

THE JOURNAL OF THE SOCIETY OF COSMETIC CHEMISTS

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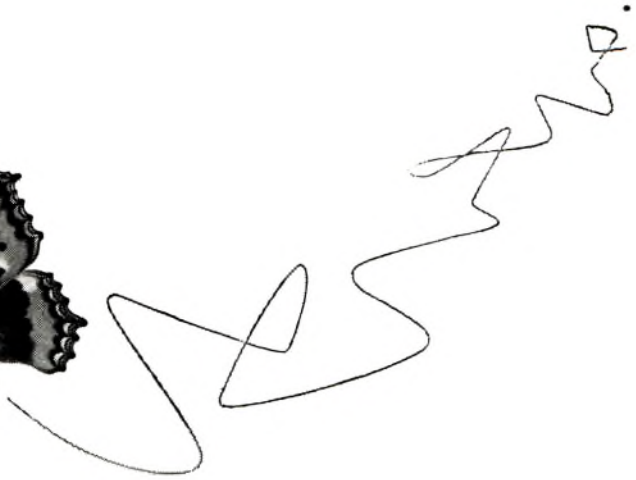
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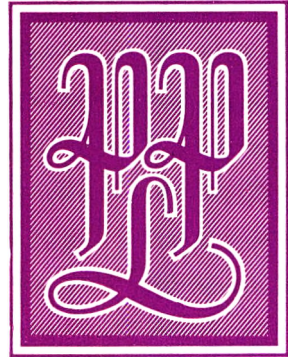
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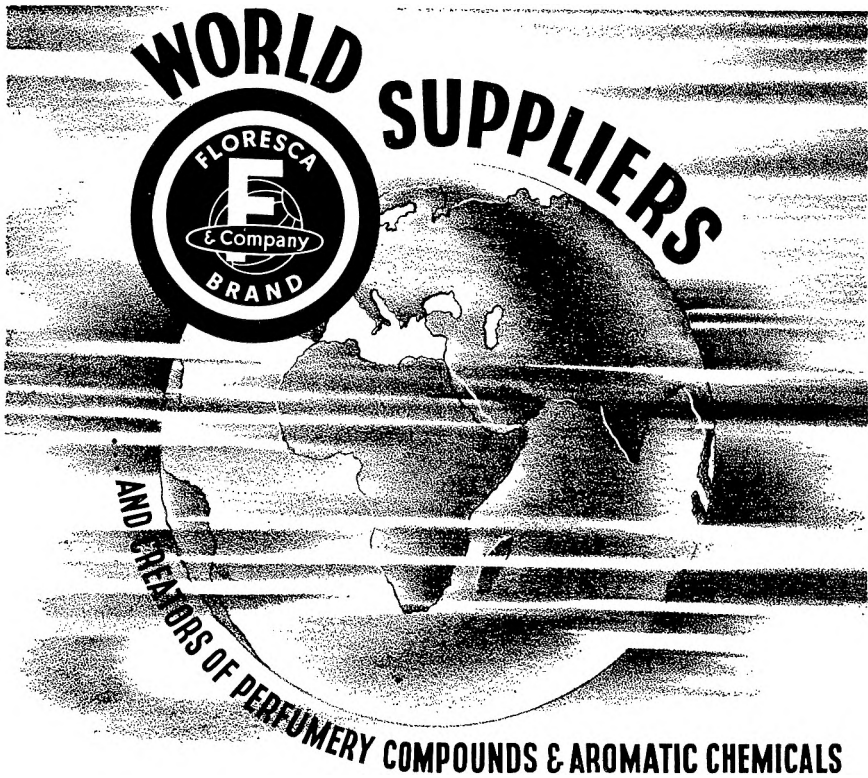


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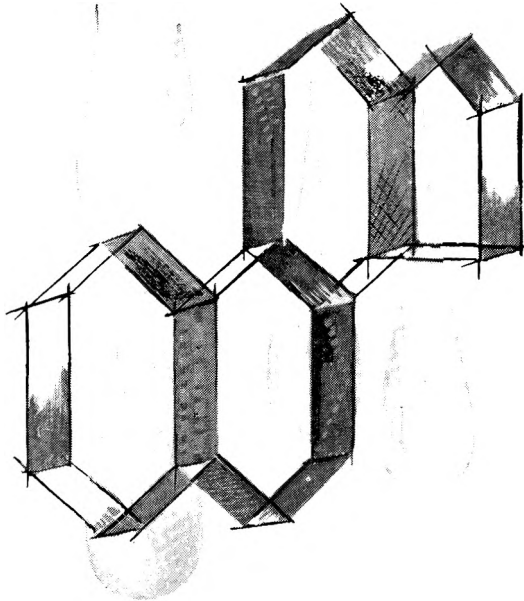
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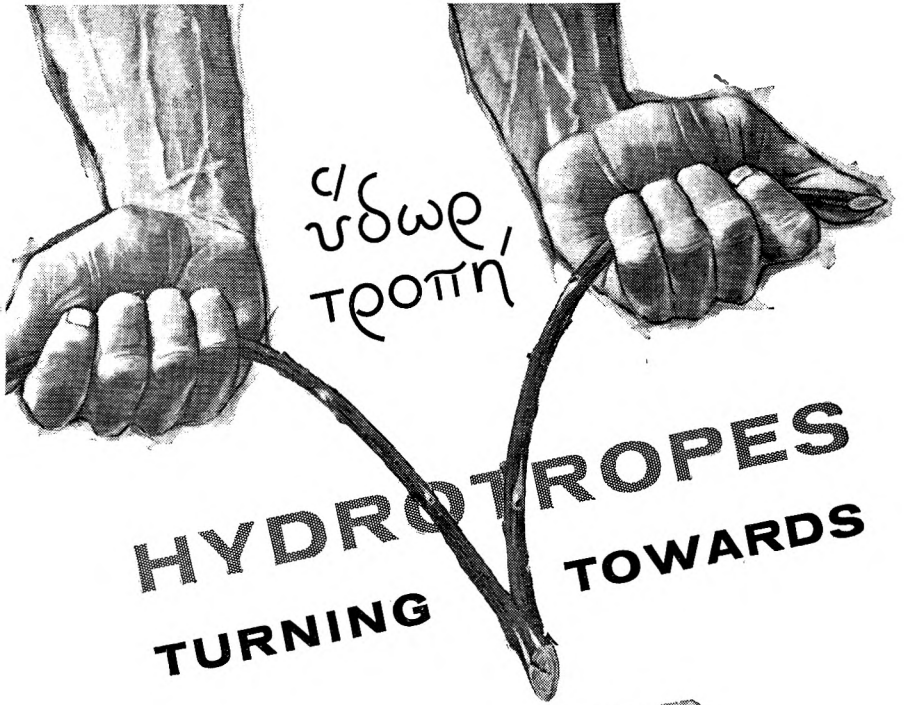


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SYNTHETIC PERFUME MATERIALS FROM PINENE

M. P. ERNI*

*Presented at the Symposium on Perfumery, organised by the Society, at
Cheltenham, Glos., on 14th November 1962.*

Not only research into unknown odorous principals of natural aromatic materials retains the attention of the perfumer. New manufacturing routes of well-established staple perfumery chemicals have also recently aroused considerable interest. The economic aspect of one of these new processes, the synthesis of certain terpene alcohols from β -pinene, is discussed. The purity of these pinene derivatives calls for a new assessment of the odour of the rose alcohols and provides the perfumer with scope for originality.

THE ADVENT of new physico-analytical methods, so fertile in the whole field of chemistry, has also made a deep impact on the industry of synthetic aromatics. Research into the finest ramifications of the immense variety of odorous material which nature offers has greatly progressed. New odorous principals have been isolated, their constitutions established and their syntheses carried out.

The perfumer follows this work with a keen interest in the hope that it will result in new, commercially available aromatic chemicals, which he may then use to produce new or better olfactive effects.

*A. Boake, Roberts & Co. Ltd., London, E.17.

But the bulk of a perfume compound still consists mainly of well-known synthetic aromatics the chemical constitutions of which are firmly established. These materials are produced in large quantities, and demand for the production of these chemicals will expand as more and more everyday retail commodities are making use of odour as a means of sales appeal.

Perfumers have a tendency to take the manufacturing processes, the sources of raw materials and the quality specification of these staple aromatics very much for granted. Continuous development is also taking place in this field. The interest of the perfumer has lately been focused on such progress since several fundamental new approaches to manufacturing routes have been made.

Probably the most ambitious among these new processes has been the synthesis of geraniol/nerol, and of linalol from myrcene. Since geraniol can be converted into citral, citronellol and citronellal, this synthesis gives access to a range of important perfume synthetics traditionally isolated from natural oils. It also furnishes intermediates for manufacturing hydroxycitronellal, and the ionones.

A long list of distinguished names of all those who have contributed to the work on pinene, myrcene and the terpene alcohols could be mentioned, but particular credit should go to two teams who have developed the industrial processes, and brought them into fruition.

Looking for new outlets for turpentine, a group of American research chemists under the direction of Bain effected the industrial production of myrcene from β -pinene. Subsequently, Bain *et al*, in particular R. L. Webb, successfully carried out the first industrial synthesis of geraniol from myrcene.

While the Americans were pressing forward with this project, a British team was studying alternative methods for the production of terpene alcohols and they also found the route from myrcene to be the most proficient. Indeed, under the direction of Carroll, British chemists succeeded in synthesising linalol from myrcene. Thus, while following different objectives, the work of the two groups was complementary. From their joint efforts, highly specialised manufacturing techniques have resulted.

In 1957, the first rose alcohols appeared on the market. Whereas nerol was offered from the start in a form containing practically no other rose alcohol, the initial qualities of synthetic geraniol and citronellol were mixtures of different rose alcohols in order to satisfy the majority of users accustomed to the traditional products. Since 1960, however, increasing quantities of the pure individual alcohols have been produced and their regular sale started this year.

In 1958 and 1959, linalyl acetate and linalol ex pinene, made their debut, and in 1961 the first batches of hydroxycitronellal and citral ex pinene, came on the market. It is a salient feature of this development that turpentine

as a raw material will gradually replace citronella, lemongrass and bois de rose, three oils whose price fluctuations are well known and the production of which is often impeded by inclement climate or political disturbances. Moreover, although the proportions of α - and β -pinene vary with their geographical origin, adequate qualities and quantities can be found not only in America but also in Europe.

The appearance on the market of products made from pinene has already had a stabilising influence on prices where the volume of production of synthetics is appreciable, i.e. for linalol, geraniol, nerol and citronellol. The production of hydroxycitronellal and citral is inadequate at the moment. But it is foreseeable that when sufficient quantities of these synthetics are available, their prices and those of the ionones will drop.

Figure 1
New synthetic routes from turpentine.

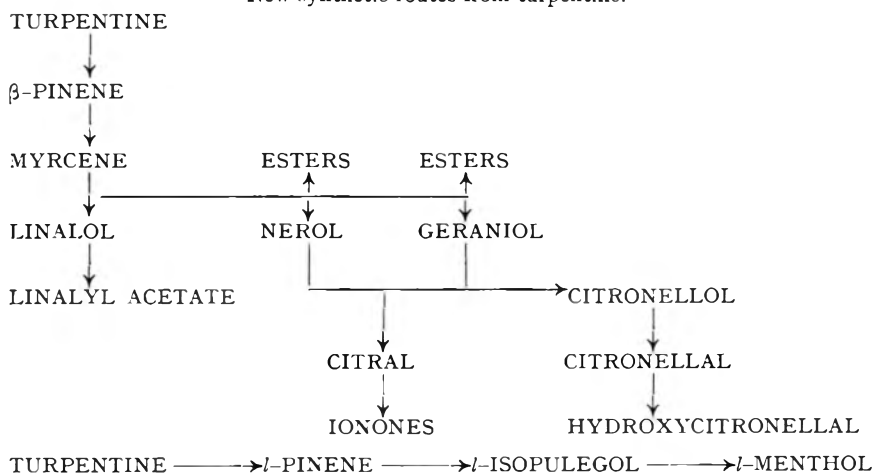
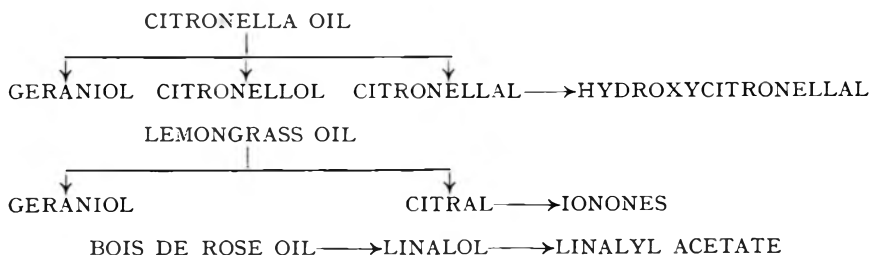


Fig. 1 outlines the new routes from turpentine, and this may be compared with the general pattern of the traditional isolation processes from natural oils shown in Fig. 2.

Figure 2
Traditional isolation from essential oils.



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The traditional rose alcohols are normally isolated from citronella, sometimes also from other natural oils. In fact, the "Geraniol" resulting from this operation is more often a by-product, the principal interest being centred on the other components of the natural oil. It is sold at a low price after a minimum of rectification. The better grade frequently contains a large proportion of citronellol, and possibly nerol.

In citronellol isolated from citronella, one normally finds geraniol. Special qualities of these two rose alcohols ex citronella are produced where extensive rectification has been carried out, but their price level handicaps their sale.

Most commercial nerols isolated from an essential oil, or derived from an isolate, contain no more than 30-70% nerol. The remainder is, for the most part, geraniol.

We therefore see that the traditional qualities of these alcohols vary to a large extent and often their commercial name indicates no more than the predominant constituent. Their common feature is a nuance, more or less accentuated, reminiscent of citronella and resulting from traces of terpenes and sesquiterpenes from the original oil.

The synthetic rose alcohols from myrcene, by their very nature, are devoid of these terpenes. They are very pure and well defined. If one compares them with their traditional counterparts this fundamental difference must be kept in mind. For example, if they appear less lasting on the smelling strip, this is explained by the absence of sesquiterpene impurities. This is simply one aspect of their purity. In preparing a composition, the perfumer will call upon oils and synthetic products which act more suitably as fixatives rather than having a citronella background.

It will also be appreciated that precise analytical specifications can be given to these new synthetics ex pinene. They will therefore fall in line with the increasing number of products which are characterised by such data. This obviates the practice of "bouquetage". Moreover, gas-liquid chromatography has significantly simplified analytical control.

We must not forget, however, that improved methods and more regular analytical control do not guarantee "absolute purity". In chemistry, as elsewhere, the "absolute" does not exist. The purest product will always contain impurities. But for the chemist this is no reason for not *aiming* at maximum purity, always on the condition that it can be obtained at reasonable cost.

The perfumer is particularly concerned with the effect of the impurities. He will certainly agree that the more a product is chemically pure the better is its chance of reflecting a true picture of its odour. But odour effect is not proportional to weight, which means that a very small amount of impurity may provoke an odour change quite out of proportion to the

actual quantities involved. Each impurity brings not only its individual odour, but the more complicated effects of exaltation or depression.

The perfumer of today is therefore not only interested in the chemical purity of a synthetic aromatic chemical. He asks for the olfactive and possibly analytical control of the unavoidable contaminations. He looks also more open-mindedly, than some of his predecessors, at the old antithesis: Nature versus Synthesis. A particular impurity is not *ipso facto* desirable because it is of natural origin. This is admirably illustrated in the case of the rose alcohols.

When examining very pure nerol, geraniol and citronellol, one is surprised how much their odours differ. The fact that in the past they were generally used together has somewhat blurred their individuality. Nerol has always intrigued perfumers; invested with a flattering reputation, the traditional product has not lived up to expectations. Today we know why, and pure nerol ex pinene has truly been a revelation. Its perfume is extremely fresh, somewhat citrus, with a delicate leafy tonality recalling the dew on a sprig of lily of the valley.

The odour of geraniol is more familiar since it is this material which is present in all the traditional rose alcohols. It should be pointed out, however, that in the pure form and freed from the musty citronella odour, it appears fresher and less straw-like.

Pure citronellol, best of all the rose alcohols, suggests the perfume of the rose. Soft and round, never too dominant, it blends as well with floral notes as with heavier perfumes.

For some years another synthetic linalol has been on the market. The prejudice towards a product not isolated from bois de rose has subsequently matured to a more realistic judgement.

From all the above synthetic alcohols, esters of analogous purity have been prepared. The same characteristic difference which was found between the rose alcohols is also reflected in their esters, modified according to the nature of the acid group. Thus the esters of citronellol have more body and are more rosy than those of geraniol which, for their part, are more powerful and aggressive. The nerol esters show variations of the delicate green note of the pure alcohol. Linalyl acetate occupies a position of prime importance in perfumery. The synthetic product is distinguished by its soft fruity note.

The latest arrivals in the series of pinene derivatives are hydroxycitronellal and citral. Obtained by a very modern technique, these aldehydes possess all the qualities of their parent alcohols, that is to say, chemical and olfactive purity.

To this short review of derivatives from pinene must also be added *laevo*-menthol obtained from α - or β -pinene. In the United States, large

quantities have already been made by this route and production in England is also anticipated. With certain of these pinene products, demand exceeds production. Important assets have recently been invested in a vast programme for expanding production capacity.

The exploitation of all the possibilities which the pinene molecule suggests to the imaginative mind of the research worker is not yet complete. It is to be hoped that the chemists who are at present working along these lines will, in the near future, develop further interesting products.

For the creative perfumer the question as to whether synthetics derived from pinene can replace the corresponding classical products is of secondary consideration compared with the originality which they offer. Since they impart a new tonality and (in the case of the rose alcohols) resolve a complex smell into distinctive, well-defined odours, these new compounds are worthy of serious attention.

(Received : 4th September 1962)

Introduction by the lecturer

Research into volatile odorous material is continuously progressing, and every year an astonishing amount of analytical information is published. Much of it is of purely academic interest, and some is deliberately incomplete. For obvious reasons one gets more discreet where work of immediate economic interest is involved, but it is only fair to say that for some years, generally speaking, there has been a distinct trend towards less secrecy. We perfumers, those attached to a supply house as well as those in the perfumery and toiletry trade, follow this trend with keen interest. New aromatic chemicals, or new bases and reconstructions of essential oils, which can be used to produce new or better olfactive effects may result. On the other hand, the production techniques, raw materials' sources and even quality specifications of the well-known traditional synthetic aromatic chemicals normally arouse less interest. It is only lately since several important materials manufactured by fundamentally new routes have appeared on the market that the perfumer's attention has been focused on this aspect.

One of these new routes is the synthesis of geraniol, nerol and linalol from β -pinene, which occurs in satisfactory proportions in turpentine. Geraniol and nerol can be converted into citral, citronellol and citronellal, so that this synthesis produces the main constituents of the following three essential oils. *Bois de rose oil*—linalol; citronella oil—geraniol, citronellol and citronellal; and lemongrass oil—citral. If to these alcohols and aldehydes we add their derivatives linalyl acetate, geranyl acetate, citronellyl acetate, hydroxycitronellal and the ionones, and *laevo*-menthol produced from the optically active pinene, we have indeed an impressive range of important perfumery materials based on turpentine.

It had long been accepted that a synthesis of the current terpene alcohols could not be a prosperous venture since traditional isolating processes seemed firmly established and raw material abundant, at least under normal political conditions. In this extremely competitive field of staple perfumery, where an output of hundreds of tons has to be considered, not only chemical ingenuity was needed, but also difficult engineering problems had to be tackled and substantial assets invested. That this problem has been successfully solved, and brought to a working industrial reality, is quite a major achievement.

The pinene products have already had a stabilising effect on the market. Even more drastic price reductions may be expected when production capacities will have been increased and are more in line with the demand. Alas, the perfumer very seldom conforms to that popular picture of a care-free artist dallying happily with Bulgarian Otto of Rose, Jasmin absolute, and similar exalted raw materials. Pencil and cost sheet are the inescapable companions of his smelling strip.

But the synthesis of the terpene alcohols from pinene has more than an economic aspect. The resulting alcohols have proved to be extremely pure, and therefore enabled the perfumer to make a new assessment of their odours. The rose alcohols, for instance, have revealed more distinctive individualities than would have been expected from the traditional isolates which, as we know, are generally mixtures of two or three alcohols. The perfumer is always on the look out for new ideas; some new twist in a field where taste conventions, technical requirements, or just price considerations very often leave him little scope for fantasy. These new pinene synthetics will be found most helpful. It seems that not only can they replace the corresponding classical products isolated from natural oils, but they also offer new tonalities and therefore an opportunity for novelty.

DISCUSSION

DR. Y.-R. NAVES: The lecturer has good reason to emphasize the interest aroused in the products which can be made from β -pinene—products which perfumers and chemists alike, are regarding as new raw materials. In fact we note that the lecturer agrees completely with the contention that these are new products, and that the perfumer is interested basically in odours and not in chemical substances as such. It is quite clear that the perfumer will appreciate the note of any of the products made from pinene as distinct from those made from alcohols from different sources.

Whilst on this subject I should like to relate a story. Some thirty years ago I prepared for Professors V. Grignand and J. Doëuvre, a sample of very highly purified *laevo*-citronellol, starting with Bulgarian Rose oil as raw

material. That product, and five commercial samples of citronellol emanating from various reputable sources, were submitted under code numbers to six of the leading perfumers of the time, examining independently. The *laevo*-citronellol, made from the Bulgarian Rose oil, was unanimously considered to be the least acceptable for the purposes for which citronellol was used at the time.

THE LECTURER : I very heartily agree with Dr. Naves about the interest of the pinene alcohols. As a perfumer I see their prime interest in their originality, in having, for instance, a really pure nerol or citronellol absolutely free from geraniol. But let us not forget that we can also mix these pure alcohols, and in some way, simulate a traditional product.

I further agree with Dr. Naves that it is impossible to obtain complete simulation of the traditional material, but I would underline that very often these products, alone or blended, can in some ways afford substitutes for traditional isolates. In fact they are probably often used as such ; but again I would like to emphasize the aspect of originality, and their value as new products.

Concerning Dr. Naves's story, I am just wondering how that highly purified product which was submitted thirty years ago, would stand up today to modern analysis by GLC, IR or NMR.

DR. Y.-R. NAVES : It may perhaps sound astonishing, but we have kept that sample for many years, and have subjected it to spectrophotometry, GLC and all the standard physical and chemical analyses. We have found it surprisingly pure, considering that it had been prepared at a time when such modern methods did not exist.

I wish to re-emphasize that the reason why the citronellol obviously was not accepted at that time was because, being so pure, it represented a new product. It was rejected because it was something unknown, something new, and perhaps in a way it can be compared with the very pure product to which you referred, that has to be looked upon in an entirely new and constructive way.

MR. A. H. RUYS : Hydroxycitronellal made from the citronellal fraction of Citronella oil Java contains *isopulegol*, and its hydrate as impurities. Should it be taken that your new hydration process is one that does not yield any *isopulegol* as a minor by-product ?

THE LECTURER : Hydroxycitronellal, ex pinene, is chemically purer than the traditional material, which does not necessarily mean olfactively purer. One has to be extremely careful about the evaluation of the olfactive quality of a hydroxycitronellal. A certain standard odour is more or less generally accepted, but it is unknown whether this traditional odour is only due to hydroxycitronellal. Perhaps it is, but we just do not know.

According to our analyst, the amount of *isopulegol* in the traditional product which we have been manufacturing ranges from 0.01—0.1%. The figures for the synthetic hydroxycitronellal are within those limits, in fact rather on the lower side.

On the basis of recent olfactive tests on the purity of hydroxycitronellal, I am inclined to state that *isopulegol* is not quite the villain it is commonly thought to be.

MR. A. D. CHESHIRE : Is it in any way possible that the observed odour differences between the natural and synthetic citronellols is due to the different proportions of α - and β -forms ?

THE LECTURER : I have smelt different products, containing both or one of the isomers, and in my opinion the differences of odour have no connection with the α - and β -forms.

DR. R. FAVRE : As users we have something to say about these new developments in the perfumery industry, which are opening up new avenues for the industry, and we ourselves welcome the advent of these new chemicals, which will help to avoid dependence on essential oils so difficult to obtain nowadays. As Dr. Naves rightly said, they should not be regarded as replacements of the old but must be considered as entirely new products. Is it really necessary for us to try always to reproduce exactly some perfumery materials which have been produced for many years in the past ? I believe that the advent of these new materials, from fresh sources, will create a revolution in the industry. Large users of perfumery materials will welcome the opportunity of obtaining supplies independently of natural sources, with the difficulties of the political situation, transport, etc. I would like to hear the opinion of the people who use these materials, but not necessarily on the question of odour, because I do not think we should always try to simulate the odours of traditional raw materials. We must be progressive and forward looking, and see exactly what other people feel about it.

MR. J. G. E. HACKFORTH-JONES : Other speakers have emphasized the differences which must always exist between terpene alcohols produced by the pinene process, and those produced by conventional methods. These differences will make it difficult to change over to pinene products in existing established formulations, but as new products the pinene-process alcohols present great interest and the nerol in particular is very fine.

Considering that ionones and methyl ionones produced by the pinene process will be made from citral which has been already substantially purified, does the lecturer feel that the end products will more closely approach ionones produced by conventional methods ?

THE LECTURER : Yes, the ionones are much further distant from the first

natural raw material. In the traditional ionones, processed from lemongrass oil, one normally does not find much of the lemongrass terpenes. I am therefore of the opinion that the new ionones will very much fall in line with the traditional ones.

MR. G. L. GARDEL : As a perfumer, I would state that when comparing with products derived from natural sources, it does not matter how good the chemistry of the synthesis really is—you can never mistake a natural product for a synthesized one. But if that fact is realised, and the perfumer keeps his mind free from any outside stimulæ, commercial or otherwise, then he is fulfilling his role. In other words, he makes use of anything that has a smell, and maybe will give him a solution to the problem he is engaged upon. Surely this is his function, the rest is more or less incidental. That is my opinion on the use of synthetic materials. The perfumer is always confronted with economic considerations, and I agree that one should not change the horse in mid-stream, because like everything else the position is subject to commercialism. Hydroxycitronellal depends a great deal on the process involved. If you knew the manufacturing processes involved, you would find they all differed, and no matter where hydroxycitronellal is obtained from, there are no two alike. This is entirely due to the manufacturing conditions.

THE USE OF GAS-LIQUID CHROMATOGRAPHY IN THE ANALYSIS OF PERFUMES AND FLAVOURS

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Presented at the Symposium on "Perfumery", organised by the Society, at Cheltenham, Glos., on 14th November 1962.

Techniques for optimum qualitative and quantitative analysis of essential oils by gas-liquid chromatography are described. Examples of the technique applied to analysing perfumes and flavours, alone and combined in products, are given. The present scope and limitations in relating chromatograms to observed odours are discussed, and two new methods of presentation of chromatograms are suggested.

INTRODUCTION

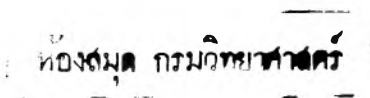
GAS-LIQUID chromatography (G.L.C.) is a physical method of analysis of mixtures of volatile compounds. It is therefore particularly suited to analysis and quality control of perfume and flavour materials. A small sample of material is vaporized in a moving gas stream and carried through a porous medium supporting a liquid. Distribution of the vapour between the gas and liquid phases promotes separation of the constituents of the original sample vapour, and the individual constituents emerge from the apparatus as separate bands of vapour which may be detected and recorded as peaks on a chart.

The cosmetic industry was, apparently, a little late in exploiting the technique to its full advantage. The reasons for the lag in application of the technique are twofold. Firstly, the highly competitive nature of cosmetic products minimised publication by the experts and much of the earlier publication in the field merely suggested what could be done but did not report progress. Secondly, the many rapid developments in G.L.C. technique within the petroleum industry were not applicable to essential oil analysis since the compounds present therein are much more labile than hydrocarbons.

More recently, much valuable work has been reported but some published chromatograms still show poor resolution or evidence of sample decomposition, indicating that optimum operating conditions are not always being chosen. Holness¹ has discussed the importance of working conditions with particular reference to lavender oils. The purpose of this paper is to provide the analyst with further examples of the choice of operating parameters for perfume and flavour analyses, and to indicate the present scope and limitations of the technique as an aid for the perfumer.

Recent reviews²⁻⁶ describe general techniques in all fields of G.L.C., while

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abstracts⁷ provide additional data on perfume and flavour analyses. Therefore, only the techniques used in this laboratory will be described without attempting to review other work in the field.

DEFINITIONS

To avoid ambiguity between the usage of some words in chemistry and in perfumery, the following meanings are implied throughout this paper :

Compound—A compound in the chemical sense ; a single molecular species.

Component or Constituent—One member of a mixture of compounds.

Blend—A mixture consisting of more than one essential oil.

Terpene—A hydrocarbon of general formula $C_{10}H_{16}$ (monoterpene), $C_{15}H_{24}$ (sesquiterpene) or $C_{20}H_{32}$ (diterpene.)

Oxy-terpene—A derivative of the above terpenes, including ethers, aldehydes, ketones, esters and alcohols.

APPARATUS

The apparatus used is of the conventional packed-column type operated isothermally. Since we are often looking for differences between the minor constituents of two samples of essential oil, the use of high-efficiency capillary columns, with their necessarily small sample injection, is considered unsuitable. High-sensitivity detectors can be used to counteract the effect of using such small sample injections, but we require all their available sensitivity for detecting low-concentration components. Programmed-temperature apparatus, designed to increase column temperature as analysis

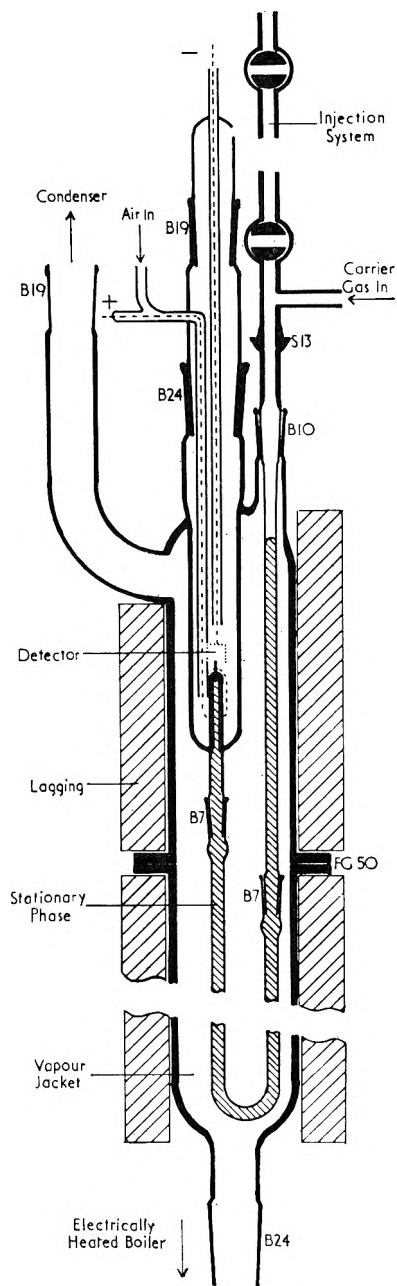


Figure 1
An all-glass analyser unit.

proceeds, is not used because it requires complicated ancillary heating equipment to ensure reproducible heating rates; moreover, the column is out of use during the cooling period. An analysis carried out on three columns operating isothermally at suitable temperatures furnishes the same information in a more reproducible manner.

One all-glass analyser unit is shown in *Fig. 1* and has been described elsewhere⁸. A simpler design, which we have used successfully for four years, has been described by Smith⁹. Apparatus of all-metal construction is also available, but is less reliable under highest-sensitivity operation. Each analyser unit incorporates a flame-ionisation detector which feeds a recorder via a simple impedance-matcher, as shown in *Fig. 2*.

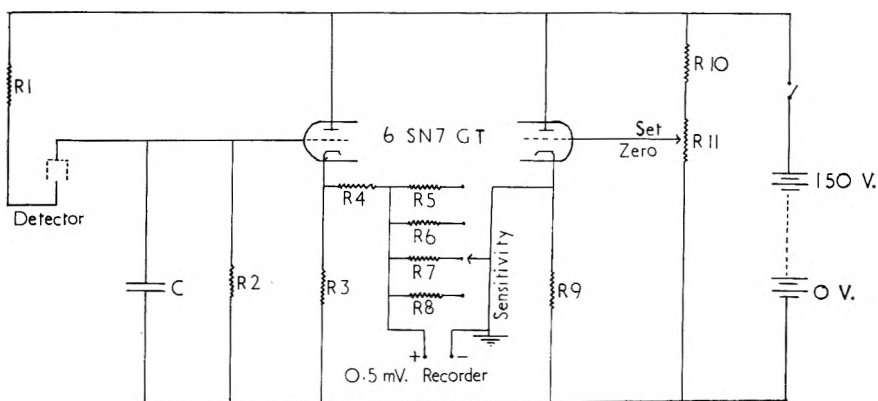


Figure 2

Impedance-matching circuit for flame-ionisation detector.

C, 1000 pF; R1, 1M Ω ; R2, 240 M Ω ; R3, R9, 50K Ω ; R4, 10K Ω ; R5, 100 Ω ; R6, 20 Ω ; R7, 4 Ω ; R8, 1 Ω ; R10, 110K Ω ; R11, 10K Ω var.

Choice of operating conditions for optimum efficiency has been discussed previously^{1,8}. The column conditions used for the work described in this paper are given in *Table 1*.

The nature of the support material has an important effect on the quality of chromatogram produced. The common choice is between ground firebrick (Johns Manville, *Sil-O-Cel C.22*) and *Celite*. For similar particle size distribution, *Celite* has two advantages in the perfume and flavour analysis field. The first advantage is that it has a much lower tendency to promote catalytic decomposition of labile compounds, e.g. β -pinene, linalyl esters. This is particularly important when semi-polar or non-polar liquid phases are being used. Secondly, *Celite* may have a favourable effect upon

Table 1 Column Conditions

Column number	1	2	3
Length x internal diameter	2.4 m x 3.6 mm	1.5 m x 3.6 mm	2.4 m x 3.6 mm
Temperature	78°C	130°C	183°C
Stationary phase	20% polyethylene glycol 400 on 60-100 mesh <i>Celite</i>	20% polyethylene glycol 400 on 60-100 mesh <i>Celite</i>	10% ethylene glycol/adipic acid polyester on 60-100 mesh <i>Celite</i>
Carrier gas	25% nitrogen, 75% hydrogen	
Detector	flame-ionisation	
Typical applications	monoterpenes ; C ₁ -C ₁₀ aldehydes, ketones, esters, alcohols, ethers.	oxy-terpenes ; sesquiterpenes ; C ₈ -C ₁₈ aldehydes, ketones, esters, alcohols, ethers.	phenols, phenol-ethers ; "non-volatile" residues ; esters, etc. >C ₁₀ .
Suitable reference compounds	limonene	menthol, citral-a	safrole, eugenol

separating power for analysis of terpene derivatives, as shown by comparing *Figs. 4b* and *5* for peppermint oils.

QUALITATIVE ANALYSIS

It may be sufficient, for quality control, merely to compare the chromatograms obtained for test samples with those of standard samples, but usually a partial or complete identification of the compounds represented by peaks is required.

Using a flame-ionisation detector, all organic compounds give a positive response. It is necessary to measure, for each peak on the chromatogram, its "retention ratio" which is defined as

$$\frac{\text{time taken for unknown to be eluted}}{\text{time taken for standard to be eluted}}$$

where times are measured from the moment of injection of sample to the centre of the appropriate peak. The standard is any suitable reference compound known to occur as a major component in one or more of the oils being analysed (e.g. menthol in peppermint oil, citral-a in lemon oil) or an added component. The standard should be chosen to be eluted near the centre of the useful part of the chromatogram.

Retention ratios observed by measurement of chromatograms may be used to determine the identity of peaks by comparison with data obtained by the following procedures :

Calibration with available compounds

Compounds believed to occur in the sample undergoing analysis should have their retention ratios determined relative to the chosen standard for each column, by chromatographing each compound mixed with the standard. The purity of the compound used for qualitative calibration is not critical.

This method is mainly of value for the more obvious compounds, e.g. menthol, menthone, menthyl acetate in peppermint oil. It does, however, pre-suppose some knowledge of the composition of the sample and many peaks will still remain unidentified.

Interpolation and extrapolation of homologous series

Logarithms of retention ratios of members of homologous series may be plotted against the number of carbon atoms in the molecule. Interpolation and extrapolation of the graph provides data for unavailable members of the series.

For flavours and perfumes containing aliphatic aldehydes, ketones, esters and alcohols, this method is valuable. It is, however, of little use for identification of unknown terpenes or oxy-terpenes since homologues do not normally occur, and at least three compounds are needed to prove the existence of a series.

Extrapolation of homologous series may be extended to isomeric forms if sufficient reference compounds are available. *Fig. 3* shows the application of this method to low molecular-weight aliphatic alcohols. Once the *n*-primary series has been plotted, other series may be drawn as parallel lines through one or more reference points.

Conversion of published data

There are, at present, no British Standard liquid phases. In spite of recommendations¹⁰, analysts still prefer to use their own "ideal" liquid phases, with the result that retention ratio data are often published for analyses on columns other than those available. An empirical correction can be applied, however, within groups of compounds, e.g. monoterpenes. The published retention ratios are plotted against the corresponding values observed for as many compounds in the group as are available. Retention ratios for other compounds can then be read from the published data via the straight-line graph. It is convenient to use log/log graph paper, and the closer the experimental conditions used approach to those published,

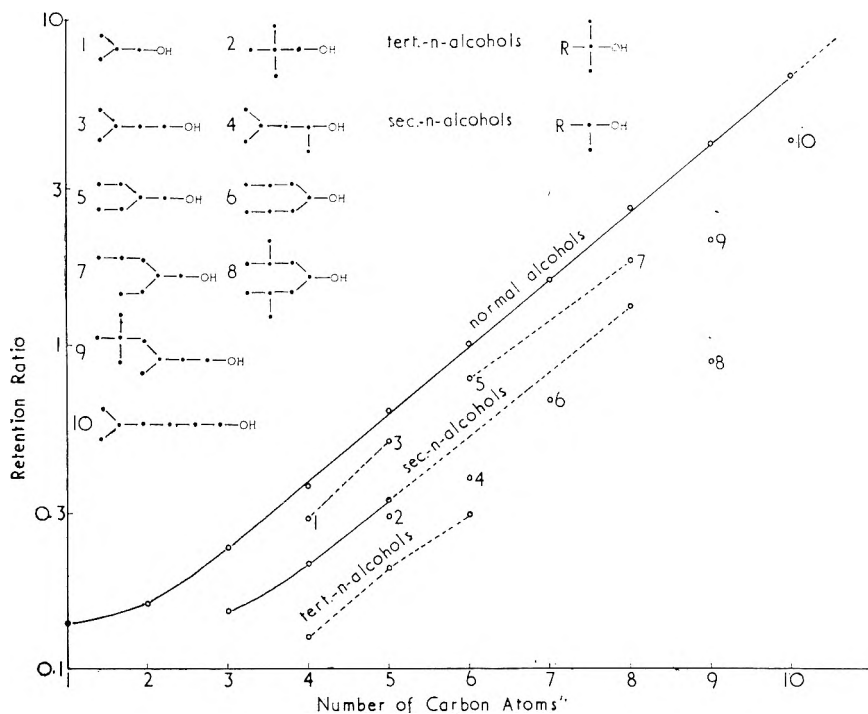


Figure 3
Retention ratios and structures of alcohols.

especially with respect to liquid phases¹⁴, the more accurate will be the converted data. In Table 2, the values read from a graph constructed with α -pinene, β -pinene and limonene as standards are compared with values

Table 2
Conversion of published retention data

Compound	RETENTION RATIO		
	Published P.E.G. 4,000 130°C	Calculated P.E.G. 400 78°C	Observed P.E.G. 400 78°C
α -pinene	0.437	—	0.352
α -fenchene	0.532	0.448	0.462
camphene	0.559	0.472	0.462
β -pinene	0.690	—	0.588
Δ^3 -carene	0.795	0.743	0.737
α -phellandrene	0.856	0.810	0.837
α -terpinene	0.914	0.884	0.901
limonene	1.000	—	1.000
β -phellandrene	1.08	1.08	1.08
γ -terpinene	1.26	1.31	1.31
terpinolene	1.53	1.67	1.64

subsequently observed by direct calibration. The published data for a polyethylene glycol 4,000 column at 130°C¹¹ is converted to the conditions of column No. 1 (*Table I*).

Where retention data is not available by any of the methods described, it is often possible to classify the compounds into chemical type with one of the following methods:

1. *Classification prior to G.L.C.*

Treatment of the sample by a suitable process before analysis enables classification of some peaks when the resultant chromatogram is compared with that of the original sample. Three examples of the procedure are given:

- (a) Alcohols may be preferentially separated from other compounds by distribution of the sample between carbon tetrachloride and propylene glycol¹². Chromatograms of the two layers are examined and compared with that of the original sample.
- (b) Separation of essential oils into hydrocarbons and oxygenated compounds by adsorption on a silica gel column is particularly useful. The hydrocarbons (terpenes, sesquiterpenes and diterpenes) are eluted with petroleum ether while the oxygenated terpenes may be displaced with ethyl acetate. Subsequent comparison of chromatograms classifies some of the peaks. Only the purest grades of silica gel should be used, and the possibility of isomerisation on the adsorbent should be borne in mind when comparing chromatograms.
- (c) Selective reagents for carbonyl compounds, e.g. Girard reagents, have restricted use in the essential oil field since some carbonyls fail to react while others decompose, e.g. camphor and citral respectively. Nevertheless, the process can be of value if supplemented with other classification tests. Chromatograms of the sample made before and after removal of carbonyls may be compared and, where possible, regenerated carbonyls can be analysed separately.

2. *Classification after G.L.C.*

- (a) After a preliminary chromatogram has been prepared, the vapours of compounds of special interest may be trapped as they are eluted during a repeat analysis. By bubbling the effluent gas from the chromatographic column via a manifold into selective reagents, the peaks may be classified into compound types¹³. We have found that such tests are reliable when there is only one functional group in the molecule. The method may be used as a guide, but must be

supported by a confirmatory test when analysing perfumery and flavour materials.

- (b) The vapours eluted from the column may be trapped in a suitable solvent for subsequent analysis by U.V. or I.R. spectroscopy.

3. *Classification during G.L.C.*

One of the simplest and most informative means of classification is the choice of a suitable liquid phase for the chromatographic column. Thermally-stable, non-volatile materials which are liquid at the temperatures of operation may be broadly classified as

- (i) non-polar, e.g. hydrocarbons, silicones,
- (ii) semi-polar, e.g. esters, polyesters, and
- (iii) polar, e.g. polyglycols, $\beta\beta'$ -oxydipropionitrile.

It should be noted that diglycerol, although strictly included in group (iii), is unsuitable as a liquid phase since its very high polarity causes most organic compounds to be virtually insoluble in it, thereby causing rapid elution of all compounds before separation has occurred.

Group (iii) is most suitable for analysis of mixtures containing several classes of compound, since the materials are eluted roughly in order of increasing polarity. For example, using column 2 (*Table I*), compounds with the same number of carbon atoms in the molecule are eluted in the order—hydrocarbons; ethers; aldehydes, ketones and esters; alcohols; phenols and acids. Since in essential oils, most compounds are of a ten-carbon skeleton, the groups are fairly well defined except that sesquiterpenes (C_{15}) are eluted in the C_{10} aldehyde/ketone/ester region (*Fig. 8b*). Within each group, elution tends to be in order of decreasing volatility.

Phenols and acids are, in general, too polar for satisfactory analysis on polar columns owing to their lengthy elution times. A semi-polar column (No. 3, *Table I*) at a higher temperature is used for these compounds.

The hydrocarbons are eluted rather quickly under the conditions of column No. 2. A longer column (No. 1, *Table I*) at lower temperature improves the separation within this group. Separation within a group could be supplemented by using a non-polar column, but it would be necessary first to isolate the group to obviate interference from other groups.

4. *Preparative-scale G.L.C.*

Apparatus designed to isolate samples of any one component or group of components^{2,3,4} can be used either to separate one group of compounds for more detailed analysis using a different stationary phase or temperature, or to isolate single compounds for analysis by other methods, e.g. spectroscopy. An isolated compound may sometimes be classified by comparing

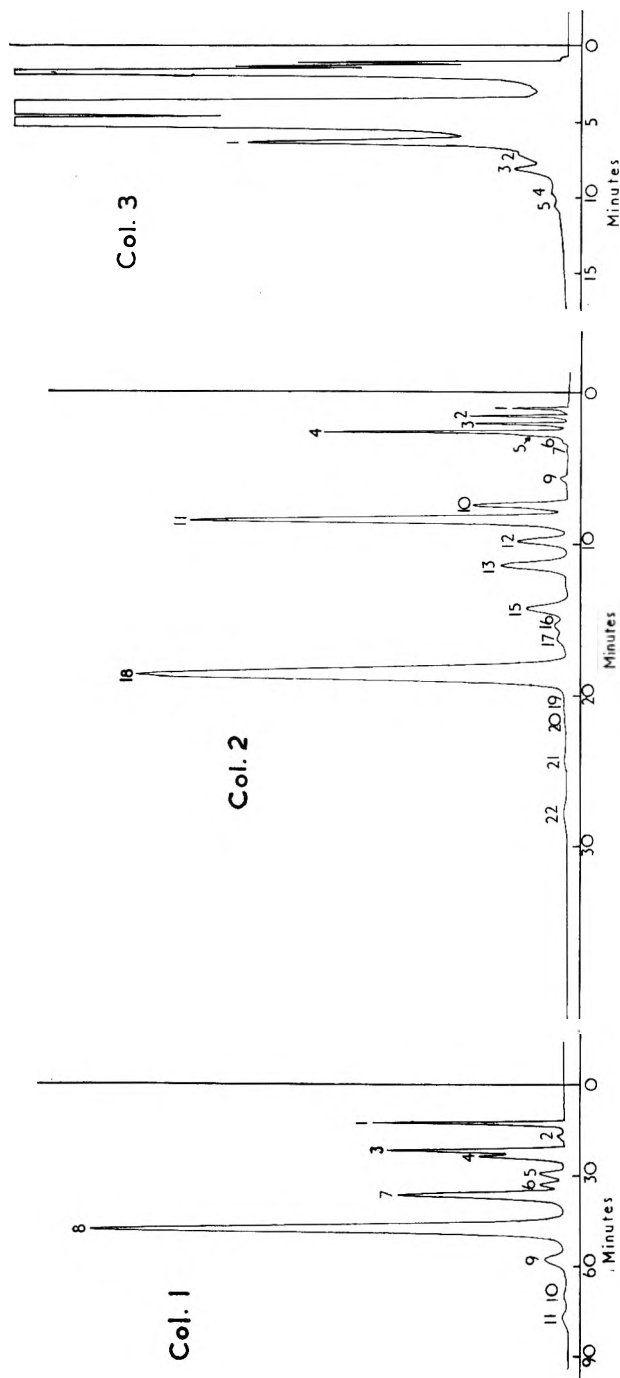


Figure 4 (c)

Figure 4 (b)

Figure 4 (a)

Peppermint oil with peaks tentatively identified:—

- (a) Column No. 1: 1 α -pinene; 2 camphene; 3 β -pinene; 4 sabinene; 5 myrcene/ α -phellandrene; 6 α -terpinene; 7 limonene; 8 cineole/ γ -terpinene; 9 *p*-cymene/terpinolene.
- (b) Column No. 2: 1 α -pinene; 2 β -pinene; 3 limonene; 4 cineole; 5 *p*-cymene; 9 octanol-3; 10 menthofuran; 11 menthone/*trans*-sabinene hydrate; 12 isomenthone; 13 menthyl acetate; 15 *neomenthol*; 17 *neoisomenthol*; 18 menthol/pulegone; 19 isomenthol; 22 carvone/piperitone.
- (c) Column No. 3: 1 pulegone; 3 carvone/piperitone; 4 benzyl alcohol.

its retention ratio relative to a standard on a non-polar (A) and on a polar (B) stationary phase¹⁴. It is necessary first to calibrate for homologous series of various types of compound and plot the log (retention ratio) on column A against the log (retention ratio) on column B, when each series will produce a different straight line. The appropriate values for the unknown compound will then fall on one of the lines, thus classifying it. This method is applicable only to compounds containing one functional group in the molecule and is therefore more likely to be of value for synthetic flavour components than for essential oils.

QUANTITATIVE ANALYSIS

The usual methods of determining concentrations of components from the areas of peaks on the chromatogram have been described previously^{2,3}. However, the need for careful calibration of the vapour detector and checking its linearity of response to increasing concentrations of vapour should be emphasised.

The sensitivity of a flame-ionisation detector is a function of its geometry¹⁵ and also varies according to the chemical type of compound being detected. In general, hydrocarbons give a larger response than oxy-compounds, but the differences become less marked as molecular weight increases. For compounds containing ten or more carbon atoms the sensitivity is nearly constant and equal for all types. Hence an approximate analysis of essential oils can be made by simply relating peak areas to concentrations. However, if the sample for analysis is known to contain low molecular-weight compounds, quantitative calibration of peak areas against concentration must be made with standard compounds or obtained from published data¹⁶.

Superimposed upon the variation of sensitivity with compound type is the variation with concentration, i.e. "non-linear response". The effect can be easily recognised by determining calibration factors for standard materials injected at various concentration levels. Non-linearity can usually be avoided by minimising the size of sample injected onto the column and operating the amplifier at high sensitivity. Large samples analysed at low sensitivity emphasise the effect and give misleading chromatograms as shown in *Fig. 6* compared with *Fig. 4b*.

QUALITY CONTROL

Individual essential oils

Chromatograms of essential oils can usually be satisfactorily made on one or more of the columns detailed in *Table 1*. Identification of peaks follows the methods described under qualitative analysis. There are, however, certain limitations which are frequently overlooked.

The importance of analysing the sample on more than one column, using a different stationary phase and/or operating temperature, is demonstrated by composite peaks which separate into two components under different conditions. Examples are given in *Table 3*.

Table 3
Resolution of composite peaks

Compound pairs	Column (<i>Table 1</i>) giving a single composite peak	Column (<i>Table 1</i>) giving two separate peaks
Menthol/pulegone	2	3
Camphor/linalol	2	1
Linalyl acetate/ bornyl acetate	1	2
Bornyl acetate/ linalyl propionate	2	1

Note that even using two columns, the presence of bornyl acetate cannot be ensured in the presence of linalyl esters. It can only be confirmed by preparative-scale isolation of the composite peak under the operating conditions of column No. 2 and then re-analysis on column No. 1.

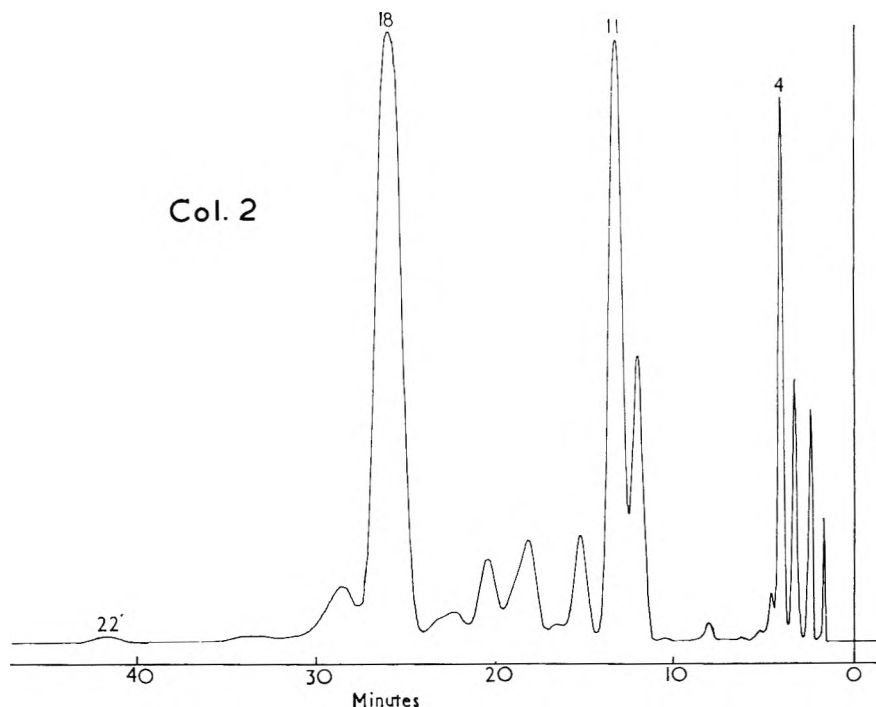


Figure 5
Peppermint oil using 60-100 mesh firebrick support. Compare resolution with *Fig. 4b* for *Celite*.

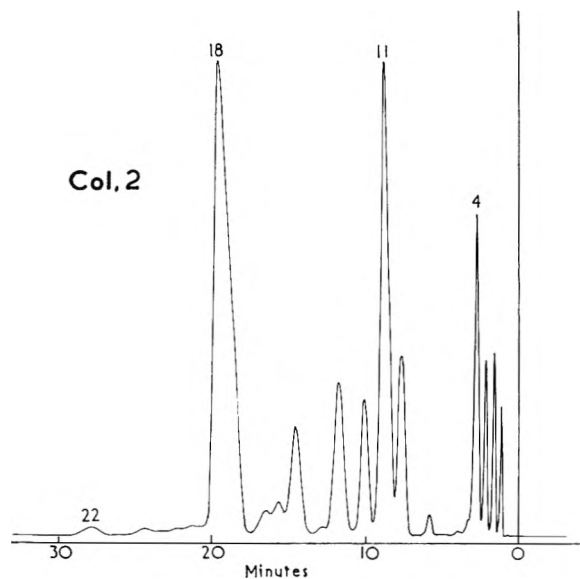


Figure 6

Peppermint oil with 0.5 μ l charge (10 x normal) at reduced sensitivity (1/5 x normal) showing non-linearity of response. Compare relative peak heights with those in Fig. 4b.

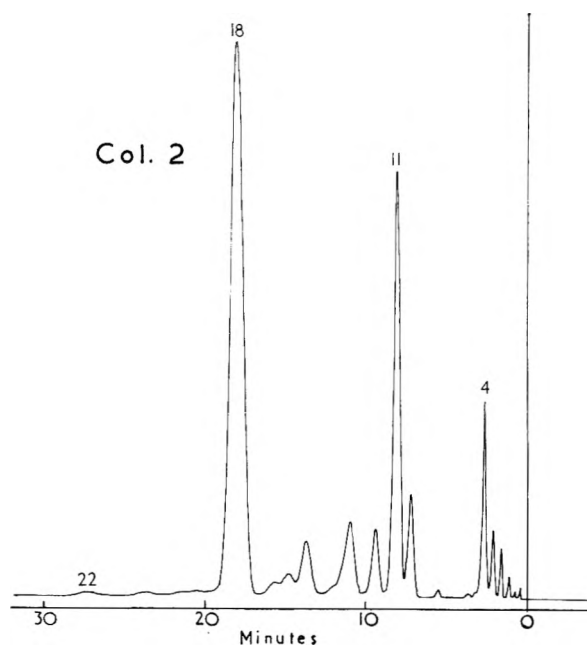


Figure 7

Peppermint oil recovered from toothpaste. Compare relative peak heights with those shown in Fig. 4b.

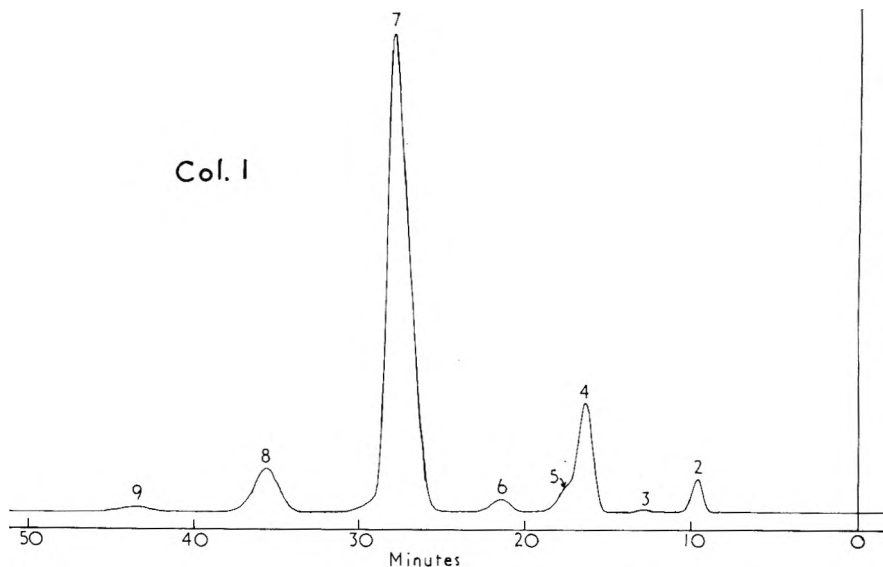


Figure 8 (a)

Lemon oil with peaks tentatively identified:—
 Column No. 1: 2 α -pinene; 3 camphene; 4 β -pinene; 5 sabinene;
 6 myrcene; 7 limonene; 8 γ -terpinene; 9 terpinolene/*p*-cymene.

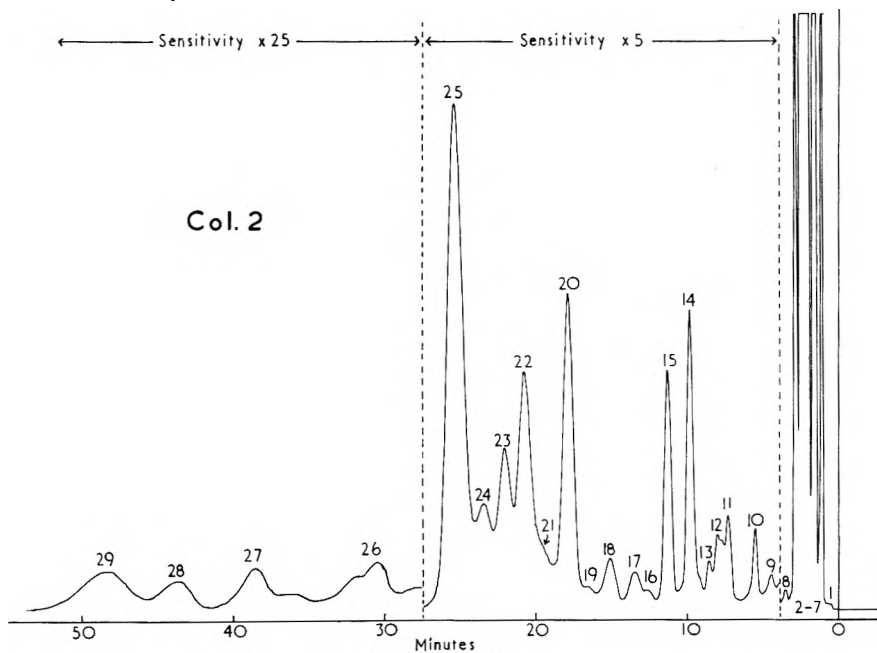


Figure 8 (b)

Column No. 2: 2-7 monoterpenes; 8 octanol; 9 methyl heptenone; 10 nonanal;
 11 octyl acetate; 12 citronellal; 13 decanal; 14 sesquiterpene X; 15 linalol/
 sesquiterpene Y; 16 linalyl propionate; 17 undecanal; 19 citronellyl acetate;
 20 sesquiterpene Z; 22 citral-b; 23 neryl acetate; 24 α -terpineol; 25 citral-a/
 geranyl acetate/carvone, 26 citronellol/decanol; 27 nerol; 29 geraniol.

There is a tendency for the "non-volatile" residues of essential oils to be overlooked, particularly if they are known to be odourless. It is possible, however, that such compounds contribute considerably to the stability of the perfume or flavour in which the oil is blended. Moreover, odourless constituents of a flavour may well affect the basic taste sensations, thus altering the overall flavour effect. Unless the analyst is concerned only with the immediate odour, the "non-volatile" portion should be isolated by conventional techniques and analysed by other methods, e.g. thin-layer chromatography, or by a suitable extension of the G.L.C. technique. We have found that "non-volatile" residues of citrus oils may be chromatographed with a slow recorder chart-speed and 16-hour analysis on column No. 2. *Fig. 8c* shows the "non-volatile" portion of a lemon oil.

It is often argued that since odoriferous compounds are necessarily volatile, the vapour over a bottle of essential oil, rather than the liquid itself, should be analysed. This supposition is, however, unfounded since the resultant chromatogram will show a high proportion of the more volatile components which are frequently less-strongly odoriferous. Further, the reasons given above for analysing the "non-volatile" fraction would have to be ignored if only the vapour phase is analysed.

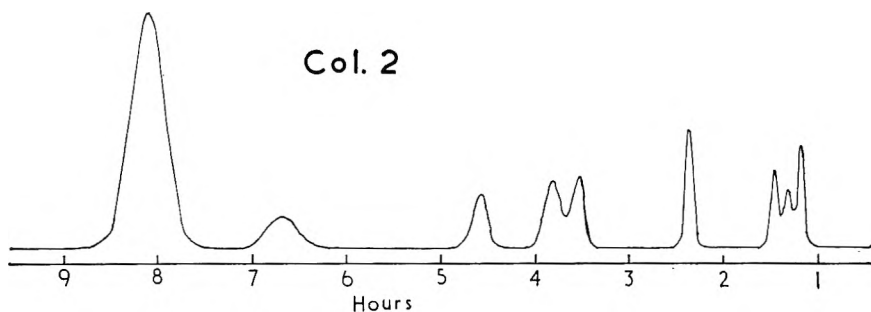


Figure 8 (c)

Column No. 2: "non-volatile" residue. The chromatogram has been drawn with exaggerated proportions of peak height to time scale, for clarity. All peaks shown are eluted after those in *Fig. 8b*. They are probably coumarin derivatives.

Certain limitations of the G.L.C. technique should be realised when analysing essential oils, otherwise misinterpretations may be made regarding the quality of the oils. The techniques described are applicable to most carbon, hydrogen and oxygen compounds. However, certain polar groups, if present in low concentration, may be adsorbed on the support and may not be visible in the resulting chromatogram. Carboxylic acids, nitrogen—and, possibly, sulphur—containing compounds may escape recognition. If

any such compounds are suspected, even in traces, they should be measured by other analytical techniques. If their presence is confirmed, the oil can be re-chromatographed by a suitably modified technique, for example :

- (a) preparation of less-polar derivatives (methyl esters of acids, acetylated amines, etc.) prior to G.L.C.,
- (b) selective extraction of the compounds of interest so that a simpler, more concentrated mixture can be analysed by G.L.C., or
- (c) analysis using, if possible, a more-polar liquid phase in the G.L.C. column.

Blended Perfumes and Flavours

Whenever possible the essential oils, synthetic mixtures and isolated compounds, which may have been blended into perfumes and flavours, should be analysed separately. Chromatograms of blends are usually so complex that interpretations are very uncertain owing to the multiplicity of overlapping peaks. Analysis under different operating conditions merely rearranges the confusion. If, however, individual oils are not available, the blend may be chromatographed in the usual way, but interpretations are usually confined to comparing chromatograms of one sample with those of another. Regions of marked differences between the chromatograms may, if required, be isolated by preparative-scale G.L.C. and may subsequently be analysed under various operating conditions, or by methods other than G.L.C.

Whole Products

It is often necessary to check perfumes and flavours in finished products. The most straightforward procedure is the injection of a sample of the product into the column. Usually, however, this course leads to column contamination by compounds of low volatility, and it is necessary to wait for a long period before the contaminants are eluted. There may be a gradual accumulation of non-volatile materials at the entrance to the column, so that columns with replaceable injection-chambers¹⁷ are of value when one is assaying specific components of the flavour or perfume.

For more detailed analysis, some prior concentration of perfume or flavour constituents is desirable. In general, extraction techniques are inefficient owing to the diverse chemical types which compose perfumes and flavours. The extracts are qualitatively, but not quantitatively, representative of the original perfume or flavour. However, chromatograms of extracts obtained from test samples may be compared directly with chromatograms similarly derived from reference samples. The method of extraction depends not only upon the type of product, but also on its

individual formula. Hence it is possible only to give some examples of extraction procedures for typical cosmetic products.

Shampoos, diluted if necessary, may be extracted with 1 : 1 mixture of diethyl ether and 40°–60°C b.p. petroleum ether. The solvent is removed under vacuum at room temperature. One must expect to find contaminants, e.g. free fatty alcohol from commercial detergents, in the perfume extract.

With toothpaste, the analyst is confronted with the added difficulty that polar constituents of the flavour are strongly adsorbed on the solid phase and therefore incompletely extracted. Solution of the solid phase in acid is unsatisfactory since carbon dioxide evolved from chalk-based pastes carries some volatile flavour materials with it, while calcium phosphate-based pastes require such strongly acid conditions that changes may occur among the flavour compounds. For qualitative comparisons, the paste may be suspended in four times its weight of water and extracted several times with ether (*Figure 7*).

Creams and emulsions, if analysed directly, suffer serious interference by the oil phase which usually dominates the chromatogram, thus masking the peaks due to the perfume. Various methods for isolating the perfume may be used, the choice depending on the nature of the emulsion. Steam distillation or solvent extraction may be suitable. Sampling of the headspace vapours above the emulsion is a simple method enabling direct analysis of the air by G.L.C., but it is important, when using this method, to carry out a blank analysis on the laboratory air since the flame-ionisation detector is very sensitive to trace contaminants. Moreover, as pointed out previously, when headspace gases are analysed, the less-volatile components will not be recorded.

Apparatus using vacuum steam-distillation, vacuum fractionation and Soxhlet extraction¹⁸ to isolate volatile fruit flavours could be equally suitable for suspensions, emulsions and solutions as long as foaming can be limited in the steam-distillation stage.

Aerosol products may be analysed directly as vapours carrying perfume, or as the liquid phase remaining after evaporation of the propellant. In the former case, the sensitivity to the perfume will be lower than when the liquid is analysed. The latter method will provide more information but contamination of the column is more likely to occur from the non-volatile components of the aerosol product.

GAS-LIQUID CHROMATOGRAPHY AND ODOUR

Correlation

The correlation of a chromatogram of an essential oil with the odour sensation produced by the oil is of prime importance to the analyst and to

the perfumer. Holness¹ has demonstrated the similarities of chromatograms for oils within the *Lavandula* genus and increasing similarities within species, varieties and strains. Such group similarities also occur within other genera. It is not in every case, however, that the major chromatographically-apparent differences correspond to obvious odour differences. The odours of lavender, lavandin and spike oils are readily correlated with relative concentrations of cineole, camphor, linalol and linalyl acetate, but in the case of citrus oils, it is no longer the major constituents (the monoterpenes) which confer the characteristic odours, but the constituents present in minor amount, e.g. citral in lemon oil. There is, however, much valuable information available in each chromatogram as long as the following sources of misinterpretation are not disregarded.

- (a) *Concentration and odour intensity*—The effect of any particular constituent upon the final odour of an oil will depend not only upon its concentration, but also upon its odour intensity or "specific odour". When two chromatograms are compared, since the peak areas are a function of concentration, we must therefore consider relative changes in peak sizes rather than absolute changes. A change in a component, X, from 1% to 2% may be just as important as a change in another component, Y, from 10% to 20%.
- (b) *Odour saturation*—It is reasonable that a fairly large change in concentration of the major constituents, especially if the characteristic odour of the oil derives therefrom, e.g. menthone and menthol in peppermint, would be less noticeable to the nose than the introduction of a foreign odour in quite low concentration.
- (c) *Odour counteraction*—The established property of odour counteraction could conceivably lead to incorrect interpretations of chromatograms. If two odorous components are absent in one oil, but present in proportions which mutually counteract in a second oil, the oils may smell similar but have quite different chromatograms.
- (d) *Odour sensitisation*—The nose may be sensitised towards some of the components of the oil when the mixture is smelt as a whole, whereas if those components were smelt as pure substances, their "specific odour" would not appear so large.

Isomers

Knowledge of the variation of odours with isomeric structures is at present mainly empirical, but since G.L.C. is capable of distinguishing between them and of isolating them in the pure state, it is probable that the next decade will see rapid strides in the science of chemical structure related to odour.

- (a) *Optical isomerism*—A few optical isomers have been resolved by G.L.C. of their diastereoisomers or by analysis using an optically-active liquid phase, but the methods are not of general applicability to essential oils. However, in the event of any doubt about the optical rotatory power of any particular peak, preparative-scale G.L.C. could be used to isolate a sample for polarimetry. Since enantiomorphs are frequently associated with contrasting essential oils, it is sometimes believed that optical isomers contribute different odours. We have examined the case of *d*-carvone (the major constituent of caraway seed oil) and *l*-carvone (the major constituent of spearmint oil). The isomers were isolated from the respective oils via the sulphite addition compound followed by fractional distillation. Polarimetric measurement showed the isomers each to be better than 99% pure. 5 mg of each isomer were then purified by "preparative-scale" G.L.C. on No. 2 analytical column, a capillary-tube trap replacing the flame-ionisation detector while the carvone was eluted. The capillaries were drained and the liquids smelt on watchglasses. Four observers agreed that the two isomers had identical caraway-like odours, and that the *d*-carvone had a distinctly more intense odour. It is interesting to note that this isomer is the one present in caraway seed oil.
- (b) *Stereoisomerism*—Stereoisomers are easily resolved by G.L.C. The four isomers of menthol (excluding enantiomorphs) are clearly separated under the conditions of column No. 2, as shown in the chromatogram of peppermint oil (*Fig. 4*). Variations in the relative quantities of these isomers could affect the odour, and particularly the flavour of the oil, without there being any other change in composition.
- (c) *Geometrical isomerism*—*Cis-trans* isomers have presented no difficulty in separation since the early days of G.L.C. Classic examples in the essential oil field are shown by citral-a/citral-b and geraniol/nerol in lemon oil analysed on column No. 2 (*Fig. 8b*). Likewise, column No. 3 will separate eugenol from the two geometrical isomers of *isoeugenol*. The separation of eugenol from *isoeugenol* is brought about by the fact that the latter is a conjugated structure.
- (d) *Double-bond position*—As in the case of eugenol and *isoeugenol*, the separation of conjugated and isolated double-bond structures is easily achieved by G.L.C. but changes in double-bond position without involving conjugation is more difficult to recognise by G.L.C. The ability to separate the isopropylene and isopropylidene (α and β) isomers of several terpene derivatives has not yet been

achieved by G.L.C., although the corresponding nonenes have recently been separated¹⁹. It should be possible to extend the method to oxy-terpenes, thus obtaining four peaks for citral and two each from geraniol and nerol.

Flavour

The effect that odourless, non-volatile components may have on the basic taste contribution of a flavour mixture has already been mentioned. When analysing flavours, therefore, it is especially important that the G.L.C. technique should be supplemented by other analytical methods. The foregoing remarks on isomerism and odour may be equally applicable to taste. Isomers of similar odour may contribute different taste sensations to a flavour, e.g. one isomer may be more bitter than another. G.L.C. can be used to control such variations once they have been recognised.

Vapour Detectors

Most users of G.L.C. today take advantage of the high sensitivity to organic vapours of the various types of ionisation detectors. The response of these detectors is proportional to the concentration of the vapour and to some function of its molecular structure. No detector is known at present which responds in proportion to the "specific odour" of a compound. Such a detector would yield a chromatogram in which, subject to the limitations described in the section entitled *Correlation*, the largest peaks corresponded to the compounds contributing most to the odour of the sample. The nearest approach to such a detector at present is the perfumer's nose. A preliminary analysis made with a flame-ionisation detector may be immediately followed by a repeat in which a heated capillary-tube, with a perfumer attached to the exit end, replaces the detector. The perfumer observes the smell at the appropriate moment in time. (The capillary is heated to avoid condensation and consequent odour tailing.)

Identification or classification of peaks is aided by the observed odours, but they cannot be used to assess the odour of the complete essential oil since so little is known at present about the additive properties of odours. Although it has been suggested that the nose is more sensitive than the best detectors towards some organic vapours, only the major constituents of a mixture can be detected by smelling the vapours eluting from the G.L.C. column. This is because the vapour has been diluted many times by air before reaching the nose. The smelling method of detection is valuable for indicating whether a particular constituent is likely to improve or degrade the odour of the complete oil, without necessarily identifying the compound.

Modern theories of the sense of smell indicate that a detector based on adsorption might be desirable, the closest approach to this being the surface potential detector used by Griffiths and Phillips²⁰. Unfortunately, this detector is non-reversible with respect to adsorbed vapours, and its sensitivity is many orders less than ionisation methods.

PRESENTATION OF DATA

The gas-liquid chromatographer frequently finds difficulty in expressing his interpretation of chromatograms in laboratory reports. Tabular presentation of tediously and, sometimes, unnecessarily calculated concentrations of each component does not give the "at-a-glance" comparison which can be made between two chromatograms. To follow a discussion of interpretations, the reader needs a graphical representation of the chromatograms before him.

Since the conditions for analysis of essential oils usually fall into three categories (*Table I*), it is possible to duplicate copies of chromatograms of various standard oils analysed under the appropriate column conditions. To each member of the staff who may be interested in G.L.C. reports, is circulated a loose-leaf folder or "Chromatogram Atlas" containing—

- (a) One copy of each chromatogram of standard oils which are frequently being analysed. Each chromatogram bears the number of the column on which the analysis was made and each peak is numbered (whether or not it has been identified).
- (b) A key defining the conditions appropriate to each column number.
- (c) A key for each chromatogram, giving the identities of peaks as known up to date.

The report writer needs only to refer to the column number and type of oil before commencing his discussion of observations made on similar oils. Peaks may be referred to by number or by name according to convenience, but it is not necessary to circulate a detailed table or a complete chromatogram with each report. Only the points of difference need be discussed about each analysis. With the chromatogram at hand, the reader can see the relative significance of the reported differences.

An alternative method of presentation designed to enable direct comparisons between chromatograms of similar oils, analysed at various times, would be of value for following seasonal changes in the essential oil industry. Owing to the inevitable ageing of liquid phases, chromatograms run weeks or months apart are not directly comparable by superimposition. The ageing process not only causes slight differences in retention ratios, and larger differences in absolute retention times, but also leads to changes in efficiency

which affect absolute and relative peak heights. The net result, to the untrained eye, is that the chromatograms are not comparable. The following method is designed to overcome these difficulties.

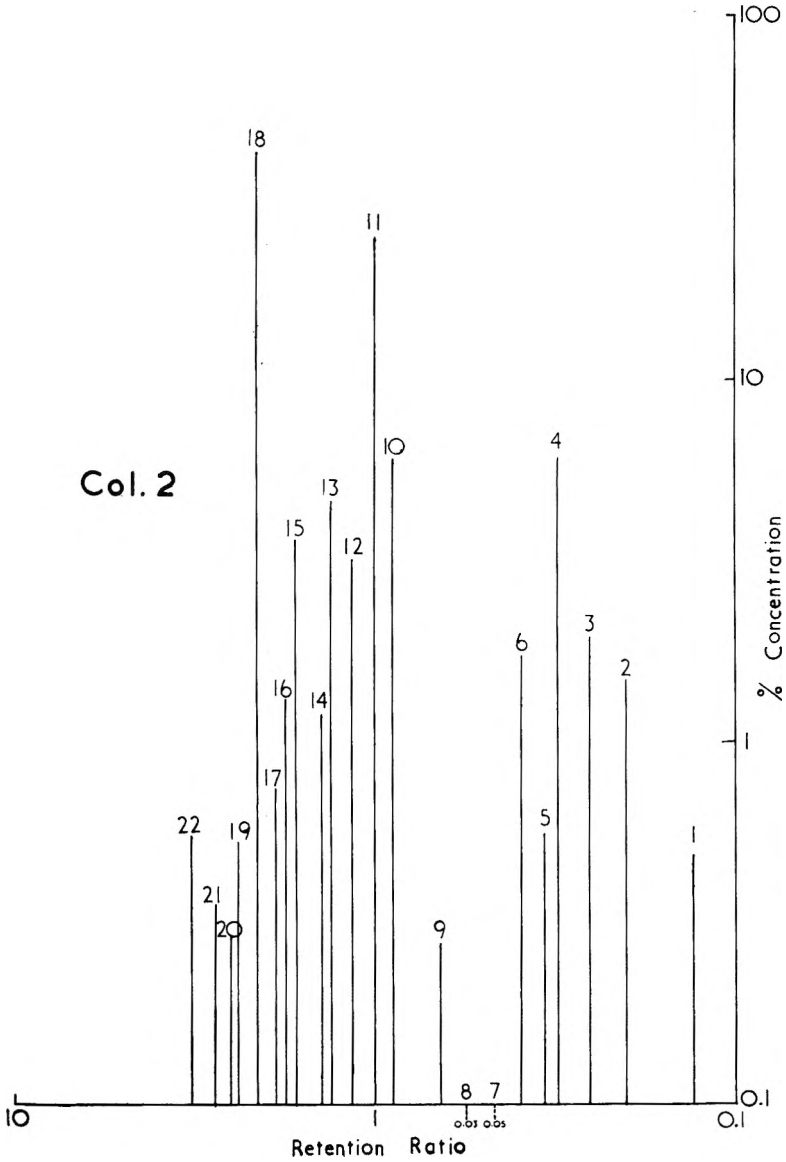


Figure 9
Peppermint oil histogram.

Chromatograms are prepared with a suitable quantitative internal standard, and the concentrations of each component are calculated. On logarithmic graph paper (3 cycles for ordinates, 2 cycles for abscissae) the standard retention ratio for each component is plotted along the abscissa (0.1 to 10) and a line representing the concentration of each component drawn parallel to the ordinate (0.1% to 100%). Values falling outside the concentration range (less than 0.1%) may be marked as red figures below the appropriate point on the abscissa. The result is a histogram representative of the original chromatogram (*Fig. 9* represents peppermint oil) with the following advantages :

- (a) The usual logarithmic spread of peaks of homologous series is neutralised, providing a more compact presentation.
- (b) Retention ratios are plotted as a standard value determined for freshly-packed columns. Ageing changes are ignored, similar compounds always being given the standard values.
- (c) As concentrations (or peak areas) are represented, the normal fall-off of peak heights as peaks become broader and flatter along the length of the chromatogram, is counteracted and later peaks appear just as important as the earlier ones at similar concentration levels.
- (d) A logarithmic presentation on the concentration ordinate enables relative changes in concentration to be determined by lengths, without considering the absolute concentration levels.
- (e) This graphical representation retains the "at-a-glance" comparison yet contains much of the information which might be compiled in a table.

ACKNOWLEDGEMENT

The authors wish to thank *The Chemist and Druggist* for permission to reproduce *Fig. 1*.

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Introduction by Mr. J. D. Cheshire

From the discussions earlier this morning it would appear that everybody now appreciates the limitations in the application of gas chromatography to perfumery. One is no longer content with looking at a number of chromatograms, comparing them and saying, "They are different, therefore the samples analysed must smell differently". We now realise that this is not so. We welcome any papers, such as the one that Dr. Naves* presented at this Symposium, emphasizing the limitations of G.L.C. and I would like to give examples of one or two other applications and limitations, going a little further than those presented in our paper.

The limitations of classical organic chemistry have been shown up by gas chromatography, and in one experiment we carried out a synthesis of *isocitral* according to Schmidt's preparation 1938-1939, where ordinary citral (which was over 99% pure) is converted to citral enol-acetate and thereafter treated with methyl alcohol and aluminium *isopropoxide* to produce *isocitral*. *isocitral* has been said to be an isomer of citral in which the double bond position is altered. The preparation we achieved had exactly the same physical constants as those given by Schmidt. The preparation was followed exactly, and we could only assume that we had produced the same material.

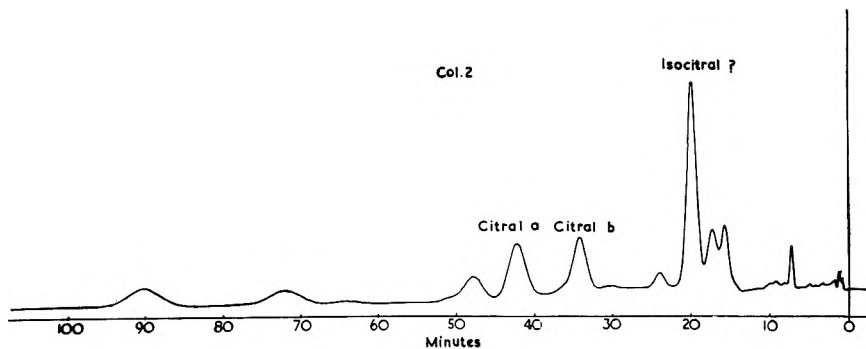


Figure 10

* *Journal* **14** 29 (1963)

It was fractionated a number of times, and no improvement on the analysis was shown. This sort of preparation shows how azeotropes can be formed that we do not recognise until we use physical methods of analysis, and *Fig. 10* shows the analysis of the resulting "isocitral"—the best fraction which we obtained. It will be noted that from the illustration there are a number of peaks, and we were only able to ascribe the identity of isocitral reasonably to the largest peak. *isoCitral* has been reputed to be the best compound giving a true lemon odour, even better than citral. We find, however, that if this largest peak in our chromatogram is indeed isocitral, there is no doubt that it does not occur to any extent in a natural lemon oil. We did not attempt to identify any structures by other methods: we were simply interested to see whether, following the preparation as given by Schmidt, this compound did actually occur in natural lemon oil. This demonstrates the fallacies that can arise with classical organic chemistry, and I hope it demonstrates one of the advantages of gas chromatography as a method of control.

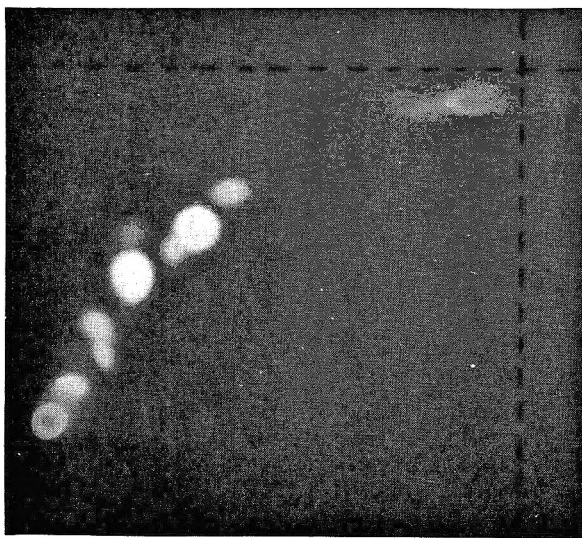


Figure 11

We have also mentioned as a limitation of gas chromatography that one should examine the non-volatile residues by some other method. We have shown in *Fig. 8(c)*, nine peaks in the gas chromatogram of the non-volatile residue of lemon oil. We have also examined this same residue by thin-layer chromatography and *Fig. 11* shows the thin-layer chromatogram examined under UV light. Being very optimistic, although we have not yet had time to confirm it, there are nine fluorescent spots which could

correspond to the nine peaks on our gas chromatogram *Fig. 8(c)*. This is the sort of auxiliary work that is required to strengthen conclusions drawn from gas chromatography. There has been some recent work, by Brown and Shyluk [*Anal. Chem.* **34** 1058 (1962)], on gas chromatography of coumarin derivatives.

The main point is that in a lemon oil, coumarins could be responsible for deterioration or ageing effects. They may have no effect on the smell but they could affect the stability of the oil. One must not overlook, therefore, the non-volatile compounds. Even if they do not actually contribute to the oil when fresh, they may affect the stability of the oil in storage, or when it is stored in a product.

A final application that we have described, where gas chromatography is applied directly to perfumery, is the smelling of peaks as they come out of the column. We have shown that if a peak in one of our chromatograms is nearly full scale one can smell most of these compounds coming out of the column. However, there is no doubt that when one is analysing only about a milligram of sample one cannot smell all the peaks that show on the chromatogram; one can only smell those that are present in major concentration. We run a pilot chromatogram to determine the times at which the various peaks are coming out. We then do a repeat analysis and attempt to smell the peaks we are interested in. We replace the detector by a capillary tube and the perfumer stands at the capillary tube smelling the peaks at the appropriate moments. This can be quite a new problem to the perfumer, who has very little time in which to make up his mind as to what he is smelling.

DISCUSSION

DR. M. H. KLOUWEN: Up to this moment the question whether there is a difference in odour of optical antipodes or not, has not been satisfactorily answered.

In the past, a number of research workers have tried to prepare optical isomers of highest purity with little success.

From the publications of high scientific standing—rare as they are in this field—I have not been able to ascertain whether the odour of optical antipodes really differs. There are two references [Rupe, H., and Wiederkehr, F., *Helv. Chim. Acta* **7** 669 (1924); Johnston, R. G., and Read, J., *J. Chem. Soc.* 236 (1934)] stating that there really is a difference; but the dates are 1924 and 1934 and we dare say that at that time traces of impurities, easily found today, could not be found at all.

In the literature we also find a number of references claiming that the odour intensity of enantiomers is different. Naves [*S.C.I. Monograph No. 1* (Staples Printers Ltd., London), 38 (1957)] has presented an excellent review on the subject.

As a result of your highly appreciated olfactive research concerning the enantiomers *d*- and *l*-carvone you conclude that the odour intensity of *d*-carvone is stronger than that of *l*-carvone, but that the odour character of both is identical. From the facts mentioned above, the conclusion should be that optical antipodes can show a difference in odour intensity but that the apparent difference in odour character has never been proved.

This conclusion is in accordance with similar effects noted in the biological and pharmaceutical fields, e.g. the action of *l*-adrenaline on blood pressure is fifteen times stronger than that of the *d*-modification.

Perhaps this phenomenon could be explained if optical activity could be proved to be present in the receptor system.

How you measure odour intensity ?

Was it done by determining the respective minimum stimuli or was your experiment carried out at higher concentrations ?

THE LECTURER : The experiments we carried out were, unfortunately, carried out about four years ago. Being a digression from our normal course of work at that time we did not pursue this line and we did not attempt to refine our simple odour tests further than already reported. The answer to your question is, therefore, that an equal quantity of each isomer, 5 mg, was chromatographed and condensed in a capillary tube at the outlet of the column. The capillaries were carefully drained on to small watch-glasses and kept covered by a second watch-glass, except while odour observations were made by four people, including one perfumer. You will realise that the observations were not statistically sound. The observations were carried out at high concentration; not at minimum odour concentrations. We felt that this work would possibly be of interest to a number of people and this is why we reported it, but we have not pursued it any further ourselves.

DR. M. H. KLOUWEN : The "histogram" you describe has already been proposed by Tesseire [*Recherches* 9 10 (1959)] in relation to oil of Clary Sage.

Do you not suppose that ageing of the column would have an influence on the reproducibility of the histogram ?

THE LECTURER : The work published by Teisseire, it is true, does give a concentration ordinate, which is a logarithmic scale. This might be as 0.1, 1, 10 and 100%. He also gives a line representing peak concentration, the concentration of each component being determined from the chromatogram. He does not, however, use the logarithmic scale on the abscissa. We do because if you have a value of 1.0 for the standard reference compound that has been chosen (preferably something occurring in the samples you are commonly analysing, e.g. menthol in peppermint or one of the citrals

in lemon oil), then it has the advantage that the presentation is compact. One is progressing from 0.1 to 1, and from 1 to 10, on this scale. It is very unlikely that anything will be more than ten times your standard. If, however, it is more than ten times, you have to choose a standard that comes out later.

Another advantage of logarithmic plotting along the abscissa is that a homologous series, which spreads out on a normal chromatogram, will come out at regular intervals on this base line, and by applying a scale rule to the histogram it is very easy to pick out the homologous series, though these compounds may not previously have been easily identified. Homologous series such as aldehydes in orange oil are readily plotted by this method.

DR. M. H. KLOUWEN : So the principle is the same, but it is easier to do in this way.

THE LECTURER : Yes, we have added the logarithmic plotting along the abscissa.

The answer to the second query is that there is a problem concerning ageing of columns, but with this representation we constantly relate retention ratios to their original values. We know by looking at the whole chromatogram that a peak is slowly shifting along one way or the other relative to our standard. We refer it back to the conditions when the column was fresh. When the column has aged to such an extent that you can no longer pick up these peaks that are drifting along in various directions, it is time to re-pack the column.

DR. Y.-R. NAVES : Personally, I am not in favour of the use of detectors which destroy the eluted substance ; as employed by you. To use such a detector, it is necessary to repeat the analysis in order to examine the eluted substances olfactively, spectrographically or chemically. In the analysis of a complex product, an exact separation of the eluted substances cannot be assured without continuous detection.

In this case, it is possible to effect detection on one part of the effluent and to study the other part olfactively, physically or chemically, but such a solution involves experimental complications when executed on the normal analytical scale.

THE LECTURER : We find that retention times are quite reproducible for consecutive chromatograms and we can therefore be sure which material is being eluted by reference to the previous chromatogram. On the analytical scale one usually needs to run a pilot analysis before it can be decided which peaks need to be identified by other methods. One is usually interested only in qualitative analysis by such methods. Choice of a suitable analytical column will therefore give the simplest quantitative analysis.

We use flame-ionization detectors because our apparatus was converted from thermo-couple detectors. These are of all-glass construction and simple maintenance is another factor. We also consider the safety in handling radioactive sources by relatively unskilled operators. Finally, the flame-ionization detector is insensitive to water. It is a fact that the argon detector depresses the sensitivity of peaks which are eluted with, or after, water.

DR. M. H. KLOUWEN: This detection method is effective, particularly if the peaks are perfectly separated. If they are not, then difficulties arise.

THE LECTURER: This is quite true, but we would not consider there would be much value in isolating peaks which were not completely separated.

DR. Y.-R. NAVES: In my opinion, the analysis of complex products such as essential oils and natural perfumes lends itself to the use of temperature programmed G.L.C. and also pre-columns, the latter to compensate for the influence of certain alterations.

I would be particularly pleased to learn your views on this subject.

THE LECTURER: We believe that temperature-programmed gas chromatography is an excellent thing in theory, but we would like to examine the economics. A complicated ancillary heating apparatus is necessary to ensure reproducible heating, and there is need for a cooling period between each analysis. The latter can be balanced by analysis on two or three isothermal columns while one is waiting for the programmed-temperature column to cool down.

We feel the main point is the difficulty of obtaining published retention data that can be applied to observations on temperature-programmed columns. This means that there is a limitation of calibrations to the compounds that one has available in one's own laboratory.

DR. Y.-R. NAVES: The use of temperature programmed G.L.C. necessitates particularly the consideration of the injection temperature. It is necessary either to achieve a certain over-heating of the injector, which is not very convenient, particularly on account of the sensitiveness of substances which are amongst the most volatile, or to arrange direct injection into the column charge, which raises other problems.

Do you have any experience of the best solution to these difficulties?

THE LECTURER: We have not studied this point in detail, but we have not noticed any decomposition of such labile compounds as linalol or linalyl esters when using a stainless steel vaporizer on our preparative-scale column (Atkinson and Tuey in "Gas Chromatography 1958", Ed. D. H. Desty,

Butterworths, London, 1958, p. 279) operating at approximately 150°C above the 130° column. Partial decomposition may be recognised fairly readily if the whole column effluent is collected, re-analysed and compared with the analysis of the starting material.

DR. Y.-R. NAVES : I would like to insist on the consideration of economic factors. The practice of chromatography must not be restricted to experts. It is better to establish simple rules and procedures which are easily carried out, so that a trained operator, using a single instrument, can examine a minimum of 20 to 22 different products in the course of one working day. Standardisation of chromatographic practice in our industry is desirable and this must not disregard economic considerations.

THE LECTURER : G.L.C. applied to routine essential oil analysis is a very reasonable suggestion but an expert must be available for the interpretation of results, and particularly for detecting faults such as ageing of liquid phase, decomposition of sample, etc.

Even when using a simplified technique, it would be optimistic to hope to analyse 20 to 22 samples in one day on a single apparatus. This would assume that each analysis takes only 20 minutes, no maintenance of the apparatus is necessary and no calculations are made beyond measurement of a few selected peaks. We believe that 10 to 12 analyses per day would be a more realistic figure for routine analysis.

MR. B. H. KINGSTON : You mentioned that the separation of α - and β -isomers of several terpene derivatives has not yet been achieved by G.L.C. In fact, for several years our research department has successfully resolved mixtures of α and β -citronellol (obtained by a synthetic route) using diglycerol at 180°C in ordinary packed columns.

Incidentally, our own evidence, based on infra-red and other measurements, suggests that the rose alcohols and related compounds exist only in the β -form—at least in nature.

DR. Y.-R. NAVES : I would like to draw attention to an error made in your paper. You state "The ability to separate the *isopropylene* and *isopropylidene* (α and β) isomers of several terpene derivatives has not yet been achieved by G.L.C." In fact, such separations (α and β citronellols, α and β linalols) were described in 1958 by me and Aldo Odermatt [*Bull. Soc. Chim. France*, 382 (1958)], and have been developed further since that time.

THE LECTURER : I would like to apologise for my oversight. We have again looked at your paper with great interest, and we have been examining the relative retention times of the α and β fractions. There have been various publications. I would like to present a few ratios to you. Dr. Naves

has done his analysis on a Perkin-Elmer "C" column which I believe is silicone oil, a non-polar column, and for citronellol he gets a ratio of α to β forms of 1 to 1.11. In each case the α form would be 1. Linalol isomers differ by 1 to 1.19. Other work in this field has shown ratios of the order of 1 to 1.14 for non-polar columns. We have examined linalol in which we did get the suggestion of two peaks from benzyldiphenyl which can be treated as a fairly non-polar column, and we get a ratio of 1 to 1.11. It is to be expected that isomerization—the movement of the double bond—will have a different effect on columns of different polarity. However, it is rather surprising to find that this similar type of α -, β -isomerization on the same liquid phase gives such different ratios for the citronellol and the linalol. The only difference between them is the shift of the double bond. Have you any suggestion why this may be so, or was I incorrect in measuring the retention ratios given in your paper?

DR. Y.-R. NAVES : Are these the relative retention times, or the relative proportions?

THE LECTURER : The relative retention times, α to β .

DR. Y.-R. NAVES : I would not expect from any theoretical consideration that the two must be of the same order.

ศาสตราจารย์ ดร. ย.ร. นเวส

PRACTICAL PERFUMERY AND INSTRUMENTATION

G. L. GARDEL*

Presented at the Symposium on "Perfumery", organised by the Society, at Cheltenham, Glos., on 14th November 1962.

Analytical instrumental methods contribute effectively to the establishment of acceptable standards of quality particularly in the field of synthetic aromatic chemicals, also for rapid control of manufacturing processes. Invaluable in pure and applied academic research, as a direct means of creating new fragrances their performance has at the present time but empirical value only.

OVER THE LAST few years many interesting and informative accounts were published in the technical press on advances in the field of pure and applied research by means of instrumentation, notably vapour phase chromatography, usually referred to as V.P.C. Most of the personnel, whether engaged in perfumery, cosmetics or other allied industries, will by now be familiar with the potential of this new tool. As usual with the advent of new developments, exaggerated claims were made for this instrument, either inspired by wishful thinking or due to imperfectly understood applications, leaving one to believe that this instrument would provide the answer for, among other things, the matching of perfume compounds. There are many technical reasons why this is not possible. This does not, however, detract in the slightest degree from the extreme usefulness of the instrument.

Technologists can be justly proud to have at their disposal such an elegant and accurate weapon for research, which, when coupled with I.R. and U.V. spectrophotometric methods, has opened avenues of approach to problems which, by the older more conventional methods of research, would possibly have taken months for their resolution. Thus the technologists have had the floor, their demonstration of the usefulness of this method is universally acknowledged, but we have failed to find among the many accounts a practising perfumer stating his or her attitude to this advance in modern instrumental analysis.

I am glad, therefore, to have this opportunity to put forward what must be of necessity my own views and beliefs as a perfumer, and perhaps find some corresponding echo from other perfumers. My views might also give the technologists some insight into the working mind of the perfumer. But

*Colgate-Palmolive, Ltd., Manchester 5, Lancs.

let us pause for a moment and re-state the function of the perfumer in society, which is, and has always been, to pander to the esthetic which creates cultural well-being ; this basic function sometimes appears to be forgotten or ignored. Perfumery has its feet firmly planted in antiquity, it is an art and not a science, its working is empirical, and no precise laws govern its practice. If we agree to this basic function, then we have to concede that the perfumer's concern is entirely with odour, and while he is working on the concept of a new fragrance such considerations as physical constants and chemical or instrumental analysis are completely meaningless, since by themselves they contribute nothing to the creation of fragrances.

The perfumer, however, realises his indebtedness to the technologist for having added to his palette many new and wonderful aromatic chemicals, thanks to the enquiring mind of the research chemist, but do not expect the perfumer to be overawed by the chemical configuration of a compound or by its molecular orientation in space to which the compound owes its odour.

Odour is the only governing factor which impresses the perfumer. This does not mean that the perfumer ignores the help that the chemist can give him—such factors as stability and discoloration indication which are of the utmost value in his work, but are by the nature of his work of secondary importance.

Many of us remember the times of yesteryear when the perfumer had to be a Jack of many trades, when he could take the time to study for himself the behaviour of his materials, which were considerably fewer, as were also the preparations for which his fragrances were required. Today he has to "remember" upwards of a thousand individual materials. When he builds a perfume complex he builds an edifice with bricks, the shape, size and dimensions of which he cannot see, but which nevertheless have to fit pretty accurately if the edifice is to stand up. You will readily appreciate, therefore, that the perfumer works on a completely different plane from the technologist who, by virtue of his academic training, moves along well-ordered theoretical rules and laws, and even though the paths he treads are unknown, he has for his guidance the object of his research. Not so the perfumer: Each step he takes is into the unknown, no rules apply, no limitations exist, even when working with familiar substances a slight change in proportions can often make or mar his efforts. He can, however, use all of the artistic licences of which he is capable, and this perhaps more than anything else makes the charm of his creativeness. No two perfumers ever approach the same problem in an identical manner, each having his own conception for a particular fragrance, their work being so completely individualistic; but it is really the end-result of their endeavours that provides the answer.

While reviewing the various papers on the subject of instrumentation as related to perfumery materials, the perfumer is left with the impression that an idea is being sold to him, to commit him to a definite course of action foreign to his way of thinking, he being gently chided that he views instrumentation with suspicion. Nothing could be further from his thoughts and no perfumer will ever refuse additional knowledge for the furtherance of his work. He will readily accept and digest any information passed to him and evaluate any samples, but he will always do so purely and simply in relation to odour, drawing on his odour memory for comparisons, or file away his impressions for future reference.

Difference of views can exist, however, particularly on the subject of essential oils as evaluated by him and the results of instrumental analysis. Given a free choice, the perfumer will always prefer to depend on his nose rather than on mechanical assessment. It must be remembered that odour is an intangible quality and we do not even know by what mechanism the sense of smell is actuated. In the single act of smelling a sample the perfumer uses all the accumulated experience of years. Why, then, try and convert him to a different way of evaluation? Instruments can be wrong, and frequently are, not because the instrument has shortcomings, but because of the human limitations which operate it. It is well known that every method of analysis must be capable of duplication if intended for universal acceptance. The potential of the instrument is still in the stage of development, changes in the stationary phase and the substrate used might produce different results for different classes of aromatic chemicals.

It might be difficult for the uninitiated to understand perfumery, but other experts know that the perfumer, with his specialised aptitude for storing information, links his memory with the odour sensation received, accepting or rejecting as the case may be. It is not the perfumer's function to pinpoint where deficiency begins and ends. It is the analyst's function to determine qualitative differences, always provided the subject is worth while pursuing. The perfumer can, and does, operate a very simple rule: "If in doubt—leave out."

I would therefore say that the value of instrumentation or any other method of analysis yet to be found, is of greater help to the research chemist, the analyst, and for the control of manufacturing processes, than to the perfumer.

The perfumer will, in my opinion, rightfully point out that he is buying odour and not physical constants, and it is hardly conceivable that a perfumed preparation is being sold on the basis of physical specifications of the perfumery material.

Standardisation of synthetic aromatic chemicals used by the perfume industry is one of the most important aspects in the elaboration of perfume

fragrances. V.P.C. is, therefore, an invaluable tool in effecting this standardisation ; it is also equally invaluable for the investigation of natural products, but since we do not even know their composition with any degree of certainty it would be difficult to talk in terms of standards. The further the chemist advances in the study of natural products, the more components are being found, and these can amount to quite spectacular numbers. Deficiencies in these trace compounds probably make the difference between a good or mediocre oil. So until all these various components have been identified and synthesised, much of the mystery that surrounds natural products will remain. There is no doubt that eventually these problems will be solved, and, as a perfumer, I feel sure that many more powerful and desirable but as yet unknown perfume materials will be added to the perfumer's range of odour.

Who knows, perhaps it will even be possible to compound fragrances by slide rule ; this, however, is pure speculation.

Even though the technologist and the perfumer appear to be on different sides of the fence, they have at least one bond in common. In their respective spheres they both serve an industry of constantly expanding scope and importance, and neither could survive on his own for very long.

As a perfumer I also feel sure that the perfumer would rather be regarded as a potential consumer if thereby he preserves his mental freedom and reserves his efforts for the creation of new fragrances for the pure enjoyment that these provide, for this is, after all, his *raison d'être*. Sometimes he creates or anticipates fashion by exercising his own originality, using new aromatic chemicals offered to him by the technologist. Sometimes he revives and stimulates interest in already existing fragrances.

Finally, I would state that the practice of perfumery is one of the most satisfying callings, often frustrating, but always stimulating in achievement.

(Received : 12th October 1962)

Introduction by the lecturer

Some four years ago when VPC first came on the market, someone blithely turned up and said that perfumers were going to be out of a job very soon. Naturally, it made my ears stand up and I started to watch what was going on around me in the field of VPC. Eventually I came to the conclusion that this instrument does not help me or anyone else to make a new perfume. I regard it as an excellent auxiliary, but it does not have to be in existence as far as I or for that matter any other perfumer is concerned. We can make good perfumes without knowing about VPC curves, or physical constants, specific gravities and so forth ; it makes no difference, we deal mainly in odours. Odour is the only factor that has

anything to do with our daily life, if it satisfies these conditions we are willing to accept any information, indeed, it is our job to know a little of everything that goes on around us concerning cosmetics, high class perfumery, cheap perfumery, etc.

That brings me to another concept of the perfumer. In the last few years the idea has gone around that the perfumer should be a chemist. I believe that this is the completely wrong outlook. The chemist's training is such that he is very orderly in his thinking and follows rules, whereas I, even when talking, do not follow any rules. I just treat the problem as it occurs to me. Order does not exist in my mind, except for odours. So when this does happen, when you appoint a chemist trained in chemical formulations to approach the problems of perfumery and he tries to relate them to structure, he will not get very far. You might just as well ask an artist (painter) to be a dyestuff chemist. When you are dealing with art and not science, mathematical rules do not apply.

We have heard various opinions about the sensitisation of the skin, stabilities, instabilities, discolourations; all these the perfumer must disregard when he creates something new. I have found, for instance, that a chemical incorporated into a piece of soap, together with traces of alkali, discolours, but in an admixture with other things this effect is not obtained. It is the same with irritation. Cinnamic aldehyde, benzaldehyde, hydroxycitronellal and others, all irritate the skin, but when you are building up—and a perfumer uses anything from 20 to 200 materials—these effects can completely disappear. So by being dogmatic on certain aspects the perfumer handicaps himself, and achieves nothing in the end. One's mind may be cluttered up with considerations of things becoming discoloured, but if you use a material that is known to discolour and try it out it may not discolour at all.

Stability is not a thing by itself. A material may possibly not be stable in a particular medium, but in association with others it is perfectly all right. I have tried for years to establish the reasons for this, but have never succeeded. On my shelves I have numerous perfumes, perfectly good on a strip of paper, but when incorporated into soap and left for a few days, the perfume completely disappears. So I return to the compound and try a new approach. Why has it happened?

I do not wish to give the impression that I oppose instrumentation. I am keenly interested in anything that furthers progress in the field of perfumery, but there are two sides to my mind: one is the interest I have in the hows, whys and wherefores, and the other is my job as perfumer. I try to make my mind a blank when I start a new project, and do not worry about cost. My first object is to produce something that is technically properly constituted and fulfils its purpose, the rest is dealt with afterwards.

This is when the troubles of the perfumer begin. We have heard of the cost of some aromatics, and this is a perfectly valid argument. In this age, when everyone wants the best value for little money it looms very large on the perfumer's horizon. The only time when he applies logic is after making something, he then starts dissecting, and perhaps even starts all over again to bring his "something" within the limits of the economics that operate. Most of us are dependent on the companies that employ us, and therefore have to conform to the aspects of the business that demand a reasonable return for the money expended.

One can see what happens when things are pushed to extremes. Music is an example that naturally comes to mind.

Every note, its duration and vibration, the exact pitch of any single instrument can be expressed in precise mathematical terms, but I have yet to hear a piece of music composed of mathematical values. The perfumer is in much the same position because he deals with intangibles. I can appreciate that any scientist, any research chemist, will hate to be confronted with something against which he cannot put an equation. In perfumery we deal with something entirely in a man's mind.

We perfumers do not even agree amongst ourselves. If two perfumers are asked for a duplication of lavender, which is not too difficult, I feel sure, that between them they might possibly have four identical materials, and the rest will be different. Yet they will come up with the same answer, or reasonably so. We do not know what actuates odour. There are many theories, but nothing proven concerning what actually happens when we smell something. Yet twelve months afterwards our memory can say "I have smelt this before". What has happened? The memory has been stored as knowledge, but how? The technicians are doing a very good job, but should not try to tell the perfumer how to do his. It is the perfumer's job to use the materials they produce.

DISCUSSION

MR. J. D. CHESHIRE : After discussing the relative merits of instrumental methods of analysis and the art of perfumery, you have stated that "the perfumer is buying odour and not physical constants".

I would like to ensure that there is no confusion between the information provided by physical constants, such as boiling point, refractive index, or specific gravity, and by physical methods of analysis such as gas chromatography or spectroscopy.

Relationships between chemical conditions and odour are at present purely empirical, as you have pointed out, but physical methods of analysis are constantly open to improvements and will eventually undoubtedly play an important role in understanding and defining odours. Physical constants,

however, provide no hope of correlation with odour, since so many compounds and mixtures yield similar values.

THE LECTURER: I agree with you, but I would also like to say that you have just pointed out the shortcoming of analysis yourself. You say that methods are always changing and becoming more accurate. At the same time you wish me to take notice of such things as specific gravity, whereas, I make the point that I am not concerned with that. I have purchased materials that were based on wet analysis, outside the standard set, and yet the odour was excellent. When I had finished my job it was accepted by everyone except by a few boys in the laboratory! At times, after working on a project for three months or more, I have wished that mathematical rules could help me. There are so many unknown factors that operate in perfumery. It is amazing—the older I get, the more I practise perfumery, the more I come to realise how little I know about it. Any perfumer who says differently, does so because he is unwilling to belittle himself. Through the years I have had many reminders that some of my ideas have been completely wrong. This should not have happened as I have been practising long enough, but it did.

DR. Y.-R. NAVES: One cannot but completely agree with your opinions. The perfumer operates with olfactive quality, and we do not really know any valid relationship between a physical or chemical property and the olfactive quality. At the most, we can associate the odorous quality with the chemically defined substance which carries the odour.

On the other hand, the technologist who must sell regularly and profitably the products required by the perfumer, cannot help but use to the best advantage instrumental techniques which identify the substance or substances determining the odour of the product.

In the current state of science and technology the use of instrumental technique has no connection with the art of perfumery.

THE LECTURER: I should like to go further with that. When the perfumer sets out to make a new compound he usually has some sort of guide, either from the management, the sales people or even from the product in hand. He already knows how far he can go. For instance, it would be completely pointless to extract a perfume of similar composition from some other product, put it through VPC, add a little guesswork, and try to reconstitute the compound. I have seen some very peculiar results arising from that method, particularly with flavours. VPC gave the result expressed as so many per cent terpene, limonene, menthol, menthone, aniseed, etc., but if one attempted to reconstitute the flavour from this information the answer would make nonsense. The instrument has faithfully recorded its results, but these bear no relationship to the actual flavour.

Not because the instrument is wrong, but because it has limitations and is still in a state of development.

The following actually happened. One supplier was asked to look again at one of the essential oils he had supplied, because VPC showed some peaks where there were none before. He naturally asked for a sample, took it back to his office and had it tested again, but could not find the peaks in question. He approached the user and said "I cannot find them, how did you?" "Oh, we cannot tell you, that is a secret!"

While so-called analysts treat these matters with secrecy, how can this claim to be a method of analysis? We are using man-made terms that do not mean the same thing. For instance, analysis does not mean the same thing to an accountant, yet by definition it means details of something, whatever it is he is trying to break down, in order to extract something. It is only to that extent that we agree. To me an analysis must be something that can be reproduced wherever there is an instrument. It is therefore up to the instrumentalists, as a body, to get together and formulate a method of procedure, even if it means using more than one stationary phase, so that everything is obtained at the same time, and it agrees with the findings of others. When an instrumentalist draws a chromatogram and this is superimposed on that of a similar oil, it will be found that with this oil, drawn from the same source, the peaks are slightly displaced, and so it is no longer accurate, is it? Dr. Naves has already said what the errors can be, so there must be quite a lot of room yet for improvement in instrumentation before it can be accepted as a tool of analysis to carry some validity. Although it may be right amongst the laboratory people, who may have some reasonable explanation, i.e. this peak is displaced for one reason or other, but it would not hold in a court of law if there is a dispute.

MR. S. J. HAWKES: The first thing I wish to say for the unfortunate technologist is that we answer the questions that you put to us. If somebody comes to me with a smell in a bottle and says "What is it?", the only thing I can do, as an analyst, is to find out what it is. Admittedly, from time to time people have sent me samples, and after I have produced its analysis, it does not smell the way the perfumer wanted it to smell.

Nevertheless, from time to time, a perfumer has sent me materials and I have sent back a result that has enabled him to work from there and find the answer to his perfumery problem. As an analyst, I cannot as yet provide the complete answer to the question "What is perfume?". It obviously contains too many substances, all of which are difficult to identify, but it can be done if I am given a few years to do it in. Nevertheless, I can chart him an answer with so many per cent of so many things,

and this I think will frequently give the perfumer or the flavouring chemist some clue as to what he is doing. I do not know to what extent this is useful, because I am not a perfumer but, nevertheless, I think it ought to be of some help to somebody.

THE LECTURER : With me it is usually the other way round. It is the analyst who comes to me and says "What is this?".

MR. S. J. HAWKES : I have done that too. Is this not a good cause for co-operation? You supply me with the mixture and I will supply the answer; we will then get together and find out what it all is.

THE LECTURER : This is precisely the point I would like to make. The analysts' outlook on the problem is different. They expect the perfumer to be subjective in his approach to perfumery, and yet at the same time practically tell him what he ought to do. To my mind the two must go together; one can not exist without the other. No technologist—no new products. No sale for our compounds—no technologist. It is not true that the perfumer is reluctant to accept instrumentation. He is very interested, but must also make use of a good deal of common sense. If something looks wrong he must not accept it.

Someone has mentioned something about eventually making perfumes by methods where the instrument has found the answer, and we then translate it into practice.

I do not think this will ever be possible. Anything creative, like writing a piece of music or poetry, is a subject in a man's mind, and it is so with perfumery. Can a machine which returns but what you feed into it, possibly give an answer? What sort of perfume is it likely to be when everyone uses exactly the same process for manufacture, uses the same standard, replaces all the essential oils with reconstitutes? There will be no great merit, everything will be classified into certain types of perfume and that will be that. No more imagination, only chemists, and no perfumers!

LETTER TO THE EDITOR

SIR,—I note that the report in the *Journal* [14 28 (1963)] of the paper by Klouwen, Kok and Ruys, omits to mention a point raised in the ensuing discussion.

Dr. Klouwen has compared the economies of the two oxalactone processes, the more recent one by Ogorodnikova *et al*, and the older one described by Collaud in Brit.Pat.490,044, solely on the basis of ease of execution.

As Dr. Klouwen drew the conclusion that the first process was more economical, I remarked that one also had to consider the fact that the second process gave a yield of 90% as against 80% in the other one. In view of the high material costs involved, this difference in yield was of sufficient importance to give an overall advantage to Collaud's process. This fact was acknowledged by Dr. Klouwen.

Yours faithfully,
Y.-R. NAVES.

Givaudan, S.A.,
Vernier-Geneve, Switzerland.

SOCIETY OF COSMETIC CHEMISTS OF GREAT BRITAIN

Election of Honorary Members

A SPECIAL MEETING was held at the Royal Society of Arts, John Adam Street, London, W.C.2, on Tuesday, 26th February 1963. 32 Members and Associates were present.

The Chair was taken by the President, Mr. G. A. C. Pitt, who called on Mr. S. J. Bush to propose the motion that

H. W. HIBBOTT, M.Sc., Ph.D., F.R.I.C., be elected an Honorary Member of the Society of Cosmetic Chemists of Great Britain.

Mr. A. Herzka seconded the motion, which was put to the vote and carried unanimously.

The Chairman then called on Mr. G. M. Howard to propose the motion that

A. W. MIDDLETON, Ph.D., F.R.I.C., be elected an Honorary Member of the Society of Cosmetic Chemists of Great Britain.

Dr. B. A. Scott seconded the motion, which was put to the vote and carried unanimously.

Increase of Membership Fees

AT THE Special Meeting held at the Royal Society of Arts, John Adam Street, London, W.C.2, on 23th February, the meeting, by an overwhelming majority, approved an increase in membership subscriptions, operative from 1st April 1963. The new rates are:

Members between the ages of 30 and 65, £4 per year. Members under the age of 30, and above the age of 65, £3 per year.

Associates £3 and £2 respectively.

Journal for Students

By a decision of the Council, students attending the Diploma Course will, in future, receive copies of the *Journal* free of charge.

1963 Programme**Lectures**

Venue: The Royal Society of Arts, John Adam Street, London, W.C.2.
Time: 7.30 p.m.

Wednesday, 15th May

W. B. Smith [Marchon Products, Ltd.]
The analysis of synthetic detergents.

Symposium on Aerosols

A SYMPOSIUM on Aerosols will be held at the Palace Hotel, Southport, Lancs., on 24th and 25th April 1963.

*Programme***Wednesday, 24th April 1963***Afternoon*

Chairman: S. J. BUSH, Esq.

- 3.00 p.m. Welcome by His Worship the Mayor of Southport,
Alderman Dr. S. J. HEPWORTH, J.P.
Opening of the Symposium by the President of the Society,
Mr. G. A. C. PITT.
- 3.15 p.m. "Hair lacquer systems"
R. C. HARRIS (*Swallowfield Aerosols Ltd., Wellington, Somerset*).
- 3.50 p.m. "Quality control of aerosol filling with particular reference to aerosol
valves"
B. HAWTIN (*Richmond Aerosols Ltd., Winsford, Cheshire*).
- 4.25 p.m. "Some factors relating to the choice of perfumes for pressurized products"
R. E. ECKTON (*Givaudan & Co. Ltd., Whyteleafe, Surrey*).
- 5.00 p.m. "Lanolin derivatives for pressurized formulations"
A. HERZKA (*Independent Consultant, London*).

Evening

- 8.30 p.m. Reception by the Mayor and Corporation of Southport.

Thursday, 25th April 1963*Morning*

Chairman: G. A. C. PITT, Esq.

- 9.00 a.m. "Physiological properties of propellants"
Dr. H. KÜBLER (*Sprühtechnik GmbH, Rheinfelden/Baden, Germany*).
- 9.35 a.m. "Flammability of propellants"
K. DIXON (*The Cooper Technical Bureau, Berkhamsted, Herts.*).
- 10.10 a.m. "Some aspects of the safety of aerosol containers"
G. F. PHILLIPS (*Laboratory of the Government Chemist, London*).
- 10.45 a.m. COFFEE.
- 11.05 a.m. "Aerosol propellants"
P. DYSON (*Imperial Chemical Industries Ltd., Runcorn, Ches.*).
- 11.40 a.m. "Corrosion in aluminium containers"
E. K. CLARKE (*Beecham Toiletry Division Ltd., Brentford, Middlesex*).
- 12.15 p.m. LUNCH.

Afternoon

- 2.00 p.m. "Brains Trust"
 M. N. CONVILLE [*Aerosol Packaging Co. Ltd., Bracknell, Berks.*].
 J. A. T. FISHER [*Aerofill Ltd., Perivale, Middlesex*].
 S. W. FRANKISH [*Imperial Chemical Industries Ltd., Runcorn, Cheshire*].
 R. A. GUNN-SMITH [*The Metal Box Co. Ltd., London*].
 J. PICKTHALL [*I.F.F. (Great Britain) Ltd., Enfield, Middlesex*].
Question Master: A. HERZKA, Esq.
- 3.45 p.m. Symposium ends.
- 4.00 p.m. TEA.

Symposium on Toxicology

A SYMPOSIUM on Toxicology will take place at the Town Hall, Leamington Spa, Warwicks., on 20th November 1963. Anyone wishing to submit a paper is requested to contact the Hon. Editor.

Annual General Meeting

This will take place on Friday, 24th May, at 7 p.m. at 55 Park Lane, London, W.1.

GENERAL NOTICES

Publication dates: The "Journal of the Society of Cosmetic Chemists" is published monthly.

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Responsibility for statements published: The Society of Cosmetic Chemists of Great Britain and its Hon. Editor assume no responsibility for statements or opinions advanced by contributors to this Journal.

Lectures: The Society shall have the right of first publication of any lecture or address delivered before it, but does not undertake to publish any given matter.

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Manuscripts: These should be in accordance with the "Directions to Authors," copies of which are available from the Hon. Editor, Ashbourne House, Alberon Gardens, London, N.W.11.

3rd INTERNATIONAL CONGRESS OF COSMETIC SCIENCE

THE 3RD CONGRESS of the International Federation of Societies of Cosmetic Chemists is being organised by the Society of Cosmetic Chemists, and will be held in New York from 21st—28th June 1964.

The American Society chose New York City because the World's Fair will be held there at that time, and Thursday, 25th June 1964, has been designated as Cosmetic Chemists' Day.

The Congress will be held on the campus of Columbia University. Anticipating that accommodation in New York during the World's Fair will be costly and scarce, the Society of Cosmetic Chemists has reserved rooms for participants in New Hall, the newest residence hall on the campus which is built, and will be operated, like a hotel during the Congress.

SCIENTIFIC PROGRAMME

The Congress will have four morning sessions, Tuesday to Friday, 23rd—26th June 1964.

Seminar Areas

- (a) *Safety Aspects of Cosmetic Usage.*
 - (1) Review of recent clinical experience.
 - (2) Advanced techniques for testing *in vivo*.
 - (3) Regulatory aspects.
 - (4) Statistical aspects.
- (b) *Instrumentation's Role in Cosmetic Research and Control.*
 - (1) Chromatography :
 - (a) Gas chromatography.
 - (b) Paper and other absorption media.
 - (2) Spectroscopy.
 - (3) Electron microscopy.
- (c) *Cosmetics versus Skin Ageing.*
 - (1) Physiology and biochemistry of the skin ageing process.
 - (2) Radiation effects.
 - (3) Action of steroids.
 - (4) Atmospheric and environmental effects.
- (d) *Cosmetics and Micro-Organisms.*
 - (1) Preservation.
 - (2) Control of skin flora.
 - (3) Microbial aspects of hair and scalp problems.
 - (4) Antibiotics versus antiseptics in cosmetics.

ACCOMMODATION

Through the generosity of the American Society of Cosmetic Chemists, members of the Society of Cosmetic Chemists of Great Britain, or of any other Society of Cosmetic Chemists affiliated to the I.F.S.C.C., will be admitted free of charge to the Congress under the "Package Deal", provided

reservations are made before **15th May 1963**. All reservations must be accompanied by a deposit which will be returned upon arrival at the Congress, or will be refunded up to 15th May 1964.

TRAVEL ARRANGEMENTS

Arrangements have been made to travel with a special flight of Aer Lingus Irish Airlines, utilising a Boeing 707 jet aircraft. If sufficient support is obtained, the cost from **London** to New York and return, will be approx. **£75** per person, and from other **European centres**, approx. **£85** to **£90** per person, irrespective of age.

The proposed departure from London, is on the morning of 21st June 1964, thus arriving in New York during the afternoon (travelling time approx. 7½ hours). The return flight, which will last 6½ hours, is scheduled to leave New York between 5th and 12th July 1964, depending on the wishes of the majority of the participants.

Participants must also return as a group and the free baggage allowance is 44 lb. All rates are subject to confirmation, because the 1964 transatlantic fare structure will not definitely be known until the autumn of this year.

No deposits are required until 31st January 1964.

Registration Forms

Anyone interested in coming to the Congress, is asked to complete the attached coupon without delay, and to send same to the Hon. Travel Organiser.

SOCIETY OF COSMETIC CHEMISTS OF GREAT BRITAIN

3rd International Congress of Cosmetic Science

New York—21st to 28th June 1964

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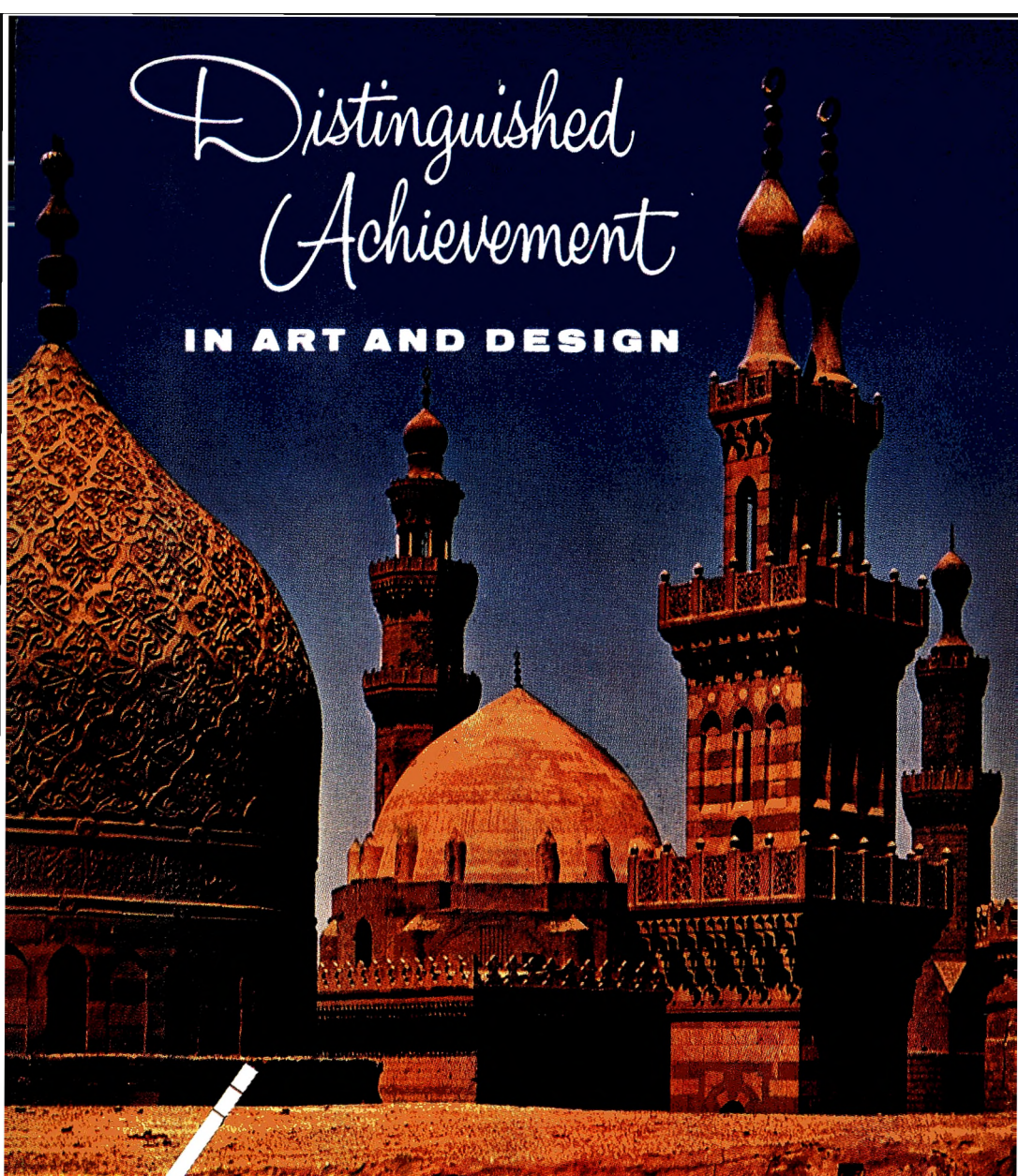
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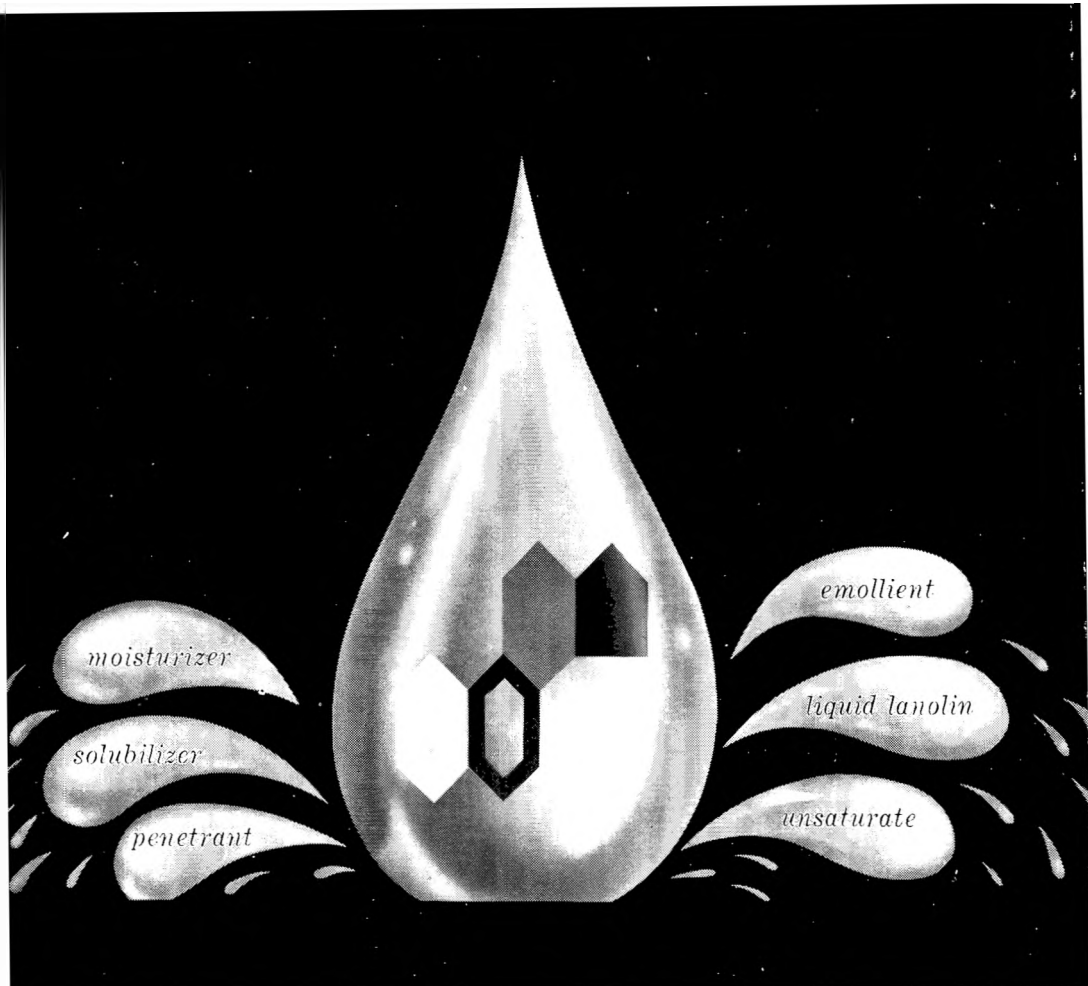
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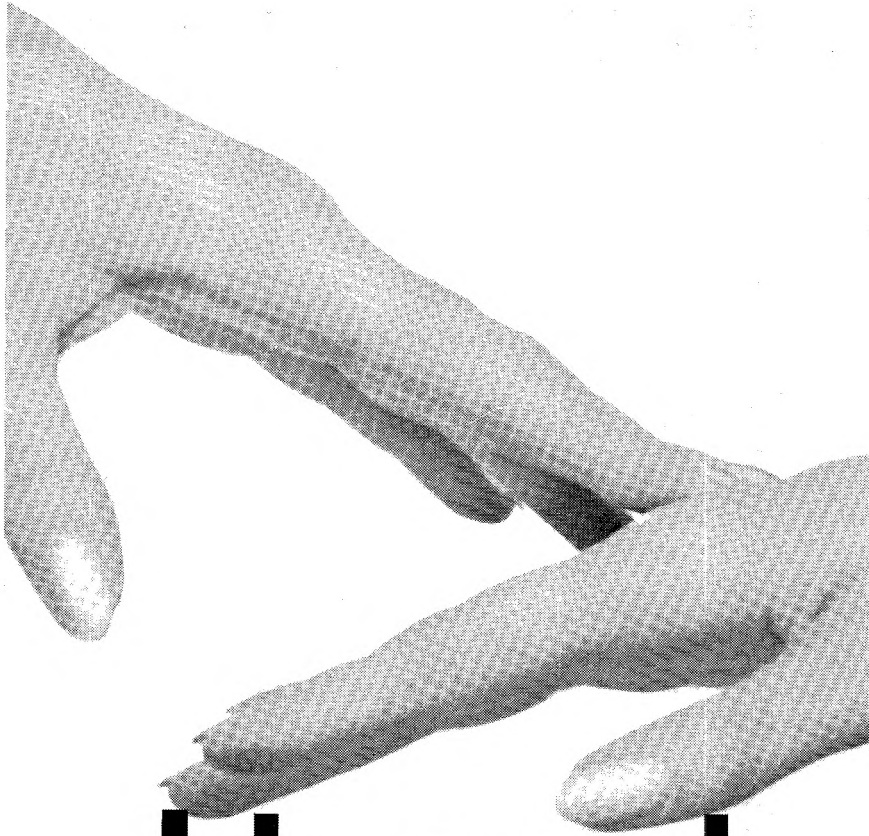
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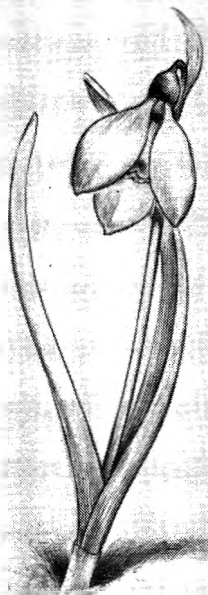


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