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Determination of Pore Volume Distribution from Size Exclusion Chromatography Data

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A method for determination of pore volume distribution from size exclusion chromatography data is proposed which is based on the supposition that a real pore structure may be represented by a set of discrete pore volume fractions, each formed by pores of one dimension only. The method has been verified on the results of measurements of porous glasses and their mixture.

Recently, works dealing with the application of size exclusion chromatography to the study of the pore structure of solid materials have been reported (1–6). A straightforward method of obtaining porosimetric information from chromatographic data had been proposed by Halász and co-workers (1–3). Their procedure is based on the assumption that the pores in some material can be, in relation to the molecule of certain size, regarded either as totally accessible or totally inaccessible; this is, of course, a gross oversimplification of the separation process. Freeman and Poinescu (4) have used the more realistic description of the separation mechanism formulated by Giddings and co-workers (7). According to their mechanism, structural parameters of the investigated porous system can be obtained from the dependence of distribution coefficient K on the size of the solute molecule. K has the meaning of the ratio of concentration of solute inside of the pore and in the mobile phase. Its relation to elution data is apparent from the equation

$$V_e = KV_p + V_0 \quad (1)$$

where V_e is the experimentally determined elution volume, V_p is the volume of pores, and V_0 is the volume of interstitial space in the chromatographic column. V_0 can be relatively easily determined as the elution volume of totally excluded solute. The problem in evaluation of K on the basis of eq 1 consists of the difficult determination of the correct value of V_p . Freeman and Poinescu (4) used as V_p the total volume of the measured sample, i.e., the sum of the volume of pores and the volume of the solid. Tsyurupa and Davankov (5), in their modification of the method, computed V_p from the elution volume of solute with the smallest molecular size for which they defined $K = 1$. But even this approach is in most cases (especially in gel materials) only a very rough approximation. Another weak point of this approach is the supposition about the monomodal shape of pore distribution, built into the basic equation. Vilenchik and co-workers (6) proposed the solution for the general shape of distribution but their method is also based on transformation of experimentally determined V_e to K .

We attempted to devise a procedure for derivation of porosimetric information from chromatographic data which would not suffer from these disadvantages. Our approach was based on the supposition that the most important unknown quantity in eq 1 is the pore volume V_p . The formulation of an equation for K in a porous network composed of identical simple pores is relatively easy (7). The difficulty consists in

the adaptation of such an equation to the real nonuniform porous network. Instead of an analytical solution of this problem, we choose a "numerical" approach. We used the set of a finite number of discrete fractions of pores, each consisting of simple pores of single size only, as a model of nonuniform porous network of investigated sample. V_e of the solute of characteristic molecular dimension L in such a porous system composed from n fractions is described by

$$V_e = \sum_{i=1}^{i=n} K^i(L) V_p^i + V_0 \quad (2)$$

Characteristic pore dimension for each fraction can be chosen in advance as a scale by which a real porous system will be described. The evaluation of investigated porous material is then reduced to the determination of the volumes of the individual fractions $V_p^1 - V_p^n$.

Adequacy of this approach and its possibilities were ascertained on the results obtained on two samples of porous glass and their mixture. These materials are exceptionally suitable for this purpose. Their rigid structure allows comparison of chromatographic measurements with results of classical porosimetric methods. Also a very narrow pore distribution is characteristic for this type material. Description of their texture can be carried out on the basis of the model of cylindrical pores. Distribution coefficient K_C for spherical molecules of diameter d_s in cylindrical pores of diameter d_p is given by the equation

$$K_C = (1 - d_s/d_p)^2 \quad (3)$$

Of course, this is valid for $d_s \leq d_p$ only; if $d_s > d_p$, $K_C = 0$.

Only exceptionally, the shape of molecules of solutes can be taken as spherical. For real molecules, we can use, instead of d_s in eq 3, their characteristic dimension L , which according to Giddings (7), governs their partitioning behavior in porous systems. For polystyrenes, the dependence of L on molecular mass M is described by the equation

$$L = am^{0.588} \quad (4)$$

For constant a , various values can be found in literature, according to the approach of individual authors (1, 2, 4, 5, 8) to this task. For this study, we used $a = 0.0246$ nm as determined by Van Kreveland and Van den Hoed (8).

EXPERIMENTAL SECTION

The chromatographic apparatus consisted of a syringe-type pump (VLD-30, Vývojové dílny ČSAV, Prague), sampling valve, stainless steel column (250 × 4.1 mm), and differential refractometer (RIDK 101, Laboratorní přístroje, Prague). In the initial stages of the experiments, the values of retention volumes were evaluated from retention time and data on the flow rate of the carrier measured at the outlet of the detector. This procedure made it possible to achieve the reproducibility of results in the range of 0.02–0.03 cm³. Later on the retention volume was calculated from the number of drops counted at the outlet of the detector (combination of DC 1002 drop counter and IT-2 integrator, both Laboratorní přístroje, Prague). In this arrangement the reproducibility was 0.01 cm³.

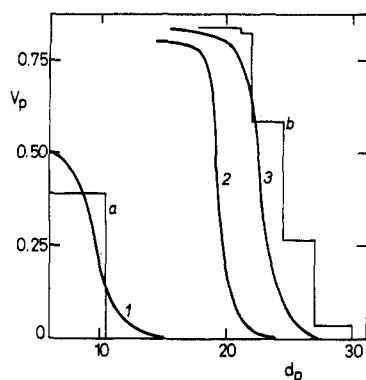


Figure 1. Cumulative pore distribution (V_p [cm³/g] against d_p [nm]) determined for CPG 00075B by nitrogen sorption (curve 1) and for CPG 00170B by mercury porosimetry (curve 2) and by nitrogen sorption (curve 3). Results obtained from chromatography data (corresponding to the models with lowest value of sum of squared errors E in Tables II and III) are shown as stepped lines a (CPG 00075B) and b (CPG 00170B).

Table I. Results of Standard Porosimetric Methods

property	CPG 00075B	CPG 00170B
Sorption of Nitrogen		
medium d_p (nm)	10.0	23.6
cumulative V_p (cm ³ g ⁻¹)	0.50	0.82
Mercury Porosimetry		
medium d_p (nm)		19.2
cumulative V_p (cm ³ g ⁻¹)		0.80
Manufacturer's Information (Method Unknown)		
medium d_p (nm)	6.9	15.9
cumulative V_p (cm ³ g ⁻¹)	0.37	0.73

Samples of porous glass CPG-10 (BDH Chemicals) were designated as CPG 00075B (lot no. 462) and CPG 00170B (lot no. 519) by the supplier. Pore distribution of these materials was determined in our institute by nitrogen sorption and in the case of sample CPG 00170B also by mercury porosimetry (9). As described in the literature (e.g., ref 10), it was found to be very narrow (Figure 1). Medium d_p and cumulative V_p computed for the model of cylindrical pores are shown in Table I. For the measurements both glasses were used as received (irregular particles of the size 120–200 mesh). According to the manufacturer's recommendation, columns were packed by the dry-filling technique. The weight of the packing was determined as the difference between the weight of the packed and the empty column.

Freshly distilled tetrahydrofuran was used as the mobile phase, and a set of polystyrene calibration standards covering the molecular mass range 570–2700000 (Pressure Chemicals Co., Pittsburgh) were used as solutes. For measurements, each sample was injected separately as 15 mm³ of a 0.5% solution in tetrahydrofuran.

RESULTS AND DISCUSSION

Interpretation of the results was performed on the assumption that there is no sorption of polystyrene standards on porous glasses and elution is influenced by steric effect only. According to the literature data (1) this supposition seems to be reasonable.

The elution limit for sample CPG 00075B was 50 000 and for sample CPG 00170B amounted to 100 000. Solutes with this and higher molecular mass did not penetrate into pores of measured glasses and their retention volumes were regarded as V_0 (Figure 2).

The range from which characteristic values of pore size of individual fractions should be chosen is indicated by the sizes of molecules of the solutes for which $V_e > V_0$. However, the

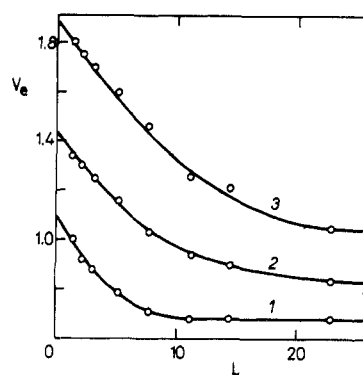


Figure 2. Elution volume data V_e [cm³/g] plotted according to effective solute size L [nm]: (1) CPG 00075B (weight of column packing 2.68 g); (2) mixture of CPG 00075B and CPG 00170B in mass ratio 1:1 (weight of column packing 2.22 g); (3) CPG 00170B (weight of column packing 1.84 g). Solid lines are calculated by using eq 2 and data from Tables II–IV corresponding to the lowest value of sum of squared errors E .

Table II. Results for Porous Glass CPG 00075B

$d_p^i = 1.5L$		$d_p^i = 2L$		$d_p^i = 2.5L$	
d_p^i , nm	V_p^i , cm ³ g ⁻¹	d_p^i , nm	V_p^i , cm ³ g ⁻¹	d_p^i , nm	V_p^i , cm ³ g ⁻¹
1.9	0.0	2.5	0.02	3.1	0.01
3.2	0.01	4.4	0.0	5.4	0.0
4.9	0.0	6.5	0.0	8.1	0.23
7.8	0.14	10.4	0.39	13.0	0.18
11.6	0.27	15.4	0.0	19.3	0.0
16.8	0.0	22.4	0.0	28.0	0.0
0.00112		E		0.00148	
0.42		Cumulative V_p (cm ³ g ⁻¹)		0.42	
		\bar{d}_p (nm)			
10.1		10.4		10.2	

selection of these characteristic sizes has to take into account low sensitivity of V_e on the presence of pores with d_p approaching L of the solute and so the range of characteristic d_p^i of individual fractions should be expanded a little above the size of molecule corresponding to the exclusion limit for the investigated material. The selection of individual values of d_p^i inside of this range was made on the basis of solute sizes L . For the assessment of the influence of selection d_p^i , we performed computation alternatively for d_p^i equal to $1.5L$, $2L$, and $2.5L$ of solutes. In such a way the results for three alternative models were obtained.

When values of pore diameter are assigned to the individual fractions from which the model of pore structure of investigated material is to be built, it is possible to compute values of K_C for each solute in each fraction. After introduction of these values into eq 2, we obtain a set of k (k is the number of solutes) linear equations containing as the unknown only volumes of pore fractions $V_p^1 - V_p^n$ (of course, it must be $k \geq n$). It would be possible to solve this set of equations analytically but in such a case the result could contain negative values of some of the roots which would be inconsistent with their physical meaning. Therefore, a numerical method was used which is based on the minimalization of the sum of squares of differences between the left and right sides of eq 2 (denoted E in Tables II–IV) at the condition that V_p^i ($i = 1, n$) ≥ 0 . It may be possible to use different algorithms for this purpose. Actual implementation depends on the availability of ready-made software. Our program was built around the published procedure BSOLV (11), based on Marquardt's algorithm (12), making possible solution of a set of equations

Table III. Results for Porous Glass CPG 00170B

$d_p^i = 1.5L$		$d_p^i = 2L$		$d_p^i = 2.5L$		a	
d_p^i , nm	V_p^i , cm ³ g ⁻¹	d_p^i , nm	V_p^i , cm ³ g ⁻¹	d_p^i , nm	V_p^i , cm ³ g ⁻¹	d_p^i , nm	V_p^i , cm ³ g ⁻¹
3.2	0.0	4.4	0.0	5.4	0.0	15.0	0.0
4.9	0.0	6.5	0.0	8.1	0.0	17.5	0.0
7.8	0.0	10.4	0.0	13.0	0.02	20.0	0.01
11.6	0.0	15.4	0.03	19.3	0.29	22.0	0.24
16.8	0.0	22.4	0.51	28.0	0.56	24.5	0.32
21.4	0.63	28.6	0.33	35.7	0.0	27.0	0.23
32.2	0.24	43.0	0.0	53.7	0.0	30.0	0.04
E							
0.0161		0.0155		0.0175		0.0132	
cumulative V_p (cm ³ g ⁻¹)							
0.87		0.87		0.87		0.84	
\bar{d}_p (nm)							
24.4		24.6		23.9		24.7	

^a Values of d_p^i adjusted after previous results.

Table IV. Results for Mixture of Glasses CPG 00075B and CPG 00170B in Mass Ratio 1:1

$d_p^i = 1.5L$			$d_p^i = 2L$			$d_p^i = 2.5L$		
d_p^i , nm	V_p^i , cm ³ g ⁻¹	\bar{d}_p , nm	d_p^i , nm	V_p^i , cm ³ g ⁻¹	\bar{d}_p , nm	d_p^i , nm	V_p^i , cm ³ g ⁻¹	\bar{d}_p , nm
3.2	0.0		4.4	0.0		5.4	0.0	
4.7	0.0		6.5	0.0		8.1	0.0	
7.8	0.0		10.4	0.16	12.4	13.0	0.30	13.0
11.6	0.22	12.3	15.4	0.10		19.3	0.03	
16.8	0.03		22.4	0.10	27.8	28.0	0.18	29.7
21.4	0.17	28.1	28.6	0.24		35.7	0.11	
34.3	0.19		45.7	0.02		57.1	0.0	
48.4	0.0		64.6	0.0		80.7	0.0	
E								
0.004 53			0.004 80			0.003 64		

with as many as nine unknowns.

Results of this treatment of elution data of polystyrenes on both porous glasses are given in Tables II and III. It is evident that these results are in agreement with the basic character of the texture of porous glasses, i.e., very narrow pore distribution. For all three examined alternative sets of pore dimensions the same medium pore diameter, \bar{d}_p (average value weighed by volumes of individual pore fractions), was obtained. This is an indication that differences between results for all three sets of pore diameters are caused only by

the different ability of individual models to conform with real pore structure. For selection of the set of results most properly representing the porous structure of the investigated material, it is possible to take into account the corresponding residual sum of squared deviations between the experimental elution volumes V_e and the values calculated by using the model of porous structure (E). It is apparently the lowest for the case when one of the considered fractions has dimensions the same as the medium pore diameter of the sample (Table II). For glass CPG 00170B this requirement was not quite fulfilled in any of three proposed pore representations. Corresponding adjustment of the model resulted in distinct improvement of the fit (last two columns of Table III). Adequacy of quantitative characterization of porous structure by the chromatographic method is confirmed by the comparison of data from Tables II and III with the results of measurements of porous glasses by classical porosimetric methods (Table I and Figure 1) (9).

The ability of the proposed method to comply with a more complicated pore size distribution was tested by measurement of the mixture of both porous glasses in a 1:1 mass ratio. Obtained data are presented in Table IV. Bimodal character of pore distribution of the mixture is shown clearly by these results and found values of pore dimensions and volumes are in reasonably good agreement with data for pure components.

Results of measurements of porous glasses confirmed the ability of the proposed method to obtain from chromatographic data structural information with accuracy comparable to well established porosimetric methods. Even information provided about the shape of pore distribution by this approach can be regarded as reliable.

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