

THE JOURNAL OF THE SOCIETY OF COSMETIC CHEMISTS

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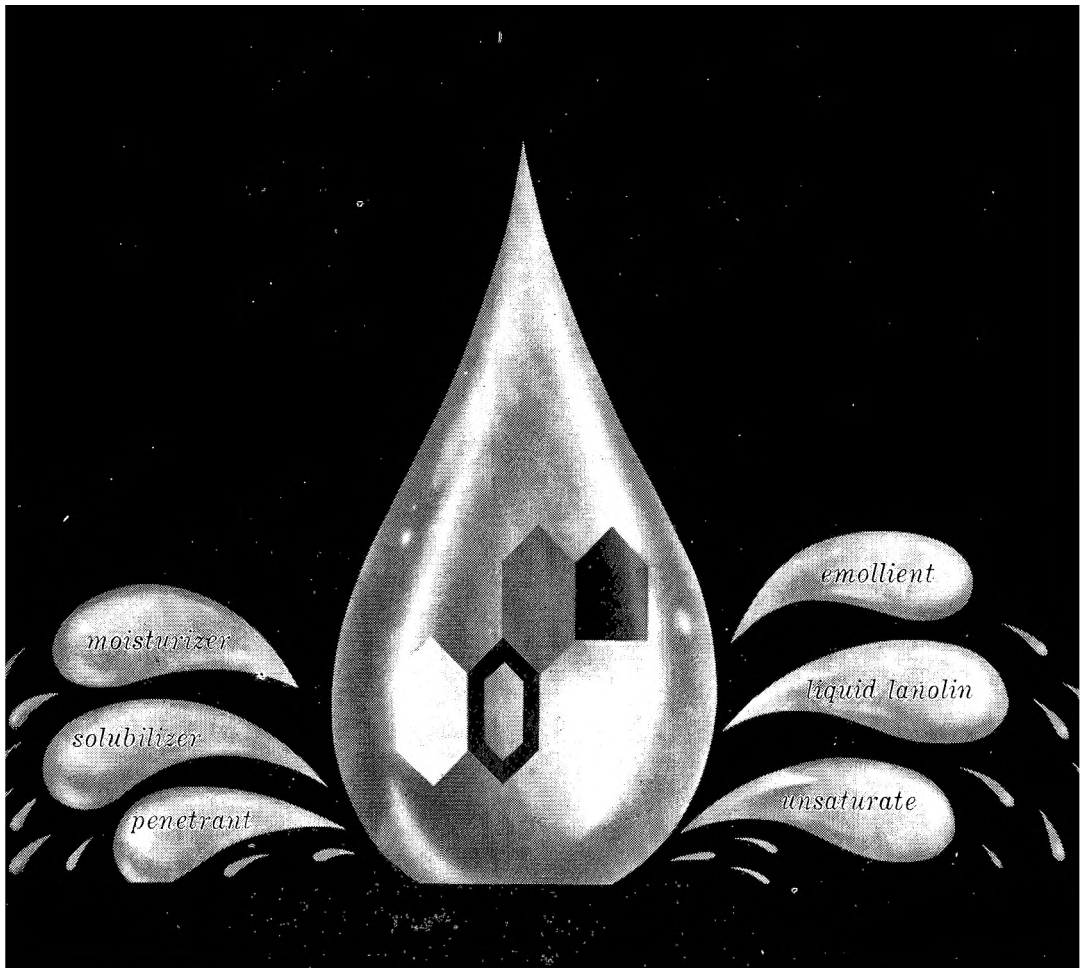
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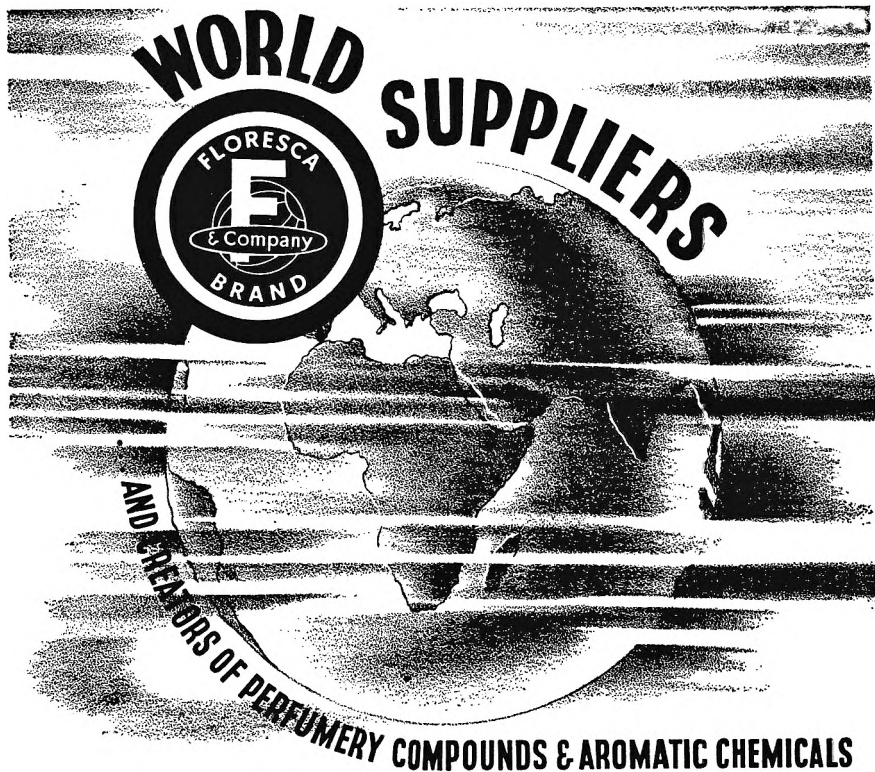
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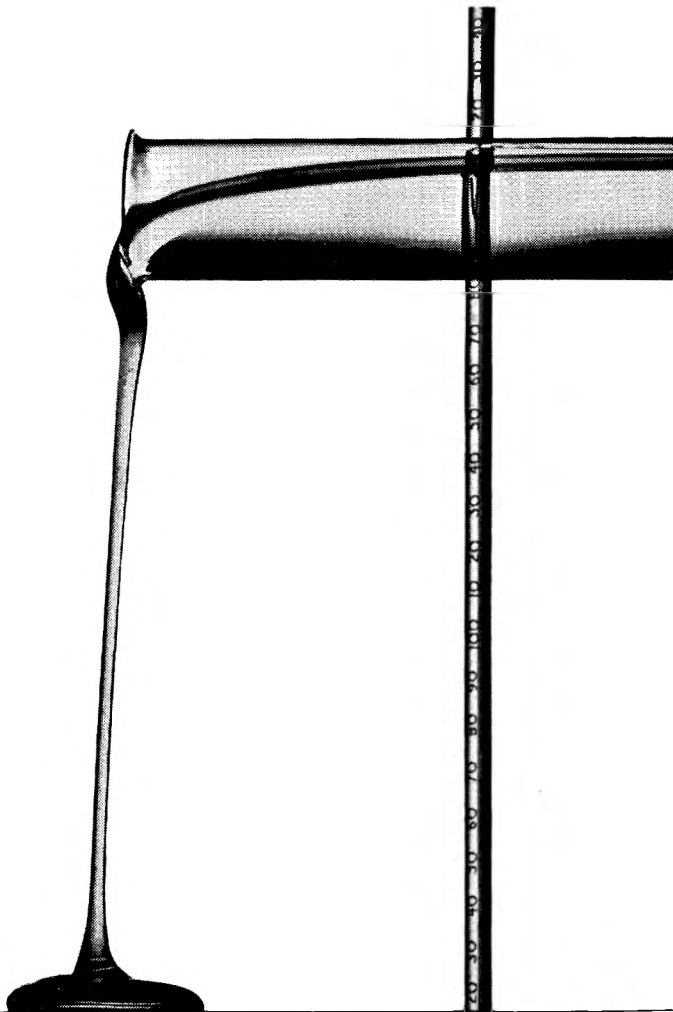


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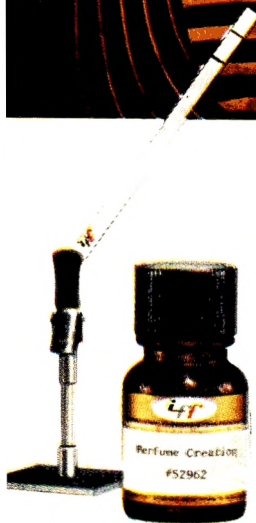


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THE JOURNAL

THE BEGINNING of 1963 marks another milestone in the history of the *Journal of the Society of Cosmetic Chemists* which henceforth will be published at monthly intervals. Six issues in the U.S.A., by the Society of Cosmetic Chemists; five issues in the United Kingdom, by the Society of Cosmetic Chemists of Great Britain; and one issue in Germany, by the Gesellschaft Deutscher Kosmetik-Chemiker e.V. By increasing the number of issues it is hoped to reduce considerably the delay between the delivery of a lecture and subsequent publication. No one can dispute that the *Journal* is unique by being published in three different countries, in at least two different languages, and yet in consecutive pagination and in a common style.

There is little doubt that the *Journal* would not have reached its present status had it not been for *MAISON G. (ED) deNAVARRÉ* who, after fifteen years as Honorary Editor of the U.S. editions, retired on 31st December 1962.

His first volume, commencing with the July 1947 issue, spanned three years and comprised five issues. During 1952, the *Journal* was published four times a year and by 1956, six times a year. In November 1951, at his instigation, the British Society published its first issue, and by 1955 was publishing two issues. During the Congress of Cosmetic Science, held in London early in 1959, the idea of a German issue was mooted, and again Ed deNavarre used all his eloquence to persuade the then small, but virile, German Society to share in the publication of the *Journal*. Upon their agreement, the frequency of publication from the other two publishing Societies was increased, and thus during each of the past three years the *Journal* has appeared nine times. Ed deNavarre was also instrumental in prevailing upon the Swiss Society of Cosmetic Chemists to publish the Decennial Index in 1961.

By thus furthering the co-operation between the various Societies, initially in the field of publication, Ed deNavarre undoubtedly laid the foundation for the work which has found its expression in the International Federation of Societies of Cosmetic Chemists, of which he became the first President.

We salute him today and trust that his wise counsel will be available to all of us in the years to come.

Words of welcome are extended to Dr. Martin M. Rieger, his successor as Hon. Editor of the U.S. editions.

THE PRINCIPLES OF WORK STUDY, WITH ONE OR TWO APPLICATIONS IN THE LABORATORY

G. A. C. PITT, M.Sc., F.R.I.C., M.B.I.M.*

A lecture delivered before the Society on 25th April 1962.

A brief account of method study and work measurement is given, and examples are cited. The relationship with other management functions is also given.

WORK STUDY is, as it says, the study of work, human work. This, however, has not always been its name. Its original names were Motion Study and Time Study. Under these names it acquired an unenviable reputation. Since the war these two have been married under the name Work Study and under this name have acquired a degree of respectability.

HISTORY

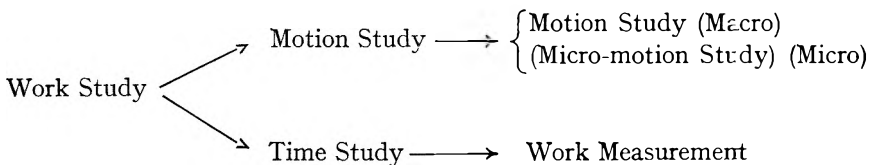
In the early part of this century, Motion Study and Time Study were not widely practised in this country. F. W. Taylor, the originator of much of these practices, succeeded in the U.S.A. but found no acceptance in this country. He accordingly moved on to the mainland of Europe where he was better received. It is incontrovertible that this was a factor in our falling behind the United States and other European countries in productivity (that is, output per worker hour) and which results in so many exhortations to increased productivity that we receive today.

TERMINOLOGY

Work Study is, in fact, Motion Study plus Time Study. These techniques have also been renamed :

Motion Study is now more generally called Method Study.

Time Study is now more generally called Work Measurement.



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METHOD STUDY

Method Study can be divided into *macro*- and *micro*- subdivisions.

Method Study on the *macro*-scale involved the study of any operation or movement lasting longer than about 3 seconds. For example, it would include a study of

- (a) factory layout ;
- (b) movement of material through a factory ;
- (c) material handling on the shop floor ;
- (d) operator work place lay-out where the operation or movement time exceeds about 3 seconds.

To assist in Method Study certain shorthand symbols have been used :

OPERATION	DENOTED BY	○
TRANSPORTATION	DENOTED BY	T
STORAGE	DENOTED BY	⌋
INSPECTION	DENOTED BY	I
DELAY	DENOTED BY	⊙

Figure 1

The basic purpose in Method Study is to reduce the amount of work to be done by detailed study of it thereby enabling the operator by various means to produce more.

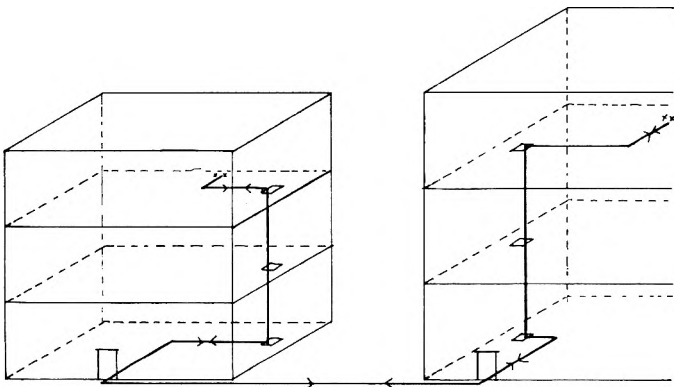


Figure 2. Path followed in original layout

Fig. 2 shows a sketch of a factory building. The lines show the flow of work through the factory.

In this case the ladies' powder room was in the right-hand building and the operators, chiefly women, worked in the left-hand building. For special reasons the ladies' powder room could not be sited inside the left-hand building in the normal way.

It will be seen that the operators had to descend from the second to the ground floor, walk to the door, discover if it were raining, walk to their lockers and put on their raincoats if it were, walk outside and down the road, up to the second floor either by lift or staircase, along a corridor. They then returned along the path by which they had come.

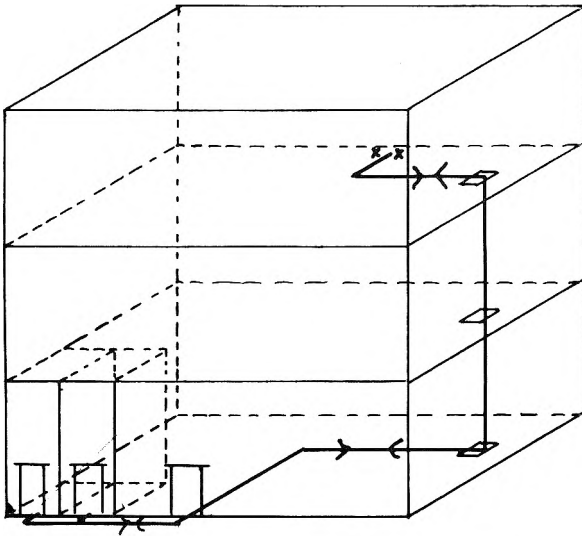


Figure 3. Path followed in improved layout

It was found possible to site the powder room in a corner of the left-hand building with access from the outside, as illustrated by *Fig. 3*. It resulted in an economy in labour amounting to, at least, in current values, £3,000 a year. This is an illustration of one type of Method Study.

One major fault that this type of analysis throws up is *backtracking*, that is, where the line of flow doubles back on itself. It is surprising how often an examination of flow lines reveals inefficiencies. Another factor of importance in flow is the frequency with which a route is followed. It may be found, for instance, that a route of 240 feet has to be followed 100 times a day, whilst

one of 120 feet is followed once a day. If these are associated with the same job, then obviously the job should be re-laid out so that the flow is reversed.

The siting of a kitchen in relation to a dining room in a restaurant is illustrative also of this principle.

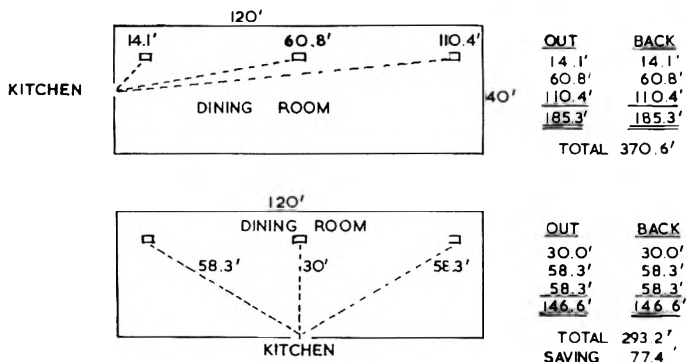


Figure 4

Fig. 4 shows the route followed by a waitress in two circumstances. It will be seen that in one case she walks 26.4% further than in the other. This may not seem much but it may mean a great deal to the waitress. If she walks these distances 200 times a day she has walked nearly 3 miles further, carrying heavy loads in the badly laid-out restaurant, and the management have wasted that amount of labour multiplied by the number of waitresses employed.

A corollary to this in the laboratory is indicated by the following, as well as by other, questions :

Is most used apparatus nearest to hand? Are most used materials nearest to hand? What is the position of the store room and balance room in relation to the laboratory or laboratories they serve? What is the path followed by Laboratory Reports? Are they typed or written? Who does it? When completed where do the various copies go? How are they transmitted? Is good use made of every copy?

Obviously, in this review of large scale Method Study the Questioning Attitude has been adopted. Briefly, this is the achieving of economies in cost by taking nothing for granted, questioning the reason for everything. In their simplest form the questions asked about an operation are :

What is the purpose of the operation? Why is it necessary to do it?

How is it done? Can it be simplified? Where is it done? Who does it? When is it done? At what stage in the sequence of operations? These questions can be asked almost indefinitely. Thus the second question could be enlarged to:

Can the operation be eliminated? Can it be combined with another operation? Can it be sub-divided and the parts worked in with other operations? Can it be done whilst the operator is forced to wait on another job?

As an illustration of this second question consider the man-machine chart illustrated by *Fig. 5*.

MAN - MACHINE CHART

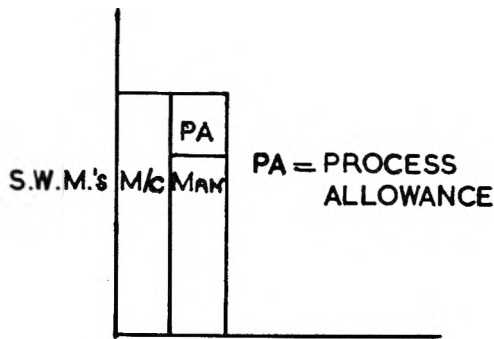


Figure 5

If part of the man's work is eliminated, consideration can be given to the man's working of two machines.

It may well be that if routine work in the laboratory is considered it will be found that a fair amount of effort may be eliminated if the organisation of the laboratory is considered in relation to the principles which have been expressed.

Method Study on the *micro*-scale is applied chiefly to the lay-out of the workplace.

The workplace must be arranged to suit the needs of the worker. The basic theory underlying Method Study is that if the workplace is arranged so that everything is to hand, and if the work is made as easy as possible then the worker will respond by a high rate of output. This arrangement has been reduced to a few simple laws:

1. The workplace should be arranged so that the work is positioned within easy reach of the operator. Thus, Method Study has been used in the surgery. The operating table is re-designed so that the instruments feed towards the surgeon's hands and everything is within easy reach of the assistants' hands.

2. Maximum output is obtained when both hands are used throughout the work cycle. When one hand only is working, the idle hand is not rested. The pianist is an example of this.

3. Operator movements should be symmetrically designed and only the hands and forearm should require to be used. Rowing is, perhaps, a good example of this. Scaffolding which rises with the house, thereby enabling the builders to be always at the correct working height, is another satisfactory example.

Historically, this type of Motion Study was developed by the Gilbreths. Frank Gilbreth was an engineer and his wife, Lilian, a psychologist. They had twelve children. Life was only possible by strict adherence to scientific management. One of their sons wrote a book "Cheaper by the Dozen" which may be familiar to some readers.

Their work was directed towards the building industry. They were responsible for the smaller type of scaffolding which rose with the building, the work of the bricklayers therefore always conforming with the Laws of Motion Economy. A higher rate of bricklaying was therefore possible. The secret of their success was the analysis of movement into detail, and they listed sixteen basic movements. Of these, or some of them, any operation could be synthesised. These detailed movements they called *Therbligs*. How these should be treated is indicated in parentheses.

Table 1
Therbligs

St.	Select (eliminate)	P(lan)	Plan (eliminate)
G.	Grasp (minimise)	PP.	Pre-position (eliminate)
TL.	Transport loaded (minimise)	RL.	Release load
P.	Position (minimise)	TE.	Transport empty (minimise)
A.	Assemble (simplify)	R.	Rest for overcoming fatigue
U.	Use (minimise)	DA.	Disassemble (simplify)
UD.	Unavoidable delay (minimise)	AD.	Avoidable delay (eliminate)
I.	Inspect	H.	Hold (eliminate)

Economy in, and ease of, movement are illustrated below by an improved method for storing laboratory record books.

The old method of keeping these record books (*Fig. 6A*) was to force them into the compartment. As the books grew in size it became increasingly difficult to put them away and to take them out. Moreover there was no place to put

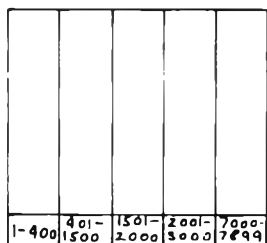
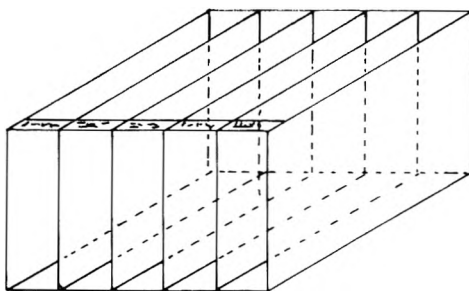


Figure 6A

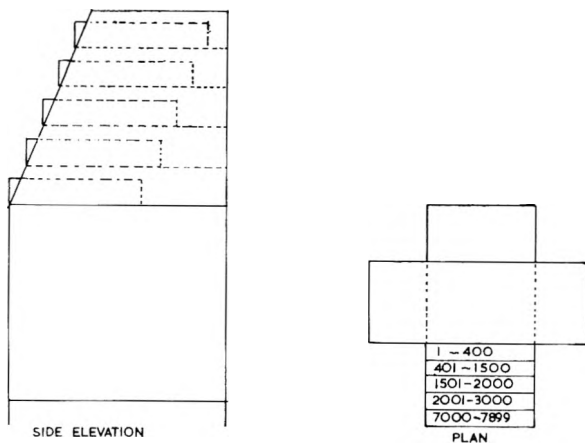


Figure 6B

them when they were opened. The top of the unit was not quite big enough. The improved stand depicted in Fig. 6B, allowed for considerable increase in the size of the books, the compartments were independent and so the books were easily stored and removed and the top flap made an excellent resting place for a book when open.

In terms of Therbligs, the new method had the following advantages :

Therblig select was reduced.

- „ grasp and transport loaded were simplified and reduced.
- „ positioning was simplified.
- „ release load was simplified.
- „ hold was eliminated.

Method Study, of course, also pays attention to conditions of lighting, heating, ventilation, worker posture, bench height and so on. Posture when seated should be upright with the back supported. Bench height should be such that the average operator can work with the forearm horizontal. Thus in a laboratory, bench height should be such that the worker's arm is horizontal when handling apparatus, i.e., ideally the bench height should be lower than it normally is.

BENCH HEIGHT & VESSELS

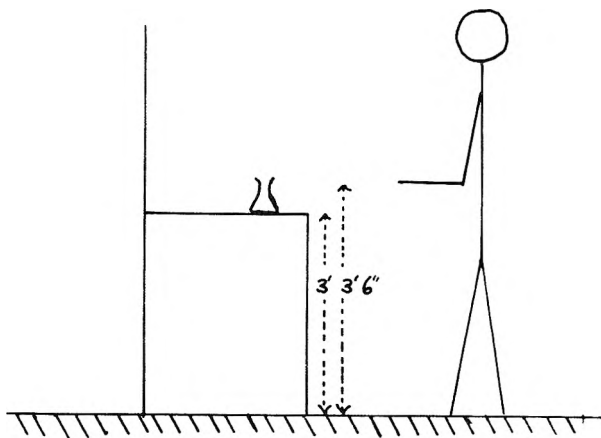


Figure 7

Method Study is most gainfully employed on repetitive work. The laboratory is not, therefore, the first field that would be considered for its application, but the attitude and principles are still applicable.

Method Study has the advantage that very little capital investment is required, and it largely results in getting the optimum from available equipment. The basis of the technique is to increase productivity, that is, output per worker hour, by reducing effort.

The co-operation of the worker is, therefore, all important if Method Study is to show significant economies.

Method Study has also been used in the assistance of disabled persons, and one large company composed of disabled persons has used it extensively. It is safe to say that many severely handicapped men and women have been helped in creative effort by the use of Method Study specially applied.

WORK MEASUREMENT

We have all read the advertisement which states that a hotel is "five minutes from the sea". What does this mean? At a walk, a run, by bicycle, by car? The time taken to do work cannot be defined merely by time alone.

Not only must the method and conditions be precisely defined, but the time selected for the work must either be derived statistically, which may be a lengthy process, or Work Measurement must be used.

Work Measurement does this by laying down an arbitrary rating scale for speed and effort, the method and conditions being recorded in detail.

Table 2
Arbitrary rating scale

30	Very slow	
40	Slow	
50	Rather slow	We do not normally rate lower than
60	Normal	30 or above 90. The one is too slow,
70	Rather fast	the other too fast
80	Fast	
90	Very fast	

One of these ratings is applied to the time observed for the work. The time for the work is then calculated from the simple formula :

$$\text{Normal time for the work} = \frac{t}{60} \times \frac{r}{60}$$

where t (seconds) is the time taken to do the work and r is the rating

It will be seen that the rate at which the work is done is arithmetically related to a norm, i.e., a 60. For example, if work is done in 10 seconds at 70 r then the time for the work is

$$\frac{10}{60} \times \frac{70}{60} = 0.194 \text{ normal minutes}$$

This is the time which would be taken for the work by a person of normal physique working with normal speed and effort. No one can expect to work

without rest so to this we add an allowance for fatigue known as "Compensating Relaxation"—10%.

$$\begin{array}{r}
 0.194 \text{ Normal Minutes} \\
 \underline{0.019 \text{ Compensating Relaxation}} \\
 \underline{\underline{0.213 \text{ Standard Work Minutes}}}
 \end{array}$$

Such an assessment of work must be subjective, and it is necessary to enlarge what 60 is. For example :

Walking by a person of normal physique in normal conditions on level ground (speed)	3 miles per hour
Walking while pulling a garden roller (speed and effort)	2 " " "
Walking while pulling a garden roller following a snake border (speed and effort plus mental attention)	1 " " "

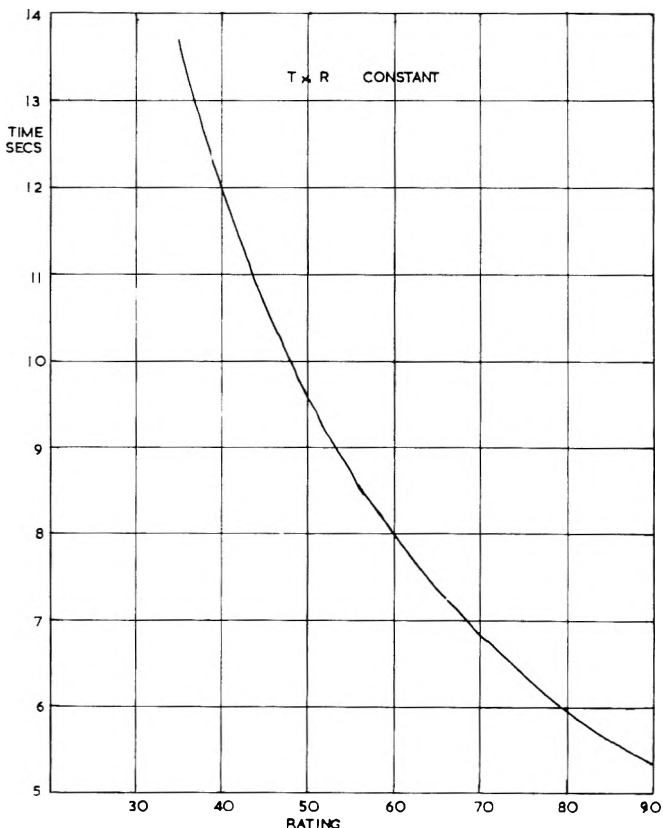


Figure 8. Ideal Rating/Time curve

Dept. <i>Laboratory</i>	Taken By <i>A.P.</i>	Date <i>4/1/62</i>	M/C Speed	File & Study
	From <i>2:30 p.m.</i> To <i>3:0 p.m.</i>			<i>II</i>
	Unit Per <i>titration</i>	Elapsed Time	Production	Sheet No. <i>1</i>

Description Description
 of of *Volumetric Titration*
 Part Operation

	Rd'g	Rat- ing	Non- Prod		Rd'g	Rat- ing	Non- Prod
A Suck up 10 cc	A	18	65	G Titrate to A	24	70	
N NaOH in pipette	B	22	80	end point	B	22	80
position over conical	C	15	80		C	15	80
flask	D	3.5	75	H Repeat G & F	D	4	70
	E	4	80	I Calculate	E	8	50
B. Run 10 cc N NaOH	F	8	75	result	F	16	60
into conical flask	G	60	60		G	34	over hot
	H	9	75		H	14	60
C. Drain pipette	I	28	-		I	35	-
for 15 seconds							
	A	28	50		A	23	65
D Pipette aside	B	23	80		B	24	70
and set down in	C	15	80		C	15	80
rack	D/E	23	} interrupted		D	4	70
E. Add 3 ml so	F	16			E	6	70
phosphoric acid	G	60	60		F	14	65
to N NaOH	H	10	50		G	37	75
	I	43	-		H	9	75
F. Read burette					I	30	-
7 record.							

Figure 9. Typical Work Measurement observation sheet

A 60 r is really the lowest rate of working acceptable to management. Since this rating is subjective, it is desirable to take as many readings and ratings by as many observers as possible.

A simple illustration from the laboratory is titration.

- (1) The job is broken up into elements, and for ease of timing and rating these are normally between 5 and 20 seconds duration. These end with what are known as *breakpoints*—actions which are readily discernible.

- (2) These elements are written down on the observation form on which Work Measurement is carried out.
- (3) The series of operations are timed and rated as previously indicated. When in "mental rhythm" with the operator's movements :

$$T \times R \text{ should equal a constant}$$

It should be noted that at this stage one is rating on a curve (*Fig. 8*), and this causes difficulties.

- (4) The times and ratings are recorded for each element and worked out as previously shown.

A typical element, its summary and working up is detailed below:

Element B

Allow contents of 10 ml pipette (*N* NaOH) to run into conical flask.

21	1	80'
22	1111	80' '' '' 75'
23	1	80'
24	1	70'
25	1	75'

Selected value : 22.0 sec at 80 rating.

- (5) The normal times for each operation are worked out similarly and listed as shown in *Table 3*.

Table 3. Element Summary sheet

Element	N.M s.	C.R.	S.W.M's.
A. Suck up 10 ml NaOH into pipette	0.354	12%	0.397
B. Allow contents of pipette to drain into conical flask	0.489	12%	0.548
C. Drain pipette for 15 sec	0.333	12%	0.373
D. Pipette aside to rack	0.078	12%	0.087
E. Add 3 drops of phenolphthalein indicator to NaOH	0.117	12%	0.131
F. Read burette and record	0.253	12%	0.283
G. Titrate to end point	0.775	12%	0.868
H. Read burette and record	0.183	12%	0.210
			2.897
	Allowance for calculation of result		0.750
			3.647

- (6) The number of titrations possible in a working day of, say, 7 hours is then determined.

Determination of the number of Titrations per day at Standard

Working day = 7 hours = 420 minutes.

Less stop/start and cleaning allowance of 25 minutes.

Net available working time = 395 minutes.

Number of titrations at standard = $\frac{395}{3.647} = 108$ (at 80r : 144)

Allowances : 50 min. approx for rest.

25 min. stop/start and cleaning up.

81 min. for calculation of result (built in).

156 min.

This procedure can be adopted for any human work. Work Measurement can also be used for comparison of methods. Care must be taken, however, that the new and improved method is given a fair trial by a trained operative.

It will be appreciated that having derived the standard time for a number of operations, the mixed number of these which can be carried out in a working day can be calculated.

One Set of Mixed Operations Calculated per day Output

If Standard Time for titration = 3.647 S.W.M.

and Standard Time for a weighing = 5.000 S.W.M.

To calculate the allowed time at standard for 10 weighings and five titrations :

For 10 weighings $5.000 \times 10 = 50$ min.

For 5 titrations $3.647 \times 5 = 18.235$ min.

Total time allowed at standard = 68.235 min.

Conversely, by taking the operations performed by a worker in a day, it is possible to compare his performance with that of another.

Mixed Operations per 7 hour day. Calculation of Rating

Suppose assistant does 10 weighings and 5 titrations in 55 minutes. At what rating has he worked ?

Formula : $\frac{\text{Time allowed}}{\text{Time taken}} \times 60 = \text{rating}$

$$\frac{68.235}{55} \times 60 = 74$$

It must be emphasised that although, in this last example, work has been taken from the laboratory, it is obviously undesirable that a laboratory

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assistant's ability should be assessed only on speed. Laboratory examples have been selected merely to illustrate the subject.

INCENTIVE BONUS

Consultants have long used a combination of Work Measurement, with the application of Incentive Bonus schemes, to show rapid returns.

The installation of an Incentive Bonus scheme is rather like having a driverless car at the top of a very steep hill with the engine off, and the hand brake released. The car is given a good push. At first the results may be impressive but unless the scheme is carefully controlled, and applied with integrity, disaster may ensue.

If the method to be used is not completely described the operator may take short cuts, thereby achieving a high output at the expense of quality.

The method of payment of bonus is shown in the following example :

$$\begin{aligned} \text{Operator's performance for week} &= 80 \\ \text{Weekly wage} &= \text{£ } 9 \\ \text{Bonus payable} &= \frac{80-60}{60} \times 9 = \text{£ } 3 \\ \text{Total pay} &= \text{£ } 12 \end{aligned}$$

Where individual bonus payments are made, payments when plotted against numbers earning them should follow a Gaussian Distribution Curve (*Fig. 10*).

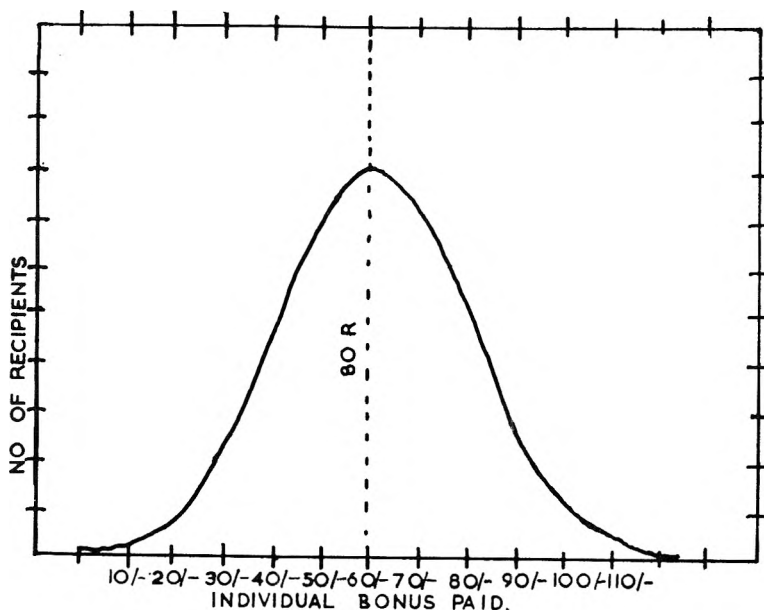


Figure 10

When standards are "loose" operators tend to restrict their output to a $33\frac{1}{3}\%$ earning so that the "easy" standard will not be re-set (*Fig 11*).

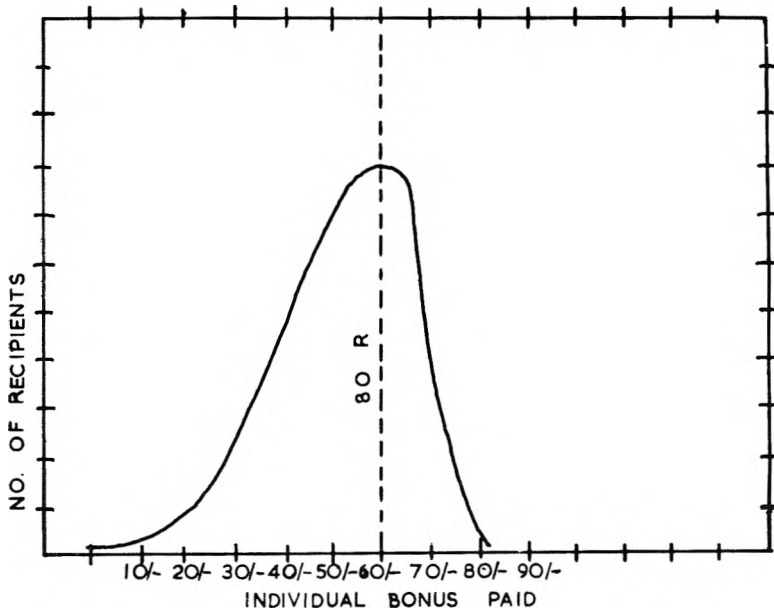


Figure 11

Method Study should be followed by Work Measurement. Incentive Bonus application is the final stage in the scheme. It is the most risky stage and should be omitted if possible.

INFORMATION SUPPLIED BY WORK STUDY DEPARTMENT TO OTHER DEPARTMENTS

Cost Accounting Department

The Costing Department needs to know standard times for standard costings. By far the best way of determining these is from Work Studies. Method Study lays down in detail *how* the job shall be done. Work Measurement shows *how long* it should take at a standard rate of working. Extension of standard times at a standard wage rate gives the standard direct labour cost for the job.

Personnel Department

Work Measurement enables the performance, over a given period, of an individual team, group, department or factory to be defined. It is therefore a measure both of supervisor and worker on an impartial basis. There is no

reason why results worked out by the Work Study Department should not be recorded in Personnel Department's records.

These results, of course, illustrate only one facet in an individual's usefulness to the employer, and should be reviewed as such.

CONCLUSION

This is only a brief and elementary account of Work Study. In this Productivity Year it may be appropriate to quote the results obtained in one group of factories in World War II.

Table 4

Labour	Reduced from 45,000 operators to 30,000 operators. 15,000 men and women transferred to the armed forces.
Output	From 30,000, double that previously obtained from 45,000.
Estimated increase in operator earnings	33.0%
Economy	£1,000,000 per year.
Cost of application	£75,000 per year.

It should be noted that much of this was obtained by chemists after a brief training in Work Study.

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CHEMICAL CONSTITUTION AND ODOUR IV. SYNTHESIS AND OLFACTIVE PROPERTIES OF 11-OXAHEXADECANOLIDE

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

The olfactive properties of the synthesised 10-, 11-, 12-, 13- and 14-oxahexadecanolides are considered. The crystalline 11-oxahexadecanolide is found to be equal in character and odour intensity to pentadecanolide, while the other liquid oxalactones are all weaker.

Previous conclusions on the correlation between structure and odour are upset by this phenomenon.

INTRODUCTION

MUSK COMPOUNDS are almost always required to complete a perfume composition. Beyond the introduction of musk odour other factors also play an important part because most commercial musk odorants possess positive fixative and exalating properties.

The importance of this group of compounds is emphasised by numerous publications in this field. Many aspects of these characteristic substances have been discussed in original articles and reviews dealing with synthesis, application, olfactive properties and physiological data. Even a few psychological effects have been described, e.g. Cardinal Richelieu did not feel inclined to work when he missed the odour of musk in his study.

The commercial importance of musk odorants probably accounts for the fact that far more research findings are being published in this field than in other subjects of research. Musks are found in different classes of organic compounds and they have been classified by Mignat¹ as follows :

1. Macrocyclic compounds.
2. Steroids.
3. Benzene derivatives—
 - (a) nitrated benzene compounds,
 - (b) non-nitrated benzene compounds,
 - (c) indane derivatives,
 - (d) tetraline derivatives.
4. Other compounds.

*N.V. Chemische Fabriek "Naarden", Naarden, Netherlands.

We do not propose to enter into details of this classification but are restricting ourselves to the macrocyclic series, and especially to the macrocyclic lactones. The well-known and valued pentadecanolide occupies a very special place in this group. From an olfactory point of view it is one of the most important components of the essential oil of *Angelica archangelica* L.² Pentadecanolide possesses a very strong musk odour with a flowery note. Ruzicka and Stoll³ already synthesized pentadecanolide in 1928; developments until 1962 have been reviewed by us⁴. Research on other macrocyclic lactones started very soon after the 1928 discovery of pentadecanolide because the synthesis was difficult and expensive. This led to the preparation of oxalactones, resembling pentadecanolide in character, but weaker in odour intensity. The oxahexadecanolides in the group of macrocyclic oxalactones have the most interesting olfactive properties.

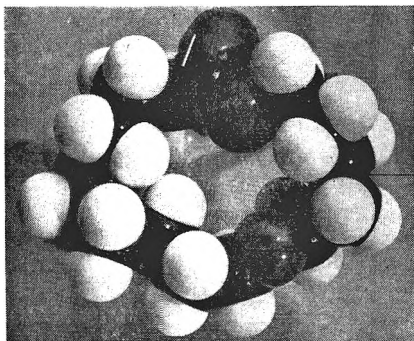


Figure 1

A Stuart model of 11-oxahexadecanolide.

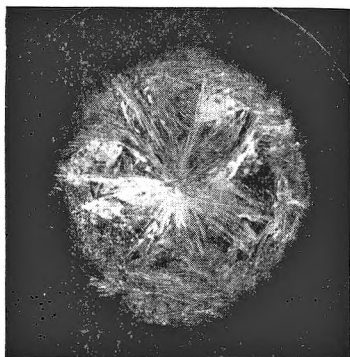


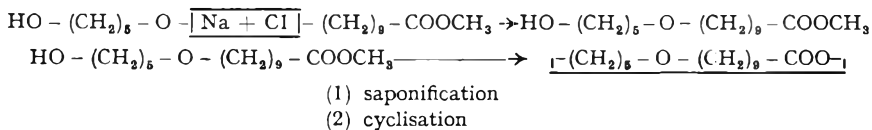
Figure 2

11-oxahexadecanolide crystals.

Only a few oxahexadecanolides have been described in the literature, viz. 6-, 10-, 12- and 13-oxahexadecanolide. We planned to synthesize all isomeric oxahexadecanolides as we expected a definite insight into the correlation between structure and odour, and we have already succeeded in preparing 10-, 11-, 12-, 13- and 14-oxahexadecanolide. Although we do not possess the data of all oxahexadecanolides, we will now deal with the synthesis and olfactive properties of the mentioned five isomers, because one of these lactones, 11-oxahexadecanolide, is equal in character and odour intensity to pentadecanolide (superior among macrocyclic lactones up to now). It is a remarkable fact that these two compounds also show a definite similarity in appearance, being crystalline with an almost identical melting point (35° and 37°). All other known oxahexadecanolides are liquids at room temperature. Correlations between structure and odour will be discussed below because 11-oxahexadecanolide showed surprising olfactive properties⁵.

EXPERIMENTAL

The isomeric oxahehexadecanolides are usually obtained by reaction of ω -halogenocarboxylic acids (esters) upon the monosodium compounds of α,ω -diols, followed by cyclisation, except in case of 15-oxahehexadecanolide. We synthesized five of them, viz. 10-, 11-, 12-, 13- and 14-oxahehexadecanolide. The 11- and 14-isomers have not yet been described in literature. Another isomer, 6-oxahehexadecanolide, has been synthesized by Nesmeyanov *et al.*⁶. The detailed descriptions are as follows:

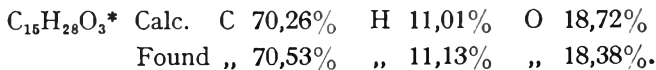
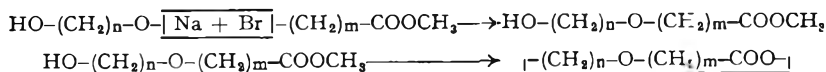
Synthesis of 11-oxahehexadecanolide.

We prepared 11-oxahehexadecanolide from 10-hydroxydecanoic acid, obtained by alkaline fission of castor oil⁷. Esterification with methanol and reaction with thionyl chloride gave us the methyl 10-chlorodecanoate⁸; b.p. 112°/3 mm; $\frac{n-20}{D}$ 1.4488. The ester was condensed in 6 hours with an equimolar quantity of monosodium pentanediolate at 150° in an excess of pentanediol.

Saponification of the reaction product yielded 76% 11-oxa-16-hydroxyhexadecanoic acid. Purification was carried out by crystallisation from benzene; m.p. 65°, neut. equiv. 275 (theoretically 274).

Cyclisation was effected according to Ogorodnikova *et al.*⁹ by converting the oxa-acid into its polymer and transesterification in vacuo at 200°. The lactone was isolated from the reaction mixture by co-distillation with glycerol.

Fractionation yielded 80% pure 11-oxahehexadecanolide, m.p. 35°.

*Synthesis of 10-, 12-, 13- and 14-oxahehexadecanolide.*

In all instances the required oxa-acids were obtained by reaction between the ω -bromocarboxylic esters and the monosodium compounds of the corresponding diols according to Stoll and Rouvé¹⁰. Cyclisation was carried out in the same manner as described above.

Table 1 shows the lactones with their refractive indices.

Table 1
Refractive indices of some oxahexadecanolides

lactone	structure	$\frac{n-20}{D}$	
		found	literature
10-Oxahexadecanolide	n=6 ; m= 8	1.4681	1.4680 ⁶
12-Oxahexadecanolide	n=4 ; m=10	1.4679	1.4678 ¹¹
13-Oxahexadecanolide	n=3 ; m=11	1.4676	1.4644 ¹²
14-Oxahexadecanolide	n=2 ; m=12	1.4683	—

*Micro-analyses by the Organic Chemistry Laboratory, University of Amsterdam, Department of Microanalysis, headed by J. P. Hubers.

OLFACTIVE PROPERTIES

Pentadecanolide has superior olfactive properties in the group of macrocyclic lactones, having a strong musk odour with a flowery note. All oxalactones synthesized in our laboratories, and 6-oxahexadecanolide, described by Nesmeyanov *et al*⁶, give similar but weaker odours than pentadecanolide with the exception of 11-oxahexadecanolide. Apart from this, the 12-, and especially the 13- and 14-isomers have a fatty note, which shows up very clearly when the substances have been on paper test strips for some time.

Curiously enough, 11-oxahexadecanolide has an odour, and other properties, which are equal to pentadecanolide in all respects. Observation of the olfactive properties of the plain substance and compositions in which it is used, underline this. This similarity will be discussed in detail in another paper that will deal with its application and properties in perfumes. Table 2 shows the lactones and their odour descriptions.

Table 2
Olfactive properties of some oxahexadecanolides and pentadecanolide

Compound	Olfactive properties
pentadecanolide	musk, strong, flowery note
10-oxahexadecanolide	musk, rather strong, flowery
11-oxahexadecanolide	musk, strong, flowery note
12-oxahexadecanolide	musk, medium, weak fatty
13-oxahexadecanolide	musk, medium, fatty note
14-oxahexadecanolide	musk, medium, fatty note

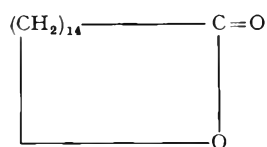
DISCUSSION

In the field of macrocyclic compounds, conclusions have been drawn and rules have been made, based on observation of correlation between odour

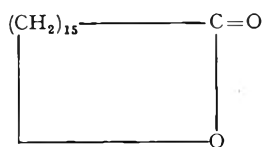
and structure. In our opinion the rules about macrocyclic ring structures containing one functional group are well-founded.

The osmophoric effect decreases down the range of lactone-, ketone-, carbonate-, anhydride- and hetero atoms (O, NH, S)¹³, but matters are more complicated if two functional groups are present in the ring. It is generally found in the literature that the introduction of a second functional group causes a decrease in odour intensity. In the series of the oxalactones this fact was accepted up to now. Exceptions to this rule are known. For instance, civettone, with a ketone group and an olefinic bond, has a much stronger odour intensity than the hydrogenated product with only one functional group. The same may be said about ambrettolide and hexadecanolide, although to a lesser degree.

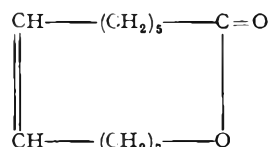
The observation of Beets and v.d. Dool¹⁴ that the introduction of an oxygen atom in macrocyclic ketones should increase the intensity of the odour is disputable. If the hetero atom is placed in the lactone position (exaltone \rightarrow pentadecanolide) then their observation is correct. In 6-oxacyclohexadecanone¹⁵, in our opinion, the odour intensity is definitely lower. We also synthesized this compound in our laboratory



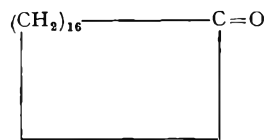
pentadecanolide



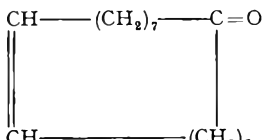
hexadecanolide



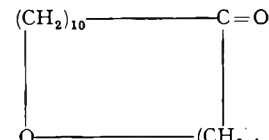
ambrettolide



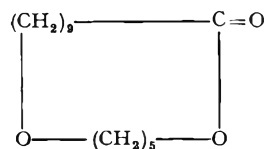
dihydrocivettone



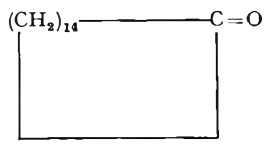
civettone



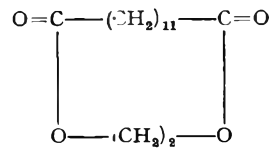
6-oxacyclohexadecanone



11-oxahexadecanolide



exaltone



ethylene brassylate

Little is said in the literature about the olfactive effect caused by relative positions of two functional groups. For this reason we wish to carry out a systematic investigation of the olfactive properties of the oxahexadecanolides. In our opinion, the place of a second osmophore may be just as important as the nature of the group.

The synthesis of these lactones led to the isomers 10-, 11-, 12-, 13- and 14-oxahexadecanolide. The fact that the 11-isomer proved to be a very strong musk compound was most unexpected.

We base our arguments on the fact that 11-oxahexadecanolide, in character as well as in intensity, is at least equal to pentadecanolide. This remarkable fact upsets a number of theories and conclusions. Stoll¹³ and, more recently, Nesmeyanov *et al*⁶ stated that the introduction of an oxygen atom decreases the intensity of a macrocyclic lactone. This applied to the hitherto known oxalactones, but the discovery of 11-oxahexadecanolide upsets this theory. Another conclusion that is based upon too little facts is that given by the Russian authors⁶, when they stated that the odour is stronger if the hetero atom in the macrocyclic lactones is further removed from the carbonyl group. Their statement was based on the difference in intensity observed between the weak 6-oxahexadecanolide and the stronger 10-oxahexadecanolide. In our series, 11-oxahexadecanolide gives a stronger odour than the isomers 12-, 13- and 14-oxahexadecanolides.

The phenomenon, reported by Beets¹⁶, that macrocyclic diesters¹⁷ have a higher intensity if the two ester groups are near to each other (ethylene brassylate), is an acceptable conclusion according to the data available to us. If this could be taken as a general rule for two functional groups, then the odour of 14-oxahexadecanolide would have to be stronger than the odour of 11-oxahexadecanolide, but the reverse applies.

We cannot explain why the intensity of 11-oxahexadecanolide is so much stronger than the intensity of the other isomers. Our knowledge of the minute differences in molecular structure is insufficient and there are more indeterminate factors that play a part when the molecule approaches the receptor surface. It is thus evident that one may only draw conclusions if the amount of systematical data is sufficient.

Basing our opinion on available data, we conclude that the introduction of an oxygen atom into pentadecanolide does not necessarily decrease the olfactive properties. Perhaps surprising olfactory discoveries will be found in other bifunctional macrocyclic systems.

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Introduction by Dr. M. H. Klouwen

Many studies have been published in the literature concerning the correlation between constitution and odour, but the majority of them do not deal with really new aspects.

Of course our paper does not pretend to bring us a step nearer to the final solution of the problem ; we only describe our results in the field of olfaction in order to discuss them in comparison with known facts. We restricted ourselves to the olfactive properties of the macrocyclic lactones having a musk odour.

For years the musk odour has been considered as a practically indisper-sable element in nearly every perfume compound. Until the second decade of this century the effects obtained with all the substitutes for natural musk were definitely inferior to that obtained with the natural product. The synthesis of Exaltone and its introduction in perfumery due to the brilliant work of Ruzicka completely changed this state of affairs. Later on, when the synthesis of the lactones from hydroxy acids became an industrial proposition, pentadecanolide started its career in perfumery.

In the years just before the second world war it was found that oxalactones having the same number of atoms in the ring, possessed an odour comparable to that of pentadecanolide and its homologues, although in every instance it had to be described as less delicate than that of penta- and hexadecanolide themselves.

It is a known fact in organic synthesis that chain-extension is far easier when, instead of a carbon atom, a hetero-atom can be utilized and so for economic reasons heterocyclic lactones met with a certain success.

In the years after the second world war, 12-oxahexadecanolide was introduced under different trade names and appreciated by many perfumers

as an element for their cheaper compounds. Comparing them to the *primus inter pares* pentadecanolide, it was found that the oxahexadecanolides are a nearer approach to its odour than the oxapentadecanolides and oxaheptadecanolides, and generally speaking they possess better "musk properties".

We planned to synthesize all oxahexadecanolides as we expected a definite insight into the correlation between structure and odour in their series. We have already succeeded in preparing five isomers, viz. 10-, 11-, 12-, 13-, and 14-oxalactones. The availability of 10-hydroxydecanoic acid, the starting material for our pentadecanolide synthesis and from which the synthesis of 11-oxahexadecanolide is easy, stimulated our interest.

From the beginning, the olfactive properties of the 11-oxalactone proved to be very promising. The quality of the odour, in strength as well as in character, is at least the same as that of pentadecanolide.

Up to now the 11-oxahexadecanolide is by far the best of the series, followed by the 10-isomer.

The 13- and 14-isomers, however, are much weaker and have unpleasant odours.

The synthesis of the oxalactones is simple. The monosodium compound of the α - ω -diol is reacted with the ω -halogenocarboxylic acid. The reaction product is subjected to one of the known cyclisation processes.

In the past some rules have been proposed for which an insufficient number of data were available.

Stoll¹³ and more recently Nesmeyanov *et al*⁶ stated that introduction of an oxygen atom in the ring diminishes the olfactive strength of a macrocyclic lactone. Up to now this may have seemed to be true, but the discovery of 11-oxahexadecanolide upsets this rule.

According to another statement based equally on too restricted a knowledge⁶, the odour is stronger when the hetero atom in the chain is further removed from the carbonyl function. This was based on the comparison of the odours of the weak 6-oxahexadecanolide and the stronger 10-oxahexadecanolide.

As a result of our observations, we can say that the odour of the 11-isomer is significantly stronger than that of the 12-, 13- and 14-isomers.

We have no explanation to offer on this point.

Our knowledge of the influence of minute differences in molecular structure is quite insufficient, and there are too many unknown factors as to what happens when the molecule approaches the receptor.

Summing up from the above we conclude :

1. Introducing an oxygen atom between the carbon atoms in pentadecanolide does not necessarily weaken the strength of the odour.

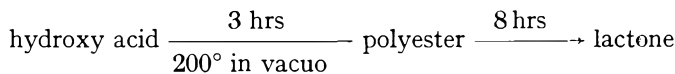
2. The place of the oxygen atom in the ring decides the olfactive properties of the molecule.
3. More information may be found after completion of our intended synthesis of the still missing isomeric oxahexadecanolides.
4. The possibility also exists that surprising discoveries in the field of olfaction will be made in other bifunctional macrocyclic systems.

DISCUSSION

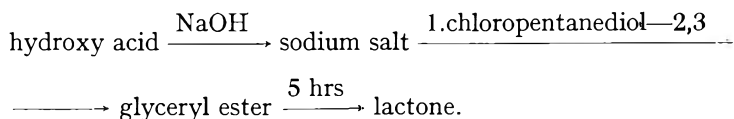
DR. Y.-R. NAVES : Since the authors refer to the process for transforming oxa-acids into lactones described by Ogorodnikova and collaborators in 1955, I would like to emphasise that this procedure is, to some extent, a backward step with respect to the process described in British Patent 490,044, and involving the cyclisation of hydroxy-16-oxa-12-hexadecanoic acid.

THE LECTURER : The difference between the two processes is that one is carried out via the polyester, while the patented method prepares a well-defined glyceryl ester as an intermediate. Lactonisation is effected in both cases by heating, in vacuo, with an alkaline catalyst in glycerol as a co-distillation component.

1. *Ogorodnikova et al*⁹



2. *British Patent 490,044*



Comparing the two methods we conclude that the former procedure is more economical because

- (a) in the second case there is one reaction step more than in the former,
- (b) the first process can be completed in a single distillation apparatus, whilst in the second the preparation of the glyceryl ester has to be carried out in a separate reaction vessel, and
- (c) prior to cyclisation it is necessary to wash the glyceryl ester with water, in order to remove the sodium chloride.

In our opinion, both lactonisation methods are in principle identical, as during transesterification the equilibrium to be obtained is essentially the same.

MR. G. J. E. HACKFORTH-JONES : The comparison between the isomers of oxahexadecanolide has proved most interesting.

Has Dr. Klouwen any observations to make concerning the odours of the corresponding oxaheptadecanolides ? I have been informed that one of these is now on the market.

THE LECTURER : In the literature three isomeric oxaheptadecanolides are described, viz. 4-oxaheptadecanolide [Beets, M. G. J., and Meerburg, W. *Rec. trav. chim.* **72** 411 (1953)]; 8-oxaheptadecanolide⁸; and 12-oxaheptadecanolide [Tong, S. T., *Soap Perfumery & Cosmetics* **26** 149 (1953)]. In our own laboratories, we prepared the 12-isomer and the unknown 11-oxaheptadecanolide. Both lactones proved to have an odour inferior to 10-, 11- and 12-oxahexadecanolide.

As far as we know, no oxaheptadecanolides have been marketed up to now.

ERRORS IN APPLICATION OF INSTRUMENTATION TO THE ANALYSIS OF PERFUMERY RAW MATERIALS

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

Problems encountered in the gas chromatographic analysis of perfumery raw materials as opposed to, for example, petroleum products are quite different. The former are complex mixtures in varying proportions of substances differentiated by functional groups, polarity and volatility.

Olfactory examination of effluents is frequently desirable, non-destructive detectors being necessary.

Inadequate equipment and techniques are responsible for many errors in identification and evaluation.

Too many publications in this field are unreliable.

GAS CHROMATOGRAPHY has rapidly become one of the most used methods of investigating perfumery raw materials, and for controlling their quality.

The apparent simplicity of the application of gas chromatography conceals from many analysts the numerous possibilities of error. They are led to rash conclusions by some misunderstanding of the physical phenomena involved, as well as by their impatient enthusiasm. That is why, like others, I am taking this opportunity of issuing a new warning, knowing that you will respond to the statements made hereunder.

I maintain that techniques which are of great service, for example, in the petroleum and natural gas industries, do not necessarily apply to the perfumery raw materials industry. The suppliers of gas chromatography apparatus either are not aware of, or prefer to ignore, this situation. There exists today an extensive range of apparatuses, very few of which are satisfactory or even almost satisfactory for the analysis of these products. As a result the industry is too often equipped with inadequate apparatus, and the work is carried out with unsuitable techniques.

Essential oils, intermediates which are made from them for the production of synthetic perfumes, and natural perfumes, are mixtures of many constituents in widely different proportions; the components differing in their volatility and chemical nature. Constituents present in low proportions can determine the quality of the odour as do impurities in synthetic perfumes.

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There does not exist, however, a chromatographic technique which is suitable for all the constituents in these mixtures, as explained below.

The forces which are brought into play during chromatography are of varying types. One molecule of the substance being analysed (A) in dilute solution in the liquid phase (S), it is surrounded only by molecules of the solvent exercising on it various forces which are, as is known, the dispersion forces of London, the induction forces of Debye, and the orientation forces of Keesom. The energy to be overcome to achieve freedom is, broadly speaking, the sum of the energies $\Sigma\epsilon_{AS}$ and the relative volatility of the two substances A and B is measured by the difference $\Sigma\epsilon_{AS} - \Sigma\epsilon_{BS}$ ¹.

The various energies involved are determined by the chemical nature of the substance and the liquid phase, and by a large number of factors acting in different ways.

Naturally, the analytical problem can be restored to a simpler level by submitting not the whole product to gas chromatography, but only fractions isolated by physical or chemical means which group together components of similar behaviour. These techniques, however, which are acceptable and even highly recommended in research, are usually too uneconomical of materials, time and money to be suitable for technical control. This handicap can be overcome in certain cases by the use of a pre-column, which retains certain types of constituents, or of a micro-reactor which changes them into substances of different behaviour.

If logarithmic graphs of the relative polarities of the charges of the columns against the relative retention times are established, it can be seen that non-polar substances give horizontal lines whilst other substances give slopes which are more or less inclined, according to the polarity². Depending on the polarity of the column, the constituents of a mixture will be more or less separated and will appear in the elute in different orders. It will therefore be apparent that according to the nature of the charge, certain constituents can be confused or overlooked. Thus the first rule for preventing errors can be established. It is desirable that the analysis of a mixture is carried out comparatively with charges of different polarities. With this objective, the use of Rohrschneider's method, starting from definite constituents, can render the greatest services. On this subject, the excellent study of Klouwen *et al*³ dealing with the separation of terpenes with columns of different polarities may be consulted.

The polarity of a column can change under the influence of time, the heating and cooling to which it is submitted, and by being maintained at elevated temperatures for long periods. The loss or the alteration undergone by the stationary phase can explain observed anomalies, but the effect of repeated heating and cooling is less easily accounted for⁴.

We find an illustration of the advantage of using comparative columns

of different polarities in the misfortunes experienced recently by von Rudloff⁵. This author announced that gas chromatography showed the presence of camphene amongst the products resulting from the dehydration of terpineol, basing his results particularly on the retention time in a rapeseed oil chromatographic column. It was in fact menthene-3, as has been shown by others⁶ who identified the effluent not only by retention time, but by IR and NMR spectra.

Temperature is another factor the variation of which is easily used to advantage in achieving separations. The logarithms of retention time are inversely proportional to the absolute temperature of the column. It therefore saves time to work at as high a temperature as possible. On the other hand it is known that the best separations are achieved at low temperatures. A compromise is therefore sought between the two requirements. It should not be forgotten, however, that the constituents of perfumery raw materials belong to classes of products which behave very differently from the point of view of the relationship between retention time and temperature. It follows that at certain temperatures the separation of some constituents is no longer possible. It is therefore important to prepare comparative chromatograms at different temperatures, as illustrated by the following example.

J. B. Roberts⁷ has demonstrated the influence of temperature by the chromatography of a specimen of hop oil at various temperatures, all other conditions being the same. Below 125° the principal constituents appeared in the following order: β -myrcene, caryophyllene, farnesene, humulene. Above 125° the order became β -myrcene, farnesene, caryophyllene, humulene. At 125° caryophyllene and farnesene were not separated.

It is evident that in the analysis of perfumery raw materials preference is given to the use of non-destructive detectors, permitting the recovery and identification of constituents, and above all their olfactive examination. The perfumer therefore is the first of the biological detectors, amongst which A. P. J. Martin⁸ has suggested cockroaches, gipsy moths, dogs, etc.

The most frequently used non-destructive detectors are thermal conductivity cells (catharometers) using hot filaments, and radiological detectors operating by ionisation. By using them it is possible to trap efficiently the elute with a view to identifying it by physical or chemical means. Modern instrumentation allows this identification to be rapid, economical and positive, with quantities of recovered substances of the order of milligrams or of micrograms. IR microspectrometry, NMR spectrography, and mass spectrography are used. The use of time-of-flight mass spectrography, whilst the power of resolution of spectrometers built on this principle (around 200) is relatively low, permits the continuous monitoring of the effluent and the

consequent detection of unresolved components^{9,10,11,12}. But a time-of-flight spectrometer is very expensive, costing around £5,000.

Whilst it is evident that the carrying out of gas-chromatography, with columns of different polarities at different temperatures, facilitates exact characterisation of a complex product and the identification of its constituents, it presupposes a knowledge of the retention times. But the relative uncertainty which surrounds the evaluation of retention times maintains the risk of confusion. We have only to consider the complex composition of most perfumery raw materials and the fact that we are acquainted with only some of the substances which could be present. We could be faced with substances previously unknown, and there is therefore the risk of confusing an unknown constituent, with a substance already encountered elsewhere. In this sense, the compositions attributed by many authors to essential oils and fractions of essential oils purely on the basis of retention time must be accepted with the greatest reserve, particularly when they result from a single chromatogram. It is essential for the elute to be identified by other methods such as IR spectrometry, NMR spectrography, and mass spectrography.

The recording of peaks obtained by the use of thermal conductivity or ionisation cells is presented in the form of a series of sigmoidal curves of which some are more or less superimposed and therefore deformed.

When the support for the liquid phase is totally inert, the peaks are symmetrical. Overloading of the column, i.e. the increase of the quantity of product injected beyond a certain value, lengthening of the column, too long an introduction time, an inadequate vapourisation temperature or the use of too high a proportion of stationary liquid in the charge, will enlarge the peaks.

Symmetry of peaks is favourable to the separation of neighbouring substances. The conditions for distinguishing peaks in relation to the differences in retention volumes have been studied by various authors. They are defined as a function of a variable t which is the same as unity of error in the theory of errors, the elution curve itself having the form of a curve of error.

The curve representing the quantity of elute in relation to the volume W of the mobile phase is, according to Martin & Synge, represented by the equation

$$Q/Q_{\max} = e^{-t^2}$$

in which e is the elongation of the recorder. The ratio decreases rapidly when t increases, and it is practically nil when $t = \pm 3$. Two substances eluted successively, and present in almost equal quantities, are therefore

well separated when $t = 6$, and if it is desired to identify a substance which is present in a minor proportion relative to another, this condition also must be satisfied. If, however, it is only necessary to distinguish two substances so as to be able to exactly measure the peak heights, it is permissible for t to be greater than 3, or better still, at least 4. With $t = 2$, it is just possible to recognise the complexity of a peak^{13,14,15}. The distinction between peaks becomes more difficult as the retention volume increases. With a column of 1,000 to 1,500 theoretical plates, it is found that the relative retention volumes must differ by about 20% for the peaks to be perfectly separated; differences of 10–15% will result in a certain confusion of peaks (shoulders, double peaks). For differences of 7% or less, the peaks are not separated^{16,17,18}.

The possible resolution of a mixture of substances in given elution time is therefore severely limited. Chromatography under ordinary conditions does not permit an assessment of the complexity of the compositions of most perfumery raw materials. The impossibility of distinguishing peaks falsifies both qualitative and quantitative analyses. A critical study of most publications devoted to gas-chromatography of essential oils illustrates this point.

Other causes of error have their origin in lack of knowledge of the properties of detectors. The non-destructive detectors, chiefly catharometers and ionisation detectors, to which reference has been made above, permit the olfactive study of the elute, and are used most often for the analysis of perfumery raw materials. The molecular percentages of the various constituents of a mixture are very frequently evaluated in accordance with a procedure, well described by Hausdorff¹⁹. "The areas for all peaks are added to give a total area which is normalised to 100 per cent. The ratio of individual areas to this total gives the mole percentage concentration directly." In this manner, according to Hausdorff, "quantitative analysis can be made directly on each recording, without knowing the instrument settings, the identity of the components present, or the components' individual calibrating constants or plots."

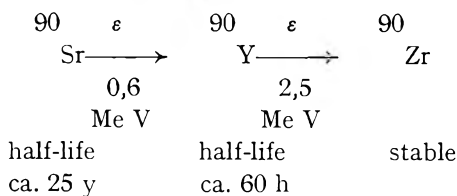
Such an enthusiastic viewpoint is acceptable only for mixtures of constituents which are similar and of the same chemical type. Applied to mixtures such as essential oils, it leads to errors amounting to as much as 15–20% of the real value.

In effect, the response of the catharometer varies with the proportion and with the type of substance. Most perfumery raw materials being mixtures of many substances in widely varying proportions, the response signal is not linear with respect to concentration. Calibration is essential if accuracy is to be obtained, less, however, where hydrogen or helium are employed as opposed to nitrogen. With moderate variations in the opera-

tional conditions, in particular in the concentration of the carrier gas, and for a large range of concentrations in the product being analysed, the calibration factor can be considered as constant. Moreover, constituents of similar type have fairly similar factors of calibration. This facilitates the analysis considerably. The calibration is effected most often by the use of internal standards. A known concentration of a standard substance, which gives an isolated uniform peak, is introduced into the sample being analysed and the responses of the detector to the standard, and to the substance being evaluated, are compared. Ideally, the two peaks should be side by side, the two products of the same type, and the concentrations of the same order of magnitude, in which case the calibration factor will approach unity. The precision of determinations by the use of an internal standard can approach $\pm 1\%$ ²⁰.

An excellent internal standard, particularly when it is desired to evaluate the percentage of a minor constituent, is the substance itself. One commences by roughly determining the percentage of the constituent by analysing the crude product, then one adds to it an equivalent percentage of the constituent in question. The two chromatograms are compared, all operating conditions being identical or very similar, notably the quantity of the product injected, the gas flow rate and the temperature, by taking as a reference the peak isolated from adjacent constituents of the substance by its retention time.

Beta Ray ionisation detectors appear to be excellent for the routine analysis of perfumery raw materials. The source of radiation most used is Strontium 90 which only produces β rays, the fission reaction being—



Normally sources of 25 m.c. are used as these are not dangerous if normal precautions are taken.

These detectors have been particularly well studied by Boer^{21,22,23,24,25}, who has claimed that "calibration is virtually unnecessary since the differential ionisation currents may be predicted from the ionisation cross sections of the component molecules." It is therefore necessary to know this parameter for each constituent.

Otvos and Stevenson²⁶ have shown by the extension of a result anticipated theoretically by Bethe²⁷ that the relative total ionisation cross sections of molecules are constitutive molecular properties, i.e., they are obtained from

the sum of the cross-sections of their constituent atoms. This is claimed to be true not only with hydrocarbons but also with compounds involving O, N, Br, etc. Nevertheless, the errors between calculated and real values become significant for types of substances frequently found in perfumery raw materials. Each type possesses broadly a corresponding proportionality factor K . In effect one has

$$T \text{ (total ionisation)} = K (n_C Q_C^i + n_H Q_H^i + n_P Q_P^i \text{ etc.})$$

where n = the number of atoms of carbon, of hydrogen, and of another atom p , and where q^i represents the ionisation cross-section of the atom in question.

Once again we are faced with the necessity of calibrating by means of internal standards when using these detectors.

A frequent problem in the analysis of perfumery raw materials is the evaluation of minor constituents. An obvious approach is to increase the sensitivity of the detectors. With ordinary equipment, the quantity normally detectable is of the order of a microgram, whether a catharometer or an ionisation cell is used. The noise level with 25 m.c. - ^{90}Sr sources amounts to approximately 0.5% of full scale deflection, so that it is about the same as that of the most sensitive type of catharometer. Noise is, however, somewhat more apparent on the β -ray charts, as it has a shorter period than in the case of a catharometer. One could think of amplifying the signal by augmenting the quantity of product injected, but in this event and even with a detector of adequate sensitivity, the trace constituent is frequently eluted with the very enlarged and diffused band of a major constituent, and becomes very difficult to measure. One can increase the efficiency of the separation by increasing the length of the column, but this also increases the size of the peaks. One is therefore left with the necessity to concentrate the impurity by preliminary gas chromatography or by a chemical pre-treatment, but this raises a number of new problems.

The error most frequently committed in the absence of internal standards is the assumption that the product utilised has entirely vaporised. In fact, perfumery raw materials such as essential oils are only partially vaporised, because they either contain heavy natural constituents or undergo changes. That is why analyses having no regard to these considerations give, for example, excessive values for lemongrass and citronella oils. In almost all cases, the use of an internal standard becomes necessary.

One should not by any means assume that all the eluted substances must be present in the same proportion, if at all, in the injected sample. In effect, under the conditions of chromatography, a certain number of original constituents can change in contact with the equipment, with the column packing or by reaction amongst themselves.

The construction material of the columns must be considered in particular. Stainless steel is used preferentially, or, in our opinion, it is even better to use glass. Monel metal and copper can give rise to variations, notably when the product being analysed is phenolic. The choice of materials for the injector and for the detector must also be considered. At high temperatures, metals can promote catalytic effects such as cracking or dissociation.

The effect of the charges (supports) has been most frequently mentioned²⁸. The use of alumina and of silica gel as the support is rarely indicated in the treatment of perfumery raw materials. Diatomaceous earth (*Celite*) and firebrick are used most often. Specially treated quartz has recently been used with advantage by Japanese workers.

β -pinene is isomerised into a mixture of α -pinene, camphene and limonene on silicone supported by firebrick or *Celite*. Aging of the columns reduces the isomerisation on firebrick and suppresses it on *Celite*. The replacement of silicone by a polyethylene glycol prevents isomerisation²⁹.

According to others, both α - and β -pinenes react when firebrick or *Celite* are employed, whereas *Chromosorb* is inert³⁰.

It has been stated that isomerisation and partial destruction of terpenes take place above 160° when silicone on *Celite* is employed and even above 140° when firebrick (*Sterchamol*) is the support³¹.

Nerol is dehydrated towards 190° on *Apiezone L* supported by acid washed *Celite*, with the formation of myrcene and ocimene³².

For the dehydration of alcohols on charges supported by firebrick and *Celite* see Liberti *et al*³³.

On a strongly polar column β -citronellal is cyclised into isopulegols to such an extent that the analysis of mixtures of α - and β -citronellals with isopulegols becomes very complex³⁴.

The mixed isopulegols and α - and β -citronellals are determined by means of a neutral *Chromosorb W* column, α -citronellal is estimated with an acidic *Celatom F.M.73* column, which transforms β -citronellal into isopulegols, and the β -citronellal is calculated by difference. Octene-1-ol-3 partially isomerises at 125° into ethylamylketone³⁵. Ethylene isomerisations which take place when firebrick is employed are almost negligible where acid-washed *Celite* (*Embacel*) is used³⁶.

Citral can be transformed by certain supports into *p*-cymene, and terpineol into dipentene³⁷.

Peroxides, which occur frequently in perfumery raw materials as the result of chemical changes, are degraded with the formation of carbonyl products, acids, etc.

The polymerisation of monomers can be retarded by the incorporation

of non-volatile inhibitors in the liquid phase. Ester interchange reactions between hydroxyl- or carbonyl-containing components and ester type liquid phases are readily observed at elevated temperatures, and can be eliminated by the use of another liquid phase or by a significantly lower operating temperature³⁸.

It is essential that the support is and remains correctly impregnated. It is almost beyond doubt that alterations in the substance being analysed, where new columns are in use, are attributable to faulty impregnation. When the support is not completely saturated by the liquid phase, it results in tailing of the peaks³⁹. Suitable pre-treatment of the support reduces the presence of active centres, de-activating it and reducing the importance of this effect⁴⁰.

Some catalytic reactions of substances with hydrogen on the platinum resistance wire of catharometers have been observed, resulting in a modification of the effluents and also in an alteration of the signal by virtue of thermal effects. If the alterations are accentuated by an increase in temperature, isomerisations of purely thermal origin can also take place (for example, ocimenes into allo-ocimenes, citrals into isocitrals, pulegone into isopulegone, carvone into spicatonone).

With fragile substances, it can be advantageous and at times even necessary, to transform them into products which are stable or more easily vaporised. One can, for example, acetylate alcohols, or convert acids into methyl esters.

The remarks made here could discourage some of the users of gas chromatography who are impatient to utilise an apparently simple analytical technique, and who are encouraged by apparatus suppliers and by publications, which in reality are superficial and misleading.

Provided the above remarks are taken into account, gas chromatography can be transformed into an analytical routine of accepted reliability and precision that lends itself to such a degree of automatic operation that work becomes rapid and does not require highly skilled operators.

The acquisition and renewal of complicated and costly apparatus, its maintenance in good condition for use, keeping in touch with progress, and the study of the diversity of original problems which are particular to the perfumery raw material industries, are hardly within the reach of analysts of small concerns or of small laboratories. It is these who must be particularly careful to formulate their conclusions with the necessary reserve.

It is useless and wrong to suppose that operational skill, which is often accompanied by a persistent error, can suffice⁴¹. Knowledge of all the phenomena that apply, attention to all accomplished progress, notably to all newly revealed causes of error, and incessant research are indispensable. The gas chromatography abstracts⁴² are useful sources of reference.

Too many uncertain results, too many well-known errors have been introduced during the last few years into the scientific and technical literature concerning odorous raw materials, in particular by the unwise or too superficial use of gas chromatography, for this warning to be neglected.

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Introduction by the lecturer

Gas liquid chromatography (GLC) has become one of the most important tools in the analysis and quality control of perfumery raw materials. Its application has, however, brought in its wake numerous difficulties and inconveniences, simply due to the lack of knowledge of some of the principles that are involved, and due to failure to take certain basic precautions. Equipment and techniques which are known, which may be quite suitable for the analysis of other products, are quite useless with perfumery raw materials because the latter comprise many constituents which differ widely in their polarities and chemical structures. One has also to take into account the added complication that certain constituents are liable to alteration in the injector, in the column, and in the detector. Because of the complexity of the perfumery materials, the diversity of the chemical characteristics of their constituents, and the even greater diversity in the relative proportions in which they are present in an oil, the identification of components and their quantitative determination impose conditions that are not always taken into account nor completely understood.

Where GLC is intended to be used for technical purposes, we ought not to neglect economic considerations either. The analysis must be made reliable, without the use of painstaking labour on the part of the probably very expensive experts. GLC must be considered merely as an analytical process. The results obtained by its use should and must be confirmed, and must be amplified by data which are obtained by means of other analytical techniques. In its instrumentation it cannot be divorced from the instrumentation of other analytical methods. The application of GLC in everyday technical analysis must go hand in hand with continuous research into better experimental conditions, and with an accumulation of experience that is subject to an equally continuous and stringent critical review.

DISCUSSION

MR. R. N. BEVITT: You have noted various changes, undergone by terpenes during gas chromatographic analysis, induced

- (i) thermally, by reaction in the gas or liquid phase, e.g., isomerisation of ocimene to allo-ocimene,

- (ii) catalytically, by adsorption at the support/liquid-phase interface, e.g., decomposition of linalol, isomerisation of β -pinene.

Decompositions of type (ii) may be prevented by the use of a liquid phase which is more polar than the components of the sample and is therefore preferentially adsorbed at the solid/liquid interface. The use of a really inert support, perhaps powdered polytetrafluorethylene, is also a possible solution.

However, a more general solution might be the use of capillary columns, which may be operated at lower temperatures and have the column material itself as the support. Do you consider that these, and other potential advantages, recommend the capillary column for general use in essential oil analysis, in spite of the reduced sensitivity brought about by the use of a necessarily small sample ?

THE LECTURER: I agree that by the use of multi-stage columns, the decomposition is likely to be reduced. Apart from that, the isomerisation must be considered as an important factor because, for example, with allo-cimenes a temperature of 140° is already sufficient to cause the change. There are other examples, such as the change of pulegone into isopulegone, and carvone into spicatonone, which are similarly caused. It is, of course, possible to use completely inert supports, such as *Haloport*, which is made by the Scientific Corporation in the United States. Although *Haloport* seems to have a very high melting point it does start to agglomerise at temperatures of 180° . It must not be forgotten that with capillary columns there are advantages and disadvantages. It is, after all, the perfumer who is working with the product, and in view of the fact that the quantities injected into a capillary column are so minute, the detection, by odour, of the minor constituents often becomes impossible. Apart from that, the very minuteness of the quantity obtained also makes it almost impossible to use physical methods such as spectrometry of various types.

Economy must not be forgotten either. I do not know what a capillary column might cost in England, but in Switzerland it would cost between £50 and £100 per unit. In view of the tremendous variety of problems that have to be handled, between 15 and 20 columns might possibly be required, and that represents quite a large investment.

DR. M. H. KLOUWEN: For the determination of retention values different authors have chosen different standard materials. In order to obtain an index system of highest practical value to science and industry it is desirable that we all agree, as much as possible, on one generally accepted system of standards.

Dr. Kovats, of the Zürich Technische Hochschule, developed a system of retention values determined in relation to the even numbered saturated

straight-chain hydrocarbons. His system may be of an even more practical value to our industry, as he is working with natural essential oils, such as lime and mandarin orange. In our opinion such a "continuous" standard has many advantages.

Whether the use of hydrocarbons as standards on columns of high polarity will still be a practical proposition remains to be seen.

For stationary phases of this description the methyl esters of the even numbered saturated straight-chain carboxylic acids could eventually be chosen.

The International Standard Organisation (ISO/TC 54) has created a sub-committee (WG 2) for the study of the problem of choosing the internal standard.

What is your opinion on this subject ?

THE LECTURER : I should like to emphasise that, in routine analysis, the depreciation resulting from the use of any one column for a large number of determinations can result in incorrect interpretation of an analysis when standard curves are used as references. The retention times for the same components are frequently altered. We, as technicians, realise that the values that are obtained by means of GLC are not absolutely exact ones, but it is not always possible to make the commercial department of a company appreciate this fact.

DR. M. H. KLOUWEN : In the GLC analysis of methyl- and ethylphenylglycidate spontaneous dehydration is observed, which in our opinion must be preceded by hydrogenation.

The conditions are—

Support :	Embacel
Liquid phase :	Apiezon L 20% W/W
Detection :	Flame ionisation
Carrier gas :	H ₂
Column temperature :	200°

Do you know of other instances where hydrogen addition has been observed or must be taken for granted, in order to explain some other reactions ?

THE LECTURER : I am not aware of any cases similar to the one quoted, but with glycidate I think it would be better to use *Reoplex 400* instead of the material suggested by you.

MR. B. H. KINGSTON : May I endorse the sentiments expressed in this and other papers on GLC techniques, that while the gas chromatograph is an extremely valuable analytical tool, great care must be exercised in the

interpretation of results. At the same time I would like to make some remarks which may be of value.

With regard to experimental technique, reference has been made to the difficulty of reconciling conditions which favour high resolution and efficiency (e.g. long columns and high temperatures), with those which facilitate reasonably short retention times, symmetrical peaks, etc. Polarity of the packing and high temperatures have been mentioned as important sources of experimental error, especially when dealing with terpene chemicals. It would seem to me that more attention should be paid to the use of capillary columns for analysing complex mixtures of both perfumes and flavours. These would have the advantages of much speedier analysis on columns of 100 feet or more, extremely high efficiency and lower operating temperatures. But above all, they dispense with the use of a solid support. Catalytic and thermal breakdown of the more sensitive aromatic components would thus be reduced.

I would also point out that errors in interpretation frequently occur when superimposing chromatograms for comparison purposes, especially with compound peaks. It is not often realised that when two or more peaks are very close together, their retention times may differ from the same peaks which have been completely separated. If single compounds or well-separated simple mixtures are used in the reference chromatogram, it should not therefore be assumed that coincidence with an unknown peak is a necessary indication of identity.

Finally, I would support the general feeling that there is a lack of reliable published retention data of interest to the aromatics industry. It should, however, be remembered that the collation of such data depends on practical support from those using this technique. The Gas Chromatography Discussion Group is well aware of such a need. Two years ago, in fact, industry and research organisations were approached for detailed information on retention times, etc. Unfortunately the response has been very poor, and, until more data is fed into this central body for conversion and tabulation, each individual will have to struggle on as best he can. This is a very unprogressive state of affairs which leads to unnecessary duplication. I feel certain that the aromatics industry as a whole could contribute to, and indeed benefit from, a much freer exchange of information of this kind.

THE LECTURER: I do not particularly favour the use of the reference chromatogram, for a number of reasons. Firstly, it is almost impossible to exactly repeat two chromatographs, using precisely the same material at almost the same time, let alone at different times, because conditions of injection, temperature and gas flow rates, are never, never exactly the same; trouble is therefore likely to be encountered if that method is used.

On the other hand, if an internal standard is injected, most of these difficulties can be avoided. If it is understood that such differences can occur with exactly the same equipment and probably the same operators, how much more difficult does it become to repeat results with different equipment and different operators. We have repeatedly found that even by putting the two samples consecutively into the same equipment, one simply does not obtain an exact reproduction of results.

Dr. Kovats has so far restricted himself to hydrocarbons which are only to some extent related to the materials encountered in our industry, but nevertheless his methods and techniques have possibilities.

Everybody agrees that publication of data is highly desirable. It seems that so far they have very largely been kept confidential, whatever the reasons may be. When I was a member of the French group of the International Standards Organisation I discussed the matter with leading members of the French industry, and with others concerned. Although they all agreed, to date the matter remains wishful thinking.

MR. J. H. MERZ: Would you agree that the difficulties with isomerisation and catalytic decomposition of terpenic compounds are largely brought upon themselves by gas chromatographers still using the operating conditions, such as high temperature, high stationary phase concentration and columns, which were necessary in the early days of relatively insensitive detectors?

Is the lower operating temperature which is possible with capillary columns nullified by the need to vaporise the sample completely by means of a flash-heater in order to achieve representative stream splitting?

THE LECTURER: With capillary columns, it would certainly be advisable and advantageous to inject directly into the column.

MR. J. H. MERZ: How can you inject such a small sample?

THE LECTURER: That is why I am against capillary columns. For our industry, there are pros and cons in capillary columns, and generally, in my opinion, the disadvantages are greater than the advantages. In matters of research, where only minute quantities might be available, the capillary column can have enormous advantages, but my comments largely refer to the technical use of the capillary column in everyday laboratory work.

It is quite true that during the development stages of GLC, the amount of liquid stationary phase has been very largely exaggerated and where initially it was used in the proportion of 30%, now it is used more often than not in the proportion of about 20%; but even so, many authors, including Dr. Klouwen, would say that 5, 3, 2 and even 1% would be enough.

One of the inter-related factors is, of course, the quality of the solid support. It is a fact that today one can get some types of *Celite* which are very easily, or relatively easily, impregnated by a very much smaller proportion of liquid phase than was previously the case.

When using two-column equipment, one of the columns is used as a reference and the other for an injection of the sample. In this way, disturbances which could be introduced by alteration of the liquid phase are corrected. Has anyone any experience on this point?

DR. M. H. KLOUWEN : We have no experience, but the new apparatus of the F. & M. Corporation possesses such a double system.

MR. J. M. BLAKEWAY : On the subject of publication of relative retention times, I believe the people who get most of this information are the essential oils manufacturers themselves, and they will spend a great deal of money identifying at least some of the minor components of essential oils. I myself cannot see them publishing this data. Does anyone think it likely that they will publish information about the minor components of some of these rarer essential oils, which would be of great interest to everybody? I feel that the academic bodies will have to publish the information in the first place, after which industry can make more general use of it. Perhaps the French School of Pharmacy, in Paris, can be persuaded to publish something initially.

MR. G. J. E. HACKFORTH-JONES : In practice we are often confronted with a choice between two oils, one of which we suspect to have been interfered with to some slight extent. For example, one might suspect the addition of 10% of the cheaper Geranium Egyptian to Geranium Bourbon, an amount, the detection of which by smell alone, would be difficult. Can you advise which type of equipment would be most suitable for the resolution of this problem?

THE LECTURER : With Oil of Geranium, which is very much more complex than many others, I, and my collaborators, have carried out a considerable amount of research, as probably has every major user of geranium oil. I have found 90 different bodies of which 60 are of interest odourwise; but it is very likely that altogether there are more than 150 constituents present in this or similar oils. In such a case, the capillary column has an advantage, and even though one would not be able to identify all the individual components with it, graphically it probably shows the number of ingredients better than most other columns. With an ordinary column under normal working conditions, i.e. with an available time of half an hour, one would not expect to get a graph containing more than about twenty-five peaks.

**SOCIETY OF COSMETIC CHEMISTS
OF GREAT BRITAIN*****Diploma Examination*****BRUNEL COLLEGE**

PAPER I

(Monday, 4th June 1962)

Candidates should answer FIVE questions. There should be no attempt to answer more than five questions.

Where possible (i) express reactions by equations, (ii) give simple sketches of apparatus used, and (iii) full explanation of symbols and equations should be given.

(Acceleration due to gravity, $g = 981 \text{ cm/sec/sec}$)

1. Oils and fats which are extracted from vegetable and animal sources are esters of glycerol and various fatty acids. Comment on the nature and properties of these fatty acids, and show how these properties can control the properties of the oil or fat.
2. Write short notes on *TWO* methods used to determine the physical properties of oils or fats. How do waxes differ from oils and fats? Discuss the practical application of waxes in cold and cleansing creams.
3. What are the four classes of surface active agents? Give examples of each class and show how these materials can be synthesised. Discuss the properties of examples of each class in relation to their practical application.
4. Recommend materials for the development of (a) a medicated shampoo, (b) a cream shampoo, (c) a conditioning shampoo, and (d) a hair bleach. What laboratory and practical assessment methods would you employ to show that the above products were satisfactory?
5. What is surface tension? Describe the capillary rise method for the determination of surface tension.
The surface tension of carbon disulphide at 19.4°C , is 33.62 dynes/cm . What is the radius of the capillary tube used in the experiment if the density of carbon disulphide at 19.4°C is 1.264 g/ml and the mean equilibrium height of liquid in the capillary tube is 4.203 cm .
6. Describe the effect of adding electrolyte to an aqueous solution of a surface active agent on (a) the surface tension, and (b) the critical micelle concentration.

7. Write short notes on *THREE* of the following :—

- (a) The effect of temperature on surface tension.
- (b) Wetting and spreading.
- (c) Surface pressure.
- (d) Why has the expected use of cationic surface active agents as detergents never been fulfilled ?

PAPER II

(Wednesday, 6th June 1962)

Candidates should answer FIVE questions. There should be no attempt to answer more than five questions.

Where possible (i) express reactions by equations, (ii) give simple sketches of apparatus used, and (iii) full explanation of symbols and equations should be given.

1. Write notes on the basic ingredients of toothpaste including their function, the basis of their selection and levels normally employed in toothpaste.
2. Write short notes on *TWO* of the following topics :—
 - (a) Factors which determine the rheological properties of emulsion systems.
 - (b) Factors which control emulsion creaming and methods of minimising this phenomenon.
 - (c) The beeswax/borax emulsion system and its application in formulation of cosmetic creams.
3. Discuss the formulation of :—
 - (a) An O/W hand cream,
 - (b) A W/O men's hairdressing :
giving a basic formula for each type of product, and indicating the function of ingredients in formulae quoted, with respect to the product user properties required.
4. Discuss the modern theories of emulsion stability with particular respect to the formulation of O/W and W/O cosmetic emulsions.
5. Describe the main methods by which essential oils, concretes and absolutes are obtained from plants.
Briefly describe the raw materials of animal origin.
6. Discuss the problems encountered in formulating suitable perfumes for,
 - (a) aerosols, (b) alcoholic perfumes (handkerchief perfumes and toilet waters), (c) creams and lotions, (d) lipsticks and (e) toilet soaps.

7. Write notes on *SIX* of the following raw materials. Include where possible details of their manufacture, properties and uses in perfumery :—

Phenyl ethyl alcohol.	Clove oil.
Benzyl acetate.	Bois de Rose oil.
Synthetic musks.	Ionones.
Geranium Bourbon Oil.	Hydroxycitronellal.

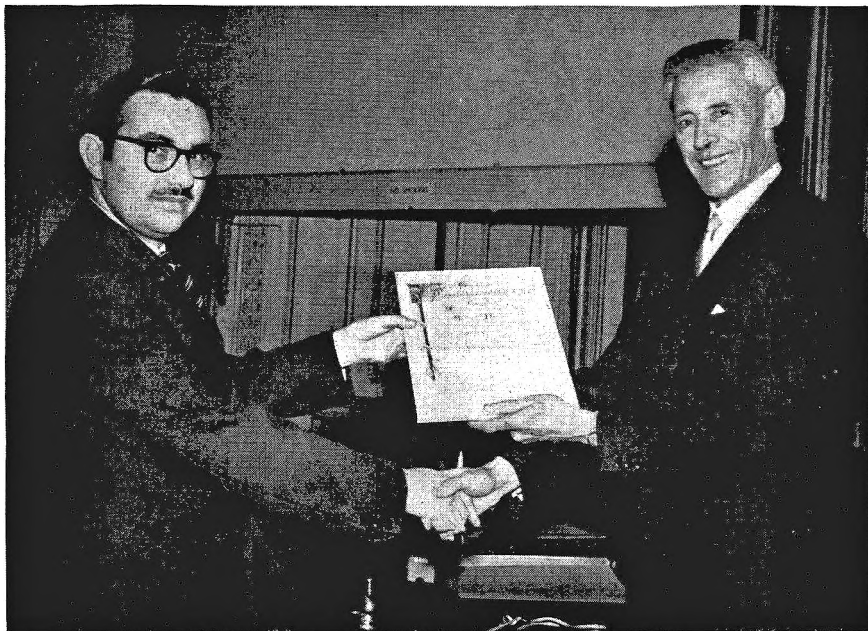
SUCCESSFUL CANDIDATES

Nine out of twelve candidates were successful. For six of the successful candidates this was only year A of the course. Diplomas were awarded to the three successful candidates who have now completed the course.

B. NICOLL
T. REMEDIAKIS
Miss J. RICHARDS

Presentation to Mr. A. Herzka

AS A TOKEN of appreciation for his work in organising the Second Congress of the International Federation of Societies of Cosmetic Chemists, The President, Mr. G. A. C. Pitt, on behalf of the Council, presented an illuminated Address and a soda-water maker, to Mr. A. Herzka on 17th December 1962.



Symposium on Perfumery

A SYMPOSIUM on Perfumery, organised by the Society, took place at Cheltenham on 13th and 14th November 1962. It was attended by 85 participants, including visitors from the Netherlands and Switzerland.

On the evening of Tuesday, 13th November, delegates attended a Civic Reception, given by His Worship the Mayor of Cheltenham, at the Pittville Pump Room.

At the morning session, the Mayor of Cheltenham, Councillor A. E. Trigg, J.P., welcomed the delegates, and the President of the Society afterwards thanked the Mayor not only for his kind words, but also for the hospitality shown to the delegates on the preceding evening. The Symposium was then formally opened by the President, Mr. G. A. C. Pitt.

Two of the papers are to be found in pages 19 and 29 of this issue, and the rest will be published in the *Journal* in due course.

1963 Programme

Lectures

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

Time: 7.30 p.m.

Friday, 25th January

L. Golberg, M.A., D.Sc., D.Phil., M.B., B.Chir., F.R.I.C.
[British Industrial Biological Research Association]
Some Problems of cosmetic and toiletry toxicology.

Tuesday, 26th February

H. Colin Davis [D. & W. Gibbs, Ltd.]
Oral hygiene, with particular reference to dental preparations.

Monday, 25th March

T. J. Elliott, B.Sc., Ph.D. [Innoxia (England), Ltd.]
Modern cosmetics—Illusions and reality.

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. Registration forms, together with final details, will be available from the General Secretary, Mrs. E. Millman, 2 Lovers Walk, London, N.3, at the end of January.

Provisional Programme

Wednesday, 24th April

Afternoon

“Hair lacquer systems.”

R. G. Harris (Swallowfield Aerosols, Ltd., Wellington, Somerset).

“Lanolin Derivatives in Aerosol Formations.”

S. C. Allen (Croda, Ltd., London, W.C.2).

“Some Factors relating to the choice of perfumes for pressurized products.”

R. E. Eckton (Givaudan & Co., Ltd., Whyteleafe, Surrey).

Evening

Civic Reception by His Worship the Mayor of Southport.

Thursday, 25th April

Morning

“Physiological Properties of Propellants.”

Dr. H. Kübler (Sprühtechnik GmbH, Rheinfelden/Baden, Germany).

“Inflammability of propellants.”

K. Dixon (Pressure Aerosols Filling Co. Ltd., Berkhamstead, Herts).

“Some Aspects of the Safety of Aerosol Containers.”

G. F. Phillips (Laboratory of the Government Chemist, London, W.C.2).

“Alcohol/Propellant Systems.”

A. Herzka (Independent Consultant, London).

“Corrosion in aluminium containers.”

E. K. Clarke (Beecham Toiletry Division Ltd., Brentford, Middx.).

Afternoon

“Brains Trust.”

M. N. Conville, J. A. T. Fisher, S. W. Frankish, R. A. Gunn-Smith,
A. Herzka, J. Pickthall.

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 General Secretary of the Society.

Annual Dinner and Dance

This will take place on Friday, 1st February, at the Cafe Royal, Regent Street, London, W.1.

Annual General Meeting

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

GENERAL NOTICES

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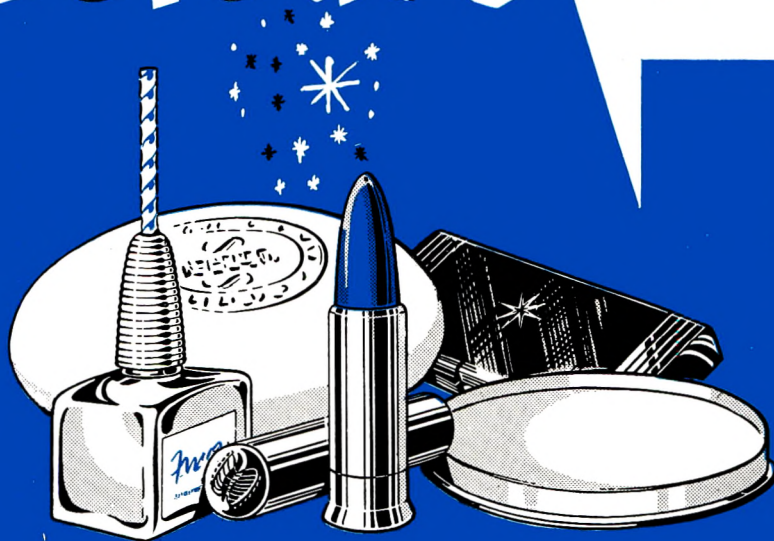
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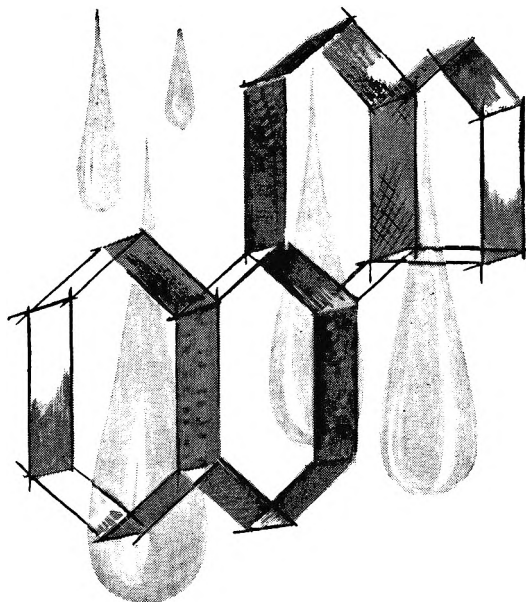
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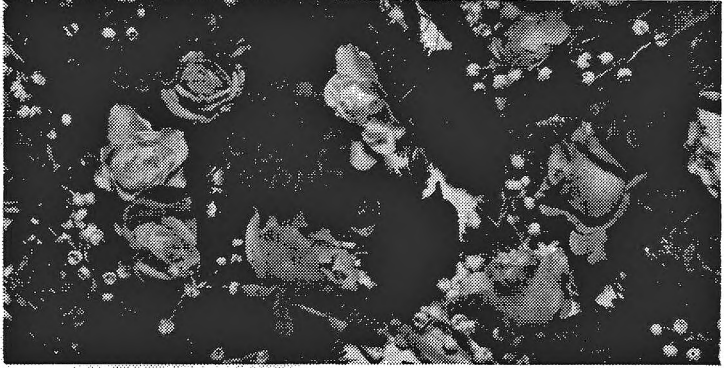
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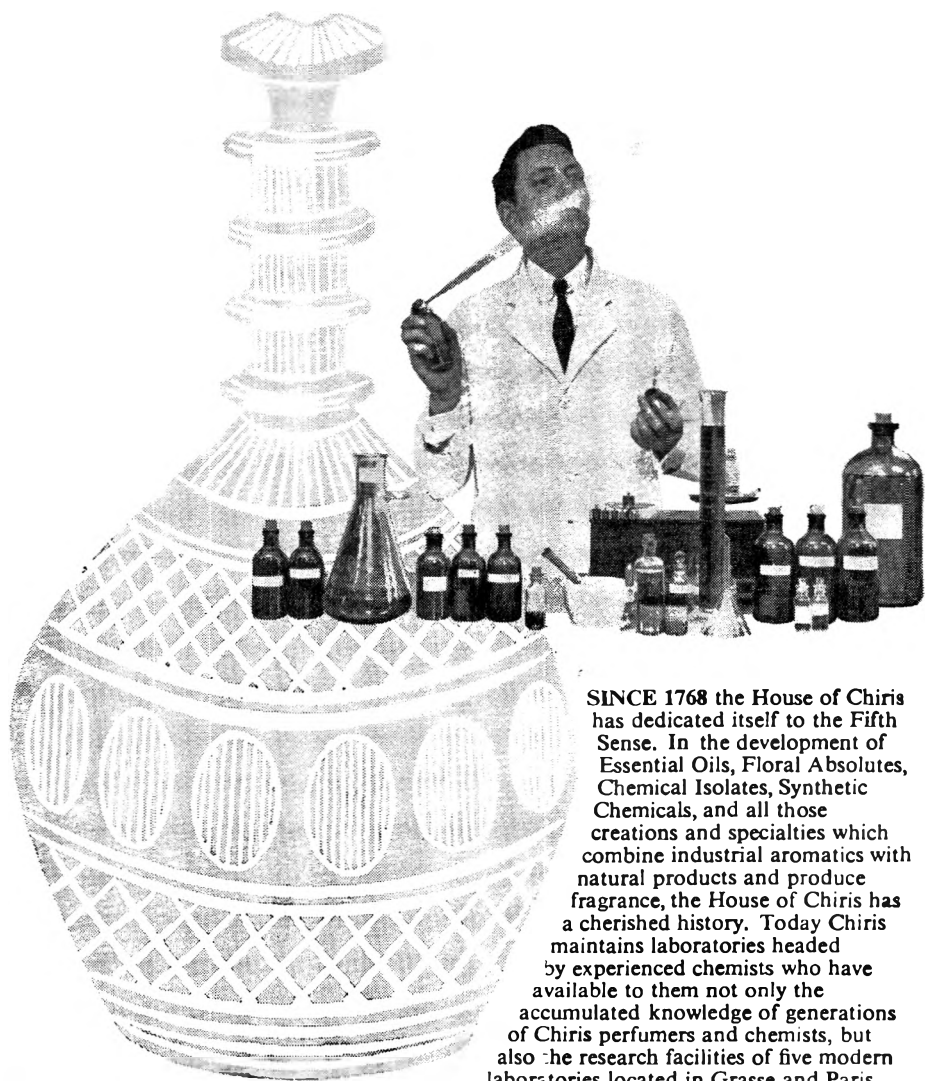
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