Evaluation of Human Body Odors:

Methods and Interpretations

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Synopsis—Annoying odors from various parts of the HUMAN BODY constitute cosmetic defects. COSMETIC TREATMENTS to remedy such defects may be based on the suppression of MALODORANT GENERATION and EMISSION, on MODIFICATION OF ODOR CHARACTER, or on both of these approaches. Measurement of the efficacy of the treatments requires a source-adapted sample collection technique and the use of appropriate sensory or analytical methods. The following are described and illustrated in this paper: measurements of odor intensity utilizing 1-butanol reference scale; measurements of the odor threshold using a dynamic dilution forced-choice triangle olfactometer; and measurements of odor character change by a multidimensional scaling of odors using a 136-descriptor list and the chi-squared statistic. The analytical techniques include use of odorograms (odor-annotated gas chromatograms) and are primarily suited for the measurement of efficacy in the suppression of malodorant emission and the evaluation of the persistence of fragrances *in vivo*.

INTRODUCTION

Excessive or annoying odors, which are caused by the emission of odorous substances from various parts of the human body, may be considered cosmetic defects. Various treatments are used to correct such defects. Antiperspirants; cleansing agents, which may be reinforced by substances that suppress proliferation of microorganisms; and fragrances that modify the character of odor are some examples of materials utilized in odor-correcting treatments.

The development of formulations and application schedules for human-body odor control requires methods which may be used to measure the efficacy of the treatments. The objective of this paper is to enumerate both some presently used methods, together with their principles, and some ex-

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amples of application to human body odor measurements. The examples serve to illustrate only—not to prove efficacy of some specific formulations.

GENERAL REMARKS

The efficacy of odor control can be measured by sensory or analytical techniques, or by a combination of both.

Sensory techniques measure the overall change in odor sensation caused by the change in emission, e.g., a reduction in the intensity of odor, or a shift in the character of odor. Analytical techniques permit one to measure the reduction in the emission of malodorants. When fragrances are used to supplement the treatment, the analytical approach cannot yet indicate the overall sensory impact; however, it is useful in following the process of the dissipation of fragrances after they have been applied.

In sensory techniques, substances reach a panelist's nose by migration through the air in the form of vapors. Vapors may be channeled directly from the source, e.g., the axillar portion of a shirt, or else they may be temporarily stored in plastic bags—a method much in use in odorous air pollution studies.

Analytical techniques must be similarly applied to emissions in vapor form, to approach composition smelled by nose. Ratios of concentrations of various odorants above perspiration are different from the ratios in the condensed perspiration: less-polar odorants exhibit higher volatility from an aqueous phase than do more-polar odorants of the same vapor pressure in a pure state. Gas-chromatographic (GC) analysis, with a vapor preconcentration step to bridge the gap between the sensitivity of nose and the most suitable detector (hydrogen-flame ionization detector), is the most used analytical technique in investigating odors.

In the sensory techniques, panelists serve as instruments. Their expectations and biases may seriously distort their judgments. It is, therefore, preferable to remove the odorous sample from its context; to use panelists who do not know the nature of the sample, and wherever possible to devise sample presentation techniques that minimize anticipation effects.

The principles of panel selection and sensory evaluation have been described elsewhere (1). A few considerations deserve stressing. Familiarity with an odor that is tested is a double-edged sword. An expert becomes quite proficient in discriminating fine nuances of odor, which he has repeatedly studied. In evaluating the efficacy of an odor control treatment, however, such familiarity becomes a liability: an expert tends to anticipate certain effects. The same applies to panelists who are quite familiar with the particular fragrance and its use in cosmetics. An individual using a certain scented product would recognize its fragrance and would be biased in rating its

effect in odor control. Well-known panel effects such as a desire to please the panel leader or to judge toward some expected result, etc., should be neutralized.

SAMPLING FROM SOURCES

When sampling from odorous emission sources, it is desirable to sample selectively, without interference from other sources. When the source is a specific part of human body, source-adapted confining devices are used.

Figure 1 depicts devices which have been used for some sources. Underarm *in vivo* may be confined by a polyethylene form (2,3). A mouthpiece is used to collect vapor samples from the mouth; high-purity air is supplied through one tube, and the vapor is removed at a controlled rate through another, while a U-tube water level manometer is used to control breathing to maintain pressure in the mouth cavity at ambient pressure. When the subject manipulates his breathing in such way, the content of lung air in the sample stabilizes at about 50 per cent. Samples of skin vapors are taken using a Teflon* cup (4). Vaginal vapor samples are taken utilizing perforated Teflon inserts (5, 6). Sampling of vapors from the entire human subject is accomplished by placing him into a glass tube on a Teflon-lined stretcher suspended within the tube (7).

With all such devices, air must be introduced at a rate commensurate with the sample removal rate and slow enough to prevent depletion of odorant content in the source. On the other hand, sampling still should be sufficiently fast so that an adequate sample size can be collected without gross inconvenience to the subject. Typical flow rates are on the order of 50 to 100 ml/min for localized sources, and 50 l./min for the subject in the tube; the duration of sampling from the mouth can hardly exceed 10 to 20 min, while longer times are possible with other sources.

The function of the confining devices is not only to temporarily isolate the source, but also to permit a more quantitative vapor sampling. Such a temporary isolation does not eliminate the presence of vapors of ambient origin in the source emission. Thus, in taking a sampling from the entire subject, components characteristic of engine exhausts and mothproofing compounds are commonly present. Care therefore must be exercised in the evaluation of data, especially in the case of analytical gas-chromatograms.

One particular problem in taking samples from human body sources is the presence of excess water vapor, which is close to the saturation point at 37°C. To avoid water condensation in the tube which leads from the source to the sample collector (such as an adsorbent or a bag), tubing should be

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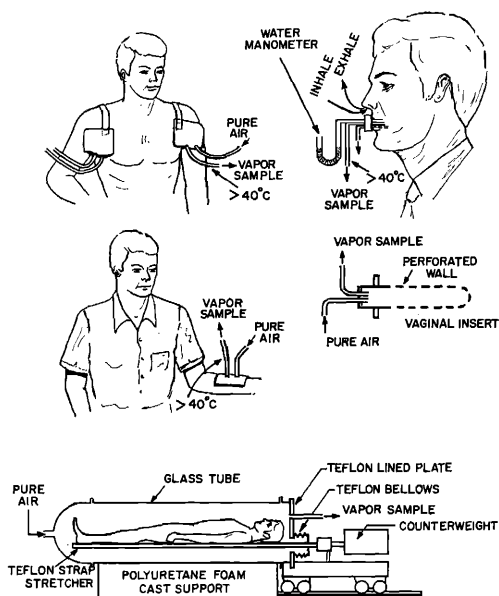*E. I. duPont de Nemours & Co., Wilmington, Del.

Figure 1. Arrangements for vapor channeling from humans to collecting devices

kept at 40°C or higher. Teflon spaghetti tubing, wrapped with a Teflon-spaghetti insulated low-voltage electrically heated resistance wire, solves this difficulty.

Several devices for accumulation and storage of samples are represented in Fig. 2. Collection of vapors from organic substances, which most odorants are, is conveniently accomplished by adsorption at surfaces of nonpolar large-surface-area organic polymers (8) (Fig. 2A). A Chromosorb 102®* is a suitable choice. Such polymers adsorb water vapor poorly, and if they are maintained above the dew point temperature of the emission during collection (40°C is a safe level) they permit collection of odorants without collecting much water. Odorants are later desorbed by heating in an inert gas and transferred to analysis in a gas chromatograph (8). Odorants such as ammonia, hydrogen sulfide, and some highly volatile organic compounds normally existing as gases are not handled too well by this collection technique and require separate arrangements. Also, this collection technique is suitable only for analytical evaluations, since an equitable reconstitution of the sample to vapors for sensory evaluation is a complex undertaking.

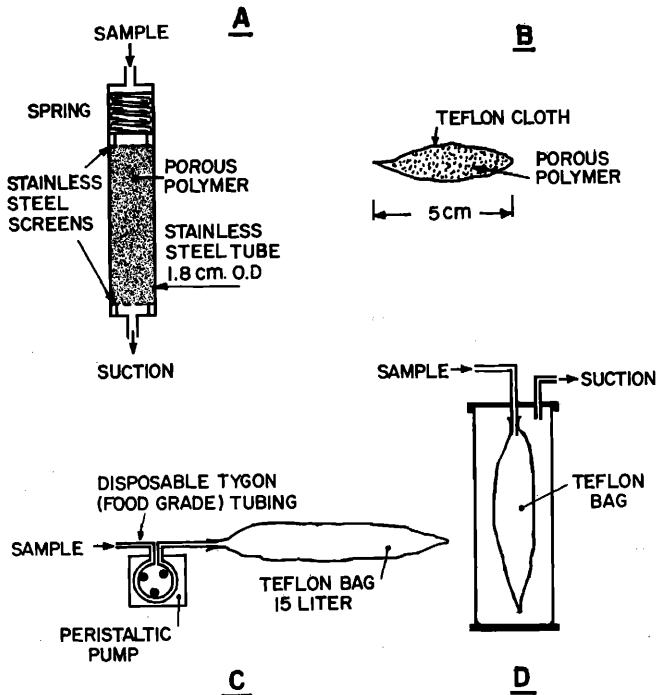*Johns-Manville, Celite Division, New York, N.Y.

Figure 2. Vapor sample collecting devices

A simplified form of vapor collector is depicted by Fig. 2B. Polymers such as those used in Fig. 2A are placed, after thorough preparation by thermal purification in an inert gas stream, in Teflon cloth bags. The resulting pads are attached to the body and effectively collect odorous vapors. After exposure, the polymer powder is removed from the bag, and the absorbed substances are desorbed and analyzed as is the case with the device shown in Fig. 2A. Again, a reconstitution of the sample for direct sensory evaluation is too complex to be practical.

Sample collection for later sensory evaluation can be accomplished by the methods presently in use in atmospheric odor measurement (Fig. 2C & D). The sample is collected into a Teflon bag either by means of a peristaltic pump (Fig. 2C), or by pulling the sample into the bag, accomplished by pumping air out of the space between the bag and a rigid cylinder surrounding the bag (Fig. 2D). In both techniques, the bag (and the peristaltic pump tubing in C) must be preconditioned to the sample before the actual sample is taken to satisfy the initial adsorption losses.

The bag method can also be used for sensory evaluation of the odors of tampons, napkins, and cotton pads worn under axillae, etc. Such sample collectors are placed into the bag, the bag is inflated with an odorless air, and left to equilibrate for 10 to 30 min. Use of this technique with samples obtained by polymer pads (Fig. 2B) has not yet been explored.

For sensory evaluation of bag samples, bags are placed in a cylinder such as the one in Fig. 2D, and the sample is pushed out by pumping air into the cylinder at a controlled rate.

SENSORY EVALUTIONS

Odor measurement is a measurement of sensation and is conducted by obtaining the responses of panelists. Odors exhibit several sensory dimensions (9-11) as follows: 1. odor intensity, of which odor threshold is a subsidiary measure, indicating the dilution of sample needed to make the odor sensation so weak that either its detectability or its recognizability is at statistical threshold value; 2. odor character or quality; and 3. hedonic value, that is the pleasantness-unpleasantness characteristic.

In the cosmetic correction of undesirable odors, detection threshold measurements have limited utility. If a fragrance is present, a reduction of malodorant emission may not be noticeable, since the threshold will relate to the odor of fragrance. Recognition threshold—that at which the malodorant character becomes recognizable as the degree of sample dilution is decreased, is a more suitable characteristic, but it is better incorporated as a part of the odor character evaluation. The odor detection threshold is, however, a useful characteristic when dealing either with the malodor or with the fragrance alone.

Odor Intensity and Threshold

Although the Weber-Fechner law is frequently utilized to express odor intensity as a function of the odorant concentration (9), the recent trend is to use another mathematical function, known as the psychophysical power law* (12-14)

$$I = kC^n$$

or

$$\log I = \log k + n \log C$$

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*It is interesting to note that at the New York Academy of Sciences 1973 conference on odors (15) not a single paper dealt with Weber's law, but many utilized the power law.

In the above, I is the psychophysical sensory magnitude of the odor sensation; C is the concentration of the odorant in air, which reaches the nose of the panelist; and K and n are coefficients. For odors, n is 0.2 to 0.8, depending on the odorant.

The consequence of this relation is that, e.g., for n = 0.5, the odorant concentration must be reduced by a factor of 4 to make the odor weaker by a factor of 2. For most odorants, a plot of log I versus log C is indeed a straight line.

Until recently, odor intensities have been recorded using some form of category scale, e.g., from 0 (no odor) to 5 (extremely strong odor) (16). Such a scale is already in proportional relation to log I and log C. Odor intensity, which is expressed in some numbers proportional to the intensity of sensation, increases by a factor of 3 to 4 per category step for the 0 to 5 scale.

The category scale creates difficulties in standardizing the meaning of the scale values. Therefore, more recently (17) an effort has been underway at the American Society of Testing Materials (ASTME) to adapt an odor referencing method in which odors are compared to odors on a scale consisting of a series of concentrations of 1-butanol. The odor of the sample is then documented to have an intensity which matches some certain concentrations of 1-butanol. Panelists readily do this, disregarding the differences in the odor character of the sample and 1-butanol. Figure 3 depicts one physical form of such scale; there are 8 scale stimuli, each next higher in 1-butanol concentration than the preceding by a factor of 2 (binary scale).

Still more recently (18) a proposal has been made to standardize the 1-butanol-referenced scale even further. Odor intensity of 250 ppm v/v in air is defined as I = 10; this odor is well noticeable in its intensity, but not too strong. Since for 1-butanol n = 0.66 (18), the following relation results

$$I = 0.261 \, (ppm \, 1\text{-butanol})^{0.66}$$

The resulting numbers, for different samples, are in an approximate ratio of the sensory odor intensities of these samples.

As an example (which will be used later) isovaleric acid (component of perspiration odors) at a concentration of 2.8 x 10^{-7} g/l. to air, was evaluated versus 1-butanol scale by 9 panelists, and its odor found to be as intense as that of 89 ppm v/v of 1-butanol in air. This corresponds, and it can be documented, as the sensory intensity of 5.

The above scale has a fixed middle point and is open on both ends. Odors of I below unity approach the odor threshold intensity.

The effect of different values of exponent n for different odorants results in a different rate of odor intensity increase with odorant concentration. Therefore, measuring odor intensities in terms of multiples of odor threshold does not give correct comparisons of the odor intensities of the sample before dilution. This is best clarified by considering the odor intensity of perspiration in the axillar area of a shirt.
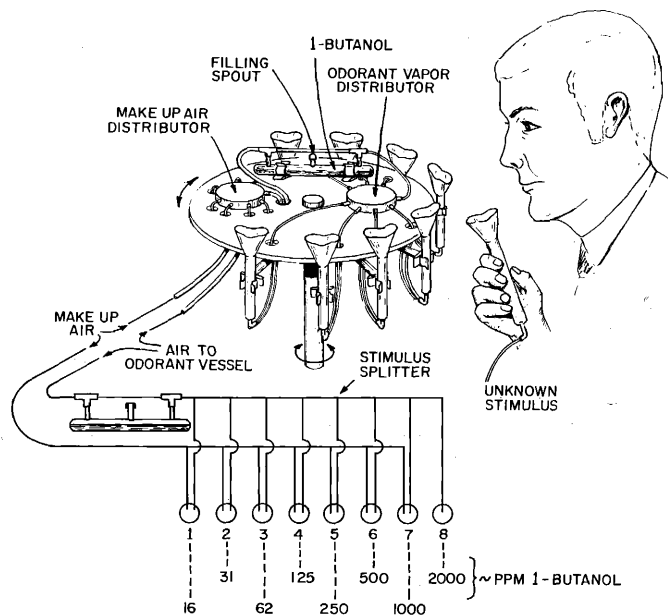
Figure 3. Odor intensity referencing scale based on 1-butanol (bottom portion represents air flow distribution scheme in the dynamic dilution binary scale olfactometer)

If one would simply smell this area of the shirt, he would deal with the "as-is" undiluted intensity of the odor. This aspect is best represented by measurements of an undiluted sample. On the other hand, odor dilution threshold comparison of two samples would give an indication on how far from the shirt the odor would be noticeable. Although both are somewhat related, the two values describe functionally different odorous properties of perspiration.

The odor threshold can be measured by a great variety of methods (19). The problem with the threshold measurements is that the odor threshold of a substance is not an exact property, such as its density or boiling point, but depends on the method of odor presentation, statistical design, sensitivities, and motivations of panelists, etc. Method used for threshold measurements in room air will not yield functionally correct values for the same odorant in the vapor space above axilla. Methods that use small volumes suffer from wall adsorption losses. Methods that use fast volumetric flows of air usually will be unsuitable for the evaluation of odors considered cosmetic defects, since the sample consumption rate would be prohibitively fast.

Similar problems exist in odorous pollution measurements on samples taken to an evaluation laboratory. Recently, for these, (20, 21) a dynamic
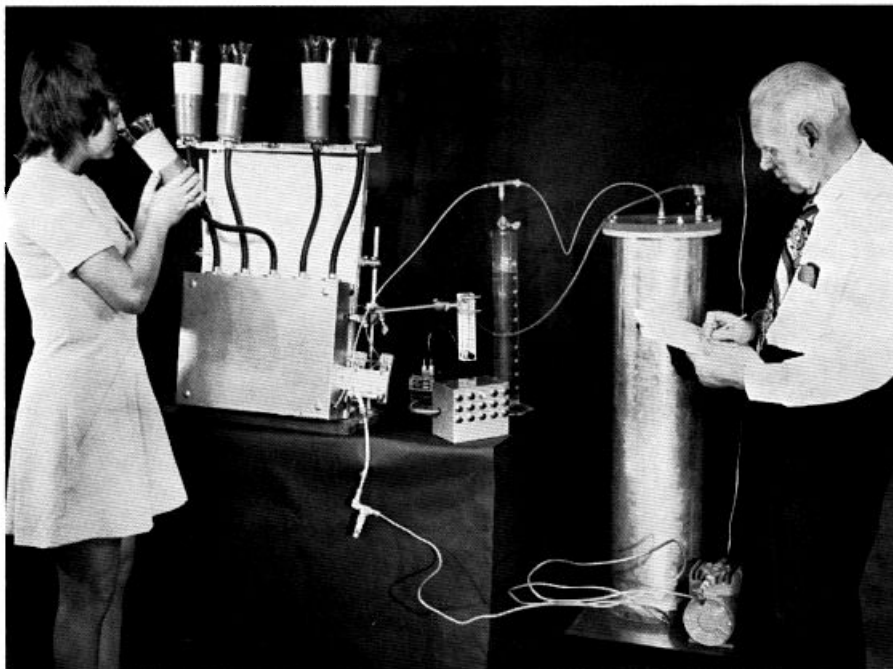
Figure 4. Evaluation of odor threshold using Dynamic Forced-Choice Triangle olfactometer (teflon bag with sample of odorous air is in metal cylinder at right)

forced-choice triangle olfactometer has been developed. Figure 4 depicts the device and the odor threshold evaluation process.

Each sample dilution level is presented at flow rate of 500 ml/min from a glass sniffing port, and is accompanied by two more ports delivering only air at the same flow rates. The three ports are mounted in a circular arrangement in a plastic cup, connected to the sample dilution module by a flexible tubing, which carries inside Teflon tubing and electrical wiring. There are 5 such cup assemblies, providing all together 5 different sample dilution levels.

The panelists proceed from the most diluted sample level toward the most concentrated sample set. It each level, they are required to select the "odd" port—that is different in smell from the two others; such design is known as forced-choice triangle design (I). The panelists signal their choice by depressing the electrical signal button next to the selected port. Lights on a panel seen only by the panel leader announce the panelist's choice. Unintentional steering of the panelist toward some specific choice is impossible in this scheme, in contrast with presentation designs where one stimulus at a time is offered.
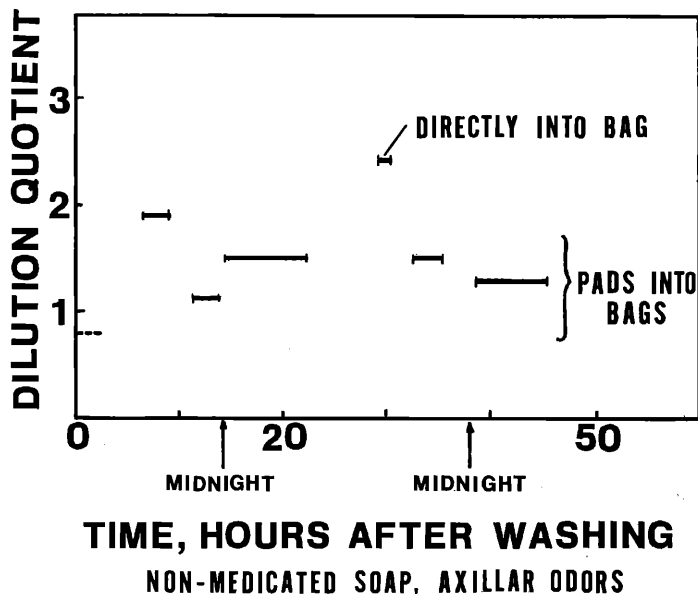
TIME, HOURS AFTER WASHING
NON-MEDICATED SOAP, AXILLAR ODORS

Figure 5. Change in odor threshold of consecutively exposed underarm pads as function of time after washing with nonmedicated soap

The dilution factor increases by a factor of 3 per level. Panelists' judgments are statistically combined and yield a group threshold termed ED_{50} (effective dosage at the 50 per cent level). Since all needed dilutions are obtained by a continuous steady-state dynamic dilution simultaneously, panelists can proceed with evaluation without waiting for any adjustments. One sample can be evaluated by a panel of 9 within 12 to 15 min, and about 10 min are needed to change to another sample.

An example of ED_{50} determinations applied to study of underarm perspiration odors is shown in Fig. 5.

The objective of the above was to explore how the underarm odor changes during the time between when one first washes with a nonmedicated soap (Ivory®*) and abstains from washing for several days. Cotton cheesecloth folded patches, 5 x 5 cm in size, were taped to both underarms of the same subject and were removed after durations of exposure indicated by the length of the segments in the figure. Exposed patches were stored in small plastic bags in a refrigerator until all samples were collected. Twenty-five hours after washing had taken place, a sample of underarm vapors was also collected directly into a 15 l. Teflon bag, using procedure shown in Fig. 2C.

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*Procter and Gamble, Cincinnati, Ohio.

For the evaluation of the dilution quotient (22), which is numerically equivalent to ED_{50} and indicates how many volumes in total one volume of odorous emission must be diluted to reach group odor threshold, both left and right patches were placed in 15 1. Teflon bag and 15 1. of nonodorous air were added (using a peristaltic pump and a wet-test gasometer at the intake into the pump to measure the volume of air added). The bags were kept at room temperature for 1 hour, to permit an equilibration of vapors between the patches and the air in the bag. Bags were then placed into the device shown in Fig. 2D and the odorous air expelled into the olfactometer shown in Fig. 4. Nine panelists then were judges, and all the samples were evaluated in the same session.

The plot of Fig. 5 indicates that during the first few hours the perspiration odor was at level below group threshold (only 4 out of 9 panelists—a statistically inadequate number—identified the undiluted-sample-containing port correctly). The odor peaked after 8 hours, then more or less stabilized at a somewhat lower level. The sample taken from the underarm and put directly into the bag showed a higher odor level; this may be expected, since some loss of odorosity results when odorants from pads distribute between the pad and the air in the bag; while with the sample taken directly into the bag with a preflush of the bag with the sample, such loss is greatly reduced. Since the pad method is logistically simpler, and would still indicate odor control efficacy on a relative basis, it is possibly preferable.

The significance of differences between the samples can be tested statistically. If the same panel has been used for all samples, the t-test-by-Difference, which compares judgments of each panelist separately, is a suitable procedure (1).

Odor Character

A cosmetic treatment may not influence odor intensity, but can modify the character of odor, either by changing the relative concentrations of malodorants, or by adding fragrances.

"Before" and "after" samples can be compared by a variety of methods (23). Most of the methods require that samples that are to be compared be available simultaneously.

Some methods, however, use reference samples, or a series of semantic descriptors, which in essence serve as references. These permit the evaluation of samples which are not available simultaneously. The procedure is less discriminating than a direct comparison, but is much simpler logistically.

In cosmetics dealing with human body odors, a wide spectrum of odors may occur—from most unpleasant to quite pleasant. Only a few odor descriptor scales encompass a wide selection of descriptors.

Table I
An Expanded List of Harper's[a] Descriptors for Characterizing of All Types of Odors

Fragrant	Oily, fatty	Aromatic	Fruity (citrus)
Sweaty	Like mothballs	Meaty (cooked)	Fruity (other)
Almond-like	Like gasoline, solvent	Sickening	Putrid, Foul, Decayed
Burnt, smoky	Cooked vegetables	Musty, earthy, moldy	Woody, resinous
Herbal, green, cut grass	Sweet	Sharp, pungent, acid	Musk-like
Etherish, anesthetic	Fishy	Camphor-like	Soapy
Sour, acid, vinegar	Spicy	Light	Garlic, onion
Like blood, raw meat	Paint-like	Heavy	Animal
Dry, powdery	Rancid	Cool, cooling	Vanilla-like
Like ammonia	Minty, peppermint	Warm	Fecal (like manure)
Disinfectant, carbolic	Sulfidic	Metallic	Floral
Perfumery	Yeasty	Eucalyptus	Strawberry-like
Malty	Cheesy	Buttery	Stale
Cinnamon-like	Honey-like	Like burnt paper	Cork-like
Popcorn	Anise (licorice)	Cologne	Lavender
Incense	Turpentine (pine oil)	Caraway	Cat-urine-like
Melony (cantaloupe, honey-dew)	Fresh green vegetables	Orange (fruit)	Bark-like, birch bark
Tar-like	Medicinal	Household gas	Rose-like
Peanut butter	Celery	Leather-like	Nutty (walnut etc.)
Violets	Burnt candle	Pear (fruit)	Fried fat
Tea-leaves	Mushroom-like	Stale tobacco smoke	Wet paper-like
Wet wool, wet dog	Pineapple (fruit)	Raw cucumber	Coffee-like
Chalky	Fresh cigarette smoke	Raw potatoe	Peach (fruit)
Mouse-like	Laurel leaves	Beery (beer-like)	Oak wood, cognac
Pepper-like	Scorched milk	Cedarwood-like	Grapefruit
Bean-like	Sewer odor	Coconut-like	Grape-juice-like
Banana-like	Sooty	Rope-like	Eggy (fresh eggs)
Burnt rubber	Crushed weeds	Seminal (sperm-like)	Bitter
Geranium leaves	Rubbery (new rubber)	Like cleaning fluid (carbona)	Cadaverous (like dead animal)
Urine-like	Bakery (fresh bread)	Cardboard-like	Raisin-like
Lemon (fruit)	Seasoning (meat)	Crushed grass	Maple (as in syrup)
Dirty linen-like	Apple (fruit)	Chocolate	Hay
Kippery (smoked fish)	Soupy	Molasses	Kerosene
Caramel	Grainy (as grain)	Sauerkraut-like	Clove-like

[a]The upper block is from Harper, with some Americanization of terms (gasoline instead of petrol, etc.).

One of the most balanced scales has been advanced by Harper (24) and consists of 44 characteristics. The odor sample is rated for the applicability of each characteric on a 0 to 5 scale.

Our work with Harper's scale indicated that odors which are quite different sometimes result in rating profiles that are not significantly distinguishable. More descriptors were needed to begin resolving such odors. Recently, the ASTM E18 Sensory Evaluation Committee collected a list of 817 descriptors which are in use by various authors and industrial organizations, and which included flavor, fragrance, cosmetics, industrial chemicals, and air pollution research and development. This material was used to expand Harper's list to 136 descriptors, Table I, where Harper's block of 44 descriptors was left intact.

A perennial problem with the odor descriptor technique is that panelists differ in their use of descriptors, either because of differences in their semantic backgrounds or in the actual perception of certain odor notes. Expanding the scale provides a broader "shopping list."

Panel training is necessary to obtain stable responses on the degree of "floral," "musty," etc. However, there is a potential danger in training the panel to respond uniformly: judgments become more and more provincial and deviate from the reality of sensory/semantic world of odor perception.

One solution to this problem is to consider each panelist's judgments separately and to use the response patterns simply to establish similarity or dissimilarity between odors, e.g., an odor before the treatment and another after the treatment.

Thus, people differ in usage of "floral," "fragrant," "perfumery," "aromatic." If panelist A rates two odors, I and II, and gives a higher floral score to I, while panelist B does not utilize "floral" but gives higher fragrant score to I, etc., indications accumulate that I is higher in the floral/fragrant/perfumery/aromatic combined dimension. This is frequently quite sufficient for guidance in the odor control efficacy evaluations.

There is another form of statistical analysis that permits overall comparisons of response patterns to two odors at at time, circumventing the need for a direct comparison of two odors. Döving (25) used the Chi-Squared statistic to compare electrophysiological responses to odors. Adaptation of this approach to semantic descriptor responses is equivalent to postulating that for a panel of 9 there may be as many as 9 different "floral" concepts, each panelist perceiving this term in a slightly different fashion. With a list of 136 descriptors and 9 panelists, there are 1224 sensory response channels. The simplest approach is to ignore the degree of response and consider only uses and nonuses.

An example to be used is an attempt to modify the malodor of isovaleric acid (a primitive model of perspiration odor) by addition of a primitive modifier, a mixture of vanillin and linalool vapors. Inspecting the distribution of

Table II

Classification of Responses on Applicability of Specific Descriptors to the Odor Character of Two Odors: 1. an Malodor;[a] and 2. Its Mixture with a Model of an Odor Modifier[b]

Number of Descriptors	
Used for malodor and mixture (21)	Used for mixture but not for malodor (41)
Used for malodor but not for mixture (39)	Not used for either of two (1123)

[a]Malodorant: isovaleric acid.
[b]Modifier: vanillin plus linalool.

sensory responses of panelists, one can classify occurrences in 4 groups. Cases where the same panelist utilized the same descriptor for characterizing the malodor as well as the malodor with the modifier added, are points of similarity between these two odors. Presumably, if a descriptor has not been used for either odor, some evidence for similarity is accumulated. Other cases, where a panelist used a certain descriptor for one odor and not for another, or in reverse, produce points for dissimilarity between the two odors. A matrix of the results are shown in Table II, where the total number in the upper left and lower right quadrants contain evidence for similarity, and the upper right and lower left quadrants contain evidence, for dissimilarity. In this form of analysis, it is not necessary that the panelists agree on the meaning of terms. They merely should be consistent in their own use of the terms.*

Utilization of this odor comparison process can be illustrated by the isovaleric acid odor example.

A mixture of 1.5×10^{-6} g/l. of linalool and 3×10^{-6} g/l. of vanillin vapors in air served as an odor modifier. Its odor intensity at 500 ml/min flow rate from a glass sniffing port of Fig. 3 was found to be equal to 5.7. It was desired to establish to what extent the odor of isovaleric acid can be modified by this mixture of fragrances.

Isovaleric acid vapor was added to the modifier stimulus concentrations higher than the acid's odor threshold concentration by factors of 10 x, 40 x, and 60 x. Table III summarizes (at 40 x) the response matrix comparisons

*Experience has shown that in the use of descriptor scales in general, panelists are somewhat more liberal in the usage of terms when exposed to scale first time. After 2 sessions and the evaluation of 15 to 25 odors, this tendency subsides to a reasonably constant level. In the application of the 136-descriptor scale, the sheer number of descriptors does not seem to present a great burden after panelists have familiarized themselves with the terms in working with the 15 to 25 odors, which are selected in such a way that a sufficient variety of odor character notes is encountered.

Table III
Comparison of Odors through Comparison of Individual Descriptor Usage Profiles
of Odors in Pairs

Panelist, Consecutive Number	Mixture (= A) versus Isovaleric Acid (= B)				Mixture (= A) versus Odor Modifier (= C)			
	Frequencies of Types of Response[a]							
	A+ B+	A+ B−	A− B+	A− A−	A+ C+	A+ C−	A− C+	A− C−
1	1	8	7		5	4	4	
2	4	2	3		2	4	1	
3	0	11	4		2	9	4	
4	4	0	3		2	2	3	
5	0	11	7		9	3	3	
6	5	1	6		1	4	7	
7	2	3	2		0	5	6	
8	1	3	4		2	3	4	
9	4	2	3		2	4	3	
Sum	21	41	39	1123	25	38	35	1126
	$\chi^2 = 109$				$\chi^2 = 170$			
	Coefficient of association = 0.09				Coefficient of association = 0.14			

[a] "+" descriptor used; "−" descriptor not used, for the particular odor by the same panelist.

for the malodor-modifier mixture versus the malodor and versus the modifier. Sum values for the left matrix are indicated in parentheses in the corresponding quadrants of Table II. Calculated Chi-Squared values (1) for this 2 x 2 contingency table are given at the bottom of Table III.

A derivative value is the coefficient of association, which for the case of 9 panelists and 136 descriptors is simply the Chi-Squared value divided by the 1224 response items. It indicates the degree of association between the two odors, and would be unity if the description matrices would completely overlap, and zero if there are no common usages of the descriptors for the two odors. In actuality, values of 0.5 to 0.7 are obtained if the same odor is evaluated in duplicate by panels not highly selected for the consistency of their responses.

Figure 6 represents the results of the modifier experiment. The malodor and the modifier are the two terminal points on each bar, placed at an arbitrary distance apart. The point representing the mixture is placed between, in such way that the distances from it to the terminal points are in inverse proportion to the ratio of the respective association coefficients. Close proximity to a point indicates close sensory association. The three experiments conducted indicate that the modifier handles the odor of the isovaleric acid quite well at tenfold odor threshold concentration of this malodorant, but begins to decrease in its efficacy at 40 x thresholds, and has completely lost
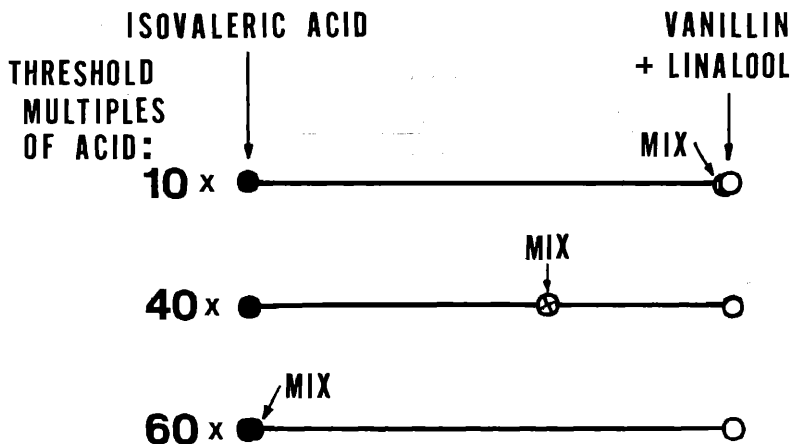
MALDODORANT: "MODIFIER:"

Figure 6. Influence of odor modifier on malodor of isovaleric acid

its usefulness at 60 x thresholds. More experiments could have established the limits of the efficacy somewhat closer.

This procedure can be applied to any cosmetic treatment where malodors are controlled by fragrances. It is not necessary that the mixture of the malodorous emission with the fragrance exhibits an odor similar to the modifier; only that the sensory complex of the malodor must be signifiantly modified. The odor of mixture may be not similar to the fragrance either, but, of course, it should be hedonically acceptable, and not only a different malodor.

Hedonic Value

The overall pleasantness/unpleasantness of the modified body odor is a function of its odor notes, but perhaps only one of these, "sickening" relates more directly to the degree of annoyance.

Testing of hedonic shifts in pairs of "before" and "after" samples is an extremely complex task. Some elementary considerations are given elsewhere (1). One is that large panels (50 to 100 panelists) must be used to judge the hedonic value. Another is that a familiarity with the formulations and brands is undesirable.

ANALYTICAL EVALUTIONS

Analytical evaluations of human odor control efficacy are based on measurements of decrease in emission of malodorants. In the case of applied

fragrances, the rates of dissipation of fragrances from part of body also can be measured.

As outlined in the discussion of odor intensity measurements, a twofold reduction in concentration of a malodorant, even if this were the only malodorant present, does not reduce the malodor intensity by a factor of 2, but rather by a fractional power of 2. A reduction in concentration by 20 to 30 per cent* usually will barely change the odor intensity sufficiently to notice that odor has weakened even if the "before" and "after" odors would be compared directly.

This reduces the demands on the reproducibility of analytical data needed for odor-related interpretations.

The most common form of analysis is gas-chromatographic, using hydrogen-flame ionization detector. This detector responds approximately proportionally to the mass of the organic substance, but does not respond to water vapor, ammonia, H_2S, CS_2, $HCOOH$, and some other compounds that contain few CH links and several heteroatoms.

To relate GC analysis data to odors, two conditions must be met. First, the gas-chromatographic sensitivity should be sufficient to obtain measurable GC peak areas even for those odorants which have a particularly low odor threshold and occur in the vapor sample at concentrations close to the threshold. Second, the GC peaks of those sample components that are most likely and significant contributors to the odor of the sample should be indicated.

These two conditions can be satisfied by a preconcentration of the sample and by using a trained analyst's nose to assay the odors of the GC-separated components at their emergence from the GC column. This sensory assaying consists of noting which components, irrespective of their peak size, exhibit particularly strong odors and characteristic odor notes (26).

Sample preconcentration should include collection of the vapors from organic substances and their separation from excess water vapor, which occurs in most samples of human body vapors. If water is not separated, the required GC sensitivity cannot be reached. As an example, analysis of the maximum possible amount of condensed perspiration yields only a few GC peaks. Collection of organic substances from several liters of perspiration vapors, without collection of water vapors, yields a sample size sufficient to obtain several dozen of GC peaks.

Collection with the gross exclusion of water is accomplished using nonpolar polymers organic polymers (Fig. 2A). It permits a several thousandfold enrichment of organic substances from vapor phase. The lowest odor thresholds are in the concentration range of 10^{-10} g/l., and such preconcentration brings even such components into GC recording range.

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*Differential threshold," related to Weber's ratio.

An analysis utilizing the above techniques results in an odorogram (6, 27, 28); a perspiration vapor odorogram is shown in Fig. 7. The areas of the GC peaks are essentially proportional to the amounts of the respective organic substances in the sample, subject to GC resolution problems. The odor character of the components reflects the judgments of the analyst. Experience has shown that there are differences in terms used by different analysts, little differences with respect to what is an unpleasant odor and somewhat poorer agreement on the relative pleasantness of neutral and pleasant odor notes. In studies where many samples of same origin must be evaluated, it is desirable to maintain the same analyst for the entire series.

To interpret odorograms of samples taken "before" and "after" some treatment, one compares the peak areas of those components which were found to be significant odorants.

This is simple only in cases where some particular odorant is well known and its GC position is also known. Decay of concentrations of known fragrance components after their application with some cosmetic preparation, falls into this class of relatively simple problems. Similarly, there may be rare cases where the principal malodorant is known and dominates the sample odor.

Usually, however, many malodorants participate in generating a cosmetic odor defect. A mass-spectrometric identification of every odor-relevant GC-resolved component in every sample is prohibitive in time and effort. In such cases, series of odorograms from the same kind of sources can be combined to obtain a better insight into the most frequently occurring malodorants from such sources (6). Figure 8 compares GC positions of malodorants found in several types of human odor sources with reasonable frequency. It appears that at least some malodorants are common to several types of sources. Hopefully, chemical identities of the malodorants indicated in Fig. 8 will be eventually established, so that odor control could be described in terms of reduction in the concentrations of some specific chemical compounds.

Meanwhile, odorograms may be compared directly. One method of comparison is to explore how each malodorant-caused GC peak has changed with the cosmetic treatment (6). Another method, somewhat less dependent on sufficient GC resolution, is a count of malodorous peaks. When the concentrations of malodorants decrease, the malodor of such components becomes less noticeable in the effluent from the GC column, and fewer GC peaks will be judged malodorous. Thus, if a GC peak was representing jointly a small amount of a malodorant and a larger amount of a compound that was not particularly odorous, the treatment may have removed the malodorant and the corresponding odor remark in the odorogram, but the GC peak size may have remained almost the same.

Figure 9 illustrates results of an earlier experiment conducted before the hexachlorophene ban. Occurrences of odorous peaks in the chromatograms
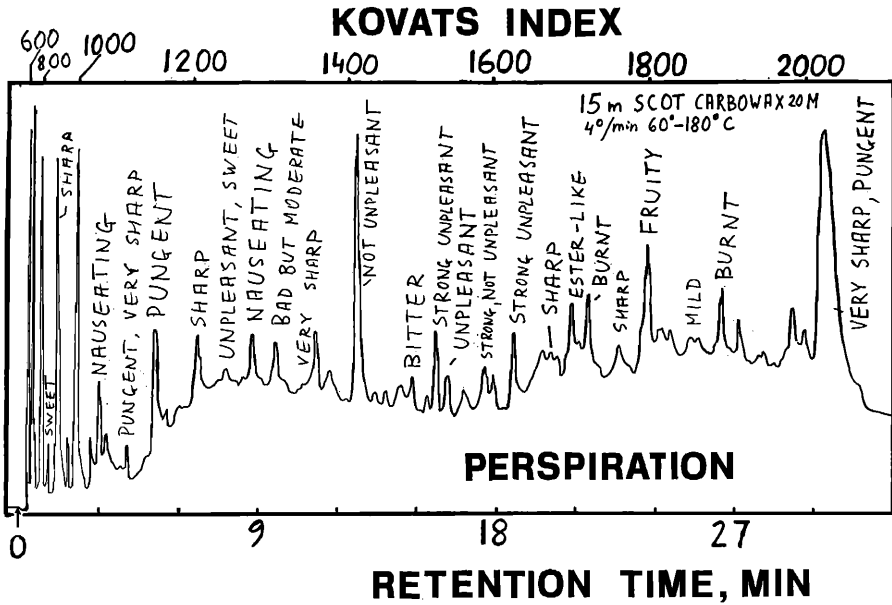
KOVATS INDEX

Figure 7. An odorogram (odor-annotated gas chromatogram) of perspiration vapor
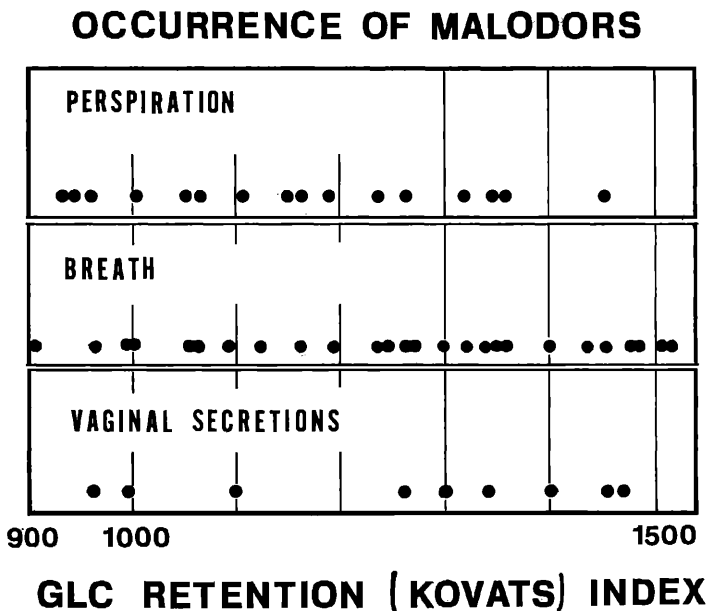
OCCURRENCE OF MALODORS

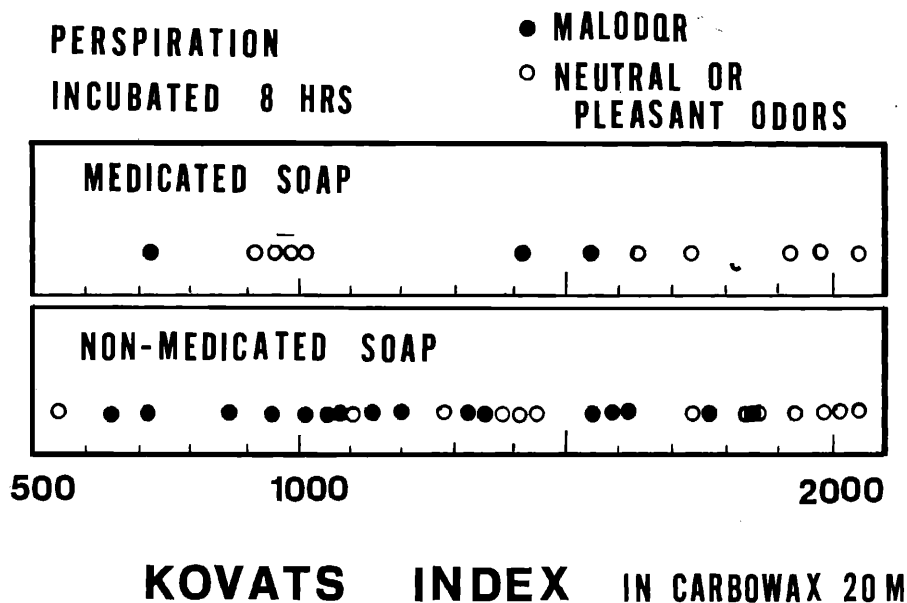Figure 8. GC distribution of malodorants in several types of human odors

Figure 9. Comparison of odorograms of incubated perspiration vapors

of two perspiration vapor samples are compared. One sample is pooled from axillae washed with a nonmedicated soap (Ivory). The other is from the opposite axillae washed with a medicated formulation. Fresh samples showed little difference, but after incubation a marked difference developed in the number of malodorous constituents.

CONCLUSION

Recent advances in the odor measurement technology, adapted to evaluate various human body odors, permit the comparison of the efficacies of cosmetic treatments in reducing or modifying the objectionability of such odors.

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