Skin Odor Value Technology for Fragrance Performance Optimization

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Since early times we have used perfume as the most intimate apparel to enhance our appeal. It clothes our skin with an invisible aura of fragrance providing it with a signature of personality and mood. Ideal fragrances are those which are a perfectly tailored match to our skin. This paper describes the methodological aspects of Givaudan-Roure's proprietary skin odor value technology and shows how it is used by perfumers in designing "haut couture" fragrances.

The Skin

Successful fragrance designers understand that skin is not just the outer layer of our body, but also a highly complex substrate. It is made up of two layers—the dermis and the epidermis.[1] The dermal layer is the outer layer which gives skin its elasticity and appearance, and protects us against physical damage. The epidermal layer is composed of four sub-layers—the stratum corneum, the granular sub-layer, the spinous sub-layer and the basal sub-layer—and it protects us against harmful substances.

The skin substrate is further complicated by having glands embedded in it. Skin has around three million sweat glands divided into two types: the eccrine glands which cool the body by secreting an electrolytic fluid, and the apocrine glands which secrete a viscid fluid. The skin also has sebaceous glands which produce a thick oily liquid. Skin can, therefore, vary in terms of its porosity, pH and lipid level. In addition, it can differ in smoothness and temperature. It is not surprising, therefore, that a perfume which smells wonderful on a friend sometimes does not smell good on you. This difference is based upon complex fragrance-skin interactions.

During a new perfume's creative development phase, our perfumers design the structure of the fragrance to perform hedonically well for the greatest number of people unless, of course, the fragrance is designed for a specific target skin type. The perfumer can measure success in tailoring the fragrance for different skin types by using a sensory panel of different skin types to compare or rate the performance of one perfume to another, commonly referred to as a benchmark, for strength and hedonics. However, while the nose is a wonderful qualitative instrument, it cannot give the quantitative detail that the perfumer requires to understand why the fragrance strength

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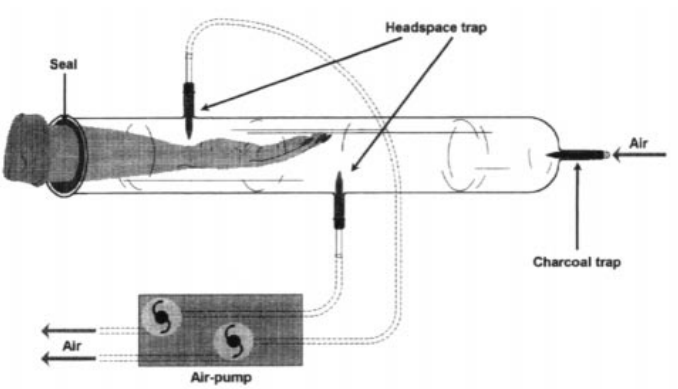

Figure 1.

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or hedonics are not as envisaged.

The principle method used is based upon the dynamic headspace technique developed to identify and quantify the volatile components responsible for the aroma of flowers, fruits and other fragrant substances.[3] Some years ago we extended this technique to measure the performance of perfumes on human skin.[4] This technique quantifies the partition of the individual fragrance components from the skin into the air. Then via our proprietary odor values[2] we can translate this partition data into an olfactive perception profile. Skin odor value technology, which is the proprietary integration of dynamic headspace and Givaudan-Roure's odor values, allows us to map the performance of a fragrance on skin to guide the perfumer in creating fragrances that perform optimally on all skin types.

Equipment

The headspace device, used so effectively to capture natural aromas, has been modified to isolate the test area of skin from the environment and allow the fragrance components that partition from the skin to be measured at various distances from it. Thus, we can establish both the substantivity and distance profile of the fragrance. The device is shown in Figure 1.

The glass sleeve is constructed out of Pyrex* glass and comfortably fits over the forearm. The open end is sealed to the upper arm with Parafilm. The sleeve contains multiple ports from which dynamic headspace samples can be taken. The ports are conveniently located over the test area of the forearm and at various distances from the test area.

A typical setup is shown in the photo on page 45. Environmental contamination is eliminated by filtering the incoming air through an activated charcoal filter placed in one of the glass sleeve ports.

The headspace samples are collected in tubes (traps) packed with an absorbent material such as Tenax, Porapak Q or activated charcoal. Normally one trap is inserted into a port directly above the treated area and adjusted to about 1 cm above the skin surface. Similarly, we can set traps along the sleeve to determine distance profiles of the fragrance. A calibrated pump is used to accurately extract a known volume of headspace. The trapped material can be removed either with a solvent or by being thermally desorbed directly into a gas chromatograph for analysis. Thermal desorption was conducted on a Perkin-Elmer ATD-400, Automatic Thermal Desorbtion instrument. The entire system is controlled by a computer using PE Nelson Turbochrom 4 software.

Typical dynamic headspace analysis involves depositing a sample onto a marked area of a subject's forearm. The sample is deposited as a solution in ethyl alcohol, using a microliter syringe. The solvent is allowed to evaporate for five minutes. The treated arm is sealed in the glass sleeve using Parafilm and an initial headspace sample taken. The subject's forearm is then removed from the headspace

* Trade name of Corning, Inc., Corning, NY

Table I. Odorants used in methodology development

Ingredient	Mol. weight	Vapor pressure (microns)
phenylethyl alcohol	122	7.5
florhydral	190	6.7
lilial	204	1.9
Fixolide	258	0.2
DEP	222	nd

nd = not determined

sleeve. The subject returns after a set time and a second headspace sample is taken.

The technique of dynamic headspace collection coupled with computer controlled thermal desorption, gas chromatography and data collection makes this a simple procedure. The use of computers to control all functions greatly reduces the error associated with manual systems.

Method

Methodology development was conducted using a test mixture of equal parts of four common odorants and diethyl pthalate (DEP) as the solvent representing different volatilities (Table 1). This was applied to the skin as a 10% ethanolic solution. The amount of each material deposited was 20 µg.

Substrate preparation: The sensitivity of dynamic headspace analysis requires special attention to prevent artifacts from the subject's personal hygiene interfering with the analysis. Initially subjects were washed with an unfragranced personal bar of soap. The headspace results obtained from washed subjects were erratic. This behavior was found to be due to the residues of the base components of the soap that would also appear in the headspace. Denatured ethyl alcohol was also found to be unsatisfactory, because the denaturant also contaminated the headspace. Artifact intervention was minimized by wiping the subject's arms 30 minutes prior to application with a towel dampened with isopropanol.

Optimization of collection time: Dynamic headspace samples do not require equilibration and can be collected over a predetermined time. The length of time and volume collected are dependent on the sensitivity of the instrumentation used for the analysis. Trials were carried out to optimize the sensitivity and reproducibility of the technique and the comfort of the test subject. The ideal length of time for sample collection was found to be between 5 and 10 minutes. The headspace volumes collected were

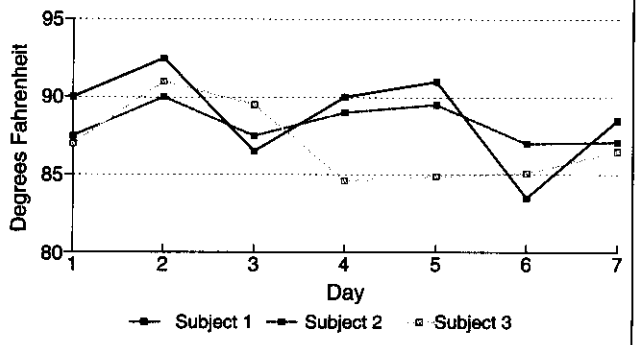

Figure 2. Variation of skin temperature on left forearm of three female subjects.

found to contain sufficient material for analysis by gas chromatography and mass spectroscopy.

Effect of temperature: A major variation in the headspace concentration was found to be due to the skin and ambient temperatures. The temperature of the skin was found to be one of the controlling factors responsible for the amount of material collected in the headspace.

The variation in skin temperature of three female subjects over a seven day period is shown in Figure 2. In this case the female subjects were left-handed and the temperature in the dominant hand tended to be higher than the other. Similar results were obtained with right-handed subjects. There also was a significant difference in skin temperatures between panelists. This temperature variation does influence the concentration of volatiles in the headspace.

To improve the reproducibilty of our technique we maintain the measurement room at a constant temperature and humidity. We also equilibrate the test subject for 20 minutes prior to taking any measurements. To obviate right-left arm temperature differences we do repeats reversing the fragrance applied.

Effect of skin type: Recent papers by Vuilleumier et al.[5,6] show the wide variation in skin characteristics but only measure fragrance evaporation rates on an average skin type. Hence, it is not known how large an effect different skin types can have on the partitioning of the fragrance components into the headspace. Experiments were, therefore, carried out to establish if skin characterization of panelists is a necessary part of skin odor value technology. To determine this, the influence of skin lipid level on fragrance partitioning into the headspace was determined. An oily skin panelist and a dry skin panelist were used. They had average skin lipid levels on the volar forearm of 6.4 and 1.3 $\mu g/cm,^2$ respectively. We found that the headspace concentrations for phenylethyl alcohol and Fixolide on oily and dry skins varied significantly.

Phenylethyl alcohol and Fixolide partition differently into the vapor phase from different skin types. The concentration of odorants in the headspace was considerably

Table II. Skin parameters of panelists

Panelist	Sebum µg/cm²	TEWL g/m²h	pH
Subject 1	2.6	3.1	4.8
Subject 2	2.4	3.9	5.0
Subject 3	2.1	4.1	4.8

Table III. Reproducibility of skin headspace measurements

Headspace results from three female subjects run in triplicate

	Average ng/l			
	Subject 1	Subject 2	Subject 3	RSD
phenylethyl alcohol	1,893	2,049	2,060	5
florhydral	411	521	492	12
lilial	163	220	224	17
DEP	36	46	62	27
Fixolide	16	6	9	50

higher on dry skin compared to oily skin. The exact mechanism of this effect is not known, but most probably the skin lipids are acting as a fixative. Thus, skin odor value technology requires the measurement of key skin parameters to help the perfumer and fragrance technologist interpret the data.

Reproducibility: Reproducibility of the methodology was determined by measuring in triplicate three female panelists, with average skin.[7] The skin parameters of sebum,[8] transepidermal water loss (TEWL)[9] and pH measured on the skin of the panelists are shown in Table II.

The headspace results of the test odorant are shown in Table III.

The reproducibility of skin headspace analysis is within acceptable limits, except for Fixolide. The high standard deviation of this ingredient is caused by its low volatility such that its headspace concentration is at the detection limits of the GC/MS system.

Application

In order to enhance the performance of an alcohol fragrance, we were seeking to improve the strength of the fragrance on the skin with time. The perfumer, using skin substantivity data bases, created a hedonically good fragrance with anticipated longevity properties. Three females selected as having "average" skin were used and the amount of fragrance partitioned into the headspace was determined by the above methodology both initially and after four hours. This was converted into a perception profile by computing the odor values from:

$$\text{Odor Value} = \frac{\text{Quantity of Odorant in Headspace (ng/l)}}{\text{Mean Odor Threshold (ng/l)}}$$

Givaudan-Roure has designed and developed dynamic air dilution olfactometers[3] to measure perception thresholds, and over the last 15 years has developed an extensive

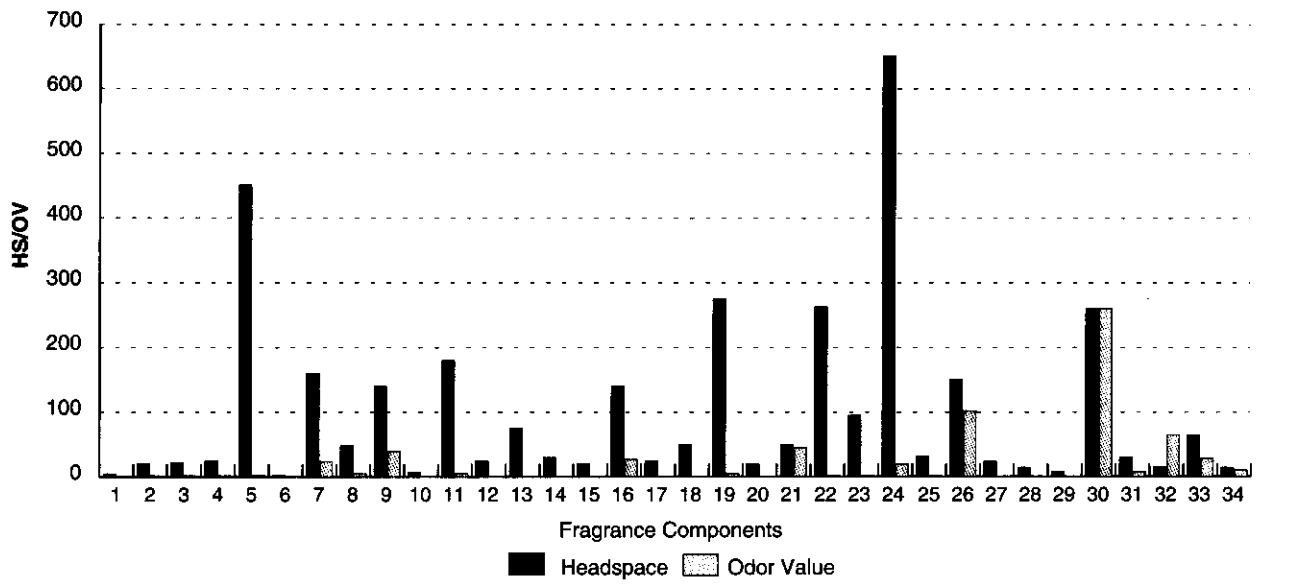

Figure 3. Skin substantivity trial 1.

database of mean threshold values of commonly used fragrance raw materials.

Figure 3 shows the headspace concentrations and odor values of the components of the experimental fragrance after four hours. The sum of the odor values of the first trial is compared to the benchmark in Figure 4. It can be seen that no improvement in longevity over the benchmark had been obtained. From Figure 3 it is evident that of the materials in the headspace only a relative few contribute meaningfully to the total odor value. The perfumer, together with the fragrance technologist, examined the data and identified those materials which easily could be adjusted to give an effective contribution to the total odor value and also enable the perfumer to maintain good hedonics of the fragrance.

The total odor value of the second trial fragrance also is compared to the benchmark in Figure 4. We can see that by rebalancing the fragrance so that more components were above their threshold in the headspace, the trial two fragrance outperforms the benchmark.

Further optimization of the hedonic characteristics can be done and the technical performance of the fragrance monitored to ensure that the performance objectives are being achieved. A similar approach is used to optimize fragrance performance on different skin types. Consider the earlier dry and oily skin example. The perfumer and fragrance technologist can match the odor values of the fragrance components in the headspace of both the dry skin and oily skin. The fragrance note is tailored to different skin types providing "haut couture" fragrances.

Conclusion

We have identified the major factors which need to be controlled in order to have a meaningful and reproducible methodology to study the interaction of fragrance and skin. The resultant skin odor value technology is proving to be a powerful tool, enabling perfumers to optimize the performance of fragrances on various skin types.

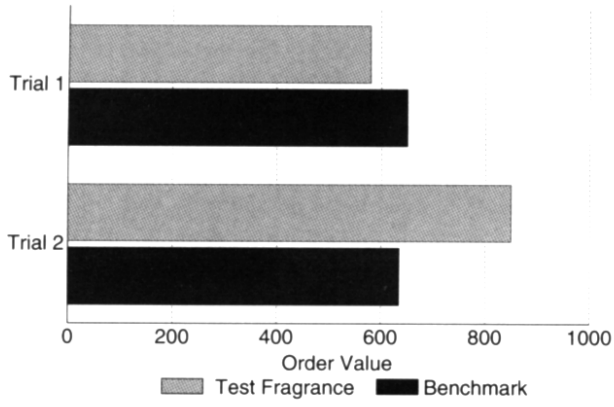

Figure 4. Total odor value with 4 hour headspace.

Acknowledgment: The authors would like to thank Andre Charles, Kathleen Sznerch and Caryl Yeager for their assistance with this project.

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