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Applicability of emanating volatile organic compounds from various forensic specimens for individual differentiation

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ABSTRACT

Trace biological materials contain volatile profiles that have yet to be evaluated to determine their value in forensic investigations. The volatiles released by different biological specimens (hand odor, hair, fingernails and saliva) collected from twenty individuals were identified using a solid phase microextraction–gas chromatography–mass spectrometry method. The human scent compounds from each specimen, per subject, were evaluated using Spearman rank correlation to assess the applicability of these compounds for the differentiation of individuals. The volatile organic compounds from each specimen type were readily identified and discriminated. When conducting inter-subject discrimination within a single specimen type, greater than 98.9% of the samples, or individuals, were differentiated for all specimen types. When conducting inter-subject discrimination among the four specimen types 99.6% of the samples were differentiated, at the 0.9 correlation coefficient threshold. Additionally, the only occurrence of cross-correlation between specimen types was observed between hair and fingernails while there were no cross-correlations with hand odor or saliva thereby demonstrating the distinctiveness of these specimens.

1. Introduction

In 2008, over 4 million violent crimes were reported within the United States [1], which included rapes/sexual assaults, robberies, aggravated assaults and simple assaults. These types of crimes are often associated with physical aggression which consequently leads to the transfer of biological materials. Bodily materials such as fingernails, hair and saliva are often collected and subsequently analyzed by comparison matches, microscopic evaluations, and/or DNA analyses. In turn, this collected trace evidence may objectively link a suspect/victim to a crime and develop important investigative leads. Another form of trace evidence that is being collected more regularly by law enforcement agencies within the United States is human scent.

Human scent is defined as the most abundant volatile organic compounds (VOCs) that are identified in the headspace of a collected scent sample [2]. The chemical constituents of human odor have been shown to be qualitatively similar among individuals, however the quantitative abundances that they are produced make them characteristic to the individual they are derived from [2–5]. A combination of the presence and abundance of VOCs produces a chemical profile that is particular to an individual and therefore can be seen as a biometric measurement [3,4].

Many factors contribute to the composition of human scent, such as genetics, diet, environment, bacteria present on the body and exogenous materials. Internally derived human scent VOCs migrate to the outside of the body through secretions from three glands, the eccrine, apocrine and sebaceous glands [6]. Eccrine glands are sweat glands that are present all over the body with the greatest density being found on the palms of hands, soles of the feet and on the forehead [7]. With nearly 2–4 million eccrine sweat glands present in the body, an individual can secrete approximately 2–4 L of sweat per hour [8]. Eccrine secretions originate as a filtrate of blood plasma and are comprised of 99% water and 1% of other chemicals (e.g., electrolytes, metabolites and waste products) [7].

Another type of sweat gland, the apocrine gland, is found in the dermis and is associated with hair follicles. These sweat glands are only found in the axillae, perineal and genitals and the secretions of these glands are regulated by hormones. Apocrine secretions are basic [9] and include lipids, steroids and proteins [10]. The sebaceous gland, which is also present on hair follicles, secretes an oily, waxy substance, called sebum. Compounds such as free fatty acids (FFA), squalene, cholesterol, wax esters, cholesteryl esters and triglycerides, were among the types of compounds identified in sebum [11]. In contrast to the apocrine glands, sebaceous glands are present all over the body and the secretions from these glands

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function to coat the surface of hair and skin preventing them from becoming dry and brittle.

Previous research has been conducted with the intention of elucidating the identities of compounds being released from skin for cosmetic, medicinal and forensic applications [4,12,13]. Curran et al. [3,4] has shown solid phase microextraction–gas chromatography–mass spectrometry (SPME–GC–MS) as a viable route for the extraction and analysis of human scent volatiles collected from hands. The resultant human scent profiles were shown to be reproducible and unique to the individual. In one study, a population of 60 individuals was sampled revealing high, medium, and low frequency compounds that demonstrated a high degree of variability among the sampled population [5]. The reported compounds included a range of functionalities, such as alcohols, acids, aldehydes, alkanes, ketones, esters, and nitrogen containing compounds [2,5]. Through the use of statistical analysis, such as Spearman rank correlations, a high level of differentiation was obtained among the subjects and their corresponding chemical profiles [4,5].

Numerous researchers have explored the chemical constituents that are derived from hands [4,5,14–17]. In forensic science, hand scent is of particular interest to investigators since 73% of collected scent evidence in the United States is comprised of items which have come into contact with hands [18]. Attention is now being turned to other biological specimens, such as head hair, fingernail clippings and saliva, which can be collected non-invasively and could possess evidentiary value as scent evidence articles.

Head hair is a human biological specimen that is frequently deposited into the environment. Hair is constructed by a durable protein called keratin. The crystalline keratin is extruded from the hair follicle and emerges as a hair shaft resulting in the appearance of hair. The average rate of growth for hair is 1 cm/month but actual rates of growth can range from 0.6 to 3.36 cm/month [19]. Secretions from the sebaceous glands, which surround the hair follicle, and eccrine sweat glands, which cover the scalp, coat the hair and impart it with characteristic odors. The use of online supercritical fluid extraction gas chromatography–mass spectrometry, revealed compounds such as acids, cholesterols, esters and squalene [20] present in human hair extract.

Similar to hair, fingernails are also composed of keratin. The nail plate originates from the nail matrix (root) and rests on a vascular nail bed, which is seen through the nail plate. A mixture of soft keratin (similar to that found in skin) and hard keratin (similar to that found in the hair follicle) have been identified within human nail plates [21]. The average growth rate of fingernails is 0.1 mm a day; however, this rate can be impeded from aging and malnutrition. Much of what is known of the composition of fingernails pertains to its elemental composition and very little, if any, research has been conducted to assess the VOCs being released by this specimen.

Saliva, also, can be deposited during acts of physical aggression, such as biting or sucking. Salivary evidence has gained usefulness for identity and drug testing because of its ease of collection and availability, being that daily saliva production averages 1.5 L in volume. Saliva is produced from three major salivary glands, which include the parotid, submandibular and sublingual glands. The glandular contributions to unstimulated saliva include, in descending order, the submandibular with 65–70%, parotid with 20%, sublingual with 7–8% and the minor salivary glands with $<$10% [22,23]. During stimulated saliva production, the parotid gland increases its contribution to over 50% of the total secretion. The constituents of saliva include: water, proteins, fatty acids, amino acids, lipids, glucose, hormones, etc. [22]. The pH of saliva is nearly neutral (about 6 or 7); however, changes in the salivary flow can fluctuate the pH, such that a decrease in flow, results in a lower pH (5.3) while an increased salivary flow raises the pH (7.8) [23]. Chemicals present in the headspace of saliva samples have previously been explored, both forensically [24], for the identification of individuals, and medicinally [25], for the diagnosis of dental diseases.

The potential use of trace biological materials, such as hair, saliva, or fingernails, as scent sources for canine use has never been evaluated. Presently, there are various countries around the world, including the United States, that employ canines for human scent detection work due to their ability of identifying and discriminating human odor. Human scent, as a form of trace evidence, can provide the investigative team with a number of key elements in a criminal case, such as following a suspect directly from the scene of a crime, determining the direction of travel of the suspect, identifying the suspect following a scent line-up procedure, identifying a particular location by scent, or recover missing persons [26].

Aside from hand odor, the value of using these biological specimens as a source for individualization has yet to be determined. Furthermore, in order for these specimens to be employed in a canine detection setting, an instrumental evaluation of the discrimination power of these forms of trace evidence needs to be conducted, as well as assessing the variability of the detected chemical profiles. Although the authors recognize the importance of sampling a larger population, in addition to analyzing the stability of odor from various biological specimens, it was not the intent of this work to present such data. The purpose of this study was to conduct a preliminary assessment on the use of novel biological specimens for identification purposes. This study utilized solid phase microextraction–gas chromatography–mass spectrometry for the extraction and analysis of volatile organic compounds that are present in the headspace of biological specimens, such as hand odor, hair, saliva, and fingernails. Qualitative, semi-quantitative and statistical evaluations were performed with VOCs detected from biological samples to evaluate the applicability of these materials as viable sources for human scent discrimination.

2. Materials and methods

2.1. Materials

This study used methanol (HPLC grade, Fisher Scientific, Pittsburgh, PA) and ethanol (AAPER Alcohol and Chemical Co., Shelbyville, KY) for the pretreatment of the collection materials. Chemical standards for external calibrations were obtained from Sigma Aldrich (St Louis, MO) or Fisher Scientific (Pittsburgh, PA). The soap used to wash the hands and forearms was natural, clear olive oil soap (Life of the Party, North Brunswick, NJ). The fragrance free shampoo was from Jason Natural Products (Culver City, CA). The gauze pads were 100% cotton, sterile, 2 in. $\times$ 2 in., 8 ply, gauze sponges (DUKAL Corporation, Syosset, NY). The cotton swabs were 6″ in length, wood stem, sterile, cotton tipped applicators (Solon Manufacturing Company, Skowhegan, ME). Nitrile rubber combs were used for the removal of hair strands from the scalp (Krest Products Corp., Leominster, MA). Plastic manicure brushes were used to clean above and underneath the fingernails (YCC Products Inc., Placentia, CA) and chrome plated steel fingernail clippers were used for the collection of fingernails (Tweezerman International, Port Washington, NY). The glass vials used were 2-mL and 10-mL, clear, screw top with PTFE/Silicone septa (SUPELCO, Bellefonte, PA). The SPME fibers used were 50/30 μm Divinylbenzene/Carboxen/Polydimethylsiloxane (CAR/DVB/PDMS; SUPELCO, Bellefonte, PA).

2.2. Pretreatment of the collection material

Prior human scent research, which utilized sorbent materials for the collection of hand odor, revealed that the collection materials, though sterile, initially possessed compounds found in human odor [2]. The pretreatment of cotton gauze for the collection of hand odor samples was conducted to ensure the removal of any background contaminants and entailed spiking the gauze pad with 1 mL of methanol and baking the gauze in an oven at 105 °C for an hour [16]. A pretreatment regime was also devised for cotton swabs used in the collection of saliva. Each swab was spiked with 250 μL of ethanol and placed in an oven at 105 °C for 1 h and then repeated. The analytical cleanliness of the cotton gauze and cotton swab was determined by SPME–GC–MS prior to sampling.