What Makes a Fragrance Substantive?

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Any answer to the question "What makes a fragrance substantive?" faces a limitation based on the fact that substantivity of perfumes can only be defined in an operational sense. The perfumer calls a fragrance or an odorant substance substantive in a perfumed product if the odor is perceptible throughout the stages of the product's application cycle. For example, in a fabric softener a substantive odorant substance would be perceptible in the detergent itself, in the wet laundry after washing, and in the dried laundry, among other stages in the product's application cycle.

The application chemist's point of view is similar. However, in attempting to get a quantitative determination of the odorant's time-dependent concentration in the headspace above the perfumed product, the modern application chemist links the headspace concentration to the odor perceived, either by calculating the number of odor value units (OV units) present in the headspace,[1] or by taking into consideration the slope of the dose-effect curves of the perfume's components.[2] It is important to note that these determinations are usually made "in praxi" for a state of equilibrium and that the storage conditions between measurements reflect the practical situation and do not necessarily represent equilibrium states.

In this article, the substantivity of fragrance is discussed as a function of the vapor pressures, perception threshold values, odor values, water solubilities and matrix factors of ten fragrance raw materials investigated mainly in view on their application in fabric softeners.

Parameters Influencing Substantivity

The key parameters influencing substantivity are compiled in Table I. They can be grouped into parameters depending only on the fragrance material, and parameters depending on both the fragrance material and the matrix (the perfumed material, or laundry in this case).[3] The latter are expressed as a summarized matrix factor which can in

Table I. Measurable odor-relevant parameters

Measurable parameters	Measuring methods	Approximate numerical range*	Application-related information
Vapor pressure	Quant. hs-analysis	0.05 - 50,000 µg/l (1:10[6])	Measure for fragrance volatility/diffusivity
Odor threshold	Olfactometry	0.002 - 2,000 ng/l (1:10[6])	Odor perception limit
Odor value	$OV = \frac{\text{hs-conc.}}{\text{thr. conc.}}$	100 - 10,000,000 (1:10[5])	Approx. numerical measure for odor intensity
Water solubility	gas chromatography	low ppm totally miscible	Odorant's behavior in water-related media
Matrix factor	$f_M = \frac{\text{hs-conc. measured}}{\text{hs-conc. calcul.}}$	0.7 - 700 (1:10[3])	How much the matrix influences the odorant's volatility

*figures of lower and upper limits taken from Givaudan-Roure's data collection of more than 1000 fragrance chemicals

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many cases be regarded as a substance-specific constant over the whole range of practical concentrations of the odorant components in the perfumed material. The matrix factor is defined as the quotient of the headspace concentration actually measured above the perfumed matrix and the headspace concentration calculated by considering the concentration of the fragrance material in the matrix and by proportionally reducing the value determined for the headspace concentration above the undiluted material.

The water solubility is of importance in more than one way: it characterizes the interaction of the fragrance material with a specific matrix (water), it is indicative of the fragrance material's polarity, and it plays a key role for every application cycle involving a distribution of the odorant components between aqueous and non-aqueous phases, which is generally the case for washing procedures.

The importance of the vapor pressure, the odor threshold and the derived odor value, finally, is obvious and needs no further comment.

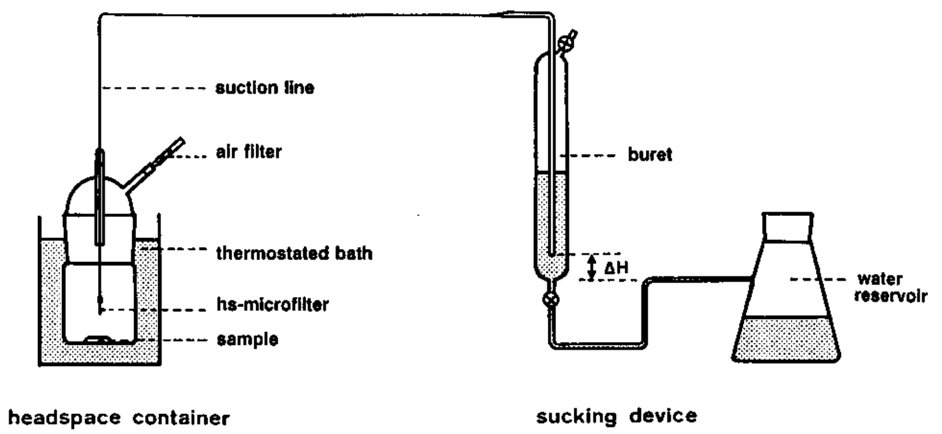

Figure 1. Apparatus for sampling headspace

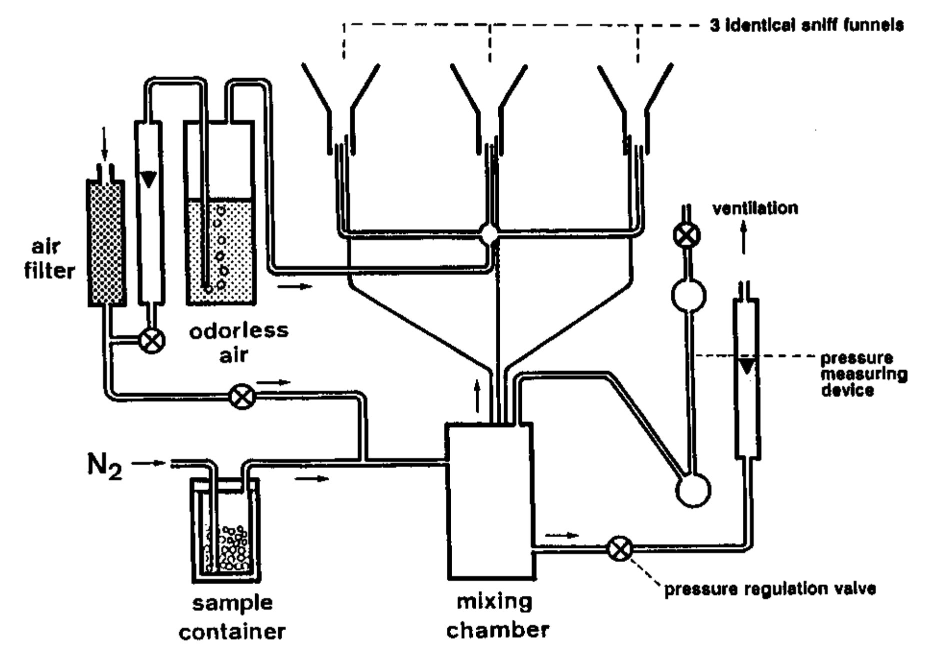

Figure 2. Dynamic air dilution olfactometer

The **vapor pressure** of an odorant or an odorant mixture is determined by using the device shown in Figure 1. The stopcock at the outlet of the buret and the adjustable height ΔH are set in such a way as to ensure a very slow flow of air from the sample container through the microfilter. This allows for maintaining a practically undisturbed equilibrium between the volatiles in the sample and in the surrounding headspace and it allows for determining precisely the headspace volume which passes the filter. The latter is afterwards eluted and the eluate is analyzed by GC.

The **odor perception threshold** is measured by having a panel work with the olfactometer shown in Figure 2. In this instrument a stream of nitrogen is saturated with the volatile sample, diluted with air and fed into the mixing chamber, where it comes into one of the capillaries injecting it into the main stream of air to be smelled. A forced choice triangle test is applied.

The **water solubility** of odorants is determined by directly injecting a saturated aqueous solution into the GC. This saturated solution is obtained by using a dialysis tube avoiding contamination of the solution by undissolved particles or microdroplets.

The **matrix factors** are determined by using the above-described device for the headspace collection. Important is a homogeneous distribution of the odorants in the matrix. This can be a problem if the matrix is a solid. In our experiment, this problem was solved by evenly distributing the fragrance and the products of the matrix's liquid phase over a septum, and then allowing the headspace materials above the septum to flow into a previously evacuated flask.

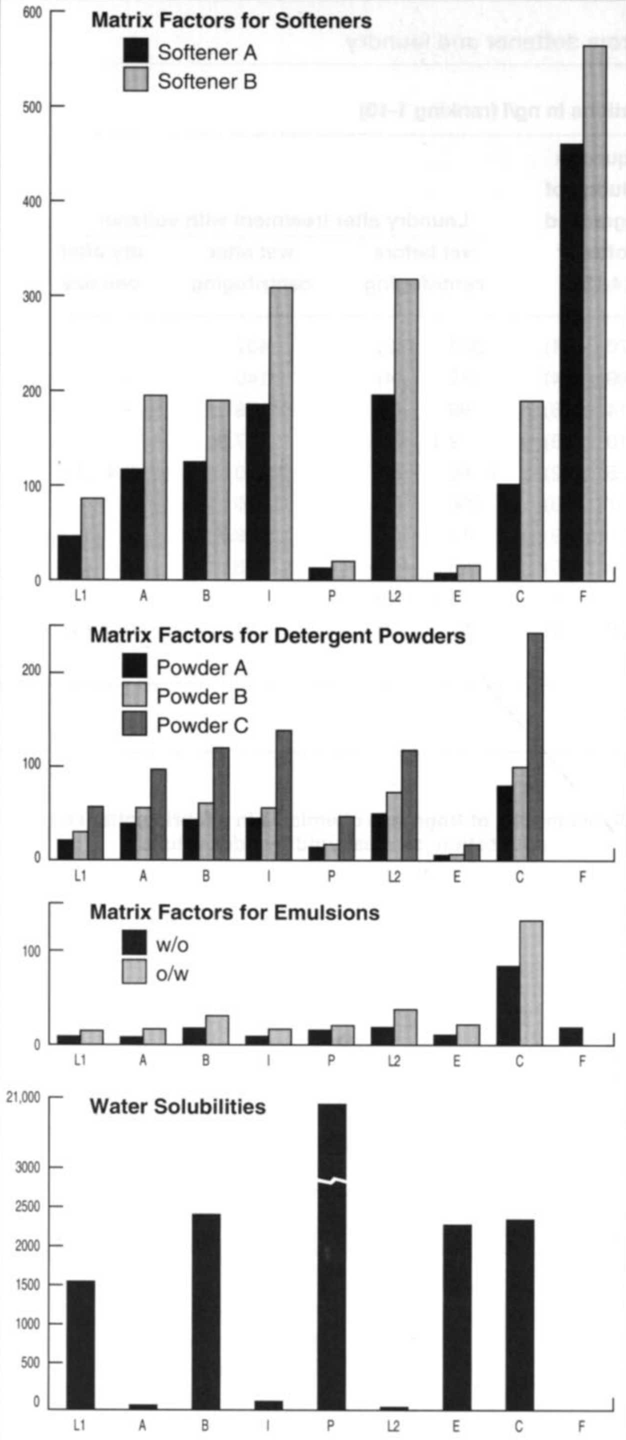

Figure 3. Matrix factors of fragrance chemicals in different types of consumer products and correlation of those factors with water solubilities in ppm

L1 = Linalool
A = Aldehyde C-12 MNA
B = Benzylacetate
I = α-Ionone
P = Phenylethanol
L2 = Lilial
E = Eugenol
C = Coumarin
F = Fixolide

The absence of values for matrix factors of fixolide in detergent powders and emulsion (o/w) is due to the fact that interference of components from the matrix made the analytical determinations of fixolide very difficult. Thus, reliable values could not be obtained for this substance.

When the detergent powder was quickly added to the flask, a cloud formed and the subsequent rotating of the flask lead reproducibly to the desired homogeneous distribution.

Results and Discussion

Figure 3 shows the matrix factors and the water solubilities of a selection of nine fragrance chemicals, part of a model perfume which was used for fragrancing seven different types of product matrices (two softeners, three detergent powders, a water-in-oil emulsion, and an oil-in-water emulsion). The following observations can be made:

- Matrix factors for all fragrance chemicals in different matrices are greater than 1. That indicates much higher odor emanation than theoretically predicted.
- Different matrices influence the emanation of a fragrance chemical to different degrees. The matrix factors for creams are between 10 and 50, for detergent powders between ~ 20 and 200, and for softeners they exceed 600.
- Drastic differences can be observed from one fragrance chemical to another within the same type of matrix.

It can be concluded that there is a direct correlation of the matrix factor and the polarity of the matrix and that there is an inverse proportionality between the fragrance chemical's polarity and the matrix factor. This reflects inter-

Table II. Fragrance emanation from softener and laundry

Headspace concentrations in ng/l (ranking 1-10)

Fragrance chemical	fragrance mixture (3.6% each component)		softener with fragrance (0.2%)		aqueous solution of fragranced softener (4.1%)		Laundry after treatment with softener: wet before centrifuging		wet after centrifuging	dry after one day	
Eucalyptol	641,270	(1)	108,310	(1)	1,070	(1)	863	(2)	437	-	
Linalool	66,280	(2)	8,340	(3)	199	(4)	179	(4)	140	-	
Benzylacetate	43,880	(3)	13,790	(2)	114	(6)	99	(6)	78	-	
Phenylethanol	21,330	(4)	661	(6)	10	(8)	9.1	(9)	7.9	-	
Aldehyde C12-MNA	10,130	(5)	4,190	(4)	925	(2)	1,180	(1)	1,060	2.4	(1)
α-Ionone	4,500	(6)	2,880	(5)	307	(3)	266	(3)	215	-	
Eugenol	3,170	(7)	132	(9)	10	(9)	10	(8)	9.7	-	
Lilial	1,190	(8)	529	(7)	159	(5)	126	(5)	108	2.0	(2)
Coumarin	1,190	(9)	152	(8)	-	(10)	1.1	(10)	-	-	
Fixolide	72	(10)	53	(10)	30	(7)	22	(7)	27	2.0	(3)

molecular interactions of fragrance materials and matrices as well as the fact that the perfume is often not really dissolved in the matrix, but forms emulsions or liquid films on the surface of solid matrix particles.

Table II displays from left to right the behavior throughout an application cycle of ten raw materials of a model mixture containing 3.6% of each component. It is observed that the relative concentration of these components in the headspace is changing. On the left (headspace above the liquid perfume) there is a strict correlation between the components' volatility (ranking in brackets) and the concentration found. This correlation is lost over the application cycle, initially (before centrifuging) mainly on the grounds of the affinity of polar (water soluble) substances to the polar matrix and afterwards mainly on the grounds of the components' volatility. This latter effect is especially important when the laundry is line-dried.

Figure 4 represents OV-histograms of the model perfume's headspace above the softener and the aqueous softener solution (upper part) and the wet, dry, and rewetted laundry (lower part). The odor values (OVs) are plotted on a logarithmic scale in order to more realistically reflect the perceived odor intensity relations. In this diagram, the single fragrance chemicals are arranged from left to right according to decreasing vapor pressures.

Already, the OVs of the single fragrance chemicals in the softener show considerable differences (between 85 and 120,000) depending on their vapor pressures, on the degree to which their volatility is influenced by the matrix effect, and on their individual threshold concentrations. The differences in OVs are still more pro-

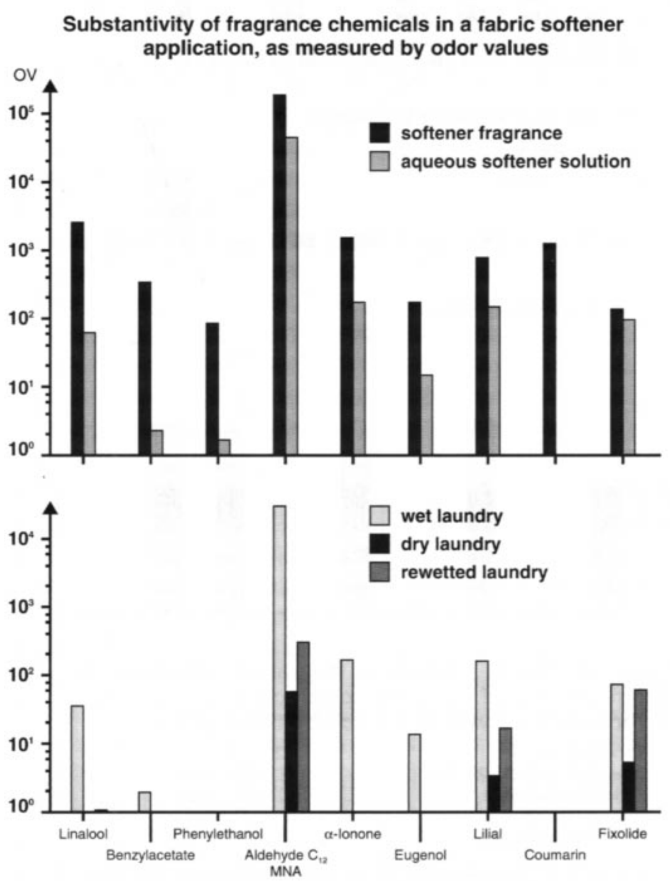

Figure 4. Substantivity of fragrance chemicals in a fabric softener application, as measured by odor values

nounced if the softener is dissolved in water. This is due to the high matrix effects on the polar fragrance chemicals of the polar medium water. For instance, the OVs of linalool, benzylacetate and eugenol are reduced by more than a factor of 10. The OVs of the most polar (water soluble) constituents, phenylethanol and coumarin, drop even more dramatically to values ≤ 1, indicating that they no longer contribute to the perceivable odor of the softener solution in water. In contrast, the OVs of the non-polar constituents are far less reduced than expected on the grounds of the 1:250 dilution of the softener in water.

Whereas the OVs above the wet laundry are nearly identical to those above the aqueous softener solution, they are drastically reduced in the case of the dry laundry: only the less volatile fragrance chemicals contribute, as expected, to the observed faint odor of dry laundry. However, volatility of a fragrance chemical cannot be the only substantivity-determining factor. The complete evaporation of water in the drying process leads to replacement of the liquid matrix (aqueous softener solution) by the solid matrix (fabric) on which the non-evaporized, less volatile fragrance chemicals remain.

The fact that α-ionone, eugenol and coumarin are not substantive on dry laundry, although they are less volatile than aldehyde C12-MNA, can again be explained by a strong matrix effect (including adsorption) of the relatively polar matrix cotton which reduces the release of polar and favors the release of non-polar (water insoluble) fragrance constituents such as aldehyde C12-MNA, lilial and fixolide. Through rewetting dry cotton, the solid matrix (cotton) is again replaced by the liquid matrix (water), which selectively increases the release of the non-polar constituents.

Conclusion

For most applications (water rinse-off application excluded), it can be concluded that a fragrance chemical can generally be regarded as substantive, if it meets the following requirements:

- A medium to low vapor pressure which prevents it from being lost in the initial phase of exposure
- A low odor threshold, which guarantees a favorable OV even in the case of a low vapor pressure
- A polarity adapted to the polarity of the product matrix (inverse correlation) which favors the release.

References

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