The Physicochemical Basis of Perfume Performance in Consumer Products

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Abstract: The literature on physicochemical aspects of perfume performance has been reviewed with emphasis on products for home and body care. Pertinent expressions related to perfume performance have been defined. For the first time a model study is presented to account for the dynamic aspects in applications of perfumed fabric softeners. A new headspace cell, which allows precise control of the atmospheric conditions and modelling of the dynamics of the drying process, has been designed. The determination of the deposition of selected fragrance chemicals and their evaporation, combined with olfactometric dose-response data, produced a reliable measurement of their performance in application.

Keywords: Dynamic headspace · Evaporation kinetics · LogP(o/w) · Perfumery · Substantivity

1. Introduction

The perfumery industry is based on a fascinating combination of art and science. Today five perfume houses supply about two thirds of the worldwide perfume business and most perfumers develop their creative talents in a small number of specialist perfume houses that supply perfumes to companies that market fine fragrances, body care and home care products. The design of perfumes for consumer products has dramatically changed during the past two decades. The traditional development of perfumes by trial and error and smelling the perfumed product in its various stages of application still continues to be the *modus operandi*, but performance data of perfume raw materials in application has increased exponentially over the past few years. The reasons for this are the following:

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a) Perfume houses need to have a guarantee of success for their New Fragrance Materials in order to spend the many millions of dollars it takes to develop and launch them.

b) Marketing companies increasingly realise that the perfume is a key ingredient in their products and often the principal one that distinguishes it from their competitors.

c) The cost of fragrance in the consumer product is not negligible, and so each ingredient in the perfume has to be efficient, cost-effective and contribute to the overall satisfaction of the consumer.

Today's perfumer is supported in his creation by a wealth of technical information, which helps him to ensure that his perfume does not just smell wonderful but that the consumer is benefiting from additional value brought by the perfume design. This ability of the perfume to enhance attributes of a product has been used for more than 30 years. The subtle odour remaining on the shirt after ironing suggests to the consumer that the shirt is not only clean and fresh but also that it is 'almost new again'; the consumer using an underarm deodorant stays 'fresh' even at the end of a hard day and the floor cleaner not only has cleaned the floor but the room remains 'clean' after many hours because of the odour of the perfume. To bring about these consumer

benefits, intense research has aimed at understanding how fragrances interact with the often complex chemical compositions of the products and the targeted substrates (*e.g.* fabric, floor, hair, skin) and how the resulting odour profiles are affected. Perfumes created using New Fragrance Materials have that distinctive success factor, and although the odour of a New Fragrance Material remains the primary feature, Secondary Properties have become an essential element in contributing to the repeat purchase of the consumer.

2. Background

Driven by the critical need of technical information for perfume design in consumer products, the physicochemical basis of fragrance performance and the measurement of odours have long been a topic of research. In a series of papers entitled 'Physical Foundations in Perfumery', Appell [1] promoted the importance of odour measurements as a quantifiable approach to perfumery; two parameters on which to base objective odour values were vapour pressure and odour intensity. Sturm and Mansfeld [2] compiled a database for the creation of substantive perfumes in the context of fabric softeners. Accordingly, the composition of the perfume after extraction with an organic solvent from the rinsed and dried fabrics

was quantitatively analysed and compared with that of the starting perfume. The amounts of the individual compounds recovered from the fabric were then compared with their retention times on a non-polar GC stationary phase (correlated with the volatility of the odorants), with the functional groups (correlated with the polarity of the odorants), with the odour characteristics, and finally with the type of fabric. The authors showed that the deposition of the perfume from the water phase onto the fabric caused a profound change of the composition, unless the perfume oil was deliberately created with only those fragrance ingredients that had been detected in the solvent extract of the rinsed and dried fabrics. As a corollary, the influence of the water solubility and the molecular weight of the odorants on their behaviour was duly emphasised. In a study of fragrance performance in fabric softener applications, Jellinek and Warnecke [3] systematically varied parameters such as the type and the concentration of cationic surfactants, additives, and the chemical structure of the perfume ingredients. The authors suggested that fragrance ingredients can associate with surfactant aggregates and that the adsorption of the fragrance onto fabric is concomitant with that of the cationic surfactants. Blakeway and Seu-Salerno [4] discussed substantivity on hair as being the partitioning of a perfume between the water phase and keratin. Blakeway [5] addressed substantivity in a more general way and described it 'as the adsorption of a perfume from an aqueous solution onto a substrate, which resists subsequent rinsing'.

A new dimension to the study of perfume behaviour was added by Etzweiler *et al.* [6] who introduced a quantitative headspace technique to monitor stability and substantivity of fragrance chemicals in typical home and body care applications. Neuner-Jehle and Etzweiler [7] and Müller *et al.* [8] combined this technique with olfactometric methods. An efficient experimental methodology was thus proposed in order to objectively quantify perfume substantivity defined as 'characteristic which ensures a perceptible odour throughout the application cycle' [7][8]. Five quantifiable parameters were associated with substantivity [7][8]: vapour pressure; odour perception limit; odour value (numerical measure for odour intensity); water solubility; matrix factor (impact of the composition and the structure of consumer products on odorant volatility). Quantitative headspace analysis in combination with the concept

of the odour value was also applied to portray fragrance behaviour on skin [9] and on hair [10]. Except for the use of electronic sensors, a recent paper on the substantivity of fragrances on cloth [11] offers no fundamentally new insights.

Model investigations concerning the physicochemical aspects of the substantivity of fragrance chemicals on laundered fabrics have been undertaken by Escher and Oliveros [12]. The overall process was divided into two consecutive steps: laundry and drying. These steps were characterised by affinity (partition coefficient of the odorant between the aqueous phase and the fabric) and tenacity (ratio of the amount of odorant on the dried fabric to the amount of odorant on the wet fabric), respectively. The term substantivity was attributed to the global effect of laundering and drying. The affinities of 15 fragrance raw materials to cotton and polyacrylonitrile fabric were measured in fabric softener and detergent solutions. The logarithm of these affinities was found to linearly increase with the logarithm of the corresponding partition coefficients between octanol and water, $\log P(o/w)$ [13], which is a calculable characteristic of the hydrophobicity of an odorant, typical values being between 1 and 7. The affinities of odorants to cotton were larger than those to polyacrylonitrile. Odorants were more abundantly transferred to fabric from softeners (cationic surfactants) than from detergents (anionic and non-ionic surfactants). The relative contribution of a number of parameters (concentration of odorant, type and concentration of surfactant, type and load of fabric, and wash temperature) was quantified within a sequence of experiments based on fractional factorial design. Besides factors inherent to the molecular structure of fragrance chemicals, *i.e.* $\log P(o/w)$ and volatility, the type of surfactant and the type of fabric were shown to have the most important impact.

The use of $c\log P(o/w)$ (= calculated $\log P(o/w)$) for the construction of enduring perfumes has been cited in the patent literature [14] but in fact these documents bring no significant new contribution to the long standing knowledge of the perfumer, nor to the findings reported in some of the earlier publications discussed above and in earlier patent literature (*e.g.* [15][16]). The latter not only recognises the importance of designing substantive perfumes to maximise the effect of *e.g.* softeners on the fabrics treated with them, but even provides examples of fragrance compositions such as those shown

in Table 1, which contain a large amounts of substantive ingredients.

Furthermore, as will be shown in Section 4 (*vide infra*), the fact that perfumes are deliberately designed with ingredients that have properties such as $\log P(o/w)$, volatility or odour threshold within specified ranges of magnitude only partially accounts for their performance.

Finally, the relation between perfume creation and physical chemistry has been recently discussed by Perring [17]. Except where partitioning is extremely discriminating, the author concluded that the single most important property for prediction of substantivity is the odorant's vapour pressure. As a practical approach, it was suggested that a method for the quantification of perfume behaviour for any given product and application combination would be to identify perfume ingredients that perform well, and then seek empirical, mathematical models which explain the behaviour of that particular system. A gradual expansion of such models was then expected to lead to a general understanding.

Table 1: Example of a substantive fragrance composition [16]

Component	Wt%
Benzyl acetate (5)	5.0
Benzyl salicylate	10.0
Coumarin	5.0
Ethyl maltol	5.0
Ethylene brassylate (= Astrotone® (3))	10.0
Galaxolide® (1) (50%)	15.0
Hexyl cinnamic aldehyde	20.0
Ionone gamma methyl	10.0
Lilial®	15.0
Patchouli	5.0
Total	100.0

3. Terminology

The terminology used in the literature to define perfume performance is by no means consistent. Attributes such as substantive, tenacious, enduring or long-lasting are often employed interchangeably and without discrimination. Therefore, an unambiguous set of meanings is an obvious necessity.

We have classified the application of perfumed consumer products depending on how the perfume is transferred from the product to the substrate.

1. The perfume is *directly applied* to the substrate together with the product (*e.g.* alcoholic solution or cream applied to skin, deodorant sprayed on skin). An unspecified period of time elapses before the next application.

2. The perfume is *transferred* from the product (*e.g.* detergent, shampoo) to the substrate (*e.g.* fabric, hair, skin, functional surface) through a wash and/or rinse process. The substrate is dried and, after an unspecified period of time, undergoes the next application cycle.

During the life cycle of a fragrance in a class 2 application (Fig. 1), the perfumer (and the consumer) identifies three important stages: the odour of the product, the odour at the stage when the substrate is wet (*wet odour impact*) and the odour at the stage when the substrate first reaches dryness (*initial dry odour impact*). We apply the expression *perceived substantivity* to the initial dry odour impact and we underline that it is *not* appropriate when used in the context of describing a wet odour impact. We restrict the use of the word *substantivity* to class 2 applications. It refers to chemicals that are *physically present* on the *dry* substrate at the end of a wash and/or rinse process [18]. Although this property is a measure of the efficiency of the transfer of odorants from a product to a substrate that has become dry, a large number of other characteristics are determinant for the appreciation of perfume performance as will be shown in Section 4.

The release of a fragrance that is perceived from a dry substrate independent of whether we deal with a class 1 or class 2 application is named *tenacity*, whereas tenacity extended over time is referred to as *long-lastingness*.

With reference to the introductory remarks, *wet* and *dry odour impact*, *perceived substantivity*, *tenacity*, and *long-lastingness* are all Secondary Properties of a perfume.

4. Perfume Performance: A New Physicochemical Strategy with Emphasis on the Dynamics

The strong demand for more efficient technical support towards perfume design prompted us to develop a new physicochemical strategy to study perfume behaviour, which we present herein for fabric softeners. Up to now, physicochemical characteristics of odorants have mostly been based on the determination
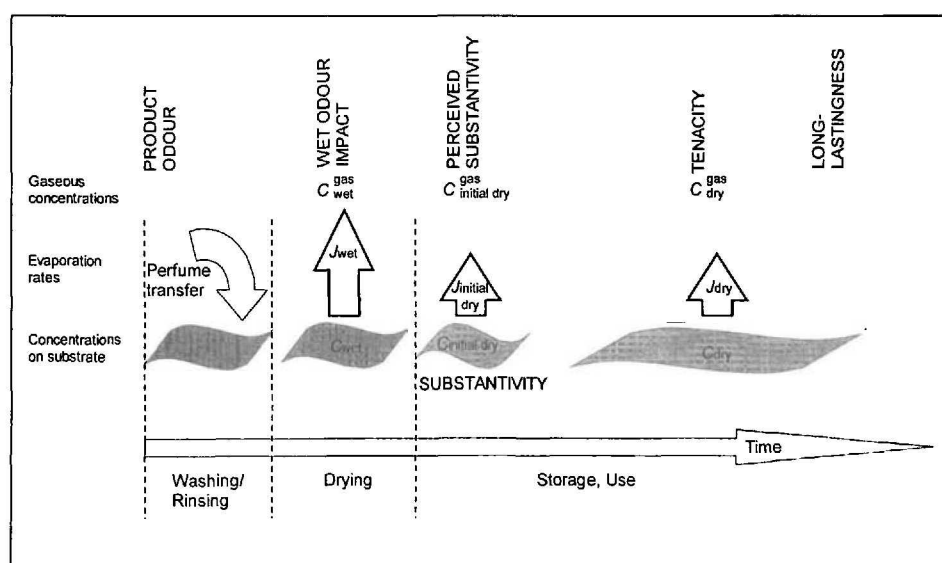

Fig. 1. Life cycle of a fragrance in a class 2 application

of equilibrium parameters such as partition coefficients (*e.g.* matrix factor [7] [8], affinity [12]). In standard application conditions, both the transfer of perfume and its subsequent evaporation are *non-equilibrium processes*. It is therefore important to consider the dynamics of the application steps and to consider mobility factors such as mass transfer coefficients and diffusion coefficients [19].

Softeners are widely used for domestic fabric care [20]. In today's European washing habits, they are brought into contact with the clothes after the main wash during the last rinse cycle. The cationic surfactants are delivered to the fabric where they produce a soft feel and control electrostatic properties. The laundered and rinsed clothes are usually line dried by which stage a pleasant odour should signal freshness. Optimisation of the fragrance design to improve such Secondary Properties of the product, as defined in the introduction, is thus of great economic importance. Using our terminology, a softener fragrance in application is characterised by its wet odour impact, its perceived substantivity (initial dry odour impact), and its long-lastingness (class 2 application).

Our strategy is based on the *design of model studies* that mimic standard applications, and is based on the experimental control of the following four steps:

a) Establishment of an experimental model that gives reproducible and relevant results. Good control of the experimental parameters throughout the process is achieved by downsizing both the rinse and the drying equipment to laboratory scale and, as dis-

cussed below, the model is designed to rigorously respect standard application conditions.

b) Quantitative determination of the fragrance transfer from the aqueous dispersion of the product to the substrate (*i.e.* fragrance deposition).

c) Quantitative analysis of the evaporation of the fragrance under controlled atmospheric conditions.

d) Translation of the gaseous concentrations to perceived intensities by means of olfactometric data.

A softener product was formulated according to standard laboratory scale procedures and perfumed at 1 wt% with a model fragrance [21]. For the present study, the six well-known fragrance ingredients 1–6, each at 10 wt% in the mixture, were selected and analysed in detail (Table 2), *i.e.* three musks (1: Galaxolide®, trademark of IFF; 2: Habanolide®, trademark of Firmenich; 3: Astrotone®, trademark of Rhône-Poulenc), 4: Hedione® (trademark of Firmenich), 5: benzyl acetate and 6: phenylethyl alcohol. Preconditioned cotton squares were mechanically stirred in diluted softener and subsequently centrifuged to mimic the final rinse cycle in European washing machines. The quantities of both the softener adhered to the fabric and the residual water at the end of the procedure were identical with those found using washing machines [22]. However, this methodology ensured far better homogeneity of the softener deposition, resulting in less scattering of the data.

The amounts of odorants deposited on the wet cotton fabric were determined from the change of their aqueous concen-

trations before and after the rinse process [23]. The deposition of the six odorants on wet cotton was found to correlate with the respective logP(o/w) data (Table 2). More precisely, the logarithm of the ratio of the amount deposited on cotton to the amount remaining in the aqueous phase depended linearly on logP(o/w) as already published for equilibrium conditions [12]. Not surprisingly, the coefficients of the linear relation differ, by a factor of about 2, from those reported [12], underlining the importance of faithfully respecting, amongst other factors, the inherent dynamic aspects of the application conditions.

The cotton squares were then transferred into a cylindrical flow cell that was newly developed to mimic line drying and subsequent storage of the washed fabrics. This cell was also designed to mimic real life conditions during the smelling process. Thus, defined atmospheric conditions were created by control of the temperature, the inlet air humidity and the convection of the airflow
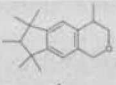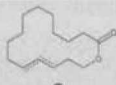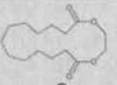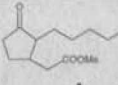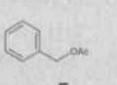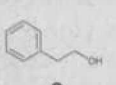
around the cotton squares. After first characterising the homogeneity of the air circulation (Fig. 2), the kinetics of the drying process were then measured. We applied a theoretical model to describe water evaporation, based on its sorption isotherm and vapour transport in the gas phase, and found that the coefficients obtained from the model were in agreement with those reported in the literature (Fig. 3). Thirdly, the forced convection that determines the transport properties of volatile molecules in the air within the cell was compared to natural convection in an open space. We thus found that the atmospheric conditions in the cell are comparable to weak convection in a mild, dry atmosphere [24].

The evaporation of the six odorants was monitored during two days by measurement of their gaseous concentrations in the outlet air stream (Fig. 4A) by quantitative purge and trap headspace analysis [25]. The initially high gaseous concentrations decreased for 6 h in parallel with the drying of the cotton square. The ob-

served decrease of concentrations varied from between one and two orders of magnitude depending on the odorant. Once the textile was dry, the gaseous concentrations remained practically stable for the rest of the experiment. An intuitive explanation for this effect was initially believed to be the rapid exhaustion of the deposited odorants during the drying of the fabric..However, such an explanation was ruled out by integrating the amounts of odorants released in the atmosphere and by monitoring the odorants' release above wet cotton during two days in an atmosphere of 100% relative humidity (Fig. 5). The decrease in the evaporation rate was due to the change in the water content of the fabrics. Possible explanations for this change are a stronger affinity of the perfume molecules to the dry fabric (an equilibrium property) and/or a smaller mobility of the perfume molecules across the treated dry fabric (a dynamic/mobility property).

A model similar to that presented to describe water evaporation from cotton

Table 2: Properties related to the chemical structure and physicochemical properties dependent on the application and performance of the six odorants

Odorant	Galaxolide®	Habanolide®	Astrotone®	Hedione®	Benzyl acetate	Phenylethyl alcohol
Structure	1	2	3	4	5	6
Molecular Weight	258	238	270	226	150	122
Properties related to the chemical structure						
Partition coefficient as logP(o/w) [a, b]	5.5	5.4	4.4	1.9	2.0	1.4
Volatility [μmol l^{-1}] as logV [a]	−2.5	−2.5	−3.6	−1.9	0.25	0.06
Physicochemical properties dependent on the application						
Deposition [%] [b]	80.0	81.0	61.0	11.5	14.9	12.0
Substantivity [%] [c]	75.0	74.0	60.0	10.9	13.9 [d]	10.9
Evaporation rates, J_{wet}/ $J_{initial\ dry}$ [ng m^{-2} s^{-1}] [e]	441 / 28	782 / 70	37 / 7	45 / 4	447 / 50	93 / 3
Performance properties expressed in odour intensities [29]						
Wet odour impact	2.4	2.3	1.5	1.7	1.2 [d]	1.7
Perceived substantivity	1.5	1.4	0.8	1.0	0	0.4
Long-lastingness [f]	1.2	0.9	0.3	0.6	0	0.5

[a] Data taken from Firmenich's in-house database.
[b] The logarithm of the ratio of the amount of odorant deposited on wet cotton fabric to the amount remaining in the aqueous phase, logK, is related to logP(o/w) by the Eqn logK = 0.36 logP(o/w) − 1.47 (R^2 = 0.985).
[c] The substantivity was determined by subtracting the integrated quantity of odorant lost by evaporation from the amount deposited (= deposition) until the cotton was dry.
[d] Uncertainty due to the high evaporation rates on wet cotton leads to unaccounted losses when the cotton is transferred from the centrifuge into the cell.
[e] The average evaporation rate J of an odorant from the cotton fabric in the cell was determined from the gaseous concentration C^{gas} [ng m^{-3}] in the outlet air stream using the following relation: $J = C \Phi/2S$, where Φ is the volumic airflow [m^3 s^{-1}] through the cell and S [m^2] the surface of the cotton square [22].
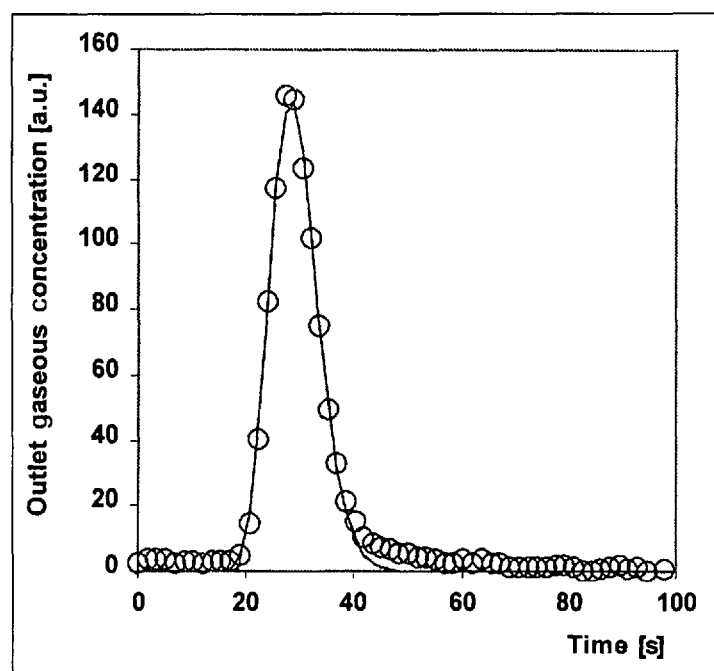[f] We characterised long-lastingness experimentally by the odour intensity after 48 h.

Fig. 2. Gaseous concentration profile of the marker at the outlet of the cell. The air flow homogeneity around the cotton fabric was assessed by the Residence Time Distribution approach commonly used to characterise reactors in chemical engineering. A gas marker is injected rapidly into the inlet, and the outlet is monitored on-line by headspace analysis. Any broadening of the peak is a sign of undesired diffusion processes in the cell; (O) Experimental points, (−) Fit with the axial diffusion model: the broadening can be represented by the axial dispersion of the flow characterised by the Peclet number $Pe = ul/D^{axial}$, where u is the linear speed of the gas flow, l the length of the cell, and D^{axial} the axial diffusion. The best fit to the experimental points gave $Pe = 84$, a value substantially higher than 1 and thus characteristic of a well-defined plug flow [30].

should also be applicable to perfume evaporation (Fig. 3, [26]). It is important to emphasise that within this model, the volatility of the odorant (gaseous concentration in equilibrium with the pure material at 25 °C) is only one of the many factors that contribute to the description of the evaporation process [27].

The contribution of the individual gaseous concentrations to the overall odour impact is interpreted in terms of the olfactometric properties of the odorants. Firmenich possesses a large in-house database of olfactive thresholds and dose-response curves that covers most of the traditional and proprietary New Fragrance Materials used in consumer products. Their characteristics can differ from one odorant to the other by several orders of magnitude. By knowing the dose-response curves of the individual odorants, any gaseous concentration of a given odorant can be converted to its corresponding perceived intensity as if it was used as a pure compound in the application [28][29]. This conversion, which is illustrated graphically in Fig. 4B, can thus dramatically change the 'physical' hierarchy of the odorants shown in Fig. 4A. We emphasise that Fig. 4B does not show the odour impact of the model fragrance as a whole, but the impact of the six individual odorants.

All six odorants in our model perfume are perceived at the wet stage (wet odour impact). Benzyl acetate (5) and Hedione® (4) have similar gaseous concentration profiles. Hedione® (4) is still perceived after 48 h whereas the gaseous concentration of benzyl acetate (5) already falls below its odour detection threshold after less than an hour. According to the terminology described in Section 3 (*vide supra*), Hedione® (4) thus has both initial dry odour impact and long-lastingness. Because the conversion in Fig. 4 is effected for single odorants of the model perfume at relatively low concentrations, it is not surprising that the resulting odour intensities come out as weak or as very weak [29]. Habanolide® (2), a recently introduced Firmenich New Fragrance Material, and Galaxolide® (1) perform well. Both have strong wet and initial dry
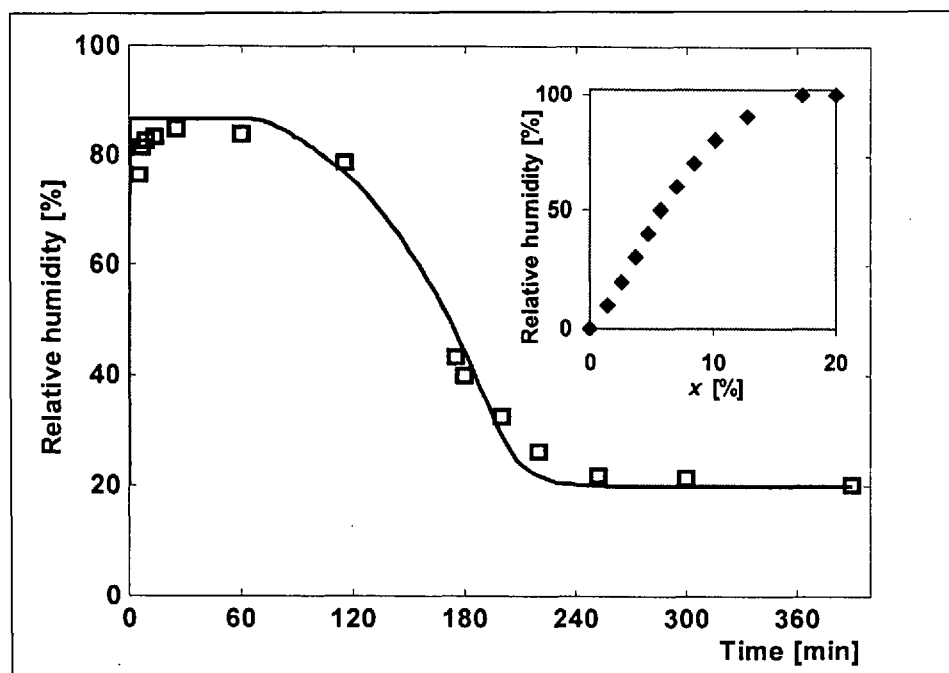

Fig. 3. Drying of the cotton square: (□) changes of the relative humidity of the outlet air stream due to water evaporation from cotton; (−) theoretical fit by numerically integrating (software Matlab, The MathWorks) the mass balance along the whole exchange surface area between cotton and air in the cell. The mass balance is based on the vapour flux J_{vapour} [ng m^{-2} s^{-1}] from the cotton to the air, for an elementary surface exchange area, located at a position y in the cell, with $J^{y}_{vapour} = k(C^{y}_{flow} − C^{y}_{layer})$, where k [m s^{-1}] is the mass transport coefficient, C^{y}_{flow} [ng m^{-3}] the concentration of water vapour in air, and C^{y}_{layer} [ng m^{-3}] its concentration in contact with the textile. The only free parameter of the model, $k = 8 \cdot 10^{-4}$ m s^{-1}, is given by the fit. The relative humidity of the inlet air is set to 20%, temperature 25 °C [26].

Insert: Water sorption isotherm on cotton; experimentally determined by Dynamic Vapour Sorption; describes the water weight fraction on cotton (x) to the relative humidity at equilibrium. The vapour concentration at 100% relative humidity is equal to 23.05 g m^{-3} at 25 °C.

odour impact, and are long-lasting. Astrotone® (3), which is also a musk chemical, performs less favourably despite the fact that the dose-response curves of the three chemicals are very similar. This may be explained by the lower deposition of Astrotone® (3) compared to those of Habanolide® (2) and Galaxolide® (1) and reflected by logP(o/w) (Table 2). Furthermore, the volatility and the resulting gaseous concentrations of Astrotone® (3) are one order of magnitude lower. As a consequence, the wet and initial dry odour impacts and the long-lastingness are all less efficient.

The performance of phenylethyl alcohol (6) is rather unexpected in view of its poor deposition (low logP(o/w)) and high volatility (Table 2). Nevertheless, with a dose-response curve very similar to that of Hedione® (4), the odour of phenylethyl alcohol (6) is perceptible, albeit weakly, until the end of the experiment.

The experimentally determined rankings of the six odorants with respect to their wet odour impact, to their perceived substantivity, and to their long-lastingness are presented in Table 2, and are fully consistent with the longstanding empirical knowledge of the perfumer. No simple correlation can be identified between the properties related to the chemical structures and the performance, which implies dynamic aspects specific to the use of the product. A discussion of the relevance of more complex psychophysical properties such as the perception of mixtures and hedonic issues is not within the scope of this article.

5. Conclusion

The strategy developed to measure fragrance performance has concentrated on:
a) Strictly controlled experimental conditions.

Fig. 5: Comparison of gaseous concentration (A) and consumption (B) of odorants between drying and wet cotton fabric. Depending on the odorant, integration of the evaporated quantities above wet cotton during 5 days (data partially shown) accounts for between 40% and 90% of the amounts deposited; (□) Habanolide®, 20% relative humidity; (○) Hedione®, 20% relative humidity; (■) Habanolide®, 100% relative humidity; (●) Hedione®, 100% relative humidity

b) Dynamic aspects of the underlying processes.
c) Interpretation of measured gaseous concentrations in terms of olfactory dose-response characteristics.

Although the study herein presented has involved only one type of product (fabric softener, class 2 application) and, for reasons of clarity, has been limited to six odorants, the results compiled in Table 2 and illustrated in Fig. 4A/4B clearly demonstrate the merit of this approach. The results take into account dynamic phenomena and are quantitative with respect to both physical characteristics (deposition, gaseous concentrations) and perceived odour intensities. For the first time, precise modelling of the drying process has allowed a rationalisation of perfume evaporation in the presence of water. This type of dynamic 'on-line' data has already proved to be successful
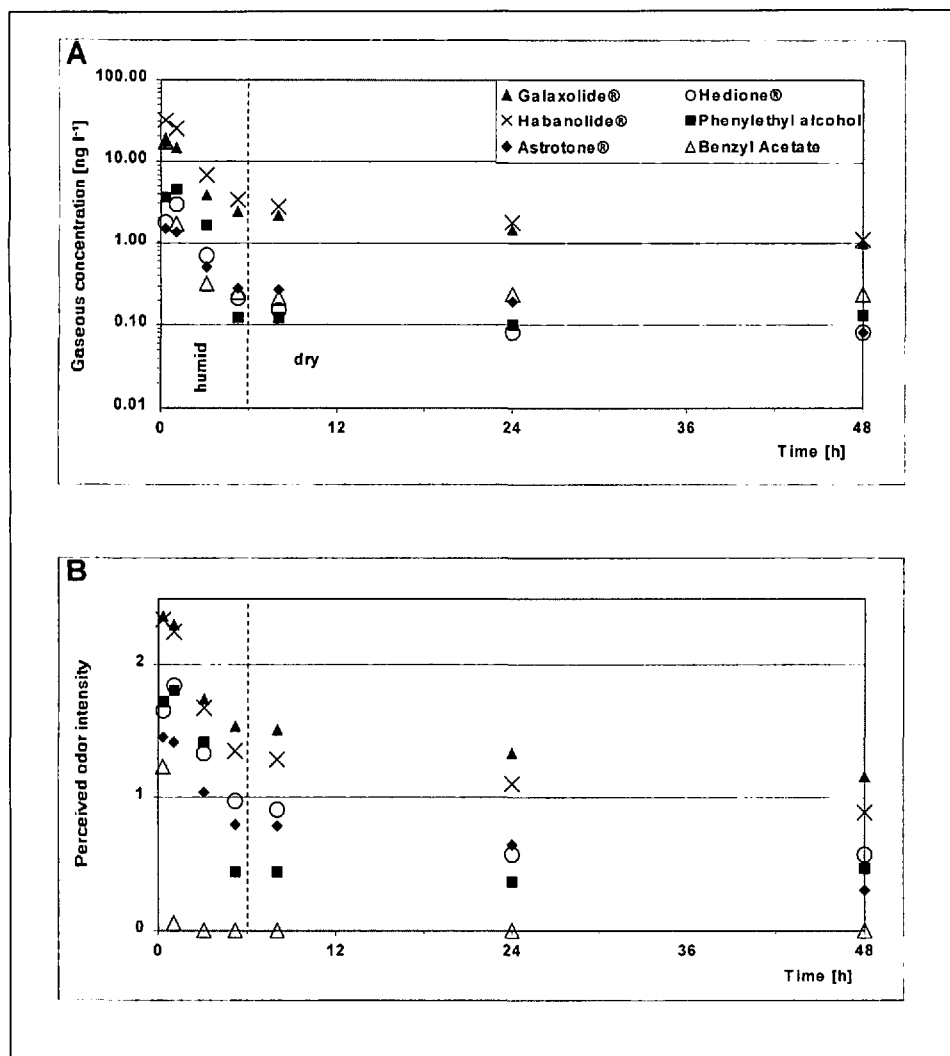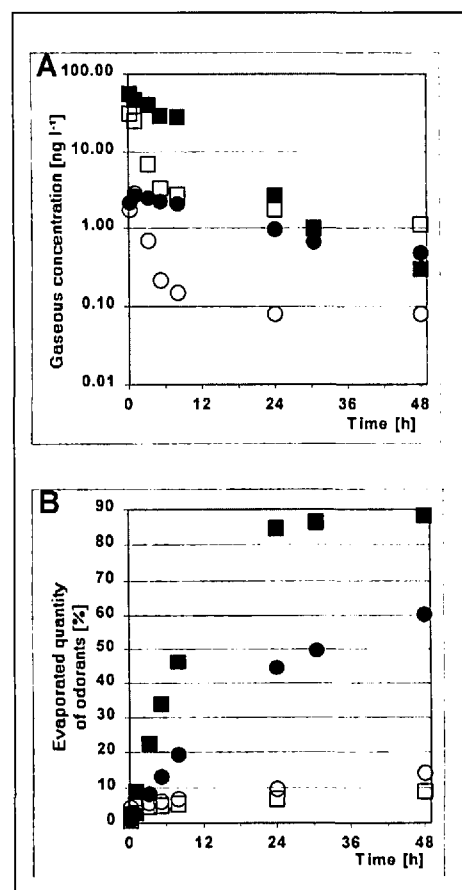
Fig. 4: Gaseous concentration of odorants measured in the outlet of the cell (A) and translation to perceived individual odor intensities [29] (B).

in guiding perfume design. Provided the experimental setup mimics accurately the application in question and is strictly controlled in all relevant aspects, meaningful data are readily generated.

Finally, special emphasis has been given to the unambiguous definition and application of attributes used to describe perfume performance *i.e.* wet odour impact, initial dry odour impact, substantivity, perceived substantivity, tenacity, and long-lastingness.

[1] L. Appell, *American Perfumer and Cosmetics* **1964**, *79* (1), 25; **1964**, *79* (2), 43; **1964**, *79* (5), 29; **1964**, *79* (11), 25; **1967**, *82* (11), 35; **1968**, *83* (11), 37; **1969**, *84* (2), 53; **1969**, *84* (3), 45; **1969**, *84* (8), 41; **1970**, *85* (10), 49.

[2] W. Sturm, G. Mansfeld, *Tenside, Deterg.* **1978**, *15*, 181.

[3] J. Jellinek, H.-U. Warnecke, *SOFW J.* **1976**, *102*, 215.

[4] J.M. Blakeway, M. Seu-Salerno, *Int. J. Cosmet. Sci.* **1983**, *5*, 15.

[5] J.M. Blakeway, *Cosmet. Toiletries* **1984**, *99*, 45; and ref. 1 cited therein.

[6] F. Etzweiler, N. Neuner-Jehle, E. Senn, *SOFW J.* **1980**, *106*, 419.

[7] N. Neuner-Jehle, F. Etzweiler, in 'Perfumes: Art, Science and Technology', Eds. P.M. Müller, D. Lamparsky, Elsevier, London, New York, **1991**, p. 153.

[8] P.M. Müller, N. Neuner-Jehle, F. Etzweiler, *Perfum. Flavor.* **1993**, *18* (4), 45.

[9] A. Baydar, T. McGee, K.L. Purzycki, *Perfum. Flavor.* **1995**, *20* (5), 45.

[10] A. Baydar, B. Bouret, A. Charles, *CTMS* **1994** (June/July), 25.

[11] X. Ormancey, S. Puech, D. Coutiere, *Perfum. Flavor.* **2000**, *25* (1), 24.

[12] S.D. Escher, E. Oliveros, *J. Am. Oil Chem. Soc.* **1994**, *71*, 31.

[13] *e.g.* A.J. Leo, *Chem. Rev. (Washington D.C.)* **1993**, *93*, 1281.

[14] *e.g.* D.R. Bacon, T. Trinh (The Procter & Gamble Company, USA), US 5500138, **1996**; P.A. Cunningham, M. Green, A.C. McRitchie (The Procter & Gamble Company, USA), WO 99/65458, **1999**; K.D.

Perring, C.F. Clements, A.P. Macmaster (Quest International B.V., NL), WO 99/18926, **1999**; E.P. Guenin, K.A. Trotzinka, L.C. Smith, J.M. Teffenhart, K.J. Mc Dermott, S.D. Shefer, A. Shefer (International Flavors & Fragrances Inc., USA), US 6156826, **2000**.

[15] J.M. Behan, C.F. Clements, D.C. Hooper, J.R. Martin, J.B. Melville, K.D. Perring (Lever Brothers Company, USA), US 5554588, **1996**, priority 08.11.1991-EP-91310360.

[16] J.M. Ladd, A.E. Nicholson, R.J. Merz, T.J. Wierenga (The Procter & Gamble Company, USA), EP 332260 B1, **1996**, priority 07.03.1988-US-164678.

[17] K.D. Perring, in 'Chem. Fragrances', Eds. D. Oybus, C. Sell, Royal Society of Chemistry, Cambridge, UK, **1999**, p. 188.

[18] The term substantivity is commonly used in the context of dyes where it stands for the affinity of a dye for a given substrate through attractive interactions.

[19] R.B. Bird, W.E. Stewart, E.N. Lightfoot, 'Transport Phenomena', John Wiley & Sons, New York, **1960**, part III.

[20] A. Jacques, C.J. Schramm, Jr., *Surfactant Sci. Ser.* **1997**, *67*, 433.

[21] Cationic esterquat surfactant (Rewoquat®) was melted at 60 °C and dispersed in hot tap water under stirring to a final concentration of 15 wt%. The surfactant aggregate size distribution of the resulting base ranged from 0.5 μm to 5 μm. The viscosity was 60 mPa s. This laboratory sample is representative of a threefold concentrated commercial softener type. The model perfume (1 wt%) was mixed with the softener base at room temperature and the mixture was sonicated for 15 min. The perfumed product was stored for one day before use.

[22] Cotton squares (28 cm x 28 cm; 17.7 g ± 0.2 g at 25 °C and 37% relative humidity) were cut from cretone cotton (Test cloth N° 221, EMPA, St Gallen, Switzerland) and conditioned over five cycles, which comprised a machine main wash with unperfumed standard detergent (ECE Colour fastness test detergent, Henkel, Düsseldorf, Germany), rinsing with water and centrifuging. The cotton squares were then line-dried and ironed. Tap water (CaCO₃ content 131 mg l⁻¹) at 25 °C was used throughout the procedure. Prior to use, the conditioned cotton squares were soaked for at least 30 min in tap water and centrifuged, then immersed in a dispersion of 0.35 g of softener in 240 g of water and mechanically stirred for 6 min. The amount of water remaining on the fabric after centrifugation was 65% of the dry fabric weight. These figures correspond to a standard European washing machine (Miele WS 5425) with 2 kg of fabric loading and 40 g of threefold concentrated fabric softener per 27 l of water in the last rinse cycle. Softener surfactant deposition was determined by fluorescence spectroscopy. A lipid membrane dye, octadecyl rhodamine B chloride (Molecular Probe, Eugene, USA) was incorporated in the surfactant aggregates at a concentration of

1 μmol. The deposition level (85%) was determined by the change of fluorescence intensity (exc/em 556/582 nm) before and after the above described procedure. Observing the fluorescence pattern on cotton further assessed the homogeneity. In contrast with the large variations observed in washing machines, it was found that uniform softener deposition was obtained.

[23] Determination of these concentrations was effected by solid phase extraction of the rinse water followed by GC-MS analysis. The values were determined with an absolute variation of 2%.

[24] The forced convection in the cell was characterised by solving k in the following equations valid for the cell geometry and flow: $Sh = (3.66^3 + 1.613^3 \, Pe \, d/l)^{1/3}$ and $Sh = k \, d/D$ whereby Sh is the Sherwood number, D the molecular diffusion coefficient [m² s⁻¹], and d and l the diameter and length of the cell. We obtained $k = 7 \times 10^{-4}$ m s⁻¹, which compares well to the value $k = 8 \times 10^{-4}$ m s⁻¹ found by fitting the experimental water evaporation from the cotton square (Fig. 3). For comparison, we found $k = 2 \times 10^{-3}$ m s⁻¹ for natural convection occurring around a freely hanging cotton square left in a room. Natural convection phenomena are generally characterised by parameter k in the range of 10^{-3} m s⁻¹ to 10^{-2} m s⁻¹. The textile was considered to be dry when the relative humidity of the air at the outlet was 20% (= relative humidity at the inlet, see Fig. 3).

[25] C. Vuilleumier, I. Flament, P. Sauvegrain, *Int. J. Cosmet. Sci.* **1995**, *17*, 61. The experimental gaseous concentrations were determined with a precision of 10% to 25%.

[26] This simple model is based on the hypothesis that the limiting factor of evaporation is the transport of the vapour in air and adequately describes our experimental data on cotton. However, more refined models might be required for fibres other than cotton.

[27] By replacing water by an odorant in the model introduced in Fig. 3 (insert), the volatility of the odorant would correspond to the gaseous concentration of water at 100% relative humidity. The remaining part of the isotherm is determined by the interaction of the odorant with the treated cotton fabric and is not linked to the volatility.

[28] L.F. Wünsche, C. Vuilleumier, U. Keller, M.P. Byfield, I.P. May, M.J. Kearney, in 'Proceedings of the 13th International Congress of Flavours, Fragrances, and Essential Oils', Istanbul, October 15–19, **1995**, Vol. 3, p. 295; AREP Publications, Istanbul 1995.

[29] The scale of perceived odour intensities ranges from 0 (no perception) to 5 (very strong). Intensity 1 corresponds to very weak perception and intensity 2 to weak perception [28].

[30] J. Villermaux, 'Génie de la réaction chimique', Technique & Documentation, Paris, **1982**, chapter 6, p. 147.