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The behaviour of perfumery ingredients in products

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Synopsis—A new technique involving the GLC ANALYSIS of PERFUMERY INGREDIENTS directly from product bases has been developed. This technique has been used to study how materials behave in SOAPS and laundry powders after storage under various conditions.

INTRODUCTION

Perfumers and cosmetic chemists have for some time been interested in predicting how perfumes will behave in the various bases into which they are to be incorporated. Until now, the perfumer has had to resort to many hours of tedious trial and error to ensure a final pleasing effect and even then he could not be certain that the effect will hold constant over months of storage under possibly adverse conditions.

Apart from simple frustration and tedium, this situation presents problems of economics. It is of little value incorporating relatively expensive ingredients in a product if they contribute nothing to the odour over time because of incompatibility with the base or because they are lost by chemical reaction or evaporation. It therefore became imperative that reliable objective methods should be developed to study these problems of behaviour in greater detail.

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HISTORY

Several workers have tried to develop instrumental analytical techniques to study the loss of perfumery ingredients, particularly with respect to soap. Sfiras and Demeilliers (1), for instance, developed a technique of analysing by glc the vapour surrounding unwrapped perfumed soap after storage under various conditions. Although some conclusions could be drawn from the data obtained, the authors were unable actually to observe what was taking place inside the soap itself.

One question they were trying to answer was which materials had the highest 'perfumery value'. Derivichian (2) had stated earlier that esters have higher perfumery values than alcohols. Sfiras and Demeilliers found from their experiments that the vapour from the soap contained higher proportions of esters (e.g. benzyl acetate) to alcohols than that which was found in the vapour from the perfuming liquid itself.

Whether this proves a higher 'perfumery value' for the esters is debatable. It could be argued that the higher proportion of esters in the vapour emitted by soap shows that these materials are lost to a greater extent and that therefore less is available for the physical transfer of perfume from the soap base to the skin. There has been conjecture that there is a virtually inexhaustible reservoir of perfume in the central core of a soap tablet and therefore the perfume ingredients are always available in their original proportion, but no concrete evidence was found to support this theory. It therefore became very desirable to discover exactly what happens inside the soap, by analysing samples directly.

TECHNIQUES OF ANALYSIS

Some early work that was carried out in Unilever involved the use of uv spectroscopy as a method of assessing the behaviour of perfumery ingredients. The materials benzophenone and anisaldehyde were incorporated separately in soap and it was found when the ingredient was extracted with aqueous isopropanol that a reasonable uv spectrum of the ingredient could be obtained. Using this technique it was proved that for those materials studied, the rate of loss of the ingredients from an unwrapped bar of soap is determined by the rate of diffusion of those materials through the soap matrix. This was achieved by measuring the concentration of the ingredients at various points along the axes from the centre to the surface. It was found that the concentration of the ingredients was highest at the centre and lowest near the surface. Had the rate of evaporation from the surface been the rate determining step, then of course the concentrations at points along the axis would have been identical.

For some ingredients that were studied, e.g. benzophenone, no measurable change in the concentration at the centre of the soap bar was observed after 24 weeks storage.

This technique had many restrictions and could not be applied generally to the study of all perfumery ingredients. Firstly, there are only a limited number of materials used in perfumery which have uv absorbing properties. Secondly, the preparation of each sample for analysis is time consuming; and, thirdly, the method does not identify possible breakdown products which may be either falsely identified as the original material or may be missed altogether. Any complex breakdown would of course be impossible to diagnose.

A more generally applicable technique was therefore required and glc appeared to be the most promising. Previous workers have used this technique, but they have all employed some cumbersome form of extraction procedure to isolate the perfume material prior to analysis. Although preliminary extraction techniques can be used for studies of a limited number of materials, it became desirable to develop a simpler, more straightforward system for studying a large number of perfumery materials under various storage conditions in different products. Such a straightforward system has been used by Proprietary Perfumes Limited for about 4000 analyses with good results.

The approach that was used was very simple. It involved placing small samples of the soap (or detergent) on the top of the glc column in the flash-heated zone, the idea being that the perfumery ingredients evaporate into the carrier gas, leaving the soap behind. Many who have tried this technique have found that the chromatogram is ruined by the presence of large peaks from the soap base, as shown in *Fig. 1.* This problem was overcome by utilizing a modified injection system. The sample is placed in a sample tube which is then inserted in the injection head; the latter is then flushed with carrier gas. Once the correct column inlet pressure is reached the sample tube is injected into the flash-heated zone of the glc column. After a short period the sample tube is removed.

In this way it was found possible to elute all of the perfumery ingredients from the sample without getting the undesired components from the base, some of which are probably produced by thermal breakdown. Complete elution of the ingredients was proved by the re-injection of the sample

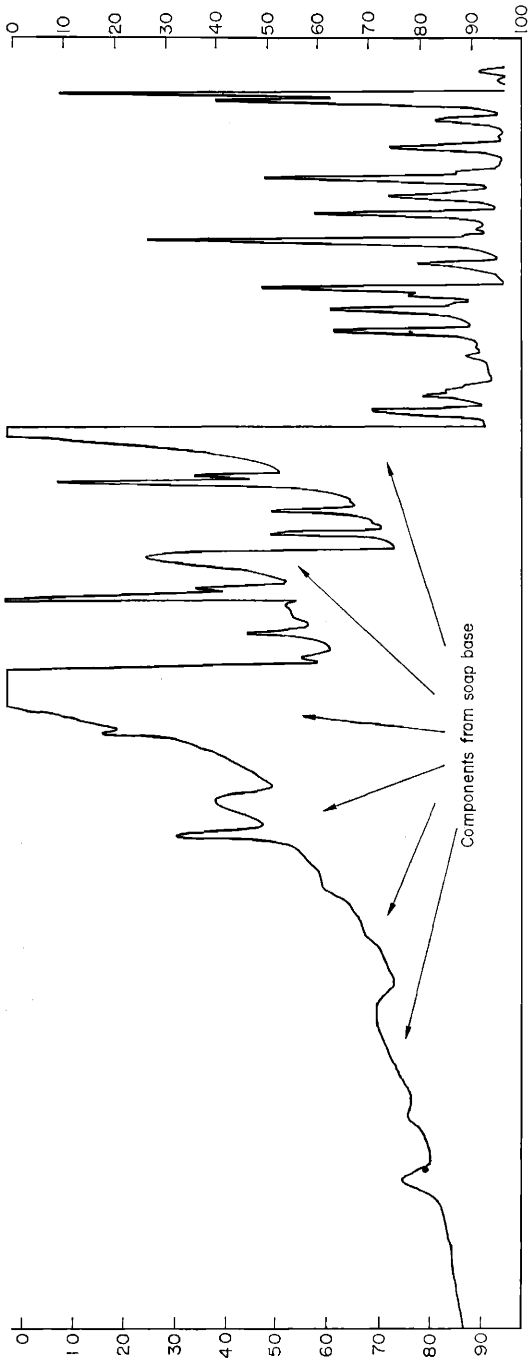

Figure 1. Chromatogram showing interference from soap base components.

when no residual traces of the ingredients could be found. Losses of the majority of perfumery materials during the weighing and sample loading procedure were minimal and a coefficient of variation of ±7% relative was obtained for the method when analysing a mixture of cineole, linalool, benzyl acetate, benzyl benzoate and diethyl phthalate in superfatted soap.

To carry out controlled storage tests it was necessary to use a stable reference material which would be incorporated into the product with the ingredient under investigation. It was also desirable that this reference material should be odourless so that parallel odour assessments could be made.

Diethyl phthalate (DEP) was selected as it is both odourless and stable in soap bars under the conditions of storage that were to be used in the test. The suitability of DEP was confirmed by incorporating a mixture of benzophenone (which had previously been shown to be stable by uv measurements) and diethyl phthalate in soap bars and analysing samples from the centre of each bar after various periods of storage.

The behaviour of each ingredient was studied in the following manner. A mixture of the ingredient and diethyl phthalate (ratio of about 1 : 1) was incorporated in superfatted soap at 0·2%; the soap was plodded into bars 3″ × 1″ and wrapped in standard glassine and glazed paper wrapping. The bars were then stored for both 12 and 24 weeks both at room temperature (*c.* 20°) and at 37°. Samples were taken from the centre of each bar and analysed by glc. Chromatograms were compared with those obtained from freshly prepared bars of perfumed soap (1 week old to allow equilibration of distribution). The incorporation and storage were arranged so that analyses could be carried out within a 24 h period.

RESULTS

Table I gives the results obtained for some common perfumery materials. Although some results have been omitted, no general conclusions could be drawn as to relationships between behaviour and chemical class except in the case of formates, which all showed a tendency to hydrolyse and produce the parent alcohol. Low boiling materials generally were lost more readily than the higher boiling materials. Samples taken from the surface layers of the wrapped bars had the same composition as those taken from the centre, which proves that any loss other than by chemical breakdown is governed, in the case of the wrapped bar, by the rate at which the ingredient migrates through the wrapper and hence into the atmosphere. Apart

Table I

Material in soap	% material incorporated present after:			
	12 weeks		24 weeks	
	at RT	at 37°C	at RT	at 37°C
Hydrocarbons				
Diphenylmethane	95	67	82	61
Camphene	62	62	50	38
Limonene	85	41	81	17
Myrcene	100	20	50	10
α-Pinene	100	40	50	4
Alcohols				
n-Nonanol	100	100	100	100
cis-*p*-tert-Butylcyclohexanol	100	100	100	100
trans-*p*-tert-Butylcyclohexanol	100	100	100	93
α-Terpineol	100	100	100	90
Borneol	100	96	100	89
Benzyl alcohol	100	87	100	81
Caryophyllene alcohol	100	81	88	75
Linalool	100	78	100	53
cis-Hex-3-enol	86	53	46	35
trans-Hex-3-enol	88	56	49	37
Esters				
Citronellyl acetate	100	100	100	88
Bornyl acetate	100	88	83	83
cis-*p*-tert-Butylcyclohexyl acetate	100	100	100	89
trans-*p*-tert-Butylcyclohexyl acetate	100	100	100	78
Terpinyl acetate	97	97	85	82
Inonyl acetate	84	56	64	49
Methyl heptine carbonate	67	31	59	13
Benzyl acetate	64	41	49	0
Benzyl formate	0	0	0	0
Citronellyl formate	0	0	0	0
Trimethylhexyl formate	0	0	0	0
Linalyl formate	0	0	0	0
Phenylethyl formate	0	0	0	0
Aldehydes				
Amylcinnamaldehyde	100	100	100	100
Hydroxycitronellal	100	100	100	98
Undecenal	100	96	100	86
Cinnamaldehyde	70	76	63	60
cis Citral, neral	95	58	68	53
trans Citral, geranial	97	58	74	52
Hydratropic aldehyde	62	36	33	16
Benzaldehyde	0	0	0	0
Phenylacetaldehyde	0	0	0	0

Table I—continued

Material in soap	% material incorporated present after:			
	12 weeks		24 weeks	
	at RT	at 37°C	at RT	at 37°C
Ketones				
α-Ionone	100	100	100	100
Benzophenone	100	100	100	100
Jasmalone	100	93	100	89
Methyl nonyl ketone	83	75	79	64
Methyl hexyl ketone	40	20	14	0
Ethyl amyl ketone	0	0	0	0
Ethers				
Amyl benzyl ether	100	100	100	79
β-Naphthyl methyl ether	94	79	96	78
Anther	100	77	73	58
Rose oxide	83	52	65	35
p-Cresyl methyl ether	100	63	80	9
Phenylethyl methyl ether	53	44	25	9

from the formates only a few materials showed signs of chemical breakdown.

Phenylacetaldehyde is so unstable that about 60% was lost 1 week after incorporation. Benzyl acetate, which has often been studied in this context in the past by others (3), is among those materials which show chemical instability, but the amount of benzyl alcohol produced does not account for all the loss and therefore evaporation must also be a contributory factor.

After the initial screening of individual materials it became interesting to examine some time-honoured beliefs that perfumers have held in connection with the behaviour of various ingredients and mixtures. For example, it has been widely believed that the behaviour of aldehydes can be improved by the addition of an alcohol, and in particular the corresponding alcohol, because of the supposed formation of hemiacetals. In order to test the validity of the argument, mixtures of the aldehyde, the corresponding alcohol and diethyl phthalate (in the ratio 1 : 1 : 1) were incorporated into soap bars and stored under the same conditions as described previously. *Table II* gives the results of the analyses and shows, within experimental error, that there is no difference in the behaviour of aldehydes with or without the alcohol.

Table II

Material in soap	% material incorporated present after			
	12 weeks		24 weeks	
	at RT	at 37°C	at RT	at 37°C
n-Octanal	80	35	30	4
n-Octanal (+ *n*-Octanol)	90	40	28	6
n-Nonanal	100	75	100	55
n-Nonanal (+ *n*-Nonanol)	100	72	100	50
Citronellal	91	93	83	59
Citronellal (+ Citronellol)	95	91	80	57
Benzaldehyde	0	0	0	0
Benzaldehyde (+ Benzyl alcohol)	0	0	0	0
	1 week			
	at RT	at 37°C		
Phenylacetaldehyde	37	0		
Phenylacetaldehyde (+ Phenylethyl alcohol)	37	0		

Another belief which was investigated was that concerning 'fixation'. It has long been thought that the addition of high boiling materials reduces the loss of low boiling ingredients from perfumes. Although this has been well established for perfumes applied to the skin it has never been proved for perfumes in products. It was possible using this method of analysis to show that even when the addition of a fixative (*Hercolyn D**) was made at a level five times that of the perfumery material, no improvement in the retention of the material in the soap could be observed.

The lack of detectable formation of hemiacetals and the ineffectiveness of fixatives in soap are not surprising when one considers the vast differences in the rates of collision between the molecules of perfumery ingredients themselves and between the ingredient molecules and the soap base molecules. The number of collisions between individual perfumery ingredient molecules would be extremely low in soap as compared with those in the essence and therefore the effects of physical or chemical interaction between such molecules would be correspondingly small. Any supposedly beneficial effects of interactions that take place in the essence before incorporation and which are reversible, as in the cases of hemiacetal formation, and the physical interactions associated with 'fixatives', will be subsequently minimized after incorporation of the essence in the product base.

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*Hercules Powder Co.

Table III

Material in laundry powder	% material incorporated present after			
	12 weeks		24 weeks	
	at RT	at 37°C/ 70% rh	at RT	at 37°C/ 70% rh
Hydrocarbons				
Diphenylmethane	62	24	72	33
Alcohols				
Phenylethyl dimethyl carbinol	100	100	100	95
Caryophyllene alcohol	100	100	100	88
Dodecanol	100	100	100	70
Decanol	100	84	92	67
Anisyl alcohol	64	40	45	19
Borneol	77	31	37	0
Benzyl alcohol	65	18	31	0
Linalool	38	8	27	0
Esters				
Musk oxalide	100	100	100	100
Benzyl benzoate	100	100	100	71
Gardocyclene	94	69	98	70
Ethyl cinnamate	59	67	63	38
Geranyl acetate	67	12	54	0
Citronellyl acetate	65	0	31	0
Benzyl acetate	18	0	13	0
Aldehydes				
Hexylcinnamaldehyde	100	100	100	100
Anisaldehyde	30	14	17	13
Hydroxycitronellal	80	40	75	0
cis Citral, neral	40	0	0	0
trans Citral, geranial	40	0	0	0
Cinnamaldehyde	28	0	0	0
Phenylacetaldehyde	20	0	7	0
Decanal	14	0	0	0
Ketones				
Versalide	100	100	100	100
Benzophenone	100	90	91	89
Celestolide	100	100	100	71
Methyl naphthyl ketone	100	100	100	71
α-Ionone	86	26	78	4
Jasmalone	92	20	72	0
Acetophenone	0	0	0	0
Ethers				
Methyl diphenyl ether	100	100	100	83
β-Naphthyl ethyl ether	93	76	97	66
Phenylethyl *n*-butyl ether	44	15	38	0
Phenylethyl amyl ether	35	0	23	0
Amyl benzyl ether	40	0	12	0

Apart from the study of the behaviour of ingredients in soap base, a similar detailed study has been carried out in laundry powders. The perfumery ingredients were incorporated individually with diethyl phthalate into a laundry powder (in this case *Persil Automatic*) at a level of 0·1%. The products were then stored in cartons for periods of both 3 and 6 months at both room temperature and 37°C/70% relative humidity. Again the incorporation and storage were so arranged as to enable the analysis to be made in a period of 24 h. The chromatograms obtained from the stored samples were compared with those from fresh samples kept in glass jars. *Table III* shows the behaviour of some common perfumery ingredients relative to diethyl phthalate.*

One can see from the table that many perfumery ingredients do not perform as well in packets of laundry powder as in wrapped soap bars. Once again similar conclusions were reached, namely that lower boiling materials are lost more readily than the higher boiling ones, and that there are no obvious links between chemical structures and stability.

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*The results are relative for it has been shown that there is loss of diethyl phthalate under the most severe conditions of 24 weeks at 37°C and 70% rh amounting to about 20%.

Table IV

Material in laundry powder	% material incorporated present after			
	12 weeks		24 weeks	
	at RT	at 37°C/ 70% rh	at RT	at 37°C/ 70% rh
n-Decanal	14	0	0	0
n-Decanal (+ *n*-Decanol)	15	0	0	0
n-Undecenal	50	0	29	0
n-Undecenal (+ *n*-Undecenol)	41	0	22	0
n-Dodecanal	83	0	74	0
n-Dodecanal (+ *n*-Dodecanol)	80	0	68	0
Linalyl acetate	32	0	12	0
Linalyl acetate (+ *Hercolyn D*)	30	0	13	0
Citronellol	100	74	74	30
Citronellol (+ *Hercolyn D*)	94	61	74	33
Cyclamen aldehyde	81	0	59	0
Cyclamen aldehyde (+ *Hercolyn D*)	80	0	49	0
Phenylethyl amyl ether	35	0	23	0
Phenylethyl amyl ether (+ *Hercolyn D*	45	0	25	0
Jasmacyclene	78	14	59	11
Jasmacyclene (+ *Hercolyn D*)	85	18	59	14

Hemiacetal formation from aldehydes and the fixative effects of *Hercolyn D* were investigated for ingredients in laundry powder and once again these effects were not demonstrable, as shown by the results in *Table IV.*

These results showed that the majority of perfumery materials do not perform well in laundry powders stored in cartons, therefore a second test was undertaken in order to differentiate between the loss by evaporation and that by chemical instability. To achieve this objective the product containing the ingredient was stored in glass jars. The results of this test are given in *Table V*, which clearly demonstrates that in the case of this particular laundry powder the loss of ingredients observed in packets was caused mainly by evaporation.

Table V

Material in laundry powder		% material incorporated present after			
		12 weeks		24 weeks	
		at RT	at 37°C/ 70% rh	at RT	at 37°C/ 70% rh
Linalool	Carton	38	8	27	0
	Glass	100	100	100	98
Phenylethyl alcohol	Carton	66	66	52	17
	Glass	100	97	93	80
Benzyl acetate	Carton	18	0	13	0
	Glass	100	83	75	50
Citronellyl acetate	Carton	65	0	31	0
	Glass	100	100	100	86
Linalyl acetate	Carton	32	0	12	0
	Glass	100	100	100	100
Citral (*cis* and *trans*)	Carton	40	0	0	0
	Glass	100	100	100	92
Dihydrojasmone	Carton	92	20	72	0
	Glass	100	79	83	37
α-Ionone	Carton	86	26	78	4
	Glass	100	100	100	93
Phenylacetaldehyde	Carton	20	0	7	0
	Glass	100	100	100	100
Amyl benzyl ether	Carton	40	0	12	0
	Glass	100	100	100	75
Phenylethyl amyl ether	Carton	35	0	23	0
	Glass	100	100	100	93
Phenylethyl *n*-butyl ether	Carton	44	15	38	0
	Glass	100	100	100	100

APPLICATION OF RESULTS

Clearly the fact that evaporation is a major cause of perfumery ingredient loss from laundry powders warrants investigations into the efficiency of various packaging materials. The loss of perfume can be as much as three times higher in the least suitable type of packet than some of the best packets used commercially, and the glc method can be of use in discovering the best package compromise in terms of effectiveness and cost.

Another area where the glc technique has found application is in market research. The ability to analyse complete perfumes directly from a product, which is possible by attaching the glc to a mass spectrometer, permits study of perfumery chemicals used in relation to market trends and fashions. This type of information is of immense value to a company in a competitive situation.

Perhaps the most valuable result of this study, however, is that it is now possible to create perfumes which are chemically stable and relatively unaffected by evaporation, even with completely new product base formulations. In these cases there are no historical data for the perfumers to call upon. More detailed investigations have shown that the materials in a complex perfume mixture behave in the same way as when ingredients are incorporated individually. Therefore it is possible to reduce the total number of analyses required by screening a large number of ingredients as a series of mixtures, thereby acquiring expert knowledge in a relatively short period.

OTHER BASE APPLICATIONS

All of the work described so far has been concerned with two major products, i.e. soaps and laundry powders. However, the technique has wider application and it has been generally employed in our laboratories in the analysis of perfumes and flavours in other bases. For example, it is possible to study the behaviour of flavours in toothpaste bases, perfumes in haircreams and in talcum powders, and the technique has even been used as a method of analysing the essential oil of lavandin directly from a single floret. The technique can in fact be used whenever an analysis is required of any volatile material present in a relatively non-volatile base.

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