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## Note

### Importance of macropores in polymer packings for gas chromatography

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The idea of using porous organic polymers as packings for gas chromatographic columns has led to new possibilities in selecting the best materials for particular separations<sup>1</sup>. Although a number of such polymers are commercially available (e.g., under trade names such as Porapak, Chromosorb and Synachrom), new materials with specific properties can be synthesized by varying the chemical nature of the polymeric skeleton, the presence or absence of polar functional groups and the texture of the porous polymer. Until now, most work has been concerned with chemical composition and its influence on the performance of the packings. Johnson and Barrall<sup>2</sup> studied the micropores (pore radii up to 10 nm) of various Porapaks and concluded that the micropore distribution has no effect on the separation properties of the packings. However, recent progress in the theory of diffusion in porous materials, made in connection with heterogeneous catalysis<sup>3,4</sup>, shows clearly that retention characteristics should depend much more on the presence of larger pores (macropores) than on micropores.

Our work has confirmed this expectation. In the series of packings that we prepared by polymerization of various monomers and cross-linking agents in the presence of pore-forming solvents (Table I), we have observed better separations and reduced tailing when the surface area of the sample was relatively low (between 15 and 60 m<sup>2</sup>/g) and the mean pore size relatively large (radii greater than 50 nm) compared with commercial preparations. The effect was dramatic in some instances. Our material PON (Table I), which in its chemical structure resembles Porapak R and N (Waters Assoc., Milford, Mass., U.S.A.)<sup>6,7</sup>, may serve as an example.

TABLE I

MONOMERS USED FOR PREPARATION OF POROUS POLYMERS

Polymer	Monomer	Cross-linking agent
KEM <sup>5</sup>	2-Cyanoethyl methacrylate	Ethylene dimethacrylate
PON	N-Vinylpyrrolidone	Divinylbenzene
PYR	Vinylpyridine	Divinylbenzene
HEM	2-Hydroxyethyl methacrylate	Ethylene dimethacrylate
MAD	Methacrylamide	Ethylene dimethacrylate
ACN	Acrylonitrile	Divinylbenzene

TABLE II  
RETENTION ON VARIOUS POLY(N-VINYLPYRROLIDONE) PACKINGS

Substance	Relative retention		Kováts index	
	PON 50*	PON 300*	Porapak R**	Porapak N***
Cyclohexane	0.06	4.81	645	625
Methanol	0.87	1.20	365	385
Water	1 <sup>§</sup>	1 <sup>§§</sup>	—	—
Ethanol	1.46	2.52	435	480
Ethyl acetate	1.97	5.35	585	700
Benzene	2.70	5.62	645	735

\* At 110°, column 0.5 × 6 mm, particle size 0.25–0.40 mm, flow-rate (H<sub>2</sub>) 120 ml/min.

\*\* At 200° (ref. 7).

\*\*\* At 175° (ref. 7).

§ Retention time 3.42 min.

§§ Retention time 3.00 min.

N-Alkylpyrrolidones form charge-transfer complexes with aromatic compounds and are used for the extraction of aromatic compounds from petroleum fractions. Therefore, a large difference in retention between aromatic and non-aromatic hydrocarbons might be expected when the pyrrolidone group is included in the polymer used as the column packing. However, published data on Porapak R and N do not show the expected selectivity (Table II, data on cyclohexane and benzene). We suspected that in materials of high surface area (as is the case with Porapaks), the surface is formed not only by active pyrrolidone groups but also by hydrocarbon chains of the polymer skeleton and of the cross-linking agent. This "hydrocarbon" fraction of the surface then serves for adsorption of non-aromatic compounds and thus increases their retention. The net effect is a decrease in selectivity for adsorption of aromatic hydrocarbons. In order to prove this hypothesis, we prepared two PON-type packings

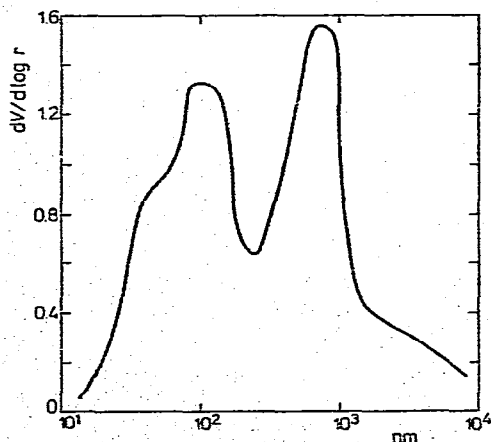


Fig. 1. Pore size distribution curve for PON 50 obtained by mercury porosimetry using a Carlo Erba porosimeter. Total pore volume, 2.01 ml/g.

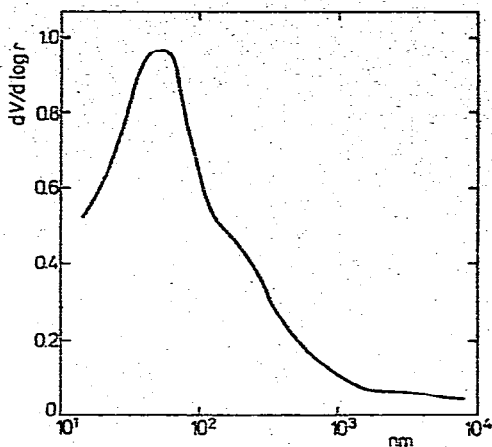


Fig. 2. Pore size distribution curve for PON 300 obtained by mercury porosimetry using a Carlo Erba porosimeter. Total pore volume, 1.21 ml/g.

that differed in their surface areas and pore size distributions (Table II and Figs. 1 and 2). The sample with a surface area of 300 m<sup>2</sup>/g (PON 300) (*i.e.*, in the range of commercial preparations<sup>6</sup>) has most pores in the range 10–100 nm, but the sample with a lower surface area of 50 m<sup>2</sup>/g (PON 50) has a large proportion of pores larger than 100 nm.

The data in Table II show the observed differences in separation abilities. Whereas the retention of water is about the same on both packings, all other compounds are eluted less easily from PON 300 than from PON 50. With PON 300 the peaks were unsymmetrical with pronounced tails. The difference in the relative re-

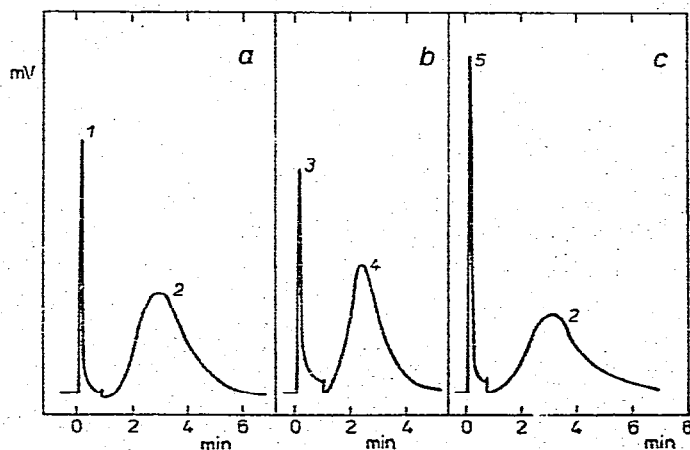


Fig. 3. Separation of aromatic and non-aromatic hydrocarbons on PON 50 packing. Column, 50 × 0.5 cm I.D.; particle size, 0.25–0.40 mm; flame-ionization detection. (a) Cyclohexane (0.1%) in benzene; 110°; N<sub>2</sub> flow-rate 37 ml/min; 0.5- $\mu$ l sample; change of sensitivity 1:100. (b) Methylcyclohexane (1%) in toluene; 140°; N<sub>2</sub> flow-rate 32 ml/min; 0.5- $\mu$ l sample; sensitivity change 1:50. (c) Isooctane (0.01%) in benzene; 110°; N<sub>2</sub> flow-rate 32 ml/min; 0.5- $\mu$ l sample; sensitivity change 1:250. Peaks: 1 = cyclohexane; 2 = benzene; 3 = methylcyclohexane; 4 = toluene; 5 = isooctane.

tentions on the two samples seems to increase with the size of the eluted molecule.

The excellent properties of PON 50 were utilized for the development of a method for the determination of trace amounts of non-aromatics in aromatic hydrocarbons. Fig. 3 shows chromatograms of such mixtures. Olefins are eluted in a single peak with saturated hydrocarbons. As the first peak is very sharp, contents of non-aromatic hydrocarbons down to 100 ppm could easily be detected. In an other case, cyclohexane admixtures with benzene in the range 0.1–1 % were analyzed with a standard deviation of 0.01 % using a gas chromatograph with a thermal conductivity detector, a temperature of 110°, hydrogen as the carrier gas, a constant volume of injected sample and calibration based on peak height.

The packing KEM, which had been applied successfully in analyses of carboxylic acids<sup>5</sup> and water<sup>8</sup>, may serve as an other example of the influence of texture. The material used in these studies had a surface area of 25 m<sup>2</sup>/g and showed a maximum at 60 nm on the pore radii distribution curve. When the conditions of polymerization were changed, the surface area was increased to 60 m<sup>2</sup>/g, the most frequent pore size decreased to 25 nm and extensive tailing appeared on the chromatograms of carboxylic acids.

We conclude that for the best performance of polymeric gas chromatographic packings, the distribution of pores should be carefully controlled. In general, broader pores should give less distortion of peaks by diffusion. However, surface area and pore size cannot be varied independently; a high surface area can be achieved only when a substantial fraction of the surface is formed by small pores. Moreover, there is probably also some dependence of the chemical composition of the surface, which is not necessarily the same as the bulk composition, on the polymerization rate and the chemical nature of the solvent used during polymerization for formation of the pores. The poor retention reproducibility of commercial polymeric packings from various batches, reported by some workers<sup>9,10</sup>, might be explained on this basis.

When considering the optimal textural parameters of a packing, we must view the chromatographic process as a complex system of interactions. We must take into account not only the strength of adsorption of the substances that are to be separated but also their relative rates of adsorption and diffusion. Therefore, mean pore radii of 60 nm have been found suitable with KEM for the separation of acids, whereas for PON and for the separation of hydrocarbons this pore size might be too small.

Other analytical applications of the materials listed in Table I are under study and will be published elsewhere.

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