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CHARACTERIZATION OF CHROMOSORB POROUS POLYMER BEAD COLUMNS BY GAS CHROMATOGRAPHIC RETENTION VALUES OF LIGHT HYDROCARBONS AND CARBON DIOXIDE

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SUMMARY

The gas chromatographic behaviour of Chromosorb "century series" porous polymer beads was investigated by analysing mixtures of gases (H_2 , CO_2 , CH_4 , C_2H_2 , C_2H_4 and C_2H_6) at different temperatures on columns filled with various types of beads (Chromosorb 101, 102, 103, 104 and 105). The adsorption enthalpies of these compounds were calculated in order to characterize the various Chromosorb types. The relative retention with respect to ethylene was used for the rapid identification of the type of Chromosorb and to compare their gas chromatographic behaviour with that of Porapak polymer beads.

INTRODUCTION

The reproducibility of gas chromatographic (GC) retention data obtained by using porous polymer beads (PPBs) has been widely discussed. In the analysis of inorganic gases, light hydrocarbons and small organic molecules, different authors have reported wide variations of absolute and relative retention times, depending on the performance of various types and batches of polymer¹.

Although many of the reported discrepancies can be explained on the basis of the temperature dependence of the retention times², other parameters that influence the column behaviour remain to be investigated: mesh size of the beads, porosity, composition and physical structure, etc. Some of these parameters are given by the producer, while others are not available to the GC user, making the choice of PPB for a given separation an art rather than a science, depending mainly on previous experience and sometimes requiring troublesome and expensive trial-and-error tests.

A general classification of the GC performance of the types of commercially available PPBs, sold by various producers under different trade names, would be very useful. A knowledge of both similarity (*i.e.*, the possibility of replacing a given stationary phase with another readily available) and difference (*i.e.*, the choice of a stationary phase having separation properties intermediate between those of different trade names) are important for the user of these packings.

Comparison of PPBs of different trade names have previously been reported.

The widest range of types was investigated by Dave³ (Chromosorb 101, 102 and 103; Porapak N, P, Q, R, S, T and Q-S; Par 1 and 2) and by Supina and Rose⁴ (Chromosorb 101, 102 and 103; Porapak N, P, R, S and T). Other papers⁵⁻⁹ report comparisons between two or three different types of Chromosorb "century series" and Porapak.

The characterization of Porapak® by analysis of light hydrocarbons was previously described¹⁰. The use of the retention time relative to ethylene, $\alpha_{C_2H_4}$, of various gases (CH₄, CO₂, C₂H₆), whose measurement is simple with respect to the determination of the thermodynamic functions (ΔH^0 , ΔG^0 and ΔS^0), permitted an evaluation of the batch-to-batch reproducibility of the column behaviour, and a semiquantitative classification of the "polarity" of the various types of Porapak. Here we report the results of a similar investigation on Chromosorb "century series"® polymer beads.

EXPERIMENTAL

Stainless-steel columns (3 m × 2.4 mm I.D.) were filled with carefully weighed amounts of Chromosorb 101, 102, 103, 104 and 105 (80–100 mesh), from different batches. A thermal conductivity detector with semi-diffusion cells (Aerograph A 350) was used at high sensitivity (filament current 250 mA) with helium carrier gas (22 cm³ min⁻¹) in order to permit analysis of the smallest possible amount of sample and to avoid peak asymmetry².

The column temperature was measured with an accuracy of $\pm 0.1^\circ\text{C}$. The flow was measured with a bubble flow meter, and the pressure at the head and at the end of the column was monitored with a mercury manometer, with an accuracy of ± 1 Torr, in order to calculate the pressure gradient correction factor, J , of James and Martin¹¹. Adjusted retention volumes, V'_R , net retention volumes, V_N , retention relative to ethylene, $\alpha_{C_2H_4}$, ΔH^0 , ΔS^0 and ΔG^0 were measured or calculated as previously described¹⁰. In the equations and discussion below, the $\alpha_{C_2H_4}$ values will be indicated, for sake of brevity, by the symbol α .

RESULTS AND DISCUSSION

As previously observed in the case of Porapak columns¹⁰, plots of $\ln V_N$ as a function of $1/T$ (reciprocal of the column's absolute temperature) were linear in the interval examined (Fig. 1). The values of the parameters p and q of the equation

$$\ln V_N = p (1/T) + q \quad (1)$$

are shown in Table I and the intersection temperatures, where the given compounds have the same retention time, calculated by solving a system of equations of the type 1, are shown in Table II, together with the temperature limits (isothermal)¹².

The α values obtained on the various Chromosorbs and typical peak shapes on 3-m (80–100 mesh) columns are shown in Fig. 2. As the experimental conditions were exactly the same as in the investigations on Porapak columns¹⁰, both the p and q values and the α values can be directly compared. Table III shows the classification of the various Chromosorb types on the basis of the α values at 30 and 50°C. The comparison of these results and of Figs. 1 and 2 with the corresponding results for the

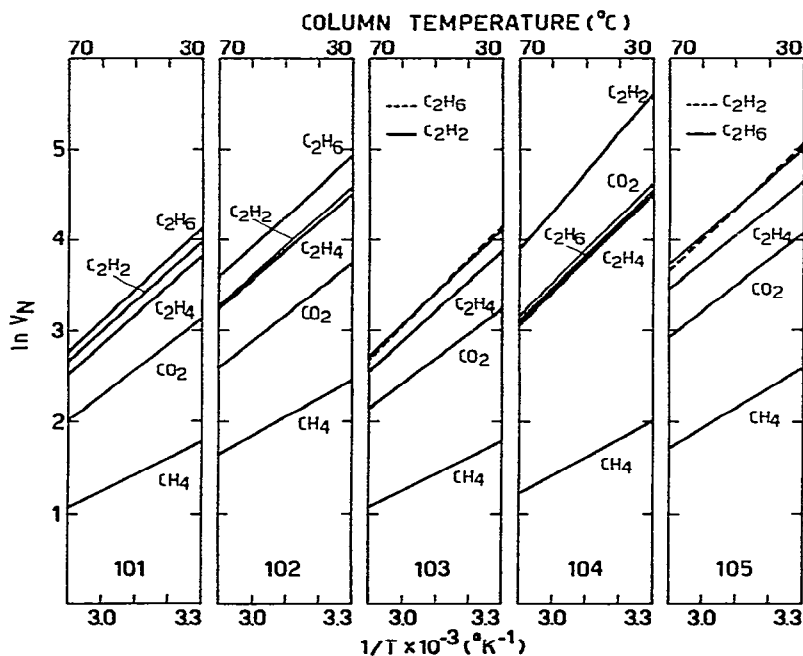


Fig. 1. Plot of $\ln V_N$ against $1/T$ on various Chromosorb "century series" (80–100 mesh). Helium flow-rate: $22 \text{ cm}^3 \text{ min}^{-1}$.

TABLE I

VALUES OF THE SLOPE (p) AND INTERCEPT (q) OF EQN. 1 FOR LIGHT HYDROCARBONS AND CO_2 ON CHROMOSORB COLUMNS

Columns: 3 m long, 80–100 mesh. Carrier gas: helium, $22 \text{ cm}^3 \text{ min}^{-1}$.

	p				
	101	102	103	104	105
CH_4	1862	2063	1835	1956	1844
CO_2	2797	2760	2680	3779	2901
C_2H_6	3227	3322	3568	3625	3023
C_2H_4	3307	3222	3304	3722	3231
C_2H_2	3413	3285	3476	4333	3500
	q				
	101	102	103	104	105
CH_4	-4.35	-4.32	-4.22	-4.41	-3.57
CO_2	-6.10	-5.37	-5.59	-7.81	-5.49
C_2H_6	-6.84	-6.02	-7.62	-7.45	-5.32
C_2H_4	-6.93	-6.08	-7.05	-7.71	-5.65
C_2H_2	-7.13	-6.22	-7.34	-8.68	-6.49

TABLE II

INTERSECTION TEMPERATURES AT WHICH TWO COMPOUNDS SHOW THE SAME RETENTION TIME ON VARIOUS CHROMOSORB "CENTURY SERIES"

Values marked with asterisks are of practical interest due to the temperature limit of the stationary phase (T_1) given by the producer¹².

Chromosorb	T_1 (°C)	Compound	Intersection temperature (°C)			
			CH_4	CO_2	C_2H_4	C_2H_2
101	300	C_2H_6	285*	324	377	252*
		C_2H_2	288*	342	679	
		C_2H_4	275*	304		
		CO_2	262*			
102	250	C_2H_6	467	586	—	—
		C_2H_2	369	340	173*	
		C_2H_4	385	372		
		CO_2	393			
103	275	C_2H_6	273*	165*	191*	55*
		C_2H_2	253*	182*	322	
		C_2H_4	246*	154*		
		CO_2	344			
104	250	C_2H_6	263	—	107*	357
		C_2H_2	284	362	305	
		C_2H_4	276	163*		
		CO_2	264			
105	250	C_2H_6	394	1842	361	49*
		C_2H_2	295	331	137*	
		C_2H_4	400	—		
		CO_2	277			

Porapak columns previously reported¹⁰ shows that the behaviour of Chromosorb 101 and 102 is similar (but not identical) to that of Porapak P and Q respectively. No intersection point of ethylene and acetylene retention times was observed on Chromosorb 102 in the considered temperature interval, while for Porapak Q the intersection point of these compounds was observed at 44°C. Resolution of ethylene and acetylene is difficult with these columns. The behaviour of Chromosorb 103 and 105 can be compared with that of Porapak S and R respectively. As shown by the parallel α plots for C_2H_2 and C_2H_6 on Chromosorb 103 and Porapak S, and by the intersection point at 49°C for Chromosorb 105, no increase in resolution is found by changing the temperature of analysis, while a satisfactory increase in the resolution between C_2H_2 and C_2H_6 is obtained by decreasing the temperature from 70 to 30°C on Porapak R. Chromosorb 104 has no analogous PPB in the Porapak series. Both Porapak N and T show a very long retention time for C_2H_2 , as Chromosorb 104 does, but the peculiar feature of 104 is the long retention of CO_2 compared with hydrocarbons. This is clearly shown by the α values of Fig. 2. Porapak N and T also retain CO_2 more strongly than other Porapaks and Chromosorbs, but this compound is always eluted before C_2H_4 .

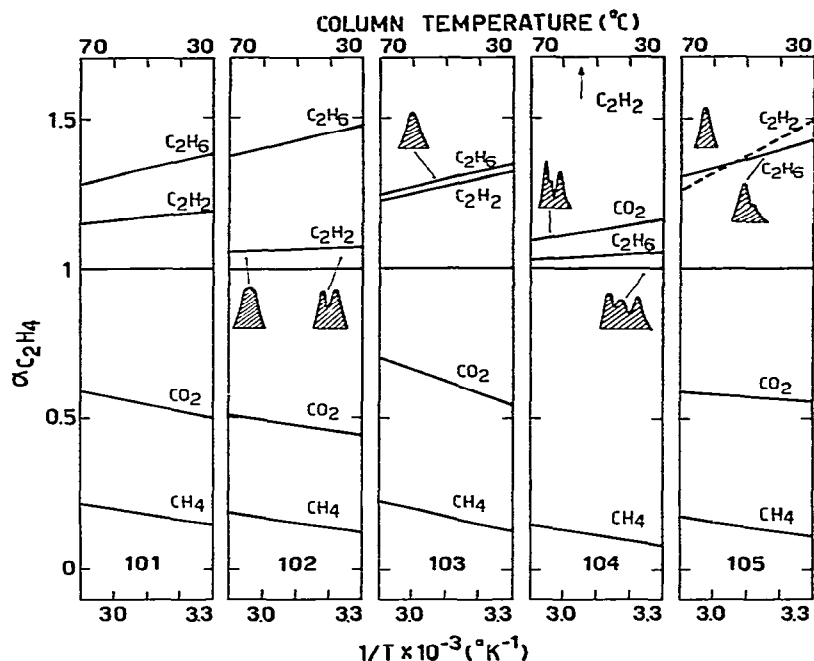


Fig. 2. Values of $\alpha_{C_2H_4}$ and peak resolution as a function of temperature on various Chromosorbs. Conditions as in Fig. 1. Acetylene off-scale on Chromosorb 104.

TABLE III

VALUES OF $\alpha_{C_2H_4}$ AT 30 AND 50°C ON VARIOUS CHROMOSORBS (80–100 MESH), USED AS A QUANTITATIVE EVALUATION OF THE "POLARITY" OF THE PHASE

Compound	Temperature (°C)	Chromosorb				
		101	102	103	104	105
CO ₂	30	0.504	0.45	0.55	1.16	0.56
	50	0.55	0.48	0.62	1.13	0.57
C ₂ H ₂	30	1.19	1.075	1.33	3.01	1.50
	50	1.17	1.07	1.27	2.62	1.37
C ₂ H ₆	30	1.39	1.48	1.35	1.05	1.42
	50	1.33	1.43	1.29	1.04	1.36

The differences and similarities between Porapak and Chromosorb obviously depend on the composition and surface area of the various beads. Unfortunately, little information is available on the chemical structure of some of the bead types. Table IV summarizes data taken from bulletins or catalogues.

The effect of the carrier gas flow-rate and of the columns length on the α values is very small, as previously observed with Porapak columns.

The linear dependence of the α values on the reciprocal of the absolute tem-

TABLE IV

CHEMICAL COMPOSITION AND SURFACE AREA OF PORAPAK AND CHROMOSORB POLYMER BEADS, TAKEN FROM CATALOGUES (WATERS AND JOHNS-MANVILLE) AND FROM REF. 16

Type	Surface area (m ² /g)	Chemical composition
Chromosorb 101	< 50	Styrene-divinylbenzene
Chromosorb 102	300-400	Styrene-divinylbenzene
Chromosorb 103	15-25	Cross-linked polystyrene
Chromosorb 104	100-200	Acrylonitrile-divinylbenzene
Chromosorb 105	600-700	Acrylic esters
Porapak N	225-350	A* + vinyl pyrrolidone
Porapak P	100-200	Styrene-divinylbenzene
Porapak Q	500-600	Ethylvinylbenzene + divinylbenzene
Porapak R	450-600	A* + vinylpyrrolidone
Porapak S	300-450	A* + vinylpyridine
Porapak T	250-350	A*

* A = Styrene-divinylbenzene or ethylvinylbenzene-divinylbenzene polymers modified with polar monomers.

perature, as a consequence of eqn. 1, permits calculation of the $\alpha(C)_i^T$ value of a compound C on the stationary phase *i* at a given absolute temperature *T*. The values of the constants *m* and *n*

$$\alpha(C)_i^T = m_i (1/T) + n_i \quad (2)$$

for the various types of Chromosorb are shown in Table V. Moreover, the behaviour of mixed columns made from various amounts of different Chromosorb types in order to obtain a change in the elution order and resolution of the various compounds can be calculated. It has been shown¹³ that the α values for a given C at a constant temperature *T* on a column prepared by mixing various amounts of two different types, *i* and *j*, of Porapak

$$\alpha(C)_{i+j}^T = (\alpha(C)_j^T - \alpha(C)_i^T)x_j + \alpha(C)_i^T \quad (3)$$

TABLE V

VALUES OF THE COEFFICIENTS OF EQNS. 2 AND 4 FOR CHROMOSORB COLUMNS

Chromosorb	CH ₄		CO ₂		C ₂ H ₂		C ₂ H ₆	
	<i>m_i</i>	<i>n_i</i>	<i>m_i</i>	<i>n_i</i>	<i>m_i</i>	<i>n_i</i>	<i>m_i</i>	<i>n_i</i>
101	-247	0.947	-231	1.267	105	0.848	262	0.523
102	-154	0.637	-168	1.003	46	0.923	268	0.601
103	-244	0.937	-377	1.791	254	0.488	276	0.437
104	-182	0.684	165	0.617	1898	-3.252	67	0.832
105	-169	0.674	-75	0.807	609	-0.513	314	0.388

where x_j is the weight fraction of the phase j and $x_i + x_j = 1$. The same behaviour, with the limits of the experimental determination of the α values for homogeneously mixed or multilayer packings¹³, has been found for Chromosorb "century series" PPBs (Fig. 3). Therefore, the α of a given compound C on a mixed column $i + j$ can be found at any temperature by a combination of eqns. 2 and 3:

$$\alpha(C)_{i+j}^T = \left[(m_j - m_i) \cdot \frac{1}{T} + n_j - n_i \right] x_j + m_i \cdot \frac{1}{T} + n_i \quad (4)$$

The preparation of mixed columns is of practical interest when PPBs of different "polarity" are used (Fig. 3). Compatibility tests must be done by mixing small amounts of the two packings in order to determine whether electrostatic effects due to the surface groups and composition of the various types of Chromosorb cause adhesion of the beads, which impairs the filling by gravity of the columns with homogeneously mixed packings. A mixed column with two non-compatible Chromosorb types can be prepared by alternately pouring small amounts of the two phases in the column, giving a multilayer packing. It has been found that such columns are similar to homogeneous columns when the number of layers increases. The behaviour of mixed Porapak-Chromosorb columns can also be calculated by using the previously published α values¹⁰. Little or no advantages are obtained by mixing packings of similar "polarity", while mixed columns of PPBs giving very different elution orders (e.g., Chromosorb 104 with Chromosorb 101, 102 or 103, see Fig. 3) can replace any column having intermediate polarity. Coupled or series columns can also be used, but

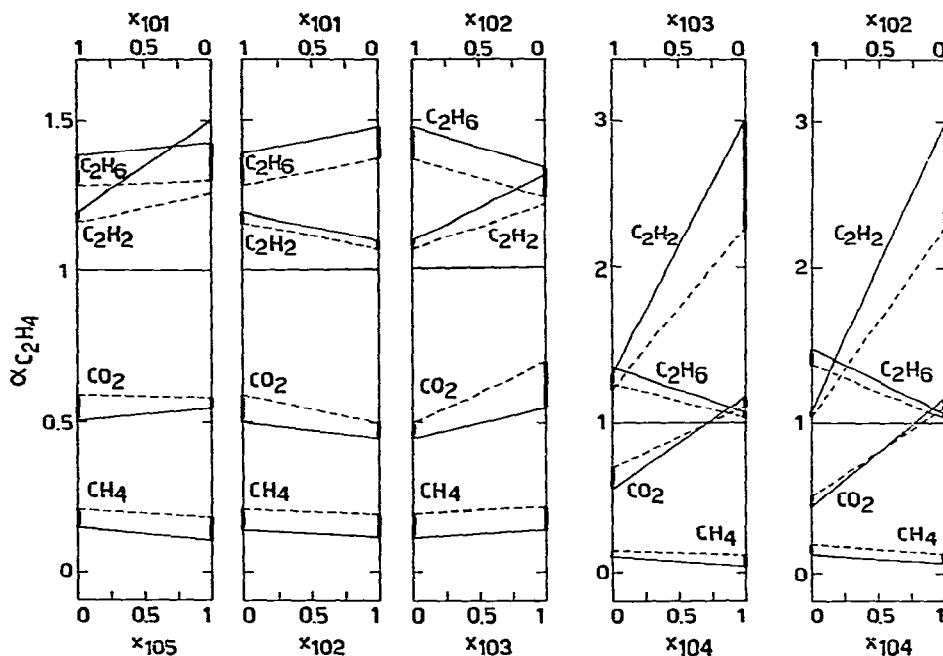


Fig. 3. Behaviour of mixed columns of various Chromosorb types at 30°C (—) and 70°C (---). Abscissa values: above, x_i ; below, x_j .

TABLE VI

VALUES OF $-\Delta H^0$ (kcal mol⁻¹) FOR LIGHT HYDROCARBONS AND CO₂ ON VARIOUS CHROMOSORBS

Conditions as in Table I.

Compound	Chromosorb				
	101	102 ^a	103	104	105
CH ₄	3.70	4.10	3.65	3.89	3.66
CO ₂	5.54	5.48	5.32	7.51	5.76
C ₂ H ₆	6.41	6.60	7.09	7.20	6.00
C ₂ H ₄	6.57	6.40	6.56	7.39	6.42
C ₂ H ₂	6.78	6.53	6.91	8.61	6.95

in this case the prevailing influence of the up-stream column working at higher pressure must be taken into account.

The thermodynamic functions were calculated as described elsewhere^{10,14,15} in order to obtain more information on the partition equilibrium and on the "polarity" of the various PPBs. Table VI shows the values of the adsorption enthalpies ($-\Delta H^0$), whose values for acetylene increase in the order Chromosorb 102, 101, 103, 105, 104, in accordance with the $\alpha_{C_2H_4}$ values of Table III, with the polarity order given by the producer¹¹ and with that obtained by analyzing a polarity mixture of acetonitrile, benzene, methyl ethyl ketone and *tert.*-butanol¹². It can be concluded that Chromosorb 102 and 104 have respectively the lowest and the highest polarity in the Chromosorb "century series" packings. The linear correlation between $-\Delta H^0$ and $\alpha_{C_2H_4}$ values (see Fig. 4) is better for the Chromosorb than for the Porapak series where

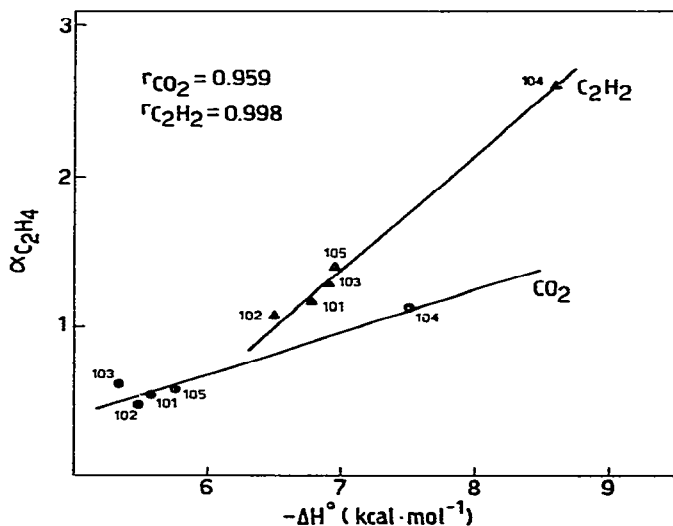


Fig. 4. Linear correlation between $\alpha_{C_2H_4}$ and $-\Delta H^0$ values of CO₂ and C₂H₂ on various Chromosorbs at 50°C. Correlation coefficients, r , are also shown.

inversion between R and S, T and N types was observed¹⁰. This is shown by the correlation coefficients, those at 50°C on Porapak type columns being 0.789 for CO₂ and 0.724 for C₂H₂, much smaller than the corresponding values for the Chromosorb "century series", shown in Fig. 4.

The dependence of the α values of C₂H₆ on the $-\Delta H^0$ values is almost random both on Porapak ($r = 0.141$) and on Chromosorb ($r = 0.678$), while a satisfactory linear correlation is found between the α and $-\Delta H^0$ values for CO₂ and C₂H₂.

CONCLUSIONS

The measured values of $\alpha_{C_2H_4}$ refer to a restricted number of batches of Chromosorb "century series" of different types. It is possible that single batches would give $\alpha_{C_2H_4}$ and $-\Delta H^0$ values which are slightly different from the values reported. In the case of the Porapaks we investigated the effect of mesh size on the $\alpha_{C_2H_4}$ values and found a variation of about 5%, that is probably of the same order of magnitude as the fluctuations due to change in mesh size of the Chromosorb beads.

This notwithstanding, the $\alpha_{C_2H_4}$ values can be used as a mean for the rough classification of the polarity of Chromosorb and Porapak PPBs and for the choice of packing or of mixed column that can replace another type of PPB not readily available for a given separation. Moreover, both for Chromosorbs and Porapaks, the measurement of the $\alpha_{C_2H_4}$ values of CO₂ and C₂H₂ at room temperature on a freshly prepared Chromosorb column permits a rapid evaluation of the reproducibility of this column with respect to that of a column previously used for the same analysis but which it is desired to replace.

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