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PAPER

CRIMINALISTICS

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The Evaluation of Human Hand Odor Volatiles on Various Textiles: A Comparison Between Contact and Noncontact Sampling Methods*,†

ABSTRACT: The focus of this study is to compare contact and noncontact human scent collection procedures across an array of textiles (cotton, rayon, polyester, and wool) to determine an optimized collection method for human scent evidence. Six subjects were sampled in triplicate for each textile and collection mode, and the samples were then analyzed through headspace solid-phase micro-extraction in combination with gas chromatography/mass spectrometry (SPME-GC/MS). Contact sampling with cotton material has been shown to be the collection method that yielded the greatest number of volatile compounds and the highest scent mass amounts. Through Spearman rank correlations, it was shown that an individual's scent profile is more reproducible within samples collected on the same textile type than between different materials. Furthermore, contact sampling with cotton fabric demonstrated the greatest reproducibility producing the lowest amount of type I and type II errors with 90.85% of the samples distinguished at the 0.9 match/no match threshold.

KEYWORDS: forensic science, human scent collection, fiber chemistries, Scent Transfer Unit (STU-100), contact and noncontact methods

In a Kelly-Frye hearing in 2004 (1), the court ruled that human scent discrimination by canine can be admitted into court as evidence if the person utilizing the technique used the correct scientific procedures and the methods used by the dog handler are reliable. To date, however, there is no optimized protocol for the collection of volatile organic compounds (VOCs) present in human scent profiles. Thus, the task of optimizing the methods used for the collection of human scent play a key role in maintaining the reliability of this investigative technique. The methodology and materials used to collect human scent differs among the countries that utilize this form of associative evidence (2). There are two main routes for the collection of human scent samples; one in which there is contact between the collection medium and the substrate and one in which there is no contact and utilizes airflow for transfer. The contact collection category includes the following: the touching of a sorbent material by an individual, the direct swiping of an individual's body regions, as well as placing a sorbent material in contact with an item that has been in contact with an individual. The noncontact collection category includes the collection of scent by placing a sorbent material near an individual for a period of time as well as utilizing the Scent Transfer Unit (STU-100) as a collection device.

The STU-100 allows for noncontact scent collection using dynamic airflow from objects or suspects without contaminating or altering the object/target of interest (3). However, the resulting volatile profiles obtained from human subjects have not been evaluated using the device. To date, there has been limited scientific validation of the STU-100 as a human scent collection device. The only peer-reviewed laboratory evaluation determined that the STU-100 effectively trapped and released chemical mixtures (a TLV40 gas mixture and colognes) in both liquid and gaseous form (4). However, only three human scent volatiles were tested (benzaldehyde, 2-nonenal and 2-ethylhexanoic acid), which were all sampled individually with the device at varying sampling times. This study does not properly evaluate the STU-100 to determine its utility as a tool to collect human scent evidence, which requires testing with human subjects whose profiles contain a multitude of volatile compounds present simultaneously.

Human Skin Volatiles

The generation of human scent is the result of various factors that together contribute to the overall body odor. In turn, one important factor is the physiology of human skin as it plays a role in the individuality of the odor sample obtained as different people have a variety of skin types and glandular activity within this organ. The human skin is composed of distinctive layers, each having characteristic physical and chemical properties dictated by function, which enable this organ to act as a permeable sheath to the human body. The epidermis is a "self-renewing" layer that has an approximate thickness of 1 mm and mostly composed of flattened cells. The dermis is located beneath the epidermis and is a composite tissue whose strength results from collagen fibers contained in a gel-like matrix of salts, water, and proteins. There is also a complex structure of connective tissue fibers located in the dermis, a network of blood vessels, sweat glands, oil-producing

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glands, and hair follicles (5). The skin can be furthered described as an intricate environment of biological functions. It exhibits different properties such as varying levels of oiliness, roughness, hydration, porosity, and pH. In turn, the skin's characteristics are also influenced by external variables including sun exposure (6).

Information gathered from studying an individual's VOC profile has many applications, including the diagnosis of disease (7), cosmetic industry (8) mosquito attractant detection (9–12) as well as for biometric purposes in a forensic context (13). The volatiles emanating from the skin surface can be described as a combination of various processes that may include the following: glandular secretions from the eccrine, apocrine, and sebaceous glandular action within the skin; external factors applied to the skin (environmental contamination, creams applied to the skin surface, as well as cosmetics and toiletries); passage of compounds from the blood vessels; and products and byproducts of skin microflora (14). It is known, however, that possible incomplete oxidation of acquired nutrients by skin microflora could result in other small volatile breakdown and elimination compounds (15–17). Studies have also entailed an understanding of what constitutes odorous intensities in different individuals. Some findings have shown that the known greater intensity of axillary odor in men for example is not due to qualitative differences in odorants or to any differences in carrier proteins, but rather in the availability of nonodorous precursor materials in apocrine secretion, which male subjects may secrete more easily (18). It has also been shown that much of the VOCs produced by the skin are released to the environment with emission patterns that are characteristic of climate conditions (19). It is also known that external factors, including eating habits, contribute to overall human odor. Havlicek et al. (20) tested the effect of meat consumption on general body odor attractiveness collecting axillary odor from several male donors. In this study, a meat or nonmeat diet was maintained for 2 weeks with the obtained results suggesting that meat consumption had a negative impact on the perceived body odor attractiveness as assessed by human sniffers.

In a recent analysis conducted by Gallagher et al. (21), approximately 100 compounds were identified and the VOC profiles of the upper back and forearm within the same individual were highly similar with noteworthy differences. Aldehydes of C8-C12 were detected in most samples for almost every subject, and the presence of ketones such as 6-methyl-5-hepten-2-one and (E)-6,10-dimethyl-5,9-undecadien-2-one were also consistent among the sampling pool. VOCs were also investigated by secondary electrospray ionization–mass spectrometry from the hand of two individuals highlighting the presence of a family of amines including trimethylamine, ethanolamine, 1-amino-2-propanol, piperidine, isobutylamine, hexylamine, heptylamine, and octylamine. Furthermore, ornithine was also reported, which had been previously reported as a constituent of sweat (22). Additional skin sampling approaches involved an online sampling device for the study of the releases of ethanol and water vapors from the thumb after dipping it for a very short period in an aqueous solution including ethanol (23). Others have used silicone elastomer sheets as skin sampling patches (14), while others have utilized glass beads to transfer secretions from the palms of hands directly into a gas chromatography/mass spectrometry (GC/MS; [9,24]).

Collection Materials

Currently Implemented Materials

Peer-reviewed scientific literature is lacking in studies performed on the collection materials that are being utilized for human scent analysis. In terms of canine evaluation, each law enforcement agency uses a different type of absorbent medium to collect human scent evidence. For example, the Federal Bureau of Investigation uses Johnson & Johnson sterile gauze while the Dutch National Police utilize King's Cotton, which is a nonsterile medium. A canine study on human scent refers to a type of ''odor-collecting cloth'' (25), yet the composition of the material is not described. Other canine work has utilized t-shirts (26) and handkerchiefs (27) for scent collection with no reasoning or description of material composition. Polyester materials have also been used for the collection and analysis of human scent by canines (28) and instrumental methods (29). Typical methods for the collection of human scent involve the use of cotton pads/gauzes in contact with the human body for different amounts of sampling times (30–33). Skin emanation analysis through instrumentation has widely utilized techniques such as solid-phase microextraction (SPME) where actual human scent is collected on cotton pads (13,34). Both canine and instrumental evaluation means vary in the type of materials used; to determine the optimized collection protocols for human scent VOCs, a comprehensive study that reaches across a broad range of materials is necessary.

Material Chemistry

Textile types can be divided into both natural and synthetic fibers. Cotton is the most commonly used natural fiber originating from a plant, but natural fibers can also come from animal sources, such as wool. Synthetic fibers are relatively new in the textile industry and include fabric such as viscose rayon, which is manufactured by modifying cellulose, which is a natural polymer found in plants (35). The long linear chains of cellulose allow hydroxyl groups to interact with hydroxyl groups on adjacent chains through hydrogen bonding and van der Waals forces. The hydrophilic nature of cotton and the effect of absorbed water on the hydrogen bonding within the fabric cause the tensile strength of cotton to change with changes in moisture. Viscose rayon fibers are made by the viscose process, which entails the use of soda cellulose, reaction with carbon disulfide, and spinning into dilute acid to regenerate the cellulose as a rayon fiber. Both cotton and rayon differ depending on the degree of polymerization, crystallinity, and orientation found within each fiber (36). The wool keratin molecule consists of a highly complex sequence of amino acids. The chemical composition of the wool fiber varies along its length. Keratin molecules are highly polar, making the fibers hygroscopic and giving the wool fabric higher moisture retention when compared to other fibers (37). Polyester fibers are a type of chemical fibers made up of any long-chain synthetic polymer. This type of fiber has low water absorbency and has therefore a lack of moisture retention (38).

The purpose of the study was to provide a limited qualitative and semiquantitative study on the types of volatiles above the headspace of a collected hand odor sample on an array of different fiber chemistry textiles and determine which textile collected the greatest number and amount of these VOCs as well as collected the human scent VOCs in a reproducible manner. Larger population studies have been conducted by the authors, which highlight both the proof of concept for a reproducible, collected human scent profile using this methodology (13) as well as a larger-scale population survey that demonstrated the inherent variability that can be observed among individuals through this collection and analysis methodology (39). Although the authors recognize the importance of taking this study to a larger population set to provide more in depth notions about the effect and/or changes of a collected odor profile across individuals, it was not the intent in this paper to present a large population analysis.

In this study, skin volatiles were analyzed from scent samples after a preliminary washing that allowed the sample to collect VOCs from the hand and forearm body regions by both contact and noncontact scent collection methods. Three female and three male subjects were evaluated with an array of both natural and synthetic materials to evaluate the types and relative quantities of VOCs present in the collected samples to determine an optimized collection technique and medium for human scent profiles.

Materials and Methods

Materials

The textiles evaluated included bleached desized mercerized cotton print cloth, spun viscose challis, spun polyester type 54, and 100% wool flannel (Test Fabrics, West Pittston, PA). All experiments utilized a $2 \times 2''$ piece of each textile type for collection procedures. The vials used to hold the collected samples were 10 mL glass, clear, screw-top vials with PTFE/Silicone septa (Supelco, Bellefonte, PA). The SPME fibers utilized were Divinylbenzene/Carboxen on polydimethylsiloxane fibers with a 50/30 μm film thickness (Supelco). Solvent utilized in the pretreatment of the fabrics prior to use was high-performance liquid chromatography (HPLC)-grade methanol (Fisher Scientific, Pittsburgh, PA). The chemical standards used for external calibration were obtained from Sigma Aldrich (St. Louis, MO) and included the following: 95% nonanal (Batch# 05223DC), 99% decanal (Batch# 086K1467), 99% 2-furancarboxaldehyde (Batch# 03920KB), 99% dodecane (Batch# 00654LC), 99% tetradecane (Batch# 13401LZ), hexadecane (Batch# 42806256), 99% 6-methyl-5-hepten-2-one (Batch# 06723DU), 97% geranylacetone (Batch# 03906JC), 99% 2-furanmethanol (Batch# 07624KC), 99.8% benzyl alcohol (Batch# 03453EC), and 98% 3,7-dimethyl-1,6-octadien-3-ol (Batch#04827PA). Alcohol pads utilized for cleaning of equipment were Deluxe Large Alcohol Prep Pads (Medline, Toronto, ON, Canada). The soap used by the subjects to wash their hands and forearms was Natural, Clear Olive Oil Soap from Life of the Party (North Brunswick, NJ). This olive oil-based fragrance-free soap has been shown previously not to contain VOCs within the headspace, which allows the analysis to be conducted with the empirical data that the detected VOCs originate from the individual sampled (40).

Collection Device (Mod-STU)

For the noncontact hand odor collection, the device used was STU-100. The STU-100 used in this study was modified from the commercially available Teflon-coated device (Bill Tolhurst Enterprises, Haw River, NC). Preliminary sampling conducted with the STU-100 demonstrated that the cleaning procedure described by the manufacturer did not prevent carryover of the standard VOC mixture. The recommended cleaning procedure involves a wipe down of the sampling hood of the STU-100 with an isopropyl alcohol swab. The sampling hood is composed of a polymer base that is Teflon coated. A custom-built modified-STU-100 sampling hood (known hereafter as the Mod-STU) was designed and developed from stainless steel. Custom stainless steel sampling plates were also designed and built to allow for the collection of multiple samples during one collection run of the device. The stainless steel hood and sampling plates are able to withstand heating at elevated temperatures allowing for the sampling surfaces of the device to be properly cleaned to ensure elimination of organic compound contamination between samplings (Fig. 1). The dimensions and general shape were paralleled from the original Teflon-coated hood that came with the device. The following schematics display the measurements for both the metal sampling plate and hood (Fig 2).

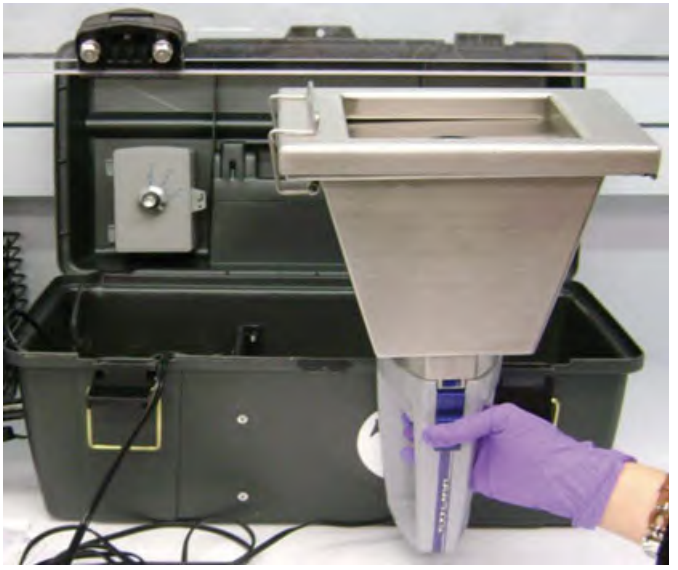

FIG. 1—*Modified Scent Transfer Unit (STU-100).*

Pretreatment of Collection Material Methods

From previous work conducted by the authors, it has been determined that even though materials used are biologically sterile, this does not equate to analytically clean. Therefore, prior to human sampling, a pretreatment procedure must be performed on the materials prior to human sampling (39,41). Pretreatment of all collection materials consisted of a direct spike with 1 mm of HPLC-grade methanol, followed by heating in the oven at a temperature of 105°C for 1 h to eliminate any remnants of possible VOCs present initially on each medium. Each material sample was analyzed by SPME-GC/MS (same method as that used for scent samples later described in text) for compound identification and verification of blank background prior to hand sampling use.

Contact Hand Odor Collection Method

Three female and three male subjects between 24 and 33 years old were sampled at indoor laboratory conditions with the four types of textiles (bleached, desized, mercerized cotton, viscose rayon, polyester, and wool). The triplicate samples per subject within each material type were taken sequentially with a 10 min break in between samples. A total of 12 samples were taken from each subject over a 4-day period, one material type per day. The sampling was conducted at the same time each sampling day; the laboratory conditions were approximately 21.8°C and a relative humidity of 48%. Table 1 depicts the sampling schedule for each subject across the evaluated collection media. The order of collection for each subject was cotton, polyester, rayon, and wool. The sampling design was chosen so that triplicate samples of any one material and method were taken on the same day to reduce intramaterial and method variation. However, this was not observed as a drawback of the experimental design, as we could observe the changes obtained from day-to-day sampling of the same person, which is relevant in field work when samples may be collected on different days, depending on the investigation. Furthermore, the backbone for conducting this line of study is to aid

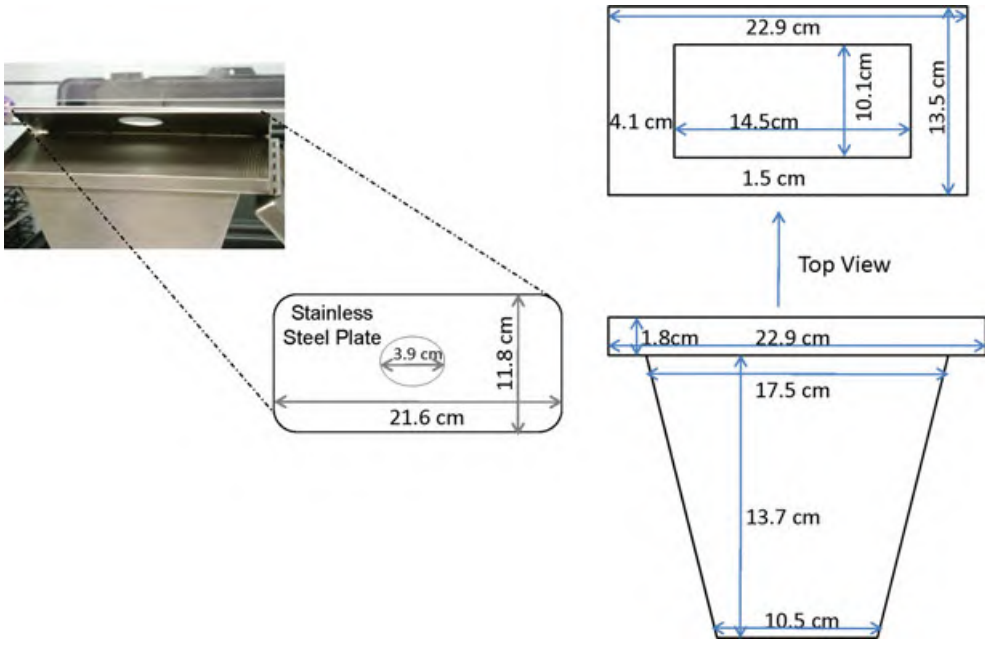

FIG. 2—*Schematics of modified Scent Transfer Unit (STU-100) sampling metal plate and hood.*

TABLE 1—*Sampling schedule for hand odor samples.*

Day Collected	Medium
Day 1	Cotton
Day 2	Polyester
Day 3	Rayon
Day 4	Wool

operational human scent canine work with collected odor samples, thus no restrictions were placed on diet or other personal hygiene procedures.

From work in the literature, there has been ample citations and references that acknowledge the importance not only of diet but also of external lifestyle changes, even genetics on the generated body odor. The reduction in compounds considered to only those previously reported in the literature to be of human origin as well as those present in multiple samples from the same individual (primary odor) during the Spearman correlations was carried out to reduce the influence of these dietary (secondary odor) and external (tertiary odor) effects on the VOCs considered.

The contact collection process consisted of washing the hands and forearms using a fragrance-free soap for 30 sec, rinsing the washed area for 2 min, air-drying for 2 min, rubbing the hands over the forearms for 5 min, and then clasping the palms of the hands together for 10 min with a pretreated $2 \times 2''$ square piece of collection material. This collection procedure was taken from previous research conducted by the authors (13,34). The pretreated $2 \times 2''$ collection material was removed from the 10-mL glass vial using tweezers that were previously swiped with alcohol pads for preliminary cleaning procedures. Each type of collection material was placed in the palms of the subject's hands. The subjects sampled themselves by holding the collection material between the palms of their hands while standing/sitting in a comfortable position for each 10-min sampling in the laboratory. The collected scent samples were then placed into 10-mL glass vials at room temperature (42) and allowed to equilibrate for 24 h prior to extraction. Prior to human sampling and to verify that VOCs from outside sources were not in the material as a result of the vial, alcohol pads, and/or the tweezers, each material was extracted for the same 21 h as the sample to provide a background evaluation before actual sampling use.

Noncontact Hand Odor Collection Method

The collection media underwent the same process for the pretreatment procedure as that mentioned earlier in the contact sampling method. For the noncontact study, the same subjects were asked to repeat the sampling with the collection materials described earlier with minor variations.

Both the metal plate and the hood were wiped with alcohol and placed overnight in an oven at 105°C to ensure the removal of contaminants prior to use. The studies were performed by a preliminary cleaning of the stainless steel hood and sampling equipment with alcohol pads. The sampling procedure was conducted in controlled laboratory conditions under a ventilated hood for each individual and performed in triplicate at the lowest airflow setting of the device for 1 min.

The airflow setting utilized throughout this study was based on preliminary experimental work utilizing the original STU-100 with a standard mixture. This standard mixture was selected based on previously reported human scent-originating compounds with various levels of occurring frequency (34). The selection of compounds for the standard mixture included high-, medium- and low-frequency occurring compounds from a variety of functional groups including aldehydes, alcohols, ketones, fatty acid methyl esters, acids, and aliphatics. The material used for this preliminary experiment was cotton and yielded important results, which included the ability of the material to trap and release the selected chemicals in a reproducible manner, with similar mass amounts being reported at the lower airflow (86.04 L/min), thus making it the point of consideration for selecting the lowest airflow as the optimal setting for sampling purposes (P. Prada, unpublished data).

Triplicate samples within each material type were taken sequentially with a 10-min break in between samples. A total of 12 samples were taken from each subject over a 4-day period, one material per day. Prior to each set of triplicate samples for each

material type, an environmental control pad was made by running the STU device at the low airflow for 1 min to monitor any compounds present in the background. The protocol for the washing/rinsing of the hands was conducted as follows: 30-sec hand washing, 2-min rinsing, 3-min air-drying, followed by 10-min rubbing of palms of hands over forearms. Subjects were then asked to open their hands after the rubbing procedure above the Mod-STU for sampling. The extended rubbing time was allotted so as to increase the regeneration of surface skin cells because the sampling approach involved no direct contact with the piece of collection material. Immediately following STU airflow sampling, collection media were removed from instrument and placed in clear 10-mL glass vials mentioned earlier for SPME-GC/MS analysis after 24 h of headspace equilibration.

Extraction and Instrumental Evaluation of Collected Hand Odor Samples (SPME-GC/MS)

Headspace extractions utilizing divinylbenzene/carboxen fibers were conducted with an exposure time of 21 h at room temperature (34). This specific fiber type was chosen in accordance with the optimal fiber for the extraction for human scent samples (40). Prior to the extraction of each collected sample, appropriate fiber blanks were performed on the analytical instrument using the same sample method to ensure proper cleaning and no cross-contamination from previous samples.

A Hewlett Packard 6890 Series GC system (Santa Clara, CA), fitted with an HP5-MS 30 m, 0.25-μm, 0.25-mm capillary column was used. The GC oven temperature was programmed as follows: 5 min at 40°C, then heating at 10°C/min up to 300°C and held for 2 min, for a total analysis time of 33 min. Helium was the carrier gas at a flow rate of 1 mL/min at an average velocity of 37 cm/sec. The analysis was conducted under splitless mode. The inlet had an initial temperature of 250°C with a pressure of 7.00 psi. The purge flow was 16.4 mL/min for a period of 2.00 min. The total flow was 20.1 mL/min. The mass spectrometer used was an HP 5973 MSD with a quadrupole mass analyzer, which was operated in electron ionization mode and scanned over a mass range of m/z 45–550 in full scan mode. Compounds were identified by both standard comparison and the NIST 98 mass spectral reference library. To quantitate the amount of compounds being extracted by the SPME fiber, an external calibration was performed using a standard mixture of previously reported human scent compounds at various concentrations (5–80 ppm) to obtain a response factor for each compound. An average response factor was then used to approximate the amount of VOCs extracted by the SPME fiber, as the slope of the line is the response factor for each analyzed compound.

Statistical Analysis Methods

Principal Component Analysis—The study being presented yielded multivariate data from each sample being collected. Important variables included not only the type of material or the collection method being utilized, but also the amounts and types of compounds being detected for each individual's volatile profile. One problem when dealing with multivariate data is that the volume may make it complex to observe patterns or relationships. In this case, principal component analysis (PCA) was used to reduce the amount of data using the data's correlation matrix. Using the correlation matrix allowed the data to be standardized having each variable equal to zero mean and unit variance. This meant that the eigenvalues obtained were equal to the number of measured variables. As the variables in this case were the detected compounds, standardization allowed for the variables to be measured with equal weight even though they were obtained through different collection methods. Although PCA shows groups of like objects, it is not always successful in doing this task. There are situations where the first principal component simply does not yield good separation between the groups under study (43).

Spearman Rank Correlation—Spearman's rank correlation is a nonparametric measure of correlation that makes no assumption on the distribution of the generated data set. Spearman rank correlations assess how well an arbitrary function could describe the relationship between two variables, without making any other assumptions about the particular nature of the relationship between the variables, such as normal distributions. In this case, the peak area of each detected compound for every collected odor sample was ranked in ascending order for each individual's chemical profile to assess the degree of similarity among the set of VOCs observed among the sampling pool. This form of statistical analysis has been previously used by the authors to explore correlation relationships among collected scent samples across a sampling pool (13,34).

Rank correlations have proven to be useful in many areas of analysis including the identification of samples of steel and cast iron, where laser-induced spectrometry was utilized for elemental characterization of the materials. In this case, rank correlation proved to be useful and reliable by analyzing the spectral "fingerprint" as the identification for the solid materials based on the use of spectral libraries (44). Similar research has been conducted for particulate geological materials where thousands of samples have to be quickly and efficiently classified in a qualitative manner, that is, whether they contain certain minerals or whether they can be attributed to a certain known mineralogical group. In this case, correlation methods are used with the goal of reliable identification of single particles that belong to different ores (45). There have been other studies that have exploited this statistical method for compositional comparison including the elemental composition of glass samples for forensic implications. In these cases, the correlation coefficients for the pairs of different metals were used to indicate the similarity among glass samples, which allowed for a compositional comparison as was the objective of the human sampling as well. This technique allows for the building and development of a database of metal pairs that can test the correlation of metal ions as new and unknown samples are introduced in the system (46).

As described in the Results section, in some occasions only the compounds that have been previously reported in the scientific literature to be of human origin (so that artifacts present because of soaps, etc., are not considered) and are present throughout multiple samples collected from the same individual (referred to as primary odor compounds) are being correlated and measured as a match/no match by specifying a threshold. This principle of restricting the compounds considered within a collected human scent profile to only those present in multiple samples collected from an individual has been justified, explained, and applied successfully in previous studies by the authors (13,39,42). Similar procedures have also been conducted in the analysis of glass samples where masking the spectra strengthen spectral similarities between samples that are the same and improve differences for the ones that are different (47).

Results/Discussion

Contact Hand Odor Collection Results

An important aspect in this study was to evaluate the textile types in relation not only to the number of collected volatiles and

TABLE 2—*Volatile organic compounds (VOCs) detected from human hand odor via contact approach separated by functional group and material type for both female (F) and male (M) subjects.*

Compound Detected	F1	F2	F3	M1	M2	M3	F1	F2	F3	M1	M2	M3	F1	F2	F3	M1	M2	M3	F1	F2	F3	M1	M2	M3
Alcohols																								
Furfuryl alcohol													x		x	x	x							
Benzyl alcohol	x	x	x			x	x	x					x	x	x	x	x	x	x		x		x	
cedrol															x									
1,6-Octadien-3-ol,3,7-dimethyl-	x	x	x	x	x	x	x			x			x	x		x		x	x		x	x		
phenyl ethyl alcohol													x											
Tridecanol																						x	x	
1-Tetradecanol		x																x						
Nonanol	x	x	x	x	x	x																		
Aldehydes																								
Heptanal													x	x	x	x	x		x		x			
Benzaldehyde		x					x	x					x	x	x				x	x	x	x	x	x
2-Decenal, (E)-	x			x	x	x							x			x								
Nonanal	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
2-Nonenal, (E)-	x	x	x			x							x		x	x								
Octanal		x	x										x			x	x		x					
Decanal	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x
Undecanal	x	x	x	x	x	x				x			x	x	x	x	x	x	x		x	x		x
2-Octenal, (E)-	x												x											
Dodecanal	x	x		x	x				x				x											
Tetradecanal				x		x	x		x					x			x			x		x		x
Lilial	x	x	x		x	x	x	x	x	x	x	x	x	x	x				x	x	x			x
Aliphatics/Aromatics																								
1-Pentadecene									x										x					
3-Dodecene, (E)-																								x
3-Octene, (E)-																						x		x
D-Limonene							x													x				
Benzene,1,3,5-trimethyl-			x											x										
Benzothiazole																x								
Naphthalene							x				x													
Dodecane	x																							
Tridecane				x					x	x		x		x	x	x	x			x	x	x		
Tetradecane	x	x	x	x	x	x	x		x	x	x	x	x	x	x	x	x	x	x	x	x	x		x
Heneicosane									x															
Pentadecane									x				x				x							
Hexadecane	x	x	x	x	x	x	x	x	x	x		x	x	x	x	x	x	x	x	x	x			x
Cyclo-tetradecane	x		x				x		x				x					x						
Cyclo-hexadecane													x					x						
Heptadecane	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x	x		x	x
Docosane									x															
Eicosane									x									x						
Octadecane	x		x				x		x				x	x	x			x	x	x	x			
Carboxylic Acids																								
Butanoic acid										x														
Dodecanoic acid																					x	x		
Pentanoic acid									x	x														
Hexanoic acid							x	x	x	x		x												
Heptanoic acid										x		x												
Octanoic acid							x	x	x	x		x		x										
Nonanoicacid		x	x		x		x	x	x	x		x												
n-Decanoicacid	x				x				x															
Hexanoicacid,2-ethyl-	x			x		x	x	x		x		x	x	x		x	x	x						x
Carboxylic Acid methyl esters																								
Acetic acid, Phenyl methyl ester													x											
Butanoic acid, methyl ester																			x					
Hexadecanoic acid, methyl ester							x						x						x		x			
Hexanedioic acid, dimethyl ester															x	x								
Octanoic acid, methyl ester	x	x				x							x	x	x	x	x	x	x					
Nonanoic acid, methyl ester	x					x							x				x							
Dodecanoic acid, methyl ester					x		x	x	x	x		x							x	x	x	x	x	x
Ketones																								
5-Hepten-2-one,6-methyl-						x								x							x			x
2-Decanone		x	x	x	x	x										x	x							
5,9 Undecadien-2-one, 6,10-dimethyl-, (E)-	x		x	x	x	x		x	x	x		x	x	x	x	x	x	x	x	x		x	x	x

collected scent mass amount, but also to indicate the types of compounds collected on each medium. A total of 58 compounds were identified in the hand odor samples collected from the six subjects studied utilizing direct contact sampling (see Table 2). As noted in the table, the list of detected compounds is separated by functional groups and by material type. Only two compounds, nonanal and

decanal, were seen in all of the sampled subjects across all material types. The presence of (E) 6,10-dimethyl-5,9-undecadien-2-one was seen in 83.33% of the cases from all the samples collected. The ketone 2-decanone was only seen in 58.33% of the samples collected on cellulosic fabrics such as cotton and rayon. It was detected for both men and women in the cotton fabric, while it was only seen in male samples in the rayon collection material. This observation in regard to this ketone being present in only the male samples and not the females can possibly be attributed to gender-specific difference of odor intensity. However, a previous population study comprised of 60 subjects utilizing cotton as a collection material reported the presence of this compound in similar frequencies between men and women, 63% and 67%, respectively (39). In this case, the collection medium of rayon is attributing distinct properties within the fiber morphology, but additionally the concentration of some compounds may be linked to intrinsic gender qualities. It has been shown that male glandular activity has greater amounts of immunoreactive proteins that lead to increased ability in glandular secretion leading to odor production (18).

Carboxylic acid methyl esters such as methyl ester dodecanoic acid were observed in 91.67% of the cases where the samples were collected on both polyester and wool fabrics, while methyl ester octanoic acid was common between cotton and rayon fiber chemistry samples in 75.00% of the cases. It has been shown that there is an inverse relationship between vapor pressure and chemical retention on fabrics (48). The differences observed within these two acid ester compounds (differing by only four carbons) on each medium may be attributed to the different vapor pressures of each compound which could effect the retention of the chemical on the specific fiber.

A common acid detected across all four material types was 2-ethyl hexanoic acid (54.17%); however, it should be noted that acids were only a dominant functional group in the polyester material. Polyester fibers demonstrate hydrophobicity and nonabsorbency, which could explain why fatty acids (which contain hydroxyl groups) are more easily released than what was observed with the cotton fabric. The polyester fabric may be able to trap these types of compounds but exhibit an easier form of release as is seen by the increased presence of acids in these types of scent samples. Acids detected in the polyester samples were typically from the C4–C12 range. Aliphatics such as tetradecane (91.67%), hexadecane (87.50%), and heptadecane (95.83%) were frequently seen across all scent samples. Only eight alcohols were seen from the samples collected, with benzyl alcohol (62.50%) and 3,7 dimethyl-1,6-octadien-3-ol (62.50%) being the most constant across all fiber types.

The contact collection method variations in the distribution of functional groups in the resulting profiles obtained among the various textiles between men and women can be elucidated in Fig. 3*a*,*b*. This variation may be resulting because of the physical characteristics of the fiber themselves, such as the scales within the wool fiber and the tubular form of cellulose fibers in cotton and rayon. These physical characteristics may influence the retention of each distinctive compound as well as affect the microbial action inherent to human sampling present on each textile. The distribution is described in relative percentage mass detected for each material type.

Aldehydes—In the direct contact approach, the majority of the mass detected for the female subjects in the cotton material was from the aldehyde functional group (62.86%). The wool and rayon fabrics also demonstrated a presence of this functional group with a 59.82% and 39.17%, respectively. For the male subjects, the contact approach using the cotton material yielded similar results as that seen with the women in which the aldehyde group yielded the highest percentage mass contribution (80.93%). Both the rayon and the wool presented similar results as seen in the female gender, whereby they collected 52.30% and 55.19%, respectively. In both genders, polyester had much smaller aldehyde percentage mass contribution with only 13.46% in the female subjects and 26.84% in the male subjects.

Alcohols—The alcohol functional group was the second highest percentage mass contributor in the two types of cellulosic fabrics, displaying 27.37% in cotton and 31.36% in the rayon samples for the female subjects. As opposed to the results with the female individuals, the male subjects did not exhibit high percentages for the alcohol group for the cotton (5.28%) or rayon (8.58%) collection media. The polyester fabric yielded 0.27% alcohol type of volatiles for the male subjects, while the female subjects displayed 8.23% for the same fabric type. The wool fabric highlighted similar ratios of alcohol contribution among both genders (women 10.06%, men 11.03%).

Ketones—Even though ketone volatiles were detected in all four material types for both genders, their percentage contribution was low in comparison with the other functional groups. For the women, the percentage mass contribution ranged between a low of 2.26% seen in the polyester to a high of 7.13% in the rayon. For the male samples, the range was slightly higher with a 5.56% in the cotton and a 14.23% contribution in the wool.

Aliphatics/Aromatics—For the female subjects, the majority of the aliphatic/aromatic types of compounds were detected in the polyester medium yielding a percentage mass of 33.07%. Rayon and cotton had percentages of 17.75% and 3.90% of the whole mass distribution. Wool also displayed these types of volatiles (16.69%). The male subjects, on the other hand, showed the aliphatic/aromatic type of VOCs in greater quantity in the rayon medium (23.28%) followed by the wool fabric (13.61%) and the polyester (13.14%).

Fatty Acids—The polyester fabric had the highest percentage mass distribution coming from the carboxylic acid group (42.19%), which was the highest amount for this functional group when compared to the other textiles in the female gender samples. For the male samples, the carboxylic acid group had the highest percentage mass as was observed from the female group results. The men collected an average of 47.09% of acids in the polyester fabric. With the contact approach, it seems that the male subjects are emanating more acidic type of volatiles in comparison with the female subjects, although in both genders the polyester material proved to be the best in trapping and consequently releasing this functional group. Our findings of high percentage mass amounts of acids in the polyester material type corroborates with similar findings within the textile industry that report an increase in short-chain carboxylic acids in the headspace above polyester fabrics after 7 days (49). The high occurrence of acidic type of VOCs among our samples also corroborates with the high odor intensity strongly associated with the polyester fabric types as has been elucidated by research groups in the textile industry compared to other textiles, such as cotton and wool (50). The other types of collection media also showed the presence of the acidic group but in much lesser percentages (1.87–4.34%).

Carboxylic Acid Methyl Esters—The amount of carboxylic acid methyl esters in the collected samples via a contact approach was

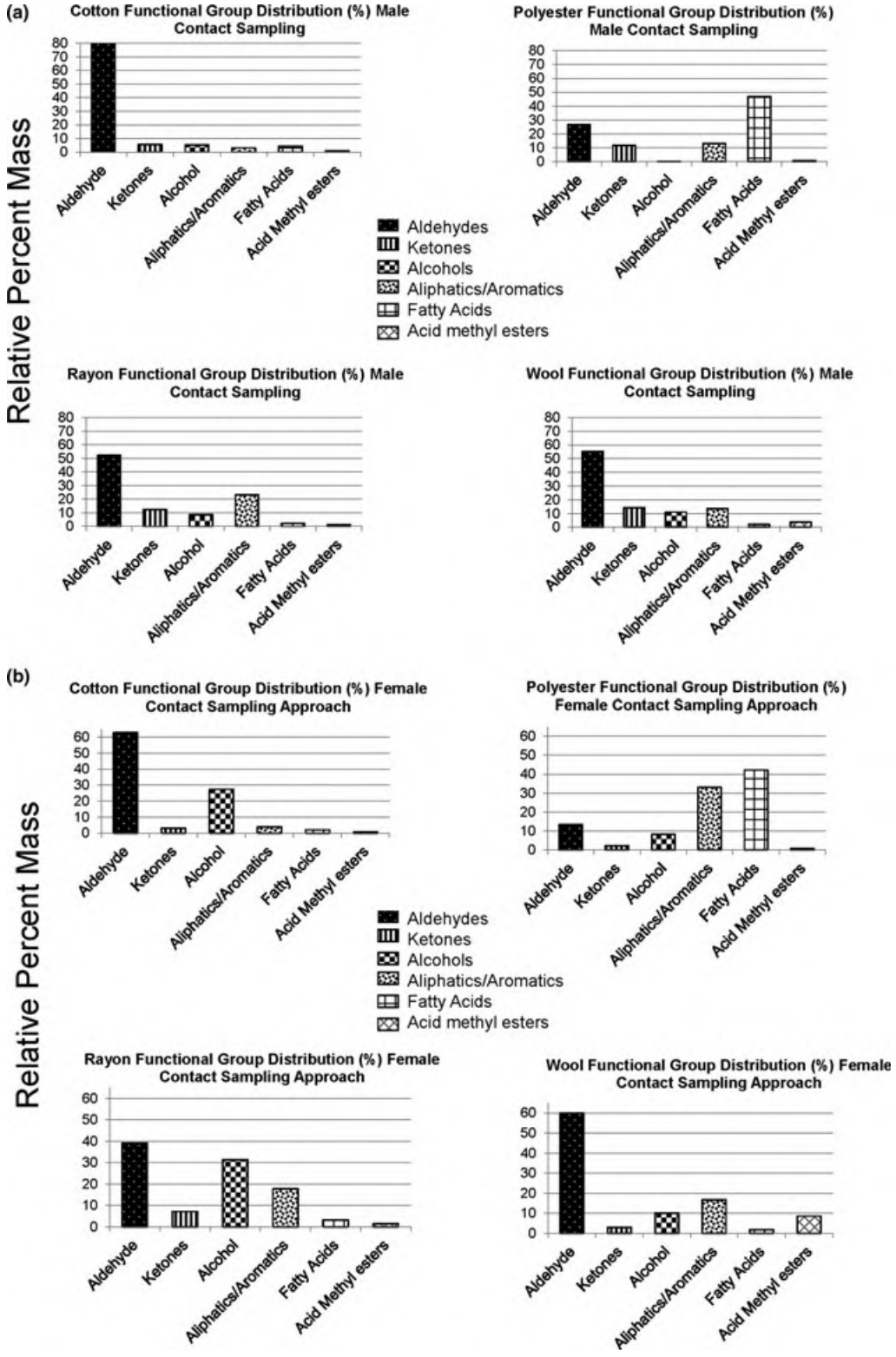

FIG. 3—*Functional group distribution in percentage mass: (a) male contact sampling; and (b) female contact sampling.*

the least reported among all the functional groups discussed thus far. It should be noted that the only fabric that detected significant amounts of these types of volatiles for both genders was the wool fabric (8.59% for the women, 3.93% for the men). For the remaining of the fiber media, the range of percentage mass detected was between a low level of 0.72% in the female cotton samples and 1.46% in the female rayon samples.

Noncontact Hand Odor Collection Results

A total of 20 compounds were detected in the hand odor samples collected with the Mod-STU device (Table 3). Even though the same subjects were tested, the results obtained varied significantly. In general, all fabric types displayed a decreased amount of VOCs present in the headspace of the scent sample, with the three

TABLE 3—*Volatile organic compounds (VOCs) detected from human hand odor via a noncontact approach separated by functional group and material type for both female (F) and male (M) subjects.*

	COTTON						POLYESTER						RAYON						WOOL					
Compound Detected	F1	F2	F3	M1	M2	M3	F1	F2	F3	M1	M2	M3	F1	F2	F3	M1	M2	M3	F1	F2	F3	M1	M2	M3
Alcohols																								
1,6-Octadien-3-ol,3,7-dimethyl-	x												x	x										
Aldehydes																								
Heptanal					x																		x	
Nonanal	x	x	x	x	x	x	x	x	x	x	x	x	x	x			x		x	x			x	x
Decanal	x	x	x	x	x	x		x	x		x	x	x	x		x	x	x	x	x	x	x	x	x
Dodecanal																							x	
Tetradecanal																			x	x	x		x	x
Lilial	x							x						x										
Aliphatics/Aromatics																								
Caryophyllene							x																	
Undecane											x													
Dodecane											x													
Tetradecane	x	x		x		x							x	x		x								
Hexadecane													x	x										
Eicosane													x											
Carboxylic Acids																								
Butanoic acid										x	x													
Hexanoic acid											x													
Hexanoicacid,2-ethyl-					x			x	x		x		x											
Carboxylic Acid methyl esters																								
Butanoic acid, methylester					x																			
Hexadecanoic acid, methylester																							x	
Ketones																								
5-Hepten-2-one,6-methyl-		x		x	x										x									
5,9-Undecadien-2-one, 6,10-dimethyl-, (E)-	x	x		x	x	x	x	x	x		x	x	x	x	x	x	x	x	x	x		x	x	x

most common detected compounds being aldehydes such as nonanal (79.17%) and decanal (87.50%), and the ketone, (E) 6,10-dimethyl-5,9-undecadien-2-one (87.50%). Polyester fabric, as seen with contact sampling, displayed a greater selection of carboxylic acids. In contrast to the direct contact sampling procedure, hand odor samples in this part of the study only displayed one alcohol, 3,7 dimethyl-1,6-octadien-3-ol (12.50%), which was found to be highly recurring in the contact method. The wool fabric had the presence of mostly aldehydes, with only two other functional groups being detected, one ketone and one acid methyl ester.

The functional group distribution among the textiles obtained through the noncontact method is shown in Fig. 4*a*,*b* separated by sex. The distribution is described in relative mass percentages for each material type between the male and the female subjects in the study.

Aldehydes—For the noncontact scent collection method, the women displayed the highest percentage mass on cotton fabric from the aldehyde group (67.01%). The polyester fabric showed 60.95% of mass distribution originating from the aldehyde group, which was a notable increase from the results observed in the contact samples. The rayon collection medium displayed 43.20% from the aldehyde group, while the wool fabric collected the least amount of aldehyde type of volatiles reporting only 38.72%. In the noncontact collection from the male hand odor samples, the aldehyde functional group was once again the most represented in the cotton (55.91%) and wool (74.98%) fabrics. When compared to the contact method, there is a clear decrease in the scent mass collected; however, the ratios in comparison with the other functional groups seem to be distributed the same in both collection methods.

Alcohols—Unlike contact sampling where alcohols were seen on all fabrics, using noncontact sampling, the alcohol functional group was only present in the two types of cellulosic fabrics in the collected female hand odor samples; 5.44% in cotton and 3.36% in the rayon samples.

Ketones—Unlike contact sampling where ketones were minor contributors, their total contribution to the observed collected scent mass was greater in the samples collected via a noncontact approach. For the female subjects, it can be noted that in both the rayon (45.26%) and the wool (61.28%) fabrics, the ketones showed the highest percentage mass contribution. They were also present in the cotton (26.06%) and the polyester (21.50%) fabrics with a lower contribution. For the male subjects, the rayon fabric collected the most ketones (68.66%) followed by cotton (36.09%), wool (21.71%) and lastly polyester (7.00%). For both genders, rayon seems to display an advantage at collecting these types of volatiles when compared to the other functional groups being reported within the collected samples.

Aliphatics/Aromatics—The aliphatic/aromatic type of volatiles for the female hand odor samples were mostly detected in the polyester material (9.05% for women and 9.13% for men). Both cotton and rayon reported lower percentage mass amounts, while the wool collection medium did not report this functional group as part of its mass distribution for neither gender.

Carboxylic Acids—As previously seen using contact sampling, noncontact sampling with the polyester material proved to be the optimal material for the detection of carboxylic acids which are not readily seen with the other fiber types. For the female subjects, 8.50% of the fatty acid mass was observed in the polyester fabric while only 0.60% was seen in the rayon. The other fiber types did not report any acidic volatiles in their profiles. As for the male

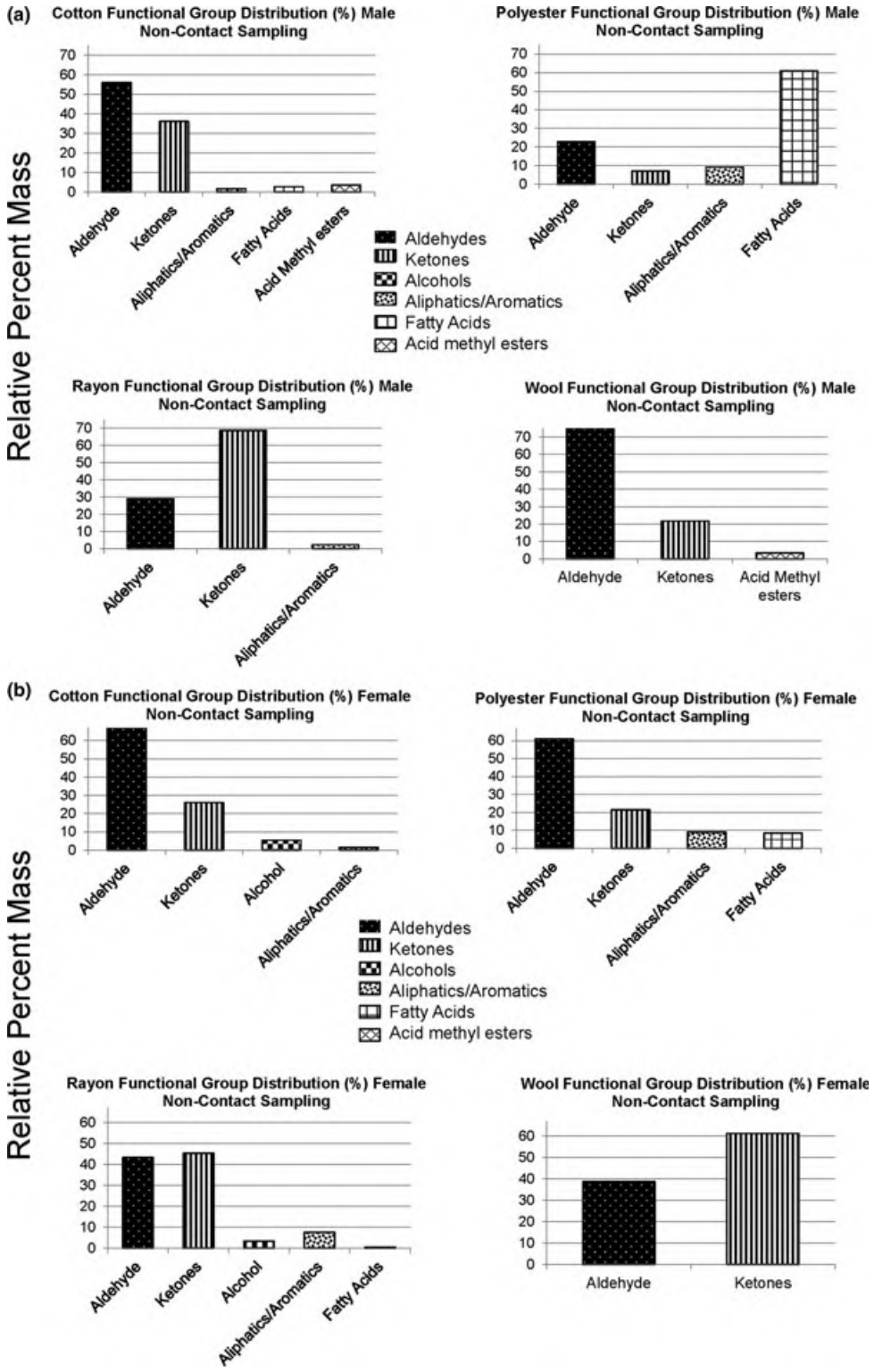

FIG. 4—*Functional group distribution in percentage mass: (a) males noncontact sampling; and (b) female noncontact sampling.*

odor samples, polyester displayed a percentage mass of 60.96% while cotton showed 2.75% of mass attributed to the acidic functional group. Both rayon and wool did not collect this functional group for any of the male samples.

Carboxylic Acid Methyl Esters—The amount of fatty acid methyl esters in the hand odor samples collected via a noncontact approach was also the least reported among all the functional groups discussed as was observed in the contact sampling method. It should be noted that only the male subjects reported any mass contribution from this functional group. This was seen in the cotton (3.54%) and in the wool (3.31%) fabrics. The female subjects had no presence of this type of volatiles in any of the fiber media tested.

Collected Scent Mass Distribution—For both the female and male subjects, the average scent amounts (triplicate) for each

TABLE 4—*Female mass distribution across fiber chemistry scent mass (ng; relative standard deviation %).*

	Contact Hand Odor Collection			Noncontact Hand Odor Collection		
	F1	F2	F3	F1	F2	F3
Cotton	274 (20)	427 (25)	232 (11)	10 (33)	5 (60)	0 (110)
Polyester	43 (18)	59 (22)	193 (57)	1 (53)	5 (51)	1 (98)
Rayon	58 (20)	72 (12)	83 (17)	5 (66)	11 (65)	2 (51)
Wool	22 (58)	17 (18)	68 (18)	1 (49)	1 (25)	0 (173)

TABLE 5—*Male mass distribution across fiber chemistry scent mass (ng; relative standard deviation %).*

	Contact Hand Odor Collection			Noncontact Hand Odor Collection		
	M1	M2	M3	M1	M2	M3
Cotton	59 (11)	83 (20)	64 (17)	1 (111)	10 (40)	2 (140)
Polyester	11 (47)	2 (80)	9 (10)	3 (17)	7 (30)	1 (65)
Rayon	24 (18)	44 (13)	19 (28)	2 (74)	8 (15)	3 (14)
Wool	82 (8)	22 (42)	6 (27)	1 (90)	9 (36)	3 (49)

corresponding material have been calculated. The reported scent mass is based on all extracted compounds that were detected in each individual sample for each collection medium under evaluation. For the female sampling group, the highest reported scent masses were seen with the cotton collection material via a contact sampling approach as can be observed in Table 4. For the noncontact sampling method, there is no distinct pattern that can be summarized; however, it is important to note that the relative standard deviations for the collected scent mass among the noncontact method (25–173%) are much higher than those reported for the contact approach (12–58%). These values emphasize the lack of reproducibility obtained within the samples taken for each material utilizing the STU-100. As Table 5 displays, across the male subjects, similar results were obtained.

The reported higher scent mass amounts within this study for both genders in the cotton fabric are supported by empirical data on the analysis of aroma chemicals on fabrics in which it is stated that these chemicals are typically released at much faster rates from polyester fibers than cotton. These results in turn are directly related to the distribution of the chemical in the external and internal fiber regions (51,52).

Statistical Analysis

Principal Component Analysis

PCA was utilized to monitor the variances in the patterns within the data groups by using three-dimensional (3D) scatterplot graphing. The PCA plots were used to monitor the different types of sampling methodologies as well as to observe the behavior of each volatile profile collected on the different fiber media. PCA was performed with all detected compounds because of the lack of common components present among the noncontact samples.

From the PCA, 3D scatterplots obtained from a single female subject (F1) and single male subject (M2; Figs 5 and 6, respectively) and including all of the collected samples from both contact and noncontact scent collection methods, a common observation was the likelihood of the samples collected on the same fiber chemistry to cluster together. Even though the samples were all collected from the same individual, the volatile chemical profile

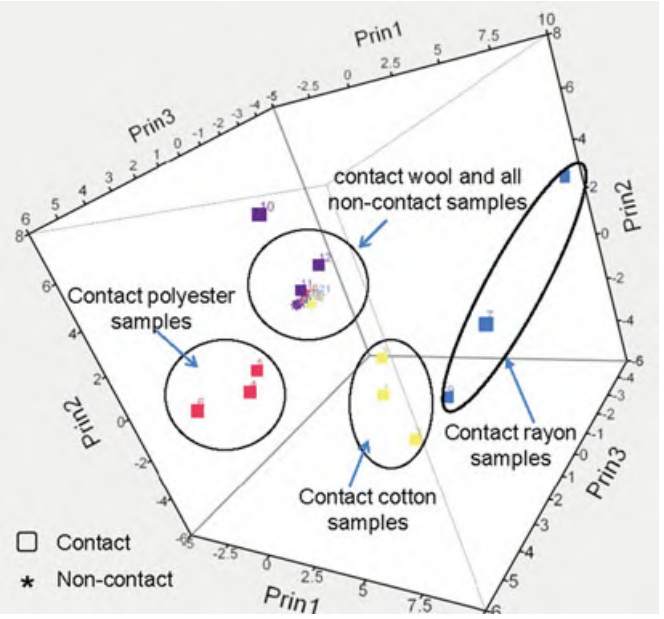

FIG. 5—*Principal component analysis (PCA) 3D scatterplot female 1 contact and noncontact collected hand odor samples.*

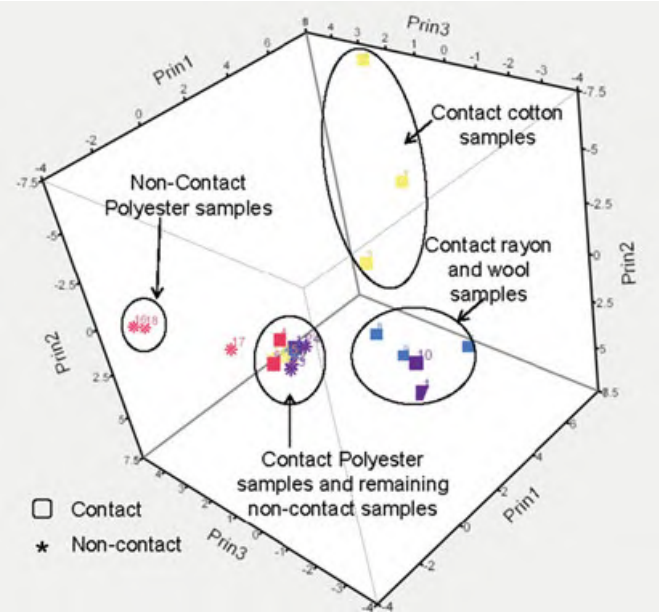

FIG. 6—*Principal component analysis (PCA) 3D scatterplot male 2 contact and noncontact collected hand odor samples.*

was different enough for each fiber medium to yield different groups in 3D space. When looking at the noncontact samples, the data clusters together in a way that is not seen with the contact samples. For both subjects, the noncontact samples stack tightly together regardless of the material utilized for sampling. The grouping observed with the Mod-STU samples could be the result of a decreased capacity to be differentiated because of the decreased number of detected compounds. Because the array in the pattern has fewer number of volatiles detected, the Mod-STU samples will therefore tend to group more closely together because of their similarity of zero values, not in volatile pattern similarity.

Spearman Rank Correlations

The clustering observed with the contact samples from both individuals described earlier only provides a measure of how the samples group in 3D space. The degree of similarity intrasubject within each triplicate set compared to the other textile types is not measured and cannot be determined in an accurate manner via PCA. Spearman rank correlations were utilized to evaluate the strength of similarity among the samples collected from the same individual as well as the ability to distinguish the collected hand odor samples among subjects as it has been previously used by the authors and determined to be a viable means to compare human scent profiles (13,34). As it relates to this study, a type I error indicates that the sample is falsely excluded at a given threshold and a type II error indicates that a particular sample is falsely included at the given threshold.

Correlations Considering all Detected VOCs

Spearman rank correlations were initially conducted for the contact samples using all of the detected compounds in the headspace of the hand odor samples. Twelve samples from the six individuals were considered producing 2556 possible pairings (72 samples in total across all textile types and subjects). As summarized in Table 6*a*, when considering a match/no match threshold of 0.9, the subjects were discriminated and identified in 69.02% of the cases (790 type I errors, 0 type II errors). When lowering the threshold to 0.8, the subjects were discriminated and identified in 69.02% of the cases (788 type I errors, 2 type II errors). At the 0.7 correlation threshold, the subjects were discriminated and identified in 69.17% of the cases (778 type I errors, 10 type II errors). The high number of type I errors underscores the fact that the choice of collection material is a variable that effects the ability to correlate and compare individual's human scent as those originating on different textiles were falsely excluded as originating from a different subject. The low presence of type II errors compared to type I errors demonstrates the variability among subject's human scent profiles. Figure 7(*a*) provides a graphical representation of the relative ratios of the all of the volatile compounds present in the human scent profiles of female 1 and male 2; intrasubject variation among the textile types can be readily determined visually. Each bar within the graph represents a distinctive hand odor sample where each color is a code for the chemical being detected and its relative peak area contribution to that particular sample as a whole.

TABLE 6—*Correlation outcomes considering all collected samples.*

0.9 Correlation Threshold	Cotton	Polyester	Rayon	Wool	Total
(*a*) Correlation Outcomes Considering All Detected VOCs Compared Across All Materials					
Type I Errors	198	196	198	198	790
Type II Errors	0	0	0	0	0
Total Errors	198	196	198	198	790
Percentage Distinguished					69.02
(*b*) Correlation Outcomes Considering Primary Odor VOCs Determined Across All Textile Materials					
Type I Errors	69	95	80	94	338
Type II Errors	12	12	12	12	48
Total Errors	81	107	92	106	386
Percentage Distinguished					84.90
(*c*) Correlation Outcomes Considering Primary Odor VOCs Based on Textile Type					
Type I Errors	176	182	180	186	724
Type II Errors	0	0	0	0	0
Total Errors	176	182	180	186	724
Percentage Distinguished					71.67

VOCs, volatile organic compounds.

Conducting the Spearman rank correlations considering only the 18 samples collected on each textile type (three samples per textile for each of the six subjects) and using all of the detected VOCs provides insight into the usefulness of each textile for discrimination. As can be observed in Table 7*a*, there is a minimal presence of type II errors as discussed earlier, indicating the low probability of falsely including someone else's sample as that of the target odor. In general, at the 0.9 match/no match threshold the highest percentage distinguished was seen with polyester at a 77.78%; at the 0.8 threshold, this was observed with both polyester and wool (both textiles had a 77.78% of the cases correctly distinguished and identified), while at the 0.7 threshold the same percentage of discrimination was achieved with polyester, rayon, and wool. This slight advantage of the other textiles when compared to cotton can be attributed to the higher number of type II errors found among the cotton samples.

Correlations Considering Primary Odor Compounds Determined Across all Material Types

Previous work by the authors has demonstrated that narrowing the compounds considered for each subject to only those common in triplicate samples or a subjects "primary odor constituents" produced a greater degree of both individualization and discrimination (13). When the volatile compounds for consideration are reduced to only those present among all 12 samples per subject hence the subject's "primary odor" compound set, a total of six compounds remain. The types of compounds determined as the primary odor components included a range of functional groups. These included alcohols such as benzyl alcohol and 3,7-dimethyl-1,6-octadien-3-ol (both reported by the authors as low-frequency occurring compounds (34), aldehydes including nonanal and decanal high frequency compounds (34), 6,10-dimethyl,5,9-undecadien-2-one (medium frequency compound) and heptadecane, a previously reported low-frequency occurring aliphatic (34). With the exception of heptadecane, all of these compounds have been previously reported by the authors to be primary odor components of hand scent samples (13).

Table 6*b* displays the summary of the Spearman correlation at the 0.9 threshold when the compounds considered across all 12 samples for a subject are reduced to only those presentage among all with no regard for differences in the collection material. At a match/no match criteria of 0.9, the percentage of subjects correctly distinguished and identified is 84.90% (338 type I errors, 48 type II errors), while at the 0.8 and 0.7 thresholds the percentage distinguished and identified is 80.20% (338 type I errors, 168 type II errors) and 86.78% (338 type I errors, 0 type II errors), respectively. As seen in Table 6*b*, when comparing the amount of errors present across the textile types, cotton is the material with the lowest number of errors. When considering the primary odor components present across all material types there is an increase of approximately 10% correctly distinguished and identified than the percentages obtained using all detected compounds. The reduction in type I errors suggests an enhanced benefit for narrowing an individual's odor components to those present among all media if the samples to be compared are not collected on a standardized type of collection material.

Considering only the 18 samples collected on each textile type and utilizing the six primary odor components across all materials for each individual allows for a closer evaluation of the discrimination power within fiber chemistry. Table 7*b* summarizes the results

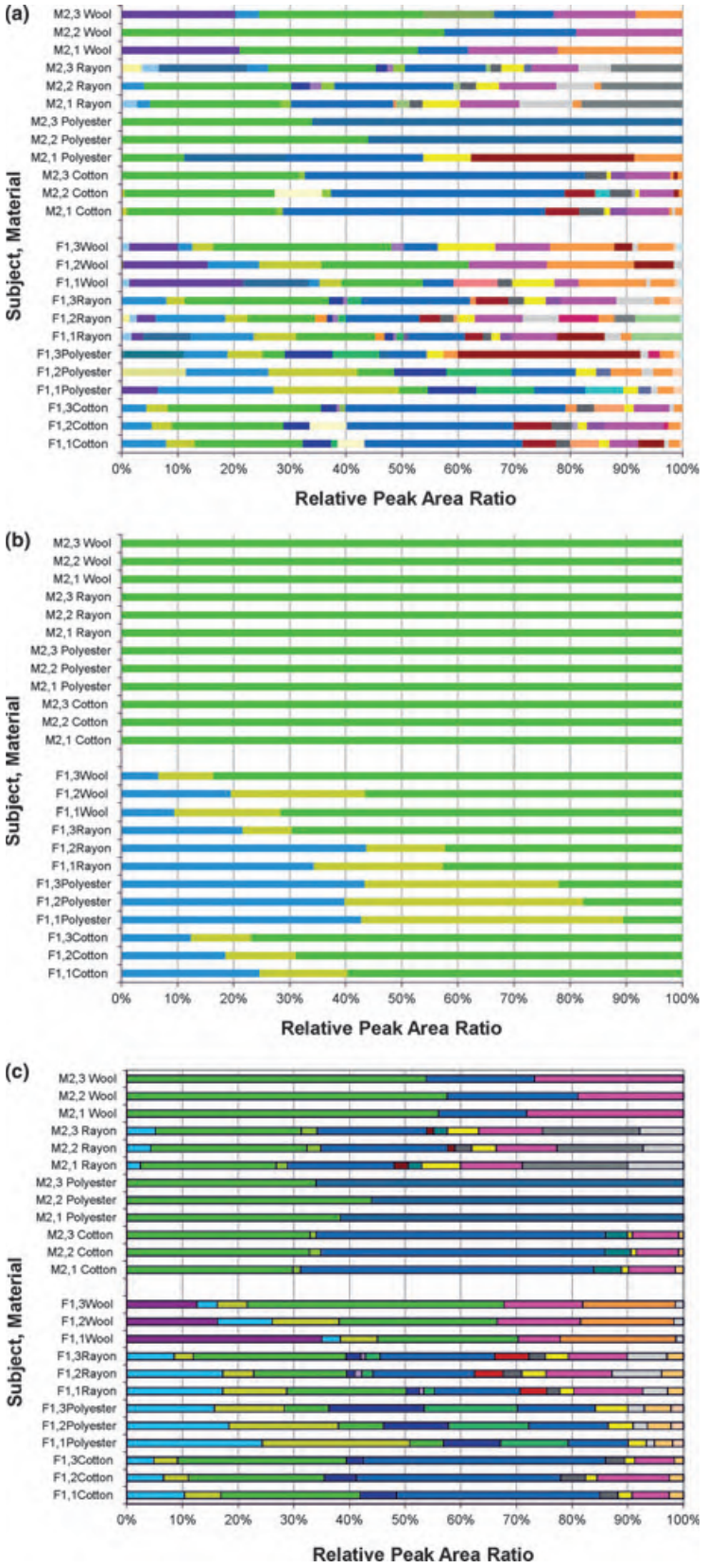

FIG. 7—*Color odor charts for female 1 and male 2: (a) displaying all compounds detected; (b) primary odor components across all fiber types; and (c) primary odor per each fiber type.*

of the Spearman correlation conducted with these samples at the 0.9 match/no match threshold. There is a significant reduction in errors across all fiber types, with cotton reporting no false exclusions (type I errors) at all thresholds evaluated. For both the 0.9 and 0.7 match/no match threshold, cotton had a 100% distinguished and identified value. As opposed to the correlation results

TABLE 7—*Correlation outcomes considering samples within a material type.*

0.9 Correlation Threshold	Cotton	Polyester	Rayon	Wool
(*a*) Correlation Outcomes Considering All Detected VOCs Compared Within Material Type				
Type I Errors	36	34	36	36
Type II Errors	0	0	0	0
Total Errors	36	34	36	36
Percentage Distinguished	76.47	77.78	76.47	76.47
(*b*) Correlation Outcomes Considering Primary Odor VOCs Determined Across All Textile Materials Compared Within Material Type				
Type I Errors	0	8	12	8
Type II Errors	0	0	0	9
Total Errors	0	8	12	17
Percentage Distinguished	100.00	94.77	92.16	88.89
(*c*) Correlation Outcomes Considering Primary Odor VOCs Based on Textile Type Compared Within Material Type				
Type I Errors	14	20	18	24
Type II Errors	0	0	0	0
Total Errors	14	20	18	24
Percentage Distinguished	90.85	86.93	88.24	84.31

VOCs, volatile organic compounds.

using all of the detected compounds, the use of an individual's primary odor components shows the increased discrimination power of the samples and thus supporting the importance of establishing an individual's primary odor profile. Both rayon and wool yielded higher incidences of type I and type II errors compared to the other textiles, demonstrating a lessened utility for employing these textiles as human scent collection media. Figure 7(*b*) shows the color odor charts for two subjects using only the primary odor components across all fiber types.

Correlations Considering Primary Odor Compounds Determined Within Each Material Type

Utilizing the Spearman rank correlation and narrowing the compounds for each individual to only those determined to be present in all three intraday samples collected per material type resulted in a total of 30 compounds that remained for consideration. These 30 compounds consisted of previous reported high-frequency (nonanal, decanal), medium-frequency (methyl ester octanoic acid, dodecane, undecanal, dodecanal, 6,10-dimethyl-5,9-undecadien-2-one), and low-frequency compounds (heptanal, benzaldehyde, benzyl alcohol, 3,7-dimethyl-1,6-octadien-3-ol, (E)-2-nonenal, nonanal, naphthalene, 2-decanone, (E)-2-decenal, tridecane, decanoic acid, tetradecane, tetradecanal, pentadecane, methyl ester dodecanoic acid, hexadecane, heptadecane). All of these compounds have been found to be primary odor VOCs of subjects in the headspace of hand odor samples from previous work conducted by the authors (13,34). Other compounds that were also found to be present as primary odor constituents of the subjects evaluated in this study included acids (hexanoic acid, octanoic acid, nonanoic acid) and an aliphatic compound (octadecane), which have not been previously reported as primary odor compounds.

Considering a match/no match threshold of 0.9, the individuals were discriminated and identified in 71.67% of the cases (724 type I errors, 0 type II errors; Table 6*c*). When a 0.8 threshold is considered, the individuals are correctly identified in 72.54% of the cases, while at the low 0.7 threshold the percentage distinguished drops to 71.99%. The minor increase in the percentage distinguished at each evaluated match/no match threshold compared to the first correlation set described earlier highlights the importance of considering a human scent baseline as is seen when only using primary odor components of an individual's scent profile. However, the high number of recurring type I errors continues to highlight the false exclusions of samples mainly as a cause of the variation in collection medium. From the correlation results obtained using the primary odor from each textile type, it can be noted that in general the samples on the cotton fabric provide with the least number of total errors at both match/no match criteria of 0.9 and 0.8. At the 0.7 threshold, polyester statistically highlights fewer occurrences of total errors including a much lower occurrence of false inclusions when compared to the other fiber types. It is evident that the discriminating power of this method can be enhanced by obtaining several samples from a subject on the same material prior to inputting into a repository of human odors and having a standard type of material that is used for sample collection.

In an effort to evaluate the utility of a standard type of collection material, a Spearman rank correlation was conducted for the population within each textile type using only the 30 compounds. A total of 18 samples from the six subjects were considered producing 153 possible pairings per each textile type. As seen from Table 7*c*, cotton had the highest percentage discrimination at the 0.9, 0.8, and 0.7 thresholds compared to the other textiles. Furthermore, cotton also represents the medium with the least total errors, while wool fabric is the textile that through statistical analysis has the greater probability of falsely including and/or excluding an individual's scent profile. When compared to the results obtained in Table 6*c*, the data in Table 7*c* displays the reduction in type I and type II errors for each textile, thereby reinforcing the importance of a standardized collection material utilized in human scent collection. Figure 7(*c*) displays a color odor chart for two subjects (man and woman) where the relative ratios of the peak areas for the primary odor compounds can be seen for all collection media.

Contact sampling with cotton material was the combination that performed the best for the six subjects in this study, both in terms of collecting the greatest number of previously reported human scent VOCs and the least amount of type I and type II errors in the produced primary odor profile. This collection method and material combination has been utilized by the authors in previous studies, which include a 60-subject population study (39) as well as a proof of concept study that validated the collection and analysis method as well as the data-handling techniques (13). The correlation data reported in this study (utilizing the optimized collection protocol) pertaining to the reproducibility of human scent profiles from multiple samples from the same subject are supported by previous studies that have utilized Spearman rank correlations to compare multiple intrasubject human scent profiles and have reported distinguishability at the 0.9 match/no match threshold as 99.54% (13). Additionally, the optimized collection method determined here was evaluated in a study that compared the effects of storage conditions on human scent samples and their resulting VOC profile (42). Furthermore, studies investigating proper storage of human scent samples also showed that pure cotton gauze materials yielded the highest similarity values as measured by 3D covariance mapping results over a 7-week storage period (42).

Conclusions

The primary focus of this study was an evaluation of direct and nondirect human scent collection techniques, with an emphasis on the optimization of collection materials composed of varied fiber chemistries.

The collection of hand odor from female and male subjects through a direct contact sampling approach yielded new insights into the types of VOCs collected when different materials are

utilized. Furthermore, the collected scent mass was shown to be obtained in the highest amounts for both male and female hand odor samples on cotton sorbent materials. Compared to noncontact sampling, the contact sampling methods yielded a higher number of volatiles, an enhancement of up to three times, as well as a higher scent mass than noncontact methods by more than an order of magnitude. These results demonstrate that an individual's observed human scent chemical profile vary considerably depending on the method used to collect scent from the same body region.

In this study, a range of textiles were evaluated, which demonstrated that cellulosic materials such as cotton and rayon provided a greater variety of functional groups being collected, while fiber media such as polyester proved optimal for the collection of acidic volatiles not readily seen among the other textile types. With both contact and noncontact scent collection methods, polyester scent samples show that male subjects emanate more acidic type of volatiles in comparison with the female subjects. Alcohol type of compounds are more readily seen in contact samples than noncontact samples for both genders, while ketones exhibit a greater mass contribution in noncontact scent samples for both male and female subjects. There was no clear indication of the optimal material to be utilized for noncontact sampling procedures. Also, it is shown that the contact and noncontact samples collected from the same subject do not demonstrate sufficient similarity among the chemical profiles to allow for individualization from the primary odor components.

Because of the low or in some cases lack of detected volatiles in noncontact hand odor samples, Spearman rank correlations were not performed for these samples; however, PCA did allow for a comparison to be made between both collection methodologies. A common observation was the likelihood of the contact samples collected on the same fiber chemistry to cluster together, while the noncontact samples regardless of fiber chemistry grouped together, which could be the result of a decreased capacity to be differentiated because of the decreased number of detected compounds. When utilizing statistical analysis such as Spearman rank correlations, contact samples were evaluated in a number of different manners to understand the utility of different textile chemistries for direct scent collection.

Using all of the detected compounds, a high number of type I errors was observed, demonstrating that the choice of collection material is a variable that effects the ability to correlate and compare individual's human scent. Furthermore, when considering only the samples on the same fiber chemistry, the use of all detected VOCs showed that cotton had the highest occurrence of possible false inclusions to occur when compared to the other fabric types. When the volatile compounds for consideration are reduced to only those present among all 12 samples per subject (primary odor compound set), a total of six compounds remained. Using this selection of compounds, there was an observed reduction in type I errors, suggesting an enhanced benefit for narrowing an individual's odor components to those present among all media if the samples to be compared are not collected on a standardized type of collection material. Utilizing these six primary odor VOCs, samples were discriminated and identified 84.90% of the cases, while 100% were discriminated and identified using only the samples within the cotton fiber type. Restricting the compounds for consideration to only those compounds present in each of the triplicate samples per subject within the same textile resulted in 30 remaining components. When each textile was considered as a group, the cotton fabric shows the lowest amount of total errors (with 90.85%, 98.69%, and 97.39% distinguished at 0.9, 0.8, and 0.7, respectively), making this textile type the top collection material performer when conducting statistical evaluations of collected human scent profiles. The importance of obtaining a human scent baseline to increase the discrimination power of this technique is reinforced here and has been shown in previous work by the authors (13).

At present, canines are utilized to associate people, places, and objects using the presence of human scent, and this study provides some indication as to what VOCs may be available to the biological detectors on a collected sample. This study demonstrates the importance of collection medium selection as well as the collection method employed in providing a reproducible human scent sample that can be used to differentiate individuals. Overall, contact sampling with cotton fabric produced the most reproducible results and the highest level of human scent discrimination.

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