Engineering Perfumes

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A new concept of perfumery ternary diagrams (PTDs), based on an analogy between perfume pyramid structure and engineering ternary diagrams, is described. These diagrams allow a fast theoretical evaluation of the odor value in the headspace for all possible concentrations of a perfume liquid mixture constituted by three fragrant components and one solvent base, thus eliminating a long trial-and-error experimental work to analyze the headspace composition. The effect of the nonidealities in the liquid phase arising from molecular interactions was analyzed, as well as the effect of ethanol in a test mixture composed of limonene, geraniol, and vanillin. A diffusion model was used to simulate the evaporation of a small and finite sample of perfume test mixture. The changes in the liquid phase and in the gas–liquid interface were followed using the PTDs developed in this work. A characteristic point of a PTD was used as the initial mixture for simulating the evaporation of the small amount of perfume as a function of time and space. The performance parameters, such as impact, tenacity, diffusion, and volume, were discussed based on these results. © 2005 American Institute of Chemical Engineers *AIChE J,* 51: 2834–2852, 2005

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Introduction

Flavor and fragrance industry

The flavor and fragrance (F&F) industry is led by a small number of big companies. In 2003, 65% of the F&F market share was attributed to ten companies from Europe, the United States, and Japan (see Figures 1a and 1b). Their total world sales volume corresponded to around \$10.5 billion; the estimated total world F&F sales market for 2003 was around \$16.3 billion.[1] The growth rate between 1979 and 2003 has continuously increased,[1] as can be seen in Figure 2. The market is very competitive and innovation is absolutely critical.

Discovery is the fountain from which new ingredients, flavors, and fragrances—and eventually consumer products—flow. New ingredients are obtained in two ways: (1) synthesizing new molecules starting from known compounds, called synthetic or artificial materials; and (2) searching in nature for new molecules and new combinations of molecules, for natural materials.[2] Compounds that are prepared by chemical means but that are identical in structure to those found in nature are known as natural identical materials. The synthesis of compounds closely related to these natural identical materials led to the discovery of ingredients that are similar in odor, but which are much easier and cheaper to make than their natural counterparts. One example is that of jasmine[3]: jasmine absolute (natural) costs \$4500–7000/kg; the natural identical materials—jasmone and methyl jasmine—cost \$450–700/kg; and the simpler cyclopentanone derivatives, \$15–70/kg. Another goal is to invent/discover more intense and more long-lasting alternatives to known odorants.

Perfume formulation

In the perfumery industry special attention is given to the performance of these materials in the composition of perfumes. These materials are commonly classified into fragrant notes that can be of three types: top, middle, and base notes. Top

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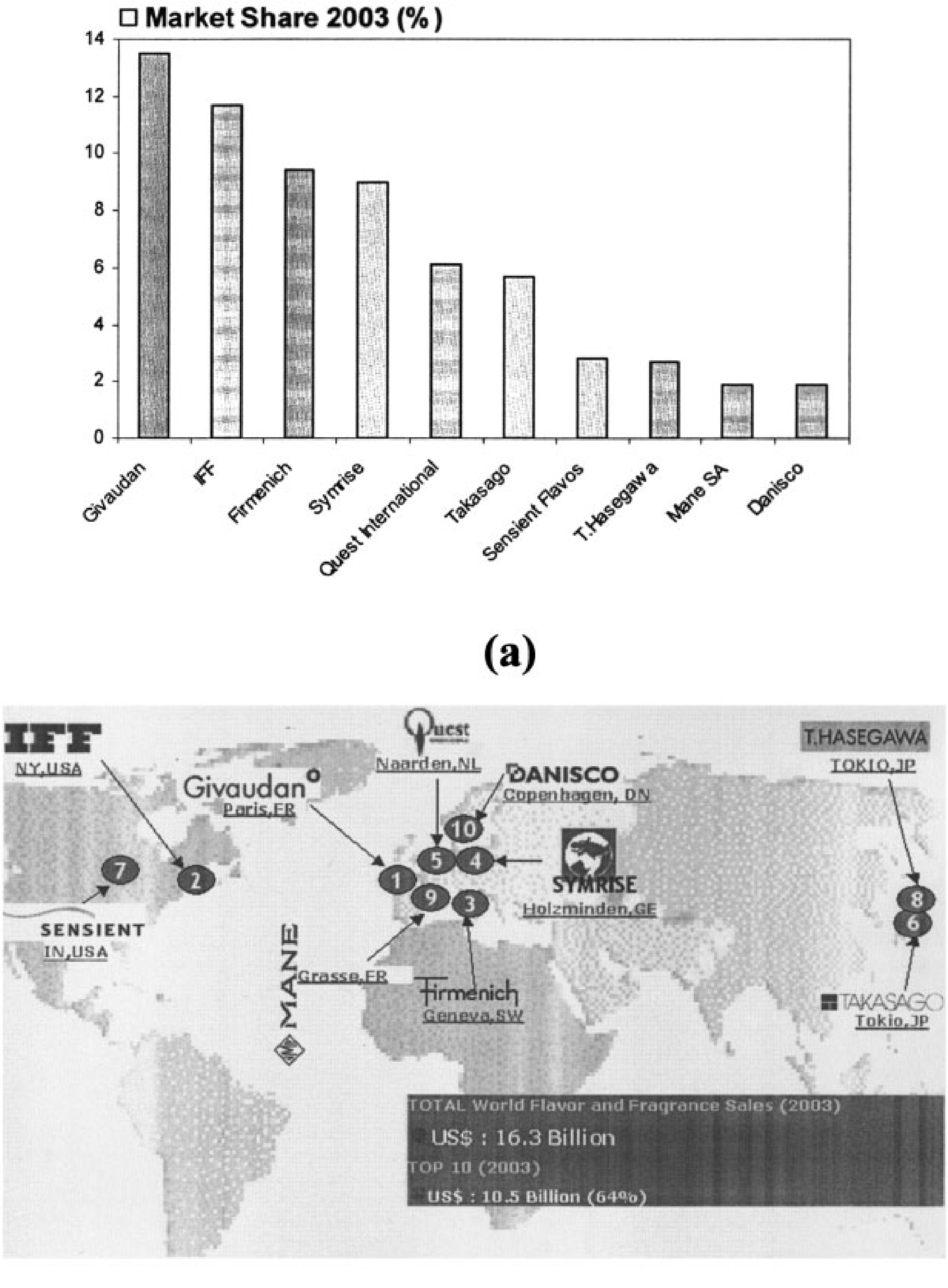


Figure 1. (a) Flavor and fragrance market share (top 10). (b) Worldwide distribution of top 10 flavor and fragrance industries.

notes are very volatile and should last no more than some minutes (or seconds, in some perfumes). Examples are citrus oils, such as lemon, lime, or menthe. Middle notes (also called heart notes) represent the body of the perfume, which are noticed some hours after application, and after top notes have disappeared. Examples are floral notes, such as rose or jasmine. Base notes have the lowest volatility, remain several hours after application (>8 h, sometimes days or months), and are used as fixatives of the whole perfume, once they lower the volatility of top and middle notes. Examples are vanillin and musk oils. Carles[4] represented the structure of a perfume as a triangle divided horizontally in three parts, each one representing top, middle, and base notes, as shown in Figure 3. The suggested proportions for each type of fragrant notes are: top, 15–25%; middle, 30–40%; and base, 45–55%.[5,6]

The different characteristics of these fragrant notes are based on the properties of their main constituents, such as volatility, odor threshold, polarity, and affinity to the liquid media and

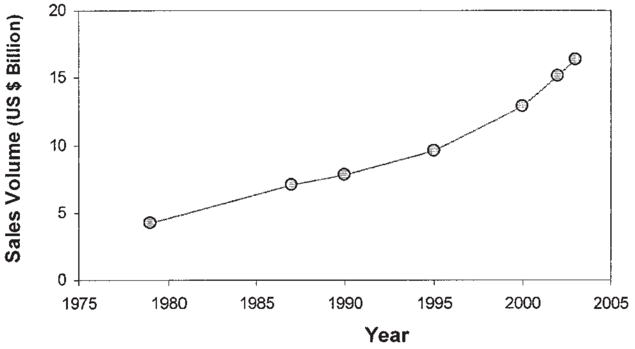


Figure 2. Flavor and fragrance sales volume since 1979.

odor value. An explanation of these terms is presented in this communication, as well as the description of the contribution of this work for the prediction of perfume mixture behavior.

For a given new chemical or new mixture/formulation, one objective that is many times looked at by the perfumery companies together with their perfumers and chemists is: *to find the minimum amount of a certain flavor or fragrance to obtain the desired effect*. If the amount is less than the optimum value the client/consumer will not perceive it and if it is higher the client/consumer can refuse to buy it for being unpleasantly intense or for having a high cost.[7] Besides, low volume means less impact on health and on the environment.[2]

Normally, famous perfumers with outstanding skills of memorizing and re-creating scents as an art have accumulated know-how over the years to satisfy users' preferences in hedonistic terms. They try with their experience to match the product quality with the requirements requested by the consumer and the feedback obtained by market research tools. In parallel, scientists have developed various systematic approaches in characterizing odors through measurable parameters, although it is not yet evident how to use the identified important parameters in the creative process: it is easier to find explanations of observed sensory phenomena than to predict them.[8]

Perfumers have evaluated fragrance performance in empirical terms over many decades. The term *performance* is generally used to denote a perfume's ability to make its presence noticed. The objective is always to achieve maximum odor effect at the lowest possible perfume dosage, especially in functional products, for both economical and technical reasons. However, the performance has been described only qualitatively over time and location. Different aspects of performance can be distinguished[7,9] (see Table 1).

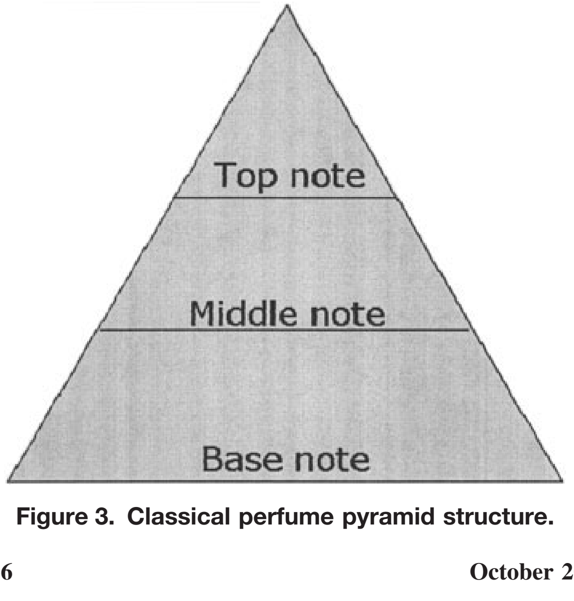


Figure 3. Classical perfume pyramid structure.

Table 1. Perfume Performance Indices

	Near the Source	At Some Distance
Soon after application	Impact	Diffusion
After some time	Tenacity	Volume

Impact refers to the efficacy of a perfume during the first moments of product performance; for example, a top note is noticed immediately when sniffing at the perfume bottle or some seconds after applying the product to the skin. *Diffusion* is a measure of the distance over which the fragrance is noticeable soon after application; high diffusion, for example, is desirable in a bath foam or a dishwashing detergent. *Tenacity* refers to the long-term effectiveness of the fragrance in the perfumed product, such as upon the skin after use of a perfume or a toilet soap. *Volume* is the effectiveness over distance, some time after application.

Such criteria have been applied over years even without being directly measurable by quantitative analytical methods. They refer to a sensory experience, which is a result of a complex superposition of individual physical phenomena occurring simultaneously, which are even known to depend on each other and finally depends on the person's individual sensitivity to register a scent perception.[8]

Measurement methods to quantitatively determine physicochemical effects, in contrast, have been well known for decades. For each molecule it is possible to acquire data of vapor pressure, activity, water solubility, partition coefficients, and many other physical properties. However, these data can be used to characterize only an isolated physical phenomenon and do not give complete information about a complex fragrance application process.[8]

On the other hand, the human odor perception is the effect of the odoriferous chemical molecules that reach the olfactory epithelium. Psychophysics explores the relationships between measurable characteristics of stimuli and their perception. Several models have been developed, especially in recent years. Nowadays, with rapid advances in computation and computer graphics, chemists can try to find novel materials by theoretical prediction of a new compound activity without synthesizing it. These predictions are mainly done using quantitative structure–activity relationships (QSAR), such as Hansch analysis,[10] osmophore approach,[11] pattern recognition,[12] and more recently other type of models such as molecular vibrations[13] and neural networks.[14]

However, the olfaction phenomenon is not yet completely understood. As an alternative, there are standard methods available to measure sensory threshold concentrations.[15] In the case of an odor as a stimulus, the only two quantitatively measurable aspects, in the current state of knowledge, are concentrations and the compositions of mixtures. Thus, the psychophysics of odor deals with measuring the perception of given odorants at different concentrations and with the perception of mixtures. A fundamental concern of psychophysicists working on olfaction has been the determination of the odor thresholds (Thr_i) of a broad array of substances.[7] Here one should mention the *detection threshold*, that is, the lowest concentration at which significant detection takes place that some odorous material is present and the *recognition threshold*, that is, the lowest concentration at which an odorant can be recognized for what it is.

These properties (detection and recognition thresholds) are commonly measured using a human panelist (generally, four or more people) and an olfactometer that records the odor threshold value for each person. Very different threshold values are obtained if the concentration of the substance has been measured in a solution, the headspace of which is smelled (such as threshold in water), or directly in the inspired air (threshold in air). In the case of solutions, the nature of the solvent strongly affects the odor threshold values. Odor threshold values based on the concentration in the air are the most meaningful values because they are independent of the medium in which the odorant was dissolved, although they are very tedious to measure, requiring an olfactometer. In the normal application of perfumes, the concentration range that comes into play lies far above the threshold values. Substances with low threshold values are generally more intense than substances with comparable vapor pressure (volatility) and higher thresholds.[7] Extensive compilations of threshold odor values, Thr_i, obtained experimentally can be found in the literature.[1,16-18]

It is known that not all the fragrant compounds that occur in a liquid or solid flavor or fragrance contribute to its aroma or scent, respectively. New experimental techniques have been developed to identify the compounds with higher intensity in the headspace in the preparation of synthetic mixtures, called *aroma models*, resembling natural products,[18] such as brewed coffee,[19] basil,[20] or wine.[21] Progress in instrumental analysis—such as gas chromatography/olfactometry (GC/O) and gas chromatography/mass spectrometry (GC-MS)—has proved to be of enormous benefit to these scientists.

A good description of how to work with a performance indicator is given by the *odor value* (OV), defined as the ratio between the concentration of that odorant component in the headspace—gas above the liquid mixture—and its odor threshold.[7] This concept is successfully used nowadays as a tool that can help to combine perfumery experience based on perception with objectively measurable parameters.[8]

The traditional classifications for single flavors and fragrances were made in terms of their volatilities. However, the behavior of one fragrant chemical or essential oil, and consequently its OV, depends largely on the medium or solvent and on the remaining fragrant components present in the perfume mixture. This is attributed to molecular size and to a great extent to physical interactions at the molecular level, such as polarity forces (ion–dipole, dipole–dipole, London forces, and hydrogen bonding forces). Generally, the affinity of a molecule to its surrounding medium is measured using the concept of activity coefficient, γ. A high value of γ implies an increased tendency for a given substance to be "pushed out" of the mixture and a low value of γ implies a low concentration in the headspace and higher retention of that substance on the liquid mixture ascribed to the higher affinity to the medium.[3] This means that one smell can change if diluted in different solvents because the volatility of the single compound and its OV will be affected in different ways. This is very important in perfume formulations once the amount of alcohol, water, or other solvent/cosmetic base can substantially influence the headspace above the liquid and, therefore, its smell.

Objectives of this work

In this work, a new methodology based on the *Perfumery Ternary Diagram* (PTD) was developed to help perfumers in the prediction of the headspace odor value for a ternary perfume mixture diluted or not in ethanol. This technique allows a fast headspace evaluation for all liquid combinations of three fragrant components and for a fixed amount of solvent. The effect of nonideality in the liquid perfume phase arising from intermolecular interactions is studied and compared with the ideal liquid perfume mixture assumption.

One diffusive model for the evaporation of a small volume of a multicomponent perfume mixture was also developed. This model considers the liquid as a nonideal solution and takes into account the changes of composition and volume during the evaporation of small volumes of liquid. Using this model and the study of the nonideality of a perfume system, a strategy for the choice of the optimal initial composition of the perfume constituents was developed. The effect of different initial perfume compositions on the headspace was studied and the obtained results were used to evaluate the performance parameters of each compound present in a test perfume mixture.

The odor value (OV) concept

A perfume system consists of a complex fragrant liquid mixture and a corresponding air phase above it, the headspace, which we smell. In this work, it is considered that:

(1) The headspace is an ideal solution, given that the components are highly diluted

$$c_i^g = \frac{y_i M_i P}{RT} \tag{1}$$

where c_i^g is the concentration of component i in the headspace, y_i is the gas-phase molar fraction of component i, P is the total gas-phase pressure, M_i is the molecular weight of i, R is the ideal gas constant, and T is the absolute temperature.

(2) The liquid is a nonideal solution because its molecules have different intermolecular forces, and the headspace is in equilibrium with the liquid perfume mixture

$$y_i = \gamma_i x_i \frac{P_i^{sat}}{P} \tag{2}$$

where y_i is the gas-phase molar fraction of component i in the headspace in equilibrium with the liquid with composition x_i, γ_i is the activity coefficient of i in the liquid, and P_i^{sat} is the saturated vapor pressure of component i. In this work, values of γ_i were calculated using the UNIFAC method, which is based on molecular group contribution.[22] This method takes into account the contribution arising from differences in molecular size and molecular shape (the combinatorial part) and the contribution arising from molecular interactions (the residual part) (see Appendix A).

Table 2. System 1: Physical Properties for Each Component in the Case Study Perfume Mixture

	Name	Molecular Formula	M_{Wi} (g/mol)	P_{Vi}* (Pa)	Thr_i* (g/m^3)	$D_{i,air}$ (m^2/s)
A	limonene	$C_{10}H_{16}$	136.2	20.5×10^{1}	2.45×10^{-3}	6.15×10^{-6}
B	geraniol	$C_{10}H_{18}O$	154.3	26.7×10^{-1}	2.48×10^{-5}	5.94×10^{-6}
C	vanillin	$C_8H_8O_3$	152.2	16.0×10^{-3}	1.87×10^{-7}	11.42×10^{-6}
S	ethanol	C_2H_6O	46.0	72.7×10^{2}	5.53×10^{-2}	10.68×10^{-6}

*From Calkin and Jellinek.[7]

The intensity of a fragrant compound i can be expressed in terms of its odor value OV_i, which is defined as[7]

$$OV_i = \frac{c_i^g}{Thr_i} \tag{3}$$

where Thr_i is the threshold concentration of i in air.

By combining Eqs. 1–3, we obtain

$$OV_i = \gamma_i x_i \left(\frac{P_i^{sat} M_i}{Thr_i}\right)\left(\frac{1}{RT}\right) \tag{4}$$

This equation relates the liquid perfume composition x_i with the human sensory response of the evaporated perfume.

In this work it is considered that one component i, present in a liquid mixture of N fragrant components, is perceived strongly by the human nose when its odor value OV_i, in the headspace above the liquid is higher than that of the others components. For example, a typical perfume has a highly volatile top note, which is noticeable when smelling the perfume bottle or until some minutes after application. It means that the odor value of the top note is higher than that of the middle and base notes. The middle note is normally noticeable only after application and after the top note has disappeared; that is, because of the decrease in the concentration of the top note, the odor value of the middle note becomes higher than that of the top note. Another special rule that a good perfume should follow is that the alcohol should never have the highest odor value, so as not to be perceived and rejected by the consumer.

Binary Perfume Mixtures

Consider a binary liquid mixture, A + B, consisting of two fragrant chemical compounds having different volatilities, each one belonging to one type of fragrant notes; that is, A represents a top note and B, a middle note. In this example, we will consider that component A is limonene and component B is geraniol.

For each mixture, there exists n_A moles of component A and n_B moles of component B. The molar fraction of A is represented by $x_A = n_A/(n_A + n_B)$ and the molar fraction of B is $x_B = n_B/(n_A + n_B)$. If there are only these two components, $x_A + x_B = 1$. For each mixture (x_A, x_B) the odor values of each component OV_A and OV_B are calculated using Eq. 4. The physical parameters of each component are shown in Table 2.

Figure 4 shows the value of the OV_i, $i = 1, 2$ as a function of $x_B = (1 - x_A)$. This plot represents the individual odor values obtained for all the combinations of A + B mixtures. We can see that below the point $x_B = 0.4$ (and $x_A = 0.6$) the highest odor value, $OV_{\max}$, is that of geraniol: $OV_{\max} = OV_B$, where $OV_{\max} = \max(OV_A, OV_B)$. Above this point the highest odor value, $OV_{\max}$, is that of limonene: $OV_{\max} = OV_A$.

In the same plot one also observes the comparison between these odor values obtained for nonideal mixtures (NI), when $\gamma_i \neq 1$, and with that obtained for ideal mixtures (I), when $\gamma_i = 1$ in Eq. 4. The greatest deviations of OV_A occur for high values of x_B and the greatest deviations of OV_B occur for high values of x_A. This result is explained by the fact that geraniol has a higher polarity than that of limonene. So, when there is a high concentration of polar molecules (geraniol) in the liquid phase the nonpolar molecules (limonene) tend to leave this liquid and vice versa. Greater differences between the molecules' polarity results in an increase in these deviations to the ideality.

The activity coefficient of a component i in a mixture, γ_i, provides a useful way of assessing the affinity of this odorant to the surrounding medium.[3] For $\gamma_i > 1$, the partial pressure of component i is higher than that predicted for an ideal solution, indicating that this volatile will be "pushed out" of the liquid system and for $\gamma_i < 1$, implies lower partial pressures of component i, less material in the gas phase than expected if we consider the liquid an ideal solution and increased retention in the liquid.

As a consequence, the odor value can change using different solvents or different quantities of each fragrant chemical for a specific multicomponent mixture. Thus, the perfumer needs to know how to increase the performance of selected materials for a given application, by choosing the right composition.

Effect of the solvent on the OV

Figure 5 shows the effect of the solvent in the odor value of each compound. In this case the solvent is ethanol (S) and the perfume is a mixture of limonene (A) and geraniol (B). The x-axis is represented by molar fractions of A and B in a basis without solvent S, respectively, $x'_A = n_A/(n_A + n_B)$ and $x'_B =$

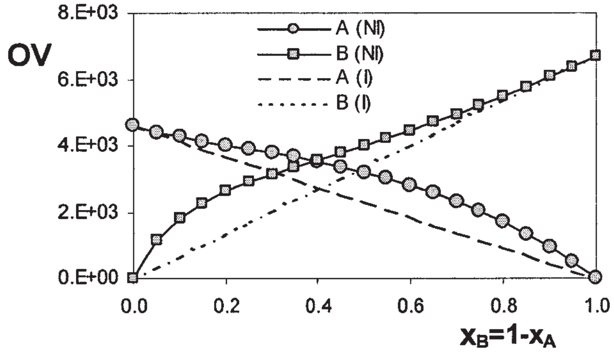


Figure 4. Variation of odor value for binary mixtures of limonene and geraniol.

Comparison between ideal model (I) and nonideal model (NI).

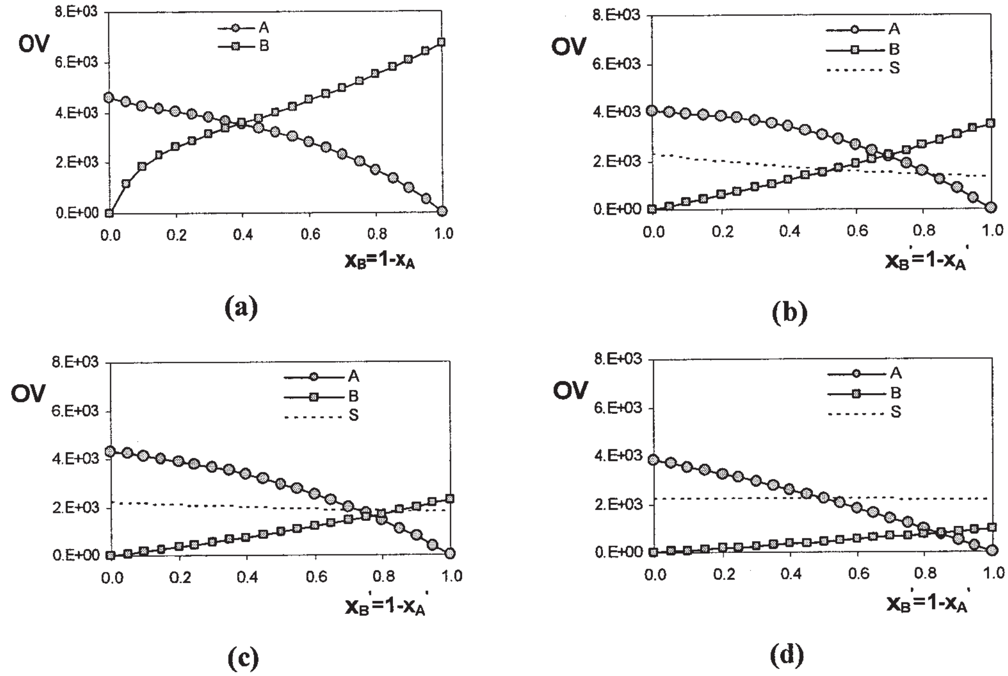


Figure 5. Effect of ethanol (S) in binary mixtures of limonene and geraniol.
(a) $x_C = 0$; (b) $x_C = 0.5$; (c) $x_C = 0.7$; (d) $x_C = 0.9$.

$n_B/(n_A + n_B)$. We see that if we want to make a mixture for which the highest OV is that of limonene we should use: $x'_A > 0.6$, when $x_S = 0$; $x'_A > 0.3$, when $x_S = 0.5$; $x'_A > 0.25$, when $x_S = 0.7$; and $x'_A > 0.5$, when $x_S = 0.9$ (for $x'_A < 0.5$ ethanol has the highest OV).

Effect of the base note on the OV

Figure 6 shows the effect of adding one base note—or fixative—to the mixture of limonene + geraniol, A + B. The base note chosen was vanillin, designated as component C. It

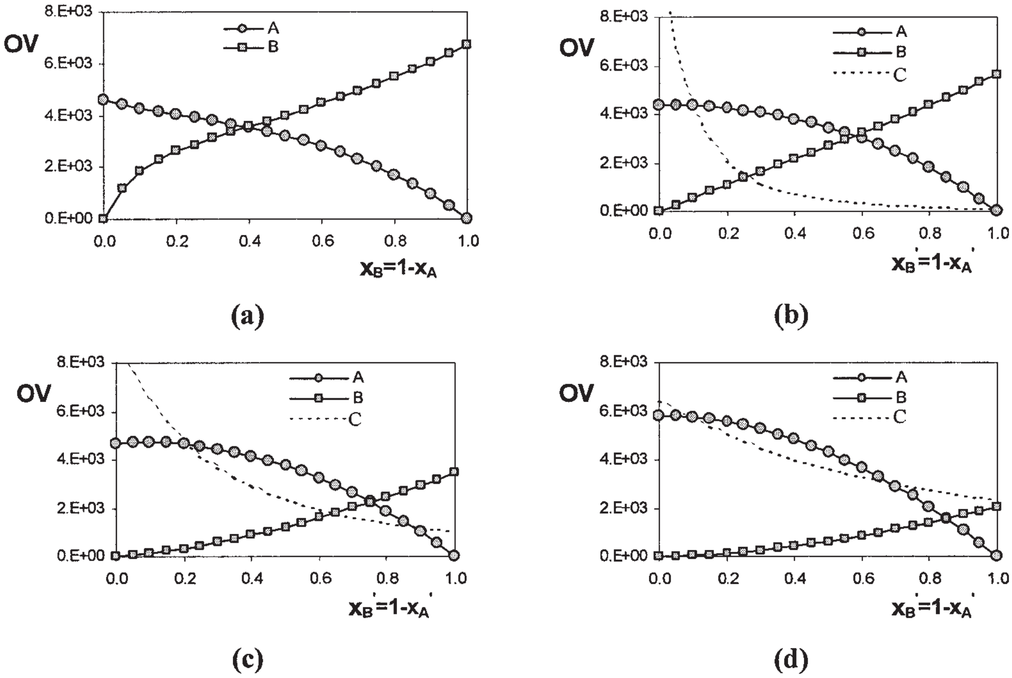


Figure 6. Effect of vanillin (C) in binary mixtures of limonene and geraniol.
(a) $x_C = 0$; (b) $x_C = 0.1$; (c) $x_C = 0.3$; (d) $x_C = 0.5$.

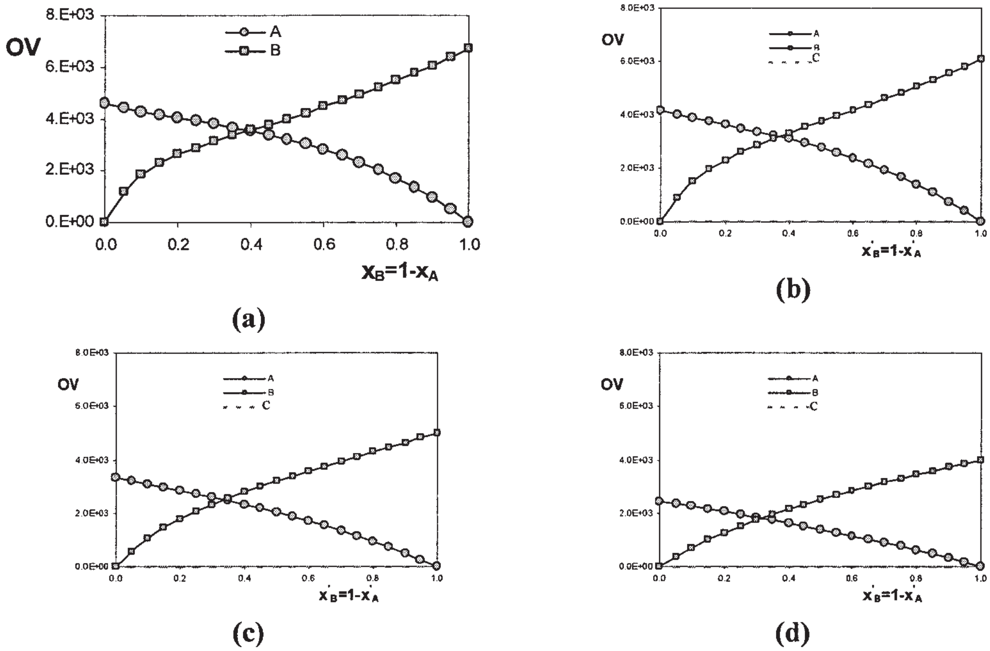


Figure 7. Effect of tonalid (C) in binary mixtures of limonene and geraniol.

(a) $x_C = 0$; (b) $x_C = 0.1$; (c) $x_C = 0.3$; (d) $x_C = 0.5$.

can be seen from Figure 6a to Figure 6d that an increase in C leads to an increase in OV_A and in a decrease in OV_B. The reason is that vanillin is a polar molecule and as its concentration increases, it tends to "push out" the molecules of the nonpolar component, limonene (A) from the liquid phase and, at the same time, to retain the more polar component, geraniol (B).

Another example is given in Figure 7, where the effect of adding a different fixative, tonalid (with a musk odor) to the same binary system, limonene + geraniol is shown. In this case, the tonalid (C) lowers the odor value of both A and B. However, because tonalid is a nonpolar compound, it will help to retain more limonene than geraniol.

Let us take as an example the case where $x'_A = 0.6$ and $x'_B = 0.4$. If we add vanillin in a molar fraction of $x_C = 0.3$, it will result in a headspace where the highest OV is that of limonene. However, if tonalid is added in the same molar fraction of $x_C = 0.3$, the highest OV in the headspace is that of geraniol.

Perfumers may use materials of low volatility in their perfumes, intending thereby to slow down the evaporation of more volatile perfume components. This is the practice commonly referred to as *fixation*. Strong mutual attraction between solvent and perfume material results in a decreased tendency of the perfume material to evaporate, and thus lowers the odor intensity of that material above the solution. Because perfume compositions are blends of perfume materials that differ widely in their polarity (even single essential oils represent such blends), the different components of a perfume are held back to differing degrees when the perfume is dissolved in a solvent. The patterns of differential holding vary greatly between different solvent systems. As a result, if a given perfume composition is dissolved in two different systems, the odor of their headspace will be distinctly different. It can therefore be stated that the odor of any perfumed product is affected by the product base in two ways: by the odor of the base itself and by the way the base, through physical attraction forces, affects the odor of the perfume.[3]

In conclusion, the choice of the fixative is very important because it will determine both the characteristic smell of the perfume and its persistence.

Ternary Perfume Mixtures

Now, let us consider a ternary liquid mixture, A + B + C, consisting of three chemical compounds having different volatilities, each one belonging to one type of fragrant notes, that is, A represents a top note, B a middle note, and C a base note. In some cases, it is also considered that a certain amount of solvent, S (in this case ethanol) is added to the mixture, thus resulting in a quaternary mixture, that will be called the *test perfume*.

The amount of each component in the test perfume is given by its molar fraction: x_A, x_B, x_C, and x_S and we will call this mixture X.

To simplify, this quaternary system is transformed into a ternary system, by recalculating the molar fractions for A, B, and C in a solvent-free basis, resulting in the new fractions

$$x'_A = \frac{x_A}{x_A + x_B + x_C}, \qquad x'_B = \frac{x_B}{x_A + x_B + x_C}$$

$$x'_C = \frac{x_C}{x_A + x_B + x_C}$$

These three quantities are then represented in a ternary diagram,[23] as shown in Figure 8.

Considering a general liquid mixture, which composition is represented by point X', the composition (solvent-free basis) of

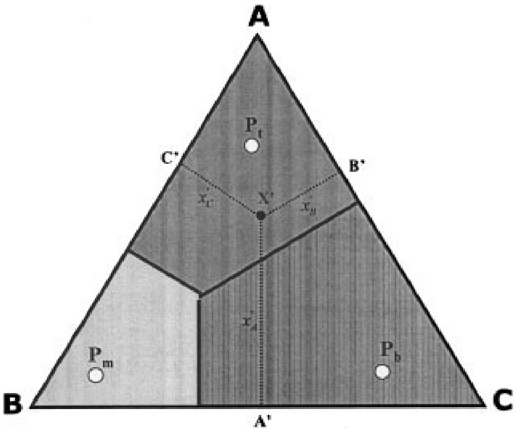


Figure 8. Scheme of a perfumery ternary diagram (PTD), and the representation of a general ternary mixture composition.

component A, x'_A, is given by the distance $\overline{X'A'}$; the composition of B, x'_B, is given by the distance $\overline{X'B'}$; and the composition of C, x'_C, is given by the distance $\overline{X'C'}$. It is considered that the mole fraction of solvent, x_S, is known and constant for each ternary diagram. As can be seen, the ternary diagram represents all liquid compositions that could be made experimentally using different quantities of A, B, and C, for a given amount of ethanol, S.

PTD concept

Now, for each liquid perfume mixture, X' (that is, each point in the ternary diagram) the odor value of each component in that mixture, OV_i, is calculated using Eq. 4. After the calculation of all the individual odor values, for a given mixture X' (represented in the ternary diagram) the maximum odor value is determined

$$OV_{\max} = \max(OV_A, OV_B, OV_C, OV_S) \qquad \text{for point } X' \tag{5}$$

After the determination of the component that has the $OV_{\max}$ for a large number of points of the ternary diagram, we obtain as a result the *Perfumery Ternary Diagram* (PTD), as shown in Figure 8. In this diagram three different areas can be distinguished, giving some highlight to the following typical composition points: P_t: $OV_{\max} = OV_A$ (dark shaded area); P_m: $OV_{\max} = OV_B$ (light shaded area); and P_b: $OV_{\max} = OV_C$ (dotted area).

Points can also exist for which the solvent has the highest odor value: $OV_{\max} = OV_S$. These points are referred to as P_s. This situation generally occurs for mixtures having a high content of solvent, as will be seen below.

Test Case

The developed PTD strategy was tested using the system: limonene (A), geraniol (B), and vanillin (C). Again, A represents a top note, B a middle note, and C a base note or fixative. In this first example, the presence of ethanol is not considered, meaning that $x'_i = x_i$, $i = A, B, C$. This mixture can be a representation of a perfume concentrate or a perfume some seconds after application, the time needed to evaporate the ethanol.

Table 2 shows properties for each component that are used for the calculation of each OV, at 25°C (298.15 K). These properties are: molecular weight, saturated vapor pressure, and odor threshold in air. It is important to note that the threshold values used in this work are mean values found in the literature, which are generally mean values over a wide number of experimental references. This fact must be taken into account when a PTD is determined, that is, the values of Thr_i should be determined by the perfumer/s that will make and test the perfume mixture composition, chosen from the PTD.

Effect of the liquid nonideality on the PTD

Figure 9 shows the resulting PTD for the ternary system chosen. Each point in the diagram represents one different liquid composition of mixture A + B + C and, by the different type of point represented, it can be seen which is the component having the highest odor value, $OV_{\max}$. It also shows the differences attributed to the effect of the nonidealities in the liquid mixture: once in the construction of these two PTDs, the values of OV_i for each point were calculated (Eq. 4) assuming (1) that the liquid solution is ideal ($\gamma_i = 1$) (Figure 9a) and (2) that the liquid solution is nonideal ($\gamma_i \neq 1$) (Figure 9b).

When comparing these two figures, it can be seen that in Figure 9a there are more points with higher OV_A, P_t, fewer points with higher OV_B, P_m, and one separate region with higher OV_C, P_b, next to corner A. This means that if we choose

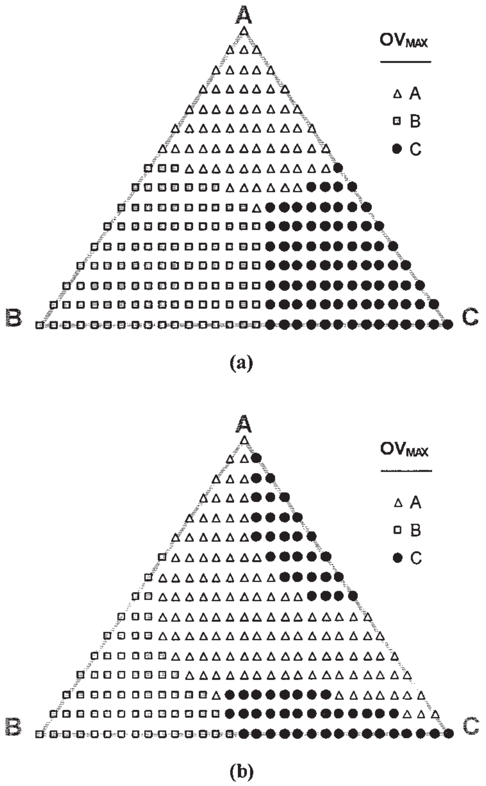


Figure 9. PTD for system (A) limonene: △; (B) geraniol: ▨; (C) vanillin: ●; ethanol: ∷ using (a) nonideal liquid solution, (b) ideal liquid solution.

one of such compositions using the simplification of ideal liquid mixtures, as a result we can have one headspace with an odor value very different from what happens in reality (nonideal solutions).

Figure 10 shows the values of OV_i, of each component separately, for each point in the PTD, that is, OV_A (Figure 10a), OV_B (Figure 10b), and OV_C (Figure 10c). Figures 11a–11c show the same values, respectively, but with the simplification of ideal liquid mixtures. For comparison between them, all PTDs have the same scale: $0 \leq OV_i \leq 11{,}000$. However, in the real liquid mixture assumption (Figure 10), the ranges of each PTD are: $0 \leq OV_A \leq 9400$, $0 \leq OV_B \leq 6696$, and $0 \leq OV_C \leq 10{,}990$. In the ideal liquid assumption (Figure 11) the ranges are: $0 \leq OV_A \leq 4605$, $0 \leq OV_B \leq 6696$, and $0 \leq OV_C \leq 5265$. When the solution is ideal (Figure 11), the contour lines are parallel and perpendicular to the pure compound because it is not taking into account the affinity to the other molecules in the mixture. This does not happen in nonideal solutions and unpredictable results appear, as can be seen in Figure 10. For example, the highest value of OV_A is not in the corner A, as would be expected, but in the region where there is a high concentration of C. This happens because the high polarity of C "pushes out" the nonpolar molecules of A.

Effect of perfume molecules polarity on the OV

Figure 12 shows the odor values obtained for the binary mixtures corresponding to the edges of the PTD in Figure 9 [both ideal (I) and nonideal (N) liquid solutions]. Figure 12a, a mixture of limonene (A) and geraniol (B) shows that the predicted OV values for nonideal solutions are higher than those obtained for ideal solutions. This means that, as mentioned earlier, we observe two molecules with different polarities, and the one in excess tends to "push out" the others. This effect is highly pronounced in a mixture of limonene (A) and vanillin (C) (Figure 12b), where the differences in polarities are even higher than those in the case of mixtures A + B. With respect to the last one, mixtures of geraniol (B) and vanillin (C) (Figure 12c), we can see that the predicted values of OV for nonideal mixtures are smaller than those obtained if the solutions were ideal because we are observing two polar molecules, with affinity one toward the other.

Effect of ethanol on the PTD

Figure 13 shows the effect of ethanol for the case study system [limonene (A), geraniol (B), and vanillin (C), together with ethanol (S)] using the developed PTDs. In each PTD shown, the molar fraction of ethanol is constant and is equal to: (a) $x_S = 0.2$, (b) $x_S = 0.5$, (c) $x_S = 0.7$, and (d) $x_S = 0.9$.

When comparing Figure 13a with Figure 9a, it can be seen that the addition of a small amount of a polar solvent, such as ethanol, increased the number of points where $OV_{\max} = OV_A$ (the liquid became even more polar), and decreased the number of points where $OV_{\max} = OV_B$ and $OV_{\max} = OV_C$. Notice that the isolated area where $OV_{\max} = OV_C$ next to corner A disappeared and now there are points where $OV_{\max} = OV_A$. This happens because the presence of ethanol in the solutions retains more of the vanillin and "pushes out" the limonene. This effect increases as the amount of ethanol also increases to $x_S = 0.5$ (see Figure 13b). However, when the amount of ethanol is

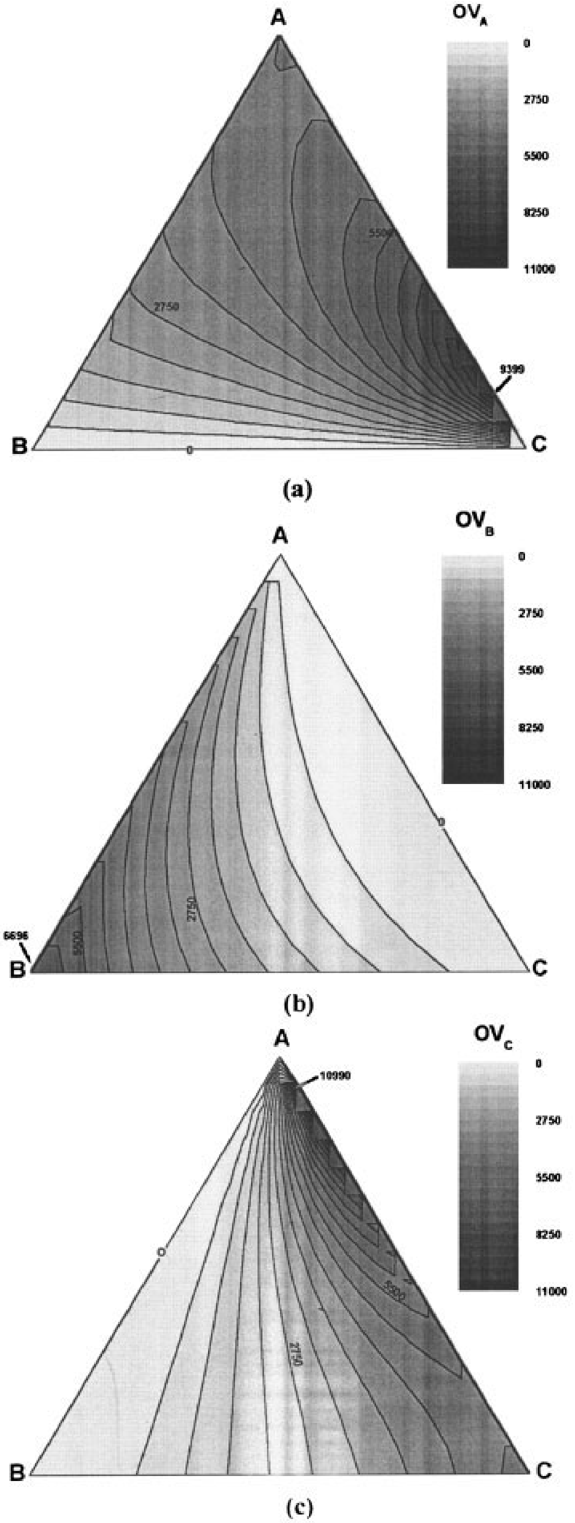
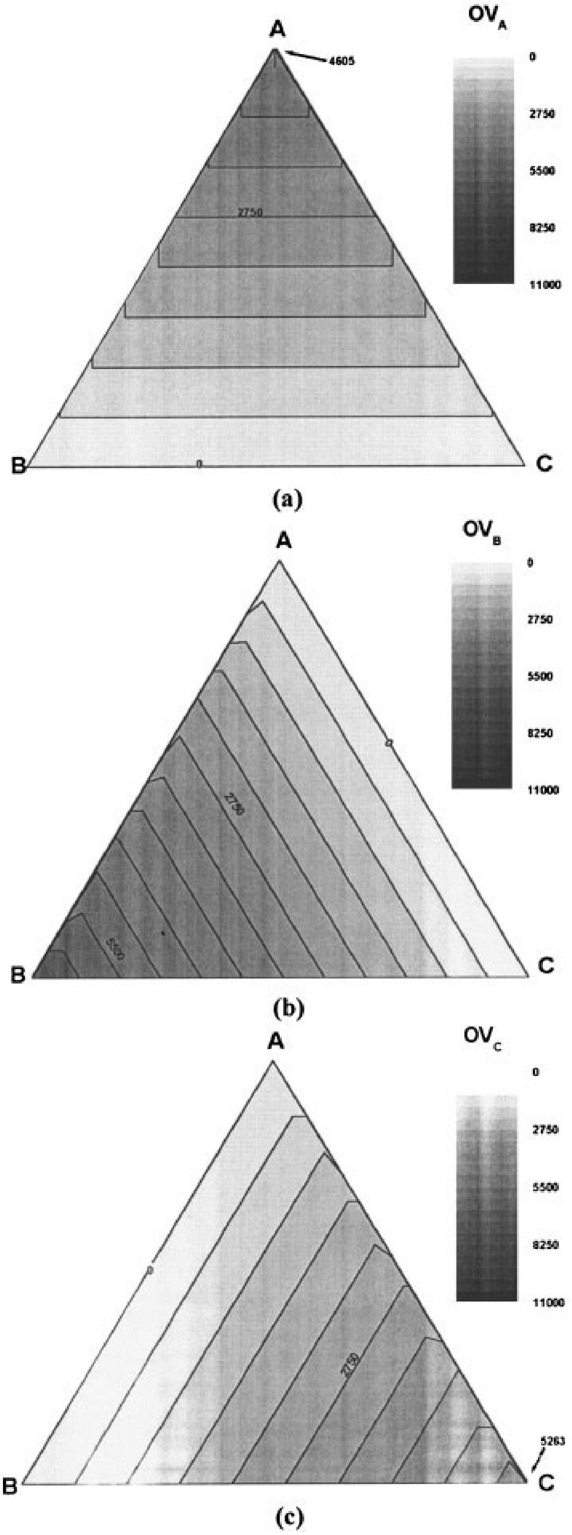


Figure 10. Variation of odor value as a function of the liquid composition and used to construct the perfumery ternary diagram of the test mixture: limonene, geraniol, and vanillin.

(a) OV_A, (b) OV_B, and (c) OV_C. The liquid is considered a nonideal solution.



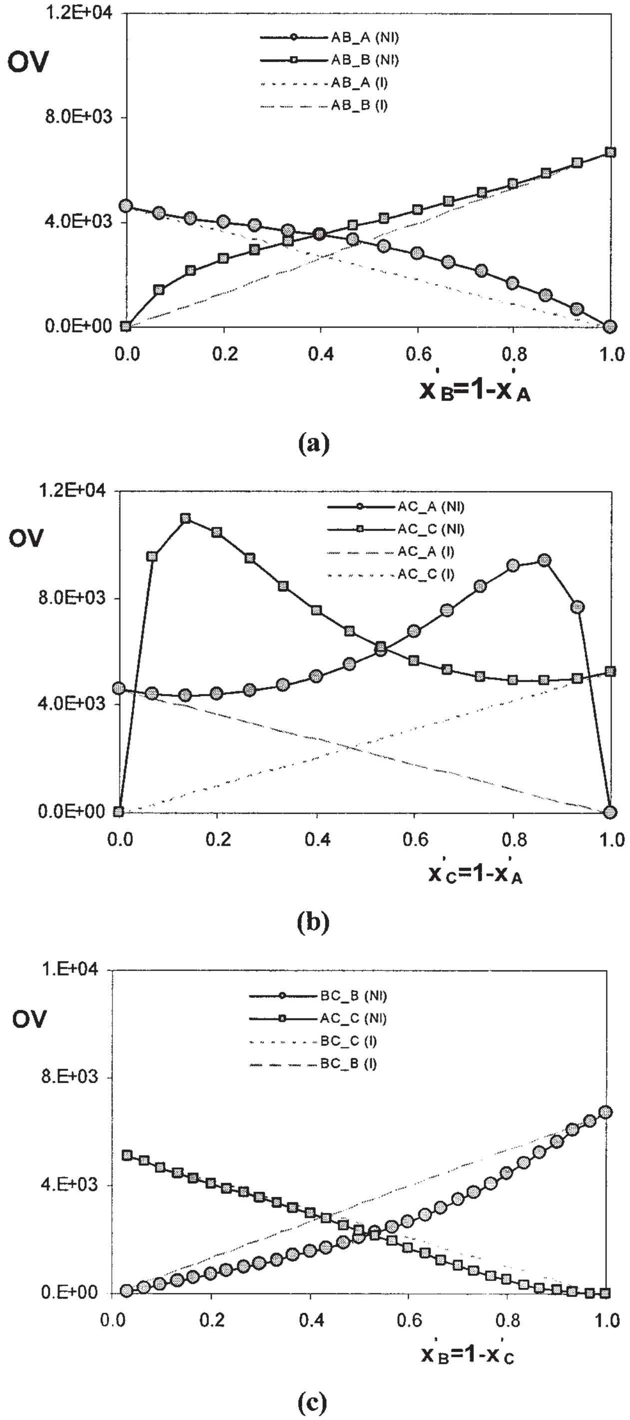
(a)

(b)

(c)

Figure 11. Variation of odor value as a function of the liquid composition and used to construct the perfumery ternary diagram of the test mixture: limonene, geraniol, and vanillin.

(a) OV_A, (b) OV_B, and (c) OV_C. The liquid is considered an ideal solution.



(a)

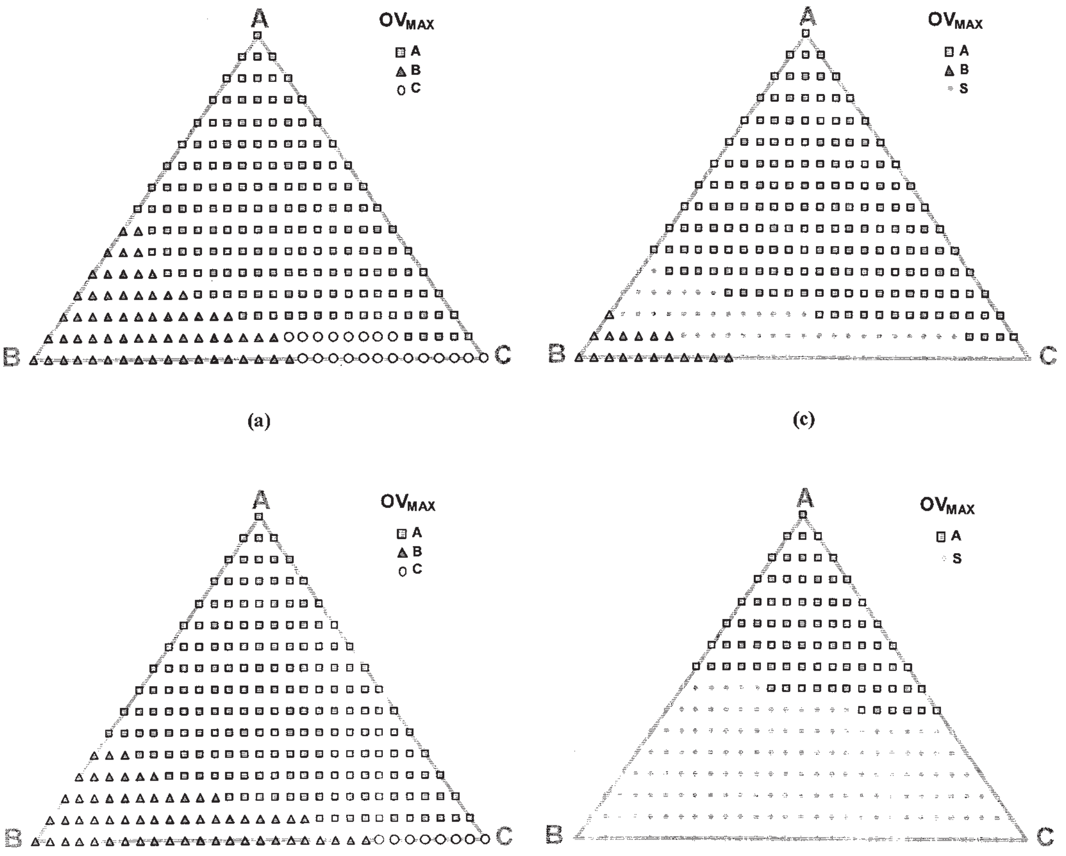
(b)

(c)

Figure 12. Variation of odor value as a function of the liquid compositions belonging to the edges of the PTD of the test mixture.

(a) Edge AB: limonene and geraniol; (b) edge AC: limonene and vanillin; (c) edge BC: limonene and vanillin.

higher, $x_S = 0.7$ (Figure 13c), there are points where $OV_{\max} = OV_S$. In this case, there is no possible solution where $OV_{\max} = OV_C$ and the values of points where $OV_{\max} = OV_B$ is very small. Finally, when $x_S = 0.9$ (Figure 13d) there are only two possibilities: points where $OV_{\max} = OV_A$ (top of the PTD, where x'_A is high) and points where $OV_{\max} = OV_S$.



(a) (c)

(b) (d)

Figure 13. Effect of ethanol (S) in the PTD of the test mixture.

(a) $x_S = 0.2$; (b) $x_S = 0.5$; (c) $x_S = 0.7$; (d) $x_S = 0.9$.

In perfumery, the effect of ethanol is important for two reasons. First, if we look to these figures from top to bottom (that is, Figures 13a, 13b, 13c, and 13d, respectively) we are simulating the addition of ethanol in the final part of the perfume composition. For a given composition of A, B, and C we can determine the maximum amount of ethanol that can be added to have the $OV_{\max}$ corresponding to the desired component, but not the ethanol. This happens, say, when sniffing perfume from a bottle: generally we want to smell the top note and never the ethanol. Second, if we look to these figures from bottom to top (that is, Figures 13d, 13c, 13b, and 13a, respectively), we are simulating the fast evaporation of ethanol, generally some seconds after application. When no ethanol exists we have to look to the PTD present in Figure 9a.

Design of a Perfume: How to Choose the Initial Mixture

As already mentioned, a typical perfume is composed of ethanol and a mixture of three types of fragrant components: top, middle, and base notes. When a perfume is applied, it is supposed that the different notes can be noticed "separately" after some time.

It was also considered above that a component *i* is perceived strongly by the human nose when its odor value OV_i in the headspace above the liquid volatile mixture is higher than that of the other components.

The composition that the perfumer can choose using the PTD concept depends mainly on what kind of perfume he/she intends to produce. Traditionally, there are two rules that are met to optimize a given perfume's behavior and for which the PTD can give an important contribution:

(1) The top note should be smelled strongly in the bottle or shortly after application. This rule can be translated as $OV_{\max} = OV_A$.

(2) The base note should be noticed long after application. It is used as a fixative of the top and middle notes and can last many hours (sometimes days or months), and can be chosen to determine the persistence of the perfume.

(3) Ethanol should not be noticed: $OV_S < OV_{\max}$.

This information can be taken directly from the PTD, thus avoiding a long trial-and-error procedure to find the optimal mixture.

Other important information can be taken from the PTD. If one wants to have a less-intense top note, a composition far from the corner A should be chosen. On the other hand, to have a high-intensity top note (such as fresh or citrus perfumes) a composition closer to corner A is used. Moreover, the PTD can be used to find the maximum fraction of ethanol to be used, for a given composition of concentrated perfume.

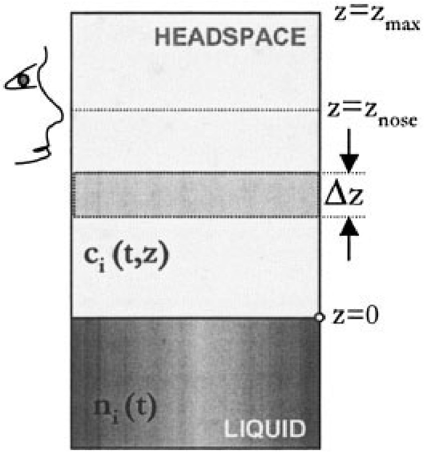


Figure 14. Scheme of the simulated gas (headspace)/ liquid perfume system.

Many other situations can be predicted using the developed PTD theory, for as many combinations there are to make one perfume. More than ever perfumers try combinations with as many innovative characteristics as possible.

Perfume Diffusion Model

A volume of liquid perfume that is evaporating in time and diffusing upward through the air above it (headspace) constitutes the following developed perfume model (Figure 14). It is considered that the liquid composition changes with time because a small amount of perfume is used. The composition of this liquid is represented by the number of moles of each species (n_i) and the headspace composition is represented by the concentration of each component (c_i) in the total air volume considered (V).

It is assumed that diffusion takes place in only one direction (z) and that the surrounding air is not soluble in the perfume mixture.

The following conditions for gas phase, liquid phase, and initial and boundary conditions, respectively, are assumed.

Gas phase

The gas phase is considered to be in a bottle of cylindrical shape and constant volume, where the perfume molecules diffuse in only one direction, z.

The solute mass in the gas phase is the result of a mass balance in the gas control volume $\Delta V = A\Delta z$, where V is the total volume of the gas phase and A is the interfacial gas–liquid area. Considering that the total volume of the gas phase V is constant, the gas phase is an ideal solution and that temperature and pressure are also constant, the unsteady-state mass balance can be represented by Fick's second law

$$\frac{\partial y_i}{\partial t} = D_{i,air}\frac{\partial^2 y_i}{\partial z^2} \tag{6}$$

where t represents time, z is the vertical distance to the gas–liquid interface, and $D_{i,air}$ is the diffusivity of solute i in the gas mixture. The value of $D_{i,air} = D$ was calculated using the method of Fuller et al.[22] (see Appendix B). This equation gives the concentration profile, that is, the variation of concentration with position and time. The value of $y_i = c_i/c_T$, where $c_T = P/RT$ is constant once the gas is considered ideal.

Liquid phase

It is considered that the concentration and volume of the liquid phase change with time t, as the multicomponent mixture vaporizes, and that the liquid solution is uniform for each value of t (perfectly stirred solution). The release of fragrant components (solutes) occurs as the result of the mass transfer from the liquid into the gas phase by diffusion, through the interfacial layer, as follows

$$\frac{dn_i}{dt} = -DAc_T\left.\frac{\partial y_i}{\partial z}\right|_{z=0} \tag{7}$$

where n_i is the number of moles of component i in the liquid.

Boundary conditions

Equation 6 is subjected to the following initial conditions:

Gas

$$t = 0 : y_i = y_{i0} = 0 \tag{8}$$

Liquid

$$t = 0 : n_i = n_{i0} \qquad \text{or} \qquad x_i = x_{i0} \tag{9}$$

where n_{i0} is the number of moles of component i in the initial perfume mixture and x_{i0} is the initial molar fraction of component i in the same initial perfume mixture.

For $t > 0$, it is assumed that the liquid phase is in equilibrium with the gas phase in contact with the interface ($z = 0$). The following boundary conditions were used

Gas

$$z = 0 : y_i = y_{i0} = \frac{\gamma_i P_i^{sat}}{P}x_i = \frac{\gamma_i P_i^{sat}}{P}\frac{n_i}{\Sigma\, n_i}$$

$$z > 0 : y_i = y_{i0} = 0 \tag{10}$$

Liquid

$$z = 0 : n_i|_t = n_i|_{t-1} - ADc_T\int_{t-1}^{i}\left.\frac{\partial y_i}{\partial z}\right|_{z=0}dt \tag{11}$$

where y_{i0} is the gas mole fraction of component i at the gas–liquid interface in equilibrium with component i in the liquid phase with mol fraction x_i.

Numerical solution

Model equations were numerically solved by using the software package PDECOL,[24] based on the method of lines, and uses orthogonal collocation in finite elements (OCFE) for the discretization of the space variable. For a ternary system there

Table 3. Initial Composition for the Gas–Liquid Case Study Perfume Mixture

Point	x_{A0}	x_{B0}	x_{C0}	γ_A	γ_B	γ_C	y_{Ao}	y_{Bo}	y_{Co}	OV_A	OV_B	OV_C
P_1	0.800	0.100	0.100	1.17	0.90	7.23	1.90E-03	2.38E-06	1.14E-07	4315	605	3808
P_2	0.667	0.167	0.167	1.40	0.63	3.86	1.89E-03	2.74E-06	1.02E-07	4297	698	3387
P_3	0.467	0.267	0.267	1.93	0.50	2.04	1.82E-03	3.53E-06	8.59E-08	4143	899	2864
P_4	0.200	0.400	0.400	3.19	0.52	1.18	1.29E-03	5.49E-06	7.43E-08	2934	1398	2475
P_5	0.733	0.200	0.067	1.22	1.13	3.25	1.82E-03	5.96E-06	3.42E-08	4133	1517	1141
P_6	0.733	0.167	0.100	1.25	0.91	4.30	1.86E-03	4.01E-06	6.78E-08	4226	1021	2262
P_7	0.733	0.133	0.133	1.27	0.73	5.14	1.89E-03	2.55E-06	1.08E-07	4305	650	3603
P_8	0.733	0.100	0.167	1.30	0.57	5.76	1.93E-03	1.49E-06	1.51E-07	4376	380	5050
P_9	0.733	0.067	0.200	1.31	0.43	6.19	1.95E-03	7.52E-07	1.95E-07	4437	191	6513
P_{10}	0.200	0.433	0.367	3.01	0.56	1.13	1.22E-03	6.33E-06	6.57E-08	2769	1610	2189

are six partial differential equations (PDEs) per section; they are discretized in the axial direction using 20 finite elements and two interior collocation points in each element; the resulting system of ordinary differential equations (ODEs) in the time variable is integrated with the solver GEARIB.[25]

For high volumes of liquid perfume phase, it is considered that the number of moles in the liquid phase is almost constant, that is, $n_i \cong n_{i0}$. This implies that the concentration in the gas phase at the gas–liquid interface, c_{i0}, is also constant. In this special situation, Eq. 6 has an analytical solution, by defining a new variable, $\zeta = z/\sqrt{4Dt}$,[26] resulting in

$$\frac{y_i - y_{i,gl}}{y_{i,\infty} - y_{i,gl}} = \operatorname{erf}(\varsigma)$$

where

$$\operatorname{erf}(\varsigma) = \frac{2}{\sqrt{\pi}} \int_0^{\varsigma} e^{-s^2} ds \tag{12}$$

One example in perfumery where this situation can occur is during the evaporation of perfume from its bottle. In this case, the volume is high and evaporation is almost negligible, and thus the concentration in the liquid phase is almost constant.

Case Study

The model was tested using a four-component mixture, representing one typical perfume. Again, this mixture consists of limonene, geraniol, and vanillin and is represented by a finite and small volume of liquid perfume, which is continuously changing with time.

Characterization of the case study system

Table 2 shows physical variables that are important for the studied evaporation model for each component and Table 3 shows the initial liquid compositions, x_{i0} for $i = A, B, C$ and the corresponding values of the liquid activity coefficients γ_i; the gas molar fraction at the gas–liquid interface in equilibrium with x_{i0} using Eq. 4, y_i; and the odor value of the headspace at this interface point, OV_i, for ten points, P_1–P_{10}. Points P_1 through P_4 are the initial values used to simulate the evaporation presented in Figures 15 and 16. These points are represented in the PTD of Figure 17. Points P_5 through P_9 are the initial values used to simulate the evaporation in Figure 18. These points are represented in the PTD of Figure 19. Finally, point P_{10} is the initial value for Figure 20 and is also represented in Figure 19.

For all points, an initial amount of test mixture was assumed: $n_{iT} = \sum n_i = 1$ mmol. The area of the gas–liquid interface, $A_{gl} = 0.071$ m^2; the pressure, $P = 10^5$ Pa; and the temperature, $T = 298.15$ K (25°C).

Effect of the top note

Figures 15a–15d show the effect of the amount of the top note A in the evaporation of the test mixture, corresponding to points P_1 through P_4 represented in Figure 17, for which the initial molar fraction of A, x_{A0} decreases and the molar fractions of B are equal to the molar fraction of C, $x_B = x_C$ (see Table 3). In all cases, the odor value of A is the maximum value, $OV_A = OV_{\max}$, during the first minutes, respectively: for point P_1 this happens over 69.6 min, for point P_2 over 49.2 min, for point P_3 over 26.4 min, and for point P_4 over 1.0 min. In all cases, after these times, $OV_C = OV_{\max}$ and component B never has a maximum odor value.

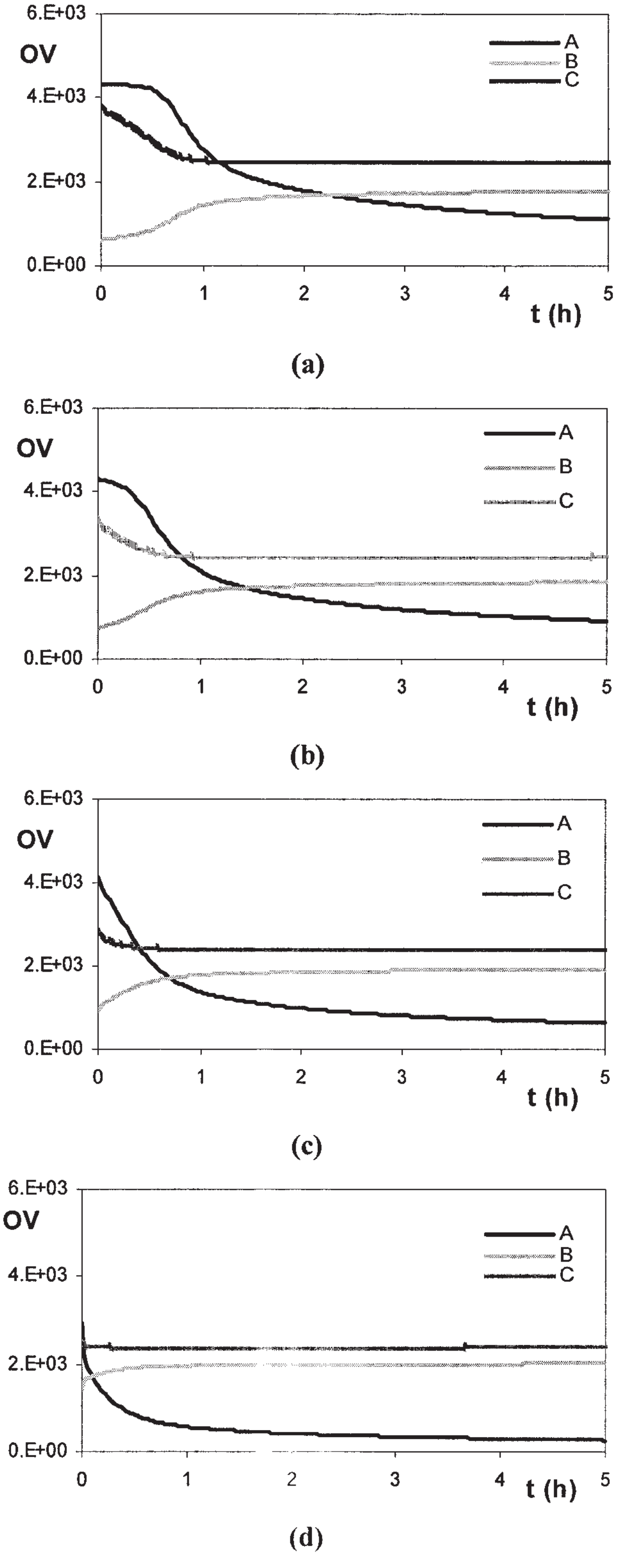
After component A has almost disappeared, it remains a solution of almost B and C. This solution is very stable, as we can observe in Figure 12c, where the odor values obtained for nonideal solutions are smaller than those obtained for the corresponding ideal solution. There are two polar molecules that tend to retain each other in the solution (γ_B and γ_C are <1 after component A has become a smaller amount) and their evaporation is very slow, because they act as fixatives of each other. Figure 16 shows, in a log timescale, the variation of odor value after some days. Component B disappears faster because its vapor pressure is higher, and the solution tends to pure C, the corner of the PTD. It can also be seen that the evaporation never passes through a point where component B has a maximum odor value. This happens, for example, when some perfumes are detected after being applied to clothes that are kept closed in a drawer or in a closet for a long time (although only the less volatile and more tenacious compounds are detected).

Figure 17 shows the location of the points P_1 through P_4 in the respective PTD, and also the "evaporation path" (lines starting from point P_i) through which two things happen during the evaporation of the test mixture:

(1) How the composition of the liquid changes

(2) What is the component that has the maximum odor value ($OV_{\max}$)

We can also see that if the starting point is P_1, the evaporation "path" passes through P_2, P_3, and P_4. This happens because the



(a)

(b)

(c)

(d)

Figure 15. Variation of odor value as a function of time using an initial composition represented by points (a) P_1, (b) P_2, (c) P_3, and (d) P_4.

volatility of A, P_{V_A}, is 77 times P_{V_B} and >12,800 times P_{V_C}. This substantial difference in volatility of the top note is the reason that the evaporation "path" is vertical in the PTD.

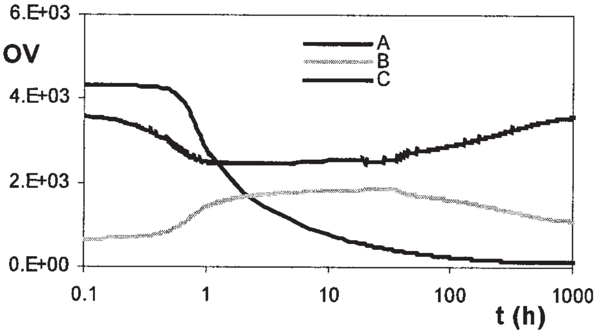


Figure 16. Variation of odor value as a function of time using an initial composition represented by point P_1 for a long time.

Effect of middle and base notes

Figure 18 shows the effect of the variation of middle and base notes, B and C, respectively, for a constant value of the top note, A, in the evaporation of the test mixture. Figures 18a–18d correspond to the evaporation of test mixtures for which the starting composition is represented by points P_5 through P_9, respectively, as indicated in Figure 19. In all cases the initial molar fraction of A is constant and equal to x_{A0} = 0.733, the molar fractions of B increases from points P_5 through P_9, and the molar fraction of C decreases from points P_5 through P_9 (see Table 3). These points belong to a horizontal line in the corresponding PTD (see Figure 19).

In the first minutes of evaporation, initial test mixtures corresponding to points P_5, P_6, and P_7 have a headspace with $OV_{\max} = OV_A$ (Figures 18a–18c), whereas initial test mixtures corresponding to points P_8 and P_9 have a headspace with $OV_{\max} = OV_C$ (Figures 18d and 18e). This behavior was previewed by the PTD theory, as observed in Figure 19.

When starting from the composition of point P_5, $OV_{\max} = OV_A$ during the first 55.2 min; after this time, $OV_{\max} = OV_B$. Starting from P_6, $OV_{\max} = OV_A$ during the first 70.8 min; after this time, $OV_{\max} = OV_B$. After a long time, $OV_{\max} = OV_C$ because the evaporation path followS the baseline of the PTD until corner C (pure C). Starting from P_7, $OV_{\max} = OV_A$ during the first 58.8 min but after this time, $OV_{\max} = OV_C$. In this last

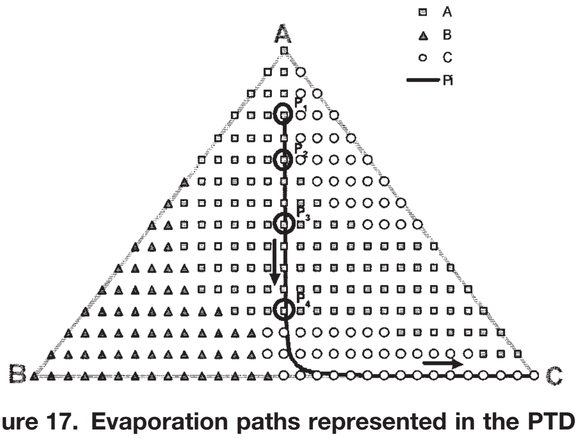
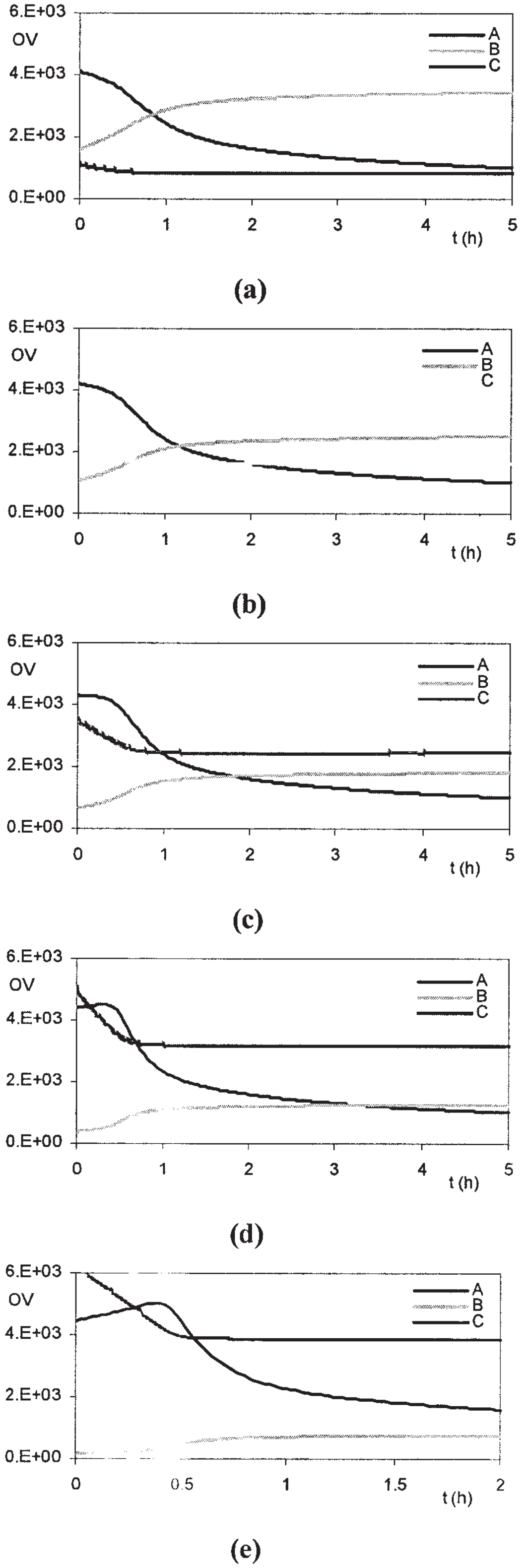


Figure 17. Evaporation paths represented in the PTD of the test mixture, for the starting compositions P_1, P_2, P_3, and P_4.



(a)

(b)

(c)

(d)

(e)

Figure 18. Variation of odor value as a function of time using an initial composition represented by points (a) P_5, (b) P_6, (c) P_7, (d) P_8, and (e) P_9.

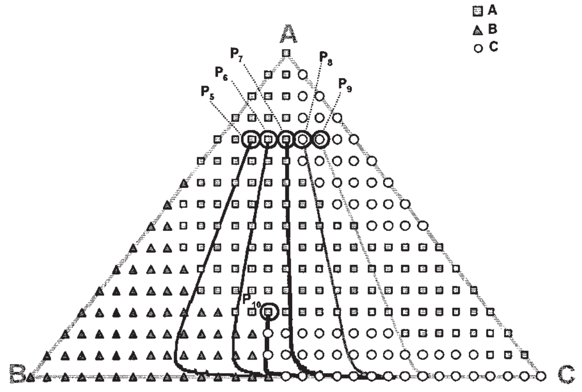


Figure 19. Evaporation paths represented in the PTD of the test mixture, for the starting compositions P_5, P_6, P_7, P_8, and P_9.

case, after limonene has decreased there was an intensification of the vanillin. Again, this effect was previewed in the corresponding PTD of Figure 19.

Figures 18d and 18e are special cases. Although the molar fraction of A is high, when starting from the composition of points P_8 and P_9, $OV_{\max} = OV_C$. This time is 10.8 min for point P_8 and 16.8 min for point P_9. After this value of time and during some time interval, $OV_{\max} = OV_A$. These intervals of time are from 10.8 to 33.6 min for point P_8 and from 16.8 to 22.8 min for point P_9. Finally, $OV_{\max} = OV_C$ and in both cases there are no points where $OV_{\max} = OV_B$.

Another special case is presented in Figure 20, where the composition of the initial test mixture is represented by point P_{10} (see Table 3, Figure 19). This evaporation path passes through *four* different phases: (1) $0 < t < 1.2$ min, $OV_{\max} = OV_A$; (2) $1.2 < t < 22.8$ min, $OV_{\max} = OV_C$; (3) 22.8 min $< t < 69.0$ h, $OV_{\max} = OV_B$; (4) $t > 69.0$ h, $OV_{\max} = OV_C$. This effect is well seen in the PTD of Figure 19.

Evaporation over distance

Figure 21 shows the concentration profiles for limonene (Figure 21a), geraniol (Figure 21b), and vanillin (Figure 21c) in the gas phase, for a distance between $z = 0$ m and $z_{\max} = 2$ m, over 2 h, obtained using Eq. 6.

The more volatile component—limonene—evaporates very quickly, as can be observed in the fast decrease of concentra-

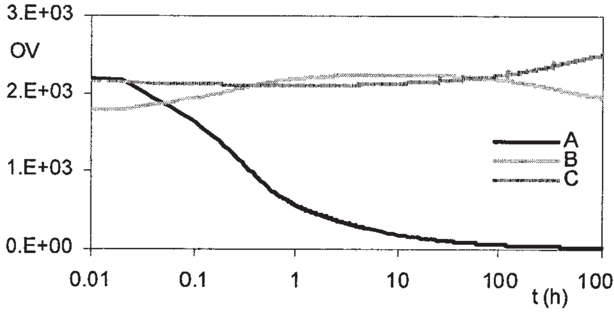


Figure 20. Variation of odor value as a function of time using an initial composition represented by point P_{10}.

tion at the interface, $z = 0$. The concentrations of geraniol and vanillin decrease more slowly because of the very low saturated vapor pressure, at the system temperature (25°C).

Notice that equilibrium at the gas–liquid interface and the remaining gas profiles are reached in a stagnant medium, where there is no convection.

Study of odor performance indexes

A study was performed concerning the odor value variation in time, at different distances, z_{nose} (see Figure 14), from the liquid mixture, that is: $z = 0$ m (gas–liquid interface) (Figure 22a), $z = 0.3$ m (Figure 22b), $z = 0.5$ m (Figure 22c), $z = 1$ m (Figure 22d), and $z = z_{\max} = 2$ m (Figure 22e). The composition of this liquid mixture is represented by point P_1 (see Table 3).

These figures can be used to illustrate the different aspects of odor performance (described in the Introduction and in Table 1): impact, tenacity, diffusion, and volume. Once more, it must be taken into account that this study is done for a small and finite volume of a perfume mixture.

Figure 22a shows the case $z = 0$ m (point at the gas–liquid interface) that represents, for example, directly smelling a perfume bottle or a paper bottler; the highest OV is that of limonene in the initial minutes, when compared to the OV of geraniol and vanillin. This means that limonene has a higher

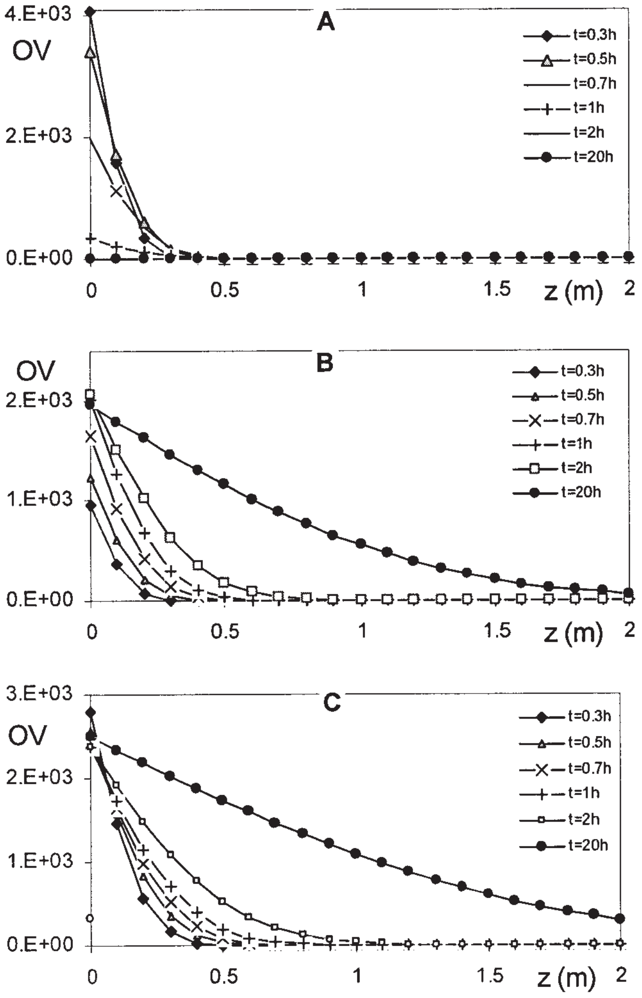


Figure 21. Odor value (OV) of each component in the gas phase, as a function of distance.

(a) Limonene, (b) geraniol, and (c) vanillin.

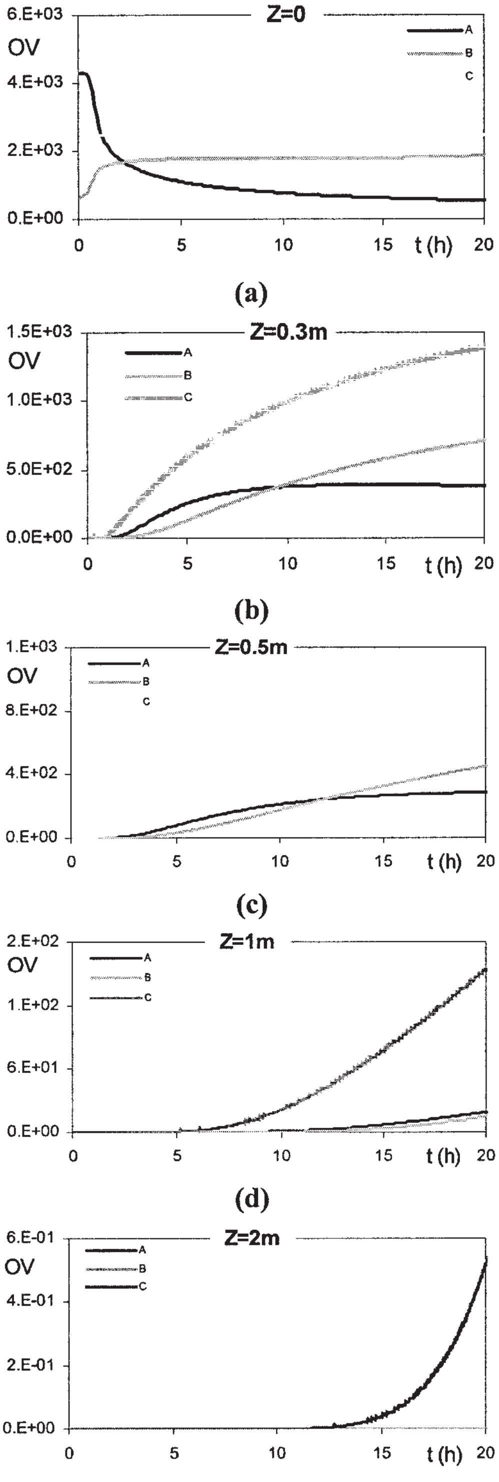


Figure 22. Variation of odor value as a function of time for different smelling distances.

(a) 0 m, (b) 0.3 m, (c) 0.5 m, (d) 1.0 m, and (e) 2.0 m.

impact than that of the other two components. However, after some time ($t > 1.2$ h), the highest OV is that of vanillin (and the OV of geraniol is similar), meaning that these two compounds—geraniol and vanillin—have a higher *tenacity* than that of limonene. They prevail in the air for a longer time because they are more persistent.

In Figures 22b and 22c we see that for a smelling distance of $0.3 < z < 0.5$ m the OV of vanillin has the highest value and the OV of limonene is still higher than that of geraniol until 9.8 and 12.1 h after application, respectively. This means that vanillin has a higher *diffusion* than that of the other two compounds; in fact, Table 2 indicates that the diffusion coefficient of vanillin in air is almost twice that of geraniol and of limonene. In these two figures and also in Figures 22d and 22e, it can be seen that the component that can reach longer distances after a long time is vanillin. Its effectiveness is higher than that of the other two compounds, thus having a higher *volume*.

Conclusions

A methodology of predicting the behavior of binary and ternary perfume mixtures in a solvent base was developed. This technique is based on the concept of *perfumery ternary diagrams* (PTDs), which allows a fast theoretical prediction of the headspace odor value (OV), for any combination of these materials in the corresponding liquid solution, without making too many experimental trial-and-error combinations. The concept of PTD was applied to the system limonene, geraniol, and vanillin. In some cases, one solvent (ethanol) was also used.

As we can see in the test example shown in this work it is not straightforward to look at the values of vapor pressure and threshold of one odorant component and define to which note—top, middle, or base—it belongs because it depends on the other molecules in the mixture. These observations mean that the choice of the right initial liquid mixture is very complex, given that there is always a simultaneous effect of molecular polarity and concentration of the component. However, the described methodology of PTD shows a simple way of studying the effect of odorant chemicals when they are simultaneously present in a mixture.

The same PTD concept also allows us to predict the evaporation path of: (1) the changes in the liquid phase; and (2) changes in the headspace, that is, which compound has a higher OV.

The simple diffusion model developed predicts the evaporation of the small perfume mixture as a function of time and distance from the application of the liquid sample. The results obtained were used to evaluate the performance criteria of the ternary perfume mixture in the headspace, based objectively on calculated odor values: impact, tenacity, diffusion, and volume, parameters that are normally established in an intuitive or experimental way, although considerably subjectively.

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Notation

A = interfacial gas–liquid area, m^2
c_i^g = concentration of component i in the headspace, mg/m^3
D = diffusivity of component i in the gas phase, m^2/s
M_i = molecular weight of i, g/mol
n_i = number of moles of component i, mol
OV_i = odor value of i
P = total pressure (Pa)
P_i^{sat} = saturated vapor pressure of component i, Pa
PTD = perfumery ternary diagram
R = ideal gas constant, Pa·m^3/mol/K
T = absolute temperature, K
t = time, s
Thr_i = odor threshold value of i, mg/m^3
V = total air volume, m^3
x_i = liquid-phase molar fraction of i
y_i = gas-phase molar fraction of component i
z = vertical distance to the gas–liquid interface, m
γ_i = activity coefficient of component i

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Appendix A: Calculation of the Activity Coefficients Using the UNIFAC Method

In this work, values of activity coefficients γ_i were calculated using the UNIFAC method, which is based on molecular group contribution for multicomponent mixtures.[22] This method takes into account the contribution arising from differences in molecular size and shape [the combinatorial part (C)] and the contribution arising from molecular interactions [the residual part (R)], expressed as

$$\ln \gamma_i = \ln \gamma_i^C + \ln \gamma_i^R \qquad \text{(A1)}$$

Determination of the combinatorial part

The combinatorial part is calculated using the following equation

$$\ln \gamma_i^C = \ln \frac{\phi_i}{x_i} + 5q_i \ln \frac{\theta_i}{\phi_i} + l_i - \frac{\phi_i}{x_i} \sum_j x_j l_j \qquad \text{(A2)}$$

where

$$l_i = 5(r_i - q_i) - (r_i - 1) \qquad \theta_i = \frac{q_i x_i}{\sum_j q_j x_j} \qquad \phi_i = \frac{r_i x_i}{\sum_j r_j x_j}$$

Table A1. UNIFAC Subgroups Volume and Area for Limonene

Molecule (i)	Subgroup (j)	Subgroup Number	Group Number	$\nu_j^{(i)}$	R_j	Q_j
Limonene	CH_3	1	1	2	0.9011	0.848
	CH_2	2	1	3	0.6744	0.540
	CH	3	1	1	0.4469	0.228
	$CH{=}C$	8	2	1	0.8886	0.676
	$CH_2{=}C$	7	2	1	1.1173	0.988

Table A2. UNIFAC Subgroups Volume and Area for Geraniol

Molecule (i)	Subgroup (j)	Subgroup Number	Group Number	$\nu_j^{(i)}$	R_j	Q_j
Geraniol	CH_3	1	1	4	0.9011	0.848
	CH_2	2	1	2	0.6744	0.540
	$CH{=}C$	8	2	2	0.8886	0.676
	OH	15	5	1	1.000	1.200

Table A3. UNIFAC Subgroups Volume and Area for Vanillin

Molecule (i)	Subgroup (j)	Subgroup Number	Group Number	$\nu_j^{(i)}$	R_j	Q_j
Vanillin	ACH	10	3	3	0.5313	0.400
	AC	11	3	2	0.3652	0.120
	ACOH	18	8	1	0.8952	0.680
	CHO	21	10	1	0.9980	0.948
	CH_3O	25	13	1	1.1450	1.088

Parameters r_i and q_i are calculated for each molecule as the sum of the group volume and area parameters, R_j and Q_j, given in Tables A1, A2, A3, and A4, as follows

$$r_i = \sum_j \nu_j^{(i)} R_j \qquad \text{and} \qquad q_i = \sum_j \nu_j^{(i)} Q_j$$

where $\nu_j^{(i)}$ is the number of groups of type j in molecule i.

Determination of the residual part

The residual part is calculated using the following equation

$$\ln \gamma_i^R = \sum_{\substack{k \\ \text{all groups}}} \nu_k^{(i)} [\ln \Gamma_k - \ln \Gamma_k^{(i)}] \qquad \text{(A3)}$$

where Γ_k is the group residual activity coefficient and $\Gamma_k^{(i)}$ is the residual activity coefficient of group k in a reference solution containing molecules only of type i

$$\ln \Gamma_k = Q_k \left[1 - \ln\left(\sum_m \theta_m \psi_{mk} \right) - \sum_m \frac{\theta_m \psi_{km}}{\theta_n \psi_{nm}} \right] \qquad \text{(A4)}$$

Equation A4 also holds for $\ln \Gamma_k^{(i)}$. In this equation, θ_m is the area fraction of group m, and the sum is over all different groups, as follows

$$\theta_m = \frac{Q_m X_m}{\sum_n Q_n X_n}$$

where X_m is the mole fraction of group m in the mixture. The group interaction parameter ψ_{mn} is given by

$$\psi_{mn} = \exp\left(-\frac{a_{mn}}{RT} \right)$$

Parameters a_{mn} and a_{nm} (in Kelvin) are shown in Table A5 for the groups used in this work: the system limonene, geraniol, vanillin, and in some cases ethanol.

Table A4. UNIFAC Subgroups Volume and Area for Ethanol

Molecule (i)	Subgroup (j)	Subgroup Number	Group Number	$\nu_j^{(i)}$	R_j	Q_j
Ethanol	CH_3	1	1	1	0.9011	0.848
	CH_2	2	1	1	0.6744	0.540
	OH	15	5	1	1.000	1.200

Table A5. UNIFAC Group–Group Interactions Parameters (in K)

u_{mn}	$n =$ 1	2	3	5	8	10	13
$m =$							
1	0	86.020	61.130	986.500	1333.000	677.000	741.400
2	−35.360	0	38.810	524.100	526.100	448.800	214.500
3	−11.120	3.446	0	636.100	1329.000	347.300	32.140
5	156.400	457.000	89.600	0	−259.700	441.800	28.060
8	275.800	217.500	25.340	−451.600	0	0	0
10	505.700	56.300	23.390	−404.800	0	0	304.100
13	83.360	26.510	52.130	237.700	0	−7.838	0

Appendix B: Calculation of the Diffusion Coefficients Using the Method of Fuller et al.

In this work, because the components are very diluted in air, the diffusion coefficient of each component i in air j was estimated using the correlation of Fuller et al.[22] for a given pressure and temperature, using the following equation

$$D'_{ij} = CT^{1.75}\frac{\sqrt{\dfrac{M_i + M_j}{M_iM_j}}}{P\{\sqrt[3]{V_i} + \sqrt[3]{V_j}\}^2} \tag{B1}$$

with T in Kelvin (K), P in Pascal (Pa), M_i and M_j in grams per mole (g/mol), and $C = 1.1013 \times 10^{-2}$; D'_{ij} is in m^2/s. The terms V_i and V_j are molecular diffusion volumes and are calculated by summing the atomic contribution in Table B1 (only the values used in this work). For example, the molecular formula of ethanol is C_2H_6O. Then, $V_{\text{ethanol}} = 2V_C + 6V_H + 1V_O$.

Table B1. Atomic and Molecular Diffusion Volumes Increments

m	V_m
C	15.9
H	2.31
O	6.11
Aromatic ring	−18.3
Air	19.7

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