

CHROM. 7145

CHARACTERIZATION OF HYDROCARBONS IN COMPLEX MIXTURES BY TWO-DIMENSIONAL PRECISION GAS CHROMATOGRAPHY

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SUMMARY

A system is described consisting of two high-resolution capillary columns of different polarity placed in series. Compounds which are not separated or incompletely separated on the first column can be resolved and characterized on the second column. The system enables the selective transfer of one or more peaks eluted from the first column on to the second column without trapping. For both columns a precision is attained corresponding to a standard deviation less than 0.05 index units for all types of hydrocarbons.

INTRODUCTION

The use of different temperatures and of different columns adds considerably to the characterization of compounds in complex mixtures¹. The possibility of overlap of retention data can be greatly reduced in this way.

A difficulty in the application of columns of different polarity for the analysis of complex mixtures is the recognition of corresponding peaks, which is complicated because of the elution order.

To solve this problem a system is developed, consisting of two high-efficiency open-hole tubular columns placed in series. It is based on the principles of counter pressure and venting between the columns²⁻⁴. The magnitude of the counter pressure and the resistance of the vent have to be carefully adjusted to the resistance of both columns and the resistance of the connections between the columns. There are no valves in the sample path, so that the dead volume associated with the use of valves is eliminated. Obviously, the absorption of sample components in the lubricants of these valves is also eliminated.

The components eluted from the first column may be selectively transferred to a second column of different polarity. In this way, compounds which are not separated or are incompletely separated on the first column can be resolved and characterized on the second column.

The precision of the retention data obtained with this system, on both columns, is of the same order as the precision obtained with single columns (S.D. < 0.05 index units). This will be demonstrated on some mixtures of hydrocarbons.

The system can also be applied to qualitative analyses of trace components.

EXPERIMENTAL

System design

The system is shown schematically in Fig. 1.

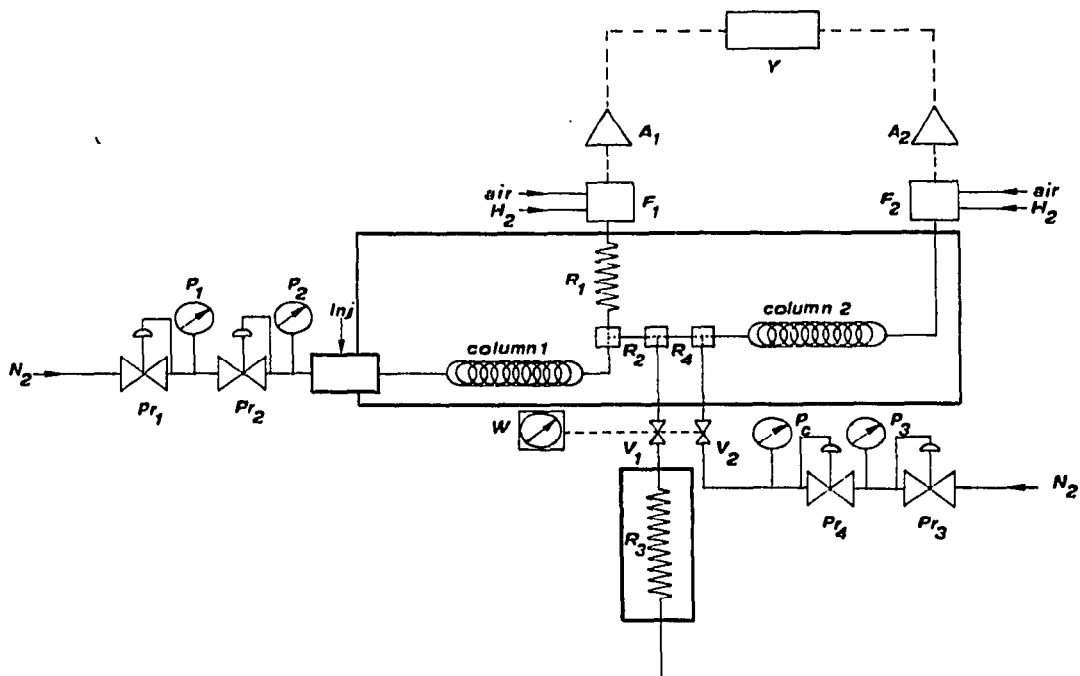


Fig. 1. Schematic diagram of the system. Pr_1 – Pr_4 = Pressure controllers; P_2 = column inlet pressure; P_c = counter pressure. F_1 , F_2 = flame ionization detectors; A_1 , A_2 = detector amplifiers; Y = recorder (two tracks); R_1 , R_2 , R_4 = restrictions (for dimensions, see Fig. 2); R_3 = stainless-steel capillary restriction, 86 m \times 0.25 mm I.D.; Inj. = inlet system; V_1 , V_2 = solenoid valves; W = time delay switch. Columns: (1) 100 m \times 0.25 mm I.D., stainless steel, squalane; (2) 75 m \times 0.25 mm I.D., stainless steel, acetyl tributyl citrate (Citroflex A4).

The dimensions of the connections (stainless-steel capillaries) between the columns, the vent and the first detector are given in Fig. 2.

To strengthen the restriction (R_1) feeding the first flame ionization detector, it is guided by a modified syringe needle as shown in Fig. 2

The carrier gas velocity is controlled by two pressure controllers (Model MB-19936; Packard-Becker, Delft, The Netherlands), placed in series. The pressure drop over the columns (P_2), which is controlled within 0.002 atm during one analysis, is registered with a high-quality differential manometer (Model FA 145; Wallace and Tiernan, Günzberg, G.F.R.). The counter pressure P_c is controlled and measured in the same way.

The temperature of the part outlined in Fig. 1 is kept constant within 0.01° by a water thermostat (Model TEV 70; Tamson, Zoetermeer, The Netherlands).

The sample is introduced into the first column via an injection system with splitter (Hamilton, Reno, Nev., U.S.A.).

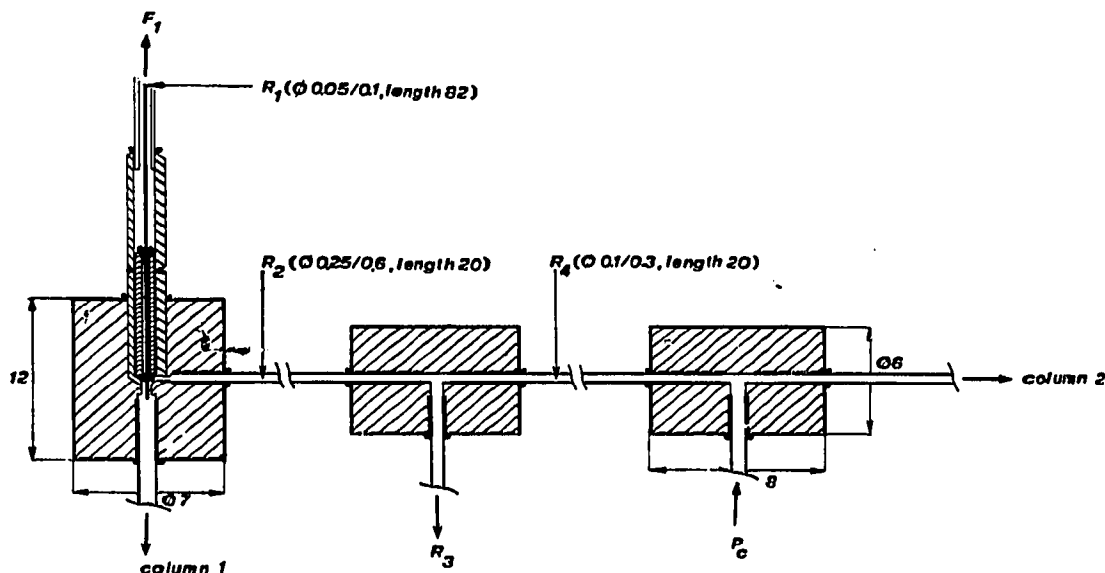


Fig. 2. Connections between the columns, vent and detector for the first column. Dimensions in millimetres.

A small part of the gas leaving the first column is split off to the first detector (F_1) via restriction R_1 . The detector signal is registered on a two-pen recorder (Y , track 1).

The rest of the eluent is led through the vent R_3 when the solenoid valves V_1 and V_2 (No. 133 A03, Lucifer Geneva, Switzerland) are open (normal situation) and is transferred to the second column when these valves are closed.

For a selective injection of a peak on to the second column these valves, which can be actuated simultaneously by the time delay switch W (Type MZ54, Schleicher, Berlin, G.F.R.), are closed during a short time (Δt). A peak, which is detected at the same time by F_1 , will be transferred during this time to the second column. The quantity of sample transferred to the second column can be controlled by variation of Δt . The peaks eluted from the second column are also registered on recorder Y (track 2).

Adjustment of counter pressure and vent resistance

The precision of retention data obtained with the system on both columns is affected by the dead volume of the connection between the columns and the constancy of the carrier gas velocity in the columns.

To avoid additional peak broadening and peak asymmetry, the dead space of the coupling between the columns is made negligibly small. As can be seen in Fig. 2, no valves are in the sample path and sharp corners at the changeover of the capillary connections are eliminated as far as necessary.

The carrier gas velocity in both columns must be independent of valves V_1 and V_2 being open or closed.

Therefore, in the first instance the resistance of the vent R_3 must be equal to the total resistance of the second column and the connection between this column

and the vent. With a vent resistance about the same as the resistance of the second column, the counter pressure, P_c , was adjusted under the following experimental conditions:

Column 1: 100 m \times 0.25 mm I.D.; stationary phase, squalane; plate number, $\approx 5 \cdot 10^5$ for *n*-hexane ($k = 0.8$). Column 2: 75 m \times 0.25 mm I.D.; stationary phase, acetyltributyl citrate; plate number, $\approx 3 \cdot 10^5$ for *n*-hexane ($k = 0.5$). Inlet pressure, 2.500 ± 0.002 atm above atmospheric pressure. Quantity of sample, about 10^{-8} g/component. Temperature, $50 \pm 0.01^\circ$.

In the ideal case the counter pressure, P_c , should fulfill the following conditions: (1) The retention time of a compound must be independent of the valves being open or closed for both columns. (2) No compounds should be transferred to the second column when these valves are open. (3) The height of the peaks on both columns should be of the same order.

In Fig. 3 the retention time of methane is given as a function of the counter pressure at 50° for both columns. Methane is chosen because the relative error in retention time is maximal for this compound.

The first condition corresponds to points A and B (Fig. 3) for the first and second column, respectively. The optimal counter pressure, which was also calculated

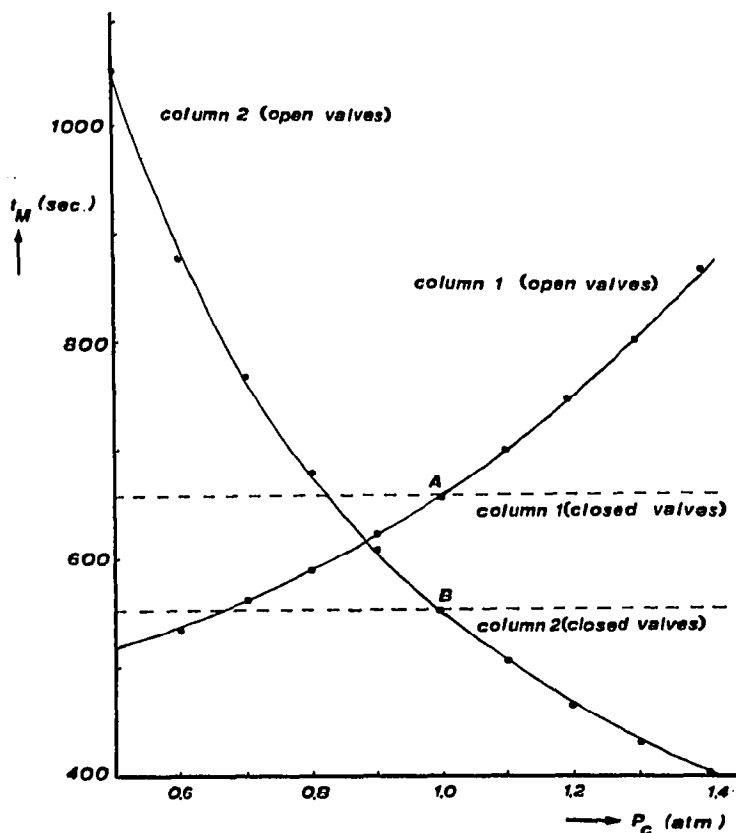


Fig. 3. Retention time of methane (t_M) as a function of counter pressure (P_c) at 50° for both columns.

by polynomial curve fitting for both points, appeared to be 1.004 atm at 50° and 0.973 atm at 70°. At these counter pressures conditions (2) and (3) are also satisfied.

The difference in t_M per column, depending on whether the valves are continuously open or closed, is about 0.4%, as can be seen in Table I. As in practice these valves will be only closed during the short time of sample transfer, this difference will be much smaller.

TABLE I
DEPENDENCE OF THE RETENTION TIME OF METHANE ON THE POSITION OF THE VALVES

	t_M (sec)			
	Column 1		Column 2	
	Open valves	Closed valves	Open valves	Closed valves
$P_c = 1.004$ atm; $T = 50^\circ$	656.8	658.3	549.3	551.3
$P_c = 0.973$ atm; $T = 70^\circ$	673.1	672.7	592.3	595.0

Measurement of retention indices on the second column

Because a selected peak is transferred to the second column at the moment its peak maximum is observed with the first detector, F_1 , the injection time is different for each peak. The injection width for the second column (Δt) was 3 sec in all cases. To enable the estimation of retention indices on the second column, methane and the bracketing n -alkanes should also be transferred to this column.

The retention time of the components on both columns is measured in the first instance as from the moment of injection on the first column. It can be seen from Fig. 4 that the adjusted retention time of a component i on the second column can be calculated by

$$t'_{i,2} = t_{i,2} - t_{i,1}^* - (t_{M,2}^* - t_{M,1})$$

where

$t'_{i,2}$ = adjusted retention time of component i on column 2

$t_{i,1}$ = retention time of component i on column 1

$t_{M,1}$ = retention time of methane on column 1

$t_{i,2}^*$ = total retention time of component i on both columns

$t_{M,2}^*$ = total retention time of methane on both columns

RESULTS AND DISCUSSION

In the first instance the potential of the system is demonstrated on a simple synthetic mixture of four hydrocarbons, the bracketing n -alkanes and methane. The composition of the mixture was chosen in such a way that three of the components were not separated on the first column, as shown in Fig. 5 (track 1). This peak, which is partly transferred to the second column, appears as expected to consist of three components. Retention indices measured on both columns at 50° are given in Table II.

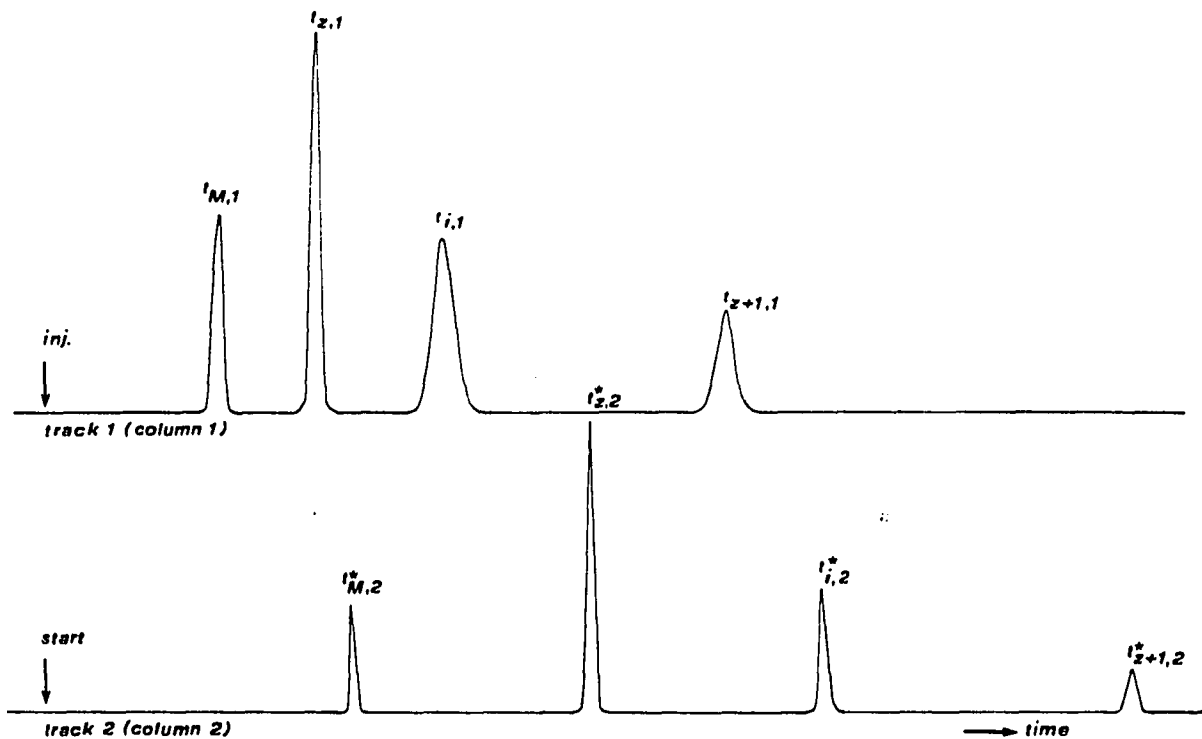


Fig. 4. Estimation of adjusted retention times on column 2. $t_{z,1}$ and $t_{z+1,1}$ are retention times of n -alkanes with z , respectively, $z+1$ carbon atoms on column 1; $t_{z,2}^*$ and $t_{z+1,2}^*$ are total retention times of these components on both columns.

Comparison of measured and tabulated retention indices⁵ on the squalane column results in three possible assignments for peak 7 + 8 + 9 (track 1), with a search window of 1.0 index unit, which is based on the separation power of the column. From the retention indices on the second column it can be concluded that peak

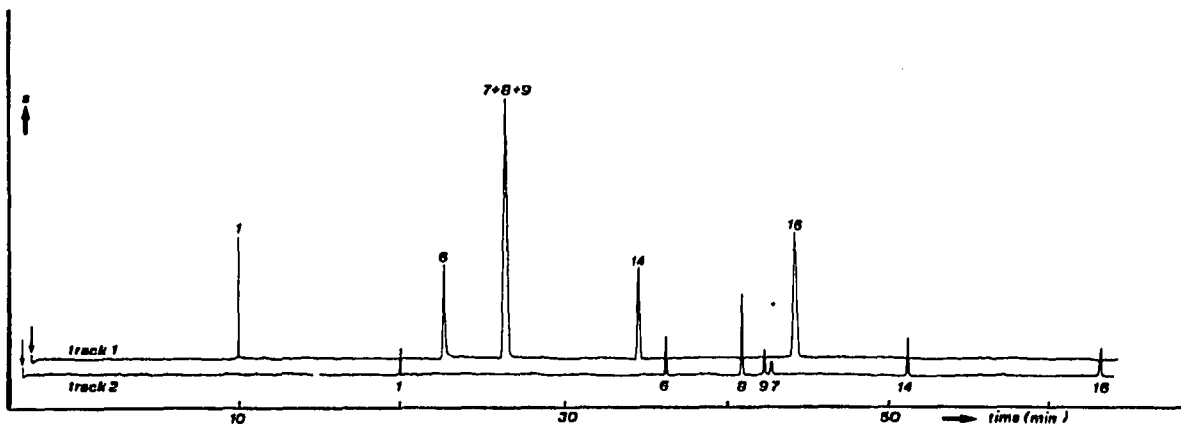


Fig. 5. Chromatogram of a mixture of four hydrocarbons (7 + 8 + 9, 14), the bracketing n -alkanes (6, 16), and methane (1). Column 1: track 1; column 2: track 2. Counter pressure, 1.004 ± 0.002 atm. For further conditions, see text.

TABLE II

COMPARISON OF RETENTION INDICES OBTAINED WITH THE SYSTEM AND TABULATED DATA AT $50 \pm 0.01^\circ$

Abbreviations: s = system, t = tabulated, sq = squalane, ac = acetyltributyl citrate. Number of measurements: 5.

Peak No.	$I_{sq,s}$	$I_{sq,t}$	Δ_{s-t}	Name	$I_{ac,s}$	$I_{ac,t}$	Δ_{s-t}
1				Methane			
6				<i>n</i> -Hexane			
7	625.49	625.12	0.37	2,3-Dimethyl-2-butene	663.27	663.35	-0.08
8		625.64	-0.15	2,2-Dimethylpentane	625.81	625.67	0.14
9		626.18	-0.69	3,3-Dimethyl-1-pentene	655.92	655.96	-0.04
14	662.62	666.63	-0.01	2-Methylhexane	666.97	666.96	0.01
16				<i>n</i> -Heptane			

7 + 8 + 9 consists of 2,3-dimethyl-2-butene, 2,2-dimethylpentane, and 3,3-dimethyl-1-pentene.

A considerable gain in time will result if more than one compound is transferred to the second column during one run. However, some troubles can be expected in this case. Depending on the combination of peak inversion and different injection times on the second column, peaks which are normally completely separated on the second column may now co-elute with another component. On the other hand, two components which are only partly separated on the first column can give rise to twin peaks on the second column (two injections). In both cases a decrease in precision can be expected, as will be demonstrated in the following example. The retention indices were measured for a synthetic mixture of thirteen hydrocarbons, the bracketing *n*-alkanes and methane with the system at 50° (Fig. 6 and Table III) and 70° (Fig. 7 and Table IV). All the components were transferred to the second column during one run.

The elution order of the components on the second column is not necessarily the same as the order of the magnitude of the retention indices on this column. This

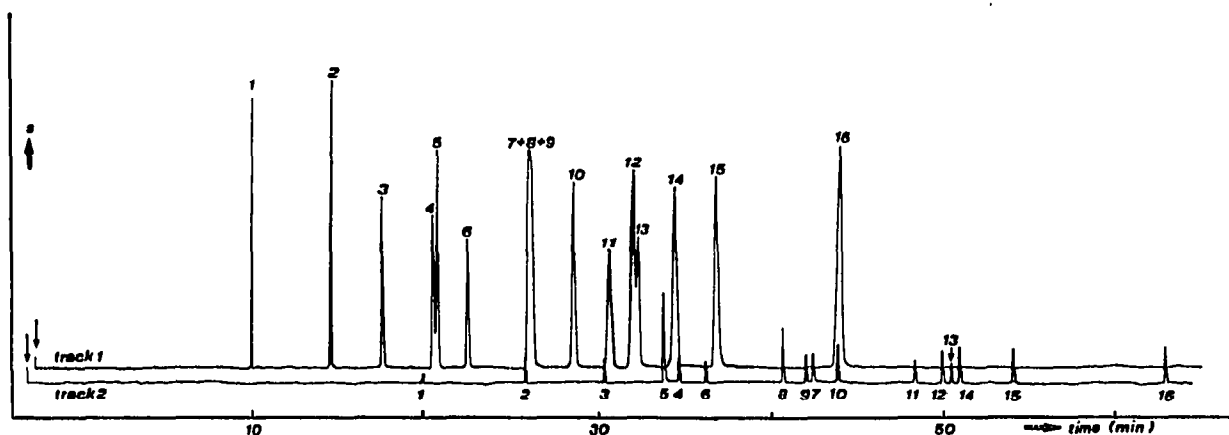


Fig. 6. Chromatogram of a mixture of hydrocarbons at 50° . Experimental conditions as in Fig. 5.

TABLE III

COMPARISON OF RETENTION INDICES OBTAINED WITH THE SYSTEM AND TABULATED VALUES AT $50 \pm 0.01^\circ$

Abbreviations: s = system, t = tabulated, sq = squalane, ac = acetyltributyl citrate, S.D. = standard deviation. Number of measurements: 5.

Peak No.	$I_{sq,s}$	S.D.	$I_{sq,t}$	Δ_{s-t}	Name	$I_{ac,s}$	S.D.	$I_{ac,t}$	Δ_{s-t}
1					Methane				
2					<i>n</i> -Pentane				
3	549.33	<0.01	549.35	-0.02	4-Methyl-1-pentene	581.29	0.03	581.38	-0.09
4	582.23	<0.01	582.25	-0.02	1-Hexene	616.78	0.04	616.87	-0.09
5	584.22	<0.01	584.24	-0.02	3-Methylpentane	585.25	0.04	585.33	-0.08
6					<i>n</i> -Hexane				
7			625.12	0.37	2,3-Dimethyl-2-butene	663.27	0.01	663.35	-0.08
8	625.49	0.02	625.64	-0.15	2,2-Dimethylpentane	625.81	0.01	625.67	0.14
9			626.18	-0.69	3,3-Dimethyl-1-pentene	655.92	0.03	655.96	-0.04
10	639.67	<0.01	639.70	-0.03	2,2,3-Trimethylbutane	641.88	0.03	641.88	0.00
11	650.39	<0.01	650.44	-0.05	2,3-Dimethyl-1-pentene	684.17	0.01	684.18	-0.01
12	656.62	<0.01	656.66	-0.04	4-Methyl- <i>trans</i> -2-hexene	684.18	0.03	684.20	-0.02
13	657.83	<0.01	657.90	-0.07	4-Methyl-1-hexene	691.20	0.04	691.21	-0.01
14	666.62	<0.01	666.63	-0.01	2-Methylhexane	666.97	0.02	666.96	0.01
15	676.21	<0.01	676.21	0.00	3-Methylhexane	677.39	0.02	677.42	-0.03
16					<i>n</i> -Heptane				

is due to the interaction of peak inversion and different injection times on the second column. This is clearly demonstrated in Tables III and IV.

In spite of the incomplete separation of components 4, 5 and 12, 13 on the first column, the influence of peak shift is only slightly noticeable for the last two components at 50° . The effect of peak inversion for components 4 and 5 is so large that they are completely separated on the second column, at both temperatures. Components 13 and 14, however, are co-eluted at 70° , resulting in decreased precision, especially for component 13.

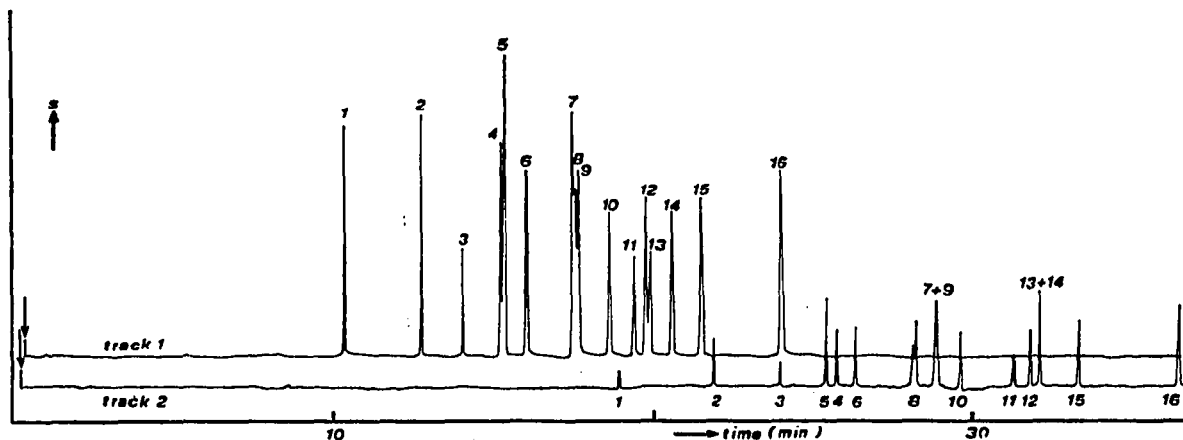


Fig. 7. Chromatogram of a mixture of hydrocarbons at 70° . Counter pressure, 0.997 ± 0.002 atm. Experimental conditions as in Fig. 5.

TABLE IV

COMPARISON OF RETENTION INDICES OBTAINED WITH THE SYSTEM AND TABULATED DATA AT $70 \pm 0.01^\circ$

Abbreviations: see Table III. Number of measurements: 4.

Peak	$I_{sq,s}$	S.D.	$I_{sq,t}$	Δ_{s-t}	$I_{ac,s}$	Name	S.D.	$I_{ac,t}$	Δ_{s-t}
1						Methane			
2						<i>n</i> -Pentane			
3	550.37	0.02	550.36	0.01	582.09	4-Methyl-1-pentene	0.05	582.03	0.06
4	582.75	0.02	582.73	0.02	616.95	1-Hexene	0.04	617.05	-0.10
5	585.14	0.01	585.14	0.00	586.18	3-Methylpentane	0.05	586.29	-0.11
6						<i>n</i> -Hexane			
7	625.67	0.01	625.65	0.02	663.25	2,3-Dimethyl-2-butene	0.16	663.35	-0.10
8			626.95		626.57	2,2-Dimethylpentane	0.27	626.96	-0.39
9	628.40	0.01	628.52	-0.12	656.62	3,3-Dimethyl-1-pentene	0.35	658.07	1.45
10	642.64	0.01	642.59	0.05	644.98	2,2,3-Trimethylbutane	0.07	645.06	-0.08
11	652.19	0.01	652.23	-0.04	685.53	2,3-Dimethyl-1-pentene	0.05	685.68	-0.13
12	657.36	0.01	657.40	-0.04	687.07	4-Methyl- <i>trans</i> -2-hexene	0.04	687.10	-0.03
13	659.19	0.01	659.25	-0.06	692.09	4-Methyl-1-hexene	0.31	692.24	-0.15
14	666.93	0.01	666.96	-0.03	667.22	2-Methylhexane	0.10	667.20	0.02
15	676.93	0.01	676.94	-0.01	677.96	3-Methylhexane	0.04	678.11	-0.15
16						<i>n</i> -Heptane			

For components 7, 8 and 9 these problems are much more complicated. At 50° , only one peak can be observed for these components. The retention index on the squalane column is strongly influenced by the peak shift. Nevertheless, these components can be characterized, as they are completely separated on the second column (track 2).

Because of a different dI/dT , these components are partly separated on the squalane column at 70° . Although they are hardly separated, the influence of peak shift on this column is very small for components 7 and 9. Interaction of peak inversion and different injection times on the second column at 70° results in a decreased precision.

For component 8 a double peak is found on the second column, which also results in decreased precision. This can be explained as follows. The transfer of a peak to the second column is started at the moment a peak maximum is observed from the first column. Because peaks 7, 8 and 9 are transferred to the second column during one run, component 8 is injected two or three times, depending on the difference in retention time of these components and the width of the injection (Δt , the time during which valves V_1 and V_2 are closed).

From the foregoing it can be concluded that a limited number of components can be transferred during one run if they are completely separated on the first column.

The precision of the retention indices obtained with the system is of the same order as the precision obtained with a single column (S.D. < 0.05 index units), as can be concluded from Tables III and IV.

ACKNOWLEDGEMENTS

The authors thank Dr. J. J. Walraven for assistance with the manuscript. Mr. C. H. Hamilton is gratefully acknowledged for a gift of the stainless-steel capillaries used in the system.

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