

## Investigation of isomeric hydrocarbons by gas–solid chromatography on graphitized thermal carbon black

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**Abstract** - Graphitized Thermal Carbon Black (GTCB) is one of the most interesting adsorbents in Gas-Solid Chromatography (GSC). It is outstanding in its ability to separate compounds with only small differences in their geometry. Otherwise it is often impossible to separate complex mixtures on GTCB-columns.

An example for the separation of isomeric octanes by GSC on GTCB is given and first results on a system of series-coupled gas-liquid and gas-solid columns are discussed.

### INTRODUCTION

There is no doubt about the fact that at present in the field of gas chromatography the capillary chromatography is of major importance. The interest in Gas-Solid Chromatography (GSC), however, has grown considerably mostly in connection with difficult separation problems. In GSC on Graphitized Thermal Carbon Black (GTCB) which is outstanding in its ability to separate compounds with only small differences in their geometry it is possible to resolve difficult to separate compounds in packed or micropacked columns. Many analytical applications and general investigations have been reported mainly by Kiselev's group in Moscow (ref. 1) and by others (ref. 2, 3, 4).

The different retention principles of Gas-Solid and Gas-Liquid Chromatography (GLC) are listed in Table 1.

The aim of this paper is to give some examples for the separation of isomeric hydrocarbons by GSC on GTCB and to discuss a way to overcome the problems which are connected with the application of GSC for the separation of complex mixtures.

TABLE 1. Retention mechanism on non-polar stationary phases

	GLC	GSC
stationary phase (properties)	squalane Poly(dimethyl)-siloxanes C <sub>87</sub> hydrocarbon	GTCB (non-porous, flat, homogeneous surface)
interactions depend on	molecule size, shape, polarizability	
stat. phase acts with the molecule	from all sides	only from one side
retention		
- depends on	vapour pressure (boiling point)	molecular shape polarizability
- increases with	increasing . boiling point . polarizability	flattening of the molecule increasing polarizability

### SEPARATION OF ISOMERIC OCTANES

The great sensitivity of GTCB to the molecule geometry will be demonstrated in Fig. 1. This figure shows a chromatogram of a mixture of isooctanes on a micropacked GTCB-column (ref. 5).

There are two peaks (9 and 10) which correspond to 3,4-dimethylhexane. This branched hydrocarbon is the analogous paraffin to the tartaric acid that led to Pasteur's discovery of enantiomerism in 1849. The 3,4-dimethylhexane molecule possesses two centers of asymmetry which are structurally equivalent. Consequently, there exist three stereoisomers: one enantiomeric pair and the meso-compound. The enantiomeric pair cannot be separated using a nonchiral stationary phase. The meso-compound is a diastereomer of these isomers. The peaks 9 and 10 correspond to the diastereomeric isomers which can be resolved in GLC only on high efficient capillary columns at low temperature.

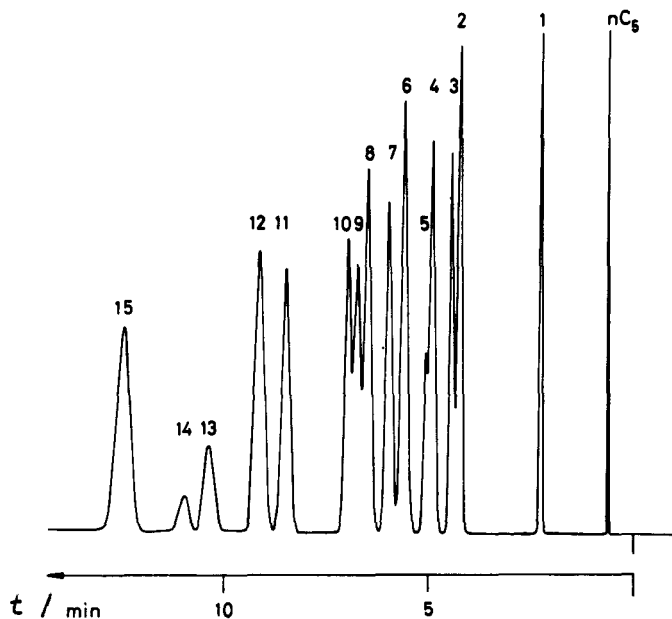


Fig. 1.  
Analysis of a mixture of isooctanes on a micropacked column with GTCB. Column length: 2.7 m, I.O.: 0.45 mm; GTCB, Sterling MI, particle size 0.09 - 0.125 mm; column temperature: 150°; carrier gas: hydrogen; inlet pressure: 5 bar (peak numbers see Table 2).

In Table 2 the retention indices of all isomeric octanes obtained on non-polar stationary phases in GSC and GLC are listed.

Nevertheless, the possibilities of separation of the isomeric mixtures are greater on GTCB than on a liquid stationary phase. The reverse side of the coin is that in a complex mixture of hydrocarbons the risk of overlapping with other components increases. Therefore a complete separation of such a mixture cannot be achieved on a single column.

### COUPLING GLC AND GSC IN SERIES

To overcome the problem mentioned above we tried to connect the high efficiency of a gas-liquid capillary column with the outstanding shape selectivity for hydrocarbons of a gas-solid micropacked column using GTCB as adsorbent. In such a series coupled system the first column, namely the capillary, has to separate the whole complex mixture whereas only the unresolved parts of the separated mixture will be transferred to the second column (GTCB) without intermediate trapping. On the second column they will be completely separated due to the different retention mechanism in GSC. So the first capillary column is used as a main column whereas the second column is applied for the separation and identification of overlapping peak groups. When realizing such a series-coupled system one has to take into account the following experimental requirements:

- two independent column ovens
- two independent carrier gas supplies
- well designed coupling unit.

Due to the progress in instrumentation such a system can now be realized with commercially available equipment, such as Sichromat 2 (SIEMENS AG, Karlsruhe, FRG, see ref. 8). The applicability of a system in which an OV-1 capillary column

TABLE 2. Retention indices of isomeric octanes in GSC on GTCB ( $I^{GTCB}$ ; ref. 5) and in GLC on Squalane ( $I^S$ ; ref. 6) and on Poly(dimethyl)siloxane ( $I^{OV-1}$ ; ref. 7).

Compound	GSC			GLC			Compound	GSC			GLC		
	No	$I^{GTCB}$ 150°C	$I^S$ 50°C	$I^{OV-1}$ 60°C	No	$I^{GTCB}$ 150°C		$I^S$ 50°C	$I^{OV-1}$ 60°C	No	$I^{GTCB}$ 150°C	$I^S$ 50°C	$I^{OV-1}$ 60°C
2.2.3.3-tetramethylbutane	1	619	726	724	2.4-dimethylhexane	8	713	732	735				
2.3.3-trimethylpentane		675	760	757	3.4-dimethylhexane	9	716)	771	771				
2.2.3-trimethylpentane	2	676	741	736	3.4-dimethylhexane	10	719)	760	761				
2.2.4-trimethylpentane	3	679	690	691	2.3-dimethylhexane		727	760	761				
3-methyl.3-ethylpentane	4	689	774	772	3-ethylhexane	11	737	772	775				
2.3.4-trimethylpentane	5	691	753	752	2.5-dimethylhexane	12	743	729	733				
2-methyl.3ethylpentane		700	762	763	4-methylheptane	13	754	767	768				
3.3-dimethylhexane	6	701	744	743	3-methylheptane	14	759	772	774				
2.2-dimethylhexane	7	706	720	723	2-methylheptane	15	770	765	767				
Retention range (Nos. 1-15)													
. index units							151	84		84			
. partial free energy of sorption G (Jmol <sup>-1</sup> )							6400	2500		2200			

Considering these retention indices the following features are discussed.

- The elution sequences obtained in adsorption and partition differ considerably.
- A complete separation of all isomers cannot be achieved on one of this non-polar stationary phases. The resolution of unresolved doublets or multiplets can only partially or cannot be improved by using polar liquid stationary phases such as polypropylene glycol (Ucon) or polyethylene glycol (Carbowax).
- The retention range, defined as the difference between the highest and the lowest retention index of the investigated group of isomers is much greater in case of GSC than in GLC. Of course, one has to consider this fact in connection with column efficiency.  
With capillary columns it is possible to distinguish between substances which differ in the retention index at about two index units. On the considerably shorter micropacked columns the index differences must be about three index units.

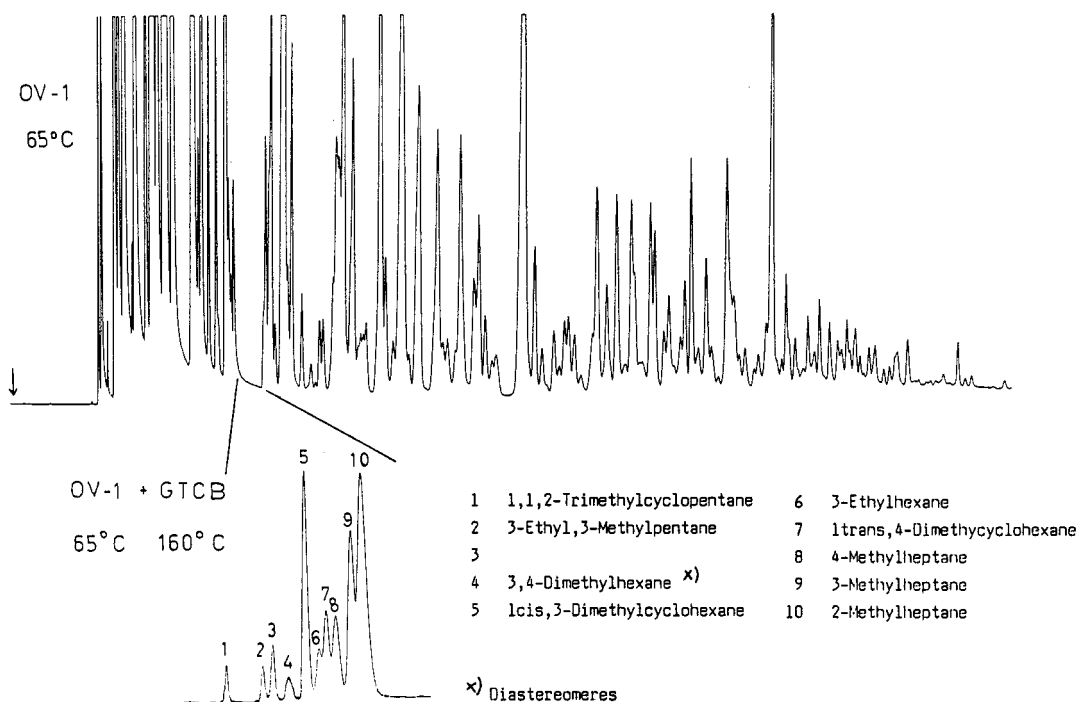


Fig. 2 Chromatogramm of a gasoline sample

TABLE 3. Retention data of isomeric xylenes on both the single columns and the coupled system (temp.: 100°C/250°C, press.: 4,5/4.0 bar hydrogen, column A: 50 m x 0.32 mm ID, OV-1; column B: 1.5 m x 1 mm micropack, carboxpack C, 0.16 - 0.20 mm)

Compound	I OV-1 100°C	t <sub>R</sub> <sub>OV-1</sub> (min)	I GTCB 250°C (ref. 9)	t <sub>R</sub> <sub>GTCB</sub> (min)	t <sub>R</sub> <sub>OV-1+GTCB</sub> (min)
o-xylene	889	6.18	836	1.50	7.68
m-xylene	866	5.67	824	1.37	7.04
p-xylene	866	5.67	840	1.52	7.19

and a GTCB micropacked column are coupled in series was proved by separating the three isomeric xylenes. As it can be seen from the index data in Table 3 the separation of m- and p-xylene is very difficult when using an OV-1 capillary, whereas the separation of o- and p-xylene is difficult when using an GTCB-column. Nevertheless we achieved a nearly complete separation of the three compounds using a system of these two columns coupled in series. The separation is achieved due to the interplay of two independent retention mechanisms. The selectivity of the system can be adjusted as required by selecting the velocities through the individual columns or the temperatures of the columns or both (ref. 10). To demonstrate the advantages of the system for the analysis of complex mixtures a gasoline sample has been used.

In the marked retention range from 766 to 776 index units the integrator found six not completely resolved peaks.

These peak group was transferred to the GTCB-column, and after optimization of GC-conditions by varying the two column temperatures and flow-rates, ten compounds (Fig. 2) could be detected.

The identification of these compounds was achieved by calculating system retention times from tabulated indices of the compounds on both columns and comparing the calculated with the measured retention times.

From our first experiments it can be deduced that two-dimensional separation using series-coupled GLC- and GSC-columns with nonpolar stationary phases represents a very promising analytical approach for the identification and quantification of components in complex hydrocarbon mixtures.

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