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SIZE EXCLUSION CHROMATOGRAPHY OF POLYMER MOLECULES ON MICROPARTICULATE SILICA GELS: A COMPARATIVE STUDY

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SUMMARY

Inverse size exclusion chromatographic procedures have been applied to silica gel packings with different pore size distributions and the resulting pore dimensions have been compared with those obtained by nitrogen capillary condensation. It is shown that the evaluation of pore sizes depends on the model which is assumed to describe the real pore texture. The empirical method developed by Halász seems to be useful in checking the adequacy of the pore model adopted. The differences in the results obtained from the chromatographic and absolute methods are discussed.

INTRODUCTION

Among the several non-conventional uses of size exclusion chromatography (SEC) is the measurement of the elution volumes of molecules having different sizes for the determination of particle porosimetry of solid packings¹⁻⁴ as an alternative to classical capillary condensation and mercury porosimetry. This application, which has been called inverse SEC¹, has great relevance for the complete characterization of porous phases employed in liquid chromatography of polymers, and hopefully will allow a deeper insight into the pore structures involved in the chromatographic analysis. Two different approaches have been reported in the use of SEC for the evaluation of pore sizes and pore size distributions: the first one^{1,4} relies on the application of a theoretical relationship for the separation of solute molecules by a random-planes pore model⁵ to the experimental distribution coefficients of standard polymer molecules; the second approach^{2,3} is based on an empirical relationship between the molar masses of monodisperse polystyrene standards generally used for column calibration and the smallest pore diameters into which the sample molecules can diffuse.

In this paper the results obtained by different inverse SEC procedures on silica gels having various pore size distributions will be compared and discussed from the point of view of both the differences in the methods and the pore model adopted.

TABLE I
 MOLAR MASSES, HYDRODYNAMIC RADII, R_h , OF THE STANDARDS ELUTED IN THE FOUR DIFFERENT LICHROSPHER COLUMNS AND d_p VALUES FROM EQN. 2

The distribution coefficients, K_{SEC} , of the standards, the pore volume frequencies, $w(K_{SEC})$, and the logarithms of the geometric mean of the consecutive d_p values are reported for each column.

Molar mass	R_h (Å)	d_p (Å)	SI 100			SI 500			SI 1000			SI 4000						
			K_{SEC}	$w(K_{SEC}) \times 100$	$\log(d_p)_m$	K_{SEC}	$w(K_{SEC}) \times 100$	$\log(d_p)_m$	K_{SEC}	$w(K_{SEC}) \times 100$	$\log(d_p)_m$	K_{SEC}	$w(K_{SEC}) \times 100$	$\log(d_p)_m$				
Toluene			9			1			1			1						
800	6		32	15.8	1.227	0.912	9	1.357	0.910	11	1.357	0.919	12.2	2.628	0.919	12.2	2.628	0.919
2200	10.5		58	49	1.635	0.785	12.3	1.841	0.890	13	1.841	0.831	31.3	2.864	0.831	31.3	2.864	0.831
4000	15		83	55.4	1.841	0.700	23	2.035	0.852	16.2	2.035	0.774	30	3.025	0.774	30	3.025	0.774
10,000	24.7		142	88	2.035	0.494	51.4	2.224	0.800	36.1	2.224	0.653	92	3.160	0.653	92	3.160	0.653
17,500	34		198	104.2	2.224	0.344	94.8	2.392	0.729	37.3	2.392	0.597	40.3	3.373	0.597	40.3	3.373	0.597
37,000	51.5		307	94.8	2.392	0.162	57.7	2.628	0.415	73	2.628	0.266	116	3.555	0.266	116	3.555	0.266
111,000	96		588	57.7	2.628	0			0.238	78.4	2.864	0.242	27	4.045	0.242	27	4.045	0.242
233,000	146		910						0.374	83.8	3.025	0.153	27	4.045	0.153	27	4.045	0.153
390,000	195		1233						0.303	83.8	3.025	0.048	27	4.045	0.048	27	4.045	0.048
670,000	264		1700						0.206	83.8	3.025	0	27	4.045	0	27	4.045	0
2,050,000	497		3280						0.024	83.8	3.025							
2,770,000	590		3920						0	83.8	3.025							
$1 \cdot 10^7$	1215		8365							83.8	3.025							
$2.6 \cdot 10^7$	2083		14,700								3.555							

EXPERIMENTAL

SEC calibration curves were determined on four commercial microparticulate silica gels (LiChrospher; SI 100, 500, 1000, 4000; E. Merck, Darmstadt, G.F.R.) having different pore size distributions and nominal particulate dimensions of 10 μm . With each gel a column (25 cm \times 0.46 cm I.D.) was prepared by dispersing the silica in methanol and packing the column by the ascending technique⁶ at a final pressure of about 10 MPa.

Chromatographic measurements were performed on a Siemens 100 liquid chromatograph equipped with a UV detector. For sample introduction a Rheodyne 7010 injection valve with a 10- μl loop was used; all the connections between the injector and column and between the column and detector were made of as short as possible low dead-volume capillary tubing (0.025 cm I.D.).

Purified tetrahydrofuran (THF) was used as mobile phase. Low dispersion polystyrene (PS) standards (ArRo Labs., Joliet, IL, and Polysciences, Warrington, PA, U.S.A.) were injected at a 0.1% (w/v) sample concentration (0.05% for the standards of highest molar mass) in THF. Toluene was used as a totally permeating solute.

The peak elution volumes of the injected samples were independent of the flow-rate over a wide range (from about 0.15 to 2.5 $\text{cm}^3 \text{min}^{-1}$). The calibrations were performed at a low flow-rate (about 0.5 $\text{cm}^3 \text{min}^{-1}$) where the elution peaks were practically symmetrical, and the solute distribution could be considered as at equilibrium. All the measurements were made in triplicate and the reproducibility of the elution volumes was better than 1%.

Surface area determinations on the porous silica gels were performed by the BET method⁷ for nitrogen sorption.

RESULTS

The distribution coefficients, K_{SEC} , of the polymer molecules in the different gels were determined from the elution volumes of the injected standards according to

$$K_{\text{SEC}} = (V_e - V_0)/(V_i - V_0) \quad (1)$$

where V_e is the standard elution volume, V_0 is the interstitial volume obtained with excluded solutes and V_i is the elution volume of a totally permeating solute. The results obtained are in Table I.

Pore dimensions by the Halász method

According to the method proposed by Halász and co-workers^{2,3} for the determination of pore distributions, the following empirical relationship holds between the weight-average molar masses, M_w , of the permeating solutes and the smallest pore diameters, d_p , in which the molecules can diffuse when they are in a good solvent:

$$d_p (\text{\AA}) = 0.62 M_w^{0.59} \quad (2)$$

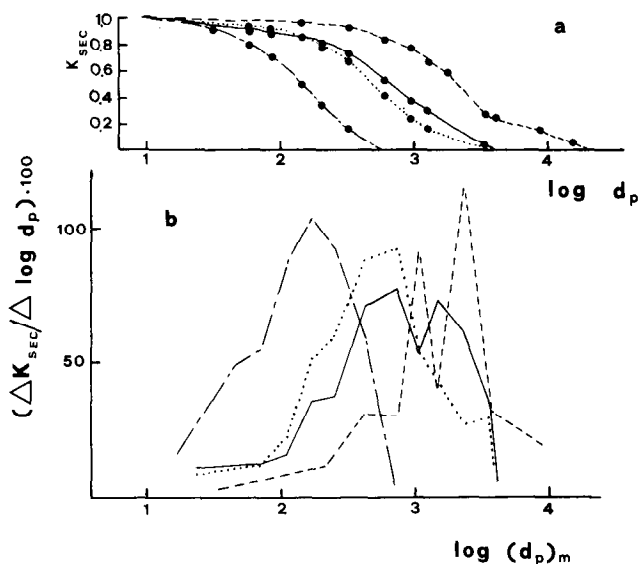


Fig. 1. Integral (a) and differential (b) pore size distributions of LiChrospher silicas according to the Halász method. Silicas: SI 100 (—•—); SI 500 (·····); SI 1000 (—■—); SI 4000 (---).

By means of eqn. 2 the usual SEC calibration curve of K_{SEC} vs. $\log M_w$ can easily be transformed into a plot of K_{SEC} against $\log d_p$. Fig. 1a shows such a plot for the different silica gels: the curves can be interpreted as integral pore size distributions. The differential distributions presented in Fig. 1b as plots of $W(K_{SEC}) = \Delta K_{SEC} / \Delta \log d_p$ were obtained by considering the differences in K_{SEC} and $\log d_p$ for two consecutive PS standards and the logarithm of the geometric mean, $(d_p)_m$, of the corresponding two consecutive d_p values. The d_p values for the injected standards, together with the values of $w(K_{SEC})$ and $\log (d_p)_m$ obtained on the four columns are reported in Table I.

From Fig. 1b it is seen that the SI 100 and 500 gels show quite regular pore size distributions around a maximum frequency value, whereas the two silica gels with larger pore sizes, SI 1000 and 4000, exhibit distributions with two separate maxima. In order to check whether such an effect could have arisen through improper column packing, several columns were prepared with the SI 4000 silica from the same batch, and in all cases the same distribution pattern was obtained.

An estimate of the chromatographic mean pore diameters, \bar{d}_p , for the investigated silica gels was obtained from the integral distribution curves of Fig. 1a by taking the values of d_p at $K_{SEC} = 0.5^3$; the results are reported in Table III.

Pore dimensions according to Giddings treatment (the Freeman method)

According to the Giddings treatment⁵ of the separation of spherical solutes by a random-planes pore structure, the dependence of the distribution coefficients of standard molecules on the solute dimensions in the solution can be expressed through the following relationship

$$-\ln K_{SEC} = A R_h \quad (3)$$

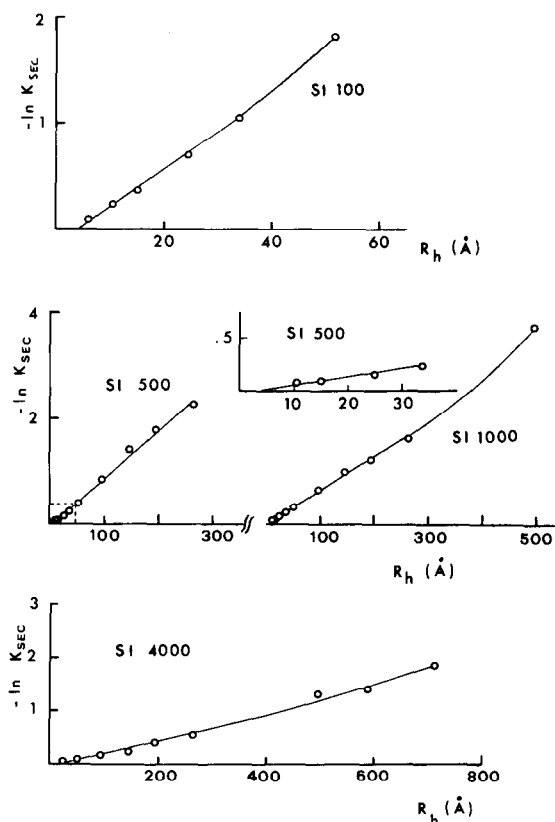


Fig. 2. Values of $-\ln K_{SEC}$ plotted against the hydrodynamic radii, R_h , of the PS standards, for the LiChrospher silicas.

where A is the surface area per unit pore volume and R_h is the hydrodynamic radius of the polymer molecules. By plotting $-\ln K_{SEC}$ vs. R_h , for a given column system, a value of A is obtained from which a mean pore dimension can be calculated, depending on the model assumed for the pore geometry.

The values of the hydrodynamic radii of the injected PS standards, obtained from the equation⁸

$$R_h (\text{Å}) = 1.37 \cdot 10^{-1} M_w^{0.564} \quad (4)$$

are reported in Table I, and are in good agreement with those calculated from the equivalent hard-sphere model⁹.

In Fig. 2 the experimental K_{SEC} values obtained for the four different silica gel columns are plotted against R_h , according to eqn. 3. The curves show two interesting characteristics: (i) deviation from linearity at the highest values of R_h ; (ii) the intercepts of the linear portions of the curves are not equal to zero (particularly for SI 100, and for SI 500 in the enlarged section of the initial part of the plot). The deviation

TABLE II

VALUES OF SURFACE AREAS, A AND S , OBTAINED BY THE FREEMAN METHOD AND FROM BET MEASUREMENTS ON THE LICHROSPHER SAMPLES

<i>Silica</i>	A ($\text{\AA}^2 \text{ cm}^{-3}$) eqn. 3	S ($\text{m}^2 \text{ g}^{-1}$) eqn. 5	S_{BET} ($\text{m}^2 \text{ g}^{-1}$)
SI 100	0.0348	360	358
SI 500	0.0091	112	65
SI 1000	0.0061	60	46
SI 4000	0.0021	20	14

from linearity derives from the inadequacy of the random-planes model when the molecule dimensions are so large that the curvature of the pore walls becomes important, and the pore walls themselves can no longer be regarded as planes. On the other hand, the non-zero of R_h at $\log K_{\text{SEC}} = 0$ arises from the fact that $K_{\text{SEC}} = 1$ for small molecules which have finite dimensions; therefore, in the real exclusion behaviour, the limit $K_{\text{SEC}} = 1$ for $R_h = 0$ predicted by eqn. 3 does not hold: the values of R_h obtained from Fig. 2, at $K_{\text{SEC}} = 1$, range from 3 to 8 \AA for the different packings.

The values of the surface areas per unit pore volume, A , have been evaluated from linear regression on the linear part of the curves of Fig. 2. The A values were then transformed into the surface areas per mass unit of the stationary phase, S ($\text{m}^2 \text{ g}^{-1}$), by means of the equation

$$S = \frac{AV_p}{\rho V_s} \cdot 10^4 \quad (5)$$

where $V_p = V_t - V_0$, $V_s = V_{\text{col}} - V_t$ is the volume of the solid gel in the total column volume, V_{col} , and ρ is the skeleton density of the gel. Values of ρ for the investigated LiChrospher have previously been reported¹⁰. In Table II are collected the values of A and S obtained from the data of Fig. 2, together with the experimental surface areas measured by the BET method on the same silica samples.

The mean pore dimensions of LiChrospher silicas have been calculated from the surface areas by the relationship

$$\bar{d}_p = 4 V_{\text{sp}}/S \quad (6)$$

by assuming uniform cylindrical non-intersecting pores⁷, where V_{sp} is the specific pore volume. The V_{sp} values of the silicas were obtained from the ratio between V_p and the weight of gel in each column¹⁰.

The mean pore dimensions obtained from eqn. 6 both by using the S values from the inverse SEC and the BET results are reported in Table III.

Pore dimensions according to Doi's treatment

Another theoretical expression for the partition of macromolecules between random porous networks and bulk liquid was proposed by Doi¹¹. He considered the pore structure generated by solid phase elements of different types (spheres, rods or

TABLE III

VALUES OF \bar{d}_p FROM BET AND FROM THE DIFFERENT INVERSE SEC METHODS FOR THE LICHROSPHER SAMPLES

Silica	Pore size (\AA)				
	Nominal	BET	Halász method	Eqn. 3	Eqn. 7
SI 100	100	116	135	116	167
SI 500	500	760	480	440	400
SI 1000	1000	860	650	660	900
SI 4000	4000	2900	2090	2000	2200

flexible chains) randomly embedded in space. The voids between the solid elements constitute the pores of the material. For flexible chain macromolecules the following approximate relation is obtained

$$-\ln K_{\text{SEC}} = \frac{2A}{\sqrt{\pi}} \cdot R + A^2 R_h^2 \alpha \quad (7)$$

where α is a constant depending on the pore geometry. Eqn. 7, taking into account the curvature of the pore wall and involving the parameter α which characterizes the pore shape, can be looked upon as a generalization of the Giddings approach.

The A values were evaluated from eqn. 7 by polynomial regression on the K_{SEC} and R_h values corresponding to the four gels investigated; the corresponding \bar{d}_p values obtained from eqns. 5 and 6 are reported in Table III.

DISCUSSION

The results in Table III show a rather wide scatter of the pore dimensions, as obtained from the different experimental approaches, around the nominal values. In particular, it appears that the SI 4000 sample has a decidedly smaller effective mean pore size than the nominal one, and that gels SI 500 and 1000 seem to have more similar porosities than expected: this last result is in agreement with the closeness of the corresponding calibration curves in Fig. 1a. The values calculated according to the Halász method are in satisfactory agreement with those calculated according to Freeman, and both these values are lower than the BET values for the SI 500, 1000 and 4000 samples. In the case of SI 100 silica, the BET, Halász, Freeman and nominal values are in reasonable agreement. The trend of the \bar{d}_p values calculated according to Doi seems less regular: the Doi value is close to the BET one (as well as to the nominal one) in the case of SI 1000, whereas in the case of the other gels the Doi values are in fair agreement with the Halász ones. Such agreement, however, is poorer than that between the Halász and the Freeman values.

It must be kept in mind that both eqns. 3 and 7 strictly apply only to the ideal models for which they have been derived. If the real pore structures are not ad-

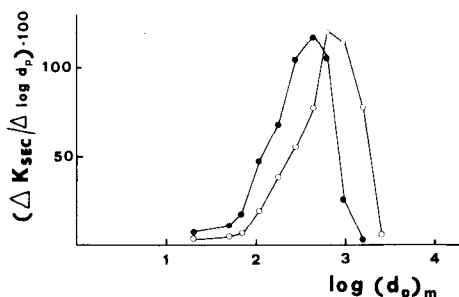


Fig. 3. Differential pore size distributions according to the Halász method for Porasil C (●) and D (○). The K_{SEC} data are taken from ref. 12.

equately represented by the random models on which these equations are based, unrealistic values of the surface areas and, consequently, of the pore sizes will result. On the other hand, the Halász method does not involve any assumption on pore shape. Then, if one can place any confidence in this method, its empirical origin notwithstanding, an indication might be obtained of the real pore shape when the \bar{d}_p values from this method agree with the \bar{d}_p values calculated from relationships based on specific pore models. In other words, the better agreement found in the present case between the Halász and the Freeman values than between the Halász and the Doi values might be taken as an indication that, for the four silica gels, the pore geometry is fairly well described by the random-planes model.

Support to such a view can be obtained by considering the two Porasil silicas (Porasil C and D) carefully investigated by Van Kreveld and Van den Hoed¹², who found an excellent agreement between the mean pore sizes measured by mercury porosimetry and those obtained by assuming a random-spheres model for the gel pores. If the data of ref. 12 are treated according to the Halász method the two well defined distributions shown in Fig. 3 are obtained. From these distributions one can calculate $\bar{d}_p = 310 \text{ \AA}$ for Porasil C and $\bar{d}_p = 630 \text{ \AA}$ for Porasil D, in fairly good agreement with the values of 330 and 700 \AA , respectively, reported by Van Kreveld and Van den Hoed. On the other hand, when the same data are treated according to the random-planes pore model (Freeman method) one obtains \bar{d}_p values as low as 180 and 440 \AA for Porasil C and D respectively. This result might be taken as evidence that these Porasil silicas are better described by the random-spheres than the random-planes pore model.

Finally, it is worth pointing out that, by assuming a random-spheres pore model for the four LiChrospher samples, one obtains \bar{d}_p values (75, 450, 540 and 1800 \AA for SI 100, 500, 1000 and 4000 respectively) which are less consistent with the values from the Halász method (Table III) than those based on eqn. 3; of course, this might be looked upon as a failure of the random-spheres model in describing the geometry of the pores of these LiChrospher samples.

The difference obtained in the mean pore size evaluation between the inverse SEC methods and the BET method requires some comment, as there are few data in the literature for a comparison of results from inverse SEC and absolute pore size measurements^{1,2}, and mainly limited to stationary phases with pore diameters up to about 400 \AA . Assuming that the inverse SEC results from eqn. 3 and from the Halász

method are reasonable, two principal effects can be regarded as responsible for the disagreement with the BET results: the limits of this last method when applied to small particles ($< 20 \mu\text{m}$) and large pore diameters ($> 400 \text{ \AA}$)², and the possibility that, owing to the different kind of experimental determination, the pore population (*i.e.*, the pore surface) explored by the chromatographic technique is not exactly the same as that "seen" by the nitrogen molecules of the BET method. If this is the case, the porosity data which are really of interest for liquid chromatographic applications should be those obtained from a suitable inverse SEC.

CONCLUSIONS

The determination of packing pore sizes by means of SEC in the inverse mode seems to give reliable results when the real pore geometry is adequately described by the model assumed in the theoretical relationships between the distribution coefficients and the dimensions of the eluted molecules. It seems possible to check the adequacy of the pore models adopted by comparison of the results with those obtained following the procedure of Halász. Notwithstanding the empirical character of the latter method, it has the advantage of avoiding any assumption on the pore structure, and furthermore gives the overall shape of the pore size distributions, which can be useful in comparing different packings or in controlling the reproducibility of the preparation of porous materials.

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REFERENCES

- 1 D. H. Freeman and I. C. Poinescu, *Anal. Chem.*, 49 (1977) 1183.
- 2 I. Halász and K. Martin, *Angew. Chem., Int. Ed. Eng.*, 17 (1978) 901.
- 3 W. Werner and I. Halász, *J. Chromatogr. Sci.*, 18 (1980) 277.
- 4 S. B. Schram and D. H. Freeman, *J. Liquid Chromatogr.*, 3 (1980) 403.
- 5 J. C. Giddings, E. Kucera, C. P. Russel and M. N. Myers, *J. Phys. Chem.*, 72 (1977) 4397.
- 6 P. A. Bristow, P. N. Brittain, C. M. Riley and B. F. Williamson, *J. Chromatogr.*, 131 (1977) 57.
- 7 S. J. Gregg and K. S. W. Sing, *Adsorption, Surface Area and Porosity*, Academy Press, New York, 1967.
- 8 W. Mandema and H. Zaldenrust, *Polymer*, 18 (1977) 835.
- 9 H. Benoit, Z. Grubisic, P. Rempp, D. Decker and J. G. Zilliox, *J. Chim. Phys. Phys.-Chim. Biol.*, 63 (1966) 1507.
- 10 O. Chiantore and M. Guaita, *J. Liquid Chromatogr.*, 5 (1982) 643.
- 11 M. Doi, *J. Chem. Soc., Farad. Trans. II*, 71 (1975) 1720.
- 12 M. E. van Kreveland and N. van den Hoed, *J. Chromatogr.*, 83 (1973) 111.