Genetics Supplement Series*, 2015. **5**: p. e7-e9.
9. Tims, S., et al., Microbial DNA fingerprinting of human fingerprints: dynamic colonization of fingertip microflora challenges human host inferences for forensic purposes. *Int J Legal Med*, 2010. **124**(5): p. 477-81.
10. Bailey, M.J., et al., Rapid detection of cocaine, benzoylecgonine and methylecgonine in fingerprints using surface mass spectrometry. *Analyst*, 2015. **140**(18): p. 6254-9.
11. Rowell, F., K. Hudson, and J. Seviour, Detection of drugs and their metabolites in dusted latent fingermarks by mass spectrometry. *Analyst*, 2009. **134**(4): p. 701-707.
12. Day, J.S., et al., The detection of drugs of abuse in fingerprints using Raman spectroscopy I: latent fingerprints. *Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy*, 2004. **60**(3): p. 563-568.
13. Buchanan, M., K. Asano, and A. Bohanon, Chemical characterization of fingerprints from adults and children. *SPIE*, 1997. **2941**: p. 89-95.
14. Kwok, Y.L., J. Gralton, and M.L. McLaws, Face touching: a frequent habit that has implications for hand hygiene. *Am J Infect Control*, 2015. **43**(2): p. 112-4.
15. *Perfumery: The psychology and biology of fragrance*, ed. S.V. Toller and G. Dodd. 1988: Springer-Science+Business Media.
16. Asano, K., et al., Chemical Composition of Fingerprints for Gender Determination. *J Forensic Sci*, 2002. **47**(4): p. 1-3.
17. Michalski, S., R. Shaler, and F.L. Dorman, The evaluation of fatty acid ratios in latent fingermarks by gas chromatography/mass spectrometry (GC/MS) analysis. *J Forensic Sci*, 2013. **58 Suppl 1**: p. S215-20.
18. de Puit, M., M. Ismail, and X. Xu, LCMS analysis of fingerprints, the amino acid profile of 20 donors. *J Forensic Sci*, 2014. **59**(2): p. 364-70.
19. Antoine, K.M., et al., Chemical differences are observed in children's versus adults' latent fingerprints as a function of time. *J Forensic Sci*, 2010. **55**(2): p. 513-8.
20. Weyermann, C., C. Roux, and C. Champod, Initial results on the composition of fingerprints and its evolution as a function of time by GC/MS analysis. *J Forensic Sci*, 2011. **56**(1): p. 102-8.
21. Archer, N.E., et al., Changes in the lipid composition of latent fingerprint residue with time after deposition on a surface. *Forensic Sci Int*, 2005. **154**(2-3): p. 224-39.

22. Girod, A., R. Ramotowski, and C. Weyermann, Composition of fingermark residue: a qualitative and quantitative review. *Forensic Sci Int*, 2012. **223**(1-3): p. 10-24.
23. Pleik, S., et al., Fatty Acid Structure and Degradation Analysis in Fingerprint Residues. *J Am Soc Mass Spectrom*, 2016. **27**(9): p. 1565-74.
24. Ricci, C., et al., Chemical Imaging of Latent Fingerprint Residues. *APPL SPECTROSC*, 2007. **61**(5): p. 514-22.
25. Girod, A., et al., Fingermark initial composition and aging using Fourier transform infrared microscopy (mu-FTIR). *Forensic Sci Int*, 2015. **254**: p. 185-96.
26. Connatser, R.M., et al., Toward surface-enhanced Raman imaging of latent fingerprints. *J Forensic Sci*, 2010. **55**(6): p. 1462-70.
27. Frick, A.A., et al., Investigations into the initial composition of latent fingermark lipids by gas chromatography-mass spectrometry. *Forensic Sci Int*, 2015. **254**: p. 133-47.
28. Emerson, B., et al., Laser desorption/ionization time-of-flight mass spectrometry of triacylglycerols and other components in fingermark samples. *J Forensic Sci*, 2011. **56**(2): p. 381-9.
29. Ferguson, L.S., et al., Direct detection of peptides and small proteins in fingerprints and determination of sex by MALDI mass spectrometry profiling. *Analyst*, 2012. **137**(20): p. 4686-92.
30. Croxton, R.S., et al., Variation in amino acid and lipid composition of latent fingerprints. *Forensic Sci Int*, 2010. **199**(1-3): p. 93-102.
31. Bailey, M.J., et al., Chemical characterization of latent fingerprints by matrix-assisted laser desorption ionization, time-of-flight secondary ion mass spectrometry, mega electron volt secondary mass spectrometry, gas chromatography/mass spectrometry, X-ray photoelectron spectroscopy, and attenuated total reflection Fourier transform infrared spectroscopic imaging: an intercomparison. *Anal Chem*, 2012. **84**(20): p. 8514-23.
32. Girod, A. and C. Weyermann, Lipid composition of fingermark residue and donor classification using GC/MS. *Forensic Sci Int*, 2014. **238**: p. 68-82.
33. Williams, D.K., C.J. Brown, and J. Bruker, Characterization of children's latent fingerprint residues by infrared microspectroscopy: forensic implications. *Forensic Sci Int*, 2011. **206**(1-3): p. 161-5.
34. Zimmermann, C.M., U.A. Laskay, and G.P. Jackson, Analysis of suspected trace human remains from an indoor concrete surface. *J Forensic Sci*, 2008. **53**(6): p. 1437-42.
35. Rostad, C.E. and W.E. Pereira, Kovats and lee retention indices determined by gas chromatography/mass spectrometry for organic compounds of environmental interest. *JHRC Journal of High Resolution Chromatography*, 1986. **9**(6): p. 328-334.
36. Desa, W.N.S.M., et al., Application of unsupervised chemometric analysis and self-organizing feature map (SOFM) for the classification of lighter fuels. *Analytical Chemistry*, 2010. **82**(15): p. 6395-6400.
37. *IBM SPSS Statistics 20 Algorithms*, ed. I. Corporation. 2011.
38. Manly, B.F.J., *Multivariate Statistical Methods A Primer*. 2005, Boca Raton, FL: Chapman & Hall/CRC.
39. Brevik, A., et al., Evaluation of the odd fatty acids 15:0 and 17:0 in serum and adipose tissue as markers of intake of milk and dairy fat. *Eur J Clin Nutr*, 2005. **59**(12): p. 1417-22.