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GAS–LIQUID CHROMATOGRAPHY AND THE PERFUMER

D. HOLNESS, B.A.*

A lecture delivered before the Society on 23rd February 1961.

Gas-liquid chromatography is an efficient separation technique which can simplify the perfumer's studies of complex raw materials. Its already numerous applications are listed, and the need for careful choice of working conditions is stressed. Examples are given of quantitative analyses and of identifications of essential oils of similar types.

THE TERM "chromatography" covers a group of closely related separation techniques, all based on partition between two phases, one fixed and one moving. Chromatographic methods are outstanding in efficiency, and have the additional merit of working under conditions which permit the safe handling of many relatively unstable compounds. Gas-liquid chromatography, distinguished by having a gas as mobile phase and a liquid as stationary phase, is applicable to substances with appreciable vapour pressures at moderate temperatures.

Perfumers frequently work with mixtures of uncertain composition (notably the essential oils) and their raw materials have odours, a property which implies some degree of volatility. Consequently chromatography has obvious applications in this field, with gas-liquid chromatography as the method of choice. The value of gas-liquid chromatography to the perfumer lies mainly in its ability to simplify his studies of mixtures. It is by no means the answer to all his problems, nor is it a sort of "artificial

*Proprietary Perfumes, Ltd., London, S.E.1.

nose" as some fanciful writers have claimed. The trained nose is a detector of a far higher degree of organization than any known gas-liquid chromatography detector. If geraniol, for instance, is fed into a gas-liquid chromatography detector, the response tells only that *some* material is there. By contrast, the perfumer's nose yields the identification "geraniol", indicating the structure down to stereochemical details! Likewise, the perfumer can name the constituents of simple mixtures which the gas-liquid chromatography detector cannot by itself show to be mixtures.

Even the best nose, however, has its limitations. It can identify only compounds of which it has had previous experience. It cannot, like the gas-liquid chromatography column, resolve mixtures into separate lots, each composed of molecules of a single kind, for examination independently of each other. It grows less sure as the complexity of the mixture increases and it is hampered by the existence of blends—so much sought after in creative perfumery—with unified odours. In quantitative evaluations the nose is an inferior performer. Furthermore, the perfumer's assessment of a material is subjective, and is therefore unjustly regarded by unskilled observers as a mere opinion which they are entitled to dispute in the absence of supporting evidence.

Perfumers have long looked for help from techniques like distillation and chemical analysis, and it is hardly surprising that nowadays many of them welcome the aid of gas-liquid chromatography, both on the analytical scale and on the preparative scale in combination with other modern instruments like the infra-red and mass spectrometers. The applications of gas-liquid chromatography to perfumery have already become so numerous that it would take too long to describe them all fully. I therefore propose only to list the ones I know of, and then to discuss in greater detail a few subjects selected to illustrate both the advantages and the limitations of this method.

Gas-liquid chromatography can be used to help perfumers

(a) In *quality control* for identification of essential oils by comparing their chromatograms with standard trace-patterns;
for comparisons of the proportions of isomers in "mixed" synthetics such as the ionones;
for checking the impurities present in synthetics and isolates;
for seeking evidence of suspected admixture or adulteration;
for checking compounded perfumes;
for investigating the causes of observed odour differences and odour changes in all kinds of raw materials;
for direct *quantitative* determinations of selected single constituents of essential oils and other raw materials.

(b) In *research* for the isolation and identification of unknown compounds present in essential oils;
for the separation of "difficult" isomers in the pure state, especially in studies of the relationships between odour and structure;
for studying reactions in experiments to develop new perfumery ingredients or to improve processes for making well-known ingredients;
for investigating the limitations of chemical methods of analysis and the causes of observed inaccuracies in them.

(c) In *manufacturing* for following and controlling the courses of reactions and fractional distillations.

Other uses may have been devised of which I have no knowledge, but even so the list is impressive enough. It will doubtless be added to in the future.

Choice of Working Conditions

In perfumery work, particularly when essential oils are studied, it is important first of all to learn how to make the best use of available equipment. Perfumers who pile on the samples without thought for the optimum capacity of their instrument must take much of the blame for their own disappointments. In the long run, time is saved when favourable conditions for achieving required separations are known.

Essential oils are among the most difficult of mixtures to which gas-liquid chromatography has yet been applied. They have very many components, which may vary over an extensive range of concentration, vapour pressure and chemical composition, and quite minor components can contribute significantly to the complete odour. *Fig. 1* is a chromatogram of components of oil of Ceylon citronella, eluted in 3 hours at 100° C. Geraniol makes up more than one quarter of the total, while the smallest peaks represent only fractional-percentage constituents. The first-eluted compounds have retention times of only a few minutes, but other substances (not all shown on the illustration) have retention times of up to 14 hours.

The diversity of possible chemical compositions gives rise to even more problems. Substances occurring in essential oils all contain carbon and hydrogen. The majority contain oxygen, a few include nitrogen, and occasionally sulphur is present. Hydrocarbons, ethers, alcohols, phenols, esters, aldehydes, ketones and lactones are commonly found. Structures include unbranched and branched chains, alicyclic, aromatic and heterocyclic rings, and some more complex bridged rings. Isomeric compounds often occur together, including stereoisomers. Resolutions of related compounds which form simple sequences rarely overtax the skill of the gas-chromatographer. *Fig. 1* shows the degree of separation obtainable with three

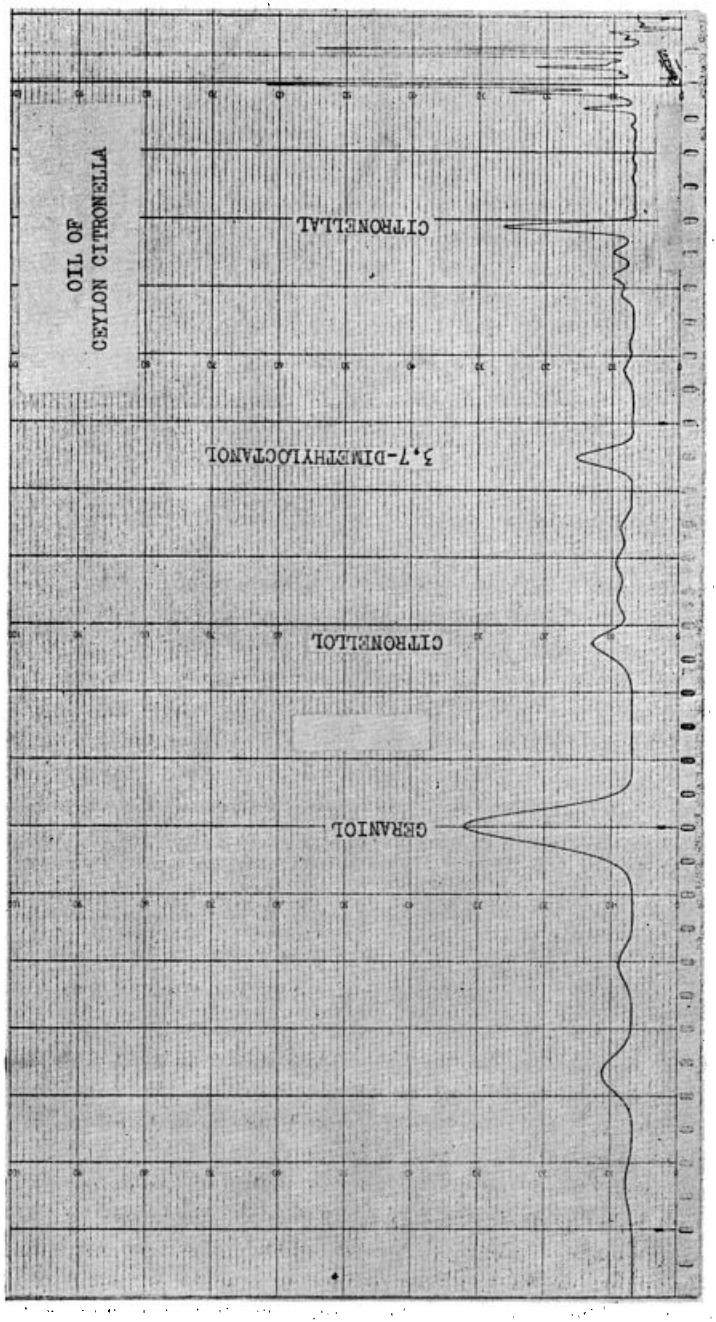
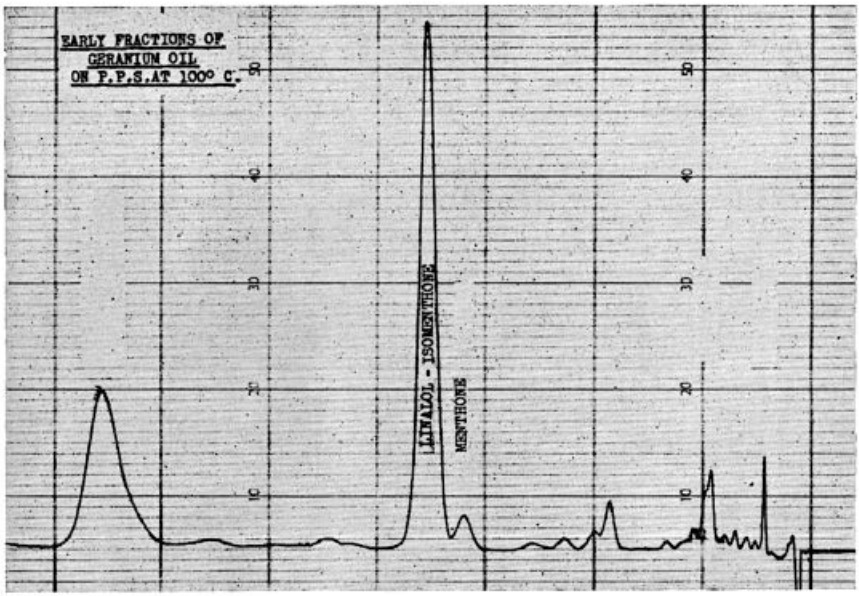
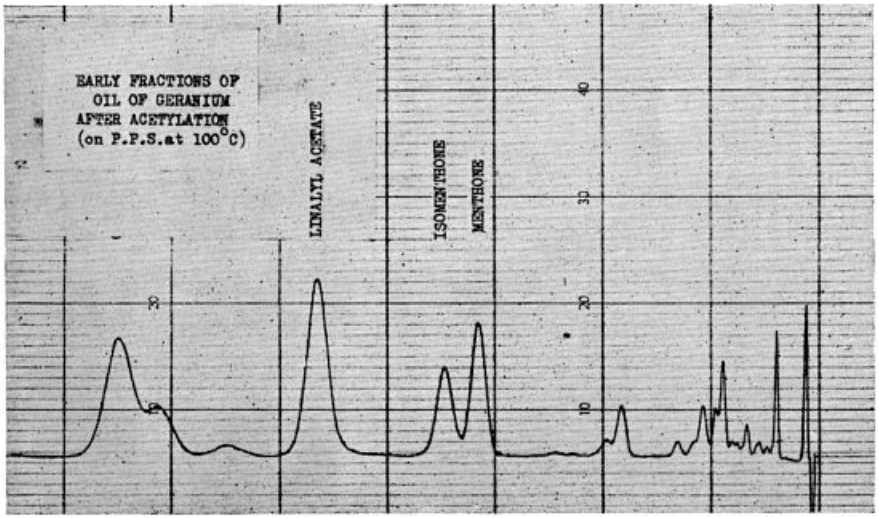


Figure 1
Oil of Ceylon citronella at 100° C.



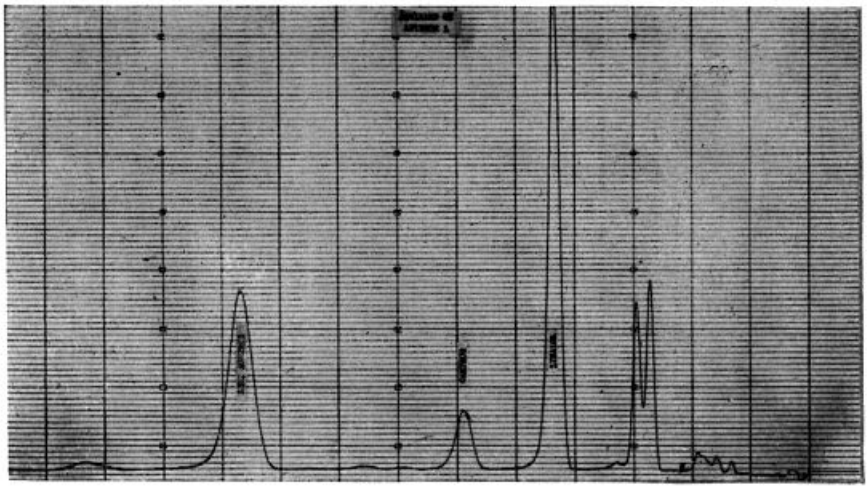
(a)



(b)

Figure 2
A "mixed" peak revealed by forming a derivative of one of its components.

of the suspect peak may be so radically altered that it becomes difficult to sort out the exact peak migrations which have taken place. *Fig. 3* shows differences between chromatograms of the same oil of lavendin on Apiezon L and on polypropylene sebacate. The reversal of elution order of linalol



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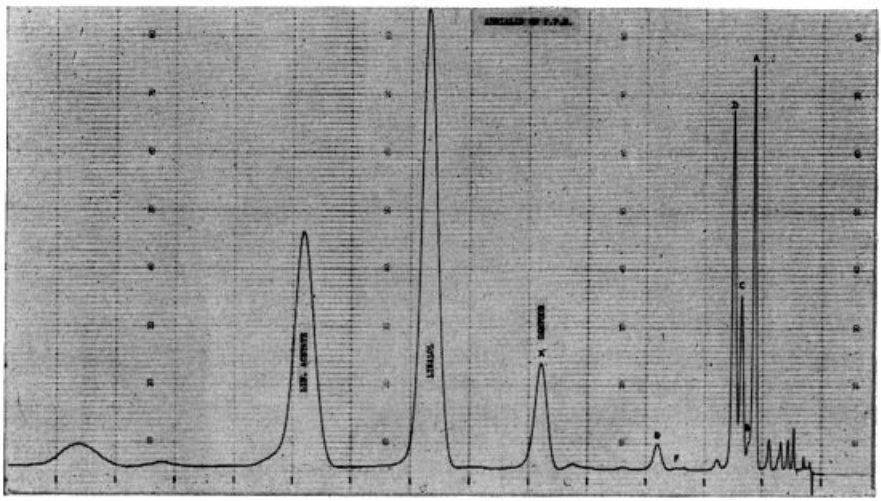


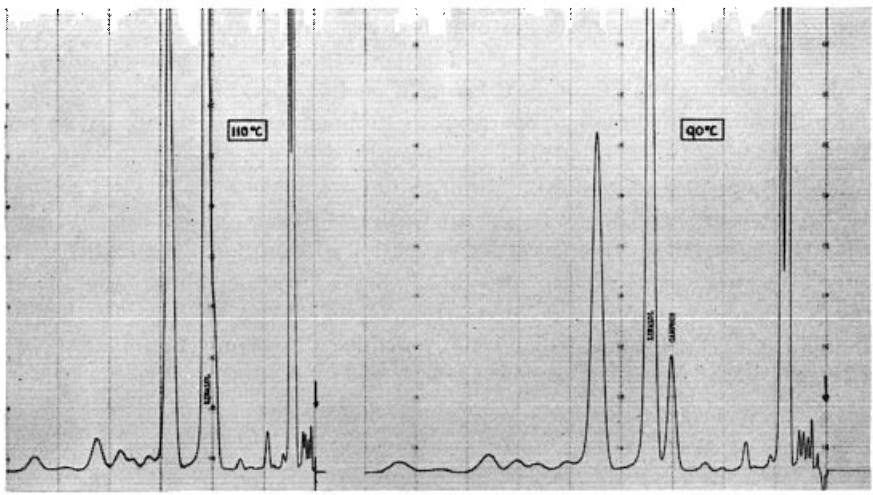
(b)

Figure 3

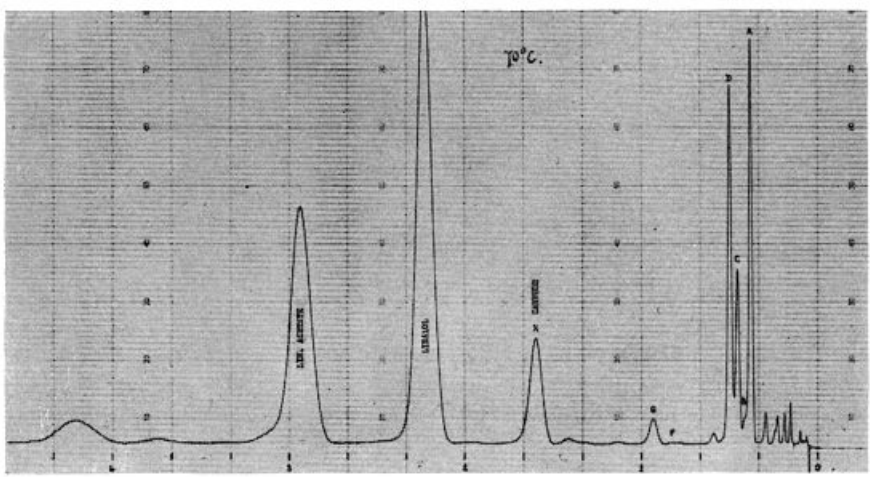
Chromatograms of the same oil of lavendin on two stationary phases of different polarity. Chart speed in *3(a)* 6″ per hour ; in *3(b)* 3″ per hour.

and camphor is indicative of the degree of change which must be anticipated. Unfortunately, available stationary phases fall mainly into a few well-defined groups. Polarity differences between group and group are rather great, while differences between the members of any one group may prove too small to be effective.

Lastly, I would like to suggest the third very simple method of running



(a)



(b)

Figure 4

Showing the effect of temperature on resolution of linalol and camphor on p.p.s. At 110°, camphor appears as a "shoulder" on the leading edge of the linalol peak.

successive chromatograms on the same polar stationary phase at varying *temperatures*. I believe that many workers with essential oils choose column temperatures too high for adequate resolution of any but the least volatile components. (Some published chromatograms have even shown clear evidence of partial thermal decomposition, indicated by a general lift of the base-line.) This predilection for high temperatures, perhaps due to impatience, may well explain why the magnitude of the effect which I propose to describe seems hitherto to have been overlooked.

At 120° C and above, the first-eluted fractions of essential oils tend to produce an unsightly jumble of concurrent peaks. Good resolution is hardly possible until the column temperature is dropped below 100° C. During a study of the early fractions of oils of lavendin on p.p.s. at 70° C, I observed a peak where no peak had occurred in chromatograms at 100° C. It proved to be camphor, which overlaps with linalol at 100° C and more. It was easy to demonstrate the increasing separation of camphor from linalol with successive reductions of temperature (*Fig. 4*). Another chromatogram of oil of geranium on p.p.s. at 70° C (*Fig. 5*) revealed a clear separation of linalol from *iso*menthone, which is not possible on the same column at 100° C (*Fig. 2*).

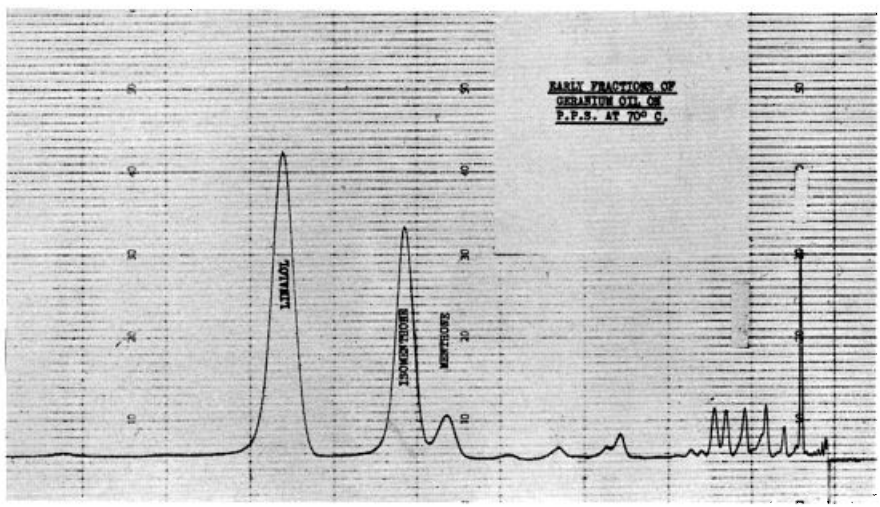


Figure 5
Separation of linalol from isomenthone by reduction of column temperature (see also *Fig. 2a*).

Peak resolution* for linalol-camphor was 0 at 120° C, 1·4 at 90° C and 3·9 at 70° C. For linalol-*iso*menthone, the figures were 0 at 100° C and

*Expressed as twice the difference between retention times, divided by the sum of the two peak widths, measured in time units.

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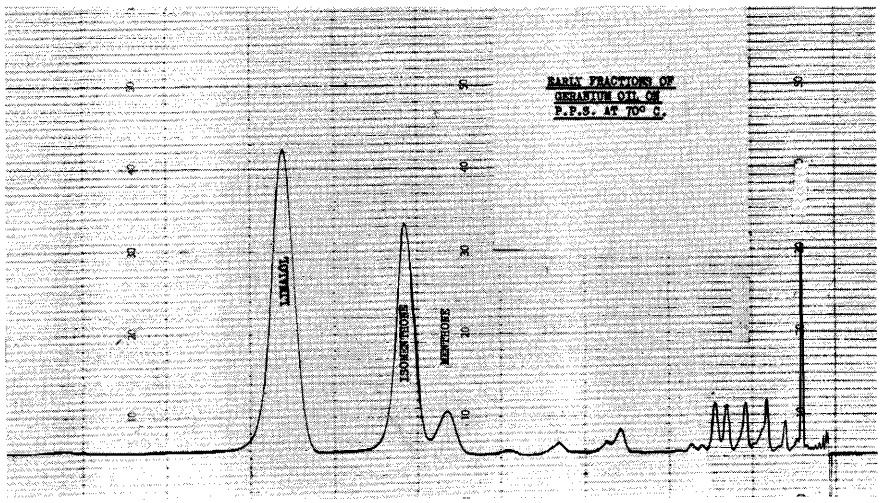

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2·4 at 70° C. The effect is not confined to dissimilar pairs like an alcohol and a ketone. On the same type of column, the resolution of geraniol/nerol increased from 2·6 at 110° C to 4·0 at 70° C; that of citral-a/citral-b from 1·9 at 110° C to 2·9 at 100° C, and that of terpineol-a/terpineol-b from 3·0 at 110° C to 5·5 at 70° C. This appears to be a retention phenomenon rather than a variation in column-efficiency, so it can work equally in reverse. For example, the peaks of nerol/citronellol are almost coincident at 70° C but not at 100° C, and bornyl acetate/linalyl acetate, separated at 100° C, overlap at 70° C.

I recommend the method to the attention of essential oil chemists as worthy of trial, particularly because it demands only the adjustment of one of the most flexible variables on any instrument—the column temperature. A better understanding of this influence of temperature on resolutions will certainly contribute considerably towards achievement of desirable "optimum" working conditions.

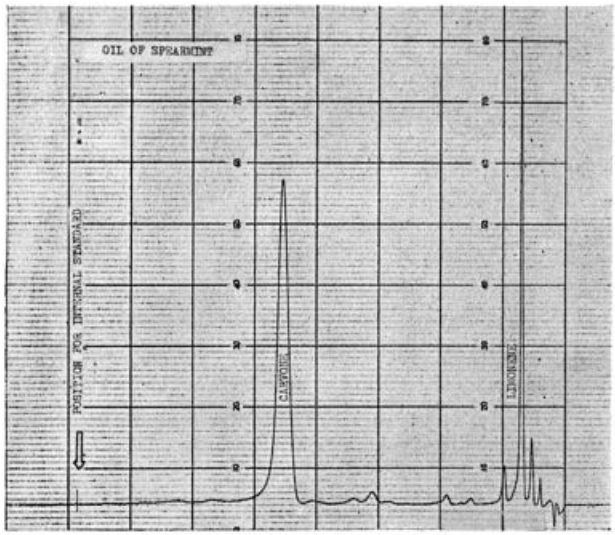
Gas-liquid Chromatography and Quantitative Analysis

Perfumers and manufacturers of perfumery ingredients are naturally interested to find out as much as possible about the composition of their raw materials. Several chemical methods of quantitative analysis have been devised, but few are really selective. They determine functional groups only. Many perfumery materials contain more than one compound with the same functional group. Their sum total may be found, but variations in their relative proportions (which may greatly affect the perfumer's assessment) cannot easily be measured. For instance, the "ester value after acetylation" has little meaning for evaluating a "citronellol", which may contain a large proportion of geraniol and dihydrocitronellol, or alternatively for a geranium oil containing geraniol, citronellol, linalol and minor amounts of other alcohols.

Gas-liquid chromatography offers the possibility of separating any chosen component of a mixture, and consequently of determining the quantity present. In theory, physical isolation followed by weighing is possible, but in practice it is difficult. Preparative-scale gas-liquid chromatography is generally less efficient than analytical-scale gas-liquid chromatography and it is not easy to trap all of the eluted material.

The more usual method is to introduce a pure reference compound (known as the "internal standard") into the sample at a known concentration, and then to compare detector responses to it, and to the ingredient which is to be determined. It is important that this ingredient be represented by an isolated, homogeneous peak, and that the peak of the internal standard occupy a position where the base-line is free from any other peak. *Fig. 6* shows how *n*-butyl benzoate may be used to determine carvone in

(a)



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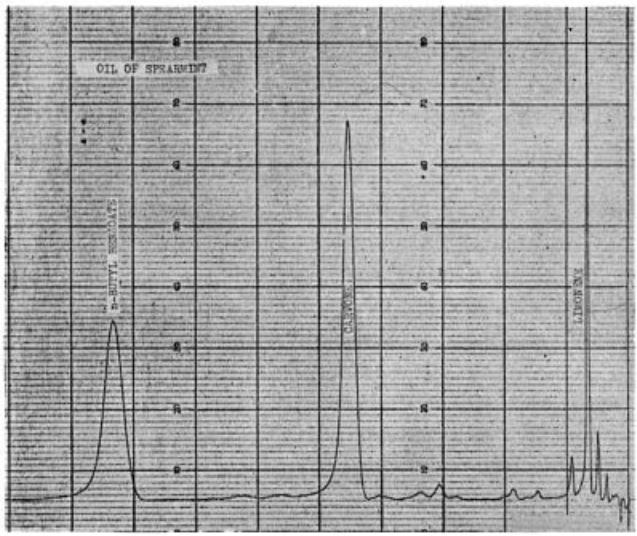
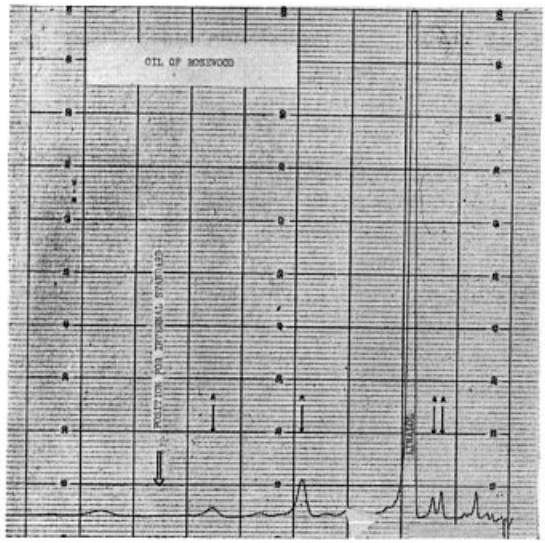


Figure 6

The determination of carvone in oil of spearmint, using *n*-butyl benzoate as internal standard. (Column temperature 100° C.)

(a)



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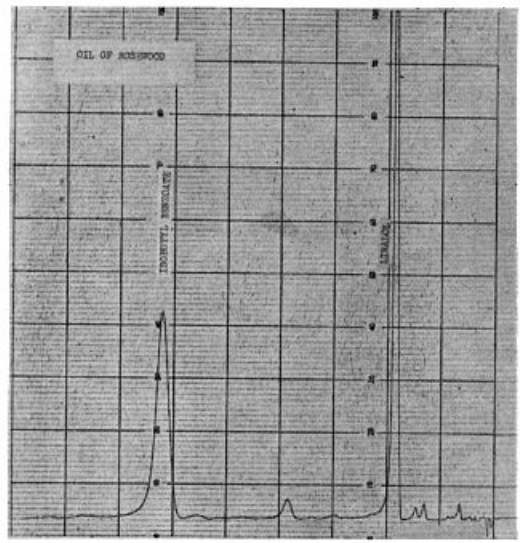


Figure 7

The determination of linalol in oil of rosewood, using *iso*butyl benzoate as internal standard. (Column temperature 100° C.)

oil of spearmint. *Fig. 7* illustrates the use of *iso*butyl benzoate to determine linalol in oil of rosewood in the presence of four other alcohols (marked by arrows) which contribute considerably towards the figure for apparent linalol content as determined by chemical methods. Detector responses to different compounds will vary, so that for accurate work, preliminary calibrations are necessary. Preparative-scale gas-liquid chromatography is of great assistance in isolating the pure components needed for calibration purposes.

Most gas-liquid chromatography equipment is designed to give differential chromatograms, in which the deflection of the pen is a function of the *concentration* of eluted material in the detector at any given time. In order to compare total amounts of selected component and internal standard, it is necessary to determine their respective peak areas. This is a source of inaccuracy which may be eliminated by the use of integral chromatograms, in which the deflection of the pen varies with the total *amount* of material which has entered the detector up to that time. Integrams consist of a series of consecutive steps, each step representing an eluted compound by a sigmoid curve whose total *height* is a function of the amount eluted. In order to increase the accuracy of height measurements it is convenient to amplify the signal while fitting the recorder with a limit switch which converts the step into a series of beats, thereby increasing the total vertical path of the pen while still keeping the recording within the confines of the chart.

Figs. 8 and *9* illustrate how citral-a and citral-b may each be determined in an oil of lemongrass. *Fig. 8* shows a differential chromatogram of this

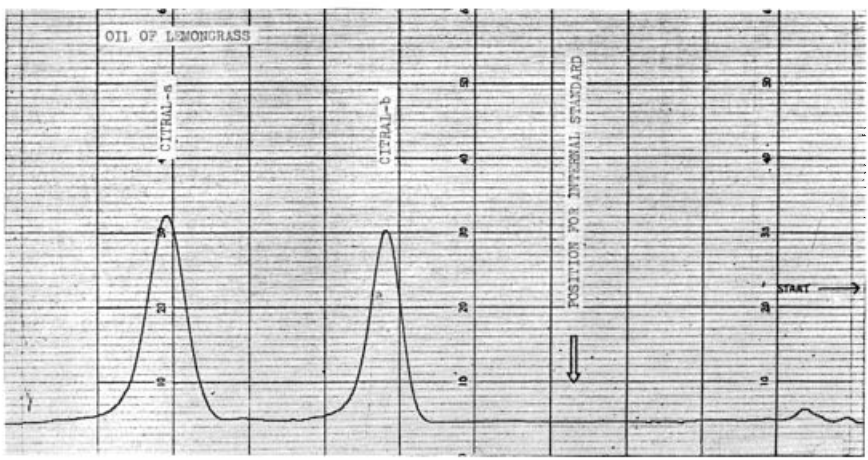


Figure 8
Chromatogram of oil of lemongrass in the neighbourhood of the citral peaks.
(Column temperature 100° C.)

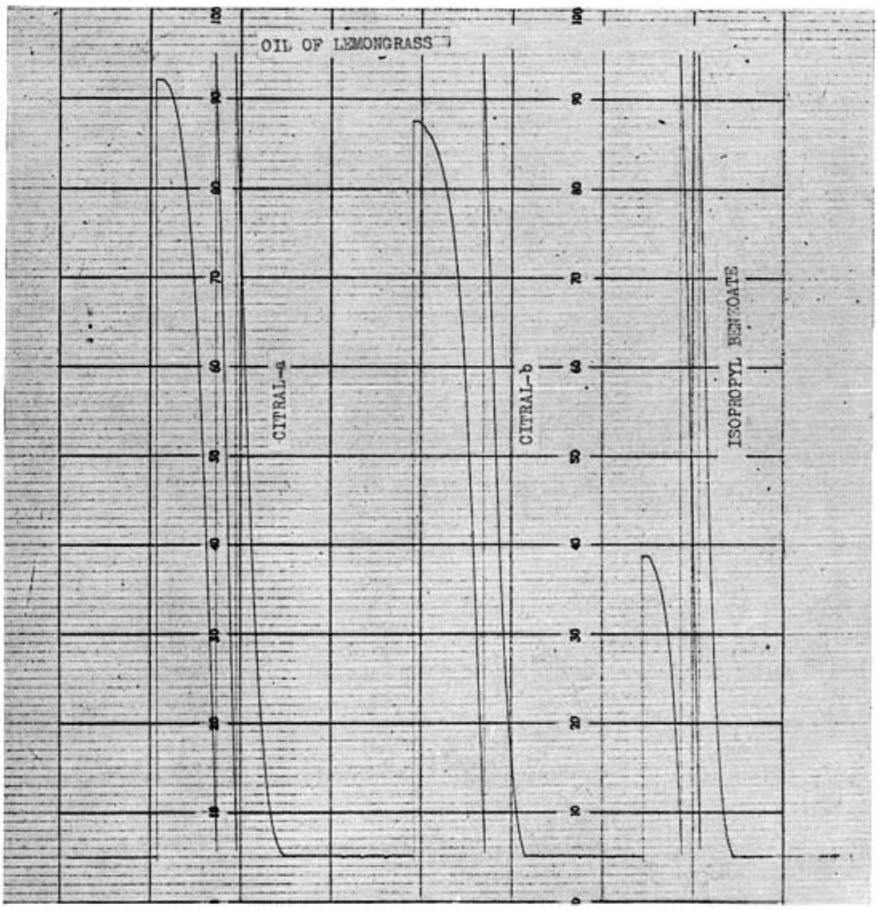


Figure 9 (*a*)
Integrams of oil of lemongrass in the neighbourhood of the citral peaks, with *iso*propyl benzoate added as internal standard.—Low magnification. (Column temperature 100°C.)

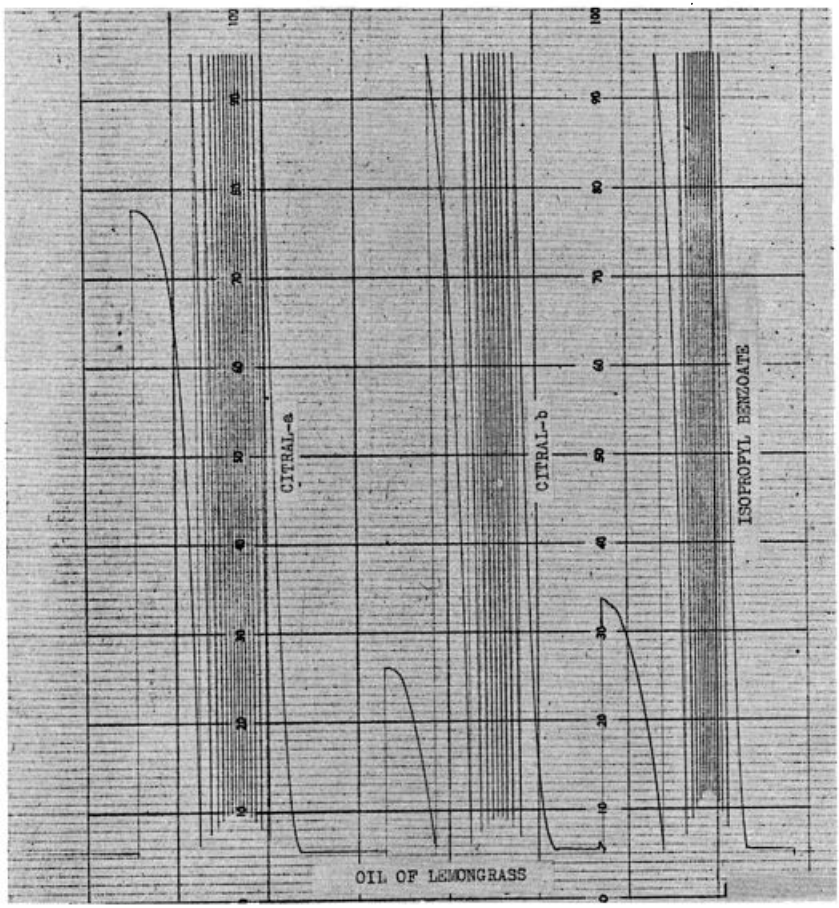


Figure 9 (*b*)
Integrams of oil of lemongrass in the neighbourhood of the citral peaks, with *iso*propyl benzoate added as internal standard.—High magnification. (Column temperature 100°C.)

oil in the neighbourhood of the two citral peaks. The internal standard, *iso*propyl benzoate, will occupy a position on the level section of base-line preceding them. *Fig. 9* shows an integram of the three compounds at low magnification, also a similar integram at higher magnification. Evaluation of the citrals depends upon linear measurements of the total traverse of the pen in the three groups.

Quantitative gas-liquid chromatography analysis is sometimes less simple in practice than in theory, because with certain essential oils it is not easy

to comply with the conditions of separation previously described. However, when gas-liquid chromatography *can* be used, it is capable of yielding more realistic results than those obtained by chemical analysis. The principle of completely isolating the component to be measured is sound from the analytical standpoint, and we may anticipate further advances in gas-liquid chromatography analysis, particularly if a more satisfactory measuring device can be discovered than the detectors now available.

Gas-liquid Chromatography and Identification of Essential Oils

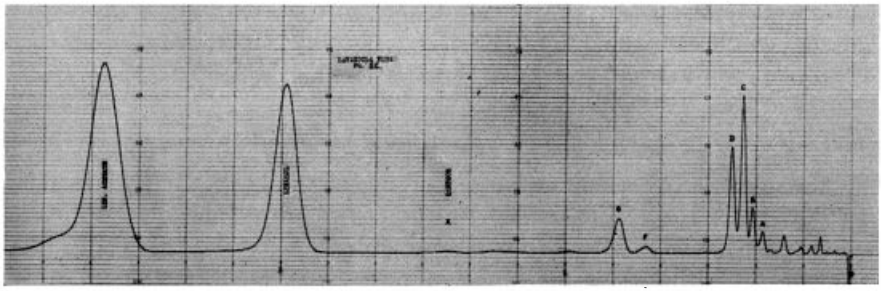
The odour of an essential oil depends upon the plant from which it is derived, but it may be modified by the environment in which the plant grew and by how, and when, the oil was extracted. On the whole, oils from species within the same genus are more likely to resemble each other than oils of plants from different genera. Oils from related hybrids, varieties or strains will tend to differ to a lesser degree. Variations due to environment and to details of manufacturing processes are usually the least marked, but perfumers can distinguish and recognise consistent odour categories, even of this order, without great difficulty. This has led to a system of classification, based upon botanical and geographical considerations, which is used for trade in essential oils.

Consistent differences of odour, however small, must be due to correspondingly consistent divergences in composition. These underlie the commonly accepted physical and chemical specifications for essential oils. Unfortunately, such specifications are almost valueless by themselves for checking the identity of essential oils because they yield so little information about details of composition. Gas-liquid chromatography, being a separation technique, can provide more reliable evidence of identity, even though the compounds which give rise to peaks on chromatograms are not all known. It remains to demonstrate what degrees of difference can be detected with certainty by gas-liquid chromatography.

My experience is that chromatograms made with good standard instruments under properly chosen conditions may be relied upon to distinguish between *any* two recognised types of essential oil, even those distilled from the same sort of plant in distinct geographical areas. Variations among samples from a single location are also detectable, though they have proved to be less characteristic and of a lower order.

Previous illustrations (*Figs. 1, 3, 6* and *7*) have shown the very distinct chromatographic patterns produced by unrelated essential oils like citronella, rosewood, spearmint and lavendin. Some similarities and differences between oils from more closely related plants are shown below. I have chosen certain oils from the genus *Lavandula,* because having collected

them myself from their distillation sites, I can vouch for their authenticity. *Fig. 10* shows the relationship between the three most important oils from this genus with respect to their more volatile constituents. Oils of spike



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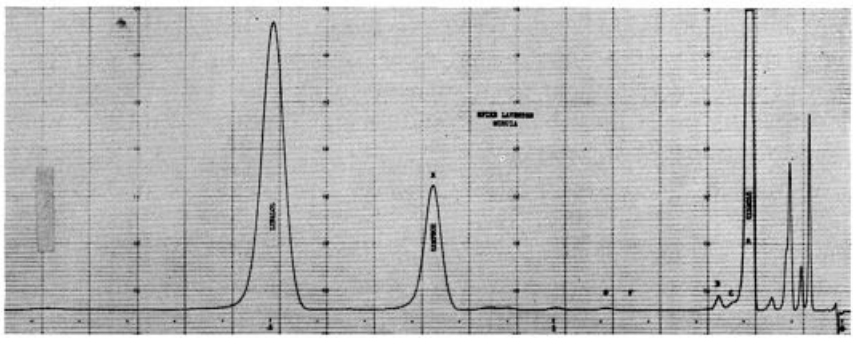

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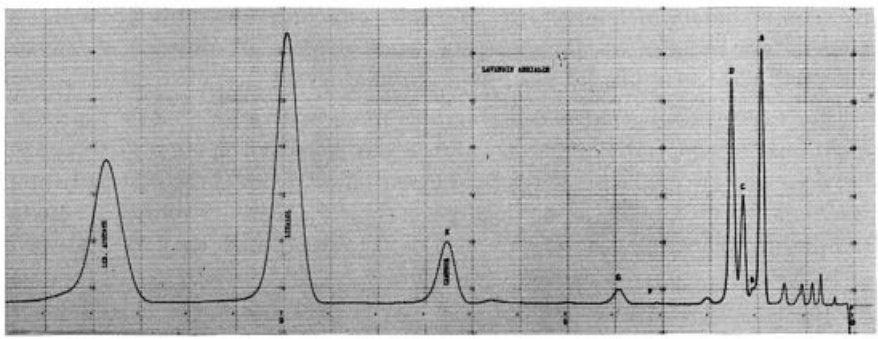
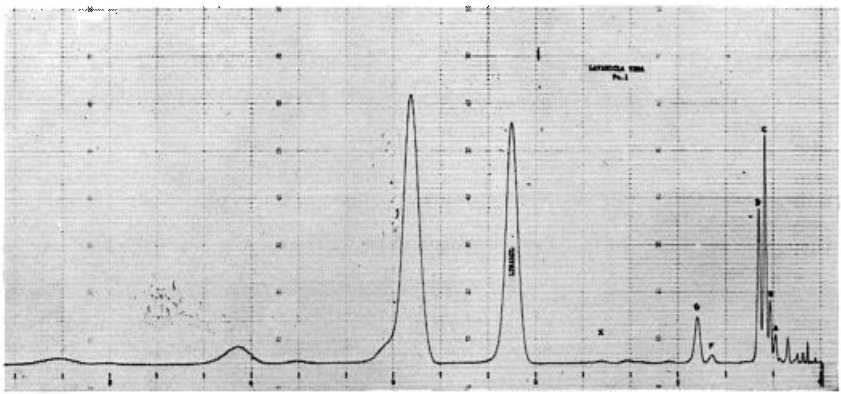


(c)

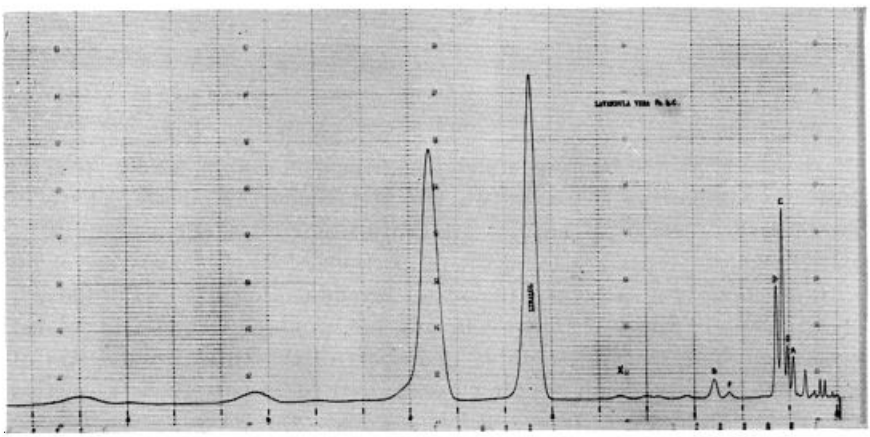
Figure 10
Comparative chromatograms of the more volatile constituents of oils of (*a*) lavender, (*b*) spike and (*c*) lavendin.

(*Lavandula latifolia*) and lavender (*Lavandula vera*) are composed in the main of the same compounds, though in very different proportions. Camphor, cineole and the early terpenes, for instance, are relatively minor constituents of oil of lavender, whereas oil of spike contains very little linalyl acetate. Lavendin is said to be a hybrid between these two species, and the chromatogram of its oil is concordant with this parentage. The illustrated differences between the three oils are both consistent and characteristic.

Several of the varieties of *Lavandula*, bred in France during recent years, have been planted and distilled on a large scale. The more important new



(a)



(b)

Figure 11
Comparative chromatograms of two different oils of ordinary lavender.

varieties of lavender are "Maillette" and "Matheronne". Those of lavendin are "Abrialis", "Super" and "Épi Carré". All these plants differ considerably in appearance from the parent types and from each other, and their oils have characteristic odours. It is interesting to compare chromatograms of their oils with those of standard oils of lavender and lavendin, and especially to compare the structures of the group of the four peaks A, B, C and D.

Fig. 11 compares two oils of ordinary lavender, differing mainly in ester content. This is shown by their chromatograms, which closely resemble each other in other respects, including Groups A—D. *Fig. 12* shows how much greater are the differences between oils of ordinary lavender and

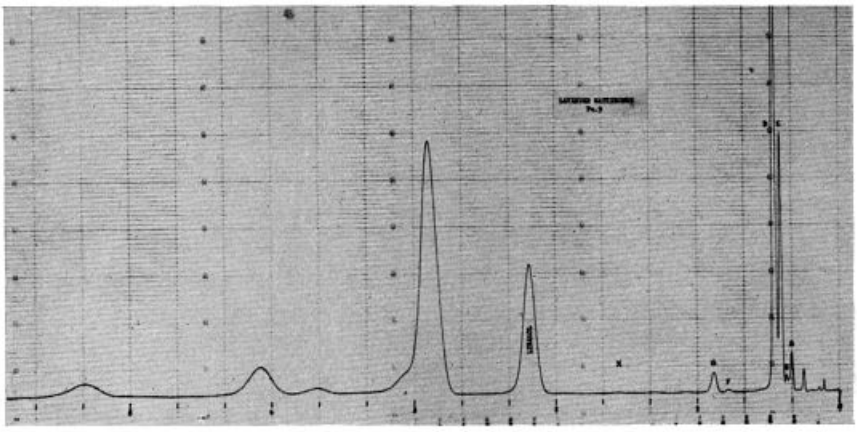
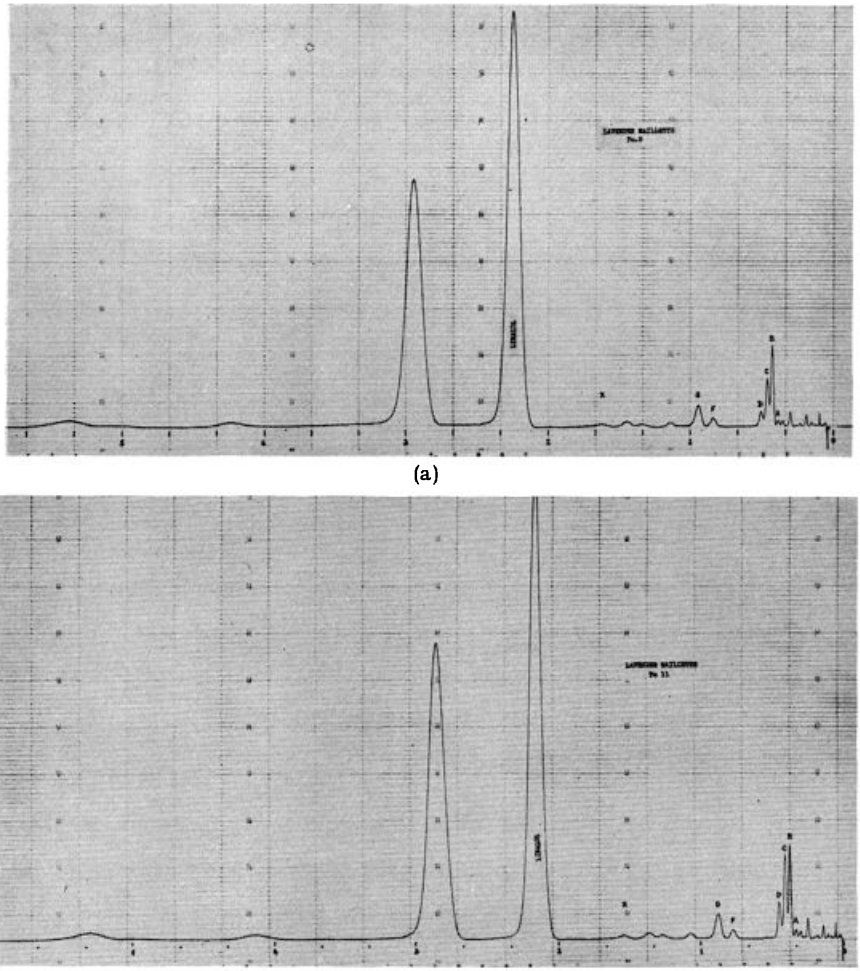


Figure 12
Chromatogram of an oil of lavender "Matheronne".

"Matheronne", these being particularly striking in Group A—D. *Fig. 13* illustrates similarities between two oils of lavender "Maillette", both of whose chromatograms also differ markedly from the previous ones. The relative size of Group A—D and the proportions of its four peaks are again quite distinct. *Fig. 14* compares oils of lavendin "Normal", "Épi Carré", "Abrialis" and "Super". These four oils, too, produce very clearly defined chromatographic patterns, notably in respect of the structure and size of Group A—D. *Fig. 15* shows the close similarities of pattern between two other oils of "abrialis".

Not only are oils of lavendin differentiated from oils of lavender by their greater content of cineole (peak A) and camphor (peak X), but in these chromatograms we may actually identify the individual oils by writing



(a)

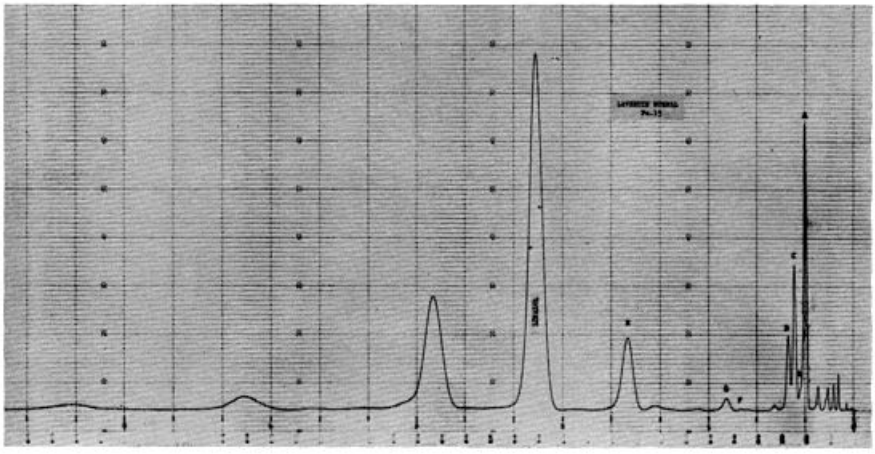
(b)

Figure 13

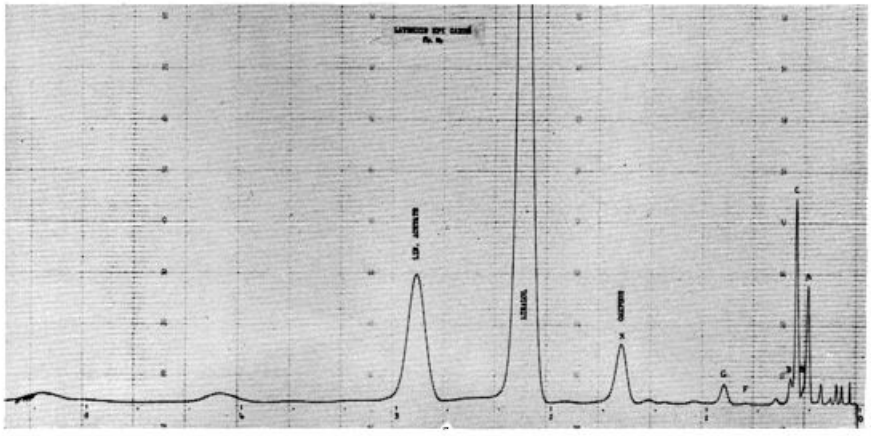
Comparative chromatograms of two oils of lavender "Maillette".

down against each of them the letters A—D in order of relative sizes of the corresponding peaks :—

LAVENDER :	Ordinary	C > D > B > A	
	"Maillette"	B > C > D > A	
	"Matheronne"	D > C > A > B	
LAVENDIN :	Normal	A > C > D > B	(Group large)
	Abrialis	D ≏ A > C > B	
	Épi Carré	C > A > D ≏ B	
	Super	A > C > D > B	(Group small)



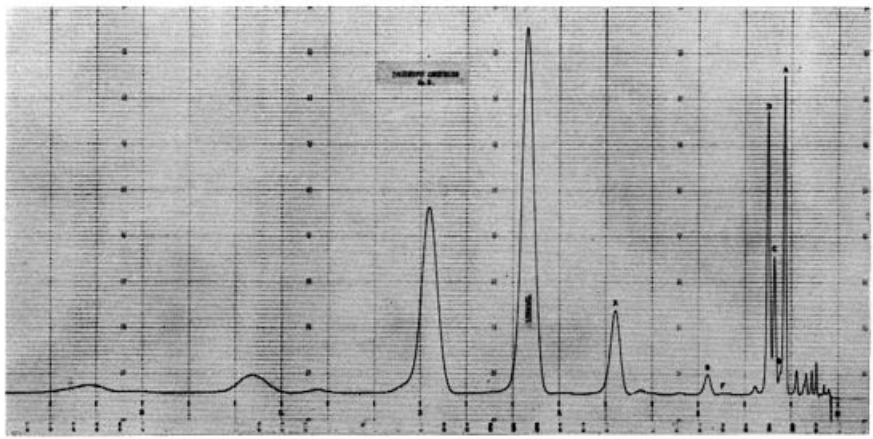
(a)



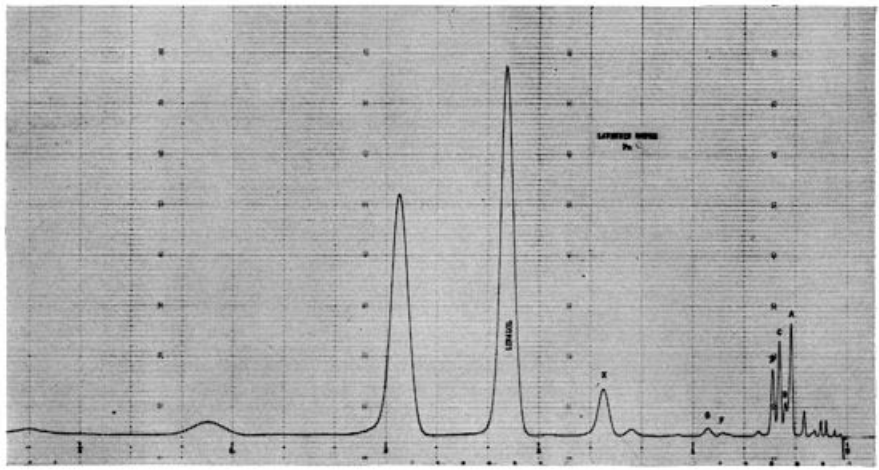
(b)

Figure 14

Comparative chromatograms of oils of four different varieties of lavendin—(*a*) "Normal", (*b*) "Épi Carré".



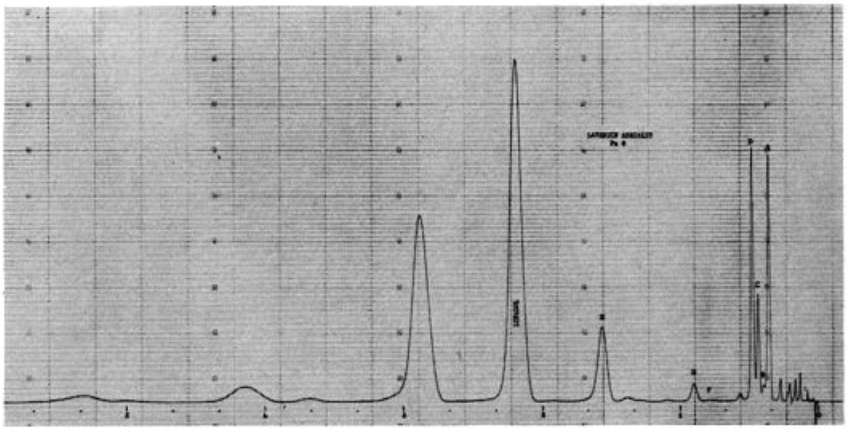
(c)



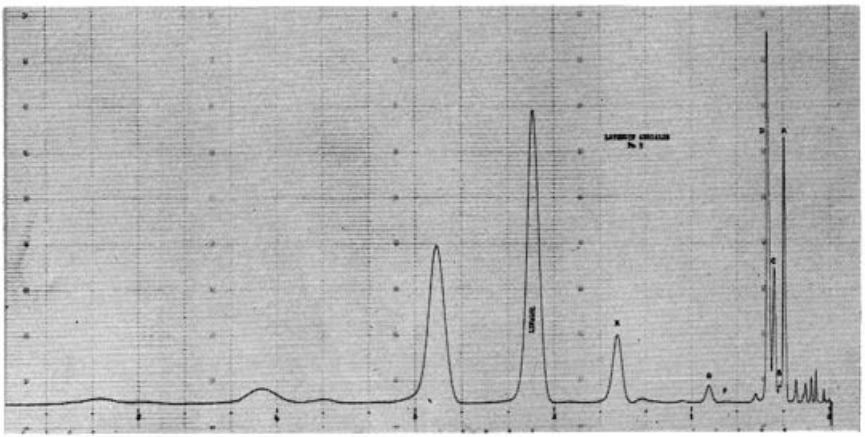
(d)

Figure 14

Comparative chromatograms of oils of four different varieties of lavendin—(c) "Abrialis", (d) "Super".



(a)

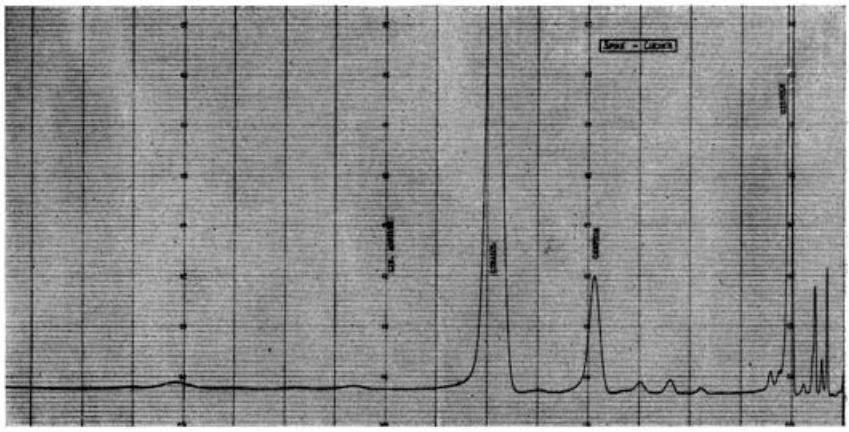


(b)

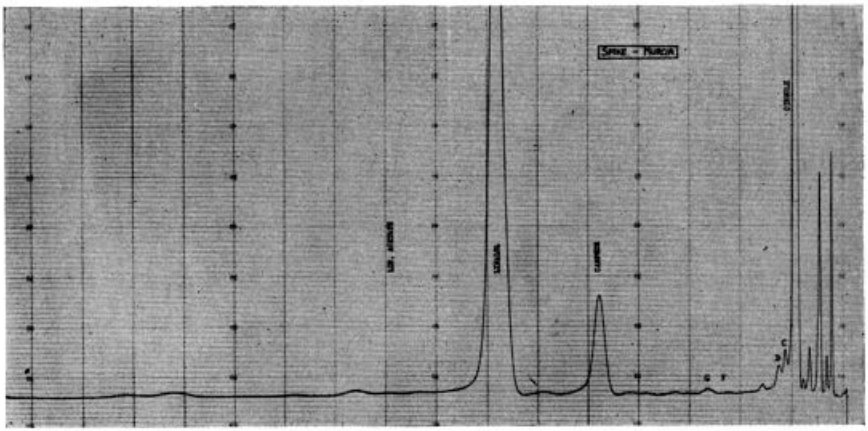
Figure 15

Comparative chromatograms of two oils of lavendin "Abrialis" (see also *Figs. 3b* and *14c*).

Except with "Normal" and "Super" (in which Groups A—D differ considerably in size) these "formulæ" are all distinct and selective. Naturally, it would need many samples, collected over a number of years, to provide conclusive evidence that such "formulæ" *always* apply. Nevertheless I am confident that geographical and seasonal variations in an oil of a given strain will rarely, if ever, prove significant by comparison with the distinctions between it and an oil of another strain. Spike lavender gives some idea of the effect of environment on essential oils. The plant grows wild throughout Spain, and only wild flowers of the one species are gathered. Stills and

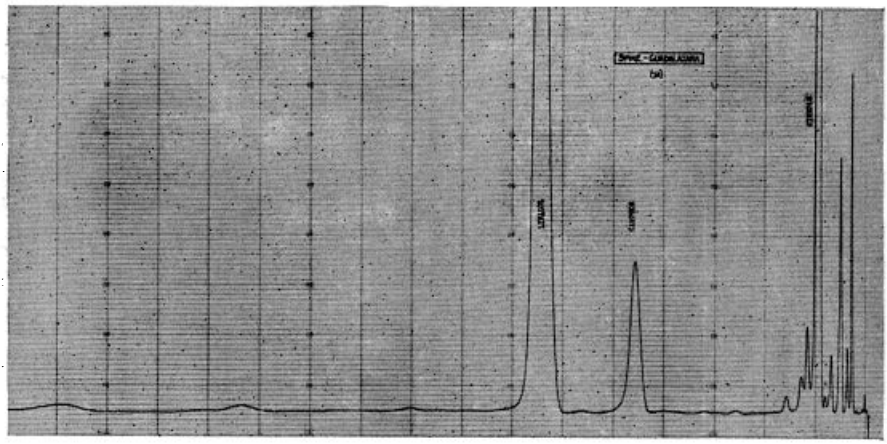


(a)

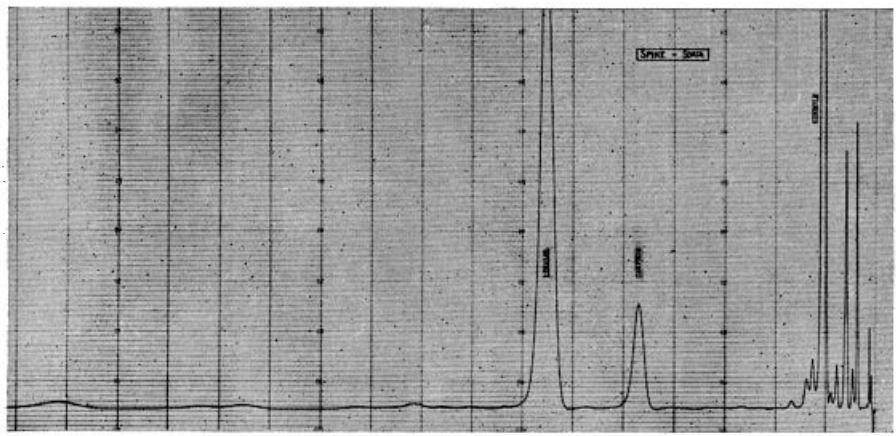


(b)

Figure 16
Comparison chromatograms of oils of spike from four different regions of Spain—(*a*) Cuenca, (*b*) Murcia.



(c)



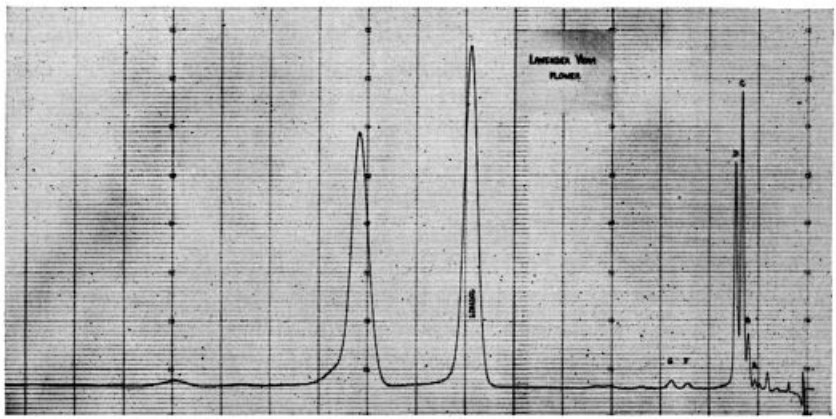
(d)

Figure 16

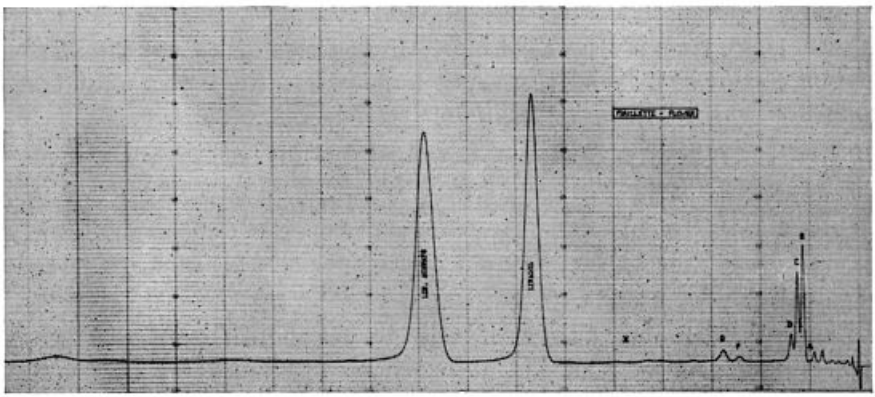
Comparison chromatograms of oils of spike from four different regions of Spain—(*c*) Guadalajara, (*d*) Soria.

distillation methods are very similar in all districts. *Fig. 16* shows that differences can exist among the early peaks of oils from various parts of the country. The group which precedes cineole varies in size, but the relative heights of its peaks cannot be used—like those of Group A—D above— to differentiate clearly between them. However, there appears to exist some tendency towards greater consistency of pattern within districts, which suggests that gas-liquid chromatography may be more critical in respect of source than is normally demanded by classifications for perfumery trade purposes.

The effect of working conditions is hardly as great in practice as might be anticipated, since factors such as still design, and time of distillation, tend to become standardized for economic reasons. Too short an extraction period decreases the relative proportions of less volatile constituents, but otherwise few significant changes are observable. In fact, chromatograms obtained directly from lavender flowers are surprisingly like those of the steam-distilled oils. *Fig. 17* shows results in two cases. In each experiment, a flower was kept for 5 minutes by a by-pass preheater at 130° C, after which the vaporized oil was flushed out and chromatographed at 70° C.



(a)



(b)

Figure 17

Chromatograms from individual lavender flowers—(a) ordinary, (b) Maillette (see also *Figs. 11* and *13*).

Minor differences exist between these, and chromatograms of the corresponding steam distilled oils (*Figs. 11* and *13*), but "formulæ" of Groups A—D are unchanged.

Flower chromatograms such as these might serve as a guide to plant breeders as well as to perfumers, and plant geneticists could no doubt make profitable use of them also.

Illustrative Chromatograms

All chromatograms reproduced in the illustrative slides were made with the standard "Pye Argon Chromatograph" and the two integrams were done with the "Pye" integrating amplifier. The column was 120 cm long, and, where not otherwise specified, it was packed with "Celite", 100–110 mesh, containing 10% w/w of "Reoplex 100" (polypropylene glycol sebacate). Column temperature was 70° C except where another temperature is stated. The carrier gas was Argon.

Acknowledgments

I should like to express my thanks to Lautier Fils, S.A. who were so good as to enable me to collect authentic samples of oils of the various strains of lavender and lavendin from distilleries in S.E. France; and to Sr. Ramón Bordas who kindly made it possible for me to visit all of the chief production areas of spike lavender oil in Spain.

(*Received : 10th March 1961*)

Discussion

Mr. H. B. Heath : Has the lecturer any information on the chromatographic picture of the one or two species of lavender grown in England, as compared with the French species and varieties ?

The Lecturer : I have not examined oils of English origin under similar working conditions.

Dr. H. W. Hibbott : The significant differences on the chromatograms seem small. Would a perfumer detect the differences which are regarded as significant ?

The Lecturer : Differences revealed by the chromatograms of oil of spike certainly seem small, but an experienced perfumer can distinguish between those particular oils. They may also vary in content of less volatile substances not shown in the illustrations, but even if they were similar in this respect, I am sure that the perfumer would have few doubts about their individuality.

MR. L. G. TOWERS : When chromatographing lavender oils at relatively low column temperatures in order to resolve as completely as possible the components of shorter retention times, what do you consider to be the minimum column temperature below which sample preheating becomes necessary ?

THE LECTURER : No significant loss of performance was observed when samples of up to 100 μg were put straight on to a column at 70° C, though at lower temperatures a preheater may be needed. The answer will probably depend upon the size of sample required for the instrument used, but in any case no harm could be caused by a sample preheater at, say, 100° C.

THE DETERMINATION OF WATER IN SHAMPOOS BY DISTILLATION

G. E. MAPSTONE, M.Sc., Ph.D., F.R.I.C.

Some shampoos, etc., foam excessively on distillation even after the addition of oleic acid. The addition of a quaternary ammonium compound in such cases allows the ready distillation of the water.

INTRODUCTION

THE DETERMINATION of water in shampoos and similar products, by distillation (*Dean and Stark Method*) presents a special problem in that such products normally contain materials of high foaming power, and frequently also a foam stabilizing agent.

Gentle spot heating of the flask just below the liquid surface can often control the foaming by circulating the flask contents and will, at all times, cause a reduction in the amount of foam present. This technique, however, requires the undivided attention of the operator and, with well foaming materials is frequently inadequate. Even when the foaming is kept under control, the solid detergents can set as a cake, as the water distils. If due care is not taken this cake can adhere to the bottom of the flask where it can either occlude water or char. This can lead to low results by the failure of all the water to distil, or to high results due to the water formed by the decomposition. Occasionally, the detergent precipitates as a fine powder which can physically stabilize the foam but, if it does happen, it is usually transient due to the tendency of the powder to agglomerate.

The addition of a non-volatile solvent that will dissolve the anhydrous detergents can reduce, and frequently overcome, these problems. Two such

*Dermacult S.A. (Pty.) Ltd., Johannesburg, South Africa.