On the design of new fragrances with perfumery radar 2.0
An approach for the prediction of the odour space

KEYWORDS: classification of perfumes, olfactory families, fragrances, odour descriptors, odour space

Abstract
The classification of perfumes into olfactory families has been performed for years based on sensorial analysis using odour descriptors. However, there is still not yet a standardized classification method universally accepted. This constraint represents simultaneously a challenge and a motivation in the search for a new and common methodology. The purpose of this review is to present the novel Perfumery Radar 2.0 methodology: a tool that starts from the composition of the liquid mixture and molecular structures of perfumery raw materials together with their corresponding olfactory qualities to predict and characterise the odour space. This tool was validated with sensorial classifications from experts using different fragrances with known compositions and commercial ones, showing a very good predictive accuracy.

INTRODUCTION
Perfume formulation comprises dozens of fragrance ingredients, each one having unique physicochemical, psychophysical and sensorial properties. These ingredients are mixed in specific proportions and combinations depending on the perfumer’s choice and can be diluted in a large variety of matrices for a final product formulation. This complex formula results in a pleasant and harmonious sensorial perception for the human nose which is sometimes difficult to describe by words from typical customers. That is the reason why perfumes are often qualitatively classified into olfactory families and nuances by perfumers who are highly trained to recognize and classify odours [1, 2]. It should be said that although humans can detect and discriminate hundreds of odorants they also have difficulty naming them when not trained [3]. A reasonable hypothesis for this phenomenon was discussed by Lorig [4], who stated that it is due to a competition within cortical regions associated to olfactory information processing and language perception. Furthermore, genomic variations are another important point generating natural knockout of specific olfactory receptors in some people that could cause phenotypic differences in olfactory acuity, perception and classification [5, 6]. Finally, it is also known for long that olfactory perception and discrimination is the result of a complex combinatorial process at the odorant-olfactory receptor level as stated by Nobel prize winners Buck and Axel [5]. Such factors can explain, at least in part, the large interpersonal variability observed in human olfaction.

From a perfumery point of view, fragrances are empirically classified into olfactory families (like citrus, floral, green, fruity, herbaceous), comprising or not subfamilies or nuances (back note from the main olfactory sensation). However, even among experts and fragrance houses (Classification des Parfums et Terminologie, The Fragrance Wheel, Drom Fragrance Circle, ScentDirect, among others – for further details see Teixeira et al. [2, 11]) fragrance classification is not unanimously recognised [7, 8, 9, 10]. But one thing is for sure: it is vital to create connections between perception and language in order to simplify the design and classification of fragrances. Toward that objective, Product Engineering may be a valuable option by bridging different scientific fields from thermodynamics and transport phenomena (physicochemical) with psychophysics (sensor). Its application to fragrance design can be preponderantly reducing the number trial and error, consumption of raw materials, and product development time [1, 2, 11]. The Perfumery Radar 2.0 is the newer version of a predictive tool recently created for the design of fragrances and classification into olfactory families, introducing some scientific grounds, thus reducing subjectivity and empiricism in this field [1, 11].

DESIGN & CLASSIFICATION OF PERFUMES
The Perfumery Radar 2.0 methodology is a novel tool recently developed for the prediction of the olfactory space from the composition of the liquid mixture and the molecular structure of each chemical ingredient together with their corresponding olfactory qualities [11]. This methodology
uses the original assumptions from its precursor, with the advantage of providing more detailed descriptions of the odour space introducing inner and outer layers of classification. In addition, this novel methodology allows the extension to all gender classes [masculine, feminine and unisex fragrances]. The Perfumery Radar 2.0 tool was validated with five in-house designed perfume mixtures, one fragrance with known composition and 36 commercial fine fragrances. The Perfumery Radar 2.0 can be divided in six steps as shown in Figure 1. The first step consists in the analytical determination of the chemical composition by gas chromatography (coupled with flame ionisation detector) and mass spectrometry (GC-FID/MS). The composition (\(x_i\), mole fraction of each fragrant ingredient) of each sample was normalised as described by Teixeira et al. (11). Thereafter, in step 2, each perfumery raw material is parameterized using the UNIFAC method for functional groups [12]. Then, it is followed by the computation of the vapour-liquid equilibrium (VLE) for all components present at the gas-liquid interface (step 3) to estimate activity coefficients (\(\gamma^i\)) in the liquid phase. From that point, the concentration of each odorant in the gas phase can be calculated using the modified Raoult’s law for VLE as shown in Equation 1 [12]:

\[
y_i P = x_i \gamma_i P^\text{sat}_i \quad (i = 1, ..., N) \tag{Equation 1}
\]

where \(y_i\) and \(x_i\) are the vapour and liquid mole fractions of component \(i\), respectively, \(\gamma_i\) is the activity coefficient for component \(i\) in the liquid phase, \(P\) is the total pressure, and \(P^\text{sat}_i\) is the saturation vapour pressure of pure component \(i\). Then, in step 4, concentrations in headspace are translated into perceived olfactory sensations, so the odour intensity for each fragrance ingredient is calculated. This is predicted using the Odour Value (OV) concept [13] which is defined as the ratio between headspace concentration, \(C^h\), and the minimum detectable concentration by the human nose - the odour detection threshold (ODT) [14,12], as expressed by Equation 2:

\[
\text{OV}_i = \frac{C^h_i}{\text{ODT}_i} \tag{Equation 2}
\]

Subsequently, combining Eq. (1) and (2), the OV can be calculated by Equation 3:

\[
\text{OV}_i = y_i x_i \left( \frac{P^\text{sat}_i M_i}{\text{ODT}_i} \right) \tag{Equation 3}
\]

where \(M_i\) is the molecular mass of component \(i\), \(R\) is the universal gas constant, and \(T\) is the absolute temperature. In this work ODT values were obtained from the compilation of literature values [15]. The classification and assignment of each perfumery raw material into specific olfactory families (for the outer, basic, and inner families) represents the next stage of this methodology (step 5). Finally, the Perfumery Radar 2.0 ends with the evaluation of the overall OV for each olfactory family (for the basic layer there are weighing factors while for the other it is calculated based on a relative percentage) and graphical representation in the Perfumery Radar (for further details see Teixeira et al. [11]).

As previously mentioned, the selection of descriptors to classify the odour space is a large controversial topic. The Perfumery Radar 2.0 (see Figure 2) uses the same eight olfactory classes from the former version (citrus, fruity, floral, green, herbaceous, musk, oriental, and woody) plus two additional classification layers: an outer layer with 7 descriptors and an inner layer with 17 descriptors [further details on this can be found in Teixeira et al. [1,2]]. Naturally, terms as warm, fresh, sweet, or cool are associated with, for example, taste or touch, but the fact is that we unconsciously bring them to the perfumery field specifically when trying to describe fragrances. In this sense, an outer layer of classification was introduced comprising the following descriptors: fresh, warm, sweet-spicy, powdery, cool/mint, watery, and ethereal. Regarding the orientation of the descriptors in the Perfumery Radar space, sweet-spicy was positioned in the bottom of the radar, thus being in accordance with some authors stating that sweet can be associated with base notes, which are highly correlated with musk, oriental, and woody olfactory families [16]. The descriptor warm is represented in the bottom part of radar as well, but it is broader than sweet-spicy, and also embraces herbaceous as previously stated by Zarzo and Stanton [16]. We found that cool/mint is linked with herbaceous and green families, while Zarzo and Stanton [16] defined it as green-citrus undertones. Powdery is associated to soft and smooth scents of some floral and musk notes and, finally, watery is associated with marine and aquatic environments (although we know that water alone is odourless). The introduction of an inner layer level of classification with 17 descriptors intends to describe in more detail information about nuances which are characteristic of each olfactory family. Therefore, the following subfamily descriptors were included in our database comprising specific characteristic fragrance ingredients: camphor, rose, pine, lemon, earthy, apple, jasmine, sandalwood, orange, vanilla, mushroom, lilac, cinnamon, pepper, banana, honey, cherry, leather, artis, chocolate, tobacco, lavender, smoky, grass, lime, myrrh, and anise. The selection of these descriptors was based on sensory descriptions from Brechbill [17] and ScentDirect [10] for each perfumery raw material, as happened for the outer layer category. In respect to gender associations, olfactory families placed on the top of the perfumery radar (fruity, floral, and green) are considered feminine.
Furthermore, chypre and fougère olfactory families are very relevant in perfumery being usually associated with feminine and masculine genders, respectively. However, there is not a clear agreement on the classification of fragrances belonging (or not) to these families. Chypre is known to be a combination of oak moss, cistus labdanum, patchouli, and bergamot as the main accord which can be categorised into woody, oriental, citrus, and fresh olfactory families (19). For this reason many fragrances belonging to this family differ in their nuances (both in terms of character and magnitude, e.g. woody can be more or less pronounced), what can explain, to some extent, discrepancies within experts’ classifications for some fragrances within this family range. Fougère, in turn, is known to be a combination of notes of citrus, lavender, sweet spices and oriental woods [8]. It is crucial that the Perfumery Radar 2.0 identifies them as noticeable dimensions of the odour space. For this reason, calculated decision criteria comprising two optimized conditions were established for the assignment of a fragrance within these families according to the predominance of their olfactory descriptors (11).

CONCLUSIONS

The Perfumery Radar 2.0 methodology combines scientific models (from thermodynamics for prediction of vapour-liquid equilibria and from psychophysics for olfactory perception) together with sensory and empirical olfactory analysis for the design and classification of perfumes. It was thoroughly validated with consumer relevant fragrances covering the whole odour space. The versatility presented by Perfumery Radar 2.0 is an asset for the design of novel perfumes; it allows changing or adding perfume families to the radar plots, including or excluding fragrant compounds, adding new data or even changing the models used. This methodology can also be considered as an efficient tool for fragrance design by reducing the time needed in the preformulation steps for the design of fragranced products, lowering the consumption of raw materials and, consequently, production costs. Finally, the Perfumery Radar 2.0 tool was created as an attempt to move perfumers toward a standard perfume family classification, thus allowing better odour communication between perfumers, scientists, and business professionals.

REFERENCES AND NOTES

5. Buck, L., Axel, R. “A Novel Multigene Family May
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