Forensic Science International 254 (2015) 133–147

Contents lists available at ScienceDirect

Forensic Science International

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

Investigations into the initial composition of latent fingermark lipids by gas chromatography–mass spectrometry

A.A. Frick [a,b], G. Chidlow [b], S.W. Lewis [a,b,*], W. van Bronswijk [b]

[a] Nanochemistry Research Institute, Curtin University, Perth 6845, WA, Australia
[b] Department of Chemistry, Curtin University, Perth 6845, WA, Australia

ARTICLE INFO

Article history:
Received 31 March 2015
Received in revised form 19 June 2015
Accepted 30 June 2015
Available online 9 July 2015

Keywords:
Latent fingermarks
Lipids
Composition
Gas chromatography–mass spectrometry

ABSTRACT

A more comprehensive understanding of the variability of latent fingermark composition is essential to improving current fingermark detection capabilities in an informed manner. Gas chromatography–mass spectrometry was used to examine the composition of the lipid fraction of latent fingermarks collected from a population of over 100 donors. Variations in the appearances of chromatograms from different donors were apparent in the relative peak sizes of compounds including free fatty acids, squalene, cholesterol and wax esters. Principal component analysis was used as an exploratory tool to explore patterns in this variation, but no correlation to donor traits could be discerned. This study also highlights the practical and inherent difficulties in collecting reproducible samples.

1. Introduction

The interaction that occurs between a latent fingermark deposit and a development reagent is directly dependent upon chemical composition. There are many variables that can contribute to latent fingermark composition, including donor traits, exogenous contaminants and deposition factors. The presence of sebum on the fingertips has significant impact on the mass of the deposited fingermark, as well as the relative proportion of lipids within the residue [1,2]. It is well established that the increase in sebum production that occurs with the onset of puberty has a dramatic effect on the lipid content of fingermarks deposited by adults compared to young children [3–6]. Significant inter-individual variation has been observed in such studies, and as a result, it has been proposed that other differences in skin surface lipid production related to age, sex, diet, metabolic disorders and skin pathology may impact upon latent fingermark composition such that the analysis of this composition may allow these traits to be inferred [1,5–7]. There is a need for a more extensive understanding of fingermark chemistry for the further development of latent fingermark detection capabilities [6,8,9].

Several studies into fingermark composition have been conducted with the aim to establish whether individual traits may be ascertained from fingermark composition, should a fingermark prove too distorted or otherwise imperfect to allow identification based on the ridge detail [1,7,10–12]. To date, gas chromatography–mass spectrometry (GC–MS) is one of the most utilised methods for investigations into the lipid fraction of latent fingermarks [5,6,13,14]. Many of these studies have been of a preliminary nature, and as such have not involved more than a small number (<30) of adult donors [1,7,8,15]. The influence of donor traits is difficult to establish from exploratory investigations, as these small donor populations allow only limited representation of different ages, sexes, ethnicities and lifestyle factors [1,12]. There are few investigations that document variation within donor populations that are large enough to provide statistically valid datasets, and that can be considered representative of a general population [5,6]. The volume of multivariate data generated by large-scale analytical studies requires multivariate statistical analysis in order to derive meaningful information from the dataset [1,7,16]. One of the most widely used multivariate statistics methods is principal component analysis (PCA) [17]. PCA simplifies the interpretation of large, complex datasets, such as infrared and ultraviolet–visible spectra or chromatograms of complex mixtures, in an objective and reproducible manner [17–20]. This is achieved by reducing data dimensionality through the transformation of multiple variables from the original datasets into a reduced number of new, orthogonal variables known as principal components (PCs), which can also be used to visualise the distribution of samples [17,19,21–23]. Such an approach has been used by Croxton et al. to highlight the compositional differences between charged and uncharged fingermarks [1].

* Corresponding author at: Department of Chemistry, Curtin University, GPO Box U1987, Perth 6845, WA, Australia. Tel.: +61 08 9266 2484.
E-mail address: S.Lewis@curtin.edu.au (S.W. Lewis).

http://dx.doi.org/10.1016/j.forsciint.2015.06.032
0379-0738/

We present a series of investigations into the variability of the initial composition of latent fingermark lipids from a statistically relevant donor population, using gas chromatography–mass spectrometry. Compounds of interest were identified from the most abundant peaks commonly encountered in most samples, in conjunction with major sebum and fingermark constituents described in the literature. Principal component analysis was performed on this data to assess the influence of intra- and inter-donor variation on fingermark composition. To this end fingermark deposits from 5 donors were collected at 2 h intervals over an 8 h period and daily at a 2–3 day interval to assess intra donor variability, and once only from 116 donors to assess intra donor variability.

2. Materials and method

2.1. Chemicals

Myristic acid (Aldrich, USA), palmitic acid (Fluka Analytical), sapienic acid (Matreya, USA), palmitoleic acid (Sigma-Aldrich, USA), stearic acid (Aldrich, USA), squalene (Sigma-Aldrich, USA), cholesterol (BDH, UK), myristyl palmitoleate (Nu-Chek Prep, Inc, USA), myristyl palmitate (Nu-Chek Prep, Inc, USA), palmityl palmitate (Nu-Chek Prep, Inc, USA), palmityl palmitoleate (Nu-Chek Prep, Inc, USA), oleyl myristate (Nu-Chek Prep, Inc, USA), USA), stearyl myristate (Nu-Chek Prep, Inc, USA), stearyl palmitoleate (Nu-Chek Prep, Inc, USA), palmityl oleate (Nu-Chek Prep, Inc, USA), stearyl palmitate (Nu-Chek Prep, Inc, USA) and dichloromethane (Macron Chemicals, USA) were used as received. A set of standard solutions of the free fatty acids, squalene, cholesterol and wax esters were prepared as individual solutions in dichloromethane in the concentration range of 0.1–50 ppm. All standard solutions were stored at −20 °C before and after analysis to prevent degradation and solvent evaporation.

2.2. Sample collection and storage

Fingermark samples were collected on filter paper circles (25 mm qualitative filter paper, Grade 1; Whatman, UK). Donors were instructed to briefly rub the tips of their middle three fingers on their forehead or nose, and then press each fingertip gently to a filter paper circle for approximately 10 s. Some donors were required to provide samples using a modified procedure where fingermarks from both hands were deposited sequentially to collect two fingermarks on each filter paper. After the donor removed their hand, the filter papers were wrapped in aluminium foil and labelled with an alphanumeric code. Donors were also asked to fill out a brief survey regarding their age, sex and substances they had recently handled. Samples were analysed within an hour of deposition, or were stored in screw-top jars and transferred to a −20 °C freezer until analysis. Samples collected at locations remote to the laboratory were stored in an ice box until they had been transported to either the laboratory or the freezer.

3. Sample preparation

Extraction of fingermark residue from the filter papers was performed in 1.75 mL glass screw-top vials (Thermo Fisher Scientific, Australia) that had been cleaned by rinsing with dichloromethane. Samples that had been stored at −20 °C were allowed to equilibrate to ambient temperature before extraction. Samples were immersed in 750 μL dichloromethane for 2 min, with gentle manual agitation to ensure that the filter papers were completely submerged in the solvent. After 2 min, the filter papers were removed and discarded, and the sample extracts were then transferred to 2 mL glass crimp top vials (Agilent Technologies, USA). The vials were sealed with aluminium crimp tops (Agilent Technologies, USA), after covering the vial opening with aluminium foil to prevent solvent extraction of plasticisers from the septa, and analysed by GC–MS. Analytical blanks consisting of clean filter papers were prepared and analysed with each set of samples.

4. Chemical analysis

Chromatographic analysis was performed on a Hewlett Packard 6890 series GC coupled with a Hewlett Packard 5973 mass selective detector (MSD), a 6890N series GC coupled with an Agilent 5973N MSD, a Hewlett Packard 6890A GC coupled with a Hewlett Packard 5973A MSD, a 6890 series GC coupled with an Agilent 5975 inert MSD, and an Agilent 7890A GC coupled with a Agilent 5975C inert XL EI/CI MSD. Full instrumental conditions are described in Table 1.

For all sample analysis, the GC oven was programmed from 40 °C, held for 1 min, then increased from 40 °C to 320 °C at 20 °C/min and held for 30 min. The inlet was operated at 320 °C in splitless mode. Helium was used as the carrier gas, at a constant flow rate of 1.1 mL/min. Typical MSD conditions were: solvent delay, 5 min; ionisation energy, 70 eV; source temperature, 230 °C; and electron multiplier voltage, 1505.9 V.

For C16:1 isomer comparisons, the GC oven was programmed (a) from 40 °C, held for 1 min, then increased from 40 °C to 260 °C at 10 °C/min and held for 35 min; (b) from 40 °C to 150 °C at 10 °C/min and held for 50 min, then increased from 150 °C to 260 °C at 10 °C/min and held for 5 min; and (c) from 40 °C to 180 °C at 10 °C/min and held for 50 min, then increased from 180 °C to 260 °C at 10 °C/min and held for 5 min. The inlet was operated at 270 °C in splitless mode. Helium was used as the carrier gas, at a constant flow of 1.1 mL/min. Typical MSD conditions were: solvent delay, 3 min; ionisation energy, 70 eV; source temperature, 230 °C; and electron multiplier voltage, 2553 V.

Table 1
Instrumental conditions for GC–MS.

	Gas chromatograph	Column type	Injector	Injection volume	Mass spectrometer
C16:1 isomer comparison	Agilent 7890A	Agilent Technologies HP-Innowax (30 m × 0.25 mm ID × 0.25 μm d_f)	Agilent 7683B series	1 μL	Agilent 5975C inert XL EI/CI MSD
Intra-donor variation (1 day)	Hewlett Packard 6890A	Agilent J&W DB-5MS (60 m × 0.25 mm ID × 0.25 μm d_f)	Hewlett Packard 6890 series injector		Hewlett Packard 5973A
Intra-donor variation (1 month)	6890 series	Phenomenex ZB-5MS (30 m × 0.25 mm ID × 1 μm d_f)	Gerstel MPS2 autosampler		Agilent 5975 inert mass selective detector
Inter-donor variation					