

CHROM. 5641

CHROMATOGRAPHIC BEHAVIOUR OF ISOMERIC COMPOUNDS ON PORAPAK P*

M. DRESSLER, O. K. GUHA AND J. JANÁK

Institute of Instrumental Analytical Chemistry, Czechoslovak Academy of Sciences, Brno (Czechoslovakia)

SUMMARY

Standard deviations of the gas-chromatographic peaks of different types of organic compounds were determined on different varieties of Porapak. An abnormality in the peaks of the branched alkanes and cycloalkanes was observed on Porapak P and PS columns. The higher was the degree of branching of the compound, the lower was its retention time and the greater was the peak broadening. Olefins, aromatics, alcohols and mercaptans did not show such behaviour. However, sulphides seemed to show a similar effect. The effects of the carrier gas flow-rate, temperature and the coating of the Porapak P on the retention behaviour of iso-octane and *n*-octane were studied.

INTRODUCTION

Porous polymers based on polystyrene have recently found extensive application as column packings for gas chromatography (GC). These materials, which have excellent separation properties, especially for gases and polar compounds, have been used for most types of organic compounds (e.g., see refs. 1 and 2). Up to now, no special attention has been devoted to the study of the separation of compounds with branched chains on this type of packing material.

From studies of the chromatographic behaviour of various types of branched-chain compounds on porous polymers, we have noticed that some types of such compounds show quite anomalous behaviour as far as chromatographic curve broadening is concerned on certain types of Porapak.

The chromatographic peak of a compound leaving the column is broadened owing to the non-ideality of the chromatographic process. In GC, diffusion phenomena and resistance to mass transfer frequently have the result that the higher the partition coefficient of a compound the greater is the broadening of the chromatographic

* This paper is part of the dissertation work of O. K. G., fulfilled during the U.N.E.S.C.O. Longterm Postgraduate Course on Modern Methods of Analytical Chemistry, 1969/70, and following a research stay at the above Institute.

TABLE I

RETENTION DISTANCES (d_R) AND STANDARD DEVIATIONS (σ) OF MODEL COMPOUNDS ON DIFFERENT POROUS POLYMER BEADS

Compound	Boiling point (°C)	Squalane		PS				Q	
		30 ml/min, $T_C = 65^\circ$		35 ml/min, $T_C = 110^\circ$		$T_C = 130^\circ$		46 ml/min, $T_C = 160^\circ$	
		d_R (cm)	σ (mm)	d_R (cm)	σ (mm)	d_R (cm)	σ (mm)	d_R (cm)	σ (mm)
Heptane	98.4					7.6	2.8		
Isooctane	99.2	8.7	4.0			9.0	14.5	11.5	5.0
2,4-Dimethyl-hexane	109.4	12.5	5.5			11.7	9.4		
4-Methyl-heptane	117.7	16.9	7.5			14.3	7.8		
Octane	125.7	22.5	9.5			17.1	6.8	18.7	7.4
tert.-Butyl alcohol	82.9			4.0	2.0				
Isobutyl alcohol	108.1			8.2	2.9			3.3	1.4
Butyl alcohol	117.6			10.4	3.3			4.0	1.6

peak of this substance. This effect is seen in the chromatograms by an increase in the standard deviation of the chromatographic curve with an increase in the retention parameters (distance, time or volume). An opposite effect, *i.e.*, a decrease in the standard deviation of the chromatographic curve with an increase in retention parameters has so far not been observed in GC. The study of such effects was the purpose of the present work.

EXPERIMENTAL

A Perkin-Elmer F 20 FE Fractometer gas chromatograph with a flame ionization detector coupled to a recorder (Honeywell Inc., U.S.A.) was used for the analysis of various types of organic compounds. Aluminium columns were used with I.D. 0.3 cm, having a length of 1 m in the case of Porapak P, PS and squalane, and 0.5 m in other cases. Column temperatures and carrier gas flow-rates are listed for individual types of compounds in the tables containing retention data. The investigated compounds were injected with a Hamilton microsyringe in amounts of *ca.* 10^{-6} g. Retention distances were measured from the sample injection.

The types of Porapak that were used (Waters Associates Inc., Framingham, Mass., U.S.A. and Synachrom, Lachema N.E., Brno, Czechoslovakia) were of the following specifications: Porapak P, 100-120 mesh, batch No. 550; Porapak PS, 80-100 mesh, batch No. 697; Porapak Q, 100-120 mesh, batch No. 558; Porapak R, 100-120 mesh, batch No. 554; Porapak S, 100-120 mesh, batch No. 601; Porapak T, 100-120 mesh, batch No. 528; Porapak N, 80-120 mesh, batch No. 661; and Synachrom E5, 60-70 mesh.

Squalane was deposited at a level of 25% on Chromosorb P, 30-60 mesh. The

S				T			N			Synachrom	
8 ml/min, $T_c = 160^\circ$		48 ml/min, $T_c = 160^\circ$		55 ml/min, $T_c = 160^\circ$		48 ml/min, $T_c = 160^\circ$		57 ml/min, $T_c = 160^\circ$			
d_R (cm)	σ (mm)	d_R (cm)	σ (mm)	d_R (cm)	σ (mm)	d_R (cm)	σ (mm)	d_R (cm)	σ (mm)	d_R (cm)	σ (mm)
7.5	3.5	10.0	4.5	6.1	3.5	11.2	5.9	3.3	2.8		
2.5	5.0	16.0	6.4	9.5	4.6	18.0	8.0	5.4	4.4		
2.0	0.8	3.0	1.2	3.0	1.5	3.5	1.6				
3.6	1.4	4.2	1.7	5.4	2.5	6.3	2.9	1.3	1.0		
4.4	1.7	5.0	2.0	6.7	3.3	7.7	3.5	1.6	1.2		

compounds were analytical-grade chemicals from Lachema N.E., Brno, Czechoslovakia, except 2,2-dimethylhexane (E. Merck A.G., Darmstadt, G.F.R.), di-*tert*-butyl sulphide, diethyl sulphide and isobutyl mercaptan (Fluka AG, Chemische Fabrik, Buchs SG, Switzerland), dibutyl sulphide (Koch-Light Laboratories Ltd., Colnbrook, Bucks., Great Britain) and diisopropyl sulphide (K & K Laboratories Inc., Plainview, N.Y., U.S.A.).

The influence of temperature and carrier gas flow-rate on the retention behaviour of the model mixture octane-isoctane was studied on a Chrom-2 gas chromatograph (Laboratory Equipment N.E., Prague, Czechoslovakia) equipped with a flame ionization detector. A stainless-steel column of length 84 cm and I.D. 0.6 cm was used. A stainless-steel column of length 50 cm and I.D. 0.4 cm was used for the study of the effect of coating on retention behaviour. The column temperature was 120° and the linear velocity of the carrier gas was 2.9 cm/sec. Model compounds were dissolved in pentane and sampled in amounts of *ca.* 10⁻⁷ g with a Hamilton microsyringe.

RESULTS

Effect of the type of Porapak used

The retention distances and standard deviations of the chromatographic curves of some alkanes and alcohols on various porous polymers as well as their boiling points are given in Table I. Data for the squalane column are also included for comparison.

On the squalane column, the retention behaviour is quite normal; the retention distance increases with increasing boiling points and the standard deviation of the chromatographic curves increases similarly. On Porapak PS, the retention distance

TABLE II

RETENTION DISTANCES (d_R) AND STANDARD DEVIATIONS (σ) OF DIFFERENT TYPES OF COMPOUNDS ON PORAPAK I

Compound	Boiling point (°C)	Column temperature (°C)					
		90		130		160	
		d_R (cm)	σ (mm)	d_R (cm)	σ (mm)	d_R (cm)	σ (mm)
<i>Alkanes</i>							
Pentane	36.1					1.7	0.5
2,3-Dimethylbutane	58.0	12.5	13.7				
3-Methylpentane	63.3	14.7	9.1				
Hexane	68.7	16.2	6.0			3.3	0.9
Heptane	98.4					6.7	2.0
Isooctane	99.2					7.2	7.3
2,2-Dimethylhexane	106.8					8.7	6.6
2,4-Dimethylhexane	109.4					9.2	5.1
4-Methylheptane	117.7					11.1	4.4
Octane	125.7					13.4	3.9
<i>Cycloalkanes</i>							
Cyclopentane	49.3					2.7	0.8
Cyclohexane	80.7					5.7	1.9
Methylcyclohexane	100.9					9.3	3.6
Cycloheptane	118-20					15.4	6.0
1,2,3-Trimethyl-cyclohexane	144-146						
Isopropylcyclohexane	154.5						
tert.-Butylcyclohexane	167.9						
<i>n</i> -Butylcyclohexane	180.9						
<i>Aromatics</i>							
Isopropylbenzene	152.4						13.5
Propylbenzene	159.4						15.7
1,2,4-Trimethylbenzene	169.4						20.4
<i>Mercaptans</i>							
Isobutyl mercaptan	88.7					7.3	2.2
Butyl mercaptan	98.4					9.0	2.5
<i>Sulphides</i>							
Diethyl sulphide	92.0						3.4
Dipropyl sulphide	141.2						9.8
Di-tert.-butyl sulphide	150.0						12.9
Dibutyl sulphide	188.0						29.6
<i>Alcohols</i>							
Isooctyl alcohol	187.6						21.4
Octyl alcohol	195.0						26.5
<i>Olefins</i>							
1-Nonene	146.9						8.1
2,6-3-Dimethylheptene							5.4
							2.1

also increases with increasing boiling point, but the standard deviation of the peaks for alkanes with branched chains decreases with increasing retention distances. This means that peak broadening is the greatest for the first peak and the least for the last peak in the chromatogram. While the standard deviation of octane on the Porapak PS column is comparable with its standard deviations on other columns, the standard deviation of isoctane is unusually large. The behaviour of alcohols is again normal. With the other types of Porapak, with the exception of Porapak P, the behaviour of both polar (alcohols) and non-polar compounds (alkanes) is also normal.

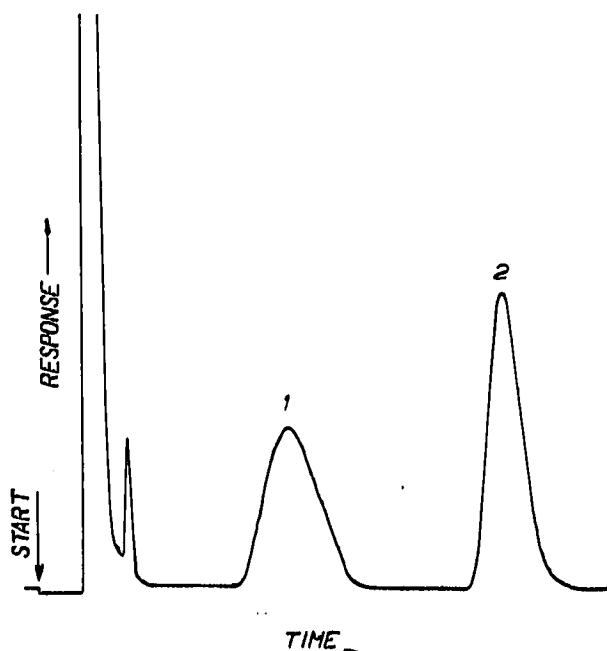


Fig. 1. Chromatogram of model pair of compounds. 1 = Isooctane; 2 = octane.

A more detailed study of this anomalous behaviour of compounds in GC was carried out on Porapak P. The results are summarized in Table II.

The behaviour of alkanes on Porapak P is similar to that on Porapak PS. The retention distance again decreases for branched-chain compounds as the boiling points decrease, but the standard deviation increases. This dependence is the same for both hexane and octane isomers and it thus seems not to be affected by the chain length. For two isomers of a compound, that which has a particular carbon atom that is more highly substituted has a higher standard deviation than the isomer with the less highly substituted carbon atom (*cf.* 2,2-dimethylhexane and 2,4-dimethylhexane). The chromatogram of the octane-isooctane mixture is shown in Fig. 1.

The behaviour of substituted cycloalkane isomers is again anomalous. The branching of the side-chain causes a higher standard deviation in comparison with the linear chain. No anomalous behaviour is obvious if the cycloalkane ring increases from

TABLE III

EFFECT OF TEMPERATURE ON STANDARD DEVIATION RATIO AND HETP OF MODEL MIXTURE ON PORAPAK P

Temperature (°C)	HETP		$\frac{\sigma_{\text{octane}}}{\sigma_{\text{isooctane}}}$
	Isooctane	Octane	
100	42.10	1.76	0.51
130	9.80	0.99	0.62
160	2.12	0.71	0.93
170	1.50	0.68	1.02
180	1.03	0.63	1.14
190	0.85	0.59	1.15
200	0.66	0.51	1.17

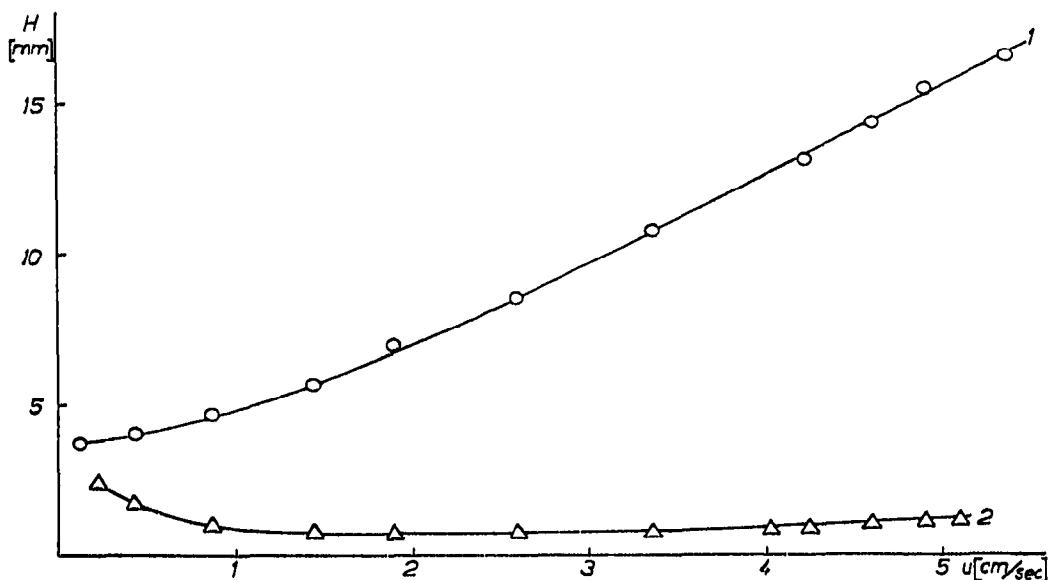


Fig. 2. Dependence of HETP (H) on the flow-rate of the carrier gas (u). Column temperature, 130° . 1 = Isooctane; 2 = octane.

methylcyclohexane to cycloheptane. The olefins, aromatics, alcohols and mercaptans studied do not show any anomalous behaviour. When the standard deviations of di-*tert*-butyl sulphide and dibutyl sulphide are compared it is obvious that the difference (1.2 mm) is too small owing to the large difference in the retention distances of this pair (16.7 cm). Sulphides thus show the same anomalous retention behaviour as alkanes and branched substituted cycloalkanes on Porapak P.

Effect of column temperature

The influence of column temperature on the ratio of the standard deviations of isoctane and octane is shown in Table III. With increasing temperature, the enormous broadening of the chromatographic peaks of isoctane decreases and above *ca.* 170° it completely disappears.

Effect of the flow-rate of the carrier gas

The influence of the flow-rate of the carrier gas on the height equivalent to a theoretical plate (HETP) is shown in Fig. 2 for isoctane-octane at 130° , where the anomalous behaviour of the compounds with branched chains appears, and in Fig. 3 at 195° , where this behaviour disappears. While the course of the dependence of HETP on the linear velocity, u , is normal for octane at 130° , it is quite exceptional for isoctane. The HETP decreases for the whole range of velocities studied with decreasing flow-rate, and the slope of the dependence (C term in the van Deemter equation) is approximately nine-fold greater than that of octane. However, the dependence of HETP on u is normal for both the compounds at 190° .

The chromatographic peaks of both isoctane and octane show tailing for larger samples. The effects of the flow-rate of the carrier gas on peak asymmetry for both compounds are illustrated by the data in Table IV. As the asymmetry of the chromatographic peaks of the compounds chromatographed on porous polymers, and also the retention volume, depend on the amount of the sample injected (e.g., see refs.

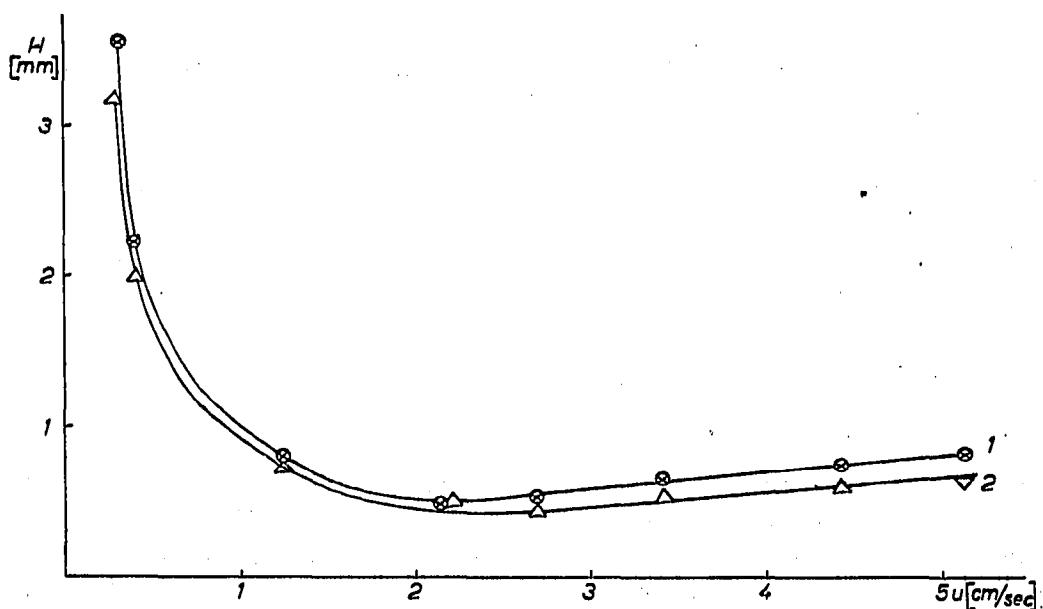


Fig. 3. Dependence of HETP (H) the flow-rate of the carrier gas (u). Column temperature, 195° .
 1 = Isooctane; 2 = octane.

3 and 4), the amount of the model mixture was always constant and larger (10^{-5} g) than in the previous cases. The peak asymmetry was expressed as the ratio of the distances of the front and the rear of a peak, as measured at one tenth of the peak height, from the perpendicular dropped from the peak maximum to the time coordinate⁴. For the isoctane peak, the asymmetry is the same for all flow-rates of the carrier gas, but the tailing of the octane peak increases with decreasing flow-rate.

Effect of coating

Porapak P was coated with various amounts of squalane and the effect of the coating on the retention volume, HETP and the ratio of the standard deviations for isoctane-octane was studied at a constant linear velocity of 2.9 cm/sec (Table V). The retention volume of both compounds decreases with increasing squalane loadings up to 10%. The behaviour of both compounds is therefore analogous to the retention behaviour of paraffinic hydrocarbons on Porapak Q coated with squalane⁵. However, at a loading of 20%, the retention volumes are larger than at a loading of 10%. The

TABLE IV

EFFECT OF FLOW-RATE OF CARRIER GAS ON PEAK ASYMMETRY

u (cm/sec)	Peak asymmetry	
	Isooctane	Octane
0.20	0.480	0.344
0.47	0.483	0.348
1.23	0.468	0.348
2.98	0.479	0.455
4.63	0.480	0.523
5.95	0.473	0.786
10.20	0.478	0.905

TABLE V

EFFECT OF COATING ON THE RETENTION VOLUME (V), STANDARD DEVIATION (σ) AND HETP

Degree of coating (%)	V		$\frac{\sigma_{\text{Isooctane}}}{\sigma_{\text{Octane}}}$	HETP	
	Isooctane	Octane		Isooctane	Octane
0	144.3	287.4	1.79	15.0	1.2
0.5	97.4	203.4	1.36	15.0	2.0
2.0	67.6	142.7	1.33	11.2	1.5
5.0	52.9	114.6	1.25	8.3	1.3
10.0	52.5	113.6	0.96	5.4	1.2
20.0	56.5	122.0	0.90	3.9	1.1

decrease and increase of the value of the retention volume as the liquid loading is increased is obviously associated with a decrease in the surface area of the Porapak and an increase in the contribution of the squalane to the overall retention of the solute. The decrease in the standard deviation for isooctane and octane, as well as of the HETP, with increase in the percentage of the liquid phase is also connected with the relative contribution of both materials.

The increase of the standard deviation of a compound with a branched chain, compared with that of the compound with a non-branched chain, manifests itself at loadings of up to about 5%. The HETP of octane increases at first (0.5% loading) and then decreases as the liquid loading is increased. In contrast to the situation⁵ with Porapak Q, the decrease occurs over the whole range of the coatings investigated with Porapak P, while the increase of the HETP in the region of 0.5% loading is much lower. For isooctane, the HETP does not increase on coating with squalane; it decreases with increase in the percentage of the liquid, but it is always larger than that for octane.

DISCUSSION

The phenomenon of the broadening of the chromatographic peak of a less-retained compound being greater than that of compounds having larger retention volumes is not known in GC for any adsorbent or stationary phase used. The anomalous retention behaviour on Porapak P described above derives from the fact that the peak broadening displayed by branched-chain compounds is abnormally enhanced compared with that for straight-chain compounds, although the branched-chain compounds have smaller retention volumes. In the case of alkanes, this peak broadening increases as the degree of chain branching and, therefore, the molar volume of the respective compound increases. For cyclic hydrocarbons, the peak broadening also increases with increasing molar volume, due either to a greater degree of branching of the aliphatic side-chain (*tert*-butylcyclohexane-*n*-butylcyclohexane) or to the substitution in the ring (1,2,3-trimethylcyclohexane-isopropylcyclohexane). The effect of the magnitude of the molar volume is also apparent for sulphides.

The phenomenon observed occurs only with Porapak P. The other types of Porapak, as well as Synachrom and Chromosorb 101 and 102, do not show this phenomenon. However, silylation of the Porapak (Porapak PS) has no effect on the anomalous behaviour. The phenomenon must therefore depend on a certain structure

of the porous polymer and on the elasticity of the structure, which is dependent on temperature. It follows from the dependence of the HETP on the flow-rate of the carrier gas that the *C* term, *i.e.*, the mass-transfer resistance, is greatly enhanced for branched-chain compounds. Therefore, it seems that the anomalous behaviour with Porapak P is not due to the phenomena that take place on the surface of the Porapak, but is due to phenomena that occur within the pores of the polymer. As the pores are gradually filled with a stationary liquid, the effect decreases.

It is not clear, at present, why the anomalous behaviour occurs only with alkanes, cycloalkanes and sulphides, and not with olefins, aromatics, alcohols and mercaptans. The fact that the effect disappears on increasing the temperature also requires further study.

The above anomalous retention behaviour of branched-chain compounds suggests, to some extent, that sieve effects occur as in gel permeation chromatography, where the peaks of the compounds with shorter retention times (compounds with higher molecular weights) display greater broadening^{6,7}.

ACKNOWLEDGEMENT

The authors express their thanks to Mr. SCHALKHAMMER, the representative of Perkin-Elmer Co., Vienna, for the loan of the GC apparatus for the U.N.E.S.C.O. course.

REFERENCES

- 1 O. L. HOLLIS, *Anal. Chem.*, 38 (1966) 309.
- 2 S. B. DAVE, *J. Chromatogr. Sci.*, 7 (1969) 389.
- 3 L. EEK AND T. GALCERÁN, *Chromatographia*, 2 (1969) 541.
- 4 T. A. GOUGH AND C. F. SIMPSON, *J. Chromatogr.*, 51 (1970) 129.
- 5 B. O. JANSSON, K. C. HALLGREN AND G. WIDMARK, *J. Chromatogr. Sci.*, 8 (1970) 398.
- 6 N. POVEY AND R. A. HOLM, *J. Chromatogr.*, 46 (1970) 33.
- 7 W. W. YAU, C. P. MALONE AND H. L. SUCHAN, *Separ. Sci.*, 5 (1970) 259.