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## USE OF CARBOWAX 20M GLASS CAPILLARY COLUMNS BELOW THEIR LOWER TEMPERATURE LIMIT\*

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### SUMMARY

The optimal separation properties of Carbowax 20M as a stationary phase in 300-m glass capillary columns at temperatures below its lower temperature limit (60°) in terms of the selectivity, efficiency and speed of the gas chromatographic analysis of isomeric C<sub>10</sub>-C<sub>13</sub> *n*-alkenes were investigated. In the separation of isomeric *n*-alkenes two possible states of the Carbowax stationary phase below 60° were used (solid state and intermediate liquid state), and the dependence of the retention of the isomers on temperature was studied. The region of the hysteresis portion of the  $I^{CW} = f(T)$  diagram permits the continuous setting of column selectivity. The efficiency of the column at temperatures below the lower temperature limit of Carbowax 20M depends on the spatial *cis-trans* configuration of *n*-alkenes and, in the solid state, for *cis*-isomers is comparable to the high efficiency of this column at higher temperatures (115°). Utilization of Carbowax 20M in the solid state made it possible to achieve faster and more complete separations of the eleven possible positional and spatial isomers of *n*-tridecenes in comparison with previous methods.

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### INTRODUCTION

The lowest temperatures of the stationary phases used in gas chromatography are generally dependent on their melting points. For Carbowax 20M, this temperature is about 60°<sup>1</sup>. When analysing compounds on columns packed with the stationary phase in the solid state (below the melting point), the efficiency is generally poor<sup>2</sup>. Vigdergauz and co-workers<sup>3,4</sup> studied the properties of packed columns at temperatures around the change of state for the stationary phase and observed changes in

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the selectivity, time of analysis and temperature dependence of the retention data. Serpinet<sup>5</sup> studied the dependence of the retention volume on temperature ( $\log V_r$  versus  $1/T$ ) in the region of the melting point of the stationary phase. As had been found by Mori<sup>6</sup>, Carbowax 20M coated on Chromosorb W is liquid at temperatures above the melting point, and below this temperature possesses the properties of a solid phase. However, Carbowax 20M chemically bonded on Chromosorb W could be regarded as a liquid phase even below 60° (the melting point of Carbowax 20M). Hysteresis in the semi-logarithmic dependence of the capacity ratio on temperature ( $\log k$  versus  $1/T$ ) has been observed by Blomberg and Wännman<sup>7</sup> in glass capillary columns coated with a relatively thick layer of Carbowax 20M at temperatures around the melting point. This fact was explained by the wide melting range as Carbowax 20M is a mixture of polyethylene glycols with molecular weights ranging from 15,000 to 20,000.

The difficult separation of long-chain *n*-alkene isomers by gas chromatography has been investigated in terms of time of separation and length and efficiency of capillary columns coated with either non-polar or polar stationary phases. For instance, all positional and spatial isomers of linear tridecene (11 components) have been resolved in 28 h on a 200-m capillary column coated with squalane at 86°<sup>8</sup>. The analysis of all isomers of *n*-tridecenes after their conversion into epoxides in a 300-m capillary column with Carbowax 20M as stationary phase has been achieved by Döring *et al.*<sup>9</sup>. The preparation of the epoxides required almost 1 day and, although the analysis was continued for about 5 h, the separation of some pairs of epoxides had still not been achieved completely to the baseline.

In this paper we consider the possible exploitation of the specific properties of glass capillary columns with Carbowax 20M as the stationary phase below its lower temperature limit for the analysis of a mixture of C<sub>10</sub>-C<sub>13</sub> *n*-alkene isomers.

## EXPERIMENTAL

A mixture of all C<sub>10</sub>-C<sub>13</sub> *n*-alkene isomers was used as a model sample. A Carlo Erba GI 452 instrument was used, equipped with a flame-ionization detector (FID) and a glass capillary column of length 300 m and I.D. 0.25 mm coated with Carbowax 20M. The column was constructed coupling three shorter columns using shrinkable PTFE tubing<sup>10</sup>. The columns were made of soft glass and the inner surface was etched with methyl trifluoroethyl ether<sup>11</sup> and coated by the dynamic method with a 10% solution of the stationary phase by means of a mercury plug<sup>12,13</sup>. The operating temperatures were between room temperature and 70°. Nitrogen and hydrogen were used as carrier gases at inlet pressures up to 0.3 MPa.

## RESULTS AND DISCUSSION

The dependence of  $\log t_R'$  on temperature ( $1/T$ ) for *cis*-2-undecene and *n*-undecane is shown in Fig. 1. The line ABC was obtained from successive isothermal runs, gradually increasing the column temperature from room temperature to 70°, and is characterized by an inflection in the region of the melting point of Carbowax 20M. The line CBD was also obtained from successive isothermal runs and gradually decreasing the temperature from 70° to room temperature, and is straight (without

an inflection) in the region of the melting point of Carbowax 20M. The dependence obtained by decreasing the temperature, even below the lower temperature limit of Carbowax 20M, is the same as that of the stationary phase in the liquid state (line CBD).

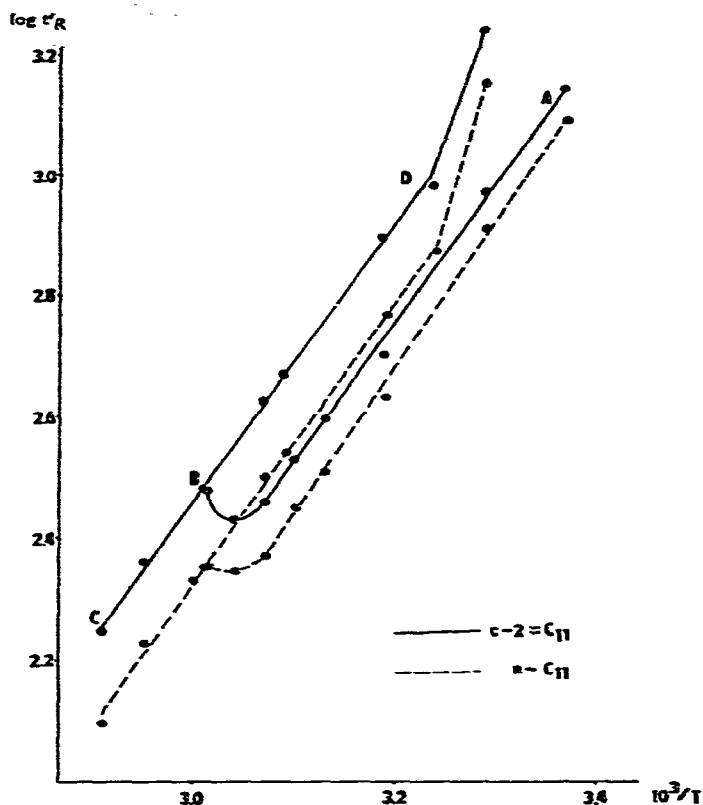


Fig. 1. Plot of  $\log t'_R$  versus  $1/T$  for *n*-undecane (broken lines) and *cis*-2-undecene (solid lines) separated in a 300-m glass capillary column coated with Carbowax 20M.

The different retention properties of the two states of the stationary phase at the same temperature below the melting point follow from Fig. 1, but the slopes of the plots of  $\log t'_R$  versus  $1/T$  are similar for both the solid and liquid states, except near the melting point. From Fig. 1 it can also be seen that the retention at a given temperature is considerably lower for Carbowax 20M in the solid than in the liquid state. Differences in the  $\log t'_R = f(1/T)$  dependences for *cis*-2-undecene and *n*-undecane are for *n*-undecane a lower inflection in the region of the melting point of Carbowax 20M, and for the same temperature smaller retention differences between the solid and liquid states of the stationary phase.

Fig. 2 shows the influence of the state of the Carbowax column on the retention of *cis*- and *trans*-isomers of 2-undecene. It can be seen that the separation of these isomers depends on the way in which the temperature is changed, either by warming or by cooling (shown by arrows). The points on the graph indicated by

vertical arrows at 50° were obtained after the column had been thermostated for 24 h. They indicate the good stability of the liquid intermediate state of the phase at this temperature. From Fig. 2 it also follows that the slope of the  $I = f(T)$  dependence is different for the two isomers ( $dI/dT$  is higher for the *cis*- than for the *trans*-isomer). The decrease in the retention indices with a decrease in the temperature of the column was greater on the column in the intermediate state than in the liquid state. It can be concluded that it is caused by the decreased polarity of the stationary phase. A decrease in polarity and retention can be explained by an increase in the amount of crystals in the stationary phase with decreasing temperature and by the change in the contributions of solution and adsorption to the retention<sup>14</sup>.

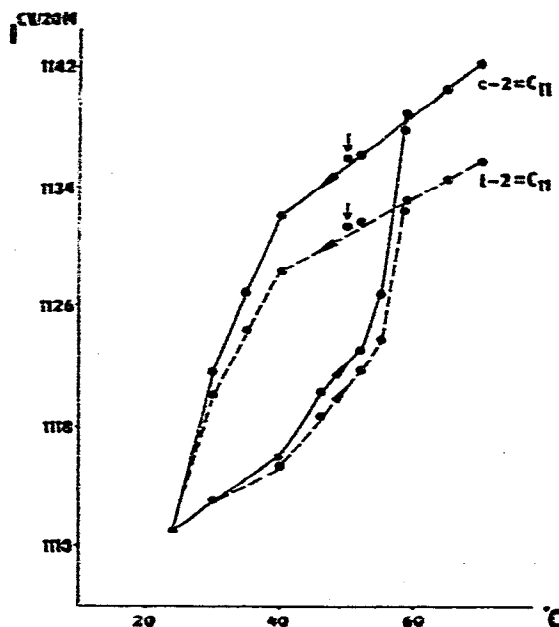


Fig. 2. Temperature dependence of retention indices of *cis*-2-undecene (solid lines) and *trans*-2-undecene (broken lines) using Carbowax 20M stationary phase in the solid and intermediate liquid states.

Table I gives the retention indices of *n*-tridecenes at 50° obtained with Carbowax 20M in the intermediate liquid state and the solid state. The retention indices measured for the liquid state are about 8 units higher than those obtained for the solid state. By a detailed analysis of the values obtained, the dependence of the differences in retention indices (corresponding to the two states of the stationary phase) on spatial factors and the position of the double bond in *n*-alkenes was found ( $\Delta I$  values are given in Table II). Thus, for *cis*-2- and *trans*-2-tridecene the difference in retention indices at 50° is 1.1 with Carbowax 20M in the solid state and 3.5 for the liquid state. As is shown in Table II, the  $\Delta I$  values for isomeric *n*-alkenes increase as the double bond shifts towards the end of the carbon chain for both *cis*- and *trans*-isomers; the  $\Delta I$  value for the 1-alkene is between the values for the *cis*-4- and

TABLE I

RETENTION INDICES OF ISOMERIC *n*-TRIDECENES, MEASURED AT 50°, USING THE INTERMEDIATE LIQUID OR SOLID STATE OF CARBOWAX 20M STATIONARY PHASE

<i>n</i> -Alkene	Retention index $I^{CW}$	
	Liquid phase	Solid phase
<i>cis</i> -6-Tridecene	1299.0	1292.3
<i>cis</i> -5-Tridecene	1301.0	1294.3
<i>cis</i> -4-Tridecene	1305.2	1298.0
<i>trans</i> -6-Tridecene	1305.2	1300.0
<i>trans</i> -5-Tridecene	1306.8	1301.5
<i>trans</i> -4-Tridecene	1307.8	1302.5
<i>cis</i> -3-Tridecene	1312.3	1304.6
<i>trans</i> -3-Tridecene	1314.1	1307.7
1-Tridecene	1315.7	1308.8
<i>trans</i> -2-Tridecene	1325.7	1317.1
<i>cis</i> -2-Tridecene	1329.2	1318.2

*cis*-5-isomers. Similar results for the dependence of the retention indices of *n*-alkenes on phase changes of Carbowax 20M were also found for C<sub>10</sub>-C<sub>12</sub> *n*-alkenes.

It follows from the above discussion that different states of the stationary phase in a single column (operated at temperatures below the melting point of the stationary phase) together with a high-efficiency separation system can be exploited to give desired changes in selectivity not only for various types of hydrocarbons (e.g., alkanes and alkenes) but also for very similar species such as geometric *cis*/*trans*- or positional isomers of *n*-alkenes. In this way it is possible to achieve effects similar to those obtained in gas chromatography using two columns of different polarity. In addition, the procedure described permits a continuous change in column selectivity in the region of the hysteresis portion of the retention diagram. Hitherto this was possible only by using several columns. The magnitude of the hysteresis effect increases with increasing polarity of the stationary phase and polarity of the

TABLE II

DIFFERENCES IN RETENTION INDICES ( $\Delta I^{CW}$ ) OF *n*-TRIDECENES, MEASURED AT 50° USING CARBOWAX 20M STATIONARY PHASE IN THE LIQUID AND SOLID STATE

<i>n</i> -Alkene	$\Delta I^{CW}$
<i>cis</i> -6-Tridecene	6.7
<i>cis</i> -5-Tridecene	6.7
<i>cis</i> -4-Tridecene	7.2
<i>cis</i> -3-Tridecene	7.7
<i>cis</i> -2-Tridecene	11.0
<i>trans</i> -6-Tridecene	5.2
<i>trans</i> -5-Tridecene	5.3
<i>trans</i> -4-Tridecene	5.3
<i>trans</i> -3-Tridecene	6.4
<i>trans</i> -2-Tridecene	8.6
1-Tridecene	6.9

TABLE III

EFFICIENCY OF 300-m GLASS CAPILLARY COLUMN COATED WITH CARBOWAX 20M IN THE LIQUID AND SOLID STATES AT 50° WITH A NITROGEN INPUT PRESSURE OF 0.3 MPa (13.6 cm/sec)

<i>n</i> -Alkene	Capacity ratio, <i>k</i>		Theoretical efficiency, <i>n</i> *		Effective efficiency, <i>N</i> *	
	Liquid phase	Solid phase	Liquid phase	Solid phase	Liquid phase	Solid phase
<i>trans</i> -2-Undecene	1.02	0.71	497,000	737,000	119,000	126,000
<i>cis</i> -2-Undecene	1.08	0.72	604,000	948,000	164,000	166,000
<i>trans</i> -2-Dodecene	2.36	1.66	419,000	424,000	207,000	163,000
<i>cis</i> -2-Dodecene	2.44	1.68	488,000	576,000	240,000	226,000

\* Values of  $n = 875,000$  and  $N = 312,000$  plates were measured for the solid-state stationary phase at 50° and  $\bar{u}_{opt} = 8.3$  cm/sec of N<sub>2</sub> for *cis*-2-dodecene with  $k = 1.49$ .

solute, and also with an increase in the thickness of the stationary phase layer and an increase in its melting interval.

The efficiencies found on the column containing Carbowax 20M below its lower temperature limit were generally lower than those found above the melting point. Values of the theoretical ( $n$ ) and effective efficiency ( $N$ ) of columns containing Carbowax 20M in the intermediate liquid state and in the solid state are given in Table III for *trans*-2- and *cis*-2-undecenes and -dodecenes (temperature 50°, input pressure of nitrogen carrier gas 0.3 MPa, linear velocity  $\bar{u} = 13.6$  cm/sec). Considering the dependence of column efficiency on capacity ratio ( $k$ ), it follows that the efficiency with the stationary phase in the solid state at 50° is slightly higher than that for the intermediate liquid state. It can be also concluded that the column efficiency depends on the spatial isomerism of *n*-alkenes and for *cis*-2-isomers it is higher than for *trans*-2-isomers. With the stationary phase in the solid state, these efficiencies differ by about 35% and in the intermediate liquid state by about 20%.

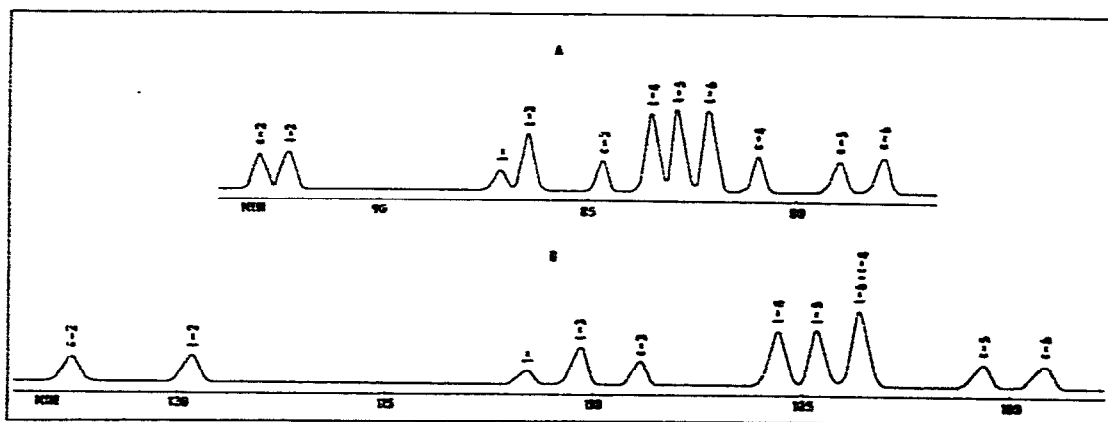


Fig. 3. Separation of isomeric *n*-tridecenes in a 300-m column coated with Carbowax 20M in (A) the solid state and (B) the intermediate liquid state. Temperature, 50°; input pressure, 0.3 MPa H<sub>2</sub>; carrier gas velocity,  $\bar{u} = 28$  cm/sec; c- denotes *cis*- and t- denotes *trans*-isomers.

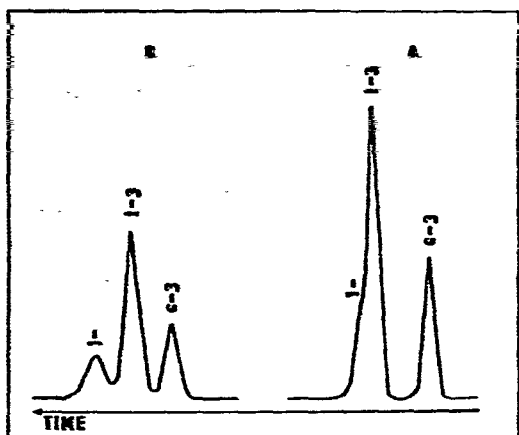


Fig. 4. Separation of *cis*-3-, *trans*-3- and 1-dodecene. Conditions as in Fig. 3.

The efficiencies found for *cis*-2-alkenes at 50° with the stationary phase in the solid state are 83% of those found with the liquid stationary phase at 115°. The higher column efficiency obtained with Carbowax 20M in the solid state is probably connected with the faster equilibration obtained when using a solid phase. In this connection, we refer to the work of Zhukhovitskii *et al.*<sup>14</sup>, who studied behaviour of sorbents containing liquid and solid stationary phases. They concluded that the height equivalent to a theoretical plate is considerably lower when using the solid instead of the liquid phase. This effect is due to a decrease in the resistance to internal diffusion.

The advantages of Carbowax 20M as a stationary phase at temperatures below its lower temperature limit are demonstrated by the separation of isomeric *n*-tridecenes in a 300-m glass capillary column (Fig. 3). It follows from the analysis at 50° using the solid-state stationary phase that the separation of all eleven isomeric

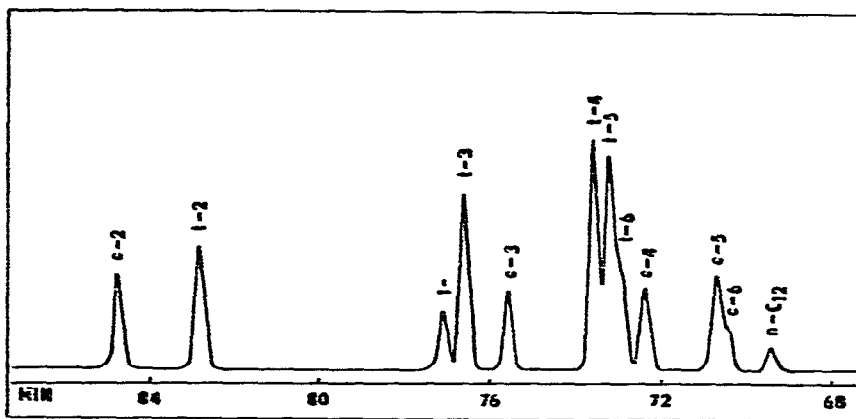


Fig. 5. Separation of isomeric *n*-dodecenes in a 300-m column coated with Carbowax 20M stationary phase in the intermediate liquid state. Temperature, 43°; input pressure, 0.3 MPa H<sub>2</sub>; carrier gas velocity,  $\bar{u} = 28$  cm/sec; c- denotes *cis*- and t- denotes *trans*-isomers; n-C<sub>12</sub> = *n*-dodecane.

*n*-tridecenes is better and faster than that under the same conditions using the liquid-state stationary phase, where *trans*-6-tridecene overlaps with *cis*-4-tridecene.

The separation of isomeric *n*-dodecenes on the same column, however is better when using liquid Carbowax 20M as the stationary phase below its lower temperature limit, as can be seen in Fig. 4. The optimal separation of all isomeric *n*-dodecenes on a Carbowax 20M column was achieved at 43° using the intermediate liquid state of the stationary phase (Fig. 5). The separation of isomeric *n*-dodecenes is more difficult than that of *n*-tridecenes. As we have shown previously<sup>8</sup>, it is caused by "new" structural features in the *n*-dodecenes (*cis*-6- and *trans*-6-positions of the double bond), and the separation of *cis*-5/*cis*-6- and *trans*-5/*trans*-6-dodecenes is troublesome. The poor separation of *trans*-4- from *trans*-5-dodecene can be explained by the propyl effect in the *trans*-4-isomer<sup>15</sup>.

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