Perfumery Quaternary Diagrams for Engineering Perfumes

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The Perfumery Ternary Diagram (PTD®) methodology predicts the headspace odor character and intensity of fragrant mixtures, applying the concept of odor value (OV) to multi-component systems. This methodology is extended here to quaternary and quinary odorant systems through the use of tetrahedric diagrams. To present this new methodology, the effect of different base notes in quaternary systems of the type (limonene + geraniol + base note + ethanol) and its forming ternary subsystems has been studied. Base notes selected were: vanillin, tonalide, ambrox, and galaxolide. The Perfumery Quaternary Diagrams (PQD) of the mixtures studied show the different headspace odor character, with ambrox and galaxolide dominating most of the composition spectrum (OV_{max}). The methodology was also applied to the quinary mixture (limonene + geraniol + vanillin + tonalide + ethanol), and the effect of different concentrations of tonalide on the headspace is presented. © 2009 American Institute of Chemical Engineers *AIChE J,* 55: 2171–2185, 2009

Keywords: product engineering, fragrance, quaternary diagram, odor value, headspace

Introduction

The development of novel and innovative products to meet consumer needs, comprises two interrelated fields of scientific knowledge in chemical engineering: what we want to produce, product engineering, and how we should produce it, process engineering.[1–4] The classical view of process engineering alone was the general path followed by chemical engineers, though it might not be sufficient on its own for product-design today.[5] Although process engineering has attained a high degree of scientific maturity over the last half century, product engineering is still growing and maturing its basis in the chemical engineering fields. Within the last decades, the chemical industry has switched from the capital intensive bulk chemicals towards the manufacture of high added-value products.[6] Hitherto, development was mainly driven by technology expansion, now it is market-driven. New trends in market innovations for the development of new products and the information technology and computational chemistry have been growing. Product engineering demands that engineers know about scientific fundamentals and technical aspects but also about customer needs and marketing.[7,8] It allows the extension of the chemical engineering methodology to product-oriented engineering, following the triplet of "molecular processes-product-process,"[9] or more recently the equation ChemEng = M^2P^2Eng (M for Molecular and Materials, P for Process and Product).[10] The objective is to develop new products that are more effective to satisfy customers' needs and/or less threatening to the environment.

The application of product engineering to Flavors and Fragrances has the crucial objective of implementing technical and scientific knowledge into a so far empiric and experimental area. In fact, the creation of perfumes is still today an art, developed by well trained perfumers, within a variety of flavor and fragrance substances. It is highly specialized and individualistic. A wide palette of raw materials in the order of thousands and differing greatly in chemical

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Table 1. Properties of the Odorant Components

	Name	Molecular formula	M_i (g/mol)	P_i^{sat} (Pa)	Thr_i (g/m^3)	$\frac{P_i^{\text{sat}} \cdot M_{wi}}{\text{Thr}_i \cdot R \cdot T}$
A	Limonene*	$C_{10}H_{16}$	136.2	20.5×10^{1}	2.45×10^{-3}	4.60×10^{3}
B	Geraniol*	$C_{10}H_{18}O$	154.3	26.7×10^{-1}	2.48×10^{-5}	6.70×10^{3}
C	Vanillin*	$C_8H_8O_3$	152.2	16.0×10^{-3}	1.87×10^{-7}	5.25×10^{3}
	Tonalide*	$C_{18}H_{26}O$	258.4	67.0×10^{-6}	1.82×10^{-5}	3.84×10^{-1}
	Ambrox	$C_{16}H_{28}O$	236.4	$12.5 \times 10^{-1\dagger}$	$2.90 \times 10^{-6\ddagger}$	4.11×10^{4}
	Galaxolide	$C_{18}H_{26}O$	258.4	$72.7 \times 10^{-3\S}$	$6.30 \times 10^{-7\P}$	1.20×10^{4}
S	Ethanol*	C_2H_6O	46.0	72.7×10^{2}	5.53×10^{-2}	2.44×10^{3}

*From Calkin & Jellinek.[22]
†From Chemspider Database.[34]
‡From Leffingwell & Associates.[25]
§From Balk and Ford.[35]
¶From Fráter et al.[36]

composition and physicochemical properties, are available to perfumers. They are typically a combination of chemicals, extracts, essential oils, and distillates that the perfumer needs to selectively choose, building the body of its perfume.[11] The experience and olfactory perception combined with creativity and inspiration are the key qualities of an experienced perfumer. After trying a number of fragrance combinations with trial and error experiments, these experts in the art of perfumery may reach a successful and unique scent.[12] This way, the key for perfume formulation is the blending of different fragrant species with the main objective of producing an esthetically pleasant scent for consumers. It is a fact that fragrances are proving increasingly popular though, even today, the creation of a perfume is a lengthy and costly process.

Products containing flavors or fragrances are complex systems where multi-component interactions between the different odorant species exist. The physical and chemical properties of the components (like molecular structure, polarity, volatility and odor strength) are factors that influence the odor behavior of a perfume. It is noteworthy to mention that the structure-odor relationship is still an issue that continues to fascinate but also frustrate fragrance chemists and psychophysicists.[13]

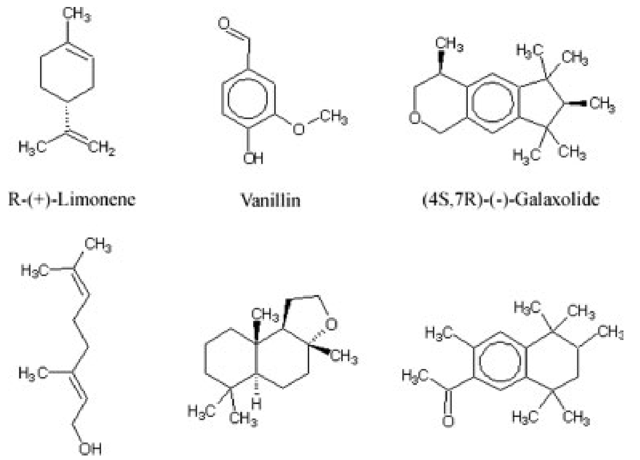

Figure 1. Chemical structures of the fragrant components.

Recently, a scientific methodology for the prediction of the odor characteristics and odor intensity in the headspace above a liquid perfume mixture of three fragrant species and a matrix of one or more components was developed.[14,15] The concept of the Perfumery Ternary Diagram (PTD®) results from the combination of the classic perfume pyramid structure and the ternary phase diagrams, especially used in the fields of engineering and physical-chemistry. Carles[16] considered a tripartite structure for perfume formulation, with three types of fragrant notes: top, middle, and base notes. The top notes are the most volatile fragrances and so, hypothetically, they would be smelled in first place, like in the first minutes after application. Then, the perceived odor would evolve into the middle or heart notes as their presence should be noticed after the top notes have disappeared, lasting for hours. The base notes would be the last to be perceived as they have the lowest volatility and so remain longer in the liquid phase. These fragrance notes are often used as fixatives as they can change the tendency of evaporation of both the top and middle notes. The base notes are smelled only some hours after application, persisting for days or

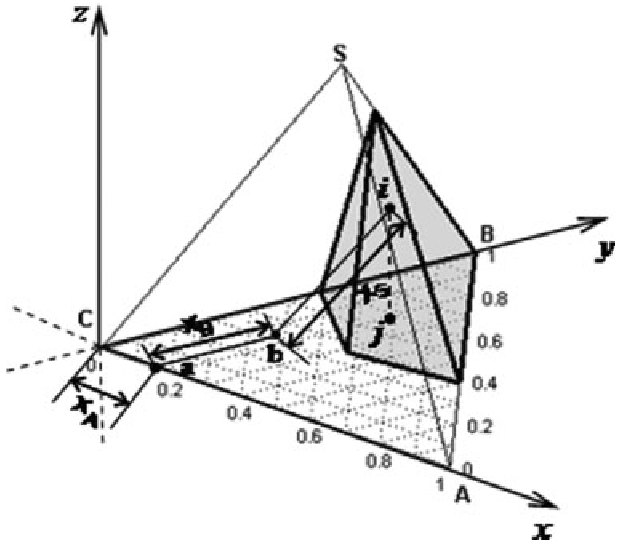

Figure 2. Relationship between the perfumery quaternary diagram (PQD) and the engineering quaternary diagrams.

Table 2. Conditions of the Nonlinear System for the PBS, PTL, and PQP

PBS: $j+k$ $\mathrm{OV}_i = \mathrm{OV}_k = \mathrm{OV}_{\max}$	PTL: $j+k+l$ $\mathrm{OV}_j = \mathrm{OV}_k = \mathrm{OV}_l = \mathrm{OV}_{\max}$	PQP: $j+k+l+m$ $\mathrm{OV}_j = \mathrm{OV}_k = \mathrm{OV}_l = \mathrm{OV}_m = \mathrm{OV}_{\max}$
$\gamma_j x_j K_j = \gamma_k x_k K_k$	$\gamma_j x_j K_j = \gamma_k > x_k K_k$	$\gamma_j x_j K_j = \gamma_k x_k K_k$
	$\gamma_k x_k K_k = \gamma_l x_l K_l$	$\gamma_k x_k K_k = \gamma_l x_l K_l$
		$\gamma_l x_l K_l = \gamma_m x_m K_m$
$\sum_{i=1}^{N} x_i = 1$	$\sum_{i=1}^{N} x_i = 1$	$\sum_{i=1}^{N} x_i = 1$
$0 \leq x_i \leq 1$	$0 \leq x_i \leq 1$	$0 \leq x_i \leq 1$

even months. The proposed pyramid structure suggested the following proportions for each type of fragrance note: top, 15–25%; middle, 30–40%; and base, 45–55%.[13,17–19] This traditional view holds that perfumes can be viewed as blends, composed of top, middle, and base notes. There are even some authors who consider the existence of some bridge notes that would make a smoother transition between the different scent notes. However, this is clearly an over-simplification because all fragrant species evaporate simultaneously but at different rates (which depend on volatility, composition, molecular structure, and molecular interactions). Thus, it is expected that they would be perceived by the human nose simultaneously but in different intensities, depending on how the receptor cells located in the nose interpret the odorant molecules.[20] Odor intensity may depend, also, on how far the perfume liquid mixture is from the nose, once it may come into account the diffusivity of each fragrance note in the air. Also of importance is the ''sampling'' mechanism of the human nose (sniffing). This last factor provokes that the fragrant components arrive to the human olfaction system in bursts, with rather important variations in composition.[21] This way, what is smelled is a blend of fragrances where the one having the highest intensity might probably be noticed more.[14,22]

In this work, the methodology, previously used for ternary fragrant mixtures, is extended to quaternary (or eventually, quinary) mixtures using tetrahedric diagrams, the Perfumery Quaternary Diagrams (PQD). The transformation from tetrahedric to Cartesian coordinates is given, and the use of the diagram to present the headspace odor character is shown. As an example, the effect of different base notes on quaternary perfume mixtures is studied. The application to quinary mixtures is also presented, showing the effect of two base notes on a quinary perfume mixture.

Methodology

The odor strength or odor intensity can be described by a quantitative parameter known as the odor value (OV). The OV[22] is defined as the ratio between the concentration of an odorant species i in the headspace, C_i^{g}, and its concentration odor threshold in air, Thr_i (both in g/m^3):

$$\mathrm{OV}_i = \frac{C_i^{\mathrm{g}}}{\mathrm{Thr}_i} \tag{1}$$

Only the volatiles with an OV higher than unity may be detected by the human nose and thus contribute to the overall scent. In what concerns to the odor threshold, it is important to consider both the detection ($\mathrm{Thr}_i^{\mathrm{d}}$) and the recognition ($\mathrm{Thr}_i^{\mathrm{r}}$) thresholds of a fragrant component i. The first gives the minimum concentration of the fragrance to be detected by the human nose, while the latter represents the lowest odorant concentration at which it is possible to recognize it.[14,22,23] The latter is perhaps the most significant, although it is not always an easy task to recognize what is smelled even when its identity is known.[23] Because of that, detection thresholds are more reliable than recognition thresholds and thus, the formers were selected to be used in this work. Extensive compilations of odor threshold values can be found in the literature for odorant substances in air and water.[22,24,25]

Using some basic thermodynamics, the concentration of the different fragrant components in the gas phase above the liquid, C_i^{g}, can be calculated from the general equation for vapor-liquid equilibria:

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

where y_i and x_i stand for the vapor and liquid mole fractions of component i, ϕ_i and γ_i for the vapor and liquid activity coefficients of component i, respectively, P for the total pressure and P_i^{sat} for the saturation pressure of pure component i. At atmospheric pressure, ideal gas behavior for the gas phase can be assumed and thus, $\phi_i = 1$. In this way, the concentration of odorant species in the headspace C_i^{g} can be calculated as:

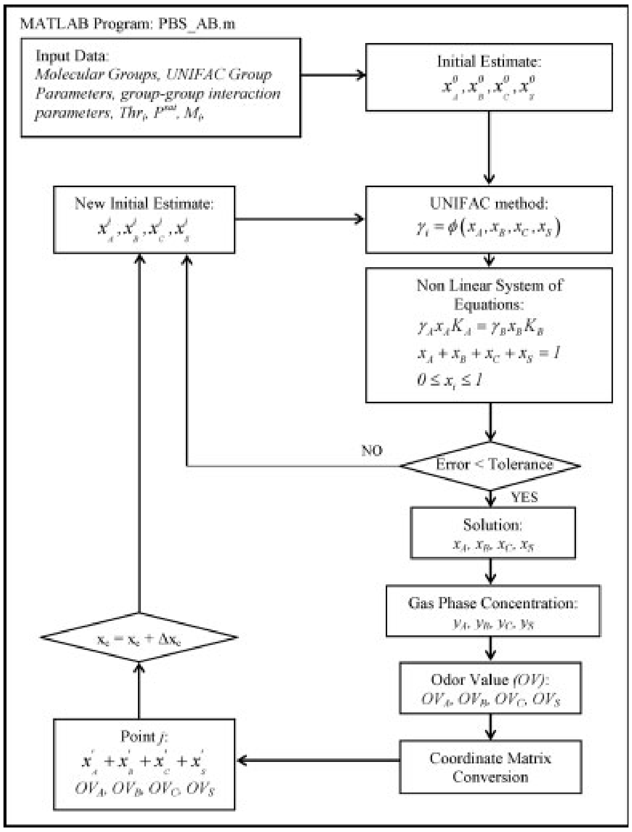

Figure 3. Iterative method for the resolution of the non-linear system of equations for the case of a PBS between a top note (A) and a middle note (B).

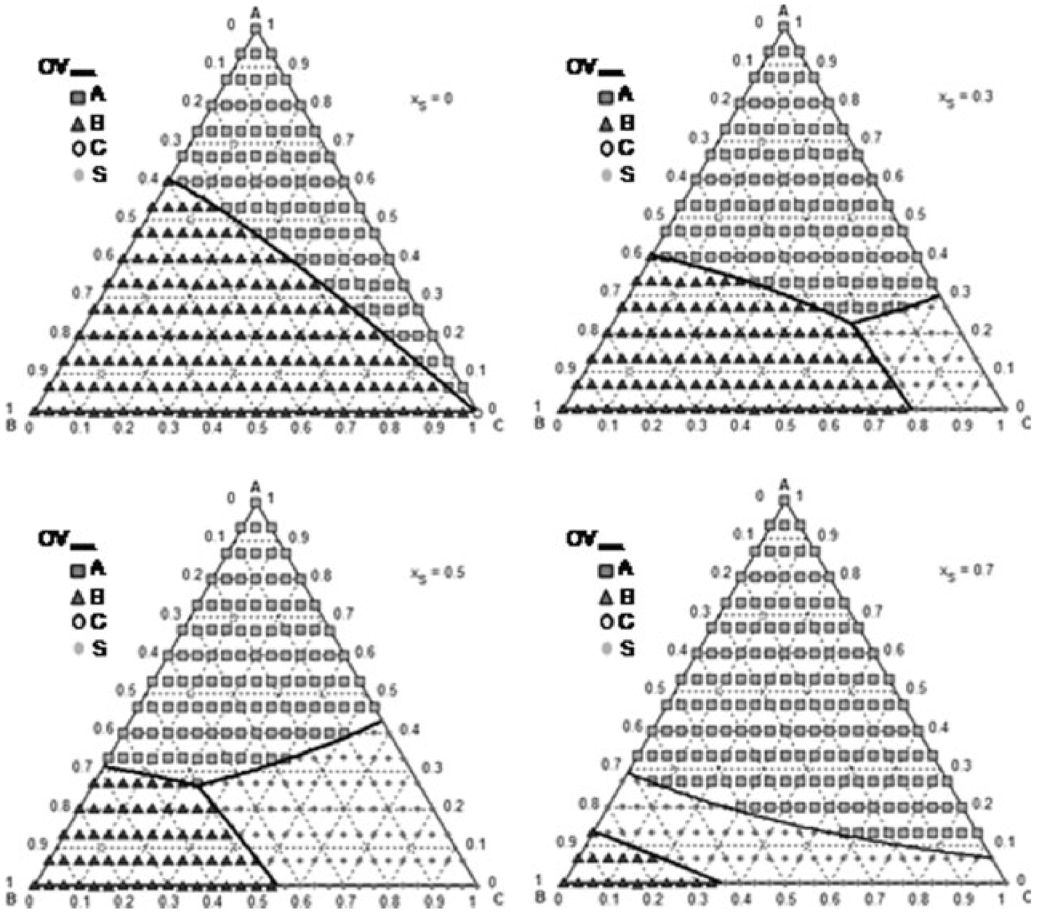

Figure 4. PTD® for different initial mole fractions of solvent in the quaternary system of limonene (A), geraniol (B), tonalide (C), and ethanol (S).

$$C_i^{\mathrm{g}} = \frac{y_i M_i P}{RT} = x_i \gamma_i \frac{M_i P_i^{\mathrm{sat}}}{RT} \tag{3}$$

where M_i is the molecular mass of component i, R is the universal gas constant, and T is the absolute temperature.

The activity coefficient (γ_i) accounts for deviations of the liquid phase from ideal behavior, reflecting the affinity and interactions of the molecule with its surrounding medium. For an ideal solution $\gamma_i = 1$, while for a nonideal solution $\gamma_i \neq 1$, evidencing deviations from the Raoult's Law. In a perfume mixture, γ_i can be understood as a measure of the tendency of a molecule i to stay in the liquid medium or to be "pushed out" into the headspace. If $\gamma_i > 1$, the concentration of the fragrant component i in the headspace will be higher than for an ideal solution, that is, the molecules will be "pushed out" from the solution into the gas phase. When $\gamma_i < 1$, lower concentrations of the odorant species i will be found in the headspace and so there is a higher retention of these odorous molecules into the liquid phase due to a higher affinity to the surrounding medium.[14]

Combining Eqs. 1 and 3, the OV of each fragrant component can be calculated as:

$$\mathrm{OV}_i = \gamma_i x_i \left(\frac{P_i^{\mathrm{sat}} M_i}{\mathrm{Thr}_i}\right)\left(\frac{1}{RT}\right) \tag{4}$$

Thus, the odor intensity of each species can be obtained from pure component data (composition in the liquid phase, molecular weight, saturated vapor pressure, and odor threshold) together with the activity coefficient (γ_i). This activity coefficient can be calculated from experimental vapor-liquid equilibrium data or with a suitable predictive method. In our calculations, we have used the UNIFAC method[26,27] for prediction of the vapor-liquid equilibrium and the activity coefficients of the fragrance components.

When considering a perfume mixture with N fragrant components, N different odor values can be calculated in the headspace, each one corresponding to a single fragrant species i. To account for the odor perception of multi-component mixtures, the Strongest Component model has been adopted: among all the odorant components present in the gas phase, the one that is strongly perceived and recognizable by the human nose is the one having the highest odor value, although there is a mixture of perceived scents in the air[28,29]:

$$\mathrm{OV}_{\max} = \max\{\mathrm{OV}_i\}, i = 1, \ldots, N \tag{5}$$

In this work, we will consider ternary to quinary perfume mixtures only, and thus Eq. 5 reduces to:

$$\mathrm{OV}_{\max} = \max\{\mathrm{OV}_{\mathrm{A}}, \mathrm{OV}_{\mathrm{B}}, \mathrm{OV}_{\mathrm{C}}, \mathrm{OV}_{\mathrm{D}}, \mathrm{OV}_{\mathrm{S}}\} \tag{6}$$

where the subscripts are defined as: A—top note, B—middle note, C and D—base notes, and S—solvent.

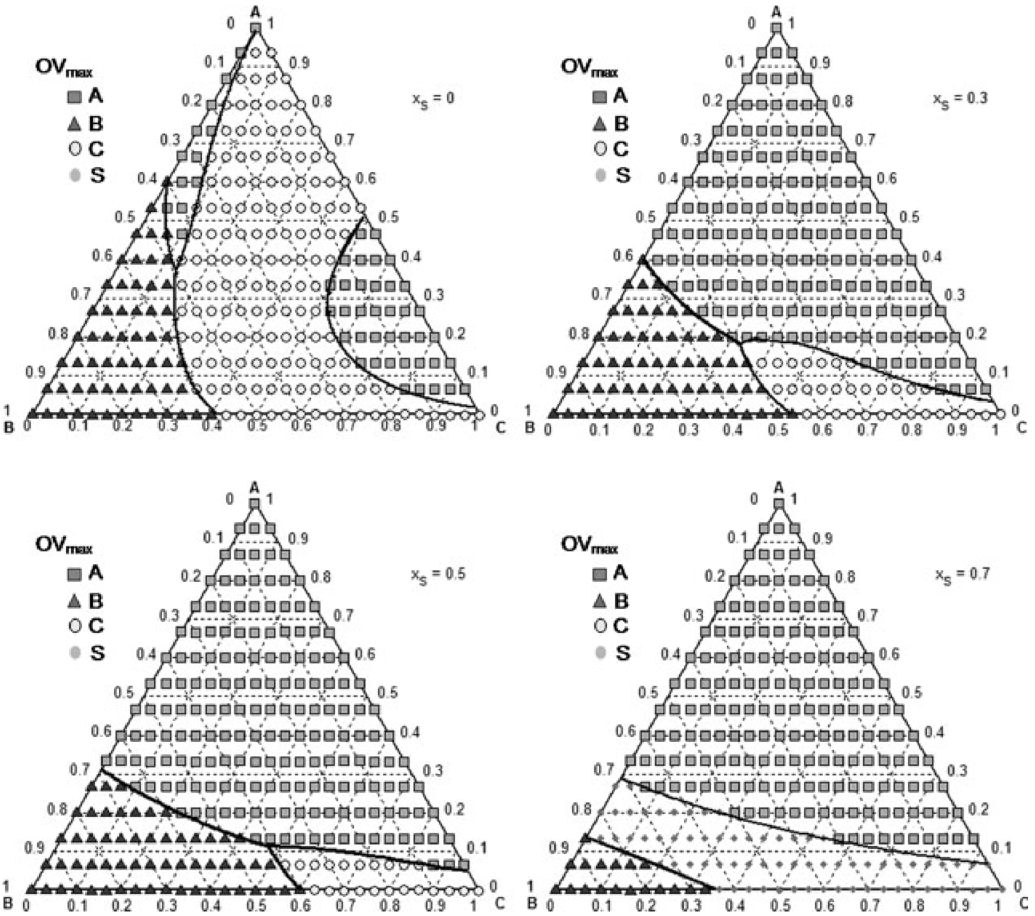

Figure 5. PTD® for different initial mole fractions of solvent in the quaternary system of limonene (A), geraniol (B), vanillin (C), and ethanol (S).

It is important to highlight that the methodology presented here is not limited to the models used. That is, different models may be used to calculate the activity coefficient (correlations such as NRTL[30] or UNIQUAC,[31] or predictive methods like ASOG[32] or COSMO-RS[33]), or to evaluate the odor intensity and perception. The models used here were selected attending to their simplicity and, most especially, the widespread availability of data needed.

Perfumery ternary diagram

The concept of PTD®[14,15] relies on the engineering ternary diagrams, where it is possible to express singular compositions by a set of ternary fractions (molar, volume, weight). In a ternary mixture, the three components, $i = A, B, C$, represent the three types of fragrant notes used in a perfume formulation: A—represents the top note, B—the middle note, and C—the base note. Some of the test mixtures considered the presence of ethanol (solvent, S) in order to differentiate from the concentrated perfume mixtures and also to simulate a real perfume formulation. For these four component systems, it is possible to define a pseudo-ternary composition using a solvent-free basis, by recalculating the ternary molar fractions of the three other components as follows:

$$x'_A = \frac{x_A}{x_A + x_B + x_C}, \quad x'_B = \frac{x_B}{x_A + x_B + x_C}, \quad x'_C = \frac{x_C}{x_A + x_B + x_C} \tag{7}$$

where x'_i indicates a pseudo-ternary composition for each of the three fragrant components (A, B, C) in the quaternary system (A, B, C, S). The studied odorant components, their chemical structures and their physical and sensorial properties are presented in Table 1 and Figure 1.

The PTD® shows which is the most strongly perceived component, the one having the maximum OV ($\mathrm{OV}_{\max}$), for a ternary perfume mixture (or even a quaternary mixture if one of the compositions is fixed). The calculation of the OV using Eq. 4 allows mapping the whole PTD® with different odor zones where the relation $\mathrm{OV}_{\max} = \mathrm{OV}_i$ for $i = A, B, C$ is valid. These odor zones represent the composition range where each odorant component dominates among all others. They are limited by the Perfumery Binary Lines (PBL) that corresponds to compositions where two different notes have the same and maximum OV. The Perfumery Ternary Points (PTP) are found at the intersection of the PBLs, where $\mathrm{OV}_A = \mathrm{OV}_B = \mathrm{OV}_C = \mathrm{OV}_{\max}$. The procedure to calculate the PBL and Perfumery Ternary Points has been explained before.[15]

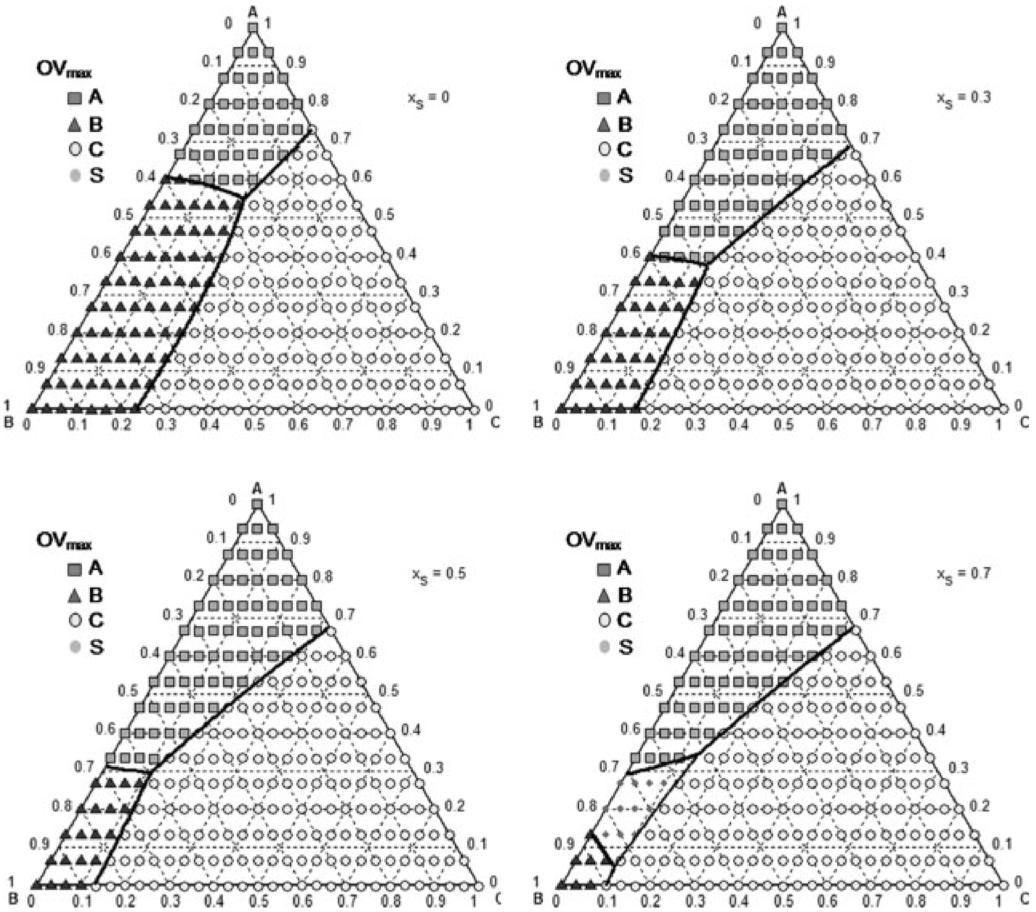

Figure 6. PTD® for different initial mole fractions of solvent in the quaternary system of limonene (A), geraniol (B), galaxolide (C), and ethanol (S).

Extension of the PTD® to the PQD

As it was previously indicated, perfumes are commonly formulated as the combination of three types of notes (top, middle, and base) with a solvent matrix. The PTD® is used to represent the odor character of a ternary fragrant mixture, and it can also be used for quaternary mixtures if the fourth component has a fixed composition (and so, the other components are represented as in a solvent-free basis). But in that way, the complete behavior of the quaternary mixture is not shown. Thus, an extension of the PTD® methodology for quaternary mixtures is needed, so that the odor character of all possible mixtures can be seen.

The regular tetrahedron has been commonly used in phase equilibria thermodynamics to represent quaternary systems. This is so because of an important property of the regular tetrahedron (similar to the equilateral triangle): the sum of the distances from a given point inside the tetrahedron to its four faces (*e.g.*, the sum of the heights of that point in respect to each face) is a constant value, *k*, and equal to the total height of the tetrahedron[37]:

$$\sum_i h_i = k \tag{8}$$

Thus, if we build a tetrahedron of unit length edges (so the edges can be used as axis to denote fraction compositions), we can use it to represent the composition (in mole, mass or volume fraction) of any quaternary system, given that:

$$\sum_i x_i = 1 \propto \sum_i h_i \tag{9}$$

where x_i stands for the composition of component *i* (in mole, mass, or volume fraction) and h_i for the height of the point inside the tetrahedron with respect to its face *i*. The vertex opposite to face *i* represents the pure component *i* in the quaternary mixture. Each edge of the tetrahedron represents a binary subsystem (composed of the two pure components at both ends of the edge), each face represents a ternary subsystem (without the component placed in the opposite vertex) and each point inside the tetrahedron represents any possible mixture of the quaternary system. All points in a plane parallel to a given face *i* are at the same distance of that face and, thus, have the same composition for component *i*.

For the construction of such a diagram, it is necessary a coordinate conversion from a system of tetrahedric coordinates (quaternary compositions, in mole, mass or volume fraction) to the three dimensional, Cartesian space. Considering a regular tetrahedron (ABCS) with unitary edges as in Figure 2, it is possible to locate any quaternary composition point $i = \phi(x_A, x_B, x_C, x_S)$ in the three dimensional space $\phi(X, Y, X)$ by summing the relative projections of each of

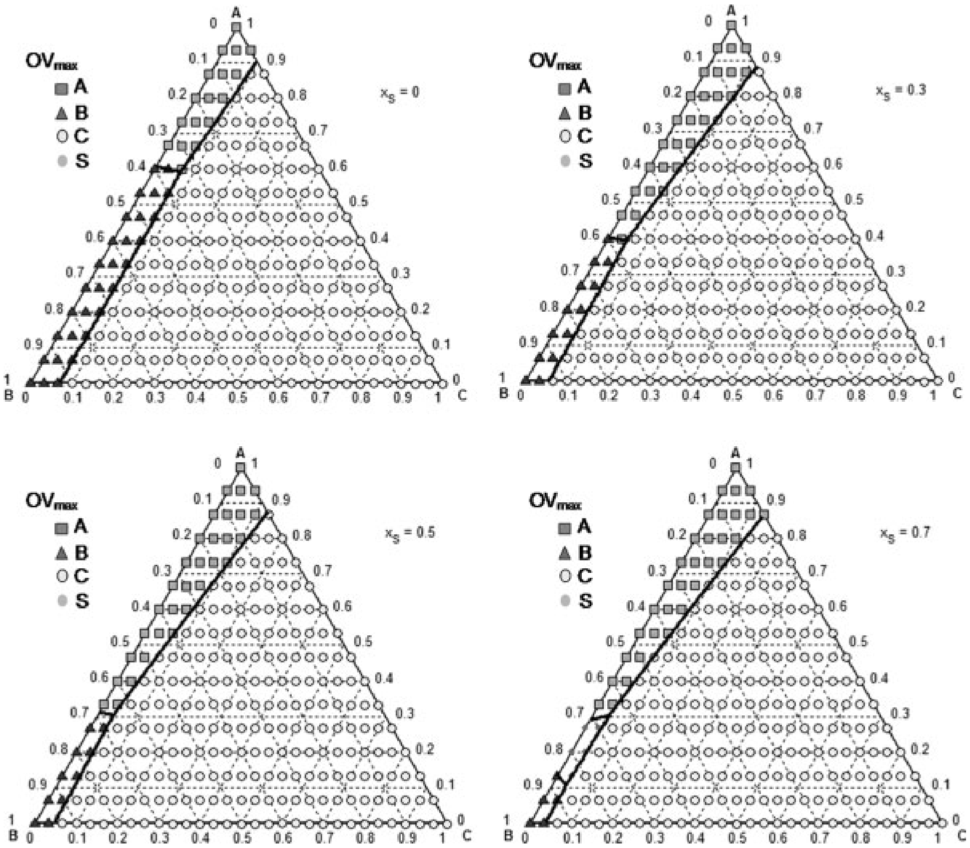

Figure 7. PTD® for different initial mole fractions of solvent in the quaternary system of limonene (A), geraniol (B), ambrox (C), and ethanol (S).

the quaternary compositions in each of the orthogonal axis (XYZ). In all the diagrams made throughout this work it was assumed the vertex C, as the origin of the orthogonal three dimensional space, that is $(X, Y, Z)|_c = (0,0,0)$. The edge $\overline{CA}$ is placed over the X axis, and the edge $\overline{CB}$ is in the XY plane. Following Wallas,[38] a schematic representation of the transformation of coordinates together with a PQD is illustrated in Figure 2.

The transformation matrix of the tetrahedric-quaternary variable system to the cartesian one, then results in the summation of the projection of the four variable system, (x_A, x_B, x_C, x_S), into an orthogonal axis (X, Y, Z) that can be mathematically traduced by:

$$\begin{bmatrix} x \\ y \\ z \end{bmatrix} = \begin{bmatrix} 1 & \cos(\pi/3) & \cos(\arctan(\sqrt{2}))\cos(\pi/6) \\ 0 & \sin(\pi/3) & \cos(\arctan(\sqrt{2}))\sin(\pi/6) \\ 0 & 0 & \sin(\arctan(\sqrt{2})) \end{bmatrix} \begin{bmatrix} x_A \\ x_B \\ x_S \end{bmatrix} \tag{10}$$

The procedure to use the tetrahedric diagrams is similar to that of the PTD®, e.g., it shows for each composition of a quaternary mixture which component has the OV_{max}. However, once the tetrahedric diagram is three-dimensional, it is divided into odor volumes where each component is the dominant note (OV_{max}) (see Figure 2).

For that purpose, the PQD covers the whole range of possible compositions between different combinations of four fragrant components presented in a liquid perfume mixture. The calculation of the odor value (OV) using Eq. 4 allows mapping the whole PQD, defining the regions where one component dominates the overall odor. The definition of the odor volumes is traduced by the relationship where $OV_{max} = OV_i$ for $i = A, B, C$, and S That is, the odor volumes are limited by surfaces where the OV_{max} is shared by two components and lines where the OV_{max} is shared by three components. The calculation of these Perfumery Binary Surfaces (PBS) and Perfumery Ternary Lines (PTL) is explained ahead. In the PQD, shown in Figure 2, it is possible to see an illustrative odor volume for component B (light shaded volume) which comprises all the quaternary compositions where the odorant species B has the maximum headspace odor value ($OV_{max} = OV_B$).

A new concept of PBS and PTL is introduced here. The distribution of the odor value (OV) for a quaternary perfume mixture represented in a PQD (Figure 2) shows that it is possible to have for each perfume system different odor volumes. These are delimited by interior PBS and externally, by the odor zones of the corresponding ternary subsystems that constitute the faces of the tetrahedric diagram.

The PBS defines the interior region of the quaternary compositions where

$$OV_{max} = OV_j = OV_k \tag{11}$$

with j, k as fragrant components and $j \neq k$. Table 2 presents the conditions for the determination of the PBS, considering a quaternary perfume system.

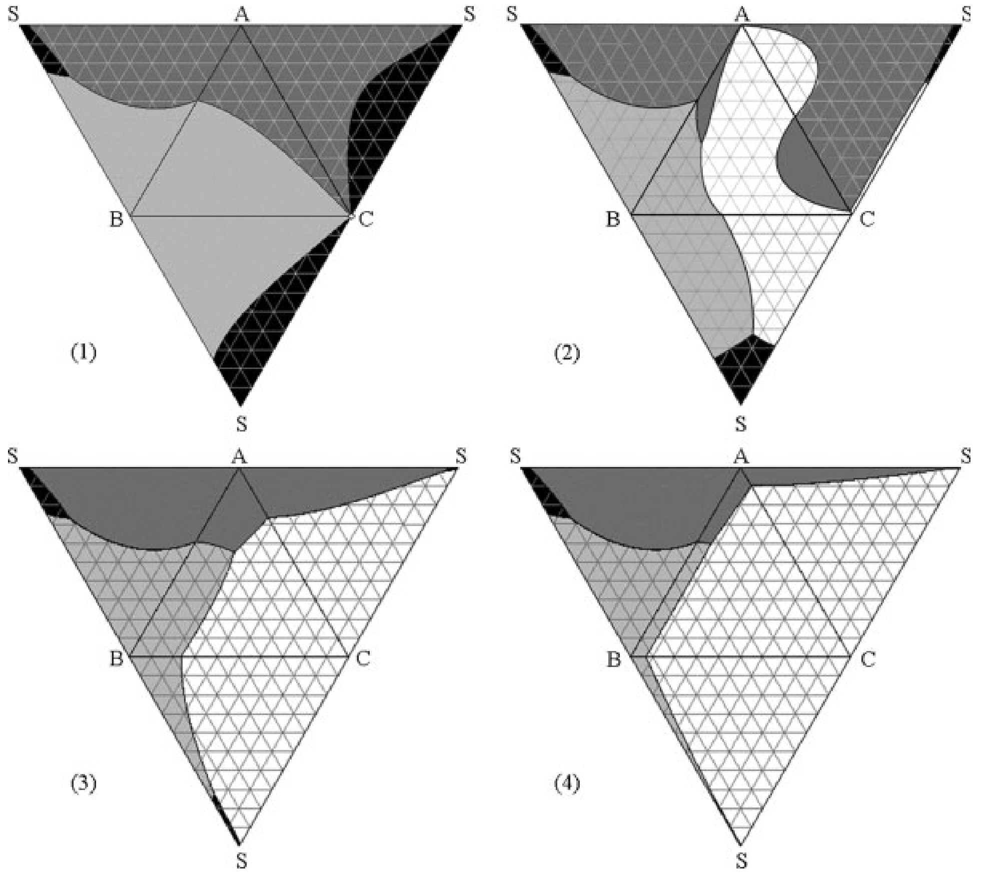

Figure 8. PTD® of the ternary subsystems for the four quaternary perfume mixtures.

The figures are the projection of the tetrahedron faces. (A) Top note (Dark gray, Limonene); (B) Middle note (Light grey, Geraniol); (C) Base note (White, 1: Tonalide, 2: Vanillin, 3: Galaxolide, 4: Ambrox); (S) Solvent (Black, Ethanol).

The PTL represent the set of quaternary compositions where remains the valid relationship

$$\mathrm{OV}_{\max} = \mathrm{OV}_j = \mathrm{OV}_k = \mathrm{OV}_l \tag{12}$$

with j, k, l as fragrant components and $j \neq k \neq l$. The PTL results from the intersection of three different PBS. This means that a PTL crosses the quaternary diagram in the thin region, where three fragrant components have the same maximum odor value ($\mathrm{OV}_{\max}$). Table 2 shows the conditions established for the PTL, considering a quaternary perfume system.

In a quaternary perfume system, it is considered that a Perfumery Quaternary Point (PQP) exists between four different fragrant components j, k, l and m when the following relationship is valid

$$\mathrm{OV}_{\max} = \mathrm{OV}_j = \mathrm{OV}_k = \mathrm{OV}_l = \mathrm{OV}_m \tag{13}$$

where j, k, l, and m are fragrant components and $j \neq k \neq l \neq m$. The composition of the PQP is also set by the intersection point of three different PTL. Moreover, for a perfumery quaternary system there is only one type of PQP which is fully determined by the conditions stated on Table 2.

The simulations for the PQD and the PTD methodologies were run using the MATLAB software. Routines and functions for the determination of the PBLs, PTPs, PBSs, and PTLs were developed in MATLAB as well as the prediction of the activity coefficients (γ_i) using the UNIFAC method. The iterative methods for solving the non-linear systems of equations were numerically computed using the optimization toolbox package from MATLAB, adapted to the nature of the problem studied.[39]

The numerical method of Levenberg-Marquardt (LM) with line search was used to solve the nonlinear system of algebraic equations. The choice of the LM method relied on its robustness and precision, although it may have occasionally poorer efficiency than other methods (i.e., higher number of function evaluations than the Gauss-Newton method, when the residual is zero at the solution). The line search algorithm uses a combined quadratic and cubic polynomial interpolation and extrapolation methods.

Although it is considered that the Levenberg-Marquardt method is more robust than the Gauss-Newton method and iteratively more efficient than an unconstrained method, the main routine was programmed to choose and shift among the different available methods for solving nonlinear systems of equations, when a solution was not found using the LM method.[40,41] This way the most efficient iterative method was dynamically selected to reach stable solutions for the system of equations.

The algorithm for the iterative methods used for the determination of the PBS is presented in Figure 3 for the case of the PBS between components A+B. Moreover, it is

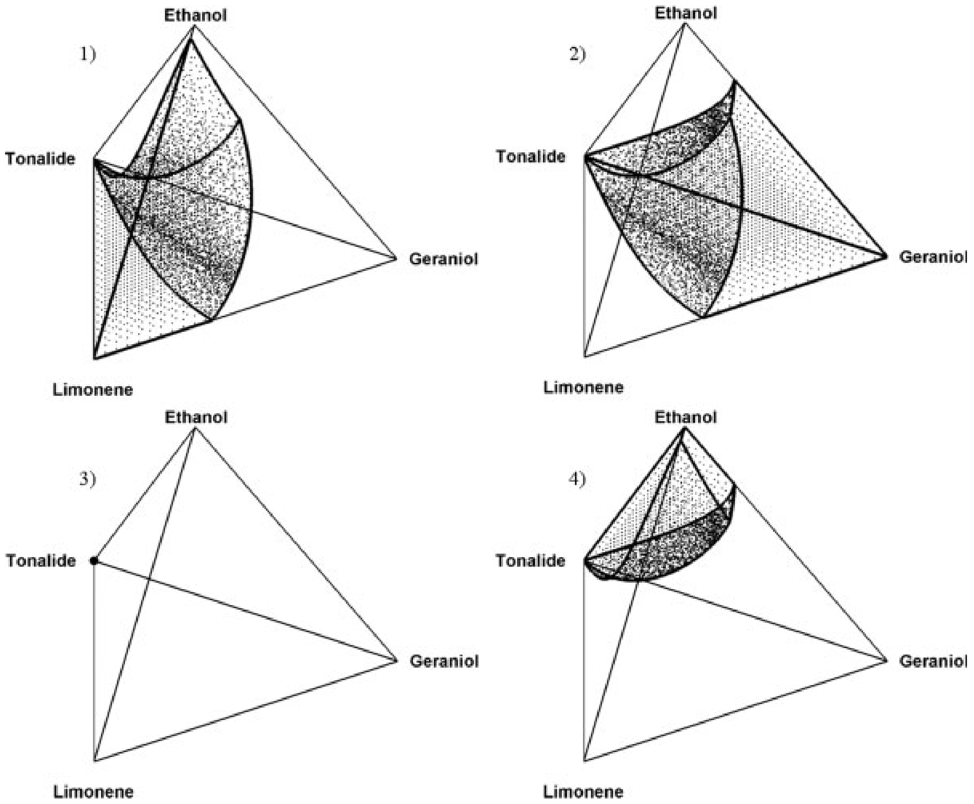

Figure 9. Perfumery fragrance volumes: (1) Limonene, (2) Geraniol, (3) Tonalide, (4) Ethanol.

important to remark that the algorithm for the PTL is analogous to the one used for the PBS, though the non-linear system of equations must be changed for the one presented in Table 2.

Effect of the base note

To illustrate the application of the PQD, the effect of different base notes on the headspace odor perception of different perfume mixtures has been studied using the proposed methodology. The top note (A—limonene), middle note (B—geraniol) and solvent (S—ethanol) were the same in the four quaternary systems studied. Four different base notes (C) were selected to be incorporated in the different quaternary systems: vanillin, tonalide, galaxolide and ambrox. The applicability of the PQD to quinary mixtures is also shown for the perfumery system: limonene, geraniol, vanillin, tonalide and ethanol. The chemical structures and some relevant physical properties of these chemicals were shown in Figure 1 and Table 1, respectively.

Application of the PTD®

The prediction of the odor character above a perfume liquid mixture is firstly analyzed to the light of the PTD® methodology. The PTDs for the different quaternary perfume systems studied in this work are presented in Figures 4 to 7 for the concentrated perfume mixtures (ethanol free) and for some selected mole fractions of ethanol in solution. These PTD® represent the cross plans of the tetrahedric diagrams at the specific height proportional to the ethanol mole fraction, thus showing the evolution of the perfume mixture as the solvent concentration rises. The PBL are also represented (solid lines), dividing the PTD® into its different odor zones. Despite this type of projections may serve to provide some insights of the quaternary behavior, it is clear that only with the PQD the whole composition range can be shown.

Nevertheless, the PTD® can be used to show the limiting behavior of the quaternary system ($A + B + C + S$), when applied to its four ternary subsystems: ($A + B + C$), ($A + B + S$), ($A + C + S$), and ($B + C + S$). As aforementioned, the four faces of the tetrahedric diagram coincide with the four ternary subsystems that compose the perfume quaternary mixture. Thus, and in order to facilitate the comprehension of the tetrahedric diagram, the PTD® of the four ternary subsystems for each perfumery quaternary system were calculated. The PTDs of the four ternary subsystems are represented together in Figure 8 as the projection of the faces of the tetrahedron. The tetrahedron can be constructed from that figure just ‘‘pushing up’’ the three outer vertices (S), so they join together in the space above the central triangle (base of the tetrahedron). It is important to mention that Figure 8 only shows the limit (faces) of the tetrahedron, thus no information about the quaternary system behavior is given.

The effect of the base note on perfume formulation can be seen in Figures 4 to 7 and especially in Figure 8, since the perceived odor character presented in the PTDs is significantly different for the perfume mixtures. On one side, it should be highlighted that tonalide will only be noticed for very high concentrations, that is nearly pure, since it has a

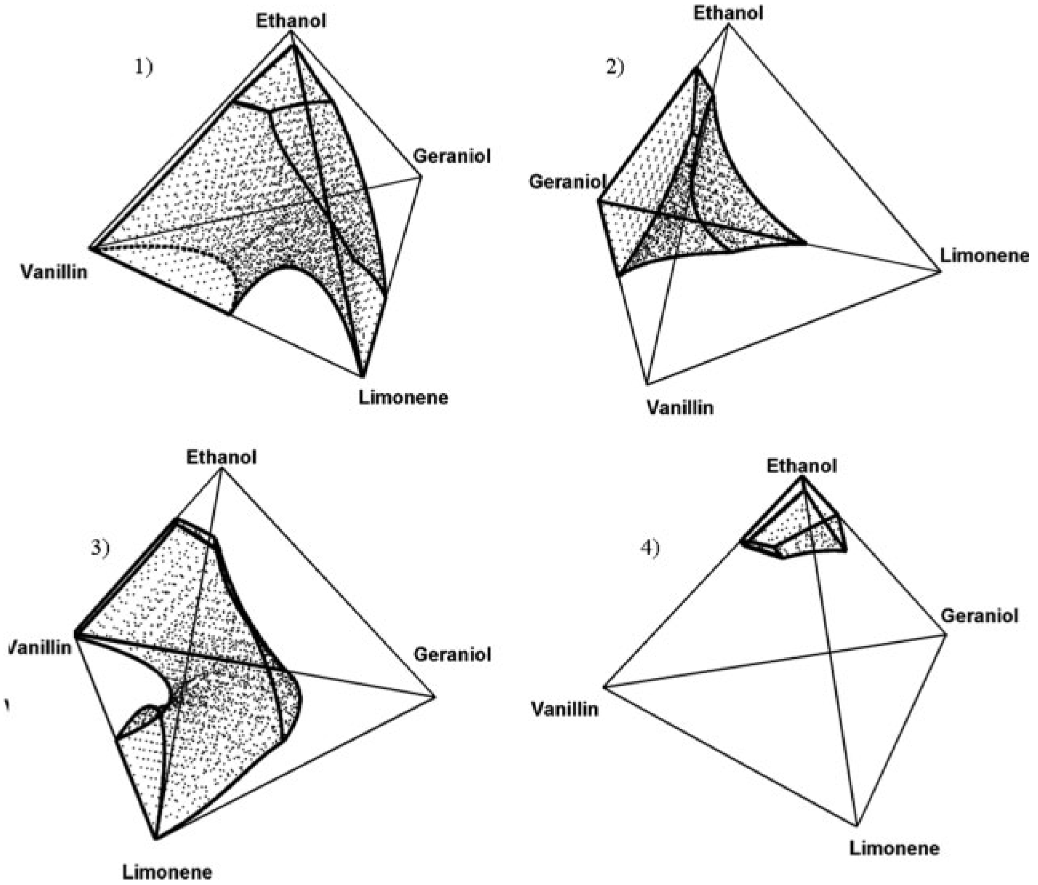

Figure 10. Perfumery fragrance volumes: (1) Limonene, (2). Geraniol, (3) Vanillin, (4) Ethanol.

very low vapor pressure (Table 1). This odorant is widely used in perfume formulations, acting as a fixative in the perfume mixture, thus influencing the molecular interactions between the different fragrant species and its vaporization behavior. On the other side, both galaxolide and ambrox present a dominant character over all other components for a wide range of compositions in the PTD®. This way, it is seen that the effect of the base note onto the odor character increases in the order of: tonalide < vanillin < galaxolide < ambrox (Figure 8—1, 2, 3, and 4, respectively).

Each PTD® on the top left side of the projection of the tetrahedron faces in Figure 8 corresponds to the ternary subsystem (A + B + S) and is equal for all four quaternary systems. As it was stated before, the diagrams in Figure 8, represent only the outside of the tetrahedron (the ternary subsystems), and no information of the inside (the quaternary system itself) is given. Thus, it shows the limiting behavior of the PTD® methodology when applied to quaternary systems. Nevertheless, it is easier to visually understand the whole tetrahedron once its outer surface is known. The PQD for the four perfume quaternary systems are shown and discussed in the next section.

Application of the PQD

To show the whole behavior of the perfume system, each fragrance odor volume is presented separately in Figures 9 to 12. The PQDs confirm what was expected from inspection of the PTD® diagrams of the ternary subsystems and quaternary mixtures (Figures 4 to 8): the size of the odor volume for the different base notes increases in the order of tonalide <<< vanillin < galaxolide < ambrox. Accordingly, the sizes of the odor volumes for the other three components in the mixture (limonene, geraniol, and ethanol) decrease as the size of the base note odor volume increases. The perception of tonalide is restricted to nearly the pure component, and it will not be sensed in almost any mixture. Galaxolide and ambrox present the largest odor volumes, which dominate most of the tetrahedric diagram (and thus, most of the composition spectrum). The size of the vanillin odor volume is somewhere in the middle. The high saturated vapor pressure of ambrox, which is of the same order of magnitude as the middle note (geraniol), is responsible for this unexpected behavior. The fact is that the ratio of $K = (P_C^{\mathrm{sat}} M_{wi})/(\mathrm{Thr}_c RT)$ presented in Table 1 that is taken into account for the calculation of the OV (see Eq. 4), is significantly high for both ambrox and galaxolide, resulting in very volatile base notes. This is why perfumers usually use them in low molar fractions or highly diluted, when they introduce these fragrances in a perfume formulation.

The factors governing the behavior of the odor value in the perfume mixtures have been detailed earlier. To provide some more insights, we can rewrite Eq. 4 as:

$$\mathrm{OV}_i = \gamma_i \cdot x_i \cdot \left(\frac{P_i^{\mathrm{sat}} \cdot M_i}{\mathrm{Thr}_i \cdot R \cdot T} \right) \tag{14}$$

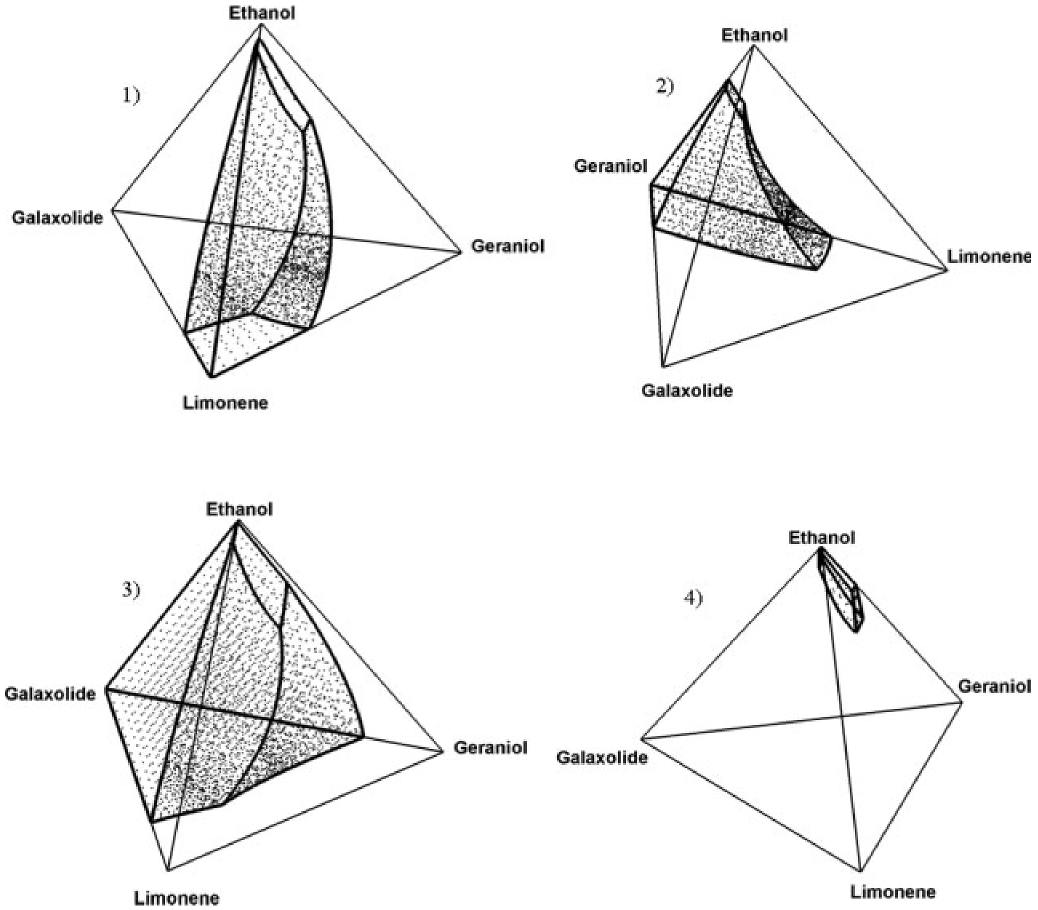

Figure 11. Perfumery fragrance volumes: (1) Limonene, (2) Geraniol, (3) Galaxolide, (4) Ethanol.

Among the three factors in Eq. 14 the composition, x_i, varies from 0 to 1, while the activity coefficient, γ_i, can vary about one or two orders of magnitude. The third factor is a constant value which depends on the experimental temperature, T, and the pure component properties (saturated vapor pressure, molecular weight and odor threshold). Table 1 presents the values of this constant (K) calculated for each odorant used in the perfume mixtures.

It is clearly seen that the value of the constant K increases in the same way as the size of odor volumes of the base notes: tonalide <<< vanillin < galaxolide < ambrox. The increase is especially significant from tonalide to vanillin, which may explain why the first can not be perceived when mixed with other fragrant components. It is to highlight also that tonalide has the lowest saturated vapor pressure and the highest odor threshold, resulting in a K value that is several orders of magnitude lower than the others. Both ambrox and galaxolide have a high ratio (Table 1) which explains why they are strongly perceived by the human nose for a wide range of perfume compositions.

Application of the PQD to perfumery quinary systems

The PQD methodology can also be extended to perfumery quinary mixtures in the same way that quaternary mixtures could be applied to the PTD® methodology, although with some limitations. When the PQD methodology is to be used with a quinary mixture, it is necessary to define pseudo-quaternary compositions. These are obtained by recalculating the quaternary molar fractions of some four fragrant components in a free basis of the fifth component, as follows:

$$\begin{aligned} x'_A &= \frac{x_A}{x_A + x_B + x_C + x_S},\ x'_B = \frac{x_B}{x_A + x_B + x_C + x_S}, \\ x'_C &= \frac{x_C}{x_A + x_B + x_C + x_S},\ x'_S = \frac{x_S}{x_A + x_B + x_C + x_S} \end{aligned} \tag{15}$$

where x'_i indicates a pseudo-quaternary composition for each of the four fragrant components (A, B, C, S) in the quinary system (A, B, C, D, S).

The predicted quinary system consists of a top note (limonene), a middle note (geraniol), two different base notes (vanillin and tonalide), and a solvent (ethanol). First, the component used at fixed compositions has to be chosen. As tonalide is only perceived when nearly pure (Figures 8 and 9) it was selected as fixed component. The PTDs for the different quinary systems simulated are presented in Figure 13, considering constant mole fractions of tonalide: $x_{\text{tonalide}} = 0.10$, $x_{\text{tonalide}} = 0.15$, and $x_{\text{tonalide}} = 0.20$, respectively. The distribution of the odor character in terms of the odor volumes for this system is presented in Figures 14 to 16 using the PQD methodology. Once more each fragrance odor volume is presented separately in order to have a better perception of the distribution of the perceived odor.

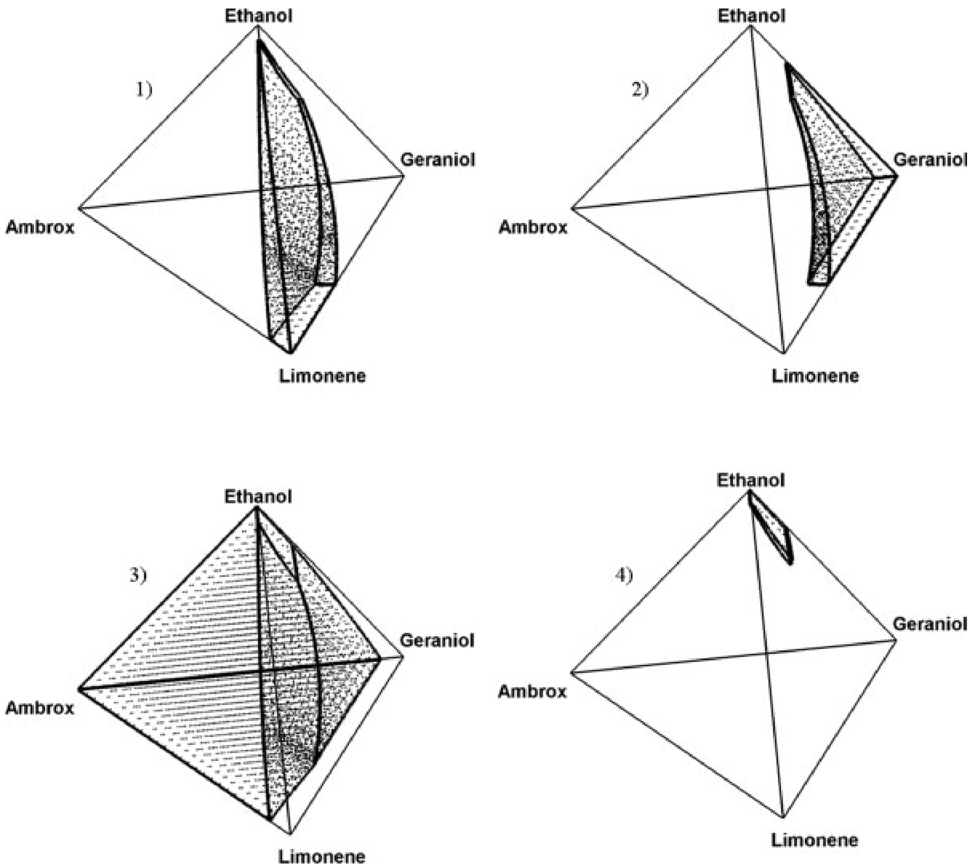

Figure 12. Perfumery fragrance volumes: (1) Limonene, (2) Geraniol, (3) Ambrox, (4) Ethanol.

For the perfume quinary system it is possible to see that incorporating a second base note (tonalide) in the perfume formulation, results in different predictions of the odor character (Figure 10 and Figures 13 to 16). This way, when the mole fraction of tonalide is increased in the perfume mixture, the odor volume for limonene tends to diminish and for $x_S = 0.20$ it is restricted to a volume near the corner of the pure component. On the opposite direction, the odor volume for vanillin increases with the concentration of tonalide in the mixture, showing that it tends to be more easily ‘‘pushed out’’ of the solution and, thus, more intensely perceived by the human nose. Middle note (geraniol) and ethanol odor volumes remain similar to those of the quaternary mixture—without tonalide (Figure 10). This indicates that the fixative properties of tonalide have a retention effect on limonene, allowing it to evaporate slower and so changing the vapor-liquid equilibrium of the perfume mixture.

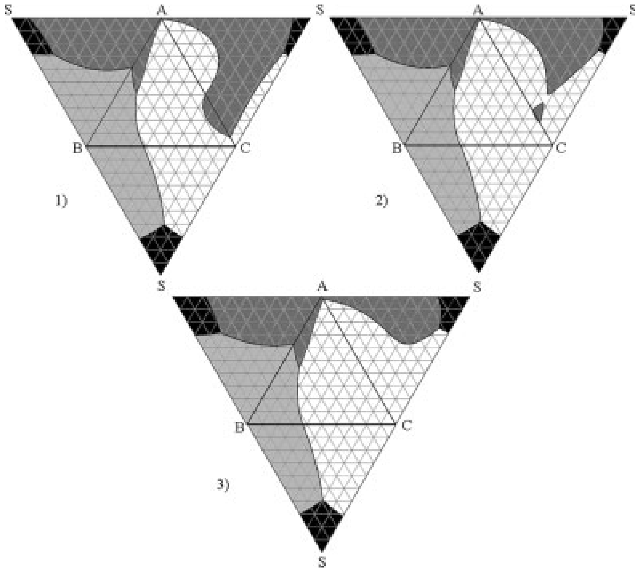

Figure 13. PTD® of the ternary subsystems for the three quinary perfume mixtures: (1) $x_{\text{tonalide}} = 0.10$, (2) $x_{\text{tonalide}} = 0.15$, 3 (3) $x_{\text{tonalide}} = 0.20$.

(A) Top note (Dark gray, Limonene); (B) Middle note (Light gray, Geraniol); (C) Base note (White, Vanillin); (S) Solvent (Black, Ethanol).

Conclusions

A methodology to describe the odor perception of quaternary perfume mixtures in the headspace has been presented. The methodology uses the concept of PQD, which are tetrahedric diagrams to represent the composition of quaternary and quinary systems. For this representation it is necessary a coordinate transformation from tetrahedric to Cartesian coordinates, which has been given.

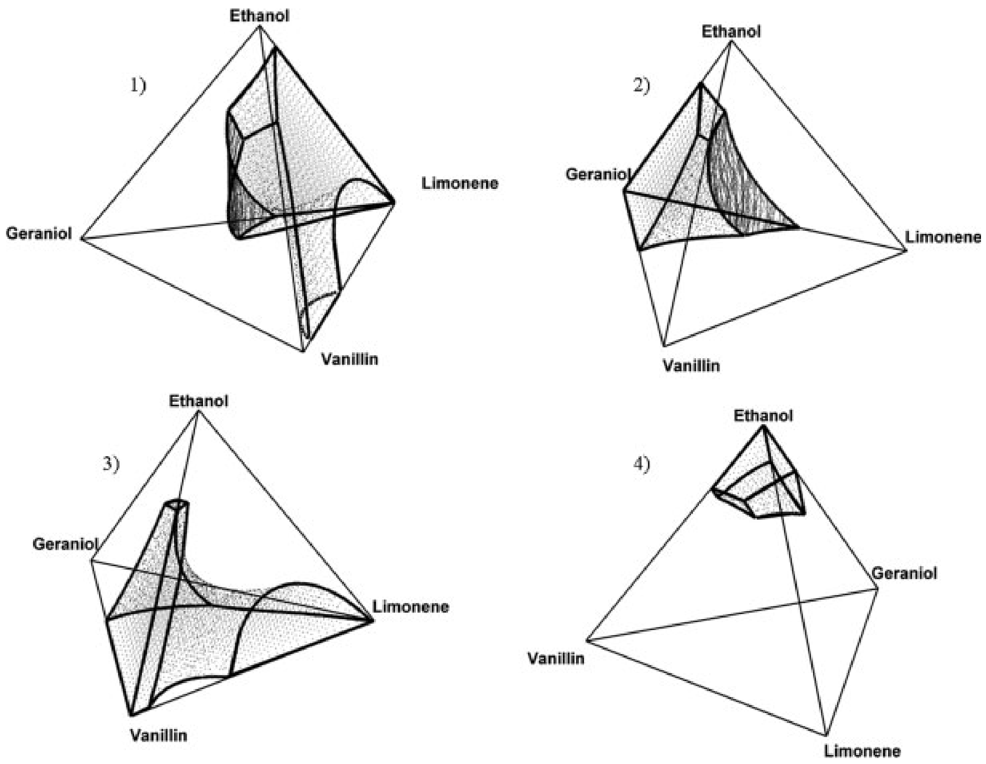

Figure 14. Odor volumes for each fragrance of the quinary mixture with $x_{\text{tonalide}} = 0.10$.

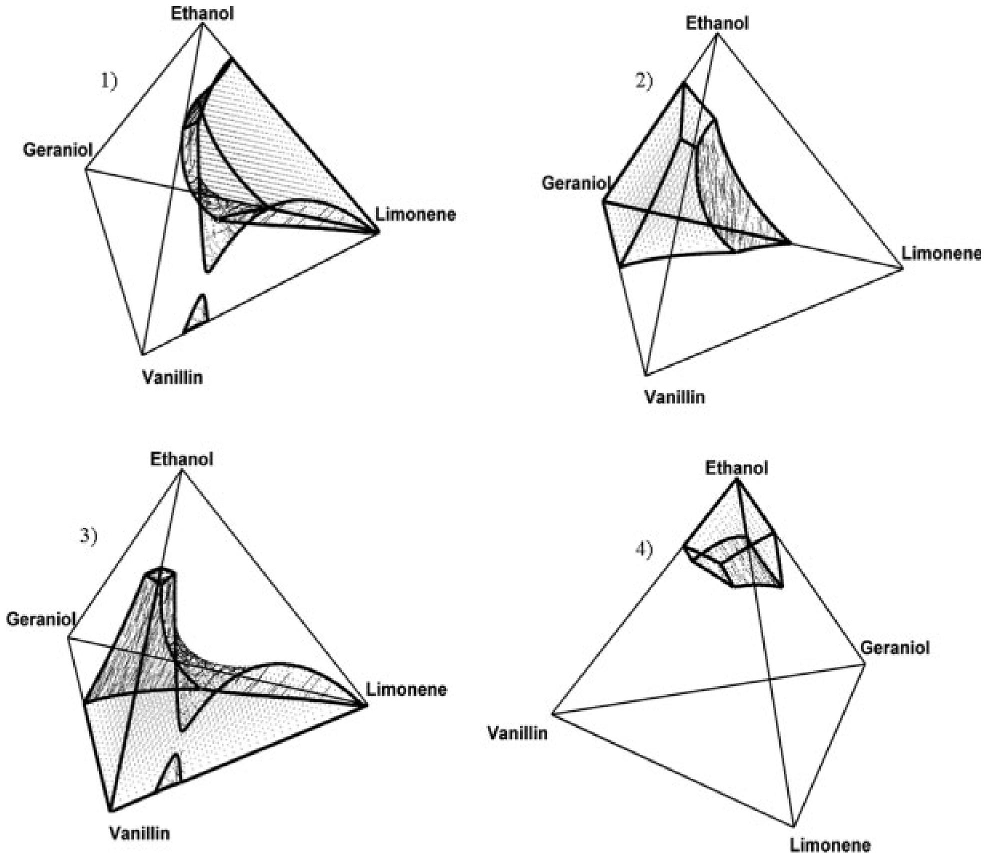

Figure 15. Odor volumes for each fragrance of the quinary mixture with $x_{\text{tonalide}} = 0.15$.

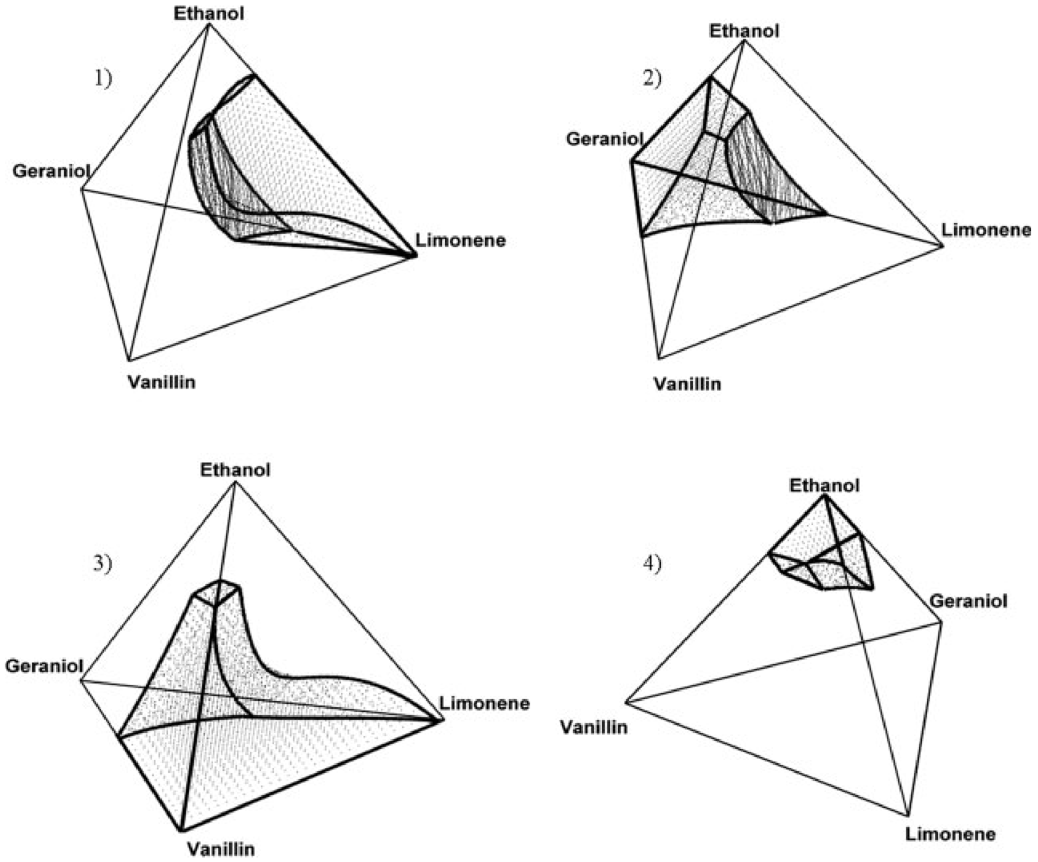

Figure 16. Odor volumes for each fragrance of the quinary mixture with $x_{\text{tonalide}} = 0.20$.

As an example of this methodology, the effect of four different base notes (Tonalide, Vanillin, Galaxolide, and Ambrox) in the perception of quaternary perfume mixtures of the type (Limonene + Geraniol + base note + Ethanol) has been studied. The odor perception through the whole composition spectrum has been calculated and is presented here. The influence of the physical–chemical properties of the pure components in the odor perception has also been interpreted.

The application of the methodology to quinary systems, keeping one component at a fixed composition, has also been shown using the system (limonene + geraniol + vanillin + tonalide + ethanol).

The methodology presented here also confirms some experimental evidences from perfume formulation: Tonalide is known in perfumery as a fixative, because it retains more volatile compounds in the perfume. The simulations presented confirm a retention effect on limonene. Galaxolide and ambrox are powerful base notes used in high dilution in perfume formulations. The strength of both base notes was also confirmed in the simulations.

This methodology is fast and convenient for the prediction of the odor perception of the headspace of perfume mixtures. In this way, repetitive trial-and-error experimental assays can be avoided in perfume formulation.

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