

# 1 An untargeted lipidomic approach for qualitative determination of latent fingerprint glycerides 2 using UPLC-IMS-QToF-MS<sup>E</sup>

3 A.A. Frick\*, C. Weyermann\*

4 École des Sciences Criminelles, Université de Lausanne, Batochime, 1015 Lausanne, Switzerland

5 E-mail: amanda.frick@unil.ch, celine.weyermann@unil.ch

6

## 7 Abstract

8 More detailed fundamental information is required about latent fingerprint composition in order to  
9 better understand fingerprint properties and their impact on detection efficiency, and the physical  
10 and chemical changes that occur with time following deposition. The composition of the glyceride  
11 fraction of latent fingerprint lipids in particular is relatively under-investigated due in part to their high  
12 structural variability and the limitations of the analytical methods most frequently utilised to  
13 investigate fingerprint composition. Here, we present an ultra performance liquid chromatography-  
14 ion mobility spectroscopy-quadrupole time-of-flight mass spectrometry (UPLC-IMS-QToF-MS<sup>E</sup>)  
15 method to characterise glycerides in charged latent fingerprints using data-independent acquisition.  
16 Di- and triglycerides were identified in fingerprint samples from a population of 10 donors, through a  
17 combination of *in silico* fragmentation and monitoring for fatty acid neutral losses. 23 diglycerides and  
18 85 families of triglycerides were identified, with significant diversity in chain length and unsaturation.  
19 21 of the most abundant triglyceride families were found to be common to most or all donors,  
20 presenting potential targets for further studies to monitor chemical and physical changes in latent  
21 fingerprints over time. Differences in relative peak intensities may be indicative of inter- and intra-  
22 donor variability. While this study represents a promising step to obtaining more in-depth information  
23 about fingerprint composition, it also highlights the complex nature of these traces.

24

## 25 Introduction

26 In recent decades, analysis of the chemical composition of latent fingerprints has seen increasing  
27 focus in forensic research, in an effort to better understand and overcome the issues facing fingerprint  
28 detection.<sup>1-6</sup> It is recognised that there is a need to identify not only the processes by which current  
29 detection techniques work, but also the factors that may cause them to fail, such as time since  
30 deposition (fingerprint age) or lack of sensitivity.<sup>7-9</sup> Other investigations have been conducted into the  
31 variability of fingerprint residue to differentiate between individuals based on characteristics such as  
32 sex or age,<sup>6, 10-13</sup> or to estimate the age of a latent fingerprint based on changes in its properties since  
33 deposition.<sup>2, 14, 15</sup>

34 The lipid fraction of fingerprint residue is of particular interest, as these non-volatile, hydrophobic  
35 compounds enable fingerprint detection on wetted substrates. This fraction has been shown to  
36 exhibit significant physical and chemical changes over time following deposition, as well as inter-donor  
37 variation.<sup>1, 4, 9, 16, 17</sup> The lipid classes identified in fingerprint residue include squalene, cholesterol, wax  
38 esters, glycerides and free fatty acids.<sup>4, 9, 18</sup> These skin surface lipids are largely derived from the  
39 secretions of the sebaceous glands, which are found in greatest density on the face and scalp, with  
40 other compounds contributed by the epidermis.<sup>19</sup> Sebaceous lipids become incorporated into  
41 fingerprint residue through incidental touching of the face and hair, and so the relative abundance of  
42 the lipid fraction can vary considerably. Significant differences may also be observed in latent

43 fingermarks deposited by adults and children, as the sebaceous glands do not become active until  
44 shortly before the onset of puberty.<sup>13, 18</sup>

45 The glycerides are one of the largest and most structurally diverse fingermark lipid classes, comprising  
46 approximately 30 % of total skin surface lipids.<sup>20, 21</sup> Mono- and diglycerides, as well as free fatty acids,  
47 are the products of bacterial lipolysis of sebaceous triglycerides (TGs) on the skin surface.<sup>22, 23</sup> The  
48 relative amounts of free fatty acids and TGs are therefore inversely proportional, and show greater  
49 inter-donor variation than other skin surface lipid components.<sup>24-26</sup> The total profile of the constituent  
50 fatty acids exhibits similar high variability.<sup>19, 27, 28</sup> In the weeks following fingermark deposition, TGs  
51 may be prone to degradation to free fatty acids,<sup>4</sup> ozonides,<sup>29</sup> and eventually shorter chain organic  
52 compounds<sup>30, 31</sup>, depending on environmental conditions. Such processes contribute to the changes  
53 in chemical and physical properties of the latent residue which can affect detectability, and may  
54 provide a basis for the estimation of the age of a latent fingermark.<sup>17, 29</sup>

55 The exact glyceride species present in human sebum or latent fingermarks remain relatively under-  
56 investigated in comparison to the smaller, more volatile sebaceous compounds which are amenable  
57 to gas chromatography (GC) separation.<sup>1, 4, 18, 32-34</sup> Despite this, TGs in particular are considered an  
58 important class in fingermark residue, as their presence provides a target for lipid-sensitive detection  
59 methods such as lipophilic dyes,<sup>35-37</sup> and may assist in the successful application of metal deposition  
60 techniques such as physical developer and single metal deposition.<sup>38, 39</sup> Saponification is traditionally  
61 utilised in the preparation of glyceride samples,<sup>40-44</sup> so while much is known about the variations in  
62 sebaceous fatty acid chain length, unsaturation and branching,<sup>19, 20</sup> their arrangement on the glycerol  
63 backbone is less clear.<sup>10, 45</sup>

64 Intact latent fingermark glycerides were first described in 2011 by Emerson *et al.*, who utilised laser  
65 desorption/ionisation tandem mass spectrometry (LDI-MS/MS) to tentatively identify 35 TG species  
66 from 43 CN:DB families (where CN denotes the total number of carbon atoms in the fatty acyl groups  
67 and DB the total number of double bonds).<sup>10</sup> The presence of numerous diglyceride (DG) species was  
68 also reported, though no structural data were presented. Numerous studies into fingermark  
69 composition have reported the presence of di- and triglycerides in samples,<sup>46-48</sup> but often limited data  
70 has been provided regarding their structures; usually only the molecular ion  $m/z$  or a generic CN:DB  
71 label is provided. Lauzon *et al.* reported a number of TG and DG structures in fingermarks using matrix-  
72 assisted laser desorption/ionisation mass spectrometry (MALDI-MS), but only 7 TGs were subjected  
73 to MS/MS.<sup>32</sup> Most recently, Pleik *et al.* examined the degradation process of unsaturated TGs by  
74 ozonolysis, focusing on a single TG.<sup>29</sup>

75 As described above, the fatty acid profile of sebaceous triglycerides has been researched extensively  
76 in the field of dermatology, but limited data is available in the literature regarding intact glycerides,  
77 due to their complexity.<sup>49, 50</sup> Michael-Jubeli *et al.* utilised high-temperature GC to separate skin surface  
78 lipids following trimethylsilylation, which enabled the characterisation of 5 monoglycerides (MGs), 7  
79 families of DGs and 35 families of TGs.<sup>27</sup> However, this approach can lead to pyrolytic decomposition  
80 of the analytes, particularly highly unsaturated species.<sup>40, 51-54</sup>

81 Liquid chromatography presents a more suitable approach for the characterisation of these lipid  
82 classes. In the context of latent fingermark analysis, it has thus far seen very limited use, with focus  
83 constrained only to a narrow range of targeted compounds.<sup>16, 29, 55</sup> Conversely, numerous methods  
84 have been developed for lipidomics analyses targeting TGs in a variety of biological samples,<sup>52</sup>  
85 including plasma and tissues,<sup>56, 57</sup> animal fats<sup>41, 58</sup> and vegetable oils.<sup>25, 40, 42, 58, 59</sup> Camera *et al.* reported  
86 a high performance liquid chromatography (HPLC)-MS method to simultaneously analyse all classes

87 comprising the 'sebum lipidome', including over 100 glycerides, demonstrating the potential of such  
88 an approach to be applied to latent fingerprints.<sup>49, 50</sup>

89 We present a method for the untargeted separation and characterisation of latent fingerprint  
90 glycerides using ultra performance liquid chromatography-ion mobility spectroscopy-quadrupole  
91 time-of-flight mass spectrometry (UPLC-IMS-QToF-MS<sup>E</sup>). Samples were collected from a small  
92 population of donors to explore the range of variation in glyceride chain lengths and unsaturation,  
93 and to identify common, abundant species as potential targets for further studies into fingerprint  
94 composition and degradation over time. Several approaches were taken to identify glyceride  
95 structures, such as *in silico* fragmentation of molecular structures previously reported in latent  
96 fingerprints and human skin surface lipids, and monitoring for neutral losses of common sebaceous  
97 fatty acids from MS<sup>E</sup> acquisition.

98

## 99 **Materials and methods**

### 100 **Chemicals**

101 Dichloromethane (GC grade; Sigma-Aldrich, Switzerland), acetonitrile (ULC/MS grade; Biosolve,  
102 France), water (LC-MS Ultra grade; Honeywell, Germany), 2-propanol (ULC/MS grade; Biosolve,  
103 France), formic acid (ULC/MS grade; Biosolve, France), ammonium formate (LC-MS Ultra grade; Fluka,  
104 Switzerland), monomyristin (MG 14:0), monopalmitolein (MG 16:1), monoolein (MG 18:1),  
105 monostearin (MG 18:0), dimyristin (DG 28:0), dipalmitolein (DG 32:2), dipalmitin (DG 32:0), diolein  
106 (DG 36:2) and distearin (DG 36:0) (all >99 %; Nu-Chek Prep, Inc, USA), tricaprilin (TG 24:0), tricaprין  
107 (TG 30:0), trilaurin (TG 36:0), trimyristin (TG 42:0) and tripalmitin (48:0) (all 99.9 %; Sigma-Aldrich,  
108 USA) were used as received.

109 Stock solutions of glycerides were prepared in dichloromethane. To determine the ability of the UPLC  
110 method to separate glycerides and the elution profiles of each glyceride class, mixed standard  
111 solutions were prepared for each class (MGs, DGs and TGs) by serial dilutions in 2:1:1  
112 isopropanol/acetonitrile/water. Mixed standard solutions were run at concentrations of 0.2  $\mu$ M and  
113 1  $\mu$ M, except for the MGs, which were prepared at 0.6  $\mu$ M and 3  $\mu$ M. Each mixed standard solution  
114 was run in triplicate, to give a maximum of 6 measurements (retention time, *m/z* and collisional cross  
115 section (CCS)) per standard compound. All standard solutions were stored at -20 °C before and after  
116 analysis to prevent degradation and solvent evaporation.

### 117 **Sample collection and storage**

118 Latent fingerprint samples were collected from 10 adult donors (21 – 37 years old) on 25 mm filter  
119 paper circles (Grade 1 qualitative filter paper; Whatman, UK). Donors were asked to refrain from  
120 handling food or chemicals, or washing hands 30 minutes prior to sampling, but were otherwise free  
121 to carry out normal activities and use of skin products. Donors were asked to provide charged  
122 fingerprints by briefly rubbing the middle three fingertips of both hands on their forehead and nose,  
123 then rubbing the fingertips of each hand together to homogenise the secretions. Three fingertips from  
124 one hand were pressed gently to individual filter paper circles for approximately ten seconds,  
125 providing a total of 30 samples (3 per donor). Samples from each donor were immediately wrapped  
126 in aluminium foil and stored in an office cupboard at ambient conditions for 24 hours prior to  
127 extraction, following the recommendations of the International Fingerprint Research Group.<sup>60</sup> A set  
128 of clean filter papers were also wrapped in aluminium foil and stored with the samples to provide  
129 analytical blanks.

## 130 **Fingerprint extraction**

131 The filter papers were individually placed in 1.75 mL glass screw-top vials (Thermo Fisher Scientific)  
132 that had been cleaned by rinsing with dichloromethane and left to air-dry. Samples were immersed in  
133 750  $\mu$ L dichloromethane for 2 minutes, with gentle manual agitation to ensure that the filter papers  
134 were completely submerged in the solvent. After 2 minutes, the extract was transferred to a second  
135 vial. Sample cleanup was performed by adding 750  $\mu$ L water and vortex mixing before allowing phase  
136 separation. The aqueous top layer was discarded, together with a small amount of the organic layer  
137 to ensure the complete removal of the water. The organic layer was evaporated under nitrogen gas  
138 until approximately 150  $\mu$ L remained. This residue was transferred to an amber glass vial containing a  
139 250  $\mu$ L glass insert, and further evaporated to dryness. The remaining residue was dissolved in 200  $\mu$ L  
140 of 2:1:1 2-propanol/acetonitrile/water with 20mM ammonium formate.

## 141 **Chemical analysis**

142 Chromatographic separation was performed using a Waters Acquity UPLC I-Class system, coupled to  
143 a Waters Vion IMS-QToF mass spectrometer (mass resolving power >40 000 FWHM) equipped with  
144 an electrospray ionisation (ESI) source. The UPLC system was equipped with a binary pump, a 96 well  
145 autosampler (maintained at 8 °C), and a temperature-controlled column compartment. Separation  
146 was performed using an Acquity UPLC CSH C<sub>18</sub> column (2.1 x 100 mm, 1.7  $\mu$ m), connected to an Acquity  
147 UPLC in-line filter to protect the column (both from Waters). The mobile phases were A) 60:40  
148 acetonitrile/water with 10 mM ammonium formate and 0.1 % formic acid and B) 90:10  
149 isopropanol/acetonitrile with 10 mM ammonium formate and 0.1 % formic acid. Gradient parameters  
150 are described in Table 1. The flow rate was maintained at 0.4 mL/min with a column temperature of  
151 55 °C. The injection volume was 1  $\mu$ L. Injections of the blank filter paper extracts were run before and  
152 after sample sets from each donor to monitor for carryover and contamination.

Time (min)	%A	%B
0.0	60	40
2.0	57	43
2.1	50	50
12.0	46	54
12.1	30	70
18.0	1	99
19.0	1	99
19.1	60	40
21.0	60	40

153 **Table 1:** UPLC mobile phase gradient parameters.

154 The ESI source was operated in positive mode, using the following parameters: the source  
155 temperature was set to 120 °C, the desolvation temperature to 600 °C, the cone gas flow to 50 L/hr,  
156 the desolvation gas flow to 1000 L/hr, and the capillary voltage to 2 kV. Data were acquired over the  
157  $m/z$  range of 50 – 1000 with a scan time of 0.2 seconds. A 200 ng/mL solution of leucine enkephalin  
158 ( $m/z$  556.2766) was used as the lock mass reference and infused into the ion source at 5 minute  
159 intervals. Data acquisition was performed using high definition MS<sup>E</sup>. The low collision energy was set  
160 at 6 eV, and the high collision energy ramp at 30 – 60 eV. Nitrogen was used as the drift gas in the IMS  
161 and as the collision gas. Ion mobility and mass calibration were performed using a Major Mix IMS/ToF  
162 Calibration Kit (Waters).

## 163 **Data processing**

164 Data were processed using UNIFI (Waters MS Technologies, Manchester, United Kingdom).  
165 Deconvolution and peak picking were performed with 4D peak detection, with a low energy intensity  
166 threshold of 250 counts and a high energy intensity threshold of 100 counts. The fraction of the  
167 chromatographic peak width applied during isotope cluster creation and high-to low energy  
168 association was 0.5. The fraction of the drift peak width applied during cluster creation and high-to  
169 low energy association was 0.5, except for critical pairs that appeared together in the low energy mass  
170 spectra. To resolve these compounds, the fractions of the drift peak width applied during cluster  
171 creation and high-to low energy association were 0.1 and 0.15, respectively.

172 A molecular database was created by uploading .mol files obtained from ChemSpider  
173 (www.chemspider.com) to UNIFI. UNIFI's MassFragment algorithm was used to match expected  
174 compound structures to deconvoluted peaks, and explain collision-induced fragmentation based on  
175 bond breakage.<sup>61, 62</sup> A total of 104 MG (8:0 – 20:0), DG (16:0 – 40:0) and TG (24:0 – 60:0) structures  
176 were selected, comprised of the glyceride standards described above, additional species reported in  
177 latent fingerprints and skin surface lipids (where constituent fatty acids were indicated),<sup>10, 49</sup> as well  
178 as monoacid species representing fatty acyl groups reported as abundant free fatty acids in latent  
179 fingerprints.<sup>9</sup> A number of isomeric DG and TG structures were included.  $[M+NH_4]^+$  and  $[M+Na]^+$  were  
180 defined as precursor ions for both TGs and DGs.  $[M-OH]^+$  was defined as an additional target precursor  
181 for DGs due to in-source fragmentation.

182 To assist in reducing the number of false positives, peaks identified based on *in silico* fragmentation  
183 were filtered based on the following criteria:  $\geq 1$  theoretical fragment observed, retention time  $\leq 18$   
184 min, mass error  $\pm 2.5$  ppm (based on expected precursor). Unidentified candidate peaks were filtered  
185 based on the following criteria:  $\geq 1$  fatty acid neutral loss (RCOOH + NH<sub>3</sub>) observed, response  $> 1000$ ,  
186 retention time 2 – 18 min, CCS  $\geq 200$  (based on observed retention times and CCS measurements of  
187 glyceride standards). Further examination of filtered candidate peaks was performed manually due to  
188 the coelution of isomeric TGs. Identification was performed based on known fragmentation pathways,  
189 i.e. the neutral loss of fatty acyl groups with ammonia from the *sn*-1, -2 or -3 positions. Candidate *m/z*  
190 were compared against calculated values for  $[M+NH_4]^+$  of TGs to ascertain CN:DB, and high energy  
191 mass spectra were examined to identify predominant 'DG-like' ions corresponding to fatty acid neutral  
192 losses. Finally, all potential glycerides were required to have a peak response at least 2.5 times higher  
193 than that of any corresponding peak in a preceding blank filter paper extract.

194

## 195 **Results and discussion**

### 196 **Nomenclature**

197 Annotation of glyceride structures in this paper follows the recommendations of Liebisch *et al.*<sup>63</sup>  
198 Glyceride classes (mono-, di-, and triglycerides) are denoted as MG, DG, and TG, respectively, followed  
199 by the CN:DB family as a generic identifier (where CN denotes the total number of carbon atoms in  
200 the fatty acyl groups and DB the total number of double bonds). Where structural information is  
201 provided, the separator '\_' is used to indicate that the *sn*-positions of the fatty acids are unknown (e.g.  
202 DG 14:0\_16:0 indicates that myristic acid and palmitic acid are present in any possible 1,2- or 1,3-DG  
203 structure), otherwise the separator '/' is used (e.g. tripalmitin may be expressed as TG 48:0 or TG  
204 16:0/16:0/16:0).

205 It should be noted that while alkyl branching has been observed in a number of sebaceous fatty acids,  
206 and several unsaturated fatty acids exist as positional isomers, the location of branches or double

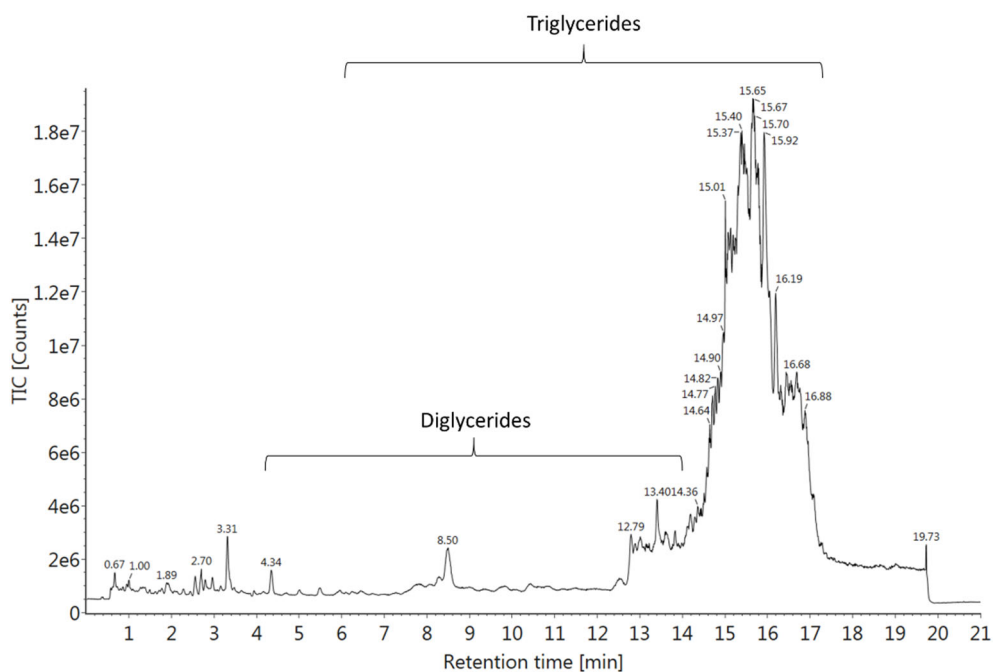
207 bonds is beyond the aims of this study, and so fatty acyl groups are referred to only by their generic  
208 CN:DB.

209

### 210 Preliminary considerations

211 Preliminary experiments showed that a limited number of sebaceous compounds other than  
212 glycerides could be readily detected using this method, primarily monounsaturated wax esters (data  
213 not shown). Other non-polar fingerprint constituents such as cholesterol, squalene and saturated wax  
214 esters exhibited very poor or no signal, likely due to the incompatibility of such compounds with ESI.<sup>64</sup>  
215 As these compounds may instead be easily analysed using GC-MS,<sup>1, 4, 12, 15, 33, 34</sup> the focus of this work  
216 was constrained only to the glyceride fraction.

217 Figure 1 shows a total ion chromatogram of a latent fingerprint, with highlighted regions indicating  
218 where DGs and TGs were eluted. Using this UPLC method, glycerides are separated based on the chain  
219 length and degree of unsaturation of their fatty acyl groups, rather than by lipid class. This is often  
220 expressed as the equivalent carbon number ( $ECN = CN - 2DB$ ), whereby mono- and polyunsaturated  
221 glycerides can be shown to have similar retention behaviour to a smaller, more saturated  
222 counterpart.<sup>41, 65, 66</sup> Complete separation can be extremely difficult to achieve for neutral lipid  
223 extracts.<sup>52, 56, 67, 68</sup> Under optimised separation conditions, resolution of TGs within an ECN group  
224 (known as 'critical pairs') can be achieved, but this comes at the cost of substantially longer run times  
225 than the method presented here.<sup>42, 69-71</sup> Complete separation of some positional isomers can require  
226 as long as several hours. The aim of this study to identify potential targets for future investigations,  
227 based on CN:DB families which are common between donors and present in high abundances. A  
228 shorter run time was thus preferred in order to acquire untargeted data from several fingerprint  
229 samples.



230

231 **Figure 1:** Total ion chromatogram of UPLC separation of latent fingerprint residue, showing elution  
232 ranges of identified di- and triglycerides.

233 MS<sup>E</sup> mass spectra of MG and DG standards were complicated by a significant peak appearing in both  
 234 the low and high collision energy mass spectra, which corresponded to a loss of a hydroxyl group from  
 235 the glycerol backbone ([M+H-H<sub>2</sub>O]<sup>+</sup>). In-source fragmentation in this manner is a known occurrence in  
 236 the analysis of DGs.<sup>49, 52, 59, 66, 72, 73</sup> Resultant signal loss was subsequently overcome by utilising this  
 237 peak as an expected ‘adduct’. Due to excessive fragmentation, MGs could not be conclusively  
 238 identified in standard solutions or fingerprint samples, as no theoretical fragments were found in the  
 239 high collision energy mass spectra. The collision energies utilised in MS<sup>E</sup> are applied to all sample ions,  
 240 and different energies cannot be selected within a method to target select fractions. It was therefore  
 241 decided not to lower the collision energy settings, as this could compromise the collisional dissociation  
 242 of the TGs.<sup>43</sup>

243 The use of *in silico* fragmentation to identify glycerides, rather than the use of standard compounds,  
 244 was chosen as an alternative approach when no standard was available, as many of the glycerides  
 245 previously identified in skin surface lipids are unavailable commercially. Furthermore, the use of  
 246 physical reference substances can create carryover issues in the UPLC system.<sup>61</sup> While an *in silico*  
 247 approach confers several advantages in these regards, other issues arise from a lack of information of  
 248 a compound’s chromatographic behaviour, namely the retention time. Without this reference  
 249 information, several peaks were identified as a single glyceride species, requiring manual examination  
 250 of the data to exclude any false positive results. By doing so, it was often found that MassFragment  
 251 was unable to conclusively identify some glycerides, due to the presence of isomers for which .mol  
 252 files had not been obtained. This was easily seen in the high energy mass spectra, due to the presence  
 253 of fragment ions corresponding to the losses of fatty acids in addition to, or instead of, those of the  
 254 proposed structure. Where a glyceride contained fatty acyls groups different to those expected from  
 255 the .mol file, MassFragment would explain observed losses as part of a fatty acid chain (where the loss  
 256 was smaller than expected) or as the loss of a fatty acid and a small fragment of another (where the  
 257 loss was larger than expected).

## 258 Diglyceride identification

259 The 5 DG standards (DG 28:0 – 36:0) eluted between 7.3 and 14 minutes, and were detected in the  
 260 low energy mass spectra as predominantly [M+H-H<sub>2</sub>O]<sup>+</sup> ions, due to in-source fragmentation as  
 261 described above (Table S1). All five standard DG compounds were detected in latent fingerprint  
 262 samples as primarily sodiated adducts. The higher proportion of sodiated adducts in sample extracts  
 263 compared to the standards can be explained by the presence of sodium originating from the eccrine  
 264 (sweat) constituents of the samples,<sup>9, 10</sup> as well as from potential sources within the laboratory such  
 265 as the filter paper substrates. A further 18 DGs were identified based on *in silico* fragmentation,  
 266 including 16 structures previously reported in human sebum.<sup>49</sup> In total, 23 DG structures were  
 267 identified, comprising 20 CN:DB families, which eluted between 4 – 14 minutes (Table 2). The observed  
 268 structures ranged from 24:0 – 36:0 with 0 – 4 double bonds. Manual examination of the high energy  
 269 mass spectra of proposed DGs was required to confirm molecular structure, as MassFragment was not  
 270 consistently able to differentiate between isomers. Isomeric DGs eluted closely together, but  
 271 exhibited sufficient chromatographic resolution for differentiation (Figure 2). While positional isomers  
 272 (i.e. 1,2-DGs and 1,3-DGs) may be resolved by HPLC,<sup>42</sup> this was not observed here.

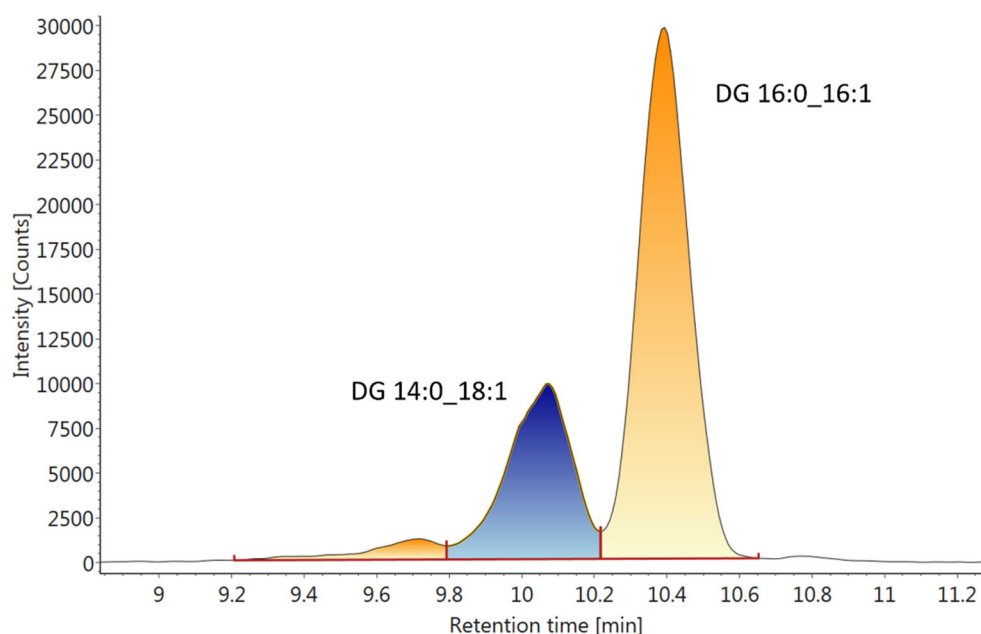
Diglyceride species	CN:DB	Average retention time (min)	Average experimental <i>m/z</i> ([M+H-H <sub>2</sub> O] <sup>+</sup> )	Average CCS (Å <sup>2</sup> ) ([M+H-H <sub>2</sub> O] <sup>+</sup> )	Average experimental <i>m/z</i> ([M+Na] <sup>+</sup> )	Average CCS (Å <sup>2</sup> ) ([M+Na] <sup>+</sup> )	Number of fingerprints [n = 30] (number of donors [n = 10])
DG 12:0_12:0	24:0	4.18	439.3780	233.6	479.3707	230.8	7 (3)
DG 12:0_14:0	26:0	5.46	467.4091	242.0	506.6519	237.5	8 (4)

DG 14:0_14:1	28:1	5.86	493.4246	245.6	533.4177	243.2	6 (2)
DG 14:1_16:1	30:2	6.29	n/a	n/a	559.4332	246.6	2 (1)
<i>DG 14:0_14:0</i>	<i>28:0</i>	<i>7.28</i>	<i>495.4408</i>	<i>249.5</i>	<i>535.4334</i>	<i>244.6</i>	<i>9 (4)</i>
DG 12:0_18:1	30:1	7.52	521.4554	252.8	561.4493	250.6	3 (2)
DG 14:0_16:1	30:1	7.78	521.4565	253.6	561.4492	250.7	11 (5)
<i>DG 16:1_16:1</i>	<i>32:2</i>	<i>8.32</i>	<i>547.4713</i>	<i>256.6</i>	<i>587.4649</i>	<i>255.4</i>	<i>18 (7)</i>
DG 18:2_18:2	36:4	8.68	599.5038	263.8	639.4959	262.8	5 (2)
DG 15:0_16:1	31:1	9.00	535.4717	257.2	575.4649	254.8	10 (5)
DG 14:0_16:0	30:0	9.70	523.4718	257.7	563.4646	252.1	20 (7)
DG 14:0_18:1	32:1	10.03	549.4876	260.7	589.4802	258.9	6 (3)
DG 16:0_16:1	32:1	10.36	549.4880	261.0	589.4801	258.5	25 (9)
DG 16:0_18:2	34:2	10.56	575.5028	264.0	615.4956	263.1	3 (1)
DG 16:1_18:1	34:2	10.75	575.5029	263.9	615.4959	263.5	13 (5)
DG 18:1_18:2	36:3	10.85	601.5190	266.8	641.5113	266.5	3 (1)
DG 15:0_16:0	31:0	11.17	536.3765	261.6	577.4799	255.4	9 (5)
DG 15:0_18:1	33:1	11.56	563.5036	264.1	603.4956	262.3	2 (1)
<i>DG 16:0_16:0</i>	<i>32:0</i>	<i>12.76</i>	<i>551.5033</i>	<i>265.4</i>	<i>591.4956</i>	<i>259.7</i>	<i>30 (10)</i>
DG 16:0_18:1	34:1	12.86	577.5193	268.0	617.5115	267.2	12 (5)
<i>DG 18:1_18:1</i>	<i>36:2</i>	<i>12.92</i>	<i>603.5343</i>	<i>271.1</i>	<i>643.5271</i>	<i>270.0</i>	<i>9 (3)</i>
DG 16:0_18:0	34:0	13.47	579.5318	271.9	619.5270	267.1	12 (5)
<i>DG 18:0_18:0</i>	<i>36:0</i>	<i>14.01</i>	<i>607.5659</i>	<i>279.2</i>	<i>647.5586</i>	<i>274.6</i>	<i>6 (2)</i>

273 **Table 2:** Diglycerides detected in latent fingerprints from 10 donors. Compounds identified using  
274 standards are indicated in italics.

275 The peak intensities of the DGs were usually very low compared to those of the TGs (total peak  
276 response of the DG fraction in a sample was typically <5 % of the total identified glycerides). Often, a  
277 DG species could not be identified in all samples from a single donor, as diagnostic fragment ions could  
278 not be detected at low signal-to-noise ratios. This is consistent with literature stating that DGs  
279 constitute a very minor proportion of the glyceride fraction of skin surface lipids, as a hydrolysis  
280 product of TGs by skin surface bacteria.<sup>20, 24, 74</sup> Only four species (DG 16:0\_16:0 (dipalmitin), DG  
281 16:0\_16:1, DG 16:0\_14:0 and DG 16:1\_16:1 (dipalmitolein)) were found to be common to over half of  
282 the donor population, with only dipalmitin found in all 30 samples.





283

284

285 **Figure 2:** Extracted ion chromatogram  $m/z$  589.4800 (DG 32:1), showing chromatographic separation  
 286 of two isomers.

287 That fewer DGs were detected in comparison to the study of Camera *et al.* (where a total of 52 DGs  
 288 were reported),<sup>49</sup> can in part be explained by the differences in the samples collected (i.e. skin surface  
 289 lipids and latent fingermarks). Skin surface lipids are typically collected by affixing an absorbent  
 290 material directly to the sampling site for an extended period of time (e.g. 30 minutes), which would  
 291 enable a larger amount of secretions to be collected as opposed to the residual amount of material  
 292 that would be collected through briefly contacting a fingertip to a porous substrate.

293 To the best of the authors' knowledge, no information has been previously reported regarding the  
 294 specific DG species in latent fingermarks. While this lipid class may not comprise a significant  
 295 proportion of recently deposited latent fingermarks, they may still be relevant in composition studies.  
 296 As with other sebaceous lipids, a correlation has been noted between the age and sex of an individual,  
 297 and the proportions of TGs and DGs in skin lipid samples.<sup>75</sup> Over time following fingermark deposition,  
 298 degradation processes may further alter this ratio.<sup>4</sup> Therefore, knowledge of the full glyceride content  
 299 of latent fingermarks will be of greater value towards understanding fingermark detection and  
 300 degradation, by identifying reactants and intermediates in degradation mechanisms.

301

### 302 Triglyceride identification

303 A great challenge to the separation and identification of TGs within a natural lipid sample is the diverse  
 304 range of structures present, including the presence of isomers within a single CN:DB family.<sup>59, 76, 77</sup> The  
 305 number of potential isomers for a given CN:DB increases with molecular weight, resulting in thousands  
 306 of total structures that could be theoretically be present in a single sample.<sup>51, 52, 78, 79</sup> For example, not  
 307 including positional isomers, 18 fatty acids have been reported in the literature as components of  
 308 human sebum and/or latent fingermarks. The resulting theoretical number of potential TG species in  
 309 a latent fingermark, disregarding isomers, exceeds 1000, and if all isomers are considered, near 6000.<sup>79</sup>  
 310 The differing relative abundances of the constituent fatty acids presents some indication as to the

311 likely higher concentration glyceride structures.<sup>80</sup> Reported TGs in human skin surface lipids range  
 312 from 27 – 94 families, comprising a wide variety of total fatty acyl chain lengths (34:0 – 60:0) and  
 313 degrees of unsaturation.<sup>27, 49, 75, 81</sup> The extremely diverse range of TG species present in human skin  
 314 presents many challenges to determining a complete catalogue in latent fingerprints. Emerson *et al.*  
 315 noted problems due to the number of TGs species (differing by numbers of double bonds) that could  
 316 occupy a single mass window specified for MS/MS experiments.<sup>10</sup>

317 The 5 TG standards (TG 24:0 – 48:0) eluted between 3.5 and 15.9 minutes, and were detected in the  
 318 low energy mass spectra as predominantly  $[M+NH_4]^+$  (Table S2). Dissociation fragments produced in  
 319 the high energy mass spectra were consistent with known fragmentation patterns of TGs. Upon  
 320 collisional activation, ammonium adducts of TGs fragment to produce ‘DG-like’ ions, resulting from  
 321 the neutral loss of each unique fatty acyl group from the *sn*-1, -2, or -3 position, plus ammonia.<sup>44, 77</sup>  
 322 This pattern of fragmentation provides a basis for the untargeted identification of TGs by monitoring  
 323 datasets for fatty acid neutral losses, when the identities of the constituent TG fatty acids are known.  
 324 While MS<sup>E</sup> and MS/MS are not sufficient to conclusively identify a TG species, due to the ambiguity of  
 325 the remaining two fatty acids, some structures may be assumed based on the most prevalent fatty  
 326 acids.<sup>10</sup> MS<sup>3</sup> is required to acquire more comprehensive structural information by fragmentation of  
 327 the resultant DG-like ion.<sup>44, 51, 52, 82</sup>

328 The fatty acid constituents of human skin lipids are unusual in the wide range of chain lengths and  
 329 structural variations that are present, including methyl branching (iso-, anteiso and other isomers) and  
 330 double bond positional isomers.<sup>20</sup> However, it should be noted that collision-induced dissociation  
 331 (CID) is not sufficient to identify structural characteristics such as double bond position or alkyl  
 332 branching, nor the *sn*-position of a fatty acid.<sup>83</sup> Table 3 lists the calculated mass losses of fatty acids  
 333 that have been identified as major components of human sebum and latent fingerprints, as both free  
 334 acids and components of glycerides.<sup>19, 20, 30, 34</sup> Up to 36 fatty acid structures originating from skin  
 335 surface TGs have been described in dermatological studies.<sup>19, 20, 84</sup> Additionally, Nicolaidis reports that  
 336 over 200 other acids are present in trace amounts, including unusually long and short fatty acids which  
 337 can be present in trace amounts in skin surface lipids.<sup>20</sup> Expected mass losses for 56 fatty acids ranging  
 338 from 2:0 – 25:2 were incorporated into the analysis method to account for fatty acid neutral losses  
 339 beyond the minimum and maximum chain lengths described above (Table S3).

Fatty acid(s)	CN:DB	RCOOH+NH <sub>3</sub> neutral loss	
		Formula	Mass (Da)
Octanoic acid (caprylic acid)	8:0	C <sub>7</sub> H <sub>15</sub> COOHNH <sub>3</sub>	161.14158
Nonanoic acid (pelargonic acid)	9:0	C <sub>8</sub> H <sub>17</sub> COOHNH <sub>3</sub>	175.15723
Decanoic acid (capric acid)	10:0	C <sub>9</sub> H <sub>19</sub> COOHNH <sub>3</sub>	189.17288
Dodecanoic acid (lauric acid)	12:0	C <sub>11</sub> H <sub>23</sub> COOHNH <sub>3</sub>	217.20418
Tridecanoic acid	13:0	C <sub>12</sub> H <sub>25</sub> COOHNH <sub>3</sub>	231.21983
Tetradecanoic acid (myristic acid)	14:0	C <sub>13</sub> H <sub>27</sub> COOHNH <sub>3</sub>	245.23548
Δ6-tetradecenoic acid	14:1	C <sub>13</sub> H <sub>25</sub> COOHNH <sub>3</sub>	243.21983
Pentadecanoic acid	15:0	C <sub>14</sub> H <sub>29</sub> COOHNH <sub>3</sub>	259.25113
Pentadecenoic acid	15:1	C <sub>14</sub> H <sub>27</sub> COOHNH <sub>3</sub>	257.23548
Hexadecanoic acid (palmitic acid)	16:0	C <sub>15</sub> H <sub>31</sub> COOHNH <sub>3</sub>	273.26678
Hexadecenoic acid (sapienic acid)	16:1	C <sub>15</sub> H <sub>29</sub> COOHNH <sub>3</sub>	271.25113
Heptadecanoic acid	17:0	C <sub>16</sub> H <sub>33</sub> COOHNH <sub>3</sub>	287.28243
Heptadecenoic acid (Δ6- and Δ8-heptadecenoic acids)	17:1	C <sub>16</sub> H <sub>31</sub> COOHNH <sub>3</sub>	285.26678
Octadecanoic acid (stearic acid)	18:0	C <sub>17</sub> H <sub>35</sub> COOHNH <sub>3</sub>	301.29808

Octadecenoic acid ( $\Delta$ 8-octadecenoic acid, oleic and petroselinic acids)	18:1	C <sub>17</sub> H <sub>33</sub> COOHNH <sub>3</sub>	299.28243
Octadecadienoic acid (sebaleic and linoleic acids)	18:2	C <sub>17</sub> H <sub>31</sub> COOHNH <sub>3</sub>	297.26678
Eicosanoic acid (arachidic acid)	20:0	C <sub>19</sub> H <sub>39</sub> COOHNH <sub>3</sub>	329.32938
$\Delta$ 10-eicosenoic acid	20:1	C <sub>19</sub> H <sub>37</sub> COOHNH <sub>3</sub>	327.31373
$\Delta$ 7,10-eicosadienoic acid	20:2	C <sub>19</sub> H <sub>35</sub> COOHNH <sub>3</sub>	325.29808

340 **Table 3:** Neutral losses of major fatty acids identified in human sebum and latent fingerprints.<sup>19, 20, 30,</sup>  
341 <sup>34</sup>

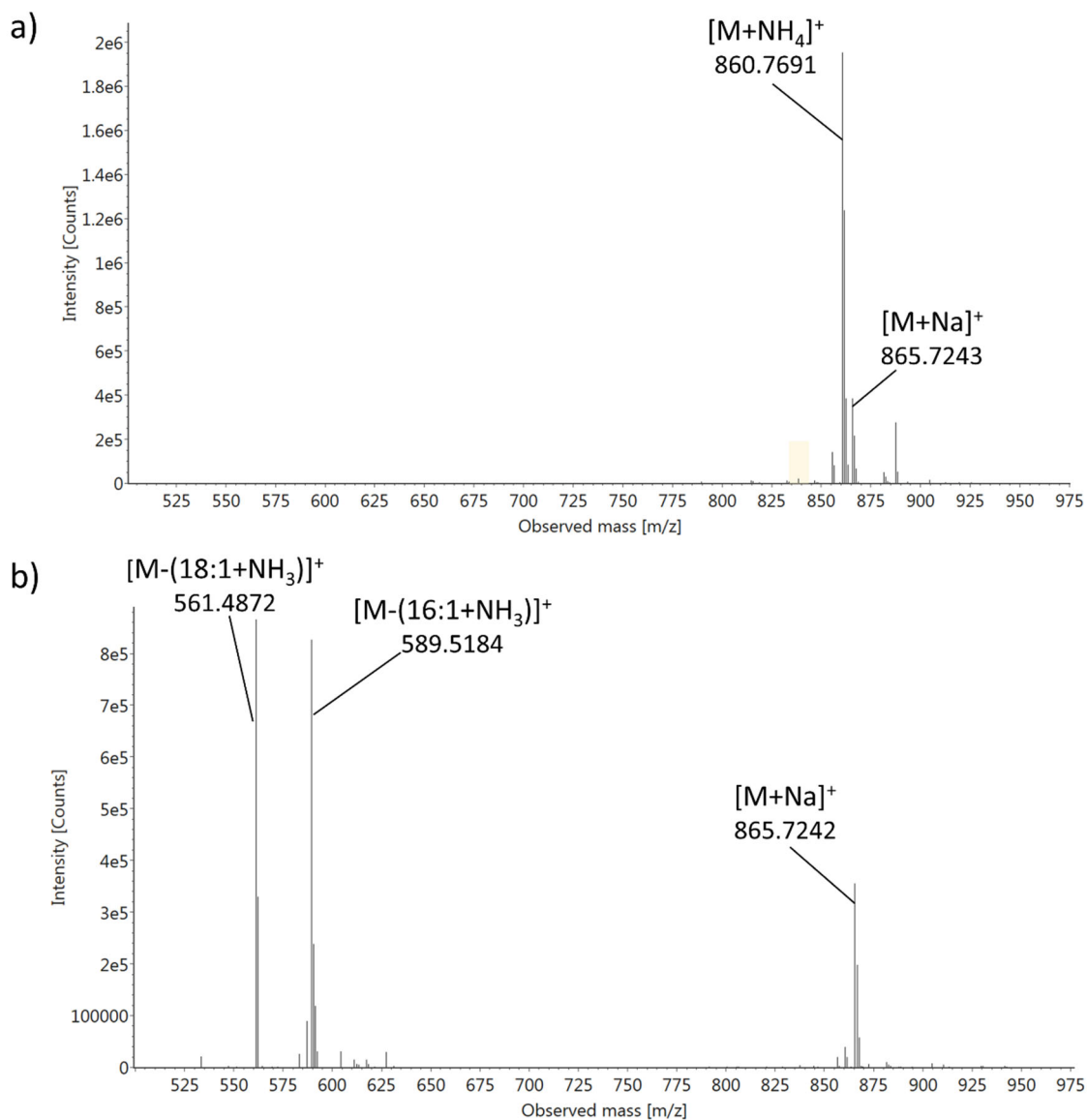
342 Fingerprint TGs were detected primarily as [M+NH<sub>4</sub>]<sup>+</sup>, with sodiated adducts comprising a minor part  
343 of the low collision energy mass spectra. TGs consistent with [M+NH<sub>4</sub>]<sup>+</sup> ions of the TG standards were  
344 identified within fingerprint samples, with the exception of tricaprilin (TG 24:0). Close to 100 peaks  
345 with *m/z* corresponding to ammoniated TGs eluted over a wide range of 6 – 17 minutes, with the  
346 greatest numbers (*ca.* 70 %) eluting between 15 – 17 minutes. Based on *in silico* fragmentation, 28  
347 families of TGs (including 21 that had previously been reported in skin surface lipids and latent  
348 fingerprints) were identified by UNIFI in 30 fingerprint samples. Manual examination of the mass  
349 spectra of identified peaks was required to identify any false positives, as identification was based only  
350 on high definition mass spectrometry measurements in lieu of reference data (i.e. retention times or  
351 CCS measurements). From these data, it could be seen that in many instances that relying only on *in*  
352 *silico* fragmentation for compound identification was insufficient, as the interpretation of MS<sup>E</sup> data  
353 was complicated by the presence of multiple fatty acid neutral losses, indicating coelution of isomeric  
354 TGs.

355 In total, 85 families of TGs were identified from the total 30 fingerprint samples (Table S4), ranging in  
356 structure from 28:0 – 60:2 and comprising 27 ECNs. The majority consisted of saturated, mono- and  
357 diunsaturated TGs, with a smaller number of polyunsaturated TGs containing up to 6 double bonds.  
358 Among the TGs showing the highest response, 21 families were identified as being common to samples  
359 from all or most of the 10 donors (Table 4). These compounds are predominantly unsaturated, and so  
360 may therefore be useful targets in the monitoring of chemical changes in fingerprint residue over  
361 time.<sup>29</sup> As a comparison, 27 TG families have been previously identified in latent fingerprints, with  
362 possible structures assigned to all but 2,<sup>10</sup> and 94 families and 142 species separately in human  
363 sebum.<sup>27, 49</sup>

364 Major observed neutral losses for all glycerides for the most part corresponded predominantly to the  
365 free fatty acid species previously reported in the literature. This is consistent with the results obtained  
366 by Emerson *et al.*,<sup>10</sup> who focused on TG species that could be elucidated from the 8 most abundant  
367 free fatty acids as reported by Nicolaides.<sup>20</sup> Up to 5 fatty acid neutral losses were observed for each  
368 TG family in a single sample, indicating isomeric species. In some cases, possible structures can be  
369 tentatively assigned, where the high energy mass spectra are relatively simple. For example, the only  
370 neutral loss observed across all samples for TG 54:6 was 18:2, indicating that the structure is most  
371 likely simply 18:2/18:2/18:2. In other instances, the observed neutral losses did not appear to  
372 correspond to the parent CN:DB; e.g. some TGs with an odd CN did not exhibit any neutral losses of  
373 odd-chain fatty acids. An example is shown in Figure 3, where the base peak in the low energy  
374 spectrum (*m/z* 860.7691) is consistent with the ammoniated adduct of TG 51:3. In the high energy  
375 mass spectrum, the two most abundant fragments (*m/z* 561.4872 and 589.5184) correspond to  
376 neutral losses of 18:1 and 16:1, respectively. The presence of an odd-chain fatty acid (possibly 17:1)  
377 may be inferred based on the CN:DB of the parent TG, but no corresponding neutral loss is observed.  
378 The loss of a fatty acid at the *sn*-1 or -3 position is demonstrably more favourable than a loss at the

379 *sn*-2 position<sup>85</sup>. It is possible that the 'missing' fatty acids are located at this position,<sup>45</sup> and are  
380 therefore less likely to be observed in CID experiments.

381



382

383 **Figure 3:** MS<sup>E</sup> spectra of *m/z* 860.7691 (TG 51:3), showing (a) the low energy mass spectrum containing  
384 ammoniated and sodiated adducts; and (b) the high energy mass spectrum containing DG-like  
385 fragments corresponding to fatty acyl neutral losses.

386 Examination of low energy spectra where several TGs were present confirmed the coelution of TG  
387 critical pairs, as described above.<sup>40, 78, 80</sup> The use of IMS confers an advantage in this regard, as  
388 coeluting TG species may be resolved on the basis of drift time, which is a reflection of differences in  
389 molecular structure and *m/z*.<sup>68, 71, 86</sup> Due to the close structural similarities between critical pairs, and  
390 therefore close drift times, it was necessary to reduce the fractions of the drift peak width for isotope  
391 clustering and high-to low energy association from the default value of 0.5. This process enabled the  
392 removal of critical pairs and their assigned fragments from the mass spectral data, facilitating the  
393 identification of fatty acyl losses for all but 6 of the 85 identified TG families.

394 While no quantification approach was used in this study, it can be inferred from the relative variations  
 395 in peak areas between samples from different donors that inter- and intra-donor variation can be  
 396 expected in glyceride profiles of latent fingerprints. Emerson *et al.* attempted to discriminate donors  
 397 by sex based on TG peak intensities, but were unable to develop a reliable method despite observing  
 398 statistically significant differences between male and female donors.<sup>10</sup> Pleik *et al.* made the  
 399 observation that monounsaturated TGs showed higher intensity than other TG components in  
 400 recently deposited fingerprints.<sup>29</sup> Similar results were reported by Camera *et al.* for human sebum  
 401 samples.<sup>49</sup> It should be noted however that the ionisation efficiency of glycerides is significantly  
 402 affected by chain length and degree of unsaturation, so that relative peak response is not necessarily  
 403 representative of concentration.<sup>42, 83</sup>

404

ECN	CN:DB	Average retention time (min)	Average experimental $m/z$ ( $[M+NH_4]^+$ )	Average CCS ( $\text{\AA}^2$ ) ( $[M+NH_4]^+$ )	Observed fatty acid neutral losses	Number of fingerprints [n = 30] (number of donors [n = 10])
42	TG 44:1	15.03	766.6915	313.1	12:0, 14:0, 14:1, 15:0, 16:0, 16:1, 18:0	30 (10)
	TG 46:2	15.09	792.7073	318.4	14:1, 15:0, 16:0, 16:1	30 (10)
	TG 48:3	15.14	818.7228	323.3	16:1, 14:1	30 (10)
43	TG 45:1	15.18	780.7072	316.7	12:0, 14:0, 14:1, 15:0, 16:0, 16:1, 17:1, 18:0	26 (10)
	TG 47:2	15.25	806.7228	322.2	14:1, 15:0, 16:1, 17:1, 18:1	30 (10)
44	TG 46:1	15.38	794.7228	320.7	12:0, 14:1, 15:0, 16:0, 16:1, 18:0, 18:1	30 (10)
	TG 48:2	15.42	820.7385	325.8	14:0, 14:1, 16:0, 16:1, 18:0, 18:1	30 (10)
	TG 50:3	15.45	846.7541	330.7	16:1, 18:0, 18:1	30 (10)
45	TG 47:1	15.52	808.7385	324.3	14:0, 14:1, 15:0, 16:0, 16:1, 18:0, 20:1	29 (10)
	TG 49:2	15.56	834.7541	329.7	15:0, 16:0, 16:1, 17:1, 18:0, 18:1, 18:2	30 (10)

46	TG 46:0	15.65	796.7385	322.4	14:0, 15:0, 16:0, 18:0	20 (8)
	TG 48:1	15.69	822.7542	327.8	14:0, 16:0, 16:1, 18:0, 18:1	30 (10)
	TG 50:2	15.72	848.7698	333.2	14:0, 16, 16:1	30 (10)
	TG 52:3	15.72	874.7854	337.5	16:0, 16:1, 18:1, 18:2	30 (10)
47	TG 47:0	15.77	810.7541	325.8	16:0, 18:0	29 (10)
	TG 49:1	15.81	836.7698	331.5	14:0, 15:0, 16:0, 16:1, 17:1, 18:1	30 (10)
	TG 51:2	15.84	862.7854	336.8	14:0 15:0, 16:0, 16:1, 17:1, 18:1, 18:2	30 (10)
48	TG 48:0	15.95	824.7698	329.8	16:0, 18:0, 20:0	23 (8)
	TG 50:1	15.97	850.7854	335.5	14:0, 16:0, 16:1, 18:0, 18:1	30 (10)
	TG 52:2	15.97	876.8009	339.9	16:0, 16:1, 18:0, 18:1	30 (10)
49	TG 51:1	16.08	864.8010	338.7	16:0, 16:1, 18:0, 18:1	30 (10)

405 **Table 4:** Triglycerides identified as major and common components in fingermarks from 10 donors.

406

#### 407 **Conclusions**

408 The glyceride fraction of human skin surface lipids exhibits a high degree of complexity, presenting  
409 challenges to the complete characterisation of latent fingermark residue. Using UPLC-IMS-QToF-MS<sup>E</sup>  
410 in a lipidomics-based approach, over 100 intact glycerides (DG 24:0 – 36:0 and TG 28:0 – 60:2), were  
411 detected in fingermarks from a population of 10 donors. This represents a more comprehensive list of  
412 the glyceride species present in fingermark samples than have been previously reported. To the  
413 authors' knowledge, specific diglyceride species in latent fingermarks have been identified for the first  
414 time, as a minor component of the total glyceride fraction. IMS enabled the use of a high-throughput  
415 UPLC method, as mass spectra of chromatographically coeluting TGs could be further resolved based  
416 on drift times.

417 This study represents a first step to better understanding the glyceride fraction of latent fingermark  
418 residue, and its potential impact on fingermark detection. Monitoring the chemical and physical  
419 changes in the lipid fraction of latent fingermarks following deposition might significantly contribute  
420 to understanding the mechanisms behind lipid-sensitive fingermark enhancement. Further studies are  
421 currently underway to examine the effect of increasing fingermark age on the glyceride composition  
422 of older samples (up to several weeks old), with a primary focus on the most common and abundant  
423 triglycerides.

424

425 **Conflicts of interest**

426 There are no conflicts to declare.

427

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436 entirely anonymised.

437

438 **References**

- 439 1. G. M. Mong, C. E. Petersen and T. R. W. Clauss, *Advanced Fingerprint Analysis Project:*  
440 *Fingerprint Constituents*, Pacific Northwest National Laboratory, Richland, 1999.
- 441 2. A. Girod, L. Xiao, B. Reedy and C. Weyermann, *Forensic Science International*, 2015, **254**,  
442 185-196.
- 443 3. S. Cadd, M. Islam, P. Manson and S. Bleay, *Science & Justice*, 2015, **55**, 219.
- 444 4. N. E. Archer, Y. Charles, J. A. Elliott and S. Jickells, *Forensic Science International*, 2005, **154**,  
445 224-239.
- 446 5. B. N. Dorakumbura, R. E. Boseley, T. Becker, D. E. Martin, A. Richter, M. J. Tobin, W. Van  
447 Bronswijk, J. Vongsvivut, M. J. Hackett and S. W. Lewis, *Analyst*, 2018, **143**, 4027-4039.
- 448 6. R. S. Croxton, M. G. Baron, D. Butler, T. Kent and V. G. Sears, *Forensic Science International*,  
449 2010, **199**, 93-102.
- 450 7. S. Chadwick, S. Moret, N. Jayashanka, C. Lennard, X. Spindler and C. Roux, *Forensic Science*  
451 *International*, 2018, **289**, 381-389.
- 452 8. S. Moret, X. Spindler, C. Lennard and C. Roux, *Forensic Science International*, 2015, **255**, 28-  
453 37.
- 454 9. A. Girod, R. Ramotowski and C. Weyermann, *Forensic Science International*, 2012, **223**, 10-  
455 24.
- 456 10. B. Emerson, J. Gidden, J. O. Lay and B. Durham, *Journal of Forensic Sciences*, 2011, **56**, 381-  
457 389.
- 458 11. A. A. Frick, G. E. Chidlow and S. W. Lewis, *Forensic Science International*, 2015, **254**, 133-147.
- 459 12. K. Asano, C. Bayne, K. Horsman and M. Buchanan, *Journal of Forensic Sciences*, 2002, **47**,  
460 805-807.
- 461 13. M. V. Buchanan, K. Asano and A. Bohanon, *Chemical characterisation of fingerprints from*  
462 *adults and children*, SPIE (International Society for Optical Engineering), Boston, 1997.
- 463 14. C. Weyermann, C. Roux and C. Champod, *Journal of Forensic Sciences*, 2011, **56**, 102-108.
- 464 15. A. Girod, A. Spyratou, D. Holmes and C. Weyermann, *Science and Justice*, 2016, **56**, 165-180.
- 465 16. K. A. Mountfort, H. Bronstein, N. Archer and S. M. Jickells, *Analytical Chemistry*, 2007, **79**,  
466 2650-2657.
- 467 17. B. N. Dorakumbura, T. Becker and S. W. Lewis, *Forensic Science International*, 2016, **267**, 16-  
468 24.
- 469 18. K. M. Antoine, S. Mortazavi, A. D. Miller and L. M. Miller, *Journal of Forensic Sciences*, 2010,  
470 **55**, 513-518.

- 471 19. Z. M. H. Marzouki, A. M. Taha and K. S. Gomaa, *Journal of Chromatography*, 1988, **425**, 11-  
472 24.
- 473 20. N. Nicolaides, *Science*, 1974, **186**, 19-26.
- 474 21. R. Ramotowski, in *Advances in Fingerprint Technology*, eds. H. Lee and R. Gaensslen, CRC  
475 Press, Boca Raton, 2ND edn., 2001, pp. 63-104.
- 476 22. N. Nicolaides and G. C. Wells, *Journal of Investigative Dermatology*, 1957, **29**, 423-433.
- 477 23. L. G. Scheimann, G. Knox, D. Sher and S. Rothman, *Journal of Investigative Dermatology*,  
478 1960, **34**, 171-174.
- 479 24. D. T. Downing, J. S. Strauss and P. E. Pochi, *Journal of Investigative Dermatology*, 1969, **53**,  
480 322-327.
- 481 25. E. Háková, V. Vrkoslav, R. Míková, K. Schwarzová-Pecková, Z. Bosáková and J. Cvačka,  
482 *Analytical and Bioanalytical Chemistry*, 2015, **407**, 5175-5188.
- 483 26. P. Ramastry, D. D.T., P. E. Pochi and J. S. Strauss, *Journal of Investigative Dermatology*, 1970,  
484 **54**, 139-144.
- 485 27. R. Michael-Jubeli, J. Bleton and A. Baillet-Gufroy, *Journal of Lipid Research*, 2011, **52**.
- 486 28. G. Sasone-Bazzano, B. Cummings, A. K. Seeler and R. M. Reisner, *British Journal of*  
487 *Dermatology*, 1980, **103**, 131-137.
- 488 29. S. Pleik, B. Spengler, D. Ram Bhandari, S. Luhn, T. Schäfer, D. Urbacha and D. Kirsch *Analyst*,  
489 2018, **143**, 1197-1209.
- 490 30. S. Pleik, B. Spengler, T. Schäfer, D. Urbacha, S. Luhn and D. Kirsch *Journal of the American*  
491 *Society for Mass Spectrometry*, 2016, **27**, 1565-1574.
- 492 31. A. Wisthaler and C. J. Weschler, *Proceedings of the National Academy of Sciences*, 2010, **107**,  
493 6568-6575.
- 494 32. N. Lauzon, M. Dufresne, V. Chauhan and P. Chaurand, *Journal of the American Society for*  
495 *Mass Spectrometry*, 2015, **26**, 878-886.
- 496 33. A. Koenig, A. Girod and C. Weyermann, *Journal of Forensic Identification*, 2011, **61**, 652-676.
- 497 34. A. Girod and C. Weyermann, *Forensic Science International*, 2014, **238**, 68-82.
- 498 35. A. Beaudoin, *Journal of Forensic Identification*, 2004, **54**, 413-421.
- 499 36. K. Braasch, M. de la Hunty, J. Deppe, X. Spindler, A. A. Cantu, P. Maynard, C. Lennard and C.  
500 Roux, *Forensic Science International*, 2013, **230**, 74-80.
- 501 37. A. A. Frick, F. Buseti, A. Cross and S. W. Lewis, *Chemical Communications*, 2014, **50**, 3341-  
502 3343.
- 503 38. M. de la Hunty, S. Moret, S. Chadwick, C. Lennard, X. Spindler and C. Roux, *Forensic Science*  
504 *International*, 2015, **257**, 481-487.
- 505 39. A. Becue, A. Scoundrianos and S. Moret, *Forensic Science International*, 2012, **219**, 39-49.
- 506 40. J. M. Bosque-Sendra, L. Cuadros-Rodríguez, C. Ruiz-Samblás and A. P. de la Mata, *Analytica*  
507 *Chimica Acta*, 2012, **724**, 1-11.
- 508 41. M. Lída, K. Netušilová, L. Franěk, H. Dvořáková, V. Vrkoslav and M. Holčapek, *Journal of*  
509 *Chromatography A*, 2011, **1218**, 7499-7510.
- 510 42. M. Holčapek, M. Lída, P. Jandera and N. Kabátová, *Journal of Separation Science*, 2005, **28**,  
511 1315-1333.
- 512 43. X. Han and R. W. Gross, *Analytical Biochemistry*, 2001, **295**, 88-100.
- 513 44. R. C. Murphy, P. F. James, A. M. McAnoy, J. Krank, E. Duchoslav and R. M. Barkley, *Analytical*  
514 *Biochemistry*, 2007, **366**, 59-70.
- 515 45. H. Kosugi and N. Ueta, *Japanese Journal of Experimental Medicine*, 1977, **47**, 335-340.
- 516 46. E. Sisco, L. T. Demoranville and G. Gillen, *Forensic Science International*, 2013, **231**, 263-269.
- 517 47. R. Bradshaw, S. Bleay, R. Wolstenholme, M. R. Clench and S. Francese, *Forensic Science*  
518 *International*, 2013, **232**, 111-124.
- 519 48. P. Hinners, K. C. O'Neill and Y. J. Lee, *Scientific Reports*, 2018, **8**, 5149.
- 520 49. E. Camera, M. Ludovici, M. Galante, J. Singra and M. Picardo, *Journal of Lipid Research*, 2010,  
521 **51**, 3377-3388.



- 522 50. E. Camera, M. Ludovici, S. Tortorella, J. Sinagra, B. Capitanio, L. Goracci and M. Picardo,  
523 *Journal of Lipid Research*, 2016, **57**, 1051-1058.
- 524 51. A. M. McAnoy, C. C. Wu and R. C. Murphy, *Journal of the American Society for Mass*  
525 *Spectrometry*, 2005, **16**, 1498-1509.
- 526 52. R. C. Murphy and S. J. Gaskell, *Journal of Biological Chemistry*, 2011, **286**, 25427–25433.
- 527 53. T. Řezanka, K. Pádrová and K. Sigler, *Analytical Biochemistry*, 2017, **524**, 3-12.
- 528 54. A. G. Solaesa, S. L. Bucio, M. T. Sanz, S. Beltrán and S. Rebolleda, *Journal of Oleo Science*,  
529 2014, **63**, 449-460.
- 530 55. B. N. Dorakumbura, PhD, (PhD thesis) Curtin University, 2017.
- 531 56. S. S. Bird, V. R. Marur, M. J. Sniatynski, H. K. Greenberg and B. S. Kristal, *Analytical Chemistry*,  
532 2011, **83**, 6648–6657.
- 533 57. K. Ikeda, Y. Oike, T. Shimizu and R. Taguchi, *Journal of Chromatography B*, 2009, **877**, 2639-  
534 2647.
- 535 58. L. Fauconnot, J. Hau, J. Aeschlimann, L. Fay and F. Dionisi, *Rapid Communications in Mass*  
536 *Spectrometry*, 2004, **18**, 218-224.
- 537 59. P. Dugo, O. Favoino, P. Q. Tranchida, G. Dugo and L. Mondello, *Journal of Chromatography*  
538 *A*, 2004, **1041**, 135-142.
- 539 60. International Fingerprint Research Group (IFRG), *Journal of Forensic Identification*, 2014, **64**,  
540 174-200.
- 541 61. A. Kaufmann, P. Butcher, K. Maden, S. Walker and M. Widmer, *Rapid Communications in*  
542 *Mass Spectrometry*, 2017, **31**, 1147-1157.
- 543 62. A. Kaufmann, P. Butcher, K. Maden, S. Walker and M. Widmer, *Journal of the American*  
544 *Society for Mass Spectrometry*, 2017, **28**, 2705-2715.
- 545 63. G. Liebisch, J. A. Vizcaíno, H. Köfeler, M. Trötz Müller, W. J. Griffiths, G. Schmitz, F. Spener  
546 and M. J. O. Wakelam, *Journal of Lipid Research*, 2013, **54**, 1523–1530.
- 547 64. K. L. Duffin, J. D. Henion and J. J. Shieh, *Analytical Chemistry*, 1991, **63**, 1781-1788.
- 548 65. R. D. Plattner, G. F. Spencer and R. Kleiman, *Journal of the American Oil Chemists' Society*,  
549 1977, **54**, 511-515.
- 550 66. M. Ovčáčíková, M. Lísa, E. Cífková and M. Holčapek, *Journal of Chromatography A*, 2016,  
551 **1450**, 76-85.
- 552 67. R. C. Murphy and P. H. Axelsen, *Mass Spectrometry Reviews*, 2011, **30**, 579-599.
- 553 68. I. Blaženović, T. Shen, S. S. Mehta, T. Kind, J. Ji, M. Piparo, F. Cacciola, M. Mondello and O.  
554 Fiehn, *Analytical Chemistry*, 2018, **90**, 10758-10764.
- 555 69. J. La Nasa, E. Ghelardi, I. Degano, F. Modugno and M. P. Colombini, *Journal of*  
556 *Chromatography A*, 2013, **1308**, 114-124.
- 557 70. M. Holčapek, P. Jandera, N. Kabátová, P. Zderadička and L. Hrubá, *Journal of*  
558 *Chromatography A*, 2003, **1010**, 195-215.
- 559 71. V. Shah, J. M. Catro-Perez, D. G. McLaren, K. B. Herath, S. F. Previs and T. P. Roddy, *Rapid*  
560 *Communications in Mass Spectrometry*, 2013, **27**, 2195-2200.
- 561 72. P. M. Hutchins, R. M. Barkley and R. C. Murphy, *Journal of Lipid Research*, 2008, **49**, 804-813.
- 562 73. H. Mu, H. Sillen and C. Hçy, *Journal of the American Oil Chemists' Society*, 2000, **77**, 1049-  
563 1060.
- 564 74. R. S. Greene, D. T. Downing, P. E. Pochi and J. S. Strauss, *Journal of Investigative*  
565 *Dermatology*, 1970, **54**, 240-247.
- 566 75. T. Sadowski, C. Klose, M. J. Gerl, A. Wójcik-Maciejewicz, R. Herzog, K. Simons, A. Reich and  
567 M. A. Surma, *Scientific Reports*, 2017, **7**, 43761.
- 568 76. X. Li and J. J. Evans, *Rapid Communications in Mass Spectrometry*, 2005, **19**, 2528-2538.
- 569 77. R. C. Murphy, in *Tandem Mass Spectrometry of Lipids: Molecular Analysis of Complex Lipids*,  
570 Royal Society of Chemistry, Cambridge, UK, 2015, ch. 4, pp. 75-104.
- 571 78. L. Ruano Miguel, M. Ulberth-Buchgraber and A. Held, *Journal of Chromatography A*, 2014,  
572 **1338**, 127-135.

- 573 79. T. Řezanka and K. Sigler, *Lipids*, 2014, **49**, 1251-1260.
- 574 80. A. Acheampong, L. N., A. Tchapla and C. Heron, *Journal of Chromatography A*, 2011, **1218**,  
575 5087-5100.
- 576 81. A. C. Kendall, M. M. Koszyczarek, E. A. Jones, P. J. Hart, M. Towers, C. E. M. Griffiths, M.  
577 Morris and A. Nicolau, *Experimental Dermatology*, 2018, **27**, 721-728.
- 578 82. M. Malone and J. J. Evans, *Lipids*, 2004, **9**, 273–284.
- 579 83. A. Triebel, M. Trötz Müller, J. Hartler, T. Stojakovic and H. C. Köfelerad, *Journal of*  
580 *Chromatography B*, 2017, **1053**, 72-80.
- 581 84. K. M. Nordstrom, J. N. Labows, K. J. McGinley and J. J. Leyden, *Journal of Investigative*  
582 *Dermatology*, 1986, **86**, 700-705.
- 583 85. E. Hvattum, *Rapid Communications in Mass Spectrometry*, 2001, **15**, 187-190.
- 584 86. C. W. N. Damen, G. Isaac, J. Langridge, T. Hankemeier and R. J. Vreeken, *Journal of Lipid*  
585 *Research*, 2014, **55**, 1772-1783.
- 586