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EFFECT OF THE MESH-SIZE DISTRIBUTION OF POROUS POLYMER BEADS ON EFFICIENCY AND SELECTIVITY OF STATIONARY PHASES

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SUMMARY

The proposed method for the classification and characterization of the gas chromatographic behaviour of stationary phases of porous polymer beads is influenced by the mesh-size distribution of the different commercial batches, which changes the number of theoretical plates, the efficiency, and the selectivity of the columns.

The true distribution of the diameters of many batches of Porapak and Chromosorb "Century Series" PPB was therefore measured and compared with the nominal mesh range. Appreciable variation in the diameters between different batches was observed, and the effective size distribution was sometimes very different from the nominal values.

The gas chromatographic behaviour of columns packed with porous polymer beads of the same type but different sizes was investigated at various temperatures and column lengths by determining the theoretical plate number, the retention values, and the selectivity of the columns.

INTRODUCTION

Stationary phases of porous polymer beads (PPB) are suitable for the analysis of inorganic gases, light hydrocarbons and polar liquid compounds[1–6]. Porapak (Waters Assoc., Framingham, MA, U.S.A.) and Chromosorb Century Series (Johns-Manville, Denver, CO, U.S.A.) PPB are widely used. Different types of the two stationary phases are produced in order to permit a satisfactory separation of many compounds of different polarity. Similar behaviour of some Porapak and Chromosorb PPB was claimed, and this should allow the use of either product with similar results. Probably owing to different preparation techniques, the gas chromatographic (GC) behaviour of Porapak and Chromosorb PPB made from the same type of polymer was found to be more or less different[7].

From the point of view of the user, some of the observed differences are more useful than the claimed similarities, because the two PPB series can be used to increase the choice of stationary phases, mainly when mixed columns are applied to the fast and complete resolution of complex mixtures[8].

The characterization of Chromosorb and Porapak PPB has been studied pre-

viously, and classifications based on retention relative to reference compounds[9-11], retention indices with respect to light paraffins[12], and comparison with standard polarity phases (squalane and apolane)[13,14] have been proposed. Liquid stationary phases with a known chemical composition are expected to behave in a predictable manner, the only possible variations being due to temperature and to the influence of the solid support used; therefore, the proposed classifications of liquid phases[15,16] permit the behaviour of a given column to be predicted within very narrow limits.

Some problems are still encountered with polymeric liquid phases (silicones, polyglycols, etc.) where the actual distribution of molecular weights may differ from the nominal value (e.g. in the Carbowax series) and from the value of the batch used for the classification. The same problem arises with PPB, as the various batches or lots may differ in molecular weight, cross-linking ratio, amount of polarity modifier, pore-size distribution, real mesh size, specific surface area of the beads and column packing density.

The effects of the size of the polymer particles and of the column-packing density on retention times and shape of the peaks have scarcely been investigated. The retention times listed by the manufacturers do not refer to specific mesh sizes, and extensive research on the GC behaviour as a function of the diameter of the beads has not been reported. Mesh sizes 50–80, 80–100 and 100–120 have generally been used, but under different experimental conditions and for various analytical purposes. A comparison based only on literature data is therefore impossible. Moreover, the effective distribution of particle diameters in a batch of PPB of a given "nominal" mesh size is probably measured by the manufacturer but is not available to the users.

In order to investigate the effect of mesh size on GC behaviour, the effective diameter distribution of Porapak and Chromosorb PPB was measured, and analyses of standard gas mixtures were accomplished by using columns filled with various sizes and known amounts of these packings, thus permitting the evaluation of the column-packing density.

EXPERIMENTAL

The effective particle sizes could not be checked by sieving the various batches of PPB, because sieves with a mesh range smaller than 20 mesh units were not commercially available, the accuracy of the existing sieves was not high enough, and electrostatic charge effects may produce agglomeration of the beads and a greater "apparent" mesh size. Therefore, the particle-size distribution was obtained by measuring the diameter of the spherical particles on 60-times-enlarged photos taken with an optical microscope (Reichert Zetopan). A graduated reference slide (1 mm divided in 100 parts) was photographed with the samples in order to permit absolute diameter measurement, independent of the reproducibility of the photo enlargement. Photos of 10–20 samples, each containing 50–200 particles, were used to measure the size distribution of each polymer batch.

The various commercial mesh ranges correspond to slightly different metric diameters, depending on the classification (Tyler, U.S., Institute of Mining and Metallurgy, etc.)[17,18]. Fig. 1 is a plot of mesh sizes vs. diameter in micrometres, taken from different sources. As the producers of the tested beads are U.S. companies, the
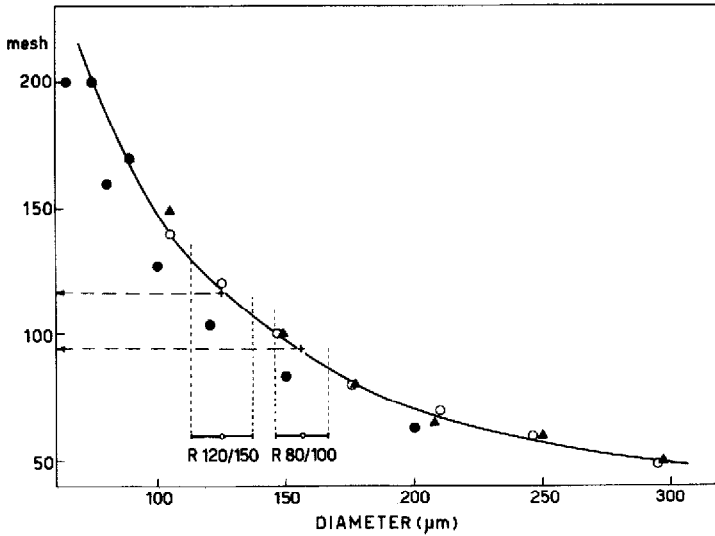
Fig. 1. Correlation between diameter and mesh size in different classifications: (O) U.S., (▲) Tyler, and (●) Institute of Mining and Metallurgy (IMM) (from refs. 17 and 18). Actual diameter ranges of Porapak R PPB used for comparison are shown (see text).

U.S./Tyler scale was used for calculation of the diameters corresponding to the mesh ranges.

The mean value between the greatest and the smallest diameter of each particle was calculated for polymers having non-spherical beads (Chromosorb 102 and 104 and Porapak Q in some mesh ranges). The histograms showing the distribution of some PPB batches are presented in Figs. 2 and 3. The average diameter, D, and the standard deviation, σ, are also shown and compared with the nominal mesh range. A general summary of the results is shown in Table I and Fig. 4. As a general rule, Porapak PPB have spherical shapes and a narrow range of diameter, whereas Chromosorb types have a more irregular appearance. Variable amounts of the various
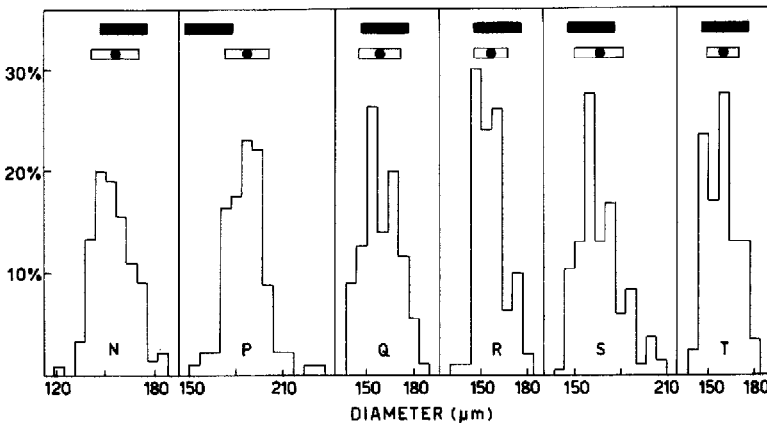

Fig. 2. Histograms showing the diameter distribution of some batches of 80–100 mesh Porapaks. Nominal interval (■), average diameter (●) and σ interval (□).
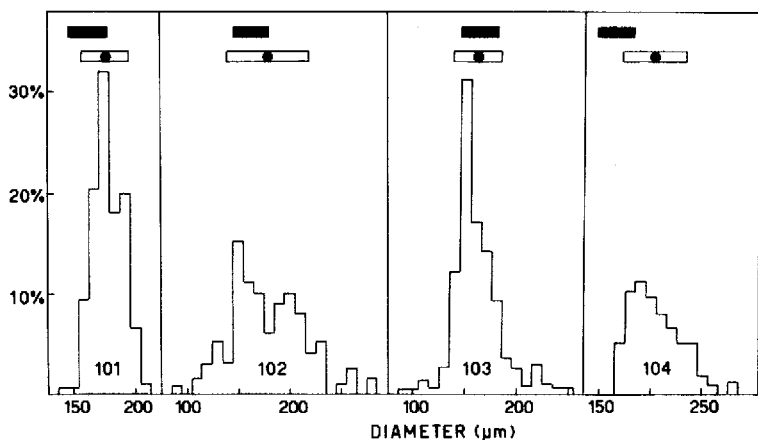
Fig. 3. Histograms showing the diameter distribution of some batches of 80–100 mesh Chromosorb "Century Series". For symbols see Fig. 2.

PPB (from 14 to 100%, with an average of 66 ± 24%) fall within the nominal mesh range.

The effect of the mesh-size distribution on the efficiency of the column was investigated by carrying out analyses of standard mixtures of methane, carbon dioxide, ethyne, ethene and ethane at temperatures ranging from 25 to 60°C, with a flow-rate of 22 cm³/min of helium. Tables II and III show the number of theoretical plates per metre, averaged for all the tested batches of every PPB type and for the whole temperature range. The difference between two columns filled with the same batch (P I and P II), the effect of the total column length (R 80–100, 3, 2, and 1 m), and the influence of the mesh size (R 80–100 and R 120–150) are also shown in Table II.

The differences between the various compounds analysed can be correlated with the different elution order and asymmetry of the peaks, depending on the polarity of the PPB, whereas the values of the σ depend on both the fluctuations between different runs and on the effects of temperature on retention time and peak shape. The columns with the narrowest mesh range showed the greatest efficiency.

The comparison between the behaviour of Porapak R 80–100 and 120–150 mesh (nominal values) was further investigated. The batches of these types of Porapak were chosen because of their narrow and symmetrical diameter distribution, confirmed by the high number of theoretical plates and by the low σ values. Whereas the 80–100 batches had an average diameter nearly coincident with the centre of the nominal mesh range, the 120–150 batch distribution was centred on the lowest value of the nominal interval, and therefore corresponds to a true 100–130 mesh range (see Fig. 1). The theoretical plate number of the smallest size batch is *ca.* 30% greater for equal column lengths.

Fig. 5 shows the linear behaviour of the values for the logarithm of the net retention value, V_N, obtained by multiplying the adjusted retention volume, V'_R, by the column pressure-gradient correction factor of Martin and James[19],

$$ j = \frac{3(P_i - P_0)^2 - 1}{2(P_i - P_0)^3 - 1} $$

TABLE I

DIAMETER DISTRIBUTION OF SOME BATCHES OF VARIOUS PPB

PPB type	Nominal value		Batch (lot)	Average diam. (μm)	±σ(%)	Minimum diam. (μm)	Nominal mesh range (%)			Maximum diam. (μm)
	Mesh	Diam. (μm)					Above	Within	Below	
Porapak										
N	80–100	147–175	1201	157 ± 15	9.6	121	18	79	3	215
			1210	143 ± 10	7.0	120	54	46	–	165
			1128	155 ± 16	10.3	125	28	63	9	190
P	80–100	147–175	1769	187 ± 14	7.5	153	–	20	80	247
Q	50–80	175–295	1016	216 ± 17	7.9	186	–	100	–	263
			1250	197 ± 23	11.9	154	18	82	–	269
	80–100	147–175	1297	159 ± 11	6.9	141	9	84	7	186
			1297★	165 ± 14	8.5	147	–	88	12	201
			1477	153 ± 10	6.5	125	15	84	1	180
			1457	157 ± 7	4.4	140	22	87	1	180
	100–120	124–147	1444	134 ± 11	8.2	102	22	62	16	154
	120–150	97–124	410	121 ± 10	8.3	102	–	68	32	154
			516	100 ± 8	8.0	70	16	84	–	180
	150–200	74–97	651	95 ± 6	6.3	83	–	69	31	115
			1423	85 ± 7	8.2	65	3	91	6	100
R	80–100	147–175	609	156 ± 10	6.4	134	2	96	2	181
	120–150	97–124	425	125 ± 12	9.6	121	18	79	3	215
S	80–100	147–175	684	167 ± 15	9.0	147	–	81	19	208
			686	151 ± 15	10.0	135	35	63	2	185
T	80–100	147–175	1797	159 ± 10	6.4	140	2	95	3	180
Chromosorb										
101	80–100	147–175	70	183 ± 20	10.9	80	2	31	67	250
102★			31274	178 ± 38	21.3	90	16	36	48	290
			2409	184 ± 29	15.8	145	41	59	22	265
			261	181 ± 26	14.4	135	–	53	47	225
			102	154 ± 14	9.1	100	21	62	17	190
103			26	161 ± 23	14.3	80	15	65	20	290
104★			2415	163 ± 30	18.4	110	30	35	35	230
105			10	129 ± 25	19.8	80	67	30	3	220
107			3	182 ± 20	11.0	130	–	14	86	210

★ Irregularly shaped beads.

as a function of the reciprocal of the absolute temperature, T. The values for the 100–130 mesh columns are higher than the corresponding values for the 80–100 mesh columns; the effect of mesh size is not the same for all of the compounds tested and, therefore, the classification according to I values is also slightly influenced (Fig. 6).

Owing to the fact that the packing density of the columns depends on the average diameter of the PPB, the columns filled with 80–100 Porapak R contained an average of 4.3 ± 0.05 g of stationary phase, and those filled with 100–130 mesh Porapak R contained 4.5 ± 0.04 g. It is known that the highest possible packing density (obtained with a face-centred cubic lattice) fills *ca.* 74% of the available volume when all the spheres have the same diameter. By taking into account the different diameters of the PPB, a slightly disordered structure results and, therefore,

TABLE II

NUMBER OF THEORETICAL PLATES PER UNIT LENGTH (n/m), AND PERCENTAGE STANDARD DEVIATION OF THE VALUES (σ) FOR THE VARIOUS COMPOUNDS ON DIFFERENT PORAPAK TYPES

Column length, 3 m; mesh size, 80–100 (except for Porapak R, where indicated).

| Porapak | N | | PI | | PII | | Q | | S | | T | | R 80–100 | | | | | | R 120–150* | |
| | | | | | | | | | | | | | 1m | | 2m | | 3m | | 3m | |
	n/m	σ	n/m	σ	n/m	σ	n/m	σ	n/m	σ	n/m	σ	n/m	σ	n/m	σ	n/m	σ	n/m	σ
Methane	580	7	500	14	530	10	420	12	580	15	740	14	410	13	510	13	710	7	920	7
Carbon dioxide	1230	3.7	850	16	890	18	590	20	1220	7	1060	7	830	15	900	9	1030	9	1390	3
Ethene	1190	12	1160	16	1030	21	360	11	1190	9	1080	20	1100	7	1050	9	1060	7	1520	4
Ethyne	1170	10	1090	20	1040	23	430	18	1090	14	1040	17	1120	8	1080	10	1200	3	1480	3
Ethane	1150	11	1190	16	1200	16	590	9	950	11	1020	13	1010	7	1030	13	1140	7	1330	5

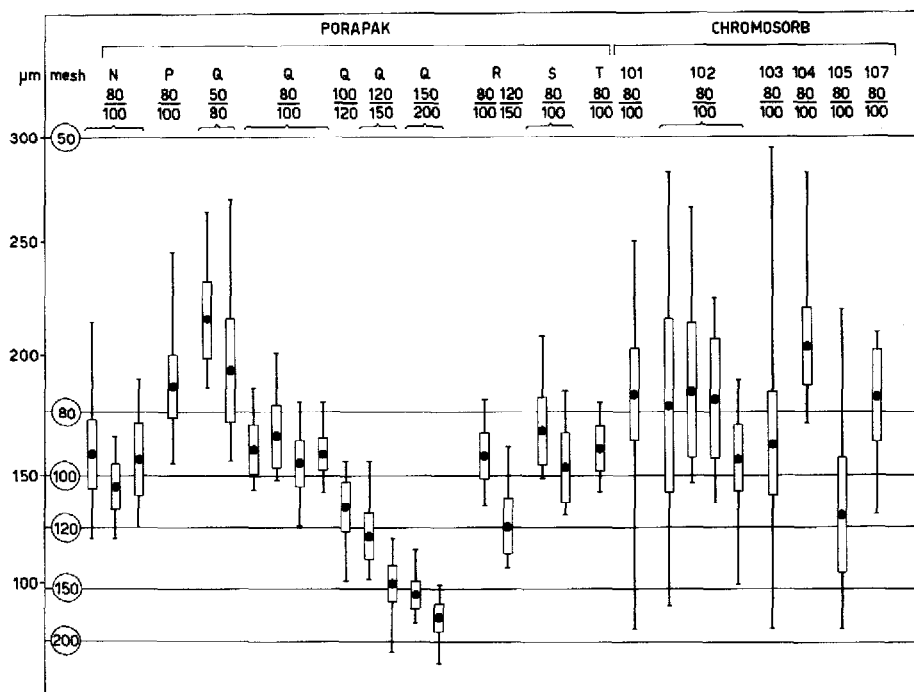* Nominal values; true mesh range 100–130 (see text).

Fig. 4. Average diameter (●), standard deviation (□) and max.–min. diameter range (|——|) of many different PPB, compared with the nominal mesh ranges.

a theoretical calculation of the void volume of the columns is difficult. On the basis of the weight of stationary phases, and under the assumption that the density, ρ, of Porapak R is independent of the mesh size, it can be concluded that the filling efficiency of the 100–130 mesh batch is *ca.* 5% higher than that of the 80–100 mesh-batch.

The use of the specific retention volume, $V_g = 273 \, V_N/W_L T_C$ (where W_L is the weight of liquid phase in the column), that corresponds to the volume of gas required to move one half the sample through a theoretical column containing 1 g of liquid phase, may not be justified for a PPB stationary phase, because it is not clear whether the separation mechanism involves the entire volume of the beads or a surface layer of varying depth, depending on the diameter, shape, and mobility of the sample molecules. In addition, the relative importance of purely diffusive phenomena, which probably predominate at low temperatures, is not known with respect to absorption and solution of the sample component in the beads, which increases with increasing temperature and thermal softening of the cross-linked polymer.

Therefore, in order to take into account the different amounts of PPB in the columns filled with different mesh ranges, and therefore the column-packing density, the net retention volumes per gram of solid stationary phase, $V_S = V_N/W$ (where W is the total weight of the PPB), were calculated. The V_S values at 30 and 60°C for the various gases and the values of the ratio $V_S(80–100):V_S(100–130)$, averaged for the V_S values from 25 to 60°C at 5°C intervals, are shown in Table IV. The change of V_S

TABLE III

NUMBER OF THEORETICAL PLATES PER UNIT LENGTH (n/m) AND PERCENTAGE STAN-
DARD DEVIATION OF THE VALUES AVERAGED OVER ALL TEMPERATURES (σ), FOR THE
VARIOUS COMPOUNDS ON DIFFERENT CHROMOSORB TYPES

Column length 3 m, mesh size 80–100.

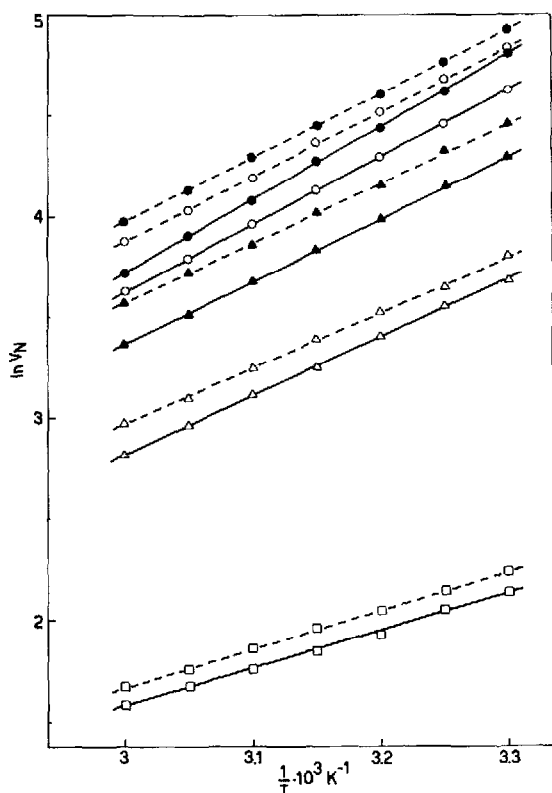| Compound	Chromosorb									
	101		102		103		104		105	
	n/m	σ	n/m	σ	n/m	σ	n/m	σ	n/m	σ
Methane	490	21	560	8	370	15	460	15	930	8
Carbon dioxide	780	15	760	8	310	28	940	7	870	6
Ethene	810	10	810	10	220	24	500	16	990	5
Ethyne	820	15	860	12	370	13	880	11	990	4
Ethane	660	7	880	6	280	22	970	8	950	3

Fig. 5. ln V_N of reference compounds as a function of $1/T$ on Porapak columns of different mesh size.
Curves: ——, 80–100 mesh; ------, 100–130 mesh). ●, ethyne; ○, ethane; ▲, ethene; △, carbon dioxide;
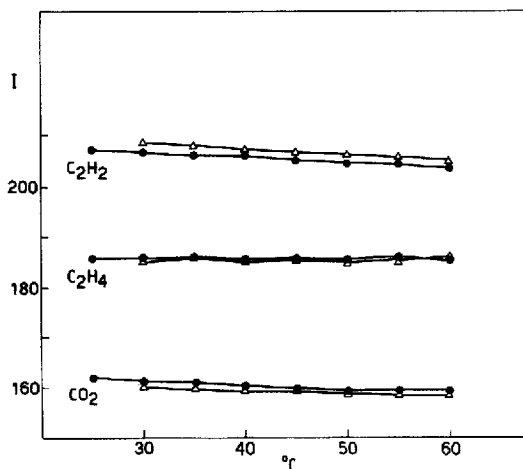□, methane.

Fig. 6. Retention index values of reference compounds as a function of temperature and mesh size. ●, 80–100 mesh; △, 100–130 mesh.

values with temperature is great, reflecting the variation in the retention time, but their ratio remains nearly constant for each compound, as shown by the small values of the standard deviation, σ.

Table IV also shows that the relative increase of V_S when changing from 80–100 to 100–130 mesh

$$\Delta V_s(\text{rel}) = \frac{V_S (100\text{–}130) - V_S (80\text{–}100)}{V_S (80\text{–}100)} \, 100$$

increases with increasing retention time, but not in proportion to it. The change of the adsorption enthalpies, ΔH°[10,20,21], which gives an idea of the molecular interactions and can be calculated from the slope of the plot ln V_N (or V_S) against $1/T$ from the equation

$$\ln V_s = \frac{-\Delta H^{\circ}}{RT} + q$$

is between 2 and 4% when changing from 80–100 to 100–130 mesh. This variation is of the order of magnitude of the experimental error and therefore the interactions of the two types of Porapak R can be assumed to be the same.

The different sensitivities of the retention volumes of the various compounds to the change of mesh size may be explained in terms of different depths of diffusion into the beads, depending on the molecular dimensions and free path with respect to the pore diameter.

The observed difference in the behaviour of batches with different mesh sizes cannot be explained merely by differences in chemical composition and specific surface areas caused by non-reproducible syntheses, because the $\Delta V_s(\text{rel})$ values between various batches of Porapak R 80–100 with average diameters close to the centre of

TABLE IV

EFFECT OF MESH SIZE ON THE BEHAVIOUR OF PORAPAK R COLUMNS

For symbols see text.

	$V_S(80-100)$		$\Delta V_S(rel)$ (%) various 80-100	$V_S(100-130)$		$\dfrac{V_S(80-100)}{V_S(100-130)}$ (average %)	$\pm\sigma$ (%)	$\Delta V_S(rel)$ (80-100 vs. 100-130) (%)	$-\Delta H°$ (80-100) (kcal mol⁻¹)	$-\Delta H°$ (100-130) (kcal mol⁻¹)	$\dfrac{\Delta V_S}{\Delta \bar{m}}$
	30°C	60°C		30°C	60°C						
Methane	1.98	1.14	±1.7	2.09	1.20	94.07 ± 1.05	1.12	5.55	3.64	3.72	0.27
Carbon dioxide	9.33	3.98	±1.9	9.89	4.34	92.04 ± 1.02	1.09	6.00	5.73	5.60	0.36
Ethene	17.16	6.77	±2.2	19.12	7.89	87.87 ± 0.96	1.09	11.42	6.21	6.00	0.55
Ethane	24.07	9.12	±2.4	27.70	10.76	85.36 ± 0.79	0.93	15.08	6.53	6.41	0.66
Ethyne	28.72	9.83	±3.8	34.84	12.05	81.77 ± 0.42	0.51	21.31	7.22	7.20	0.83

the nominal mesh range were appreciably smaller than the observed variation between 80–100 and 100–130 mesh (see Table IV, second column).

The observed increase in ΔV_s(rel) follows the behaviour of the b term of the Van der Waals' equation (due to the finite volume of the molecules and to their general incompressibility)[22], which increases in the order methane < carbon dioxide < ethyne < ethene < ethane, except for ethyne, which shows a greater increase in V_s, but can be correlated with the linear and rigid structure of the molecule. Therefore, the V_s(rel) increase can be correlated with the increasing difficulty of the sample molecules to permeate the bead volume, which reduces their interaction with the large beads, decreasing the retention times on the 80–100 polymer. One can expect that a complete interaction of all sample molecules, independent of their size, with the entire bead should only be possible for very small PPB, as confirmed by the increasing theoretical plate number. On the other hand, very small mesh sizes cause a high packing density and require a very high input pressure.

From the practical point of view, the effect of mesh-size variation on the classification of the PPB can be evaluated by taking into account that, in terms of retention index values, the observed ΔV_s(rel) between 80–100 and 100–130 correspond to *ca.* ± 2 index units (IU) at 30°C and ± 1.5 IU at 60°C. By dividing ΔV_s(rel) by the difference between the average mesh size of the two Porapak R batches, $\Delta \bar{m}$, (156 μm corresponding to 95 mesh, 125 μm to 117 mesh) the percentage variation of the retention for each mesh unit is obtained (see Table IV).

The effect of a variation of *ca.* 0.1 IU per mesh on the PPB characterization based on I values is negligible when the average diameter of any given PPB batch falls within the nominal mesh range and for the most widely used 80–100 mesh PPB. In many of the batches tested (see Table I and Fig. 4) the $\Delta \bar{m}$ between the true mesh average and the centre of the nominal interval is smaller than 20 and, therefore, the variation in I is probably within ± 2 IU. On the other hand, when different mesh-size intervals are compared, and when compounds showing opposite changes of their I values (*e.g.* carbon dioxide and ethyne in the test mixture) are analysed, differences in the I values of *ca.* 5–10 IU can be expected that are two to three times greater than the observed differences between various batches of the same mesh size. In this instance, the validity of any classification based on retention times or indices may be strongly reduced when different batches of unknown mesh-size distribution are compared.

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