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Fragrance Profiling on Skin after Cosmetic Application

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Keywords

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Abstract

Understanding the persistence and perception of sensory-active compounds on skin is critical for evaluating the performance of cosmetic products. Conventional sampling approaches, such as solvent swabbing, glass beads, solid phase microextraction (SPME), and sorbent tubes, have drawbacks. They can be invasive, challenging to implement, and/or insensitive to the volatiles that drive perception. Thin film-solid phase microextraction (TF-SPME) provides a direct approach to sampling fragrance behavior on the skin surface. The flexible, high-capacity film easily conforms to the skin surface, enabling collection under real-world conditions without solvents or skin disruption. The results reveal how formulation composition and skin interaction influence the presence and perception of volatile compounds over time. These findings offer valuable insights into product development, enabling formulators to optimize fragrance profiles and enhance consumer experience.

Introduction

Fragrance performance on skin is a critical determinant of consumer perception and product acceptance in cosmetic formulations. While fragrances are typically designed and evaluated as neat mixtures or within product matrices, their sensory impact is ultimately governed by how volatile components are released, transformed, and persist on the skin over time. Skin is a chemically and biologically active surface influenced by temperature, moisture, lipids, and the resident microbiota, all of which can alter the fragrance composition after application. As a result, analytical approaches that fail to capture on-skin behavior may overlook key transformations responsible for off-odors, loss of character, or reduced longevity.

Traditional methods for sampling fragrances from skin, such as solvent extraction, glass beads, or gauze swabbing followed by solid phase microextraction (SPME) [1], often suffer from poor selectivity, matrix interference from lotion bases, and limited sensitivity for highly volatile compounds. In addition, these approaches can disrupt the skin surface or introduce competition effects during extraction, complicating the interpretation of time-resolved fragrance profiles. There is therefore a strong need for minimally invasive, reproducible sampling techniques that more accurately reflect skin following cosmetic application.

Thin film-solid phase microextraction (TF-SPME) offers several advantages for on-skin fragrance analysis, including a larger sorbent surface area, enhanced extraction capacity, and improved sensitivity relative to conventional fiber-based SPME. TF-SPME enables comprehensive, solvent-free profiling of volatile and semi-volatile fragrance components. In addition, it is well-suited for time-series measurements, allowing the evolution of top, middle, and base notes to be monitored directly on the skin.

In this study, TF-SPME was evaluated as an on-skin sampling technique for cosmetic fragrance analysis. Background contribution from the sampling materials was assessed, matrix interference was evaluated, and potential skin-mediated chemical transformations were investigated by comparison

GERSTEL AppNote 305

with an inert surface. TF-SPME performance was further benchmarked against a commonly used gauze-based SPME approach, and method reproducibility was assessed. Finally, a time-series study was conducted to characterize the temporal release of fragrance notes following lotion application, demonstrating the utility of TF-SPME for realistic, time-resolved fragrance evaluation.

Experimental

Instrumentation

GERSTEL MPS Universal Platform with SPME on Agilent 8890/5977B GC-MSD as shown in Figure 1.

Analysis Conditions Universal Platform

SPME fiber	50/30 DVB/CAR/PDMS; 23 gauge; 1 cm
MPS	35 °C incubation/extraction temperature
	2 min incubation time
	60 min extraction time
	250 rpm agitation speed
CIS 4	Splitless
	Purge flow to split vent: 30 mL/min at 1.2 min
	250 °C; isothermal
TF-SPME	HLB/PDMS
TDU 2	Splitless, 60 mL/min
	40 °C; 720 °C/min; 250 °C (5 min)
CIS 4	Tenax® TA-filled liner
	Solvent vent, 10:1 split
	-30 °C; 12 °C/sec; 280 °C (3 min)

Analysis Conditions Agilent 8890 GC

Column	30 m HP-5MS UI (Agilent)
	d_i = 0.25 mm, d_f = 0.25 µm
Pneumatics	He; P_i = 15.73 psi
	Constant flow = 1.3 mL/min
Oven	40 °C; 5 °C/min; 280 °C (2 min)

Analysis Conditions 5977B MSD

Mode	Scan
Scan	40 – 350 m/z

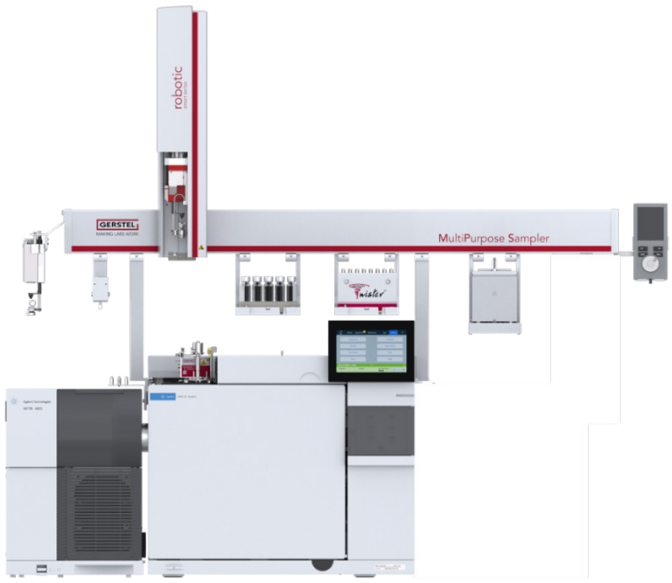

Figure 1: MPS Universal Platform with SPME.

Sample Preparation

A lavender- and honey-scented lotion, stainless-steel wire mesh, paper medical tape, sterilized wound covers, and gauze pads were purchased from a local store. For TF-SPME sampling, approximately 250 mg of lotion was weighed and applied to the forearm. Immediately after lotion application, a 35 x 35 mm mesh piece was placed directly on the forearm, with the TF-SPME membrane on top, to elevate it slightly off the skin. The TF-SPME and mesh were secured with a sterile wound cover and paper medical tape. The sampling scheme is shown in Figure 2. The TF-SPME was collected after 15 minutes and placed in an empty TDU tube for analysis.

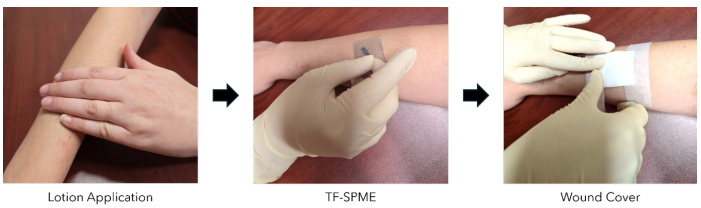

Figure 2: TF-SPME sampling.

The SPME sampling procedure was adapted from the literature [2]. Approximately 250 mg of lotion was weighed and applied to the forearm. Immediately after the lotion application, a 25 x 25 mm piece of gauze was placed directly on the forearm and secured with paper medical tape. The gauze was collected after 15 minutes and placed in a 20 mL screw-capped vial.

GERSTEL AppNote 305

Sample Introduction

The TF-SPME membranes were desorbed in splitless mode with a helium flow of 60 mL/min at 250 °C for 5 minutes. Analytes were trapped in the CIS 4 inlet on a Tenax® TA-filled liner at -30 °C. When desorption was complete, the analytes were transferred to the column in split (10:1) mode by heating the inlet rapidly to 280 °C.

The gauze in 20 mL screw-capped vials was placed on a VT15 tray on the MPS for SPME extraction. The samples were incubated at 35 °C for 2 minutes with an agitation speed of 250 rpm. Then, the sample headspace was extracted for 60 minutes. The analytes were trapped on a CAR/DVB/PDMS 1 cm fiber. The SPME fiber was desorbed at 250 °C in the CIS 4 inlet in splitless mode for 3 minutes.

Results and Discussion

Skin sampling was performed, without lotion application, to assess the background of the sampling materials and the skin. Figure 3 shows the total ion chromatogram (TIC) of the TF-SPME background sampling. The chromatographic signal is low and is comprised mainly of siloxanes, which can be attributed to the PDMS phase in the sorbent material. Several vinyl benzene derivatives are also observed, attributable to the HLB phase in the material. The remaining peaks, limonene, tetradecane, hexadecane, and hexadecanoic acid, are common metabolites that may originate from the mesh, wound cover, or skin.

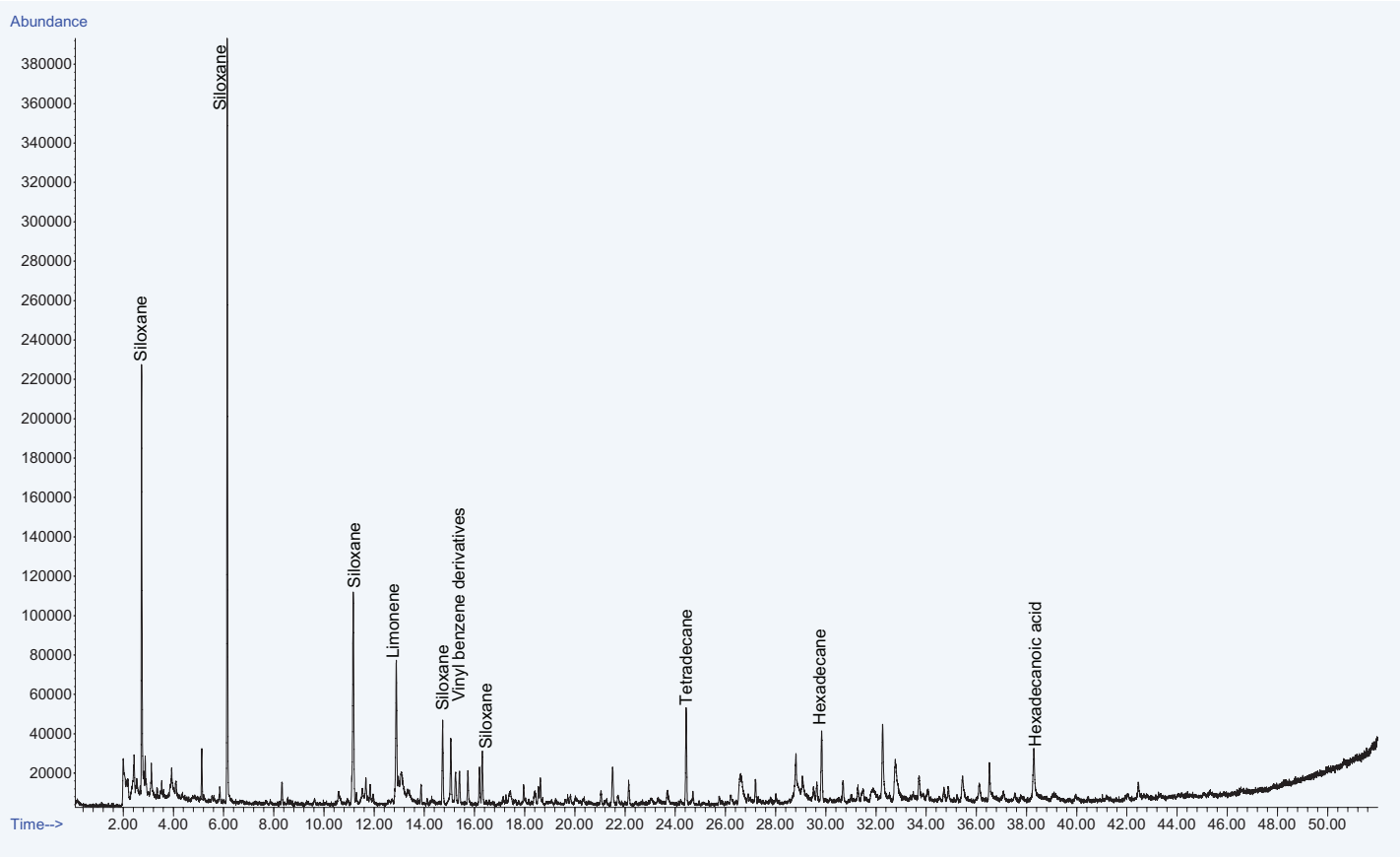

Figure 3: TIC of TF-SPME background sampling.

GERSTEL AppNote 305

The TF-SPME sampling methodology was evaluated with and without the wire mesh in place. Figure 4 shows a stacked view of the TICs for fragrance sampling with (top) and without (bottom) the mesh. An increase in the peak signal is observed in the latter part of the chromatogram when the mesh is absent, or when the TF-SPME remains in direct contact with the skin surface. The compounds present, including hexadecanoic acid, octadecanoic acid, C12-C15 alkyl benzoates, and hexadecyl octanoate, are attributable to the lotion base rather than the fragrance composition. Due to the high concentration and low volatility of these components, subsequent sorbent blanks showed significant carryover. Several instrument blanks and sorbent conditioning cycles were necessary to return the background to a clean state. Lifting the TF-SPME membrane slightly off the skin with the mesh enables more efficient analysis of fragrance components by removing most of the lotion's less-volatile matrix.

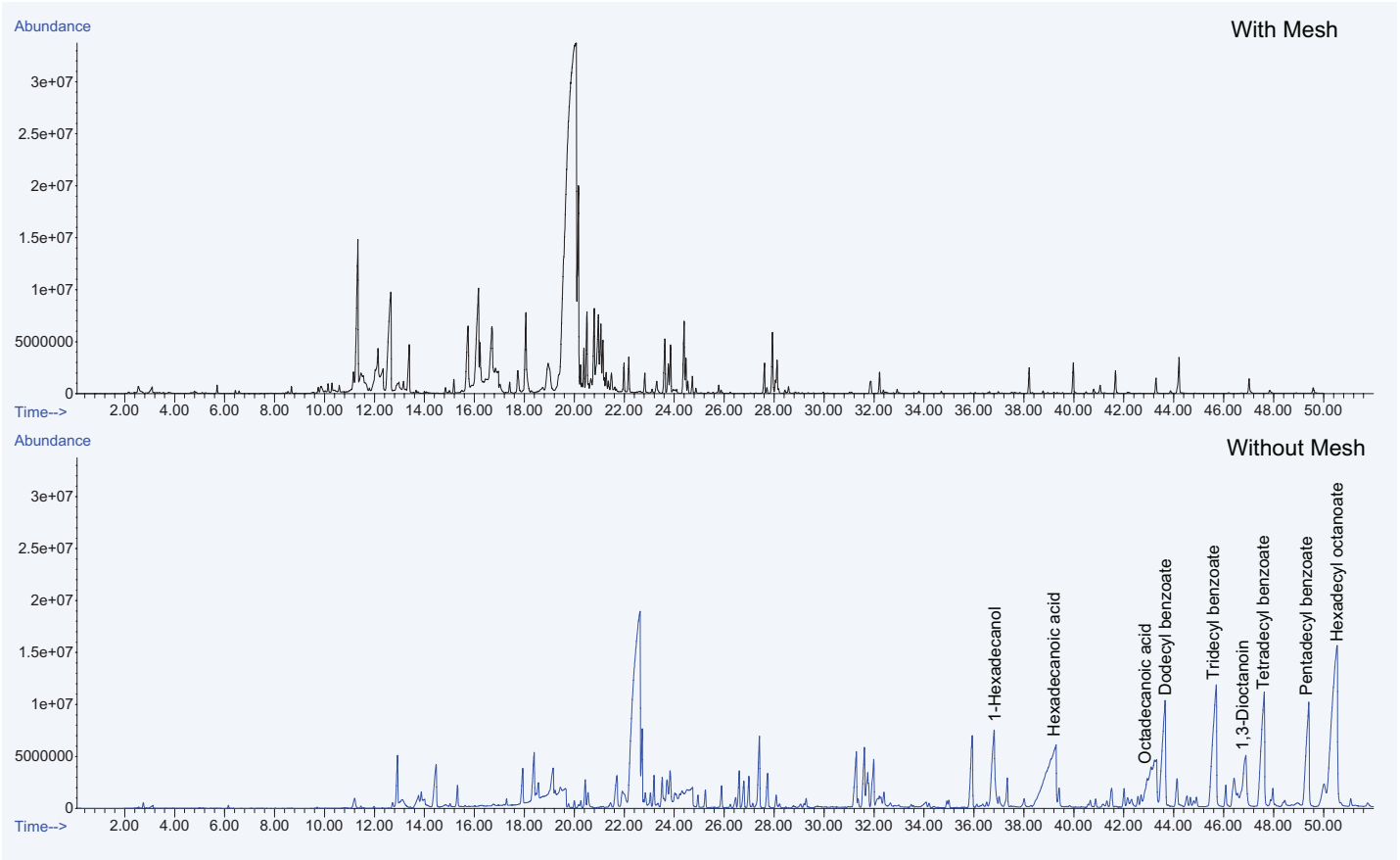

Figure 4: Stacked view of the TICs for fragrance sampling with (top) and without (bottom) the mesh.

GERSTEL AppNote 305

To determine any reactions between the lotion and the skin, TF-SPME sampling was performed on an inert surface. The lotion was spread on the bottom of a 10 mL screw-capped vial, and sampling was performed for 15 minutes at 35 °C, simulating skin surface temperature, with the TF-SPME membrane suspended in the vial. Figure 5 shows the stacked view of TICs for the fragrance sampling on skin (top) and in the vial (bottom). The chromatograms from ~10 mins onwards are nearly identical. However, the first 10 minutes differ significantly. Notably, several alcohols are present in the vial that are not on the skin, including 2-propen-1-ol, 1-butanol, 3-methyl-1-butanol, and 1-hexanol. In addition, while the ethyl esters are present in both, they are at much higher levels in the vial. In contrast, several short-chain fatty acids, such as acetic, propanoic, and butanoic acid, were detected on the skin but were absent in the vial. These carboxylic acids could form through alcohol oxidation or ester hydrolysis on the skin surface. These acids have low odor thresholds, meaning they can be smelled at concentrations between 6 and 0.2 ppb in air [3]. These compounds are often associated with acetic, cheesy, rancid, and vomit-like odors [4]. If too much is produced, consumers may complain of off-odors in the lotion, emphasizing the importance of on-skin testing for cosmetic product formulations.

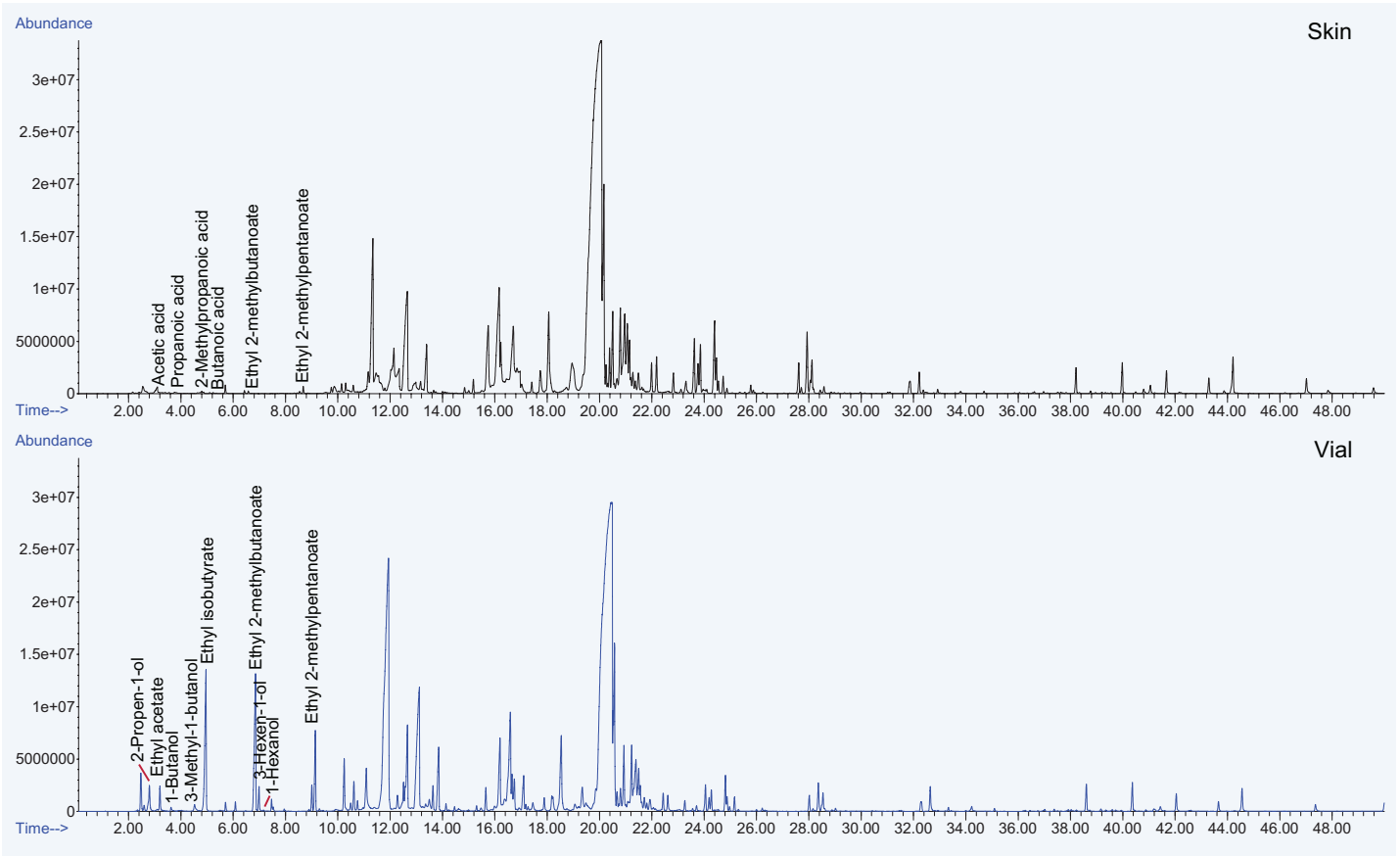

Figure 5: Stacked view of the TICs for fragrance sampling on skin (top) and in the vial (bottom).

GERSTEL AppNote 305

The TF-SPME methodology was compared with a commonly used skin sampling technique, in which volatiles are extracted from the skin using gauze [1,2]. Then the gauze is extracted by traditional SPME for GC-MS analysis. Figure 6 shows the stacked view of TICs of TF-SPME sampling (top) and SPME sampling (bottom). The overall fragrance profile is similar between the two techniques. However, of the 177 analytes detected by TF-SPME, 43 were not detected by SPME, whereas only four were unique to SPME. In addition, many other analytes are extracted in higher amounts by TF-SPME, especially those that elute earlier in the chromatogram, as shown in Figure 6. These analytes are subject to competitive effects on the SPME fiber because of the limited sorption phase available relative to the TF-SPME membrane.

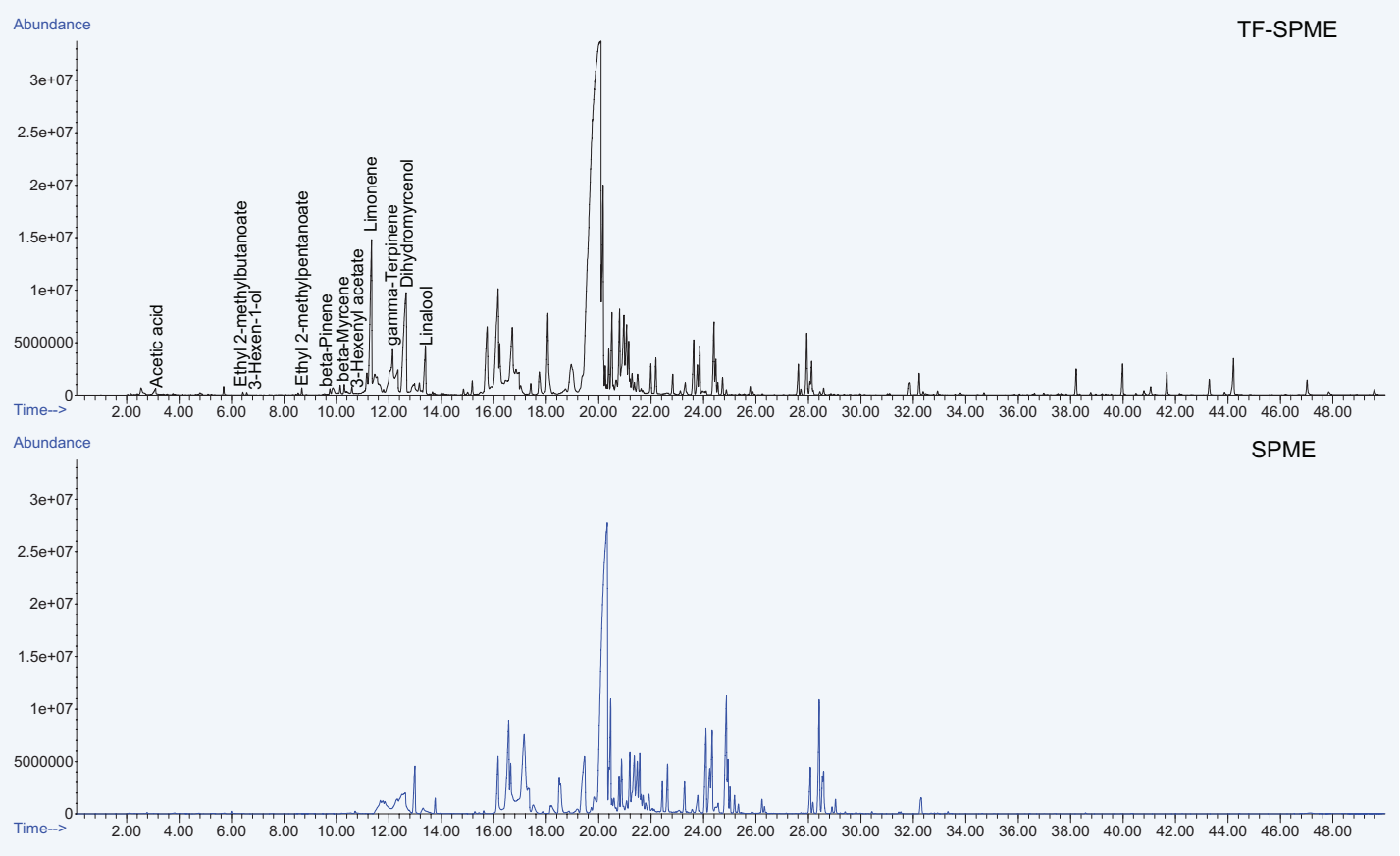

Figure 6: Stacked view of TICs of TF-SPME sampling (top) and SPME sampling (bottom).

GERSTEL AppNote 305

The TF-SPME sampling approach was evaluated for reproducibility. Figure 7 shows a stacked view of TICs of three replicate TF-SPME extractions. In the first replicate, the lotion's base components at the end of the chromatogram are present at a higher signal than in the next two replicates. During sampling, the TF-SPME membrane may have briefly contacted the skin, resulting in greater extraction of these compounds. However, the overall fragrance profile shows good consistency of results. Table 1 shows the percent relative standard deviation (%RSD) of replicate measurements for selected fragrance analytes. Overall reproducibility is excellent, with most analytes' %RSD values below 10%. The values could be improved by outlining a specific area on the forearm to ensure more consistent lotion application and by taking greater care during TF-SPME placement and removal.

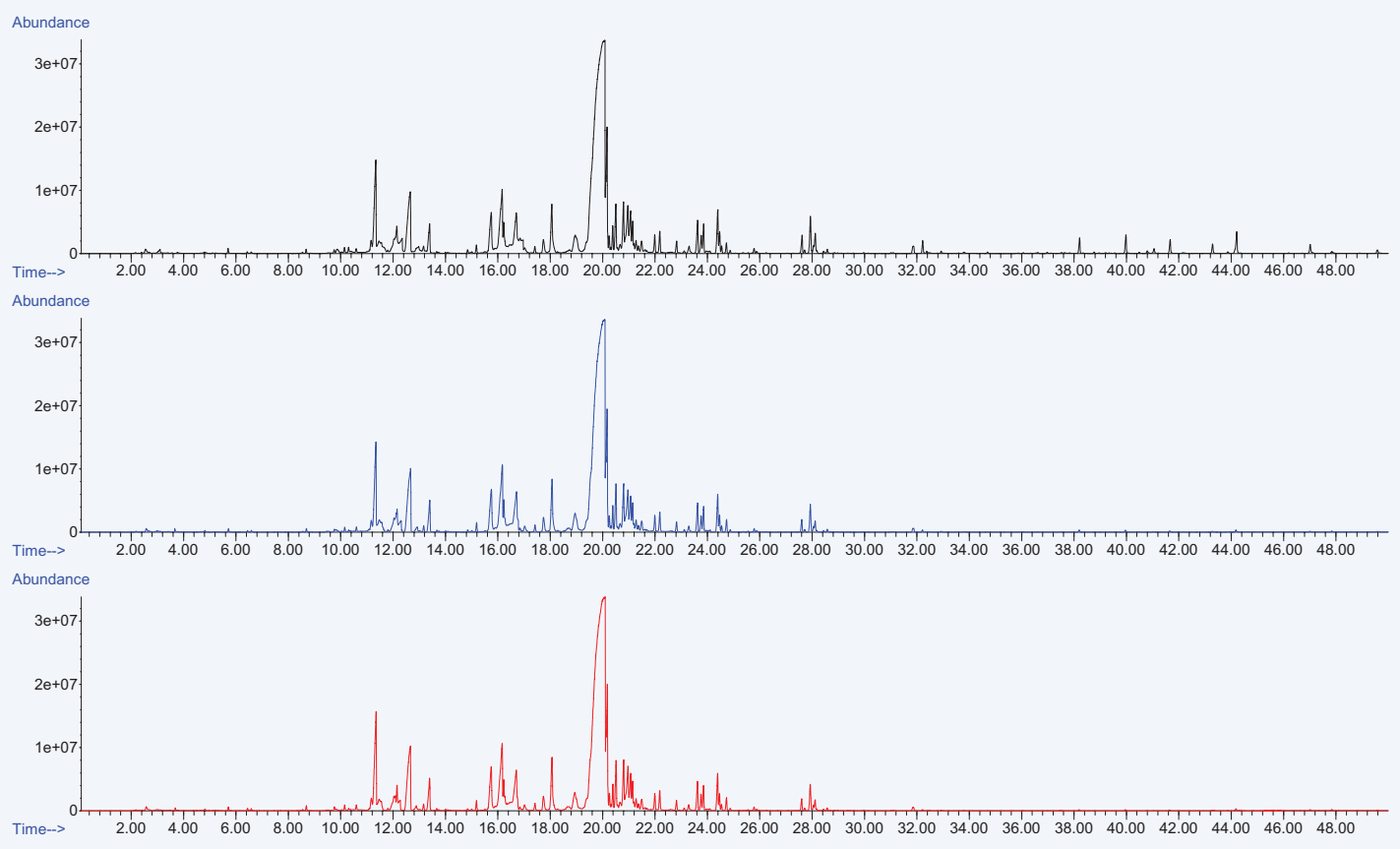

Figure 7: Stacked view of TICs of TF-SPME sampling replicates.

GERSTEL AppNote 305

Table 1: % RSDs for TF-SPME replicates.

Compound	RT (min)	%RSD
Ethyl isobutyrate	4.64	10.3
Butanoic acid	5.22	1.97
3-Hexen-1-ol	6.58	11.5
Citronellene	8.84	7.81
β-Pinene	9.75	7.29
6-Methyl-5-hepten-2-one	10.03	8.55
Limonene	11.34	9.30
β-Ocimene	11.80	4.63
Isoamyl butyrate	12.02	3.22
Dihydromyrcenol	12.65	4.03
Linalool	13.39	4.86
Rose oxide	13.67	7.92
Methyl octanoate	14.00	2.73
Benzyl acetate	15.18	6.79
Octanoic acid	16.95	16.31
Citronellol	17.03	2.69
α,α-Dimethylbenzenepropanol	18.95	8.09
Geranyl acetate	21.15	5.94
Ananolide	22.18	7.76
γ-Decalactone	23.31	13.1
β-Ionone	23.77	9.66
α-Methylionone	24.55	6.29
2-Methylbutyl salicylate	24.87	14.7
Heliotropyl acetone	25.55	6.57
Methyl dihydrojasmonate	28.18	13.5
Benzyl octanoate	29.56	10.9

A time-series sampling approach was used to evaluate how the fragrance profile changes over time. Figure 8 shows the stacked view of TICs from time-series sampling. The 15-minute sampling was performed immediately after lotion application (hour 0) and 1, 3, 5, and 9 hours after application. A significant reduction in the overall signal is seen after the first hour. Table 2 lists some fragrance analytes that are no longer detectable after the first hour. These analytes exhibit fruity, citrus, tropical, and green aromas [4], which constitute the top notes of the fragrance profile. The top notes are typically the most volatile analytes that give a fragrance its first impression. Table 3 shows example analytes that are no longer detected in the 3-5 hour window. Their aromas are floral, lavender, rose, green, and woody [4], which describe the middle or heart notes of the fragrance profile. The middle notes are the core of the profile and define the fragrance's main characteristics. Lastly, Table 4 lists fragrance analytes that remain present 9 hours after application. These are woody, musky, floral, and lily aromas [4], which are the base notes of the fragrance. The base notes give depth to a fragrance and are meant to last for hours or even days. By utilizing an easy to implement time-series approach, the evolution of the fragrance profile is readily seen.

GERSTEL AppNote 305

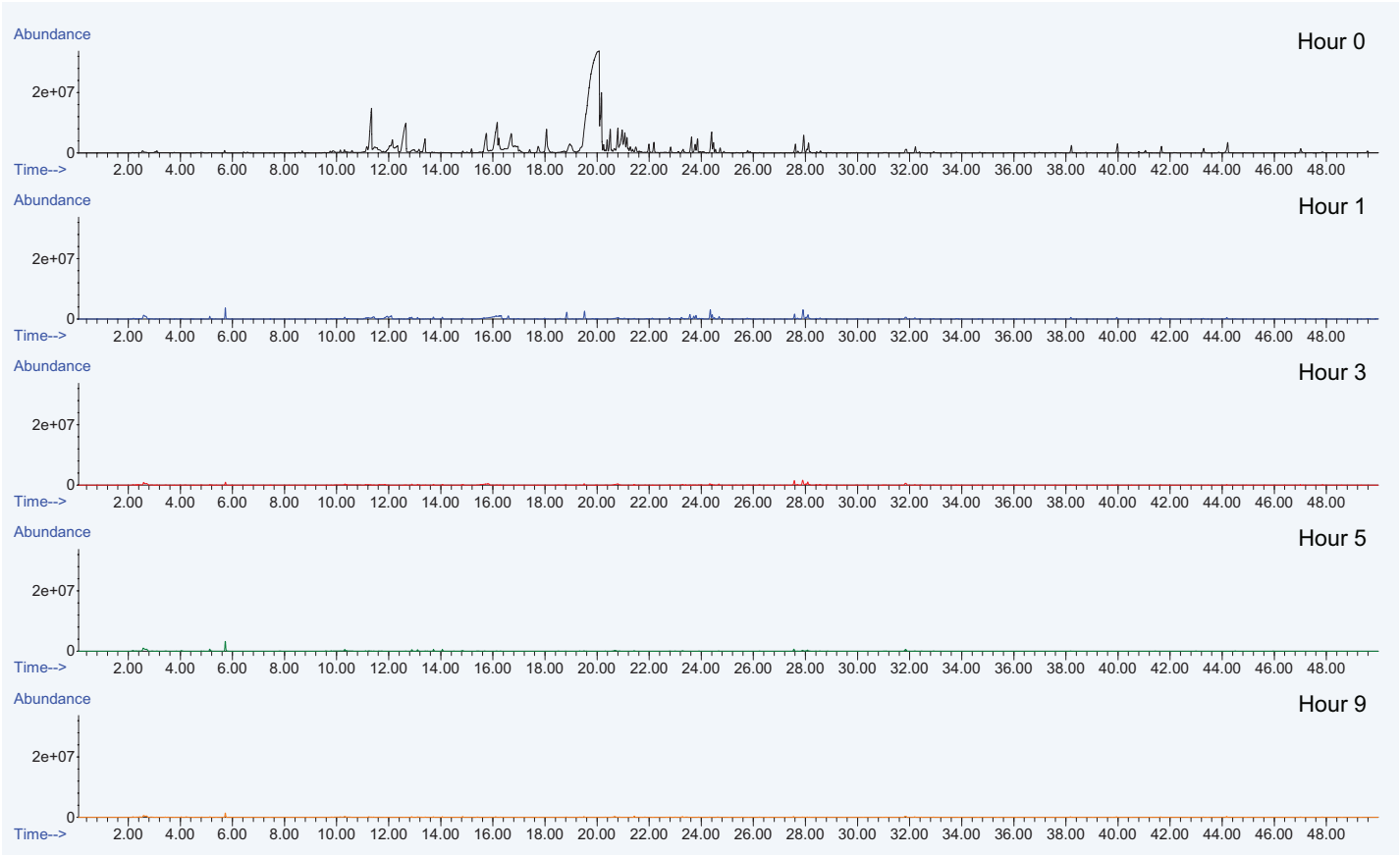

Figure 8: Stacked view of TICs of TF-SPME time series sampling.

Table 2: % Example top note analytes.

Compound	Aroma [3]
Ethyl isobutanoate	ethereal, fruity, rummy
Ethyl 2-methylbutanoate	fruity, berry, tropical
3-Hexen-1-ol	green, leafy
Ethyl 2-methylpentanoate	green, melon, waxy
Citronellene	rose, herbal, citrus
6-Methyl-5-hepten-2-one	citrus, green, lemongrass
3Z-Hexenyl acetate	green, fruity, banana
Limonene	citrus, herbal, terpenic
Isoamyl butyrate	green, tropical, banana
Rose oxide	rose, green, fresh
Methyl octanoate	waxy, green, orange
Benzyl acetate	fruity, jasmine, fresh

Table 3: % Example middle note analytes.

Compound	Aroma [3]
β-Ocimene	tropical, green, woody
Linalool	floral, lemon, lavender
2-Phenoxyethanol	rose, balsamic
Citronellol	rose, citrus, waxy
Linalyl acetate	green, citrus, lavender
4-Methoxybenzaldehyde	powdery, hawthorn, balsamic
Geranyl acetate	rose, lavender, green
3Z-Hexenyl 3Z-hexanoate	green, fruity, pear
Ananolide	pineapple, waxy, green
2-Phenoxyethyl isobutyrate	fruity, rose, honey
α-Methylionone	woody, orris, violet
2-Methylbutyl salicylate	berry, woody, orchid

GERSTEL AppNote 305

Table 4: % Example base note analytes.

Compound	Aroma [3]
Hydroxycitronellal	lily, tropical, green
Cyclamen aldehyde	floral, rhubarb, green
α-Isomethyl ionone	woody, violet, raspberry
β-Ionone	woody, orris, berry
Lilial	lily, green, powdery
Heliotropyl acetone	raspberry, floral, powdery
3Z-Hexenyl salicylate	herbaceous, lily
Hexyl salicylate	fresh, herbal, orchid
Methyl dihydrojasmonate	jasmine, citrus, woody
Benzyl octanoate	herbal, peach, floral
Ambrox	woody, musky, amber
Galaxolide	musky, floral

Conclusions

This study demonstrates that TF-SPME provides a robust, sensitive, and reproducible approach for characterizing fragrance compositions directly on skin while minimizing matrix interference from cosmetic bases. Background experiments confirmed that the sampling materials contribute minimal signal, and the use of a wire mesh effectively limits the extraction of low-volatility lotion components, reducing carryover and improving analytical selectivity for fragrance volatiles. Comparative experiments on skin versus an inert surface highlight the importance of on-skin testing, revealing skin-mediated chemical transformations that generate low-odor-threshold fatty acids that can cause off-odors and consumer complaints. Relative to conventional gauze-based SPME sampling, TF-SPME captured a broader range of analytes at higher abundance, particularly for early-eluting, more volatile compounds, while maintaining excellent reproducibility across replicates. Finally, time-series sampling clearly resolved the temporal evolution of top, middle, and base notes, illustrating how fragrance profiles change over hours following application. Collectively, these results establish TF-SPME as a powerful tool for realistic, time-resolved evaluation of cosmetic fragrances on skin, supporting formulation optimization, stability assessment, and improved prediction of consumer sensory experience. Future studies should include olfactory detection (GC-O) to link aroma descriptors to chemical identities and determine at which time point an analyte falls below its odor detection threshold. In addition, GC-O can be used to identify fragrance compounds that may be present below the instrument's detection limits.

References

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