

CHROM. 12,879

GAS CHROMATOGRAPHIC ANALYSIS OF LIGHT HYDROCARBONS FOR THE CHARACTERIZATION OF PORAPAK COLUMNS

GIANRICO CASTELLO* and GIUSEPPINA D'AMATO

Istituto di Chimica Industriale, Università di Genova, Corso Europa 30, I-16132 Genova (Italy)

(First received March 10th, 1980; revised manuscript received April 8th, 1980)

SUMMARY

The gas chromatographic behaviour of various types of porous polymer beads (Porapak N, P, Q, R, S and T) was investigated by analysing mixtures of gases (H_2 , CO_2 , CH_4 , C_2H_4 and C_2H_6) at different temperatures. The values of ΔH° , ΔS° and ΔG° of solution for these compounds were calculated, in order to characterize the various Porapak types. The relative retention with respect to ethylene can also be used for the rapid identification of the type of Porapak and to ensure reproducibility of the behaviour of columns made with beads belonging to different batches.

INTRODUCTION

PorapakTM stationary phases are porous polymer beads, modified to give different retention characteristics. By incorporating polar monomers into the basic polymer they can be used for a wide range of gas chromatographic (GC) separations.

The analysis of light hydrocarbons and permanent gases was facilitated by the use of these packings, owing to their stability and selectivity. Unfortunately, poor reproducibility of the retention times in the analysis of these substances was observed¹⁻³. As an example, Hollis³, in an extensive review of the most significant works on the use of polymer beads, reported that C_2 hydrocarbons can be eluted in different orders depending on the type of Porapak used and the temperature. In a study of the effect of temperature⁴ it was found that the adjusted retention times, t'_R , of the compounds change with the temperature of the column in different ways, depending on the type of Porapak. Various compounds may have the same t'_R values in a particular temperature range, making the separation impossible, while below or above this range the elution order is altered. Appropriate types of Porapak must therefore be used for the GC separation of ethane, ethylene and acetylene in the presence of hydrogen, air, carbon dioxide and methane in order to permit a satisfactory analysis of the mixture in a wide temperature range. Mixed columns sometimes have to be used to achieve the desired results^{5,6}.

Batch-to-batch variation of the polymer beads makes the preparation of columns with identical behaviour difficult. This may cause problems with routine analyses of gas streams, performed in different laboratories and factories⁷. Replace-

ment of an old or contaminated column with a new one having the same characteristics may also be a problem. When data systems and computers are used for the evaluation of the chromatograms and for process control, unwanted changes in the behaviour of the column may produce large errors and require time-consuming modification of the software.

A method that permits a simple and rapid characterization of the properties of a polymer column is therefore useful for many practical applications. The producer (Waters Assoc., Milford, MA, U.S.A.) lists the Porapak's in order of increasing polarity on the basis of the elution time of water with respect to hydrocarbons; water is progressively moved from an elution position just after ethane for Porapak Q to elution with the butenes on Porapak T. Available data⁸ give various polarity orders depending on the hydrocarbon used as a reference and on the temperature. Although the effect of temperature has been previously investigated⁴ and the experimental values measured at various temperatures can therefore be corrected, the choice of the reference standard substances has a considerable influence on the resulting polarity order. The order Porapak Q, P, R, S, N, T is generally accepted (not taking into account the S or silanized types), but numerical values of the polarity are still subject to uncertainty.

Previous methods for the characterization of porous polyaromatic beads used in GC⁹⁻¹⁵ involved the use of liquid standard samples that were analysed at high temperatures. The results obtained cannot be applied easily to analyses at room temperature. As various types of Porapak behave differently in the separation of light hydrocarbons (mainly C₂) and inorganic gases, the analysis of a suitable mixture of these compounds can be used for the characterization of these stationary phases.

EXPERIMENTAL

Stainless-steel columns (3 m × 2.4 mm I.D.) were carefully washed, dried under a flow of nitrogen and filled by gravity under vibration with Porapak N, P, Q, R, S and T (80–100 mesh) from different batches. Some tests were also made with other mesh sizes. The weight of packing in each column was carefully measured.

Thermal conductivity detectors with semi-diffusion cells (Aerograph A350) and flow-through microcells (Varian 1420) were used. The pressures at the head and the end of the columns were monitored with a mercury manometer and the flow-rate (22 ml min⁻¹ of helium) measured with a bubble flow meter. The column temperature was known with an accuracy of ±0.1°C.

The samples (mixtures of H₂, air, CO₂, CH₄, C₂H₆, C₂H₄ and C₂H₂) were diluted with pure helium and injected by means of a gas sampling valve directly connected to the column in order to avoid the dead volume of the injector. Each sample was repeatedly analysed at temperature intervals of 5°C in the range 30–70°C. The smallest possible amount of each gas was injected in order to avoid peak asymmetry⁴.

The adjusted retention volumes (V'_R) were calculated by subtracting from the uncorrected retention times the hold-up volume, V'_M , taken to equal the retention volume of hydrogen, practically corresponding to that of helium⁴. The net retention volumes, V'_N , were calculated by using the equation

$$V'_N = JV'_R \quad (1)$$

where J is the pressure gradient correction factor of James and Martin¹⁶ and was calculated from the equation

$$J = \frac{3(P_1/P_0)^2 - 1}{2(P_1/P_0)^3 - 1} \quad (2)$$

where P_1 and P_0 are the absolute pressures at the column inlet and outlet, respectively.

RESULTS AND DISCUSSION

The plots of $\ln V_N$ as a function of $1/T$ (T = absolute temperature of the column) were linear for all Porapaks and for all analysed gases in the temperature range studied (see Fig. 1). Intersecting lines show that two compounds have the

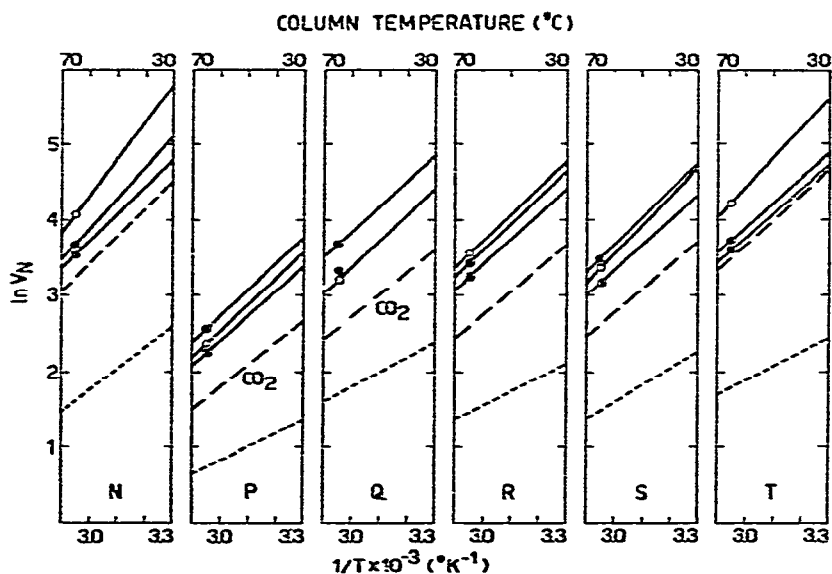


Fig. 1. Plot of $\ln V_N$ against $1/T$ on various Porapaks (80–100 mesh). Helium flow-rate: 22 ml min^{-1} . ---, CH_4 ; - · -, CO_2 ; ●, C_2H_6 ; ■, C_2H_4 ; ○, C_2H_2 .

same retention time and therefore cannot be resolved with this stationary phase at temperatures near the intersection point. By solving an appropriate system of equations of the type

$$\ln V_{N(1)} = p_1 \cdot \frac{1}{T} + q_1 \quad (3a)$$

$$\ln V_{N(2)} = p_2 \cdot \frac{1}{T} + q_2 \quad (3b)$$

etc., the intersection temperature for each sample pair can be calculated and the usefulness of the various Porapaks for the separation of a given mixture can be evaluated. Table I shows the values of p and q and Table II the calculated intersection temperatures.

TABLE I
VALUES OF THE SLOPE (p) AND INTERCEPT (q) OF THE EQUATION $\ln V_N = p \cdot 1/T + q$ FOR LIGHT HYDROCARBONS AND CO₂, ON
PORAPAK N, P, Q, R, S AND T COLUMNS (3 m LONG, 80-100 MESH, CARRIER GAS HE AT 22 ml min⁻¹)

Compound	q											
	N	P	Q	R	S	T	N	P	Q	R	S	T
CH ₄	2472	1820	1873	1839	2152	1836	-5.61	-4.61	-3.80	-3.93	-4.86	-3.68
CO ₂	3621	2855	2875	2935	2129	3374	-7.42	-6.73	-5.88	-5.98	-6.62	-6.49
C ₂ H ₆	3854	3509	3298	3331	3531	3296	-7.63	-7.80	-6.02	-6.34	-6.91	-6.01
C ₃ H ₈	3661	3293	2918	3156	3318	3205	-7.26	-7.44	-5.25	-6.10	-6.59	-5.87
C ₄ H ₁₀	4481	3403	3128	3680	3721	3985	-9.04	-7.67	-5.88	-7.31	-7.60	-7.30

TABLE II

INTERSECTION TEMPERATURES (°C) AT WHICH TWO COMPOUNDS SHOW THE SAME RETENTION TIME ON VARIOUS PORAPAKS
 Values marked with asterisks are of practical interest due to temperature limit of the stationary phase (T_1) given by the producer.

Porapak	T_1 (°C)	Porapak						T_1 (°C)					
		CH ₄	CO ₂	C ₂ H ₄	C ₃ H ₄	C ₃ H ₆	C ₃ H ₈						
N	190							CH ₄	CO ₂	C ₂ H ₄	C ₃ H ₄	C ₃ H ₆	C ₃ H ₈
			412	864	260	157*			257*	338	334		512
		C ₂ H ₆	305	244	178*			C ₂ H ₆	246*	313	225*		
		C ₃ H ₈	445	—				C ₂ H ₄	247*	340			
		C ₃ H ₆	361					CO ₂	216*				
Q	250							CH ₄	CO ₂	C ₂ H ₄	C ₃ H ₄	C ₃ H ₆	C ₃ H ₈
			369	2770	217*	1017			348	852	466		85*
		C ₂ H ₆	326	∞	44*			C ₂ H ₆	272*	288*	159*		
		C ₃ H ₈	450	—				C ₂ H ₄	335	1650			
		C ₃ H ₆	208*					CO ₂	261*				
S	250							CH ₄	CO ₂	C ₂ H ₄	C ₃ H ₄	C ₃ H ₆	C ₃ H ₈
			400	1123	395	0.8*			348	-1.7*	338		273
		C ₂ H ₆	299	330	125*			C ₂ H ₆	319	485	265		
		C ₃ H ₈	401	—				C ₂ H ₄	348	-108			
		C ₃ H ₆	282*					CO ₂	271				

Obviously, the separation of a given pair of compounds showing an intersection point is influenced by the resolution of the column, *i.e.*, by its length and by the mesh size of the stationary phase. The separation is therefore impossible within a certain temperature range near the intersection point. This is exemplified by the series of chromatograms in Fig. 2, which show the behaviour of Porapak P in the range 30–70°C. In order to permit an easy comparison, the retention values and the peak widths are reported as $\alpha_{C_2H_4}$ values [$\alpha_{C_2H_4} = t'_R(X)/t'_R(C_2H_4)$], *i.e.*, as the relative retention of a compound X with respect of ethylene, which was chosen as the reference compound owing to the small dependence of its retention time on temperature, confirmed by the lower values of the slope p in Table I. Although the calculated intersection point between C_2H_4 and C_2H_6 is above 300°C, a resolution of only 40% is achieved at 70°C, owing to the increasing widths (b_x) of the peaks with respect to their retention times. Extrapolation of the trends of both $\alpha_{C_2H_4}$ and b_x shows that at 120–150°C a single peak will be obtained from C_2H_4 and C_2H_6 on the column used. Of course, increasing resolution is ensured by using a longer column and a smaller mesh size.

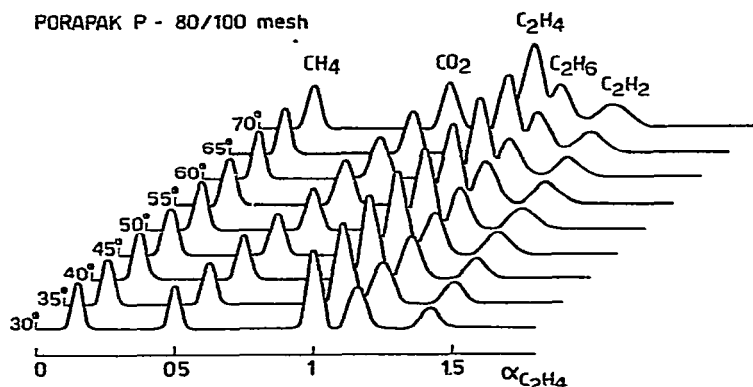


Fig. 2. Change of peak resolution as a function of temperature. Column: Porapak P (80–100 mesh) from 30 to 70°C.

Fig. 3 shows $\alpha_{C_2H_4}$ values obtained on the various Porapaks and typical peak shapes on 3-m 80–100-mesh columns. The behaviour of the $\alpha_{C_2H_4}$ values is typical for the various Porapaks and, at a given temperature, permits any Porapak type to be identified by giving a “fingerprint” of the separation properties of the stationary phases towards a simple gas mixture.

The calculation of the α values, obtained from the ratio of the adjusted retention times or volumes, may be more complex than the determination of the separation factor A , given by the ratio of absolute retention times. This is due to the fact that dead times, t_M , cannot be determined, as normally in GC by measuring the retention time of air, because Porapak columns retain O_2 and N_2 more than helium. As seen previously⁴, the addition of hydrogen to the test mixture permits the measurement of t_M with good accuracy, because the retention times of H_2 and He are almost identical at temperatures above 20°C, as shown by using N_2 as the carrier gas. Notwithstanding this slight additional complexity, the calculation of α is con-

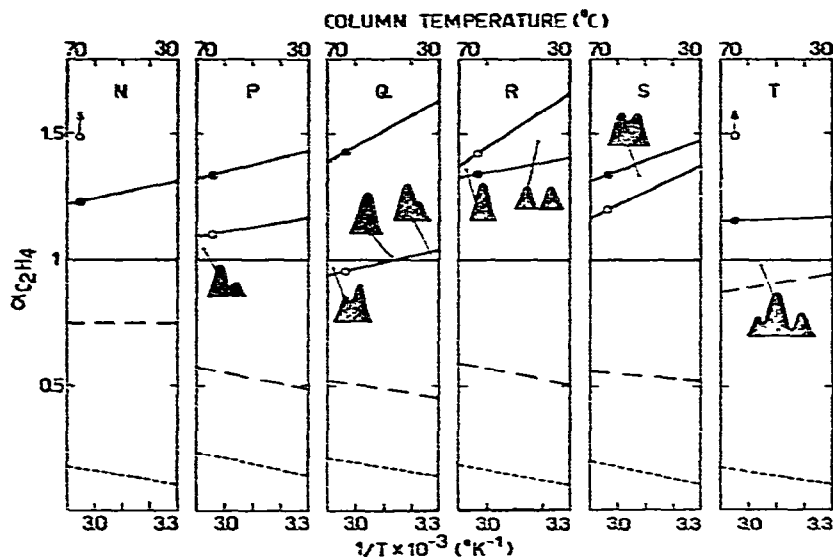


Fig. 3. Peak resolution as a function of temperature on various Porapak. Conditions and symbols as in Fig. 1. Acetylene off-scale on Porapak N and T.

venient because it yields values that are less dependent than A on experimental conditions. As an example, Table III shows the mean values and the standard deviations, σ , of $\alpha_{C_2H_4}$ on a Porapak R column (80–100 mesh) at 30°C as a function of the carrier gas flow-rate (between 10 and 70 ml min⁻¹) and of the column length (between 0.5 and 3 m). The variations are very small: the $\alpha_{C_2H_4}$ values are less dependent on the carrier gas flow-rate than on the column length, especially for very short columns. This may be due to the inherent errors in the measurements of short retention times. On increasing the mesh size of the Porapak the $\alpha_{C_2H_4}$ values increase (a variation of about 5–8% was observed between 80–100 and 120–150 mesh), but their ratios and relative values remain almost constant.

Table IV shows an example of classification of the various Porapaks on the basis of the $\alpha_{C_2H_4}$ values at 30 and 50°C. The $\alpha_{C_2H_4}$ values for acetylene follow the "polarity" order given by the producer, except for R and S types, which show an inversion. A batch of Porapak, sold as R type, showed a different behaviour, giving

TABLE III

EFFECT OF CARRIER GAS FLOW-RATE (φ) AND OF THE COLUMN LENGTH (L) ON THE $\alpha_{C_2H_4}$ VALUES

Porapak R, 80–100 mesh, at 30°C.

Compound	$\bar{\alpha}_{C_2H_4}$	σ		
		$\Delta\varphi$ 10–70 ml min ⁻¹	ΔL 1–3 m	ΔL 0.5–3 m
CH ₄	0.130	±0.002	±0.009	±0.020
CO ₂	0.549	±0.003	±0.009	±0.012
C ₂ H ₂	1.401	±0.007	±0.006	±0.006
C ₂ H ₄	1.669	±0.006	±0.002	±0.007

TABLE IV

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

Compound	Temperature (°C)	Porapak					
		Q	P	R	S	N	T
CO ₂	30	0.44	0.49	0.54	0.53	0.74	0.94
	50	0.49	0.55	0.56	0.55	0.74	0.90
C ₂ H ₂	30	1.03	1.16	1.67	1.37	2.34	3.12
	50	0.99	1.14	1.50	1.26	1.97	2.69
C ₂ H ₆	30	1.62	1.43	1.40	1.47	1.30	1.18
	50	1.45	1.38	1.36	1.40	1.26	1.16

$\alpha_{C_2H_4}$ values for acetylene lower than the corresponding values on the S type. It is not yet clear whether this was due to improper packaging or to any variation of behaviour due to other reasons.

The reported $\alpha_{C_2H_4}$ values, taking into account the corrections for temperature, made on the basis of the $\ln V_N$ versus $1/T$ plots, permit a quantitative evaluation of the behaviour of the various Porapak types. It should be noted that the α values, sometimes indicated as "solvent efficiency" values, correspond to the ratio of the partition coefficients, K , for the various compounds on any given stationary phase. At identical carrier gas flow-rates and pressures, by injecting identical, very small sample volumes, the amount of solute per unit volume of gas phase can be considered constant and the α values are therefore proportional to the amounts of solute dissolved per unit volume of any stationary phase.

By following the procedure suggested by some workers^{17,18}, the sample-stationary phase interactions could also be investigated by measuring the values of the thermodynamic properties of solution. The linear dependence of $\ln V_N$ on $1/T$ permits the determination of their values, as V_N in a gas-solid chromatographic system is related to the partition coefficient by

$$V_N = K W_S \quad (4)$$

where W_S is the weight of the packing material and K is related to the partial molar free energy (ΔG^0):

$$\Delta G^0 = \Delta H^0 - T\Delta S^0 = -RT \ln K \quad (5)$$

By using the equation

$$\ln V_N = \frac{-\Delta H^0}{RT} + q = \frac{-\Delta H^0}{RT} + \frac{\Delta S^0}{R} + \ln W_S \quad (6)$$

the values of ΔH^0 can be calculated from the slope (p) of the plot $\ln V_N$ against $1/T$. If the weight of the packing material W_S is known, ΔS^0 can be calculated from the values of the intercept q , and ΔG^0 can also be found.

The validity of this approach depends on the exact nature of the mechanism of retention. It is generally thought that the retention mechanism on porous polymers is complex and that both adsorption and solution mechanisms are involved¹⁸. As the

above calculation of thermodynamic functions assumes that equilibrium occurs, the exact nature of this equilibrium has to be known. If dissolution phenomena predominate, and involve the whole bulk material, the suggested approach may be considered exhaustive, and the weight of stationary phase is a relevant parameter. On the other hand, if the sorption mechanism involved is adsorption rather than bulk dissolution¹⁹, then it is not the weight but the surface area (macro- and micropores) that is of importance. In this instance, the use of eqn. 6 for the calculation of ΔS^0 and ΔG^0 may be questionable, while the determination of the adsorption enthalpies (ΔH^0) will give an idea of the molecular interactions, regardless of the physical state of the column packing where these interactions take place, and will permit a comparison of the behaviour of the various Porapak types with the reported literature data. This is not a completely correct approach, but is certainly a good approximation.

Table V gives the values of $-\Delta H^0$ for the various gases analysed on different Porapak types. They are of the same order of magnitude as those calculated by Czubyrt and Gesser¹⁷ for CH₄ and CO₂ on Porapak S, taking into account the difference in the experimental conditions and the reliability of the results in the determination of thermodynamic properties by GC when different operators and instruments are involved²⁰.

TABLE V

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

Conditions as in Table I.

Compound	Porapak					
	N	P	Q	R	S	T
CH ₄	4.92	3.62	3.72	3.65	4.28	3.65
CO ₂	7.19	5.67	5.71	5.83	6.22	6.70
C ₂ H ₆	7.66	6.97	6.55	6.62	7.02	6.55
C ₂ H ₄	7.27	6.54	5.80	6.37	6.59	6.37
C ₂ H ₂	8.90	6.76	6.20	7.31	7.39	7.92

Depending on the substances taken as a reference (CO₂, C₂H₄, C₂H₂) a different order of interaction can be deduced from the ΔH^0 values for Porapak P and Q, while the order Porapak R, S, T and N is shown by all of the sample gases. The ΔS^0 and ΔG^0 values, calculated formally with eqn. 6 with the hypothesis of a pure "partition" equilibrium, also are of the same order of magnitude as the values previously found¹⁷, but their use for the classification of the various Porapaks leads to different "polarity" orders. Therefore, the usefulness of the calculation of thermodynamic functions for the characterization and classification of polymer beads is questionable in the absence of any information on what parts of the stationary phase are accessible to the solute and on the type of equilibrium that is predominant depending on the type of solute, type of Porapak and temperature.

Measurements of the thermodynamic parameters over a wider range of particle sizes and porosity are therefore necessary in order to elucidate the separation mechanism and to evaluate the usefulness of a thermodynamic approach for the characterization of porous polymers.

CONCLUSIONS

We do not feel that the values of $\alpha_{C_2H_4}$ that we measured represent the true mean values of all of the possible batches of the different Porapak types available. The maximum variation that we have observed between the tested batches of the same type was about 3–6%, *i.e.*, the same order of magnitude as the fluctuations due to change in mesh size. On the other hand, single batches of Porapak Q and R gave values of $\alpha_{C_2H_4}$ differing from the mean values and it is therefore possible that a greater variation could be observed over a larger range of samples.

A wider evaluation of the $\alpha_{C_2H_4}$, ΔH^0 , ΔS^0 and ΔG^0 values for a large number of batches was beyond the scope of this work, taking into account the high price of the stationary phases and the time needed for the accurate determination of the thermodynamic functions.

The practical usefulness of the $\alpha_{C_2H_4}$ values is due to the fact that columns with similar values for CO_2 , C_2H_6 and C_2H_2 showed a reasonable reproducibility of the behaviour if used for the analysis of both gaseous and liquid samples at various temperatures. The routine measurement of the $\alpha_{C_2H_4}$ values for all freshly prepared Porapak columns permitted a prior evaluation of the reproducibility of the column behaviour, thus avoiding unexpected results when these columns were used in complex multi-column systems with computerized data acquisition.

A standard classification of the various batches of Porapak on the basis of α (or ΔH^0) values, should avoid uncertainty in the choice of a given Porapak type for routine analyses. As the measurement of $\alpha_{C_2H_4}$ values is relatively simple, in comparison with the troublesome determination of the thermodynamic properties of solution, the collection of data from many laboratories that use polyaromatic beads for GC would permit an evaluation of the usefulness of the $\alpha_{C_2H_4}$ values for a general classification of these stationary phases.

REFERENCES

- 1 T. A. Gough and C. F. Simpson, *J. Chromatogr.*, 51 (1970) 129.
- 2 M. Dressler, R. Vespalec and J. Janák, *J. Chromatogr.*, 59 (1971) 423.
- 3 O. L. Hollis, *J. Chromatogr. Sci.*, 11 (1973) 335.
- 4 G. Castello, G. D'Amato and G. Canciani, *Ann. Chim. (Rome)*, 68 (1978) 255.
- 5 G. Castello, P. Canepa and M. Nicchia, *Ann. Chim. (Rome)*, 68 (1978) 543.
- 6 G. Castello and G. D'Amato, *Ann. Chim. (Rome)*, 69 (1969) 541.
- 7 G. Castello and M. Riccio, *Fuel*, 57 (1978) 469.
- 8 "Porapak" Technical Data, Water Assoc., Milford, MA, U.S.A., 1965.
- 9 K. Sakodinsky, *Chromatographia*, 1 (1968) 483.
- 10 W. R. Supina and L. P. Rose, *J. Chromatogr. Sci.*, 7 (1969) 192.
- 11 S. B. Dave, *J. Chromatogr. Sci.*, 7 (1969) 389.
- 12 H. L. Gearhart and M. F. Burke, *J. Chromatogr. Sci.*, 15 (1977) 1.
- 13 J. R. Lindsay Smith, A. H. H. Tameesh and D. J. Waddington, *J. Chromatogr.*, 148 (1978) 353.
- 14 J. R. Lindsay Smith, A. H. H. Tameesh and D. J. Waddington, *J. Chromatogr.*, 151 (1978) 21.
- 15 J. R. Lindsay Smith, A. H. H. Tameesh and D. J. Waddington, *J. Chromatogr.*, 151 (1978) 27.
- 16 A. T. James and A. J. P. Martin, *Biochem. J.*, 50 (1952) 679.
- 17 J. Czubyrt and H. D. Gesser, *J. Chromatogr.*, 59 (1971) 1.
- 18 F. M. Zado and J. Fabecic, *J. Chromatogr.*, 51 (1970) 37.
- 19 N. R. Rakshieva, J. Novák, S. Wičar and J. Janák, *J. Chromatogr.*, 91 (1974) 51.
- 20 E. F. Meyer and F. A. Balocchi, *Anal. Chem.*, 49 (1977) 1029.