A Chemically Relevant Artificial Fingerprint Material for the Cross Comparison of Mass Spectrometry Techniques

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Research was conducted at the National Institute of Standards & Technology

Acknowledgements: The authors would like to thank Matthew Staymates for his work on the artificial fingerprint stamp. This work was supported by the Science and Technology Explosives Division of the U.S. Department of Homeland Security under interagency agreement HSHQDC-12-X-0024 with the National Institute of Standards and Technology.

Abstract

The development of a chemically relevant artificial fingerprint material as well as a preliminary method for artificial fingerprint deposition for mass spectrometric analysis and chemical imaging is presented. The material is an emulsified combination of artificial eccrine and sebaceous components designed to mimic the chemical profile of a latent fingerprint. In order to deposit this material in a manner that resembles a latent fingerprint, an artificial fingerprint stamp, created using 3-D printing, was used. Development of this material was spurred by the inability to cross-compare mass spectrometric techniques using real fingerprint deposits because of their inherent heterogeneity. To determine how well this material mimicked the chemical composition of actual fingerprint deposits, ambient ionization mass spectrometry and secondary ion mass spectrometry techniques were used to compare the signatures of the artificial and real fingerprint deposits. Chemical imaging comparisons of the artificial fingerprints across different imaging platforms are also presented as well a comparison using fingerprint development agents. The use of a material such as this may provide a way to compare the capabilities of different techniques in analyzing a sample as complex as a fingerprint as well as providing a method to create fingerprints with controlled amounts of exogenous material for research and technique validation purposes.

Keywords

Latent Fingerprints, Mass Spectrometry, Chemical Imaging

Introduction

Fingerprint analysis in a forensic setting has traditionally focused on understanding the structure and formation of fingerprint ridges, as well as establishing methods for the cross-comparison of fingerprint deposits. Additionally, research has also focused on how to locate invisible, or latent, fingerprints and make them visible using various developing agents. However, with the recent proliferation of sophisticated analytical techniques into the forensic science community, the chemical structure and makeup of latent fingerprint deposits has begun to be investigated [1–7]. One pitfall of evaluating and cross-comparing the techniques that study the chemical make-up of fingerprint deposits is the inherent variability in the chemical signature from one individual to another. Chemical signatures of an individual's fingerprint have been shown to be altered by factors such as diet, gender, age, medical conditions, application of cosmetics or lotion, and frequency of hand washing [1,2,7–10]. Because of this variability, as the chemical makeup of fingerprint deposits is probed further, and more techniques are developed to understand the chemistry in the deposits, there is a need to establish a fingerprint deposit with a known and reproducible chemical makeup. Furthermore, when it is of interest to examine fingerprints contaminated with potentially hazardous material, such as explosives and narcotics, an artificial fingerprint would allow for mitigation of hazards from direct contact by providing a method to create artificial fingerprints doped with these hazardous materials.

Though fingerprint deposits do vary amongst the population and even the individual, there are a number of components, and classes of components that are found in a large majority of fingerprints. Fingerprint deposits are generally composed of two different types of secretions – eccrine and sebaceous[2]. Eccrine secretions, also known as sweat, are secreted by the eccrine glands, located on the fingers and palms of the hands, and have been found to contain 98 % to 99

% water by mass [1,2]. The additional 1 % to 2 % by mass of the eccrine excretion has been found to contain numerous inorganic and organic compounds. Major groups within these classes of compounds include inorganic salts, amino acids, and proteins [1,2,10,11]. Other trace compound classes which are found in eccrine secretions include lipids, enzymes, immunoglobins, and vitamins as well as pharmaceuticals and metabolites [12–14]. Over four hundred individual compounds have been identified and associated with the eccrine secretions [2].

The second major type of secretion present in a fingerprint is the sebaceous secretion, also known as sebum. Sebum is secreted by the sebaceous glands located next to hair follicles [4]. Sebum components are commonly broken down into five classes of organic components: glycerides and free fatty acids, wax esters, cholesterol, squalene, and cholesterol esters [1,2]. Free fatty acids and glycerides are the most abundant component of sebum in adults, accounting for over 50 % by mass. Squalene, cholesterol, and cholesterol esters are found at lower weight percentages, typically below 10 % by mass, in adults but can have significantly higher proportions in the sebum of children. Additional, trace level components in sebaceous secretions include compounds such as phospholipids, alkanes, piperidines, and ketones [1,2,5,15,16].

Since the composition of a fingerprint deposit is variable and can contain hundreds of different compounds and salts, it would be extremely difficult to replicate the entire chemical composition of such a material. However, as the chemical composition of these deposits are probed and evaluated by a number of different analytical techniques, there is currently no way to accurately cross-compare techniques. Therefore, the material discussed herein aims to provide an artificial deposit which can be used to evaluate and cross-compare techniques using a reproducible material with a composition that is known – instead of relying on actual fingerprint deposits of unknown chemical makeup.

Areas of research which can be explored using this material include providing a standard platform for the cross-comparison of chemical imaging techniques, understanding the chemical changes in fingerprints as a function of time and environment, determining the chemical processes responsible for visualization of latent fingerprints, and providing a material to be used to represent a complex matrix in the detection of other compounds such as metabolites or exogenous components. Also, since the substance is made in-house, the chemical composition can be altered to remove, add, or change the concentration of individual components if desired, allowing for the inclusion or exclusion of components which could be useful in a number of different applications, such as trace contraband detection. While previous studies have been completed to create artificial sweat and sebum [17,18], these works have mainly focused on cosmetic applications, and have not focused on incorporating both excretion types into one inclusive material.

The development of this material was focused on the chemicals that are present in fingerprints at concentrations that can be detected by a number of different analytical techniques such as secondary ion mass spectrometry (SIMS) [19–21], atmospheric ionization mass spectrometry (AI-MS) [22–26], and gas chromatography mass spectrometry (GC/MS) [10,27]. From an extensive literature search and analysis of the chemical compositions of actual fingerprints, a list of the prevalent and readily detected fingerprint constituents was established and used as a basis for development of the material along with cross-comparison on these platforms with actual fingerprint deposits. This work outlines the method for the production of the artificial fingerprint material, as well as the production of artificial fingerprint stamps used to create artificial fingerprint deposits. A comparison of chemical signature of the material to actual fingerprints is then presented using both AI-MS and SIMS techniques. In addition to a chemical comparison, a comparison of chemical images produced by these techniques is presented, highlighting how the material can be used to analyze samples that are and are not doped with additional material. A brief comparison on the ability to develop artificial fingerprints using traditional development techniques is also presented.

Materials and Methods

Emulsion Development

To prepare the sweat solution, the components listed in Table 1 (total of 19) were dissolved into 990 mL of deionized water, in a 1000 mL volumetric flask. These compounds represented two of the three major classes of eccrine components; inorganic salts and amino acids. Proteins were not incorporated into the artificial eccrine material because of their low concentration and infrequent use as a target component in mass spectrometric fingerprint analysis, though they could easily be incorporated if desired. The sample was then sonicated for fifteen minutes to ensure complete mixing. After sonication, the solution was balanced to a pH of 5.5, the approximate pH of sweat [12], using 5 M NaOH and 12 M HCl (Sigma-Aldrich, St. Louis, MO, USA). The solution was then brought to volume, with deionized water, and sonicated for an additional fifteen minutes.

[Insert Table 1 near here]

To create the sebum, the 23 chemicals were used (Table 2), incorporating compounds from each of the five major classes present in sebaceous secretions. The sebum was produced by mixing the chemicals listed in Table 2 in a 20 mL amber vial using sonication. The heat produced from sonication (which raised the temperature of the mixture to approximately 35 ^{0}C) was sufficient to liquefy all solid components and allow for complete mixing.

[Insert Table 2 near here]

The goal of this work was to create a single fingerprint material which incorporated the major components of both eccrine and sebaceous secretions. In order to accomplish this, an emulsion of the artificial eccrine and sebaceous secretions was produced by adding equal amounts, by weight, of the artificial eccrine and sebaceous materials. Additionally an emulsifying agent, Steareth-20, (Sigma-Aldrich) was added at 0.5 % by mass to ensure homogeneity. The emulsion was then sonicated for fifteen minutes. Steareth-20 is an emulsifying agent commonly found in cosmetics and hand creams and is an exogenous material that has been detected in real fingerprint deposits [28]. The final, 1:1 eccrine-sebum emulsion had the consistency of a cosmetic lotion, allowing it to be easily applied to surfaces, fingers, or artificial fingerprint stamps. If a dilute emulsion was desired, the material could be diluted in water or an organic solvent such as methanol.

Artificial Fingers

Artificial fingerprint deposits were produced by pipetting a known amount of the emulsified mixture (2 µL to 5 µL) onto a glass slide. If the fingerprint was doped, 5 µg of the dopant (RDX, lead, barium, or antimony) were also pipetted onto the glass slide. A fingerprint stamp, details on the construction of which are presented elsewhere [29], was wiped over the fingerprint material to load the finger with the emulsion and then subsequently pressed down onto the surface of interest to produce a fingerprint. Real fingerprints were prepared by loading the finger with sebaceous material by rubbing the forehead, followed by deposition onto the surface of interest, allowing for enough sebaceous material to be present for analysis.

SIMS Operating Parameters:

In order to compare the chemical signature of the artificial fingerprint material to that of actual fingerprints, three different mass spectrometry techniques, secondary ion mass spectrometry (SIMS), desorption electrospray ionization mass spectrometry (DESI-MS), and laser desorption ionization mass spectrometry (LDI-MS) were used. The SIMS system that was used was a Cameca ims-4f (Gennevilliers Cedex, France) coupled with an IonOptika (Hampshire, England) C_{60} primary ion source. Preparation of samples for analysis by SIMS was completed by depositing the sample onto 2.54 cm circular silicon wafers. Analysis of the samples was completed on a CAMECA ims-4f (Madison, WI, USA) equipped with an IonOptika C_{60} primary ion source (Gennevilliers Cedex, France). Instrument parameters included a primary ion accelerating voltage of 10 keV, a 500 µm x 500 µm raster, a 250 µm x 250 µm imaging field, and a primary ion current of approximately 1×10^{-10} A. Mass spectrum parameters included a scan range of 0 *m/z* to 600 *m/z* with 1800 cycles at an integration time of 0.1 s/cycle. Both positive and negative secondary ion scans were completed.

DESI-MS Operating Parameters:

DESI-MS analysis was completed by depositing fingerprints directly onto double sided tape (Scotch, 3M) that was mounted to a clean glass microscope slide. The ionization source used was a Prosolia DESI source (Indianapolis, IN, USA) coupled to an ABSciex 4000 Q Trap mass spectrometer (Framington, MA, USA). Source parameters included a spray voltage of ±4000 V, N_2 carrier gas at a pressure of 5.5 bar, an incidence angle of approximately 40 ^{0}, and a solvent flow rate of 4.6 µL/min. The solvent used was a 50 : 50 methanol : water mixture. Mass spectrometer parameters included an inlet temperature of 200 ^{0}C and a scan range of 100 *m/z* to 800 *m/z*, at one second per scan, with 30 scans summed. Both positive and negative ion mass spectra were collected.

DESI-MS Imaging Parameters:

The DESI-MS analyses incorporated an ABSciex (Framington, MA, USA) QTrap 4000 mass spectrometer coupled with a Prosolia (Indianapolis, IN, USA) DESI source. Detailed parameters on the mass spectral imaging procedures can be found elsewhere [22,25]. Briefly, instrumental parameters identical to those in the above reference were used, however, in this instance the sample was scanned, at a rate of 350 µm/sec, in a perpendicular motion with respect to the mass spectrometer inlet. A small scan window (275 *m/z* – 290 *m/z*) was collected every 0.285 sec so that 100 µm x 100 µm pixels of data were collected. After each row was scanned, the sample was translated back to the home position and the next row (100 µm deeper than the previous) was scanned. In this configuration every line corresponded to a data file and every pixel to a single MS scan. The combined data was then transformed from the native ABSciex file type to a readable single file which was opened in MSiReader [30].

LDI-MS Operating & Imaging Parameters:

The LDI-MS analyses incorporated an ABSciex (Framington, MA, USA) QTrap 4000 mass spectrometer coupled with a MassTech (Columbia, MD, USA) AP-MALDI source. LDI-MS analysis was completed by depositing fingerprints directly onto Non-Focus Array Plates (Hudson Surface Technology, Old Tappan, NJ, USA). Source parameters included an Nd:Yag laser (355 nm wavelength) with a laser attenuation of 75 %, a laser repetition rate of 150 Hz, and an applied plate voltage of ±3000 V. Mass spectrometer parameters included an inlet temperature of 150 ^{0}C and a scan range of 30 *m/z* to 600 *m/z*, at two seconds per scan, with 30 scans summed. Both positive and negative ion mass spectra were collected.

Imaging procedures for the LDI-MS experiment are nearly identical to those of the DESI-MS setup. Differences included a scan rate of 0.420 µm/sec and a mass spectral window of 30 *m/z* – 40 *m/z* for the potassium ion scan or a split scan ranges of 120 *m/z* – 130 *m/z*, 135 *m/z* – 145 *m/z*, and 204 *m/z* – 214 *m/z* for the scan of lead, barium, and antimony. In all instances, the total scan time per pixel was 0.217 s.

Fingerprint Developing Procedures:

Latent prints deposited on glass microscope slides were developed using black fingerprint powder (Regular Silk Black Powder) and fluorescent (YELLOWescent Fluorescent Fingerprint Powder) fingerprint powders (Sirchie Co., Youngsville, NC, USA). Latent prints deposited on bond paper (Navigator premium multipurpose ultrabright) were developed using solutions of ninhydrin or 1,2-indanedione. To prepare the ninhydrin working solution, 5 g of ninhydrin (Evident Crime Scene Products, Union Hall, VA, USA) was mixed into 45 mL ethanol (Fisher Chemical, Pittsburgh, PA, USA), 2 mL ethyl acetate (Fisher Chemical, Pittsburgh, PA, USA), and 5 mL glacial acetic acid (Sigma-Aldrich); to this solution, 1 L of Novec™ HFE7100 (3M, St. Paul, MN, USA) was added for the final dilution step. The 1,2-indanedione working solution was prepared by dissolving 2 g of 1,2-indanedione (Sirchie Co.) in 70 mL ethyl acetate and mixing with 930 mL Novec™ HFE7100 (3M). These working solutions were applied individually to the bond paper by spraying the surface until it was thoroughly wetted. After air-drying, the papers were placed in a drying oven at 90 °C for 20 minutes.

Latent prints deposited on clear packing tape (Scotch Brand, 3M) were developed using cyanoacrylate or gentian violet. To develop with superglue, the tapes were hung in a 0.05 m^3

cabinet with 150 mg cyanoacrylate (Adhesive Systems RP100, Frankfort, IL, USA) in an aluminum dish on a hot plate heated to 110 °C. The tapes were allowed to fume for 10 minutes, and the cabinet was vented for 10 additional minutes prior to opening. After development with cyanoacrylate, the developed prints were rinsed with a methanol-based solution of rhodamine 6G for enhanced visualization. The rhodamine 6G working solution consisted of 5 mg rhodamine 6G (Sigma-Aldrich) in 500 mL methanol (Fisher Chemical). The gentian violet working solution was prepared by adding 1 g gentian violet to 1 L distilled water. The tapes were dipped into a shallow bath of gentian violet working solution, and then rinsed with a gentle stream of water.

Results and Discussion

Comparison of the Chemical Signatures of Real and Artificial Fingerprints

To compare the chemical signatures of the artificial material to actual fingerprint deposits, chemical analysis of both sample types was completed using SIMS, DESI-MS, and LDI-MS. These three techniques highlighted that the artificial material was chemically similar, though not chemically identical, to actual fingerprint deposits.

Figure 1 illustrates the chemical similarities between the actual fingerprint and emulsion when analyzed by SIMS in negative ionization mode. SIMS provides the benefit of simultaneous analysis of organic and inorganic constituents within a sample without changing instrumental parameters. Furthermore, the use of the C_{60} cluster ion source provided low fragmentation of molecules because of the dispersed energy of the primary ion cluster upon impact. This produced a mass spectrum dominated by molecular ion peaks, not fragment ions. The negative ion SIMS mass spectra (Figure 1) highlighted the comparison of the anionic species present in the samples as well as several amino acids and fatty acids. The make-up of the longer chain fatty acids (mass range 200 *m/z* to 350 *m/z*) was nearly identical with the exception of heptadecanoic acid ($[M\text{-}H]^-$, 269 *m/z*), present in actual fingerprints but not in the artificial material. The amino acid signature (mass range 70 *m/z* to 150 *m/z*) was also similar between the actual fingerprint and the artificial material. The positive ion mass spectrum (Figure 2) provided information predominantly on the inorganics, such as sodium and potassium, and several other organic components such as amino acids, cholesterol, and squalene that were found in both the actual fingerprint and the artificial emulsion. Like the negative ion SIMS spectra, the positive ion spectral comparison between the actual and artificial fingerprint deposits showed excellent agreement, indicating similar chemical composition. The major difference in the positive ion SIMS spectra, was the presence of additional peaks present in the 200 *m/z* to 600 *m/z* range of the artificial material. Those peaks were attributed to the emulsifying agent, Steareth-20.

[Insert Figures 1 & 2 near here]

A comparison of the chemical compositions via negative ion DESI-MS was also completed (Figure 3). Like SIMS, the DESI-MS comparison further strengthened the chemical similarity between the actual and artificial materials. Since DESI-MS analysis was completed under ambient conditions, detection of semi-volatile components such as short chain length and unsaturated fatty acids was easily accomplished. The inorganic profile of the fingerprint, however, could not be probed in this configuration. Stronger peaks for the glycerides, present in the range beyond 400 *m/z*, could be seen in the artificial material spectrum and was likely due to a higher mass of sample deposited onto the sampling surface than that of the actual fingerprint deposit.

[Insert Figure 3 near here]

LDI-MS, utilizing a high in-source collision induced dissociation voltage, provided a method to observe the inorganic fraction of a fingerprint under ambient conditions, and also illustrated a high degree of agreement between the real and artificial fingerprint deposits (Figure 4). Overall, the mass spectrometric techniques highlighted the close resemblance of the chemical composition of the sebum-sweat emulsion to the composition of actual fingerprint deposits.

[Insert Figure 4 near here]

Chemical Imaging Comparison

Another emerging area of fingerprint analysis is the chemical imaging of these deposits in order to obtain spatial information regarding the constituents in the fingerprints. Several different mass spectral techniques, namely SIMS [19,20,20,21] and ambient ionization based techniques [6,23,25,26,31–33], have been shown to be capable of resolving the fingerprint ridges and valleys of deposited fingerprints. There are a number of potential benefits of being able to obtain such information, including age dating of fingerprint deposits, determination of deposition order [6], and the capability to complete simultaneous biometric and chemical analysis. In order to compare these many techniques, however, the same, or approximately the same, fingerprint should be used to truly examine metrics such as spatial resolution, spatial detection limits, and quality of the obtained chemical images. To highlight how this material, and corresponding stamp, could be used to fill this role, artificial fingerprints were deposited onto double sided tape and MALDI plates for chemical imaging by DESI-MS and LDI-MS respectively. Both doped and non-doped fingerprints were deposited. Fingerprints analyzed by DESI-MS were doped with cyclotrimethylenetrinitramine (RDX), while fingerprint analyzed by LDI-MS were doped with a combination of lead, barium, and antimony. The images that were obtained, as well as an optical image of the starting deposited, are highlighted in Figure 5. It was evident from these images that both techniques were capable of resolving fingerprint ridges and valleys. Furthermore, as is highlighted in Figure 5C and 5F, it was possible for these techniques to detect and spatially resolve both the endogenous and exogenous components of a fingerprint. While this demonstration highlights the capability of this material to be used as a chemical imaging comparison tool, future work will focus on completing cross-comparisons of imaging techniques to truly understand the strengths and weaknesses of particular techniques in completing this type of complicated analysis.

Latent Fingerprint Development Comparison

In order to evaluate the ability of the artificial material to be developed in a manner similar to actual fingerprints, artificial fingerprints, using the ballistics gelatin stamps, were deposited onto surfaces, next to actual fingerprints and subjected to a number of different latent fingerprint development techniques. The techniques chosen included black powder, fluorescent powder, cyanoacrylate fuming followed by rhodamine 6G treatment, gentian violet, ninhydrin, and 1,2-indandione. The first three techniques were explored because of their widespread use in the field as physical developers. Gentian violet was tested because it reacts with the sebaceous components of fingerprints while ninhydrin and 1,2-indandione were chosen to test the reaction with amino acids [2]. Figure 6 illustrates the results of developing both the real and artificial fingerprints with each of the development techniques. Using all of the techniques listed, artificial fingerprints were able to be developed, indicating proper reaction with the chemical agents for techniques like ninhydrin and gentian violet. To understand if the detail created by the artificial fingerprints was less than those created by actual fingerprints, the real and artificial fingerprints were examined by a certified latent fingerprint examiner, from the Defense Forensic

Science Center (Fort Gillem, Georgia, USA) and the quality of the artificial fingerprint was determined to equal to or better than that of the real fingerprint in all cases. This indicates that the ability to use the artificial material as a method to study fingerprint development is possible. Current work is now focusing on expanding the range of developing agents tested as well as the ability of aged artificial fingerprints to develop in a similar manner to aged actual fingerprints.

[Insert Figure 6 near here]

Conclusions

A chemically relevant artificial fingerprint material has been established. Unlike prior work to create such a material, this method combined artificial sebaceous and eccrine secretions using an emulsification process to produce a material that contains major components of both secretions at chemically relevant concentrations and pH compared to real fingerprints pre-loaded with sebum. Chemical signatures of the actual and artificial fingerprint deposits were shown to widely agree and, though not identical, were similar enough to be used as a test material either for broad chemical detection capabilities or as an imaging standard. Another benefit of this material was that it was made in-house which allowed for the ability to incorporate additional materials to create a doped fingerprint (Figure 5). It is believed that this material has a wide range of potential applications including a standard for cross comparison of chemical analysis and chemical imaging of fingerprints, a material to evaluate new or existing visual developing agents (Figure 6), and a background matrix to supply realistic test materials for trace contraband detection. Current work is now focusing on developing a way to better quantify a method of doping the material, understanding the stability of the material, understanding how the material ages, evaluating the efficacy of developing techniques, exploring ways to enhance the precision of fingerprint deposits to create a more reproducible artificial fingerprint and fingerprint stamp, and completing a true cross-comparison of mass spectral imaging techniques.

References

[1] Girod A, Ramotowski R, Weyermann C. Composition of fingermark residue: A qualitative and quantitative review, Forensic Sci. Int. 2012;223:10–24.

[2] Lee H. Advances in Fingerprint Technology. 2nd ed. Boca Raton (FL): CRC Press; 2001.

[3] Archer NE, Charles Y, Elliott JA, Jickells S. Changes in the lipid composition of latent fingerprint residue with time after deposition on a surface. Forensic Sci. Int. 2005;154:224–239.

[4] Jacobsen E, Billings JK, Frantz RA, Kinney CK, Stewart ME, Downing DT. Age-Related Changes in Sebaceous Wax Ester Secretion Rates in Men and Women. J Investig Dermatol. 1985;85:483–485.

[5] Antoine KM, Mortazavi S, Miller AD, Miller LD. Chemical Differences Are Observed in Children's Versus Adults' Latent Fingerprints as a Function of Time. J. Forensic Sci. 2010;55: 513–518.

[6] Bright NJ, Webb RP, Bleay S, Hinder S, Ward NI, Watts JF, et al. Determination of the Deposition Order of Overlapping Latent Fingerprints and Inks Using Secondary Ion Mass Spectrometry. Anal Chem. 2012;84(9):4083 - 4087.

[7] Hemmila A, McGill J, Ritter D. Fourier Transform Infrared Reflectance Spectra of Latent Fingerprints: A Biometric Gauge for the Age of an Individual. J. Forensic Sci. 2008;53:369–376.

[8] Mong GM, Petersen CE, Clauss TRW. Advanced Fingerprint Analysis Project Fingerprint Constituents. 1999. Available from: http://www.osti.gov/bridge/servlets/purl/14172-SQLzxz/webviewable/.

[9] Boddis AM, Russell DA. Simultaneous development and detection of drug metabolites in latent fingermarks using antibody–magnetic particle conjugates. Anal. Methods. 2011;3:519–523.

[10] Croxton RS, Baron MG, Butler D, Kent T, Sears VG. Variation in amino acid and lipid composition of latent fingerprints. Forensic Sci. Int. 2010;199:93–102.

[11] Asbaugh DR. Quantitative and Qualitative Friction Ridge Analysis: An Introduction to Basic and Advanced Ridgeology. Boca Raton (FL): CRC Press; 1999.

[12] Parnas J, Flachs H, Gram L, Wuurtz-JØrgensen A. Excretion of antiepileptic drugs in sweat. Acta Neurol. Scand. 2009;58:197–204.

[13] Barnes AJ, Smith ML, Kacinko SL, Schwilke EW, Cone EJ, Moolchan ET, et al. Excretion of Methamphetamine and Amphetamine in Human Sweat Following Controlled Oral Methamphetamine Administration. Clin. Chem. 2008;54:172–180.

[14] De La Torre R, Pichini S. Usefulness of Sweat Testing for the Detection of Cannabis Smoke. Clin. Chem. 2004;50:1961–1962.

[15] Downing DT, Strauss JS, Pochi PE. Variability in the Chemical Composition of Human Skin Surface Lipids. J. Invest. Dermatol. 1969;53:322–327.

[16] Wolstenholme R, Bradshaw R, Clench MR, Francese S. Study of latent fingermarks by matrix-assisted laser desorption/ionisation mass spectrometry imaging of endogenous lipids. Rapid Commun. Mass Spectrom. 2009;23:3031–3039.

[17] Stefaniak AB, Harvey CJ, Wertz PW. Formulation and stability of a novel artificial sebum under conditions of storage and use. Int. J. Cosmet. Sci. 2010;32:347–355.

[18] Wertz PW. Human synthetic sebum formulation and stability under conditions of use and storage. Int. J. Cosmet. Sci. 2009;31:21–25.

[19] Bailey MJ, Jones BN, Hinder S, Watts J, Bleay S, Webb RP. Depth profiling of fingerprint and ink signals by SIMS and MeV SIMS. Nucl. Instrum. Methods Phys. Res. Sect. B Beam Interact. Mater. At. 2010;268:1929–1932.

[20] Szynkowska MI, Czerski K, Rogowski J, Paryjczak T, Parczewski A. ToF-SIMS application in the visualization and analysis of fingerprints after contact with amphetamine drugs. Forensic Sci. Int. 2009;184:e24–26.

[21] Sisco E, Demoranville LT, Gillen G. Evaluation of C60 secondary ion mass spectrometry for the chemical analysis and imaging of fingerprints. Forensic Sci. Int. 2013;231:263–269.
[22] Forbes TP, Brewer TM, Gillen G. Desorption electro-flow focusing ionization of explosives and narcotics for ambient pressure mass spectrometry. Analyst. 2013;138:5665–5673.
[23] Ifa DR, Manicke NE, Dill AL, Cooks RG. Latent fingerprint chemical imaging by mass spectrometry. Science. 2008;321:805.
[24] Eberlin LS, Liu X, Ferreira CR, Santagata S, Agar NYR, Cooks RG. Desorption Electrospray Ionization then MALDI Mass Spectrometry Imaging of Lipid and Protein Distributions in Single Tissue Sections. Anal Chem. 2011;83:8366–8371.
[25] Forbes TP, Sisco E. Chemical imaging of artificial fingerprints by desorption electro-flow focusing ionization mass spectrometry. Analyst. 2014;139:2982–2985.
[26] Forbes TP, Sisco E, Mass Spectrometry Detection and Imaging of Inorganic and Organic Explosive Device Signatures Using Desorption Electro-Flow Focusing Ionization. Anal. Chem. 2014;86:7788–7797.
[27] Croxton RS, Baron MG, Butler D, Kent T, Sears VG. Development of a GC-MS Method for the Simultaneous Analysis of Latent Fingerprint Components. J. Forensic Sci. 2006;51:1329–1333.
[28] Fruijtier-Pölloth C. Safety assessment on polyethylene glycols (PEGs) and their derivatives as used in cosmetic products. Toxicology. 2005;214:1–38.
[29] Staymates JL, Orandi S, Staymates ME, Gillen G. Method for combined biometric and chemical analysis of human fingerprints. Int. J. Ion Mobil. Spectrom. 2014;17:69–72.
[30] Robichaud G, Garrard KP, Barry JA, Muddiman DC. MSiReader: An Open-Source Interface to View and Analyze High Resolving Power MS Imaging Files on Matlab Platform. J. Am. Soc. Mass Spectrom. 2013;24:718–721.
[31] Bailey MJ, Ismail M, Bleay S, Bright N, Elad ML, Cohen Y, et al. Enhanced imaging of developed fingerprints using mass spectrometry imaging. Analyst. 2013;138:6246.
[32] Miki A, Katagi M, Kamata T, Zaitsu K, Tatsuno M, Nakanishi T, et al. MALDI-TOF and MALDI-FTICR imaging mass spectrometry of methamphetamine incorporated into hair. J. Mass Spectrom. 2011;46:411–416.
[33] Mirabelli MF, Chramow A, Cabral EC, Ifa DR, Analysis of sexual assault evidence by desorption electrospray ionization mass spectrometry. J. Mass Spectrom. 2013;48:774–778.

Tables

Chemical	**Amount (mg)**
Inorganic Salts	
Potassium Chloride[1]	1,400
Sodium Chloride[1]	1,300
Sodium Bicarbonate[1]	250
Ammonium Hydroxide[1]	175
Magnesium Chloride[1]	40
Amino Acids	
Serine[2]	275
Glycine[2]	135
Ornithine[2]	110
Alanine[2]	80
Aspartic Acid[2]	40
Threonine[2]	40
Histidine[2]	40
Valine[2]	30
Leucine[2]	30
Other Components	
Lactic Acid[1]	1,900
Urea[1]	500
Pyruvic Acid[1]	20
Acetic Acid[3]	5
Hexanoic Acid[1]	5

Table 1. Components and amounts used to create artificial sweat. Superscripts indicate the chemical supplier. Suppliers included ^{1}Sigma-Aldrich (St. Louis, MO, USA), ^{2}Carolina Chemicals (Burlington, NC, USA), and ^{3}J.T. Baker (Center Valley, PA, USA).

Chemical	Amount (mg)	Chemical	Amount (mg)
Free Fatty Acids		**Triglycerides**	
Hexanoic Acid^{1*}	50	Triolein^{1*}	275
Heptanoic Acid^{1*}	50	Tricaprylin^4	20
Octanoic Acid^{1*}	50	Tricaprin^4	20
Nonanoic Acid^{1*}	50	Trilaurin^4	20
Dodecanoic Acid^1	50	Trimyristin^4	20
Tridecanoic Acid^1	50	Tripalmitin^4	20
Myristic Acid^1	50	**Other Components**	
Pentadecanoic Acid^1	50	Squalene^{3*}	120
Palmitic Acid^1	55	Cholesterol^1	30
Stearic Acid^2	55	Cholesterol n-Decanoate^1 (Cholesterol Ester)	40
Arachidic Acid^1	50		
Linoleic Acid^{3*}	55	Cetyl Palmitate^1 (Wax Ester)	155
Oleic Acid^{1*}	55		

Table 2. Components and amounts used to create artificial sebum. Superscripts indicate the chemical supplier. Suppliers included ^{1}Sigma-Aldrich (St. Louis, MO, USA), ^{2}KIC (New Paltz, NY, USA), ^{3}Fluka (Buchs, Switzerland), and ^{4}Supelco (Bellefonte, PA, USA). Compounds with an asterisk (*) were liquid at room temperature.

Figure Captions

Figure 1. Negative secondary ion SIMS mass spectral comparison of an actual fingerprint (top / black) to the artificial fingerprint emulsion (bottom / grey). Select peaks of interest are numbered with their assignments listed.

Figure 2. Positive secondary ion SIMS mass spectral comparison of an actual fingerprint (black) to the artificial fingerprint emulsion (grey). Select peaks of interest are numbered with their assignments listed. Peaks with arrows indicate those produced from the emulsifying agent, Steareth-20.

Figure 3. Negative ion DESI-MS mass spectral comparison of an actual fingerprint to the artificial fingerprint emulsion. Select peaks of interest are numbered with their assignments listed.

Figure 4. Positive LDI-MS mass spectral comparison of an actual fingerprint (black) to the artificial fingerprint emulsion (grey). Select peaks of interest are numbered with their assignments listed.

Figure 5. Examples of chemical imaging of artificial fingerprints by mass spectrometry. An optical pictograph of the artificial fingerprint deposit (A.) along with LDI-MS examples (B. & C.) and a DESI-MS example (D. – F.). The LDI-MS image (B.) is of the potassium ion distribution (39 *m/z*, K^+) while image (C.) highlights an expanded overlay image of an artificial fingerprint doped with lead (blue, 208 *m/z*), barium (red, 138 *m/z*), and antimony (green, 121 *m/z*). The DESI-MS example highlights a fingerprint (D., oleic acid, 281 *m/z*, $[M-H]^-$) doped with RDX (E., 284 *m./z* $[M+NO_3]^-$). An overlay of the two signals is shown in (F.) (red and green representing the oleic acid and RDX signals respectively). In all images, a brighter color indicates higher peak intensity.

Figure 6. Comparison of real (top) and artificial (bottom) fingerprints developed using black fingerprint powder (A.), fluorescent fingerprint powder (B.), cyanoacrylate fuming followed by treatment with rhodamine 6G (C.), crystal violet (D.), 1,2-indanedione (E.), and ninhydrin (F.). For these comparisons a ballistics gelatin copy of the actual finger was used instead of the 3-D printed mold.