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CLASSIFICATION OF THE "POLARITY" OF POROUS POLYMER BEAD COLUMNS FOR GAS CHROMATOGRAPHY AT HIGH TEMPERATURE BY ANALYSIS OF STANDARD POLARITY PROBES

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SUMMARY

The classification of the "polarity" of Porapak and Chromosorb "Century Series" porous polymer bead (PPB) stationary phases was made on the basis of the retention index values of Rohrschneider's and some of McReynolds' polarity probes (ethanol, butanol, pyridine, nitromethane, 1-nitropropane, benzene, methyl ethyl ketone and methyl propyl ketone).

Except for Porapak T and Chromosorb 107 and 108, the average polarities, calculated from the sum of the ΔI values of selected probes with respect of the less polar PPB Chromosorb 106, were fairly constant during the ageing of the columns. The "polarity order" obtained from the average polarities determined with butanol, benzene, methyl propyl ketone and pyridine (at 200°C) was: Chromosorb 106, Porapak Q, Chromosorb 102, Porapak R and Chromosorb 105, Porapak N, Chromosorb 101, Porapak P, Chromosorb 103, Chromosorb 104. Increasing polarities with column ageing were shown by Chromosorb 107, Porapak T and Chromosorb 108. Linear relationships between the polarity order at low temperature, calculated by gaseous probes, and the high-temperature polarity order were found when PPBs of similar chemical composition were considered.

INTRODUCTION

The classification of the "polarity" of the stationary phases used in gas chromatography (GC) involves complex thermodynamic aspects and, when completely achieved, will give useful information on the separation mechanisms. The state of the art on this topic is still open to discussion but, from the point of view of practical application, any classification system should reveal the similarities and differences of a great number of phases, reduce the number of phases being used and assist the gas chromatographer to select the best phase for a given separation or to replace with a similar one a phase not readily available.

For liquid phases, the polarity was determined by using selected "polarity probes" by Rohrschneider¹ (benzene, ethanol, methyl ethyl ketone, nitromethane and pyridine) and by McReynolds² (benzene, butanol, 2-pentanone, nitropropane,

pyridine, 2-methyl-2-pentanol, iodobutane, 2-octyne, 1,4-dioxane and *cis*-hydrindane). Generally, the first five probes proposed by McReynolds are used for classification and their ΔI values with respect to the retention index on squalane (taken as the standard non-polar liquid phase), ΔI_{sq} , are listed in many catalogues of GC accessories and materials, and provide information on selective interactions and on the general polarity of one particular liquid phase compared to another.

Some attempts were made to apply the McReynolds polarity scale to porous polymer beads (PPBs) used as stationary phases^{3,4}. Negative values of ΔI_{sq} found for some polarity probes, implying that some PPBs are less polar than squalane, led to the conclusion that graphitized thermal carbon black (GTCB) could be used to replace squalane as the standard non-polar solid phase⁶. Another polarity mixture (acetonitrile, benzene, methyl ethyl ketone, *tert.*-butanol) was used for the classification of Chromosorb PPBs⁷, probably owing to the close values of the boiling points of these probes, but no correlation with any reference phase was made and ΔI values were not calculated.

In previous papers⁸⁻¹⁰ the characterization of PPBs by using relative retention, α , or retention index values, I , was accomplished at low temperature, and a polarity order obtained with Porapak Q being used as the "less-polar" reference phase. The use of a commercial porous polymer as the reference phase may lead to uncertainty in the numerical values of the polarity, expressed in terms of ΔI_Q (the difference between the I values on any given phase and those on Porapak Q), because retention data on commercial polymers may change from batch to batch.

Previous researches showed that many of the variations between retention data on PPBs reported in the literature were probably due to the influence of the analytical parameters, *e.g.*, temperature and carrier gas flow-rate¹¹, mesh size⁸, amount of injected sample¹¹, previous ageing¹² and contamination of the column. In addition, some experiments with GTCB showed that the batch-to-batch variations of retention times on this solid adsorbent were similar to those observed on thermally stable PPBs, Porapak Q, N, R and Chromosorb 106, thus not justifying the choice of a reference phase so chemically different to the PPBs.

An "internal reference" polarity scale, however, with the ΔI values of liquid probes calculated with respect to the PPB showing the smallest values of retention index, seems to be precise enough for comparing the behaviour of commercial PPBs, in order to permit the choice of the best phase for a given separation and the selection of a packing nearly equivalent to another not readily available. On the other hand, the classification of PPBs at room temperature, while useful for column selection in gas analysis, should be modified at high temperature owing to the increasing importance of absorption and solution phenomena with respect to adsorption.

The Chromosorb "century series" and Porapak PPBs were therefore characterized at 200°C by using Rohrschneider's and McReynolds' probes, and the results were compared with the classification obtained by using methane, ethane, ethylene, acetylene and carbon dioxide at low temperature¹⁰.

EXPERIMENTAL

All the columns were made with stainless steel (3 m × 2.4 mm I.D.), packed with Porapak and Chromosorb PPBs (80-10 mesh). A Varian 3760 gas chromato-

graph was used, at $200 \pm 1^\circ\text{C}$, with a constant helium flow-rate of 22 ml min^{-1} . monitored before and after each run and corrected when necessary. Direct on-column injections of the samples ($0.2\text{--}0.4 \mu\text{l}$) were accomplished by means of Hamilton microsyringes. A high-sensitivity thermal conductivity detector was used and the results were monitored by a Varian CDS-111C data system. The accuracy of measurement of the retention times was $\pm 0.01 \text{ min}$ and the adjusted retention times, t'_R , were calculated with respect to the retention time of air, corresponding, at 200°C , to that of helium, as shown by using hydrogen as the carrier gas in some runs.

Rohrshneider's probes, ethanol (ETA), methyl ethyl ketone (MEK), nitromethane (NM), benzene (BE) and pyridine (PY), and some of McReynolds, butanol (BUA), methyl propyl ketone (MPK) and 1-nitropropane (1NP), were injected along with $\text{C}_5\text{--C}_{11}$ linear alkanes, in suitable mixtures to avoid peak interferences. Sometimes, in order to obtain small and regular peaks when injecting mixtures containing few probes and alkanes, xylene (which is eluted after all the peaks of interest) was used as a solvent.

The retention index values, I , were measured on freshly prepared PPB columns and the analyses were repeated at regular intervals during an ageing period up to 25 days, as it was previously shown that the retention times of some compounds on some PPBs change with column ageing¹². A BASIC program was used for the calculations (Commodore CBM 4016 mini-computer).

RESULTS AND DISCUSSION

The majority of the PPBs tested showed a linear dependence of the adjusted retention times, t'_R , and retention index values, I , as a function of the ageing time, t .

Tables I and II show the values of the initial adjusted retention times, $t'_R(0)$, and of the coefficients, a and b , for linear alkanes

$$\log t'_R = a + bt \quad (1)$$

on all of the Porapak and on Chromosorb 101, 102, 104, 105 and 106. Table III shows the values of t'_R of linear alkanes at various ageing times on Chromosorb 103, 107 and 108, which show a non-linear dependence on t .

Tables IV and V show the values of the initial retention index, I_0 , and of the slope, k , of the equation

$$I = I_0 + kt \quad (2)$$

for the various polarity probes on the columns showing a linear relationship between I and t . Chromosorb 103 belongs to this group, notwithstanding the non-linearity of the $\log t'_R$ plot. Table VI shows the I values at various ageing times for Chromosorb 107 and 108 only.

Figs. 1 and 2 show the trends in I values as a function of t on different PPBs, representing typical behaviours with respect to eqn. 2, as shown by the slope values in Tables IV and V, and which can be summarized as follows:

(1) Chromosorb 102 and 106, Porapak N, Q, R, S (alcohols and pyridine show tailing peaks on Porapak Q and S; the correlation coefficients of eqn. 2 are small) produce horizontal plots

TABLE II
VALUES OF $t_R(0)$ AND OF a AND b FOR LINEAR ALKANES ON CHROMOSORB PPBs SHOWING THE LINEAR RELATIONSHIP BETWEEN $\log t_R$ AND AGEING TIME, t

Alkane	$t_R(0)$ (min)					a					$b \times 10^4$				
	101	102	104	105	106	101	102	104	105	106	101	102	104	105	106
<i>n</i> -Pentane	1.00	2.61	0.74	-0.20	9.88	0.0002	0.42	-0.13	0.63	0.99	11.2	8.1	4.33	-11.61	8.11
<i>n</i> -Hexane	1.79	5.07	1.20	8.26	20.25	0.25	0.70	0.08	0.92	1.31	14.2	9.4	6.93	9.63	11.01
<i>n</i> -Heptane	3.15	9.70	1.90	15.79	41.58	0.50	0.99	0.28	1.20	1.62	18.3	11.5	9.22	9.81	11.45
<i>n</i> -Octane	5.52	18.44	3.04	29.95	85.23	0.74	1.26	0.48	1.48	1.93	22.2	14.4	8.14	5.69	10.20
<i>n</i> -Nonane	9.75		4.77			0.99		0.68			18.5		10.96		
<i>n</i> -Decane			7.48					0.87					7.86		
<i>n</i> -Undecane			11.53					1.06					0.80		

TABLE III

ADJUSTED RETENTION TIMES, $t'_R(\text{min})$, OF LINEAR ALKANES AT VARIOUS AGEING TIMES, t , ON CHROMOSORB PPBs SHOWING THE NON-LINEAR DEPENDENCE OF $\log t'_R$ ON t (SEE FIG. 2)

	Chromosorb 103 aged for			Chromosorb 107 aged for			Chromosorb 108 aged for		
	0	8	22 days	0	10	22 days	0	10	22 days
<i>Alkane</i>									
<i>n</i> -Pentane	0.61	0.64	0.67	3.34	2.66	2.52	1.53	1.03	0.87
<i>n</i> -Hexane	1.04	1.12	1.16	6.51	4.99	4.68	2.75	1.78	1.48
<i>n</i> -Heptane	1.73	1.90	2.01	12.52	9.15	8.49	4.91	2.99	2.47
<i>n</i> -Octane	2.89	3.23	3.39	23.90	16.57	15.21	7.36	4.97	4.07
<i>n</i> -Nonane	4.78	5.37	5.78	36.34	30.00	27.26	12.05	8.21	6.72
<i>n</i> -Decane	8.56	9.41	9.73				18.51	13.53	11.14

(2) Chromosorb 104 and 105 and Porapak P show the plots for some probes to be horizontal, with others slightly increasing

(3) Chromosorb 101 shows the plots for some probes to be horizontal with others slightly decreasing

(4) Porapak T shows that all of the plots linearly increase

(5) Chromosorb 107 and 108 shows that all of the plots increase, but not linearly

(6) Chromosorb 103, which, as seen above, shows a non-linear dependence of $\log t'_R$ on t , yields I values which are linear as a function of ageing time: the plots for ethanol and butanol increase, those for benzene and pyridine decrease and those for methyl ethyl and methyl propyl ketone are horizontal.

The PPBs to be used as the reference for the calculation of the ΔI values should be either Porapak Q or Chromosorb 106, which show the lowest I_0 and k values. Porapak Q was used as the reference phase for the classification at low temperature¹⁰, but unfortunately the peaks of alcohols and pyridine showed appreciable tailing and the calculations of their I values was therefore subject to uncertainty (see Table IV). Furthermore, the I_0 values on Chromosorb 106 are slightly smaller than on Porapak Q and Chromosorb 106 was therefore chosen as the "less polar" reference in order to give positive ΔI values for all the tested PPBs, which are shown in Table VII and were calculated from

$$\Delta I_{200}^{106}(\text{X}) = I_{200}^c(\text{X}) - I_{200}^{106}(\text{X}) \quad (3)$$

where according to proposed nomenclature rules¹³, c indicates the type of column used and X the polarity probe. For the sake of simplicity, the temperature indication will be omitted in the following discussion.

When the change of the I values with column ageing was small, *i.e.*, when the value of the slope of eqn. 2, k , was ≤ 0.3 , the ΔI^{106} values were calculated from the I^c values averaged over the entire ageing time; when the values of k were greater than 0.3 or when the I^c plots were not linear (Chromosorb 107 and 108), the "initial" and "final" (after 22 days) I^c values were used for the calculations. The ΔI^{106} values for nitromethane and 1-nitropropane on Porapak S and Chromosorb 103 are not shown

TABLE V
VALUES OF I_0 AND OF k FOR THE POLARITY PROBES ON THE VARIOUS CHROMOSORB PBs SHOWING THE LINEAR DEPENDENCE OF I
ON THE AGEING TIME, t

For symbols of probes see Table IV.

Probe	I_0										k									
	101	102	103	104	105	106	101	102	103	104	105	106	101	102	103	104	105	106		
ETA	469.0	410.0	549.5	703.7	438.6	374.9	-0.054	0.012	0.449	0.225	0.450	-0.056	-0.054	0.012	0.449	0.225	0.450	-0.056		
MEK	625.9	573.8	682.9	870.0	598.1	550.2	-0.136	0.014	0.005	0.108	0.321	-0.019	-0.136	0.014	0.005	0.108	0.321	-0.019		
NM	618.5	520.8	*	982.5	547.6	465.2	-0.341	-0.046	-	-0.090	0.106	-0.093	-0.341	-0.046	-	-0.090	0.106	-0.093		
BE	723.3	648.7	763.6	860.9	647.7	616.7	-0.348	-0.054	-0.336	0.063	-0.010	-0.036	-0.348	-0.054	-0.336	0.063	-0.010	-0.036		
BUA	676.8	624.3	758.9	927.8	660.8	599.9	-0.131	0.038	0.336	0.085	0.349	-0.054	-0.131	0.038	0.336	0.085	0.349	-0.054		
MPK	715.3	668.2	770.1	960.7	690.5	646.8	-0.149	0.029	-0.063	0.036	0.409	-0.030	-0.149	0.029	-0.063	0.036	0.409	-0.030		
PY	814.9	722.6	883.7	1075.7	745.9	673.0	-0.299	-0.025	-0.403	0.315	0.913	-0.052	-0.299	-0.025	-0.403	0.315	0.913	-0.052		
INP	777.5	697.7	*	1124.1	728.0	658.5	-0.305	-0.058	-	0.279	0.153	-0.046	-0.305	-0.058	-	0.279	0.153	-0.046		

* Reacts with the stationary phase, giving multiple or very broad peaks.

TABLE VI

VALUES OF THE RETENTION INDEX, I , OF THE POLARITY PROBES ON CHROMOSORB PPBs SHOWING THE NON-LINEAR DEPENDENCE OF I ON AGEING TIME, t

Symbols as in Table IV.

Probe	Chromosorb 107 aged for			Chromosorb 108 aged for		
	0	10	22 days	0	10	22 days
ETA	514	525	537	568	595	603
MEK	656	681	688	715	729	735
NM	644	683	692	744	782	793
BE	670	698	708	748	764	771
BUA	738	758	766	814	825	834
MPK	753	779	787	808	820	829
PY	812	831	844	903	926	935
INP	838	860	872	923	942	950

because these compounds gave multiple or very broad peaks on these columns, probably due to reaction with the stationary phase.

The “average polarity” of each PPB in the Rohrschneider (R) and McReynolds (MR) reference systems was determined from the sum of the ΔI values of the respective probes, Σ_R^5 and Σ_{MR}^2 . Owing to the fact that nitromethane and nitropropane yield multiple or very broad peaks by reacting with Porapak S and Chromosorb 103, this classification would not be used for these PPBs. The sums of the ΔI values, except those for NM and NP, *i.e.*, Σ_R^4 and Σ_{MR}^4 , were therefore calculated, and are compared with the Σ_R^5 and Σ_{MR}^5 values in Table VIII, where the PPBs are listed in

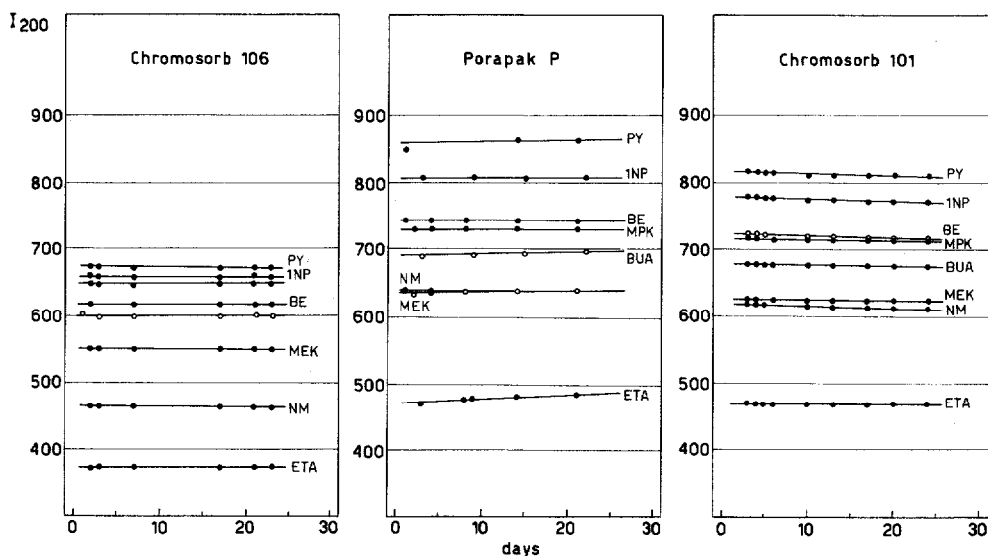


Fig. 1. Values of the retention index, I_{200} , of Rohrschneider and McReynolds polarity probes on PPBs showing constant values of I_{200} as a function of the ageing time at 200°C. For symbols of the probes see Table IV and text.

TABLE VII
 VALUES OF M_{200}^{106} (SEE EQN. 3) OF THE VARIOUS POLARITY PROBES
 When two values are shown, the upper one refers to new and the lower one to the aged column (22 days at 200°C under helium flow).

	ETA	MEK	NM	BE	BUA	MPK	PY	INP
<i>Porapak</i>	N	115.6	85.5	150.3	49.8	108.2	83	97.7
		96.8						126
	P	114.8	91	176.5	129.9	98.9	84.9	175.5
		26.7	4	15.9	7.3	10.1	3.7	196.2
	Q	87.2	47.2	96.0	31.5	77.2	45.5	14.6
		70.3	31.9	*	17.6	52.5	32.5	68.8
	179	155	265.9	113.5	182.9	152.8	40.8	73.7
	244.7	199	362.5	161.7	244.5	189.3	187.4	*
							272.5	292.5
								317.8
<i>Chromosorb</i>	101	94.1	74.3	155.7	107.4	75.9	66.3	144.3
		35.6	24	148.7	100.4			138.0
	102	174.1	133	56.2	31.9	25.4	21.4	49.6
		184		*	146.9	160.4	122.2	212.4
	103	332.5	321.5	516.8	140.2	167.2		203.4
		63.7	47.6		245.6	329.6	314.1	404.5
	104	76.9	56.8	84.9	31.4	61.5	45.3	414.9
		0	0	0	0	71.2	55.2	73.5
	105	139.8	106.3	179.6	54.2	0	0	97.5
		158.4	138.2	227.6	91.8	139	105.5	0
	106	194.2	165.2	280.0	131.9	167.9	139.9	140.1
		228.4	184.7	329.0	155.0	214.8	161.3	171.7
					234.6	181.9	230.7	
							262.4	
								180.5
								214
								265.3
								292.3

* Reacts with stationary phase, giving multiple or very broad peaks.

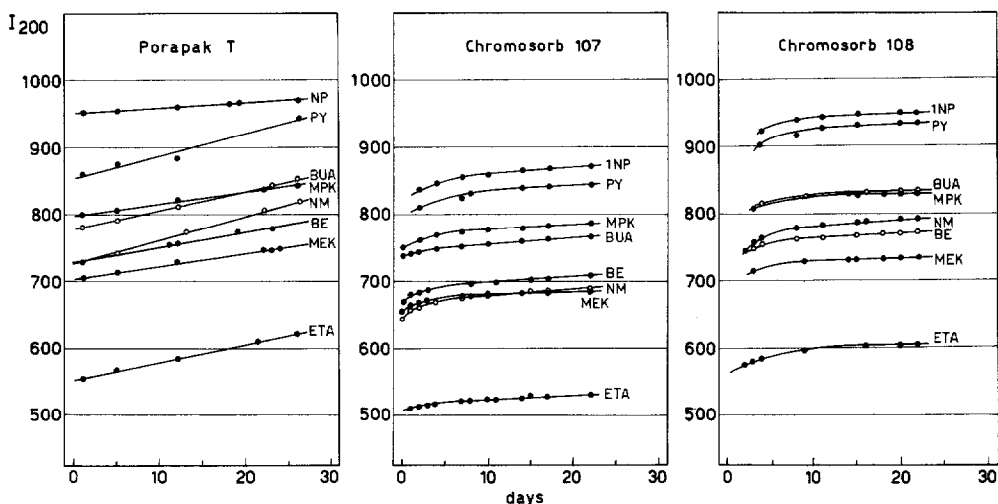


Fig. 2. Values of the retention index, I_{200} , of Rohrschneider and McReynolds polarity probes on PPBs that show increasing or non-linear values of I_{200} as a function of the ageing time at 200°C. For symbols of the probes see Table IV and text.

order of increasing initial Σ_{MR}^5 values. The values obtained by summing the ΔI values measured on "aged" columns are also shown. The order of average polarity is the same in both R and MR classifications, and the ratios $\Sigma_{MR}^5/\Sigma_{MR}^4$ and Σ_R^5/Σ_R^4 are sufficiently constant to show that the sums of the ΔI values of the probes except NM and NP can be used for the classification of the average polarity of all the PPBs, including Porapak S and Chromosorb 103.

Fig. 3 (left) shows the behaviour of the Σ_{MR}^4 values as a function of the ageing time and (right) compares the high temperature polarity scale based on Σ_{MR}^4 with the low temperature polarity order obtained from ΔI_{30}^O values of C_2H_2 (ref. 9). The changes due to the column ageing are shown. A linear correlation including all of the PPBs was not observed, while the polarity order at high temperature follows reasonably well than at low temperature when PPBs of similar chemical compositions are considered. The lines, calculated by the least squares method in Fig. 3 correspond to: (a) polystyrene, styrene-divinylbenzene and ethylvinylbenzene-divinylbenzene polymers (Porapak Q and P, Chromosorb 101, 102, 103 and 106); (b) acrylic polymers (Chromosorb 105, 107 and 108); (c) vinylpyridine and vinylpyrrolidone PPBs (Porapak N, R and S). The correlation coefficients are respectively: $r(a) = 0.936$; $r(b) = 0.892$; $r(c) = 0.999$.

CONCLUSIONS

The use of the ΔI system for the classification of the polarity of the various commercial PPBs at high temperature yields comparable results when both Rohrschneider's and McReynolds' polarity probes are used. The change of the retention index values on some PPBs with column ageing at high temperature results in a change of the polarity order only for the following PPB pairs: Porapak T and Chromosorb 108, Porapak P and Chromosorb 7, Porapak R and Chromosorb 105, as

TABLE VIII

VALUES OF THE AVERAGE POLARITIES OF VARIOUS PPBs, DETERMINED FROM THE SUM OF ΔI_{200}^{I06} VALUES OF THE POLARITY PROBES

Σ_R^5 = Sum of ΔI for ETA, MEK, NM, BE and PY; Σ_R^4 = sum of ΔI for ETA, MEK, BE and PY; Σ_{MR}^5 = sum of ΔI for BUA, MPK, 1NP, BE and PY; Σ_{MR}^4 = sum of ΔI for BUA, MPK, BE and PY. When two values are shown, the upper one refers to new and the lower one to aged columns (22 days at 200°C under helium flow).

Chromosorb or Porapak	Σ_{MR}^5	Σ_{MR}^4	$\Sigma_{MR}^5/\Sigma_{MR}^4$	Σ_R^5	Σ_R^4	Σ_R^5/Σ_R^4
106	0	0	—	0	0	—
Q	38.4	35.7	1.08	68.5	52.6	1.30
102	167.2	128.3	1.30	197.3	141.1	1.40
S	—	143.4	—	—	160.6	—
	283.7	211.7	1.34	301.1	216.2	1.39
105	327.3	255.3	1.28	347.5	262.6	1.32
R	296.7	223.0	1.33	330.7	234.7	1.41
N	464.7	338.7	1.37	498.9	348.6	1.43
	515.4	393.9	1.31	575.8	420.1	1.37
101	494.7	380.6	1.30	555.5	406.8	1.37
	619.3	438.8	1.41	620.0	440.4	1.41
107	785.3	571.3	1.37	787.7	560.1	1.41
	639.6	489.2	1.31	671.5	495.0	1.36
P	660.3	509.9	1.29	708.4	531.9	1.33
	929.1	636.6	1.46	900.8	634.9	1.42
T	1185.8	868.0	1.37	1240.4	877.9	1.41
	—	641.9	—	—	666.4	—
103	1004.0	633.0	—	—	660.6	—
	738.7	738.7	1.36	1002.0	722.0	1.39
108	1126.2	833.9	1.35	1159.5	830.5	1.40
	1760.9	1293.8	1.36	1820.9	1304.1	1.40
104	1780.2	1304.2	1.36	1831.3	1314.5	1.39

shown by the values in Table VIII and by the left-hand diagram of Fig. 3. However, two of these pairs show practically the same selectivity either at low or at high temperature, and the corresponding columns can therefore be used for equivalent chromatographic separations (compare the I_0 and k values in Tables IV and V, and the plots for Porapak T and Chromosorb 108 in Fig. 3). Porapak P and Chromosorb 107, which have similar values of the average polarities (Σ^5 and Σ^4) at high temperature, behave differently at room temperature, as shown by the right-hand diagram of Fig. 3. Moreover, the comparison of their plots of retention index vs. ageing time (Figs. 1 and 2) shows that benzene and pyridine are more strongly retained on styrene-divinylbenzene Porapak P than on the acrylic ester Chromosorb 107.

With the exceptions discussed above, the high temperature polarity order obtained either with Rohrschneider's or McReynolds' probes by using Chromosorb 106 as the "less-polar" reference shows little dependence on the ageing of the columns and can therefore be used as a guide for the choice of phase or for the preparation of mixed or composite columns.

The approximate comparison obtained by using the "average polarities" as Σ^4 and Σ^5 (Table VIII and Fig. 3) can be further enhanced by knowledge of the initial retention index values, I_0 , and of the slope, k , of the linear dependence of the be-

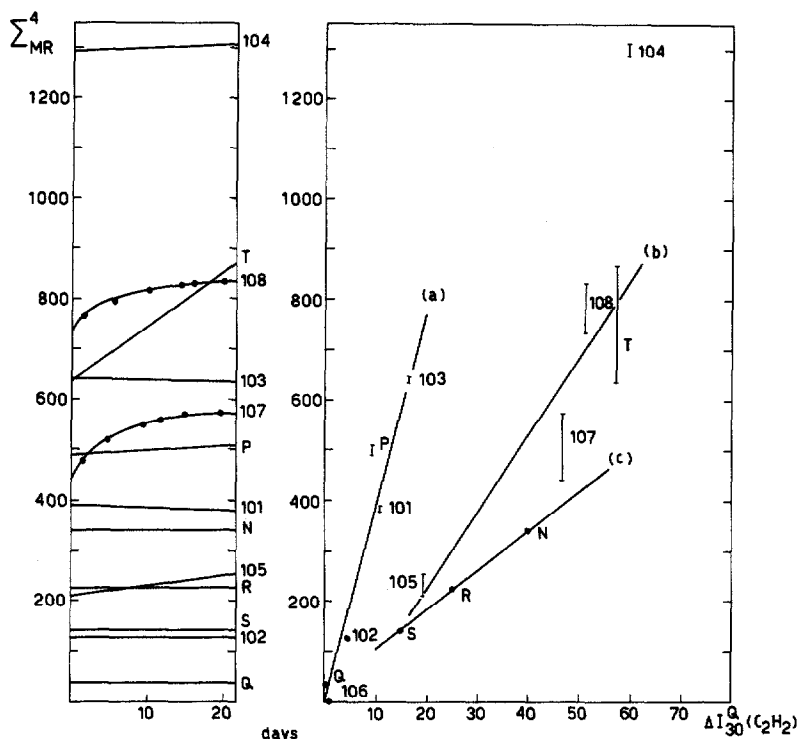


Fig. 3. Average polarity, at 200°C, Σ_{MR}^4 , calculated from the sum of ΔI_{200}^{106} values of butanol, benzene, methyl propyl ketone and pyridine, as a function of ageing time, t , (left), and of the polarity order at low temperature, $\Delta I_{30}(C_2H_2)$ (right). Least-squares lines for polystyrene (a), acrylic (b) and vinylpyridine (c) polymers are shown.

haviour of the various probes on column ageing. Within the limits of the polarity classification based on ΔI values of reference probes, whose choice was founded on valid considerations but cannot take into account all of the possible solute-solvent and surface interactions, this method seems to be precise enough to be recommended for the classification of further PPB phases produced in the future.

The polarity order previously obtained at low temperatures by using light gases as probes⁹ corresponds to that measured with liquid probes at high temperature as far as polymers with similar chemical compositions are concerned and, owing to the ease of its use, can still be convenient for preliminary investigations on the behaviour of PPB stationary phases.

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