

THE GAS CHROMATOGRAPH  
WITH  
HUMAN SENSOR: PERFUMER MODEL

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*Introduction*

The image of the traditional perfumer is difficult to describe. In the first place, there are relatively few perfumers in the world, and they are generally not classified according to their abilities as strictly creative perfumers, control perfumers, or those most capable of performing duplication. A perfumer is, however, an artistic person with a highly developed discriminatory sense of smell.

It is not unusual to find perfumers with an excellent range of odor memory covering hundreds of synthetic and natural raw materials. These he can identify accurately by name, or at least characterize quite accurately when presented to him as unknown raw materials. In this paper, we will report our attempts to employ and develop these skills in a new way, that is, in conjunction with a gas chromatograph.

The perfume chemist has found vapor phase chromatography to be one of the most useful tools for the rapid analysis and evaluation of many complex perfumes and essential oils. Since its inception in 1952, much has been accomplished to improve and enhance the effectiveness of this powerful component separator. In fact, more than 4,000 publications have appeared since the original publication by James and Martin.

Because of the limitations of space, we are assuming in this paper that the functional characteristics of the vapor phase chromatograph are known or are available to the reader. The electronic sensing device which transmits the information to the recorder, is commonly equipped with a "thermal conductivity detector," "flame ionization detector," or "beta-ray ionization detector."

*The Human Sensor*

This paper describes the results obtained when a vapor phase chromatograph is equipped with a "perfumer detector" supplementing the electronic "thermal conductivity cell." The information we will give here may be duplicated in any laboratory using the same equipment and conditions employed in our experiments. We cannot supply the "perfumer detector."

We have investigated the feasibility, usefulness, and advantages of having a perfumer (human sensor) smelling and analyzing the helium stream as it leaves the gas chromatograph.

The smelling and characterization of the larger odorous components eluted from the gas chromatograph is done routinely in many laboratories, as is the collecting or trapping of these materials. However, we are unaware of any published data investigating the capability of a professional perfumer, serving as a human sensor, in smelling and identifying the exit gases. We have examined the accuracy of identification as well as the limitations of such a professional perfumer using this technique and established his usefulness to the chemist operating the vapor phase chromatograph in the evaluation of its chromatograms.

More important than the utilization of the perfumer's odor memory, we also hoped to achieve a furtherance of the perfumer's knowledge of all the odor components contained in a single commercial aromatic or in a natural essential oil, so that he might learn the relationship between the pure major and minor components and the influence the pure minor constituents would have upon the odor complex. Except in rare instances, perfumers are only familiar with the aromatic chemical components when surrounded by minor impurities, both desirable and undesirable. Since the knowledge of the effects of minor components leads to creative thinking, we look upon this technique as opening new horizons for the perfumer.

We began our investigation by designing a clear plastic cover and suspended it over the perfumer's head to avoid the confusing influence of outside odors (FIGURE 1). A heated, insulated tube extended from the gas chromatograph exit port, under the cover, and up to the perfumer's nose. A vacuum system led to the top of the plastic cover to remove the gases after they had passed the perfumer's nose.

As we expected, several disadvantages appeared with this system. It was inconvenient for the perfumer in that he had to maintain a continuously stationary position to prevent burning his nose on the heated tubing, and while in this position, he could not conveniently write or dictate his odor impressions. In addition, the pull of the vacuum not only removed the exit gases, but brought in unwanted outside odors. It did, however, demonstrate the workability of the idea. Unfortunately, it also confirmed the acute sensitivity of the nose to heat as well as to odor.

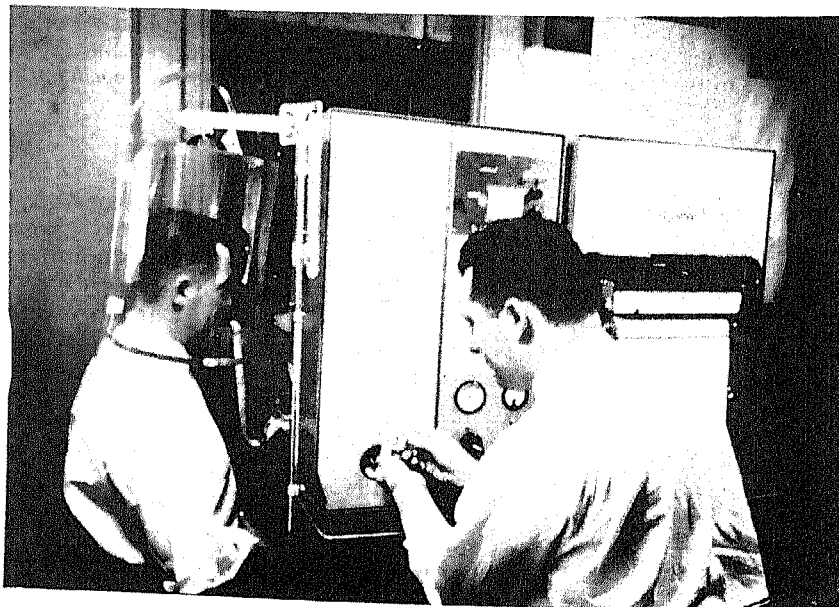


FIGURE 1. Original smelling hood.

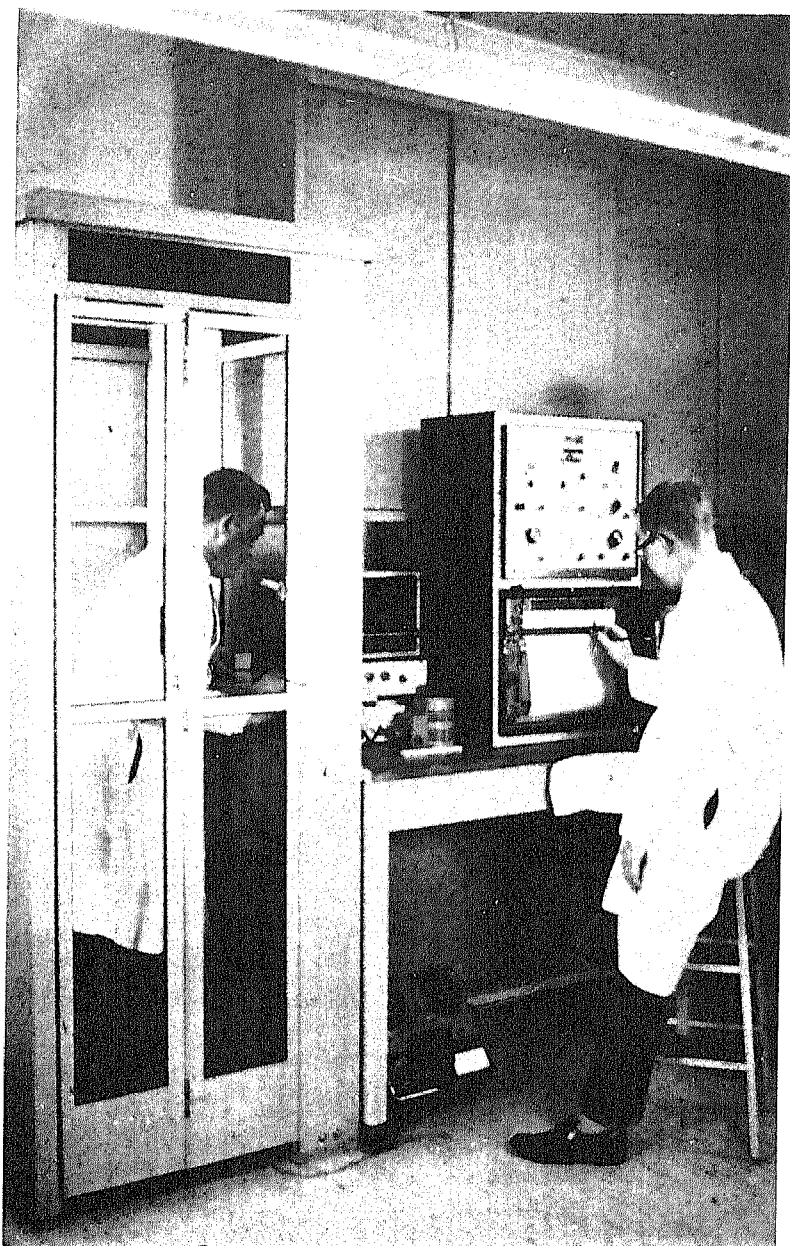


FIGURE 2. The "bird cage" and VPC.

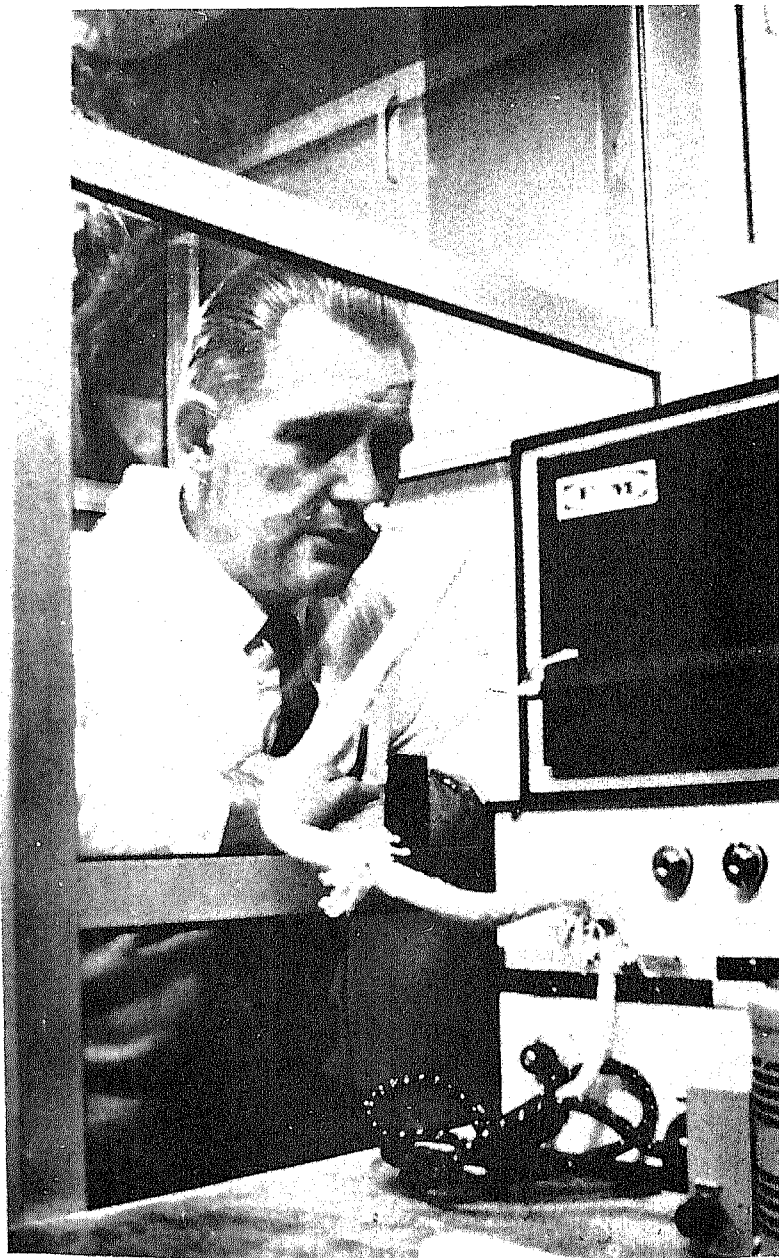


FIGURE 3. Heated exit tube.

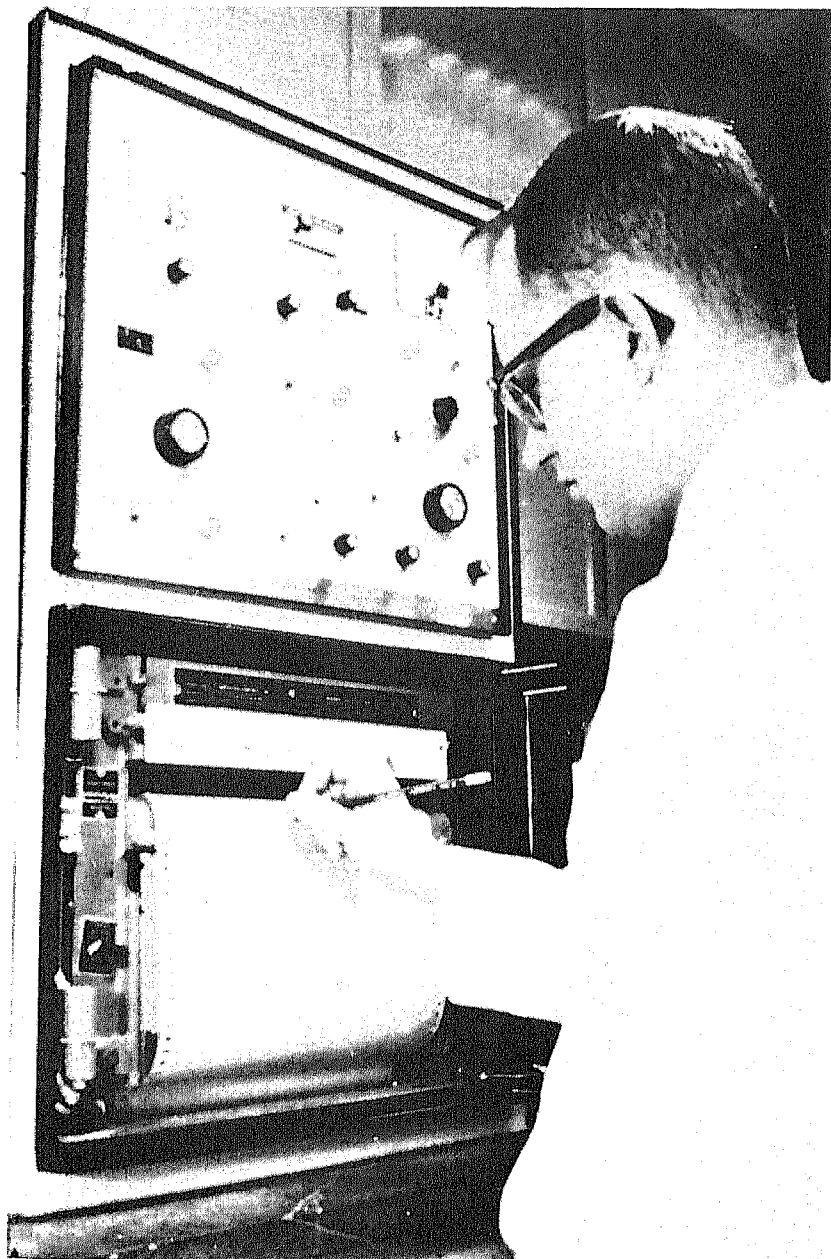


FIGURE 4. The F & M, No. 720 VPC.

We circumvented these problems by employing a telephone booth rather than the plastic cover, and christened it the "bird cage." This is illustrated in FIGURE 2. The exit port of the gas chromatograph was attached to the "bird cage" with stainless steel tubing.

The tubing was heated by resistance wire to maintain the same temperature as the chromatographic column in order to prevent condensation of the eluted components (FIGURE 3). The telephone booth permitted the perfumer to sit comfortably and quietly with his nose immediately above the exit of the tube and to fully concentrate on transmitting his odor impressions. These impressions were either written down along with the observed time taken from a stop watch or dictated into the microphone of a tape recorder. The microphone allows the perfumer to devote his undivided attention to describing the odors in the emerging gas stream.

The components were detected by the perfumer almost exactly at the time the peak was charted by the recorder. The recorder used is shown in FIGURE 4. With the more volatile components, the vapor was detected as the pen was recording the front half of the peak while with the higher boiling materials, the odor was observed as the pen was registering the back side of the peak.

We began our study with the standardization of the human sensor, that is, the familiarization of the perfumer with the pure single aromatics and natural isolates that are commonly used in our perfumery work. The aromatics when eluted in this highly purified state gave clear, highly diffusive notes. They possessed a fineness that might easily excite the expert perfumer who is accustomed only to the commercial aromatic chemical or isolate containing several "fellow travelers" which, like fleas, must be accepted with the dog.

The relative retention times of these materials were determined and are listed in TABLE 1. (For TABLE 1, covering more than 150 aromatics, see Pages 717-719) *Relative* retention times were calculated rather than *absolute* times to eliminate the variables of flow rate, column length, and the ratio of liquid phase to inert support. While these variables affect the absolute retention times, they have little effect on the relative retention time. Column temperatures, however, affect relative retention time data and are always specified.

After this preliminary work, the perfumer's ability to distinguish and identify the components of known mixtures was tested. We began by examining single functional group mixtures of five components and progressed to complex mixed functional groups.

It was encouraging to find that in a system of 15 resolved components, appearing in rapid succession, the perfumer was able to distinguish each peak and correctly identify the *majority* of them. The average results of several of these tests with various 15 component functional group mixtures show the perfumer correctly identifying by chemical name, 10 out of 15.

In FIGURE 5, the perfumer's identification is listed first and when incorrectly identified, it is followed in parenthesis by the correct identification. It can be noted that the perfumer also characterized three minor impurities (Peaks 2, 4, and 6) which were not added intentionally, but were "fellow travelers." These are listed as unknown although the perfumer recorded his odor impression.

The accuracy is more remarkable when it is considered that with many of the mistakenly identified peaks, a material was named that was very close in odor. In FIGURE 6, Peak 11 was described as isborneol rather than borneol. Proper identification was easily possible with the use of the retention time tables.

TABLE I  
ORDER OF RELATIVE RETENTION TIMES

Part A			
Column temperature 160°C. isothermal; linalool = 1.00			
Pentane	0.007	Isooctylacetate	0.67
Dimethyl sulfide	0.034	Methyl heptanol	
Isobutyraldehyde	0.042	(2-methyl-1-hepten-6-ol)	0.68
Acetone	0.045	Dihydromyrcenol	0.71
Ethyl formate	0.048	Furfural	0.80
Nonane	0.064	n-Octyl acetate	0.81
Ethyl propionate	0.081	Alpha-citronellal	0.85
Diacetyl	0.11	Beta-citronellal	0.86
Trans-p-menthane	0.12	Menthone	0.93
Propyl propionate	0.12	n-Decaldehyde (aldehyde C-10)	0.94
Tricylcene	0.13	Indene	0.99
Alpha-pinene	0.14	Linalool (Reference Standard)	1.00
n-Butyl acetate	0.14	n-Octyl alcohol (alcohol C-8)	1.03
n-Caproaldehyde (aldehyde C-6)	0.15	Isomenthone	1.03
3-p-Mentene	0.16	Benzaldehyde	1.10
n-Butyl alcohol	0.16	Linalyl acetate	1.16
Camphene	0.17	Camphor	1.18
Amyl acetate	0.17	Myrcenyl acetate	1.27
Di-n-propyl ketone	0.18	Isopulegol	1.31
Allyl acetone	0.18	Linalyl formate	1.38
Beta-pinene	0.21	Methyl nonyl ketone	1.43
Myrcene	0.22	Bornyl acetate	1.44
3-Carene	0.23	Isobornyl acetate	1.48
n-Heptaldehyde (aldehyde C-7)	0.24	Aldehyde C-11 (undecylic)	1.48
Alpha-phellandrene	0.25	Linalyl propionate	1.48
n-Amyl alcohol	0.26	Beta-terpineol	1.54
Cumene	0.27	Methyl n-nonyl acetaldehyde	
Limonene	0.28	(aldehyde C-12 MNA)	1.58
2-Hexen-1-al (leaf aldehyde)	0.29	Menthol	1.58
1,8-Cineol	0.31	Furfuryl alcohol	1.60
Ethyl amyl ketone	0.33	Methyl benzoate	1.62
Dibutyl sulfide	0.36	Caryophyllene	1.65
Styrene	0.36	n-Nonyl alcohol (alcohol C-9)	1.67
Methyl hexyl ketone	0.37	Dimethyloctanol	
p-Cymene	0.38	(3,7-dimethyl-1-octanol)	1.68
n-Caprylaldehyde (octanal)	0.38	Methyl heptene carbonate	
n-Amyl-n-butyrate	0.41	(methyl 2-octynoate)	1.70
Terpinolene	0.41	Isovaleric acid (unsym.)	1.79
Linalyl methyl ether	0.44	Citronellyl acetate	1.81
Cis or trans-2-hexen-1-ol		Acetophenone	1.81
(beta-gamma-hexenol)	0.44	Aldehyde C-11 (undecylenic)	1.85
Methyl heptenone		Isoborneol	1.89
(2-methyl-1-hepten-6-one)	0.46	Pulegone	1.90
Cis-3-hexen-1-ol	0.49	n-Decyl acetate	1.99
3-Octanol	0.50	Beta-citral (neral)	2.00
n-Heptyl acetate	0.52	Alpha-terpineol	2.05
Cis-rose oxide	0.53	Linalyl butyrate	2.05
Allo-ocimene (minor isomer)	0.53	Borneol	2.15
Cis or trans-2-hexen-1-ol		Alpha-terpinyl acetate	2.20
(beta-gamma-hexenol)	0.54	n-Dodecaldehyde (aldehyde C-12)	2.29
Tetrahydrocitraal (dimethyloctanal)	0.58	Benzyl acetate	2.41
Trans-rose oxide	0.58	Alpha-citral (geranial)	2.43
n-Nonaldehyde (aldehyde C-9)	0.60	n-Decyl alcohol (alcohol C-10)	2.49
Alloocimene (major isomer)	0.60	Piperitone	2.56
Tetrahydrolinalool	0.61	Carvone	2.60
3-Hydroxy-2,2,6-trimethyl-6-vinyl		Citronellol	2.61
tetrahydropyran	0.67	Geranyl formate	2.61

TABLE 1 (Continued)

Geranyl acetate	2.67	Benzyl alcohol	3.91
Alpha-terpinyl propionate	2.78	Alpha-ionone	3.97
Methyl acetophenone	2.96	Phenylethyl alcohol	4.79
Nerol	3.09	Hydroxycitronellal	
Allyl cyclohexane propionate	3.28	(7-hydroxy-3,7-dimethyloctanal)	5.18
Geranyl propionate	3.48	Diphenyl oxide	7.53
Geraniol	3.65	p-Cresol	8.71
Order of functional groups			
Column temperature 160°C. isothermal; linalool = 1.000			
Hydrocarbons			
Pentane	0.007	Cumene	0.27
Nonane	0.064	Limonene	0.28
Trans-p-menthane	0.12	Styrene	0.36
Tricyclene	0.13	p-Cymene	0.38
Alpha-pinene	0.14	Terpinolene	0.41
Camphene	0.17	Allo-ocimene (minor isomer)	0.53
Beta-pinene	0.21	Allo-ocimene (major isomer)	0.60
Myrcene	0.22	Indene	0.99
3-Carene	0.23	Caryophyllene	1.65
Alpha-phellandrene	0.25		
Alcohols and phenols			
Ethanol	0.055	Beta-terpineol	1.54
n-Butyl alcohol	0.16	Menthol	1.58
n-Amyl alcohol	0.26	Furfuryl alcohol	1.60
Cis or trans-2-hexen-1-ol (beta-gamma-hexanol)	0.44	n-Nonyl alcohol (alcohol C-9)	1.67
Cis-3-hexen-1-ol	0.49	Dimethyl octanol	1.68
3-Octanol	0.50	Isoborneol	1.89
Cis or trans-2-hexen-1-ol (beta-gamma-hexanol)	0.54	Alpha-terpineol	2.05
Tetrahydrolinalool	0.61	n-Decyl alcohol (alcohol C-10)	2.49
Methyl heptenol	0.68	Citronellol	2.61
Dihydromyrcenol	0.71	Nerol	3.09
Linalool	1.00	Geraniol	3.65
n-Octyl alcohol (Alcohol C-8)	1.03	Benzyl alcohol	3.91
Isopulegol	1.31	Phenylethyl alcohol	4.79
		p-Cresol	8.71
Aldehydes			
Isobutyraldehyde	0.042	Benzaldehyde	1.10
n-Caproaldehyde (aldehyde C-6)	0.15	Aldehyde C-11 (undecylic)	1.48
n-Heptaldehyde (aldehyde C-7)	0.24	Methyl-n-nonyl acetaldehyde (aldehyde C-12 MNA)	1.58
2-Hexen-1-ol (leaf aldehyde)	0.29	Aldehyde C-11 (undecylenic)	1.85
n-Caprylaldehyde (aldehyde C-8)	0.38	Beta-citral (neral)	2.00
Furfural	0.80	n-Dodecaldehyde (aldehyde C-12)	2.29
Alpha-citronellal	0.85	Alpha-citral (geranial)	2.43
Beta-citronellal	0.86	Hydroxycitronellal	5.18
n-Decaldehyde (aldehyde C-10)	0.94		
Ketones			
Acetone	0.045	Menthone	0.93
Diacetyl	0.11	Isomenthone	1.03
Allyl acetone	0.18	Camphor	1.18
Di-n-propyl ketone	0.18	Methyl nonyl ketone	1.43
Ethyl amyl ketone	0.33	Acetophenone	1.81
Methyl hexyl ketone	0.37	Pulegone	1.90
Methyl heptenone (2-methyl- 1-hepten-6-ol)	0.46		



TABLE 1 (Continued)

Esters			
Ethyl formate	0.048	Methyl benzoate	1.62
Ethyl propionate	0.081	Methyl heptine carbonate	1.70
Propyl propionate	0.12	Citronellyl acetate	1.81
Butyl acetate	0.14	Amyl caprylate	1.86
Amyl acetate	0.17	Decyl acetate	1.99
Amyl butyrate	0.41	Linalyl butyrate	2.05
Heptyl acetate	0.52	Alpha-terpinyl acetate	2.20
Isooctyl acetate	0.67	Benzyl acetate	2.41
Octyl acetate	0.81	Geranyl formate	2.61
Linalyl acetate	1.16	Geranyl acetate	2.66
Myrcenyl acetate	1.27	Alpha-terpinyl propionate	2.78
Linalyl propionate	1.48	Allyl cyclohexane propionate	3.28
Linalyl isobutyrate	1.48	Geranyl propionate	3.48
Miscellaneous			
Dimethyl sulfide	0.034	Trans-rose oxide	0.58
1,8-Cineol	0.31	3-Hydroxy-2,2,6-trimethyl- 6-vinyl tetra-hydropyran	0.67
Dibutyl sulfide	0.36	Isovaleric acid	1.79
Linalyl methyl ether	0.44	Diphenyl oxide	8.71
Cis-rose oxide	0.53		
Part B			
Column temperature 100°C. isothermal; beta-pinene = 1.00			
Pentane	0.020	Alpha-phellandrene	1.34
Ethanol	0.26	Cumene	1.38
Benzene	0.35	Alpha-terpinene	1.45
Tricyclene	0.56	Limonene	1.62
Trans-p-menthane	0.58	Cineol	1.72
Alpha-pinene	0.60	p-Cymene	2.43
3-p-Menthane	0.75	Aldehyde C-8	2.59
Camphene	0.79	Terpinolene	2.63
Beta-pinene	1.00	Alloocimene (minor isomer)	4.19
3-Carene	1.24	Alloocimene (major isomer)	4.78
Myrcene	1.24		
Part C			
Column temperature 185°C. isothermal; carvone = 1.00			
Estragole	0.76	Gamma-ionone	1.61
Carvone	1.00	Phenylethyl alcohol	1.67
Cis-anethole	1.03	Alpha-methylionone	1.84
Trans-anethole	1.29	Beta-ionone	1.95
Alpha-ionone	1.47	Gamma-n-methylionone	2.04
Alpha-isomethylionone	1.48	Beta-n-methylionone	2.44
Beta-isomethylionone	1.60	Anisic aldehyde	2.62

Operating conditions: instrument, F & M Model 720 gas chromatograph; stationary liquid phase, carbowax 20 M.; solid support; chromosorb P mesh size 35/80; concn. stationary phase, 20 per cent (weight); column length, six feet; column tubing, stainless steel, one-quarter inch O.D.; gas flow, 50 ml./min.; temperature °C., 100, 160, 185; injection port °C., 210; block °C., 200; bridge power, 180 ma.

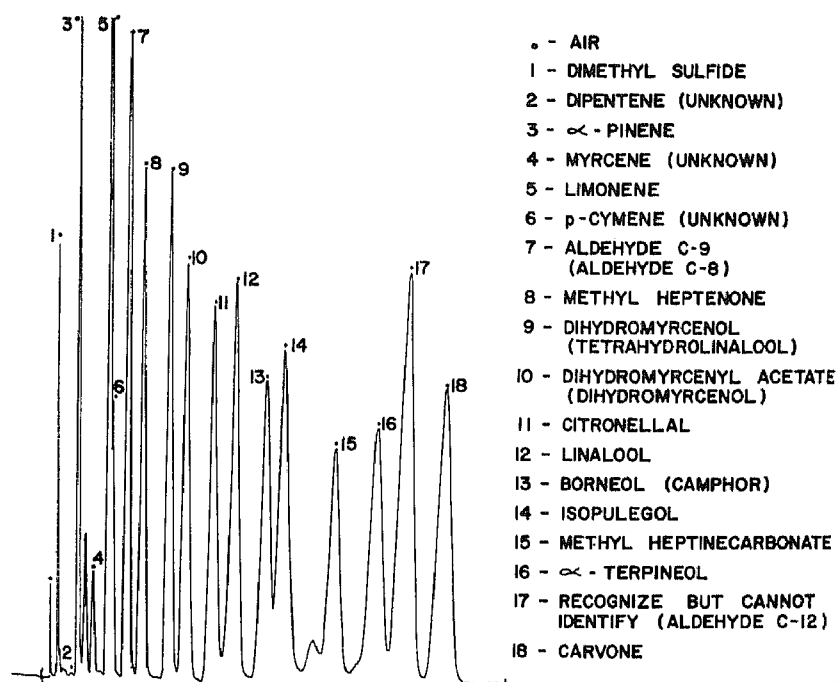


FIGURE 5. Fifteen component mixed functional groups. F & M model 720; column: six feet, carbowax 20 M.; programmed:  $160^{\circ}$  @  $1^{\circ}/\text{min.}$ ; sample:  $4\lambda$ .

#### Practical Threshold

An effort was made to establish the *limits* to which the human sensor could detect and identify the components. In establishing these thresholds, varying concentrations of ethanolic solutions of both mild and strong odor bodies were prepared. By varying the concentration of the solution and the size of sample injection, an approximate threshold was determined.

The point at which the human sensor could just detect and identify the sample was taken as the practical threshold. In the case of the stronger odor bodies, such as methyl heptene carbonate, a one microliter ( $1 \times 10^{-3}$  ml.) sample size was detected and identified, although present in only a few parts per one hundred thousand. At this concentration, the instrument, having a detector consisting of a thermal conductivity cell employing a heated metal filament, did *not* record a peak. In TABLE 2 the thresholds are listed in order of per cent of compound in the ethanolic solution at a one microliter sample size. The parts per one hundred thousand at this sample size are listed along with the milligrams and number of molecules that this sample size constitutes.

It is extremely important, we believe, to avoid conditioning the perfumer's mind before his entering the "bird cage." All work reported here was "blind" evaluation on the part of the perfumer. The sample was not identified until after the experiment was performed; we think this is critical if the odor identification is to be helpful to the chemist. It also places a tremendous burden on the per-

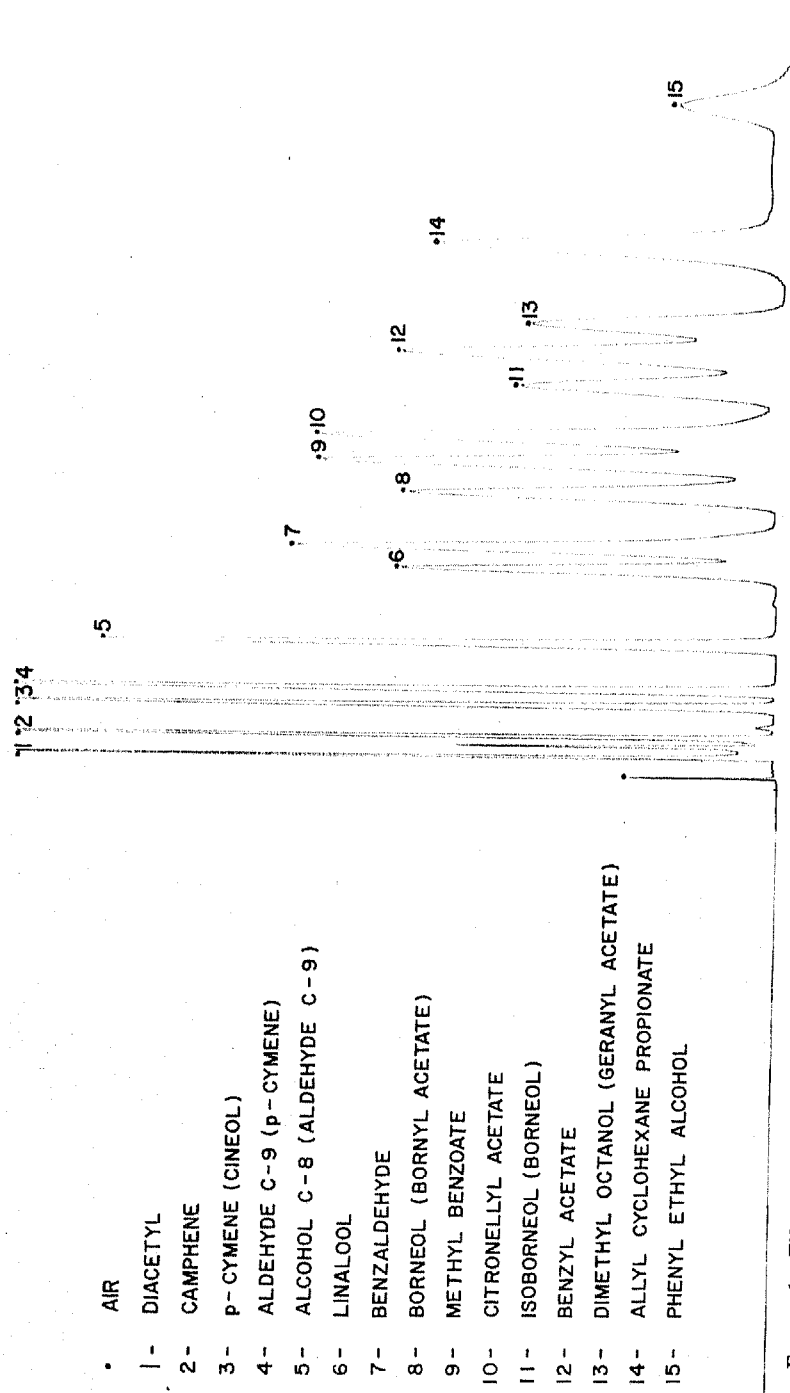


FIGURE 6. Fifteen component mixed functional groups. Conditions: six foot carbowax 20 m. column; programmed for 160° C. at 1°/min.; 4γ sample size.

TABLE 2  
 PRACTICAL THRESHOLDS

Compound	Per cent of compound in ethanol detected at a 1 $\lambda$ sample size	Milligrams	Molecules	Parts per 100,000; 1 $\lambda$ sample size
Methyl heptene carbonate	$6.0 \times 10^{-3}$	$4.8 \times 10^{-8}$	$1.9 \times 10^{11}$	6.0
Cineol	$7.8 \times 10^{-3}$	$6.2 \times 10^{-8}$	$2.4 \times 10^{11}$	7.8
Dibutyl Sulfide	$1.1 \times 10^{-2}$	$8.8 \times 10^{-8}$	$3.6 \times 10^{11}$	11
Citronellal	$6.5 \times 10^{-2}$	$5.2 \times 10^{-7}$	$2.0 \times 10^{12}$	65
Methyl heptenone	$7.9 \times 10^{-2}$	$6.3 \times 10^{-7}$	$3.0 \times 10^{12}$	79
Aldehyde C-9	$1.2 \times 10^{-1}$	$9.6 \times 10^{-7}$	$4.1 \times 10^{12}$	120
Limonene	$7.2 \times 10^{-1}$	$5.8 \times 10^{-6}$	$2.6 \times 10^{13}$	720
Linalool	1.4	$1.1 \times 10^{-5}$	$4.3 \times 10^{13}$	1,400

fumer's nose, his training, and his skill in achieving almost instant odor recognition during the fleeting moments when a few molecules reach his nasal receptors.

With the foregoing data, we have attempted to demonstrate that a professional perfumer can effectively detect and identify the trace quantities of aromatic chemicals in the eluted helium stream from the gas chromatograph. We feel that this technique offers unique advantages to both the perfumer and the chemist.

To the perfumer, it offers the opportunity to judge the effects of the pure components and single isomers previously unobtainable. He can judge the effects of odor bodies which have yet to be isolated or discovered.

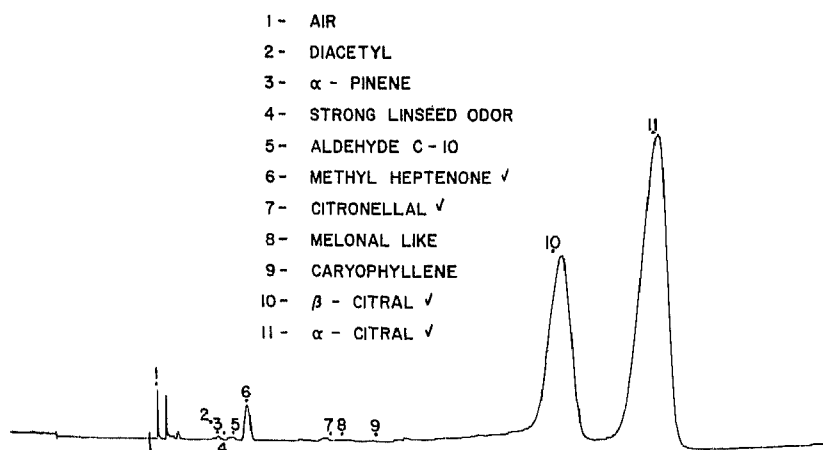


FIGURE 7. Citral *ex* lemongrass. Denotes that the relative retention time confirms the odor description. Conditions: six-foot carbowax 20 M. column; column temperature, 160° C. (isothermal); 2 $\lambda$  sample size at attenuation 8.

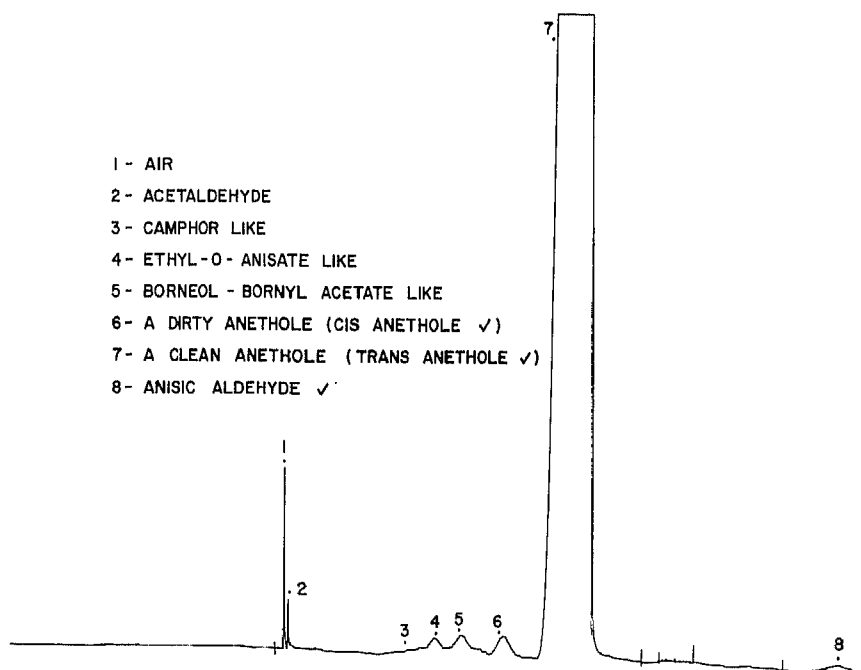


FIGURE 8. Anethole *ex* pine oil. ✓ Denotes that peak was confirmed by retention time. Conditions: six-foot carbowax 20 M. column; column temperature, 185° C. (isothermal); 4λ sample size at attenuation 2.

To the chemist, the technique frequently provides rapid identification of many materials not easily recognized because no retention time data is available. When this identification by the perfumer can be supported by the retention time data, we have reasonably sound evidence that the identification is correct.

Some practical examples of this technique are illustrated in the analyses of commercial citral and anethole (see FIGURES 7 and 8, respectively). With commercial citral, the perfumer, for the first time, became aware of the odors of pure beta and alpha isomers, free of traces of citronellal and methyl heptenone. Since the perfumer was positive in his identification of the methyl heptenone and citronellal and those assignments were supported by retention times, this provided the chemist with a fair amount of evidence in identifying these two components. Beta citral resembles citronellal in odor. It offers a fine example of the utility of powerful related odor components in pushing, without obvious alteration, a major note. The time for the analysis of the citral was about 30 minutes.

The anethole analysis arose from a need to explain a definite, but a very slight difference, in organoleptic quality between two samples, both of which presumably originated with pine oil. By a normal gas chromatographic run, each sample analyzed better than 99 per cent anethole. The infrared spectra could be superimposed on one another. However, with the electronic detector at highest sensitivity and a larger sample size, several small peaks appeared. These small components were easily detected by the human sensor. By comparison with the retention times of known compounds, several identifications were made. Thus, the

odor of *cis* anethole was revealed to the perfumer, and anisic aldehyde was correctly identified as the organoleptic quality factor. One sample contained three times as much anisic aldehyde as the other. This may have been due to age or longer exposure to the atmosphere, since on such exposure, the anisic aldehyde content increases. It was, therefore, possible to establish quantitative limits for the component, anisic aldehyde, which in tenths of one per cent affects organoleptic quality of a 99. + per cent pure material.

The human sensor can also aid the chemist by judging whether or not a supposedly "single peak" is completely resolved by characterizing both sides of such a single peak, and whether or not decomposition or isomerization is occurring. In addition, new odor bodies may be uncovered, which, if interesting enough, could be isolated and investigated.

Of course, there are many peaks which the perfumer is unable to identify or even closely characterize. However, at this point, we still firmly feel that the technique offers much to both the perfumer and the chemist.

Further work will involve the collection of more retention data on several columns, the development of trapping techniques, and the graphing of homologous series versus retention time data. With this data, it is possible to project new compounds not now available.