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In Situ Surface Sampling of Biological Objects and Preconcentration of Their Volatiles for Chromatographic Analysis

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This report describes a rolling stir bar sampling procedure for volatile organic compounds (VOCs) present on various biological surfaces. In combination with thermal desorption/gas chromatography/mass spectrometry, this analytical technique was initially tested for quantitative profiling of human skin VOCs. It is also applicable to additional hydrophobic surfaces such as agricultural products, plant materials, and bird feathers. Use of embedded internal standards provides highly reproducible and quantitative results for a wide variety of sampled trace components. The samples of collected human skin VOCs and standards were found stable under cool storage conditions for at least 14 days, making this approach suitable for field biological and agricultural studies. Additionally, this methodology appears to have potential for forensic and toxicological investigations, as suggested through the analyses of VOC profiles of the human thumb prints recovered from a nonbiological smooth surface.

Animals and plants emit volatile organic compounds (VOCs) into their respective microenvironments. While some of these VOCs are just metabolic products of the biologically complex organisms, certain substances could carry useful signaling information pertaining to a variety of biological functions. For example, natural plant defenses against herbivores and insects are known to be mediated through odorants on the plant surfaces. Infestation by the plant-eating herbivores can trigger production of VOCs in the fruit, which, in turn, attract the herbivore predators.[1−3] Gland-originated odors emitting from animal skin can be essential for chemical communication within a species.[4] Even in humans, the natural body odors might have signaling function, as they have been reported to affect mood[5,6] and the physiological state of other individuals.[6−9]

Methods of studying the chemical nature of VOCs on various biological surfaces are a challenge due to their low levels and mixture complexity. Typically, some form of preconcentration (e.g., adsorption) is first in order, to be followed by a mixture separation in the gas phase and either a highly sensitive universal detection or a specific monitoring of selected solutes. Capillary gas chromatography (GC), combined with mass spectrometry (GC/MS) or a selective GC detector, have primarily been the methods of choice for the analytical task. The proven merits of gas-phase methods and GC/MS notwithstanding, quantitative measurements of VOC profiles, originating from biological surfaces, have largely been hampered by the lack of suitable preconcentration matrixes. Among other investigations, this has been particularly evident with the attempts to analyze organics originating from human skin.

A classical method for collection of human skin volatiles involves the use of cotton pads attached to skin for different time periods, followed by a solvent extraction step[10,11] or trapping of VOCs into a Tenax GC-type adsorbent.[11] Other approaches have included pumping air or inert gas directly to the axillary area and collecting volatiles from the circulating flow into an adsorbent trap.[11−13] The literature of recent years is also replete with examples where specific skin constituents were determined: a novel on-line sampling device was described for the measurement

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of ethanol in human sweat by capillary GC,[14] while glass beads were proven effective in transferring effectively mosquito-attracting skin constituents[15,16] from palms of hands to GC/MS. The so-called "electronic nose" (a semiconductor-based detector) has been demonstrated useful in detection of a human axillary constituent, 5α-androst-16-en-3-one.[17] In terms of profiling human skin volatiles, a method utilizing solid-phase microextraction (SPME) was also described.[18] A subject held a hand inside the 6-L container, purged with nitrogen, while SPME sample collection of VOCs was performed. In yet another report, human underarm volatiles were collected on the pads previously purified through supercritical fluid extraction, followed by SPME extraction. Volatiles were collected from the pads in the headspace mode using separate vials.[19]

Most previously described methods have been largely qualitative, since collection techniques lack the reproducibility necessary for precise quantitative measurements of VOCs. Comprehensive studies of the VOC emanations from biological and other surfaces demand analytical reproducibility together with high-throughput techniques for statistical evaluations that most reported methodologies do not meet. Consequently, we have developed a versatile and quantitative collection technique for VOCs on surfaces that involves the previously described principles of stir bar sorptive extraction.[20−22]

This report describes a new device for the surface sampling, presents its analytical attributes, and demonstrates its wide applicability. The essential part of the described device is a stir bar coated with a poly(dimethylsiloxane) (PDMS) matrix, which can be rolled over a determined area of a biological surface (human skin, oily fruit, vegetable surfaces, etc.) while collecting a representative sample of VOCs that had been entrapped on such surfaces. Additionally, we demonstrate its use in a qualitative detection of VOCs from latent human fingerprints collected on a mirror surface. For quantification purposes, the stir bar can be previously impregnated with suitable internal standards.

EXPERIMENTAL SECTION

Reagents and Materials. All retention standard compounds were purchased from Sigma-Aldrich Chemical Co. (Milwaukee, WI). Stir bars (Twister, 10 mm, 0.5-mm film thickness, 24-μL PDMS volume) used for sample collection were provided by Gerstel GmbH (Mülheim an der Ruhr, Germany). The stir bars were conditioned prior to and between individual runs in the TC-2 tube conditioner (Gerstel GmbH) at 300 °C under purified helium stream. Volatile and semivolatile compounds were collected from surfaces using a clean stir bar inserted into a special roller device designed especially for the purpose of VOC profiling of human skin (Figure 1). Here, a Teflon handle accommodates adjustable jaws. An easily replaceable stir bar can be fastened between the jaws by a spring and a nut in such a way that a stir bar rolls freely when moved on the surface.

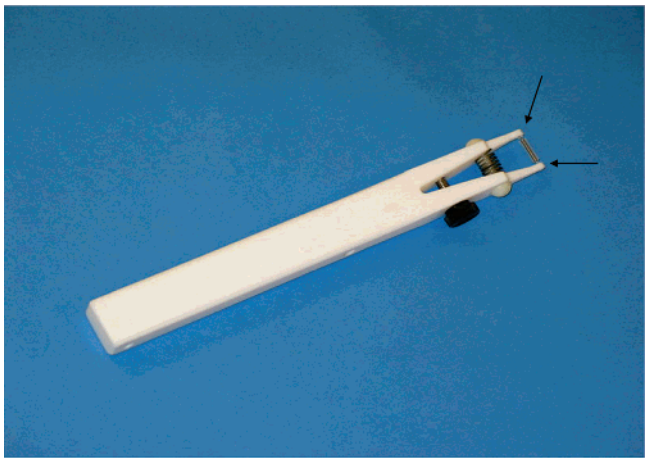

Figure 1. Schematic of the roller device designed for the stir bar surface sampling. Arrows show the attachment points of the stir bar between the jaws of this device.

Preparation of Embedded Internal Standards. High-purity water (OmniSolvEM Science, Gibbstown, NJ) was placed (2 mL) in precleaned, 20-mL scintillation vials. As an internal standard, 8 ng of 7-tridecanone (Aldrich, Milwaukee, WI) and 50 ng of ^{13}C-labeled benzyl alcohol (Cambridge Isotope Laboratories, Inc., Andover, MA) were added in 5 μL of methanol to each vial, followed by the addition of a preconditioned stir bar. Stirring speed was 850+ rpm on the Variomag Multipoint HP 15 stir plate (H+P Labortechnic, Oberschleissheim, Germany). Prior to extraction, all glassware was washed with acetone and dried at 80 °C. After extraction, the stir bars were stored in the individual vials inside a refrigerator prior to sample collection for up to 20 days.

Human Skin Samples. A pilot study for collection of human skin samples from five healthy female and male volunteers was approved by Indiana University Human Subjects Committee. A preconditioned stir bar with embedded internal standards was placed in the collection device, and two separate 5-cm-long stretches of the inner arm skin were rolled over with a stir bar (10-cm^2 skin area). The stir bar was subsequently dropped from the collection device and placed either in a clean thermal desorption tube for the immediate analysis by GC/MS or in a capped Twister glass vial, while the samples were stored in the refrigerator until analysis for up to 14 days.

Oily Plant Surfaces. A peeled pink grapefruit was divided into segments, and a surface in one segment was rolled over with the stir bar in ∼4-cm^2 surface area. Similarly, after a yellow onion was dissected, the stir bar was rolled over the cut cross-sectional surface. These plant samples were analyzed during the day when sampling was performed.

Bird Feather Surface. A wing feather of a dark-eyed junco (*Junco hyemalis*) bird was sampled, rolling a stir bar gently over a ∼4-cm^2 surface area of its length. Sample-containing stir bars were subsequently stored in a refrigerator. The analyses were performed within 48 h.

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Human Latent Fingerprints. A thumb fingerprint of human volunteers was pressed on the surface of a clean mirror. A stir bar was rolled over the print four times in collecting the deposited materials.

Analytical Instruments. The GC equipment for quantitative analysis consisted of the Agilent 6890N gas chromatograph connected to 5973i MSD mass spectrometer (Agilent Technologies, Inc., Wilmington, DE) with the thermal desorption autosampler and cooled injection system (TDSA-CIS 4 from Gerstel). Positive electron ionization mode at 70 eV was used with the scanning rate of 4.51 scans/s over the mass range of 35−350 amu. A MSD transfer line temperature was set at 280 °C. The ion source and quadrupole temperatures were set at 230 and 150 °C, respectively. Separation was performed by a DB-5MS (20 m × 0.18 mm, i.d., 0.18-μm film thickness) capillary column from Agilent (J&W Scientific, Folsom, CA). Samples were thermally desorbed in a TDSA automated system, followed by injection into the column with a cooled injection assembly, CIS-4. The TDSA was operated in splitless mode. The TDSA temperature program for desorption was 20 °C (hold for 0.5 min) and then a 60 °C/min ramp to 250 °C (final hold of 3 min). Temperature of the transfer line was set at 280 °C. The CIS-4 was cooled with liquid nitrogen to −80 °C. After desorption and cryotrapping, CIS-4 was heated at 12 °C/s to 280 °C, with the hold time of 10 min. The CIS-4 inlet was operated in the solvent vent mode, a vent pressure of 14 psi, a vent flow of 50 mL/min, and a purge flow of 50 mL/min. The temperature program in the GC operation was 50 °C for 1 min, then an increase to 160 °C at a rate of 5 °C/min, followed by the second ramp at a rate of 3 °C/min to 200 °C (hold time, 10 min). The carrier gas head pressure was 14 psi (flow rate, 0.7 mL/min at constant flow mode and under retention time locking conditions).

Element-selective compound profiling was performed with a GC 6890 instrument using an atomic emission detector (AED, model G2350A) from Agilent Technologies (Wilmington, DE) and a TDSA-CIS-4 (Gerstel). The separation was accomplished with a HP-5MS (30 m × 0.25 mm, i.d., 0.25-μm film thickness) capillary column from Agilent. Samples were thermally desorbed in a TDSA automated system, followed by injection into the column with a cooled injection assembly under the same conditions as described above for the GC/MS analysis, except that the CIS-4 was cooled with liquid nitrogen to −60 °C. The GC oven temperature program consisted of an initial hold at 50 °C for 2 min, then an increase to 200 °C at of 3 °C/min, followed by a final hold of 12 min. The carrier gas head pressure was 14 psi (flow rate, 1.2 mL/min). The GC unit was operated in the constant flow mode. The emission lines for carbon (193 nm), sulfur (181 nm), and nitrogen (174 nm) were monitored during the atomic plasma emission detection.

RESULTS AND DISCUSSION

General Considerations. Quantitative sample acquisition of the representative compounds from the surface of human skin can have considerable value in fundamental physiological studies and even a clinical diagnostic potential.[23] Reflecting the internal physiological state of a mammal (including microbial activity), different members of animal species, not surprisingly, exhibit characteristic skin odors with a distinct chemosignaling function (species-specific, hormone-dependent, individual recognition, etc.).[24,25] On the evolutionary scale, the vital importance of this chemosignaling function may have been largely lost in humans, although some recent studies do support the notion of olfactory communication in *Homo sapiens*.[7,8,26] Body odors in humans may also have their genetic attributes,[27] while a resident microflora can significantly contribute to their occurrence, qualitatively or quantitatively.[28,29] Metabolic state of the body (e.g., during certain diseases states) can also alter the body volatile odors.[30]

Acquiring a "representative profile" of the VOC emanations from human skin has been complicated by (a) mixed gland types present on any parts of the body with a different density and (b) substances retained on the skin surface due to environmental influences (soaps, shampoos, deodorants, perfumes, tobacco smoke, etc.) Our skin surfaces contain four different types of glands: sebaceous, eccrine (sweat), apocrine, and apoeccrine. Their anatomical distribution varies, as is likely a local chemical composition.[31] Sebaceous glands prominently feature various mixtures of lipids, such as triglycerides, fatty acids and their metabolites, waxy esters, cholesterol, and squalene.[32] Sweat gland secretions contain primarily water, although salts and antimicrobial peptides are also present.[33,34] The apocrine gland's function appears associated with adrenergic innervation and is believed to be a major source of odoriferous secretions including volatile steroids.[35−37] The recently described apoeccrine gland functions[30,35] have been less defined, but they seem to be a composite of eccrine and apocrine gland functions. Thus, depending on a sampled area of skin, VOC concentrations may vary due to a local distribution of different glands: for example, with fingertips containing only sweat glands, or the underarm (axillary) areas featuring all four types of glands.[30]

The primary impetus for this study has been the need to develop a high- throughput, reproducible procedure for evaluating VOC profiles, repeatedly sampled from the underarm areas of ∼200 human volunteers in a distinct geographical location. While the results of this study, linking VOC profiles to genetic factors

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Table 1. Reproducibility of Integrated Peak Areas (PA) for Selected Volatile Compounds Collected from the Arm of a Female Subject

Rt (min)	compound	PA × 10^6 sample 1	sample 2	sample 3	sample 4	average	SD[a] 10^6	RDS,[b] %
9.97	nonanal	0.383	0.341	0.382	0.317	0.356	0.032	9.0
12.78	decanal	0.186	0.193	0.169	0.176	0.181	0.011	6.1
19.19	geranylacetone	0.173	0.171	0.152	0.156	0.163	0.011	6.7
19.82	1-dodecanol	0.472	0.532	0.362	0.384	0.437	0.079	18.1
29.98	1-hexadecanol	2.085	2.222	1.764	1.819	1.972	0.217	11.0

[a] Standard deviation. [b] Relative standard deviation.

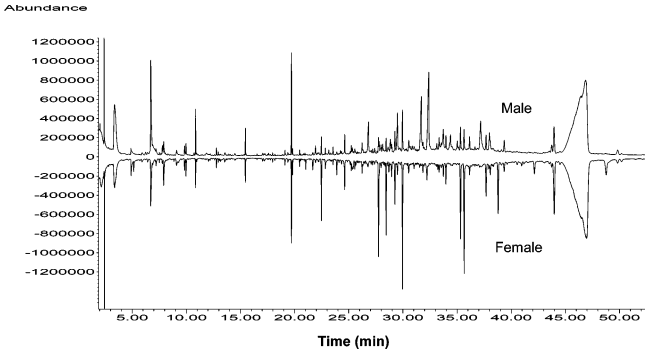

Figure 2. Comparison of TICs of skin surface VOCs for male (upper profile) and female (inverse profile) human subjects. Analytical conditions for GC/MS are described in text. IS 1, internal standards, ^{13}C-labeled benzyl alcohol; IS 2, 7-tridecanone.

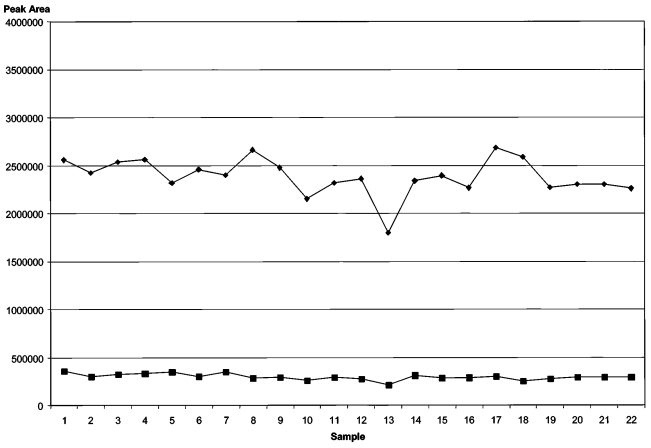

Figure 3. Variation in the peak areas of two embedded internal standards, ^{13}C-labeled benzyl alcohol and 7-tridecanone (n = 22).

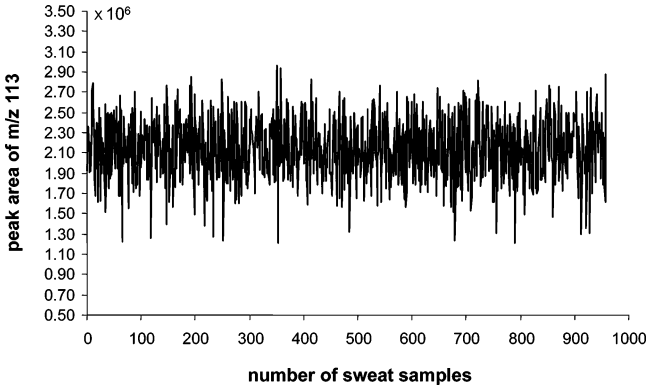

Figure 4. Long-term reproducibility (14.3%, RSD, n = 960) of the peak area measurements of 7-tridecanone (peak area × 10^6) over the 3-month analysis period. (The figure used with permission of the coauthors of ref 38).

and microflora, will be described elsewhere,[38] we report here the methodological aspects of this procedure, as developed through the assistance of five apparently healthy volunteers of both genders. To overcome the difficulties with a different distribution of skin cell types, all samples were consistently acquired from the same location on the inner forearm of these individuals.

Skin VOC Chromatographic Profiles. As seen in Figure 2, with representative chromatograms obtained from one male and one female volunteer, the profiles of VOCs generated from a direct skin sampling are fairly complex. Approximately 100 main components (out of ~400 GC/MS-detectable compounds altogether[38]) could be either positively or tentatively identified (data not shown) through GC/MS, with typical compound classes of aldehydes, ketones, fatty acids, and alcohols being present, not unlike those seen in previous studies using underarm collection pads.[36,37] The late-eluting broad (overloaded) peak seen in all chromatograms is squalene, a ubiquitous waxy constituent of the skin surface, likely originating from sebum secreted by the sebaceous glands (also, a precursor for cholesterol among other metabolites). As tentatively seen in our limited set of human volunteers (and confirmed in a large set of data[38] later), there was a considerable individual-to-individual variation in these profiles, while repeated samples from one person remained relatively stable. An example of the repeated sampling results for selected compounds in one person is shown in Table 1.

Human VOC profile components for five individuals (three samples for each individual), taken from the same area on the inner arm surface during a working day varied between 3 and 25%, RSD. Similar results (4−30%, RDS) were obtained from the same individuals on four consecutive days of sampling (one sample per day).

Taking into account the possibility of somewhat different gland distributions on the skin surface[30] and possible physiological fluctuations during any day, this repeatability is considered quite reasonable. In fact, our results of the skin compound variability over consecutive days are comparable with those obtained by Bernier et al. in their skin mosquito attractant studies (12−24%, RSD).[39]

To be able to account for the individual variations in the generation of VOCs by different humans, or the microbes

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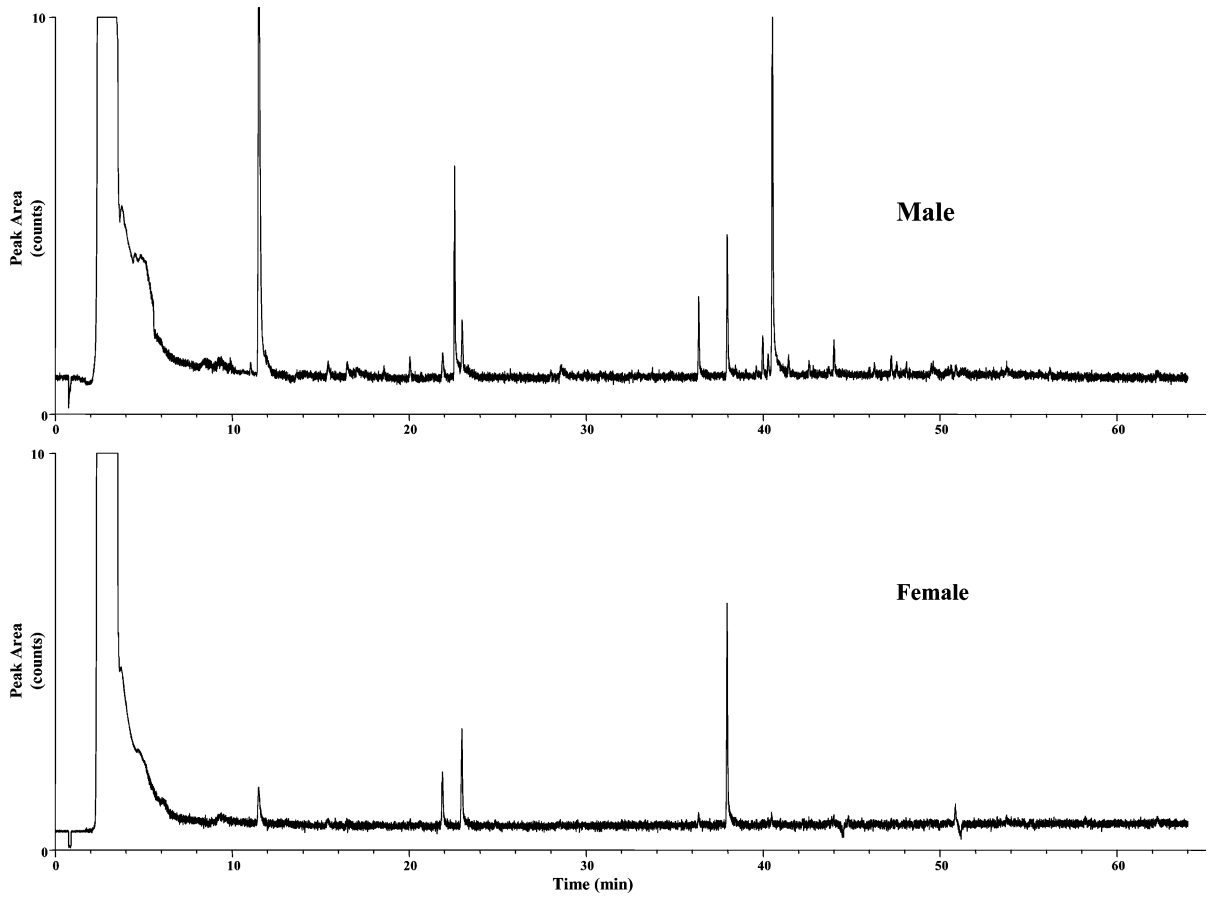

Figure 5. Selective sulfur line measurements (181 nm) of the male and female skin VOC profiles by GC-AED. Analytical conditions are described in text. Compounds were not identified.

modifying their VOC profiles, one must utilize reference compounds (internal standards) within the analytical scheme. Owing to their minimum interference with the eluting sample peaks, our embedded internal standards, ^{13}C-labeled benzyl alcohol and 7-tridecanone, have provided the means for quantitative comparisons through peak area ratios. Additionally, by embedding the internal standards inside the polymer sorption material, human skin exposure has been minimized. As seen in Figure 3, the short-term reproducibility in the peak areas of these embedded internal standards over a 5-day period, or 22 samples, was ±11.2%, RDS for ^{13}C-labeled benzyl alcohol and ±8.1% for 7-tridecanone. This procedure was even more helpful in a large population sampling study, over a prolonged analysis period,[38] normalizing possible variations and small differences due to sampling and instrumental responses. In the study, the measurements extended over 3-months time (n = 960), while the internal standard variations were remarkably low, ±14.7 and ±14.3% for ^{13}C-benzyl alcohol and 7-tridecanone, respectively (see Figure 4).[38]

As a different means of profiling VOCs from human skin, we have utilized an element-specific detector for monitoring sulfur-containing compounds. Human skin is expected to contain some sulfur compounds, possibly originating from the interaction of bacterial microflora and various skin constituents as well as some sulfur compounds that might originate from diet. Qualitatively, the skin sulfur compounds collected with the stir bar surface sampling technique were monitored at 181-nm emission line in the GC-atomic emission detection (AED) mode. Representative sulfur profiles for male and female subjects are shown in Figure 5. Typically, male subjects showed a larger number of peaks and greater abundance of sulfur compounds in their profiles compared to females.

Considerations on Sampling Principles. Human skin represents a morphologically and biochemically heterogeneous system in which metabolically derived (endogenous), microbially transformed, and exogenous (environmental) compounds become intermixed and partitioned into its hydrophilic and hydrophobic (lipid) regions. To devise a "universal" or a comprehensive sampling matrix that would register the compounds of a wide polarity range and molecular mass is thus nearly impossible. The equilibrium sampling procedures that are based on a transfer of volatiles into an adsorbent, followed by chromatographic analysis, have the distinct advantage of a bias against the large (nonvolatile) molecules, thus selectively sampling the VOCs for analysis. Apart from the inherent quantification problems associated with this analytical alternative[40,41] and the cumbersome nature of sampling in high-throughput studies, these procedures do not guarantee reproducibility (due to losses in adsorbent tubes and formation of analytical artifacts). Direct contact sampling techniques thus appear practically more favorable, so long as absorption rather than adsorption of sample molecules is chiefly present, combined

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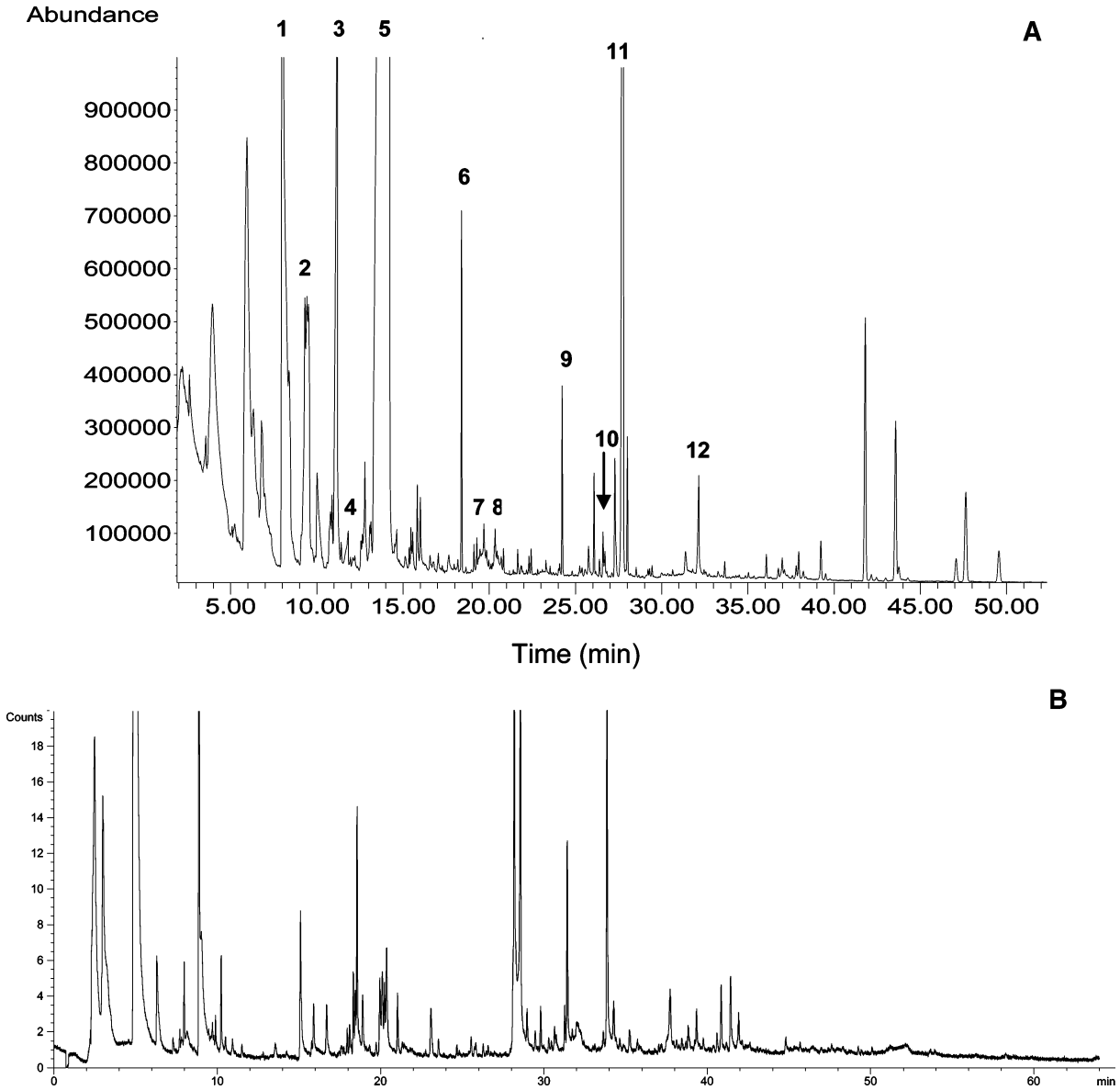

Figure 6. (A) GC/MS TIC of the volatile compound profile collected from the surface of a juicy grapefruit. Analytical conditions are described in text. Numbers indicate selected identified compounds 1, limonene; 2, 3, 5, Maillard reaction products; 4, benzoic acid; 6, caryophyllene; 7−9, various sesquiterpenes; 10, myristic acid; 11, nootkatone (an essential grapefruit flavor); 12, palmitic acid. (B) A sulfur line (181 nm) measurement of the sulfur profile from the cut surface of a yellow onion by GC-AED. Analytical conditions are described in text.

with the efficient and reproducible thermal desorption processes for VOCs.

The described sampling method offers distinct advantages over the previously described procedures. Foremost, it is amenable to performing reproducible sampling and optimum analyses at two geographically separate sites, at a relatively high sampling rate. A repeated screening of ~200 individuals at a European location, followed by shipping the acquired samples to the United States for a highly automated, quantitative analysis,[38] has been made possible through the development of this sampling approach. Using the stir bars coated with a hydrophobic polysiloxane film, very polar skin constituents (salts, peptides, sugars, etc.) are largely restricted from partitioning into this layer, although many moderately polar constituents such as fatty acids and alcohols are present (due to their proportional partitioning into the stir bar coating) in a quantifiable, "representative" substance profile. Since the relative rather than absolute quantification has been the primary objective of our population screening,[38] this methodology appears appropriate. While the stir bar procedure is obviously less comprehensive than the previously described use of glass beads,[15,16] where the surface adsorption is the major sampling mode, it also reduces appearance of asymmetrical, large peaks such as glycerol and lactic acid, which may obscure certain parts of the chromatogram when the medium-polarity GC separation phases are being used.

What level of reproducibility can be expected for sampling a large surface of human skin? While the underarm pads and similar VOC-transfer media were found useful in both physiological studies and the earlier identifications of human emanations, they cannot generally meet the requirements of quantitative metabolic profiling because of (a) variable contact of the sampled skin with sampling matrix, (b) difficulties of a quantitative translocation of VOCs to the injection port of a gas chromatograph, and (c) a substantial interference from ubiquitous background contaminants

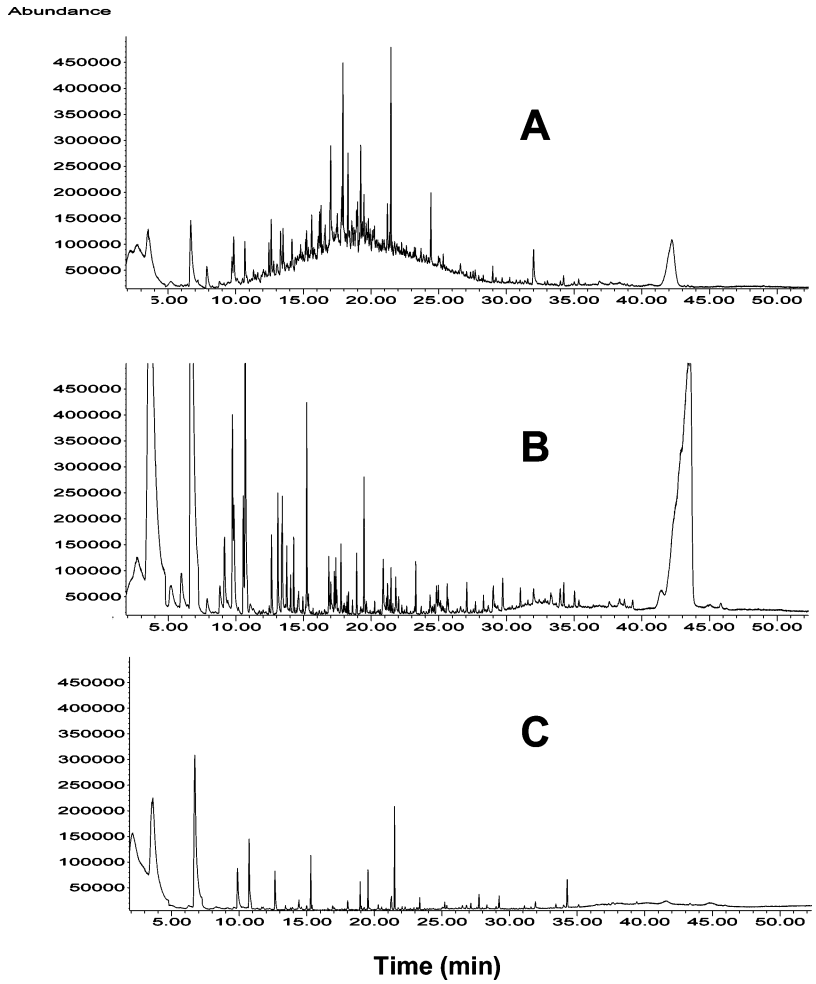

Figure 7. Comparison of VOCs of the latent fingerprints collected from the mirror surface by a stir bar using a roller device. GC/MS TICs for A−C refer to fingerprints of three different individuals.

("chemical noise") originating from both the pad materials and the solvents used to extract these for preconcentration. Conversely, rolling a stir bar (if necessary, repeatedly) over an area of skin provides reproducible sampling, as evidenced in this work.

How do the VOCs become concentrated (absorbed) onto the surface of a stir bar membrane? While a conventional stir bar extraction in its aqueous and headspace modes typically requires 30−45 min to reach a sorption equilibrium,[20] our direct skin VOC sampling method requires only 10−12 s. Even when a very thin layer of skin is being sampled during the experiment, similar equilibrium conditions can hardly be reached. Serendipitously, we believe, Nature has provided us with a unique preconcentration medium already before the stir bar application: a skin lipid layer, undoubtedly different in its content among different subjects, is being "mopped" by the stir bar element, transferring VOCs, with some lipids, to the sampling surface. Indirect evidence for this is the regular appearance of the squalene peak (see Figure 2) and a periodical (albeit not too frequent) need to clean the inlet sections of our GC/MS unit from contamination deposits. Still, this minor drawback did not appear to negatively effect quantification of a large study (more than 1000 samples), with only two interruptions for the system maintenance within a 3-month period.[38] Serendipitously, the presence of lipids on a polysiloxane stir bar surface is likely to preserve the chemical individuality of VOCs over extended time periods: with up to 20-day storages in a cool refrigerator, we observed no significant quantitative changes in substance profiles (data not shown).

Applications to Other Hydrophobic Surfaces. While the primary impetus for this work has been to develop a quantitative profiling technique for human skin VOCs, we can envision many other applications where a vigorous quantification and a rapid assessment of dynamic concentration changes on such surfaces could not be previously met. For example, certain quality parameters (like flavors and aromas) of fruits and vegetables during different maturation stages[42] can easily be measured. We demonstrate this briefly with the examples of a peeled grapefruit and a freshly cut onion. Importantly, such samples could be collected in field studies and safely analyzed by GC/MS at a different location.

Figure 6A shows a total ion current (TIC) chromatogram of VOCs collected on the moist surface of a pealed grapefruit. A cursory inspection of the separated components and their mass spectra revealed a number of typical plant constituents, such as terpenic and sesquiterpenic compounds, in addition to several furan and pyrane derivatives (data not shown). Figure 6B is a chromatogram consisting of compounds from a freshly cut yellow onion surface, using the sulfur-sensitive atomic emission detector. Many plant-originated, sulfur-containing compounds have been

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of a wide interest due to their health attributes. Increasing their levels for health and aroma benefits has been a genetic target for some time.[43,44] While the sulfur organic profile shown in Figure 6B is evidently complex, no attempts were made in this work to identify these VOCs further.

Another area of potential exploration for this sampling technique is chemical communication in bird species. As hypothesized in the recent literature,[45−47] bird wing feather surfaces can be an important source of chemosignaling substances within a species. Our preliminary studies of VOCs in preen gland composition[48] strongly suggest that VOC profiles change due to hormones and breeding season. Bird feathers are known to contain some of the preen oil, functioning similarly to mammalian sebaceous gland secretions,[46] while birds purposely apply the preen gland oily material on their feathers with their bill. It appeared to us that the rolling stir bar technique could be uniquely applied to sampling directly VOCs on the feather surface, presumably the site of chemosignal emission. The GC/MS data (results not shown) resulted in identification of several components that were previously seen in the preen glands.[48]

Related to our human skin studies, we investigated whether a human thumb print on a clean mirror surface could provide enough VOC material, to be transferred via a rolling stir bar, for a GC/MS analysis. Human fingerprints, considered by the standards of forensic science to be characteristic individual "signatures", typically contain finger sweat compounds (often supplemented by additional materials from a person's face or hair after contact). Additionally, environmental compounds (those originated from food, personal care products, contact materials, etc.) are expected to be found in human fingerprints. While different visualization techniques are the norm in judging human fingerprints,[49,50] only a few reports describe chemical or biochemical analysis of fingerprint content: typically, performing a DNA analysis,[51] or judging the presence of certain chemical warfare agents.[52] It was interesting for us to speculate whether different individuals could feature their unique "chemical fingerprints". As shown in Figure 7 with three different volunteers, there is a distinct possibility for this, and perhaps some forensic potential. Obviously, the detected VOCs are a composite of a person's own metabolic processes and environmental influences.

CONCLUSION

A rolling stir bar technique has been developed to facilitate reproducible and quantitative comparison of human skin VOC profiles. Internal standards can be embedded into the sorptive layer prior to sampling. The stability of samples under reasonable storage conditions and extended time periods allows the analyses to be performed in a location different from that of sample collections. Additionally, the described methodologies may have some potential for clinical and forensic investigations involving different means of sampling from skin.

Similar surface sampling conditions seem applicable to quantitative investigations of the VOC composition of other biological surfaces, such as those of plant materials (e.g., fruits and vegetables) and bird feathers. This, combined with the sample stability under reasonable conditions, suggests a potential utility of this technique in agricultural and biological field studies. Our preliminary studies also indicate that volatile and semivolatile compounds from human fingerprints can be analytically recovered from solid surfaces. This general approach may be applicable to toxicological and forensic investigations.

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