

## Notes

---

CHROM. 538I

### Reproducibility of retention data on porous polystyrene polymers (Porapak)

A new type of adsorbent — an organic porous polymer based on polystyrene — was developed for gas chromatography (GC) by HOLLIS<sup>1-3</sup>. These materials, manufactured under various commercial names such as Porapak, Chromosorb 101-105, Synchrom, Polypak, etc., have excellent separation properties, especially for compounds of polar character, and their application has therefore been fairly widespread. They have also recently been employed in thin-layer<sup>4</sup> and liquid<sup>5</sup> chromatography.

Numerous papers exist in the literature, in which retention data<sup>2,3,6-9</sup> are tabulated in the form of specific retention volumes, relative retention volumes, and Kováts' indexes. In addition the manufacturers of these materials give many retention data<sup>10,11</sup> in their leaflets. The measurement of physical characteristics based on retention data<sup>12</sup> has also been carried out on polymer materials of Porapak type.

It is known that reproducible batch preparation of polymers and adsorbents is not an easy matter generally. Individual papers dealing with separations on Porapak express, in some cases, different opinions concerning the use of this material for the separation of certain compounds, e.g. the separation<sup>11,13</sup> of a mixture of nitrogen, oxygen, carbon monoxide and argon. GOUGH AND SIMPSON<sup>14</sup> have recently shown that the retention behaviour of compounds on Porapak may differ in certain cases depending on the polymer conditioning. Their data are, however, presented for temperatures higher than those recommended by the manufacturers in many cases, and the differences may thus be caused by changes in the Porapak resulting from the high temperature used.

As a result of this, we have compared tabulated retention data published by different authors and carried out measurements of retention data and separation factors of model mixtures on different batches of Porapak Q and on Porapak Q conditioned in various ways, by means of gas and liquid chromatography.

#### *Experimental*

The surface areas of individual Porapak samples were measured by the dynamic desorption method<sup>15</sup> in an apparatus for the determination of the specific surface area of adsorbents<sup>16</sup>. Weights of 7-9 mg were used for the surface area measurements.

The analysis of a model mixture by GC was carried out in a Becker Delft Multigraph 409 gas chromatograph. The column used was 80 cm long and had an I.D. of 0.3 cm. The column temperature was 32°, the carrier gas flow rate was 30 ml of H<sub>2</sub> per min. A thermal conductivity detector was used for detection of the separated substances. A mixture of ethylene, propylene and water vapour was used as the model mixture. The compounds were sampled in amounts of about  $5 \times 10^{-7}$  mole. In all cases, the column packing was prepared in such a way that the Porapak Q was con-

ditioned in the column for 15 h in a flow of nitrogen at the appropriate temperature, and then the column was emptied and repacked with the conditioned polymer.

The analysis by liquid chromatography was carried out in an apparatus of own design. Degassed *n*-hexane was used as the mobile phase. A damping system, described by LOCKE<sup>17</sup>, was employed to balance pressure pulses generated by the MC 300 piston pump (Mikrotechna N.E., Prague, Czechoslovakia). Porapak samples were filled into straight stainless steel columns, 50 cm long and 0.2 cm I.D. A capacity detector<sup>18</sup> was used for the detection. In order to decrease the broadening of the chromatographic peaks<sup>19</sup>, the capillary connecting the column and the detector was shaped. The measurements were carried out at room temperature. Dead volume of the column was measured by the injection of *n*-octane. 2- $\mu$ l samples of a mixture of dibutyl phthalate (DBP), benzyl alcohol, and benzene, were used for the measurements of the retention times; the flow rate of the mobile phase was 0.33 ml/min. Thermal processing of the Porapak samples was the same as for the gas chromatographic measurements. The conditioned sample was washed with mobile phase overnight at room temperature.

### Results

The relative retention volumes of the compounds measured by various authors on different types of Porapak are shown in Table I. All the retention volumes are

TABLE I  
RELATIVE RETENTION VOLUMES OF MODEL GASES ON DIFFERENT TYPES OF PORAPAK  
Propene = 1.00.

Compound	Porapak type	Relative retention volumes							
		32°			26°		30°		32°
		ref. 3	ref. 2	$\Delta\%$	ref. 10	$\Delta\%$	ref. 11	$\Delta\%$	
H <sub>2</sub> O	P	0.982	0.961	- 2	0.976	- 1	0.942	- 4	
	Q	0.364	0.356	- 2	0.369	+ 1	0.331	- 8	
	R	2.67	2.67	0	2.67	0	1.77	-34	
	S	1.28	1.27	- 1	1.28	0	1.37	+ 7	
	T	4.05	3.94	- 3	4.07	+ 1	3.31	-28	
C <sub>2</sub> H <sub>4</sub>	P	0.257	0.286	+11	0.254	- 1	0.324	+26	
	Q	0.141	0.142	+ 1	0.144	+ 2	0.179	+27	
	R	0.167	0.159	- 5	0.171	+ 2	0.203	+22	
	S	0.154	0.168	+ 9	0.154	0	0.188	+22	
	T	0.143	0.150	+ 5	0.141	- 1	0.182	+27	
C <sub>3</sub> H <sub>8</sub>	P	1.59	1.65	+ 4	1.58	- 1	1.00	-27	
	Q	1.30	1.30	0	1.31	+ 1	1.12	-14	
	R	1.21	1.21	0	1.22	+ 1	1.13	- 7	
	S	1.11	1.12	+ 1	1.11	0	1.11	0	
	T	0.870	0.860	- 1	0.890	+ 2	1.00	+15	
CH <sub>3</sub> Cl	P	1.73	1.96	+13	1.72	- 1	1.51	-13	
	Q	1.17	1.17	0	1.19	+ 2	0.890	-24	
	R	—	—	—	—	—	1.29	—	
	S	1.32	1.32	0	1.31	- 1	1.30	- 2	
	T	1.80	—	—	1.85	+ 3	1.64	- 9	
C <sub>2</sub> H <sub>2</sub>	P	0.203	0.327	+12	0.292	0	0.381	+30	
	Q	0.141	0.142	+ 1	0.144	+ 2	0.148	+ 5	
	R	0.253	0.262	+ 4	0.257	+ 2	0.262	+ 4	
	S	0.185	0.211	+14	0.192	+ 4	0.223	+21	
	T	0.353	0.394	+12	0.407	+15	0.407	+15	

relative to propene. The relative retention volumes can differ by as much as 20 % or more without considering the type of Porapak. Small differences (up to 6°) in the temperature of the measurement<sup>2,3,10,11</sup> are, however, not large enough to explain the differences in the data tabulated, especially as the greatest differences have been found at the same operating temperature *cf.* refs. 3 and 11.

Relative retention volumes of some other compounds, in this case by entirely different authors<sup>7,9,10</sup>, are compared in Table II. The retention data are given relative to ethyl alcohol. The deviations are large and are to 77 % in the case of propionic acid and ethylene glycol. These differences in retention volumes are due to different authors and thus obviously also to the different samples of Porapak Q being used. The same as has been said above holds for the influence of the difference in temperature, which is 6 or 7°.

Relative retention volumes of ethene and water relative to propene and peak resolution *R* for the pair propene-water measured by the authors for different batches of Porapak Q and for different conditioning temperatures are presented in Table III.

TABLE II  
RELATIVE RETENTION VOLUMES ON PORAPAK Q  
Ethanol = 1.00.

Compound	Relative retention volume				
	157°		Δ%	163°	
	ref. 10	ref. 9		ref. 7	Δ%
Methanol	0.500	0.375	-25	0.615	+23
Isopropanol	1.73	2.00	+16	1.38	-20
<i>n</i> -Propanol	2.27	2.81	+24	2.15	-5
<i>tert.</i> -Butanol	2.77	3.25	+17	—	—
Ethylether	2.23	2.50	+12	—	—
Formic acid	0.932	—	—	1.38	+48
Acetic acid	1.96	—	—	2.92	+49
Propionic acid	4.77	—	—	8.46	+77
Ethylene glycol	4.77	—	—	8.46	+77
Propylene glycol	8.41	—	—	13.85	+65
Benzene	6.59	—	—	5.38	-18
Hexane	6.14	—	—	9.23	+50
Cyclohexane	7.73	—	—	10.77	+39
Acetone	1.59	—	—	2.15	+35

TABLE III  
RELATIVE RETENTION VOLUMES AND PEAK RESOLUTION OF MODEL GASES ON PORAPAK Q OF DIFFERENT PRODUCTION BATCHES AND CONDITIONING PROCEDURES MEASURED BY GAS CHROMATOGRAPHY

Batch No.	Conditioning temperature (°C)	Specific surface area (m <sup>2</sup> /g)	Relative retention volumes		Peak resolution <i>R</i> propene/water
			Ethylene	Water	
516	25	530	0.129	0.725	1.80
516	190	648	0.130	0.730	1.70
555	25	592	0.123	0.610	2.40
555	190	621	0.125	0.516	3.40
631	25	550	0.128	0.535	2.98
631	190	655	0.130	0.525	3.08

When the Porapak was conditioned at 190° the relative retention volume of water was 0.516 for Porapak batch No. 555; 0.525 for batch No. 631 and even 0.730 for batch No. 516. The peak resolution decreases in the opposite direction. The influence of different conditioning on the relative retention volume and peak resolution varies according to different batches. While being very small with the batches Nos. 516 and 631 (the differences seem to be caused by the error of the measurements), this effect is quite obvious with batch No. 555. The change in peak resolution is also quite considerable. These changes are illustrated in Fig. 1.

The specific surface areas differ to a certain extent, but any evidence of a relationship between the changes in the retention behaviour of various substances and the specific surface area of the Porapak does not seem to exist (Table III).

TABLE IV

RELATIVE RETENTION VOLUMES AND PEAK RESOLUTION OF MODEL SUBSTANCES ON PORAPAK Q OF DIFFERENT PRODUCTION BATCHES AND CONDITIONING PROCEDURES MEASURED BY LIQUID CHROMATOGRAPHY

Batch No.	Conditioning temperature (°C)	Relative retention volume		Peak resolution <i>R</i>	
		DBP	Benzyl alcohol	DBP/benzene	Benzyl alcohol/DBP
516	25	4.07	14.0	1.10	1.67
516	190	4.10	14.2	1.21	1.74
631	190	2.36	8.95	0.56	1.36

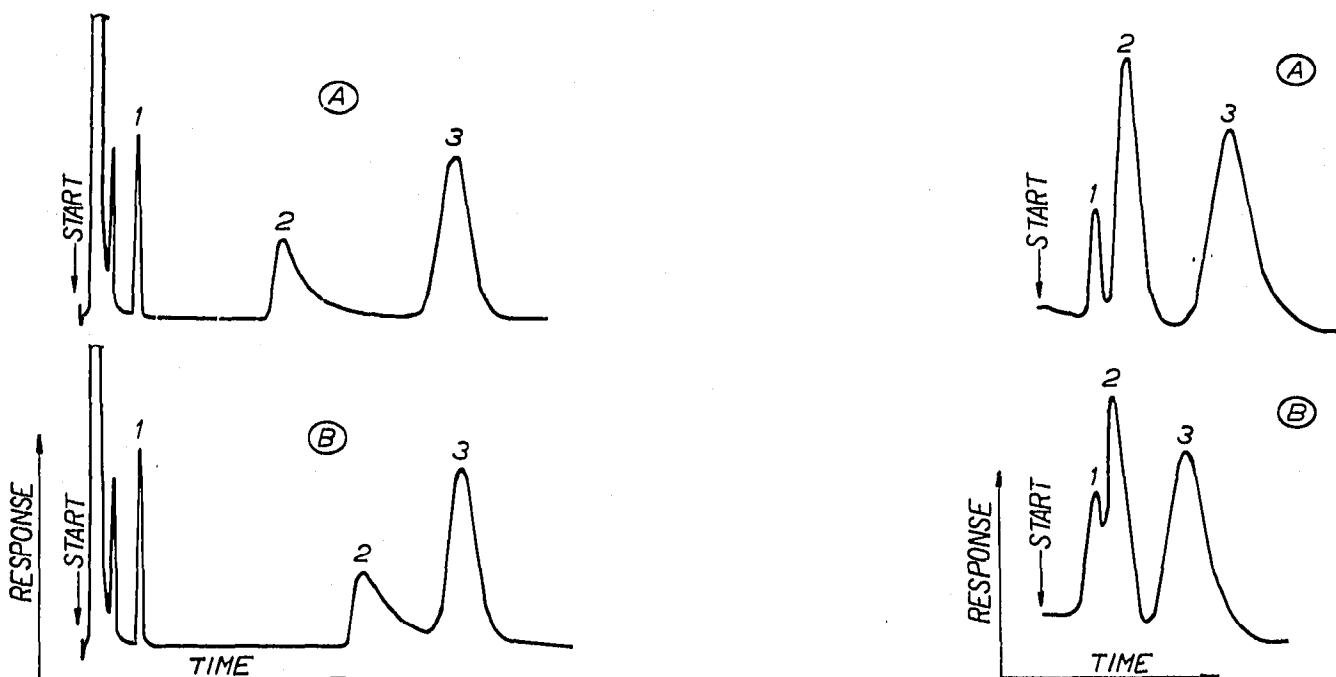


Fig. 1. Gas chromatogram of a model mixture on Porapak Q conditioned at 190°. 1 = Ethylene; 2 = water; 3 = propene. A = Batch No. 631; B = batch No. 516.

Fig. 2. Liquid chromatogram of model mixture on Porapak Q conditioned at 190°. 1 = Benzene; 2 = DBP, 3 = benzyl alcohol. A = batch No. 516; B = batch No. 631.

The results of the measurements carried out by liquid chromatography are summarised in Table IV. Relative retention volumes of DBP and benzyl alcohol, related to the retention volume of benzene, which was almost constant for all the samples, do not change substantially with different conditioning of the same polymer batch. However, the relative retention volume of DBP decreased by 42 % and that of benzyl alcohol by 37 % on using the polymer from another production batch. Similar changes could also be found in peak resolution. While different ways of conditioning change the *R* value by 5–10 %, the differences are substantially larger when polymer of another production batch is used. The chromatograms of the mixture mentioned are shown in Fig. 2.

Retention volumes of polar compounds (DPB, benzyl alcohol) on batch No. 631 obviously decrease when compared with the retention volumes of the same compounds on batch No. 516. The same effect may be found for the elution of water on the same materials (Fig. 1) in GC.

### Conclusions

From the data presented for retention volumes and peak resolution of model compounds on Porapak Q it is evident that they differ substantially depending on the individual batch used and in some cases also on the method of conditioning both in gas and liquid chromatography. The differences in retention data are so large that the tabulated retention data taken from the literature or those measured on a certain batch of Porapak or as subject to certain conditioning cannot be used practically for the qualitative identification of compounds on other batches. Any measurements of physical characteristics on the basis of retention data are also evidently only valid for the given material measured and have only an instructive significance for the general comparison of various types of Porapak.

We wish to thank Dr. D. KOUŘILOVÁ and Mrs. M. ROUDNÁ for the specific surface area measurements.

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

M. DRESSLER  
R. VESPALEC  
J. JANÁK

- 1 O. L. HOLLIS, *Anal. Chem.*, 38 (1966) 309.
- 2 O. L. HOLLIS AND W. V. HAYES, in A. B. LITTLEWOOD (Editor), *Gas Chromatography 1966*, Inst. Petrol., London, 1967, p. 57.
- 3 O. L. HOLLIS AND W. V. HAYES, *J. Gas Chromatogr.*, 4 (1966) 235.
- 4 J. JANÁK, *Chem. Ind.*, (1964) 1137.
- 5 J. JANÁK, Z. JAGARIĆ AND M. DRESSLER, *J. Chromatogr.*, 53 (1970) 525.
- 6 S. B. DAVE, *J. Chromatogr. Sci.*, 7 (1969) 389.
- 7 J. D. BURGER, *J. Gas Chromatogr.*, 6 (1968) 177.
- 8 J. R. L. SMITH AND D. J. WADDINGTON, *Anal. Chem.*, 40 (1968) 522.
- 9 J. R. LINDSAY SMITH AND D. J. WADDINGTON, *J. Chromatogr.*, 36 (1968) 145.
- 10 *Porapak*, Waters Associates, Inc., leaflets, 1965.
- 11 *Chromatography Packings, Components, Instruments and Services*, Waters Associates, Inc., leaflets, 1970.
- 12 F. M. ZADO AND J. FABECIĆ, *J. Chromatogr.*, 51 (1970) 37.
- 13 R. VESPALEC, J. MORÁVEK AND I. PIETRIK, *Elaboration of the First Foundations for the Control of Carbon Dioxide Circuits*, Research Report No. 00060401, Power Research Institute, Prague, Laboratory Jaslovské Bohunice, 1968.

- 14 T. A. GOUGH AND C. F. SIMPSON, *J. Chromatogr.*, 51 (1970) 129.
- 15 F. M. NELSEN AND F. T. EGGERTSEN, *Anal. Chem.*, 30 (1958) 1387.
- 16 D. KOUŘILOVÁ AND M. KREJČÍ, *Chem. Listy*, in press.
- 17 D. C. LOCKE, *J. Gas Chromatogr.*, 5 (1967) 202.
- 18 R. VESPALEC AND K. HÁNA, *J. Chromatogr.*, in press.
- 19 I. HALÁSZ, H. O. GERLACH, A. KRONENSEIN AND P. WALKING, *Z. Anal. Chem.*, 234 (1968) 98

Received March 24th, 1971

*J. Chromatogr.*, 59 (1971) 423-428