Micro pore structure of porous polymer columns

The use of beads of porous aromatic hydrocarbon polymers as packing for gas chromatographic columns was first reported by HOLLIS[1]. These packings, with various registered trade names such as Porapak and Par, have been widely used, particularly for samples containing water[2]. HOLLIS[1] cited surface area and rigidity as important factors which affect the separation performance of porous polymers. Surface areas were reported from less than 1 m^2/g up to 660 m^2/g although the polymers that produced useful separations were in the 100–600 m^2/g range. It is well known that the various porous polymers exhibit quite different separating ability; see for example the widely varying relative retention times in Table I. There appears to have been no investigation of other parameters of the beads such as pore size distribution, average pore diameters, etc.

This study was undertaken to see if there were significant variations in these parameters.

TABLE I

RELATIVE RETENTION TIMES FOR POROUS POLYMER

Compound	*Retention times relative to ethane*[3]				*Retention times relative to water*[1]			
	Porapak Q	*Porapak R*	*Porapak S*	*Porapak T*	*Porapak Q*	*Porapak R*	*Porapak S*	*Porapak T*
Air	0.09	0.07	0.10	0.10	0.049	0.0073	0.0175	0.004
Carbon dioxide	0.33	0.39	0.38	0.79	0.187	0.0335	0.0670	0.0327
Methane	0.15	0.15	0.16	0.15	0.083	0.0126	0.0286	0.0064
Ethane	1.00	1.00	1.00	1.00	0.562	0.0862	0.175	0.0414
Propane	6.4	5.3	5.0	5.2	3.58	0.454	0.873	0.215
Acetylene	0.69	1.10	0.08	2.38	0.388	0.0946	0.145	0.0982
Ethylene	0.69	0.73	0.07	0.86	0.388	0.0627	0.121	0.0354
Propylene	4.9	4.4	4.5	5.9	2.75	0.375	0.783	0.247

Experimental

The porous polymers were "Porapak" Q, R, S and T, 80–100 mesh, supplied by Waters Associates Inc., Framingham, Mass. The adsorption and desorption isotherms were determined with the use of an automated isotherm apparatus ("Adsorptomat", American Instrument Company, Silver Springs, Md.) based on a design of BALLOU AND DOOLEN[4]. Nitrogen was used as an adsorbant. The samples were pretreated under vacuum as follows: Q, R and S for 2 h at 445°F, T for 2 h at 335°F in a previously described apparatus[5].

A computer program was used to calculate surface areas from the adsorption isotherm and pore size distributions from the desorption isotherms by conventional methods[6,7] with the exception that an exact cylindrical pore model was substituted for the usual approximate model. The surface areas were computed from six points in the pressure range $0.05 < P/P_0 < 0.35$ by a least square analysis. The desorption isotherms had 45 points at approximately equal pressure increments in the range $0.10 < P/P_0 < 0.99$.

Results and discussion

Table II lists surface areas, micro pore volumes, micro pore diameters, and average particle diameters for the four Porapaks. The micro pore volume is defined here as the volume of all pores with a radius of less than 500 Å. The average micro pore diameter is then computed from:

Average micro pore diameter Å = (4 × volume/area) × 10^4

An average particle diameter can be obtained from the area and skeletal density by:

Average particle diameter (Å) = (6×10^4)/(area × density)

assuming a spherical shape for the particles. Fig. 1 is a plot of dV/dR *vs.* pore radius, where V is the micro pore volume and R is the micro pore radius.

TABLE II

PHYSICAL PROPERTIES OF PORAPAK

Porapak	*Surface area* (m^2/g)	*Micro pore volume* (cc/g)	*Average micro pore diameter* (Å)	*Average particle diameter* (Å)
Q	634	1.185	74.8	111
R	547	1.035	75.6	101
S	536	1.017	76.0	79.4
T	306	0.701	91.4	163

From Table II a marked difference in the surface area for Porapak T in contrast to Q, R and S is shown. There is a considerably lower value for the available micro pore volume for the same polymer. The distribution of pore size is quite different for Q and T as shown in Fig. 1 with T containing a significantly greater number of larger pores. The detailed distributions of Q, R, and S differ only slightly, and the average micro pore diameters are essentially the same. Considering the relatively nonpolar

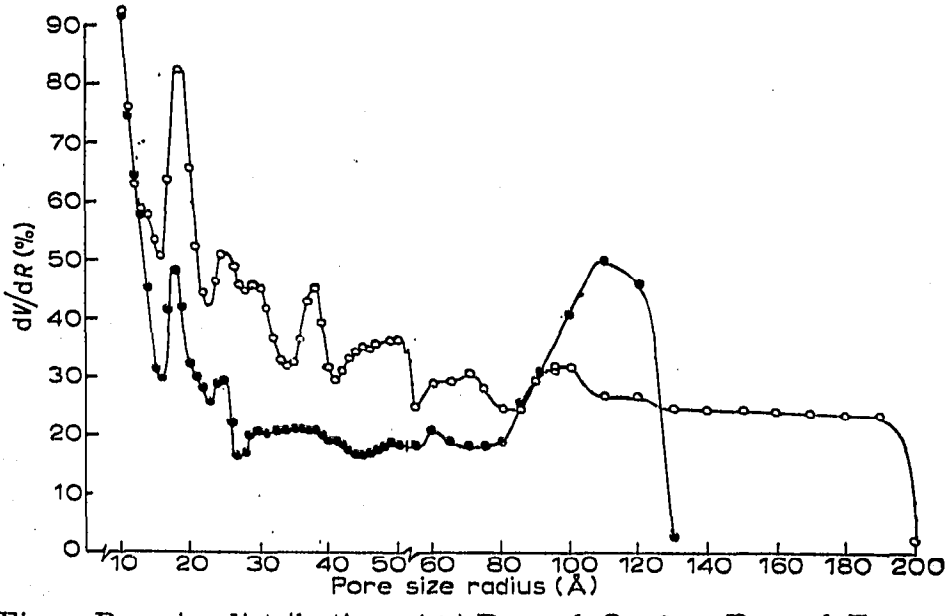

Fig. 1. Pore size distributions. (○) Porapak Q; ● = Porapak T.

compounds methane, ethane, and propane referred to ethane, see Table I, the separations for all four packings are quite similar. It is only for the more polar compounds that differences become marked. There appear to be no significant differences in separations that depend on either total micro pore volume or an average micro pore size. Thus, the controlling factor for separations evidently is a function of the nature of the porous polymer other than its micro pore structure.

Chevron Research Company,
Richmond, Calif. (U.S.A.)

JULIAN F. JOHNSON
EDWARD M. BARRALL II

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A stream splitter for liquid chromatography

In the use of a detector for monitoring the effluent during column chromatography, it is often necessary to divert part of the effluent stream through the detector. The device here described was constructed easily from readily available materials for use with a Barber-Colman liquid chromatography detector[1]. It is adaptable to any system requiring the diversion of a small and variable portion of the effluent stream for analysis.

The splitter utilizes a piece of 1 cm I. D. stainless steel tubing and a 20 gauge stainless steel syringe needle with luer hub. A hole is drilled into the side of the tubing and the needle soldered into place as shown in Fig. 1.

The flow rate through the sampling tube, and thus the size of the sample relative to the main stream can be regulated by adjusting the height of the splitter above the detector.

The effluent stream is directed into the hub of the needle as shown. The excess liquid overflows the hub and is directed into the receiver through the lower portion of the tube. The sample from the needle flows into the detector through a piece of small diameter Teflon* tubing. The luer hub is large enough to allow positioning of the

* References to specific products of commercial manufacture are for illustration and do not constitute endorsement by the U. S. Department of Agriculture.