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THEORETICAL ASPECTS OF THE PORE DISTRIBUTION AND ITS DETERMINATION BY SIZE-EXCLUSION CHROMATOGRAPHY

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SUMMARY

A generalized treatment of the pore-distribution problem is proposed with no reference to the geometrical form of the pores. The actual pore-size distribution is clearly defined and distinguished from the commonly known pore-volume distribution which can be determined experimentally. A relationship between the two distributions is derived and the possibility of obtaining them from size exclusion chromatography data is demonstrated with silica gels intended for use in high-performance liquid chromatography. The important numerical characteristics of the distributions, *e.g.*, mean value, standard deviation or variance, have been evaluated by applying the method of moments. The results obtained and the distributions for selected silica gels are discussed.

INTRODUCTION

All commonly used methods of determining the pore distribution of dispersive materials, *e.g.*, capillary condensation, mercury porosimetry and size-exclusion chromatography (SEC), actually yield the relative pore-volume distribution

$$W(\varphi) = dV/V_\text{P}d\varphi \tag{1}$$

where V is the volume of pores of diameter φ falling within the range φ to $\varphi + d\varphi$ and V_P is the total volume of all pores in the material studied. This function is often incorrectly called the pore-size distribution, which strictly corresponds to

$$D(\varphi) = dN_\varphi/Nd\varphi \tag{2}$$

where N_φ is the number of pores whose diameters fall within φ to $\varphi + d\varphi$ and N is the number of all pores.

In the present paper the functions represented by eqns. 1 and 2 will be distinguished as the pore-volume distribution and actual pore-size distribution, respectively. Unfortunately, in contrast to $W(\varphi)$, there are no methods of experimentally determining $D(\varphi)$. However, by applying a generalized approach to the pore-distribution problem that does not require assumptions about the pore geometry, a

relationship between the two distributions can be derived which enables the determination of $D(\varphi)$ if $W(\varphi)$ is obtained experimentally. The possibility of determining $D(\varphi)$ by using SEC measurements is demonstrated with silica gels intended for use in high-performance liquid chromatography (HPLC).

THEORETICAL

Pore-size distribution problem

It is well known that the pores of solid materials are of various shapes and sizes. The form of the pores and their dimensions are mutually related. To obviate the limitations arising from the pore shape, one commonly defines the linear size of the pores via the so-called hydraulic diameter, φ_h

$$\varphi_h = 2V_p/A_p \tag{3}$$

where V_p and A_p are the volume and the surface area of a pore or of a group of equal pores[1,2]. Practically, it is more convenient to employ the so-called effective diameter, φ, defined as $\varphi = 2\varphi_h$ for a cylindrical pore.

In order to define φ without reference to the form of the pores, the relationship

$$\varphi = h\varphi_h \tag{4}$$

is introduced, where h will be called the pore-shape parameter. Usually, the pores of a solid are of equal or nearly equal form, being conditioned by the solid's origin. From relationships 3 and 4, a constant value of h ($h > 0$) corresponds to pores of equal shape, *e.g.*, $h = 2$ holds for cylindrical pores. If the pores are of nearly equal form as is commonly observed, then h must be considered as an average corresponding to an average pore shape.

In the following, the effective pore diameter, φ, defined by relationship 4, will also be called the pore diameter. Since φ has arbitrary values in a continuous interval, it can be considered as a random quantity characterized by a distribution, $D(\varphi)$. The main problem in each experimental study of a porous material is to plot the differential function of the pore distribution which yields maximum information concerning the structure of the material. From a theoretical point of view, however, it is interesting to derive some explicit expression of this function, thus facilitating the pore-structure investigations.

Combining relationships 3 and 4 yields:

$$V_p = (\varphi/2h)A_p \tag{5}$$

It is known that the surface area of a pore, A_p, is a function of φ. Here it will be described by the general expression

$$A_p = qa^{2-n}\varphi^n \tag{6}$$

where n is a positive real number dependent on the pore shape and called the pore-shape index, q is a dimensionless constant and a is a numerical parameter. It is

obvious that eqn. 6 originates from the evidence that A_p has dimensions of [length]^2, while φ has a dimension of [length]. Thus, a should also have a dimension of [length] to satisfy the equation:

$$[\text{length}]^2 = [-] \cdot [\text{length}]^{2-n} \cdot [\text{length}]^n$$

Theoretically, this equation holds for each arbitrary value of n. However, taking into account that the surface area of a solid is determined only by those pores representing open cavities, it follows that $n < 2$, a value corresponding to the closed spherical form. For cylindrical pores, it can be shown that $n = 1$, while for pores of any form, $0 < n < 2$.

Since both h and n are pore-shape dependent, it is logical to postulate the existence of a relationship between them. For example, for cylindrical or spherical pores, $h = n + 1$. For pores of arbitrary shape, however, it is difficult to derive a common relationship. Later, this problem wil be discussed again when considering the results obtained.

Combination of eqns. 5 and 6 leads to a general expression for the volume, V_p, of a pore having diameter φ:

$$V_p = (qa^{2-n}/2h)\varphi^{n+1} \tag{7}$$

Remembering that φ is a random quantity characterized by a density function, $D(\varphi)$, we can use the last expression to define the volume, V, of all pores whose diameters fall within the range 0 to φ_v

$$V = N \int_0^{\varphi_v} V_p D(\varphi) d\varphi$$

or taking account of eqn. 7:

$$V = (qa^{2-n}N/2h) \int_0^{\varphi_v} \varphi^{n+1} D(\varphi) d\varphi \tag{8}$$

The upper integration limit, φ_v, in eqn. 8 is a variable, which can take any value of φ. When $\varphi_v = \infty$

$$V_P = (qa^{2-n}N/2h)J_{n+1} \tag{9}$$

where

$$J_{n+1} \equiv \int_0^\infty \varphi^{n+1} D(\varphi) d\varphi \tag{10}$$

and V_P, as mentioned above, is the total pore volume.

Let us further differentiate eqn. 8 as follows:

$$dV/d\varphi_v = (qa^{2-n}N/2h)(d/d\varphi_v) \int_0^{\varphi_v} \varphi^{n+1}D(\varphi)d\varphi$$

According to the Leibnitz–Newton theorem[3]:

$$dV/d\varphi_v = (qa^{2-n}N/2h)\varphi_v^{n+1}D(\varphi_v)$$

Since φ_v can be equal to each φ value, we may write:

$$dV/d\varphi = (qa^{2-n}N/2h)\varphi^{n+1}D(\varphi) \tag{11}$$

Dividing eqn. 11 by eqn. 9, and taking account of expression 1, we obtain the important relationship:

$$W(\varphi) \equiv dV/V_P d\varphi = (\varphi^{n+1}/J_{n+1})D(\varphi) \tag{12}$$

It follows from eqn. 12 that the pore-volume distribution, $W(\varphi)$, depends on the actual pore-size distribution, $D(\varphi)$, as well as on the pore-shape index, n, reflecting the influence of the real pore geometry. For a certain porous material, however, neither $W(\varphi)$ nor $D(\varphi)$ can be expressed in an explicit form. Bearing in mind the importance of both functions when studying the pore structure, it would be very useful to be able to obtain them, even approximately.

So defined, the problem can be solved in a satisfactory way. Thus, the methods of determining the pore-volume distribution involve plotting an experimental $W(\varphi)$ curve. In principle, the latter can be approximated more or less precisely by a polynomial or even by a known differential function. Having this expression at our disposal, we can define $D(\varphi)$ approximately by rearranging eqn. 12:

$$D(\varphi) = J_{n+1}\varphi^{-(n+1)}W(\varphi) \tag{13}$$

In practice, in order to employ eqn. 13 it is necessary to know the value of the J_{n+1} integral. Obviously, eqn. 10 is inapplicable because J_{n+1} depends on $D(\varphi)$. Eqn. 13 is therefore integrated as follows:

$$\int_0^\infty D(\varphi)d\varphi = J_{n+1} \int_0^\infty \varphi^{-(n+1)}W(\varphi)d\varphi$$

Taking into consideration that $D(\varphi)$ is a density distribution function, it is evident that the left-hand-side integral is unity. Hence

$$J_{n+1} = 1/\int_0^\infty \varphi^{-(n+1)}W(\varphi)d\varphi \tag{14}$$

and if n is known, J_{n+1} can be evaluated.

For detailed determination of the actual pore-size distribution it is necessary to obtain its most important numerical characteristics, *e.g.*, the mean value, $\bar{\varphi}_D$, the standard deviation, σ_D (or the variance, σ_D^2), and the maximum, $\bar{\varphi}_{D,\text{max}}$. According to the well known method of moments[3], the mean value is defined as the first initial moment of $D(\varphi)$. Taking into account eqn. 13, we can write:

$$\bar{\varphi}_D \equiv \int_0^\infty \varphi D(\varphi)\mathrm{d}\varphi = J_{n+1} \int_0^\infty \varphi^{-n}W(\varphi)\mathrm{d}\varphi \tag{15}$$

On the other hand, the variance is defined as

$$\sigma_D^2 = \overline{\varphi_D^2} - (\bar{\varphi}_D)^2 \tag{16}$$

where $\overline{\varphi_D^2}$ represents the second initial moment of $D(\varphi)$, *i.e.*:

$$\overline{\varphi_D^2} \equiv \int_0^\infty \varphi^2 D(\varphi)\mathrm{d}\varphi = J_{n+1} \int_0^\infty \varphi^{1-n}W(\varphi)\mathrm{d}\varphi \tag{17}$$

Finally, to estimate the maximum, $\bar{\varphi}_{D,\text{max}}$, it is enough to plot the distribution $D(\varphi)$ or to nullify its first derivative, $\mathrm{d}D(\varphi)/\mathrm{d}\varphi$, and to solve this equation with respect to φ.

Eqns. 15–17 enable the evaluation of the numerical characteristics only if the n value is available. In practice, the pores are commonly regarded as cylindrical capillaries, thus $n = 1$. In general, n is unknown and unfortunately cannot easily be determined. Special procedures for evaluating n must be developed depending on the methods used for determining the pore-volume distribution. An appropriate procedure for SEC is described below.

Using eqn. 6 and taking into account that φ is randomly distributed, it can be shown also that the total surface area, A_P, of a porous material is

$$A_P = qa^{2-n}NJ_n \tag{18}$$

where, in accordance with eqn. 13:

$$J_n \equiv \int_0^\infty \varphi^n D(\varphi)\mathrm{d}\varphi = J_{n+1} \int_0^\infty \varphi^{-1}W(\varphi)\mathrm{d}\varphi \tag{19}$$

Further, combination of eqns. 18 and 19 leads to

$$h = A_P/2V_P \int_0^\infty \varphi^{-1}W(\varphi)\mathrm{d}\varphi \tag{20}$$

which enables an independent evaluation of the pore-shape parameter, if both A_P and V_P are determined experimentally. Attention has to be paid however to the dimensions of the quantities, e.g., if A_P, V_P and φ are expressed in cm^2, cm^3 .and nm, respectively, then the right-hand-side of eqn. 20 must be multiplied by a factor of 10^{-7}.

SEC method of determining the pore-volume distribution

This method has been developed by Halász and Martin[4,5] as an useful technique exhibiting substantial advantages over the commonly used "classical" methods of determining the pore-volume distribution, e.g., capillary condensation and mercury porosimetry. It has been applied to studies of the porous structure of rigid solids such as silica, alumina, tungsten oxide, etc.[6,7], as well as of non-rigid solids swellable in various solvents, e.g., polymers and ion exchangers[8-11]. The principles and boundary conditions of the method have been described[5], therefore only a brief explanation will be given below.

Conventional HPLC equipment is used, the material studied being packed into a column by "dry" or "slurry" techniques depending on the particle size. Medium polar and polar solvents, e.g., dichloromethane, tetrahydrofuran, dimethylformamide or even water, can be employed as mobile phases. A suitable set of samples of known molecular masses is necessary which are well soluble in the corresponding eluent. The samples are used as standards when determining the pore-volume distribution.

For rigid solids a set of twelve linear polystyrene standards (PSt) of different polymerization grades is applied, their molecular masses ranging from 600 to $3.7 \cdot 10^6$ units and their polymolecularity being less than 1.1 (ref. 5). Referring to the conclusions of Van Kreveld and Van den Hoed[12] concerning the equivalent-sphere approximation of the dissolved random-coil PSt molecules, the effective "hard-sphere" diameter, φ'_k, of the kth standard can be evaluated from

$$\varphi'_k \, [nm] = 0.0246 M_k^{0.588} \quad (k = 1, 2, \ldots, 12) \tag{21}$$

where M_k is molecular mass of the standard. As found by Halász and Martin[5], however, the pore-volume distribution curve obtained by using the calculated φ'_k values does not agree in respect of the position of the maximum with the curves obtainable by the "classical" methods. To fit the results of the SEC method with those of the other methods they proposed the equation

$$\varphi''_k \, [nm] = 0.062 M_k^{0.59} \quad (k = 1, 2, \ldots, 12) \tag{22}$$

thus ascribing to the kth PSt an exclusion value, φ''_k. The latter is interpreted as the minimum effective pore diameter which exerts no steric hindrance to penetration of the corresponding PSt molecules.

The φ''_k values are about 2.5 times greater than those of φ'_k. This leads to a better coincidence of the distribution curves obtained by SEC and by the other methods, at least in respect of the positions of their maxima. However, the SEC distribution curve appears to be considerably broader than the corresponding "classically" obtained curves. Halász and Martin[5] attempted to explain this by pointing

out that the boundary conditions for SEC are quite different from those of the "classical" methods. As noted by Knox and Scott[13], the exact explanation follows from the fundamental concepts of SEC.

It is known that the molecular separation obtained by SEC is due to the different degrees of permeation of the available pore volume of the column packing by molecules of different sizes[14]. Hence, the void volume of a column is considered as a sum of the total pore volume, V_P, of the packing and the extra-particle volume, V_Z. The elution volume, V_{Ek}, of the kth PSt standard is given by

$$V_{Ek} = V_Z + V_P K_k \tag{23}$$

where K_k is the so-called exclusion coefficient of the standard. Obviously, small molecules, e.g., those of the eluent, that permeate virtually all pores will have an elution volume equal to the void volume, i.e., their exclusion coefficient will be unity. In practice, it is convenient to use benzene as a "zeroth" standard ($k = 0$), because its molecules are comparable in size with those of the eluent. Then, $K_0 = 1$ and $V_{E0} = V_Z + V_P$. Large molecules (like those of PSt 12), which cannot permeate the available pores, are totally excluded, i.e., $K_{12} = 0$, and hence, $V_{E12} = V_Z$. For the other standards, k, between benzene and PSt 12, $0 < K_k < 1$, and the corresponding elution volume, V_{Ek}, is smaller the greater is the molecular mass (or φ'_k) of the standard. Taking this into account, the total pore volume of a column material can be evaluated from

$$V_P = V_{E0} - V_{E12} \tag{24}$$

The accuracy of eqn. 24 will be discussed later.

Generally, the exclusion coefficient, K, is interpreted as the ratio of the pore volume, accessible to the mass centre of the penetrating "hard-sphere" molecule, to the total pore volume of the column packing[12,14]. Considering different models of pore geometry[12,13,15], K can be represented by corresponding expressions that enable calculation of the K_k values for the different standards. A comparison of the calculated and experimental K_k values allows the adequacy of the pore-shape model to be evaluated. As noted by Knox and Scott[13]: "Indeed, the rather slight improvement in going from the simplest model of a uniform cylindrical pore to the most complex model of random size touching spheres is something of a disappointment". That is why the authors proposed the model of cylindrical pores, taking into account that the pore size is randomly distributed. Thus, the small but definite loss in accuracy is compensated by the simplicity of the calculations connected with the SEC determination of the pore-volume distribution.

As shown in the previous section, the need to apply any model of pore geometry has been avoided by generalizing the definitions of both the effective pore diameter, φ (eqn. 4), and the pore surface area, A_p (eqn. 6). In accordance with eqn. 7, the volume of a pore accessible to a PSt molecule of diameter φ'_k can be defined as

$$V_{pk} = (qa^{2-n}/2h)(\varphi - \varphi'_k)^{n+1} \tag{25}$$

providing $\varphi \geqslant \varphi'_k$. Then, the exclusion coefficient, K_k, from this pore can be obtained by dividing eqn. 25 with eqn. 7:

$$K_k \equiv V_{pk}/V_p = \left(1 - \frac{\varphi'_k}{\varphi}\right)^{n+1} \tag{26}$$

Bearing in mind the random distribution of φ, we can generalize eqn. 26 for all pores having $\varphi \geqslant \varphi'_k$, i.e.:

$$K_k = \int_{\varphi=\varphi'_k}^{\varphi=\varphi_m} \left(1 - \frac{\varphi'_k}{\varphi}\right)^{n+1} W(\varphi)d\varphi \qquad (k = 0, 1, 2, \ldots, 12) \tag{27}$$

The upper integration limit, φ_m, in eqn. 27 must be carefully estimated in order to account for the widest pores. Hence, the values of φ_m for porous solids can considerably differ, e.g., from 300 to 1000 nm or more.

Eqn. 27 is essential for deriving the approximate expression for the pore-volume distribution function, $W(\varphi)$, since φ'_k are known and the K_k values are obtainable from SEC measurements. Using a familiar expansion of the binomial, $(1 - \varphi'_k/\varphi)^{n+1}$, to an infinite series we obtain:

$$\left(1 - \frac{\varphi'_k}{\varphi}\right)^{n+1} = 1 - (n+1)\frac{\varphi'_k}{\varphi} + \frac{(n+1)n}{2!}\left(\frac{\varphi'_k}{\varphi}\right)^2 - \frac{(n+1)n(n-1)}{3!}\left(\frac{\varphi'_k}{\varphi}\right)^3 + \ldots$$

For simplicity, only the first three terms will be considered. Thus, eqn. 27 can be rearranged to:

$$K_k = \int_{\varphi'_k}^{\varphi_m} W(\varphi)d\varphi - (n+1)\int_{\varphi'_k}^{\varphi_m} \frac{\varphi'_k}{\varphi} W(\varphi)d\varphi + \frac{(n+1)n}{2}\int_{\varphi'_k}^{\varphi_m}\left(\frac{\varphi'_k}{\varphi}\right)^2 W(\varphi)d\varphi \tag{28}$$

A three-fold differentiation of eqn. 28 with respect to φ'_k leads to:

$$\frac{n(1-n)}{2}\cdot\frac{d^2W(\varphi'_k)}{d\varphi'^2_k} - \frac{(n^2-1)}{\varphi'_k}\cdot\frac{dW(\varphi'_k)}{d\varphi'_k} - \frac{(n+1)}{\varphi'^2_k}\cdot W(\varphi'_k) = \frac{d^3K_k}{d\varphi'^3_k}$$

Bearing in mind that this holds for each PSt standard, k, and that the φ'_k values correspond to the minimum diameters, φ, of the pores accessible to the PSt molecules, we can generalize the equation as follows:

$$\frac{n(1-n)}{2}\cdot\frac{d^2W(\varphi)}{d\varphi^2} - \frac{(n^2-1)}{\varphi}\cdot\frac{dW(\varphi)}{d\varphi} - \frac{(n+1)}{\varphi^2}\cdot W(\varphi) = \frac{d^3K}{d\varphi^3} \tag{29}$$

For cylindrical pores where $n = 1$, we immediately obtain the solution of eqn. 29, i.e., the pore-volume distribution function

$$W(\varphi) = -\frac{\varphi^2}{2}\cdot\frac{d^3K}{d\varphi^3} \tag{30}$$

which is identical with that derived by Knox and Scott[13]. For pores of arbitrary geometry, when $0 < n < 1$ or $1 < n < 2$, eqn. 29 must be solved in respect of $W(\varphi)$, following the rules for non-homogeneous differential equations of second order.

Thus, it can be shown that eqn. 29 has two additional solutions dependent on the value of n. When $n < 1$

$$W(\varphi) = C_1\varphi^{-\alpha+\lambda} + C_2\varphi^{-\alpha-\lambda} + G\varphi^2 \cdot \frac{d^3K}{d\varphi^3} \tag{31}$$

where

$$\alpha = (n + 1)/n \tag{31a}$$

$$\lambda = \left[1 + \frac{1}{n^2} - \frac{4}{n(n-1)} \right]^{1/2} \tag{31b}$$

When $n > 1$

$$W(\varphi) = C_1'\varphi^{-\alpha} \cos(\lambda'\ln\varphi) + C_2'\varphi^{-\alpha} \sin(\lambda'\ln\varphi) + G\varphi^2 \cdot \frac{d^3K}{d\varphi^3} \tag{32}$$

where

$$\lambda' = \left[\frac{4}{n(n-1)} - \frac{1}{n^2} - 1 \right]^{1/2} \tag{32a}$$

In eqns. 31 and 32, C_1, C_2, C_1' and C_2' are adjustable constants, whose determination will be discussed later, and

$$G = -2/[4-n(n-1)] \tag{33}$$

Summarizing:

(1) The representations 30, 31 and 32 of $W(\varphi)$ correspond to three different cases when the pore-shape index can be either $n=1$ or $n<1$ or $n>1$

(2) Two of the representations contain adjustable constants (C_1, C_2, C_1', C_2'), as well as parameters dependent on the value of n (α, λ, λ', G)

(3) To transform the $W(\varphi)$ representations in explicit form it is necessary to derive an expression for $d^3K/d\varphi^3$. This is possible if the $K(\varphi')$ dependence for the whole set of PSt standards is known

Hence, in order to apply the derived representations, we need first to find an appropriate approximation of the $K(\varphi')$ dependence and secondly, to propose a reliable procedure for evaluating the pore-shape index, n. These are the two main problems to be discussed further. Since the type of the $K(\varphi')$ dependence is entirely connected with the pore structure of the material studied, the problem of approximating this dependence will be considered in the discussion of the silica gels intended for use in HPLC. The next section will deal with the problem of evaluating n, assuming the $W(\varphi)$ distribution function is represented in an explicit form.

Procedure for evaluating the pore-shape index

Since it is difficult to obtain preliminary information concerning n for any material, we do not know which of the three $W(\varphi)$ representations to employ. Moreover, no relationship is available for the calculation of n on the basis of the experimental data. Hence, the only possibility for evaluating n is the employment of an iterative calculation procedure.

For the first iteration step it is assumed that $n = 1$. Using eqn. 30, the exclusion coefficients, K_k^c, are calculated by solving numerically the integral in eqn. 27. For this purpose the equation is represented as

$$K_k^c = \sum_{\varphi = \varphi_k'}^{\varphi = \varphi_m} \left(1 - \frac{\varphi_k'}{\varphi}\right)^{n+1} W(\varphi)\Delta\varphi \qquad (k = 0, 1, 2, \ldots, 12) \tag{34}$$

where $\Delta\varphi$ is the length of the integration subinterval, e.g., $\Delta\varphi = 1$ nm. Since the SEC-measured values, K_k^m, are known:

$$\Delta K_k = K_k^m - K_k^c \qquad (k = 0, 1, 2, \ldots, 12) \tag{35}$$

Furthermore, differentiation of eqn. 34 with respect to n leads to an expression for the partial derivatives:

$$\frac{\partial K_k}{\partial n} = \sum_{\varphi_k'}^{\varphi_m} \left(1 - \frac{\varphi_k'}{\varphi}\right)^{n+1} W(\varphi)\ln\left(1 - \frac{\varphi_k'}{\varphi}\right)\Delta\varphi +$$

$$\sum_{\varphi_k'}^{\varphi_m} \left(1 - \frac{\varphi_k'}{\varphi}\right)^{n+1} \frac{\partial W(\varphi)}{\partial n} \Delta\varphi \tag{36}$$

Having the $\partial K_k/\partial n$ values at our disposal, the following simple system of equations can be compiled

$$\frac{\partial K_0}{\partial n} \cdot \Delta n = \Delta K_0$$

$$\frac{\partial K_1}{\partial n} \cdot \Delta n = \Delta K_1 \tag{37}$$

$$\vdots$$

$$\frac{\partial K_{12}}{\partial n} \cdot \Delta n = \Delta K_{12}$$

where Δn is a correction to be added to n.

System 37 is overdetermined and can easily be solved in respect of Δn by applying matrix algebra. Then, the correction

$$\Delta n = \frac{\sum\limits_{k=0}^{12} (\partial K_k/\partial n)\Delta K_k}{\sum\limits_{k=0}^{12} (\partial K_k/\partial n)^2}$$

is determined by the least squares method and after addition to the previous value of n according to

$$n_{i+1} = n_i + (\Delta n)_i \qquad (i = 1, 2, 3, \ldots, \text{etc.}) \tag{38}$$

gives the corrected value of n for the next iteration step, $i+1$. Thus, after the first iteration step, depending on the porous material, Δn can be negative or positive and hence, $n < 1$ or $n > 1$, respectively.

To generalize the procedure for the next steps, eqns. 31 and 32 wil be expressed in the common form

$$W(\varphi) = C_1 f_1(\varphi) + C_2 f_2(\varphi) + GA(\varphi) \tag{39}$$

where $f_1(\varphi)$, $f_2(\varphi)$ and $A(\varphi)$ are the corresponding functions in the above mentioned equations, while G is calculable from eqn. 33. Constants C_1 and C_2 are adjusted so as to satisfy the conditions

$$W(\varphi_0) = 0 \quad \text{and} \quad \int_{\varphi_0}^{\varphi_m} W(\varphi)\mathrm{d}\varphi = 1 \tag{40}$$

where φ_0 is the value of the smallest pore diameter available. For a variety of porous materials, φ_0 is easy to estimate, e.g., for silica gels it cannot be less than 0.1 nm. Thus the following equations are obtained

$$C_1 f_1(\varphi_0) + C_2 f_2(\varphi_0) = -GA(\varphi_0) \tag{41}$$

$$C_1 \int_{\varphi_0}^{\varphi_m} f_1(\varphi)\mathrm{d}\varphi + C_2 \int_{\varphi_0}^{\varphi_m} f_2(\varphi)\mathrm{d}\varphi = 1 - G \int_{\varphi_0}^{\varphi_m} A(\varphi)\mathrm{d}\varphi$$

which can be solved numerically in respect of the constants C_1 and C_2, again employing matrix algebra.

Once calculated for a certain value of n, C_1 and C_2 are used in the next iteration step with the corresponding $W(\varphi)$ representation to obtain the values of the $\partial K_k/\partial n$ derivatives according to eqn. 36. Determination of the correction Δn by solving the system 37 leads to a new refinement of n (eqn. 38), etc. In order to control the efficiency of the iterative procedure a criterion, F_{cr}, is calculated at each iteration step:

$$F_{cr} = \sum_{k=0}^{12} | \Delta K_k / K_k^{\mathrm{m}} |$$ (42)

During the iteration steps, F_{cr} gradually decreases to a minimum value corresponding to the best fit of the calculated to the experimentally measured K_k values. Then, the iteration procedure is terminated and the last value of n is used in the evaluation of both the pore-volume and the actual pore-size distributions, as well as for determining their important numerical characteristics.

EXPERIMENTAL

Apparatus

The liquid chromatographic equipment is described elsewhere[16,17]. The columns were drilled stainless-steel tubes (300 mm × 4.2 mm I.D.). Both the column and the eluent container were thermostatted with circulated water during the measurements at 22.0 ± 0.1°C.

Reagents

The sorbents were commercially available silica gels intended for use in HPLC: Si-60, Si-100 and Si-200 (E. Merck, Darmstadt, F.R.G.). Their physical characteristics are presented in Table I.

Dichloromethane purified by distillation was used as the eluent, and special care was taken to keep it relatively dry (water content less than 80 ppm). Benzene and twelve PSt standards (Waters Assoc., Milford, MA, U.S.A.) were dissolved in dichloromethane to give 0.1% solutions, from which approximately 10 μl were injected.

Procedures

All sorbents were packed into the columns by using a modified "slurry" technique[17]. Before the measurements, the columns were extensively washed with dichloromethane. The mass of the packing was determined by unpacking the column after use and weighing the vacuum-dried material. The volumes of the empty columns

TABLE I

PHYSICAL CHARACTERISTICS OF SELECTED SILICA GELS

Silica	Mean particle size* (μm)	Specific surface area** (m^2/g)	Specific pore volume (cm^3/g)
Si-60	10	355	0.742
Si-100	10	308	1.00
Si-200	10	167	0.736

* Irregular particles.
** Measured by Veba-Chemie (Gelsenkirchen, F.R.G.)

were estimated by weighing the empty columns and again when filled with distilled water.

The measurements for a given sorbent were carried out at constant temperature and flow-rate, the latter ranging from 1 to 2 ml/min for the different silicas. The elution times of the standards were measured at the corresponding peak maxima, while the elution volumes, V_{Ek}, were obtained by multiplying the times by the flow-rate selected. The V_{Ek} values were then employed for calculating the K_k values from eqn. 23. For comparison, the pore-volume distributions of the selected silica gels were obtained by nitrogen capillary condensation, using a home-made apparatus.

All calculations, including those of the $K(\varphi')$ dependence for the sorbents, the iterative evaluation of the pore-shape index, n, and the $W(\varphi)$ and $D(\varphi)$ distributions and their characteristics, were performed by means of a Model 9845 computer (Hewlett-Packard, Palo Alto, CA, U.S.A.), using the author's BASIC programs.

RESULTS AND DISCUSSION

Approximation of the $K(\varphi')$ dependence for silica gels

Initialy, the $K(\varphi')$ dependence was approximated by a 5–7 degree polynomial using the K_k values determined by SEC and the corresponding φ'_k values of the PSt standards calculated from eqn. 21 as proposed by Van Kreveld and Van den Hoed[12] with tetrahydrofuran as the eluent. However, the correlations obtained were poor, giving two or three negative K_k^c values for all silica gels examined. Finally, the approximation

$$K_k = 1/(1 + b\varphi'^m_k) \tag{43}$$

was found to be sufficiently representative and convenient as regards the determination of the parameters b and m. Rearrangement of eqn. 43 yields the linear regression

$$m \log \varphi'_k + \log b = \log \left(\frac{1}{K_k} - 1 \right) \tag{44}$$

enabling the evaluation of both b and m.

As is evident from eqn. 44, it was not possible to employ both the K_0 and K_{12} values, which when calculated from SEC data are always unity and zero, respectively. The regression calculations for each silica gel were performed by using φ'_k and K_k values for the standards $k = 1, 2, \ldots, 11$. Having b and m values at our disposal, the corresponding K_0 and K_{12} coefficients can be recalculated from eqn. 44 by introducing the values of φ'_0 and φ'_{12}, respectively.

Further, the calculated $W(\varphi)$ distributions were found to differ from those obtained by nitrogen capillary condensation, especially in respect of the positions of their maxima. The calculated maxima occurred at considerably lower φ values than the experimentally obtained ones. The data published by Van Kreveld and Van den Hoed[12] for K_k determined by SEC for both Poracil C and D with tetrahydrofuran as eluent were then employed. Since the φ'_k values of the PSt standards used by these authors were also available, the described calculation procedure was applied to their

TABLE II

COMPARISON OF THE CALCULATED MEAN PORE DIAMETER OBTAINED IN THIS WORK
WITH PREVIOUS RESULTS FOR TWO TYPES OF PORASIL

Eluent: tetrahydrofuran.

Silica	Calculated mean pore diameter (nm)		Pore diameter range* (nm)
	This work	Ref. 12	
Porasil C	29.7	33	20–40
Porasil D	60.4	69	40–80

* Data given by the manufacturer and cited in ref. 12.

silica gels. The good agreement between the pore diameters calculated here and the
pore diameter ranges given by the manufacturer, as well as with the mean values
calculated by the authors on the basis of their "random touching spheres" model, is
evident from Table II.

This immediately shows that the φ'_k values calculated from eqn. 21 hold only
if the SEC measurements are performed with tetrahydrofuran. In the case of di-
chloromethane, the dependence of φ'_k on M_k for the dissolved PSt molecules remains
similar (as indirectly illustrated by Halász and Martin[5] wit eqn. 22), however slightly
greater φ'_k values are expected. Since there was no experimentally verified φ'_k (M_k)
dependence in the case of dichloromethane, an attempt was made to determine it by
"trial-and-error" refinements. For this purpose, pore-volume distribution data (from
nitrogen capillary condensation) for a spherically shaped silica, Be 74/3, were em-
ployed, kindly supplied by Professor K. Unger, University of Mainz. This silica is
quite different from the irregularly shaped silica gels examined in the present study.
The φ'_k (M_k) dependence was fitted in order to obtain a coincidence of the $W(\varphi)$
maximum of Be 74/3 (calculated from SEC data) with that determined by capillary
condensation for the same silica. Thus, the equation

$$\varphi'_k \text{ [nm]} = 0.0412 \, M_k^{0.588} \qquad (k = 1, 2, \ldots, 12) \qquad (45)$$

was obtained which does not depend on the SEC data for the silica gels. Using the
φ'_k values estimated from eqn. 45, excellent agreement was obtained between the
calculated and the experimentally determined $W(\varphi)$ distributions of the silica gels
studied. Hence, it seems quite possible that PSt molecules having the same molecular
mass can exhibit different dimensions when dissolved in various solvents. Taking this
into consideration, only the φ'_k values calculated from eqn. 45 were employed. They
are listed in Table III together with the corresponding molecular masses of the PSt
standards.

Fig. 1 illustrates the $K(\varphi')$ dependence for the selected silica gels. The curves
obey eqn. 43, while the points correspond to the SEC data. The adequacy of the
approximation is visible and the good agreement is confirmed by the calculated cor-
relation coefficients; the latter are close to unity as demonstrated in Table IV which
also lists the calculated parameters b and m.

TABLE III

DATA FOR POLYSTYRENE STANDARDS

k = Serial number of standard; M_R = weight-averaged molecular mass; φ'_k = effective diameter of polystyrene molecule calculated from eqn. 45.

Standard	k	M_k	φ'_k (nm)
Benzene	0	78	0.538
PSt 1	1	600	1.77
PSt 2	2	2100	3.70
PSt 3	3	3550	5.03
PSt 4	4	10 000	9.26
PSt 5	5	20 800	14.2
PSt 6	6	36 000	19.7
PSt 7	7	111 000	38.1
PSt 8	8	200 000	53.9
PSt 9	9	498 000	92.1
PSt 10	10	867 000	128
PSt 11	11	2 610 000	244
PSt 12	12	3 700 000	299
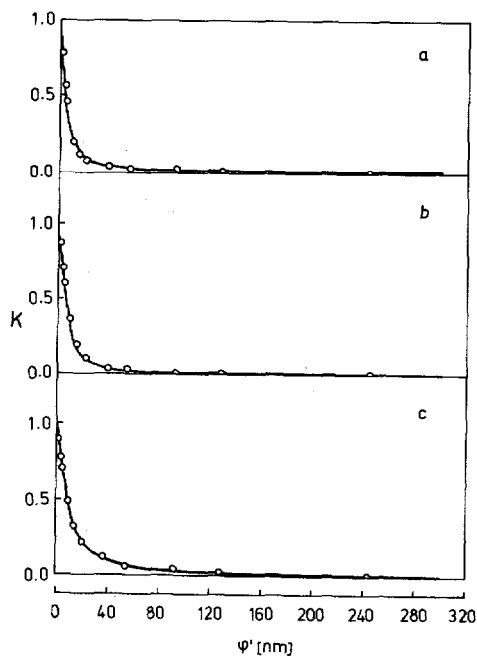
Fig. 1. Approximated $K(\varphi')$ dependence for the selected silica gels: (a) Si-60; (b) Si-100; (c) Si-200. All curves are calculated according to eqn. 43. The points correspond to the SEC data.

TABLE IV

DATA CONCERNING THE APPROXIMATION OF THE $K(\varphi')$ DEPENDENCE FOR SELECTED SILICA GELS

Silica	Parameter*		Correlation coefficient
	b	m	
Si-60	0.1672	1.302	0.9789
Si-100	0.08795	1.309	0.9871
Si-200	0.05111	1.396	0.9939

* Calculated from the linear regression, eqn. 44.

Determination of the total pore volume

As pointed out, eqn. 24 enables the evaluation of the total pore volume, V_P, of a material studied by SEC. From a theoretical point of view, however, this equation appears to be an approximation. It could be assumed that pores of diameters less than 0.5 nm are present in many porous materials, especially in silicas. Since the diameter of benzene (the "zeroth" standard) is a little greater than 0.5 nm, it cannot penetrate these narrowest pores, so that their volume remains inaccessible. Hence, the elution volume of benzene, V_{E0}, should be less than theoretically expected. On the other hand, extremely large pores ($\varphi > 300$ nm) in the porous media may also be available. Then, the molecules of the last PSt standard ($k = 12$) will not be totally excluded and their elution volume, V_{E12}, will be a little greater than that expected. Thus, eqn. 24 would give V_P values smaller than is actually possible.

Another source of inaccuracy in eqn. 24 is the *a priori* assumption of $K_0 = 1$ and $K_{12} = 0$. Even if no pores of $\varphi < 0.5$ and $\varphi > 300$ nm are present in the material, it is theoretically impossible to obtain $K_0 = 1$. Because of the finite (although small) dimensions of the benzene molecule, the pore volume accessible to its mass centre is always less than the actual pore volume and hence, K_0 becomes close to (but definitely smaller than) unity.

These problems have been discussed by Van Kreveld and Van den Hoed[12], who found that the measured elution volumes differ from the actual ones in average by about 1%. It is, of course, possible to employ "classical" methods to determine V_P. However, mercury porosimetry does not allow a correct measurement of the volume of pores whose diameters are less than 7 nm. Similar difficulties arise with the method of capilary condensation which permits correct measurement only of pores having φ between 2 and 30 nm. Hence, strictly speaking, there is no method of exactly determining the total pore volume of a porous material. According to my experience, the best results might still be expected from the SEC method, because it enables measurements over a quite broad φ interval, *e.g.*, 0.5–400 nm, accounting for the evidence that K_{12} could have an extraordinarily small value and yet satisfy the inequality $K_{12} > 0$. Thus, if an appropriate approximation of the $K(\varphi')$ dependence has been found, then a reliable estimation of K_0 and K_{12} should be achieved that will facilitate the evaluation of V_P via:

$$V_P = (V_{E0} - V_{E12})/(K_0 - K_{12}) \tag{46}$$

The application of eqn. 46 requires the employment of smoothed K_k values instead of those initially determined from eqns. 23 and 24. However, the calculated $W(\varphi)$ and $D(\varphi)$ disributions differ negligibly from those calculated without any refinement of the initial K_k values. Therefore, in this study, eqn. 24 was used for evaluating the total pore volumes. The calculated V_P values were found to be about 1–3.5% greater than those obtained by nitrogen capillary condensation. Obviously, it may be assumed that eqn. 24 is a reliable approximation giving V_P values of an entirely sufficient accuracy for practical purposes.

Pore-volume and pore-size distributions

Figs. 2–4 illustrate the obtained $W(\varphi)$ and $D(\varphi)$ distributions (curves 1 and 2, respectively) for the silica gels examined. All the distributions are bimodal, thus indicating that two groups of pores determine the structure of the sorbents. The φ axes of the plots are scaled logarithmically so as to cover the full range from 0.5 to 400 nm. However, the curves appear to be perturbed specifically, thus giving a distorted picture of the ratio of the two groups of pores present. In Fig. 5 the corresponding pore distributions for Si-60 silica are partially drawn with a linear φ axis to demonstrate the actual ratio. A comparison of Figs. 2 and 5 makes the difference obvious. From the distributions obtained it can be estimated that the pores of $\varphi \leqslant 2.1$ nm represent 26% of the pores in Si-60, while their common volume comprises only 3.8% of the total pore volume. Analogous calculations for the other two sorbents show that the narrower pores ($\varphi \leqslant 3.4$ nm for Si-100 and $\varphi \leqslant 5.3$ nm for Si-200) constitute a considerable fraction of all open cavities (36 and 42%, respectively),
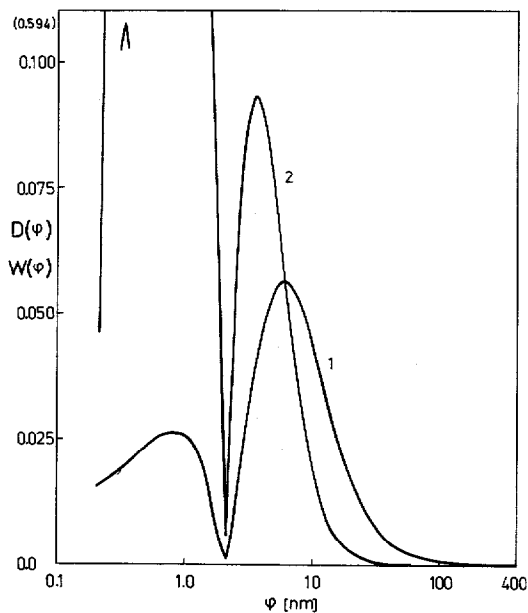

Fig. 2. Calculated $W(\varphi)$ (1) and $D(\varphi)$ (2) distribution curves for Si-60 silica.
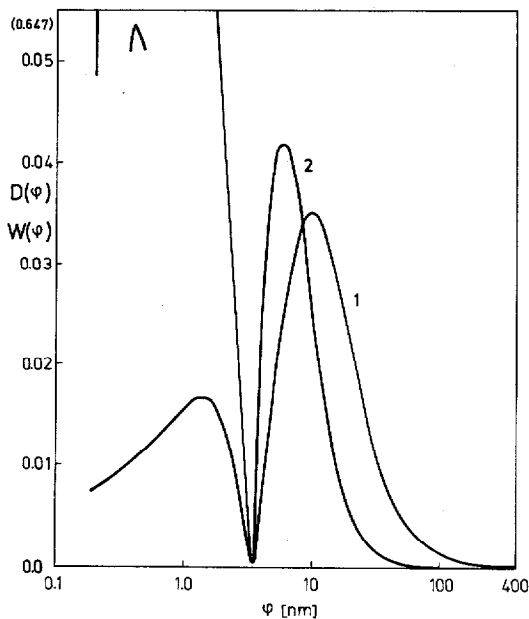
Fig. 3. Calculated $W(\varphi)$ (1) and $D(\varphi)$ (2) distribution curves for Si-100 silica.
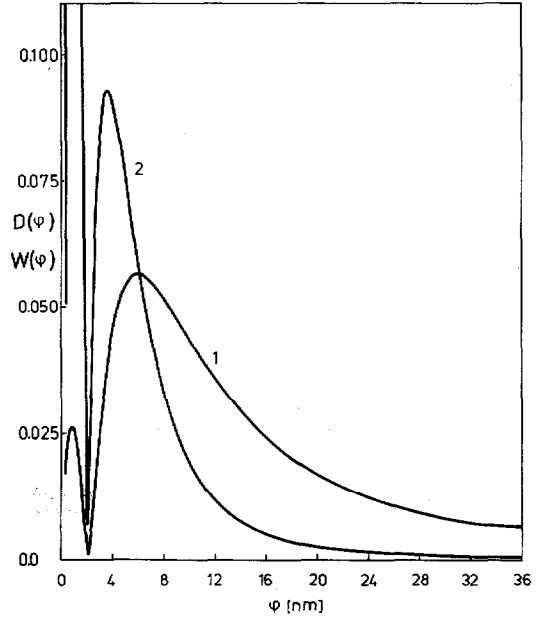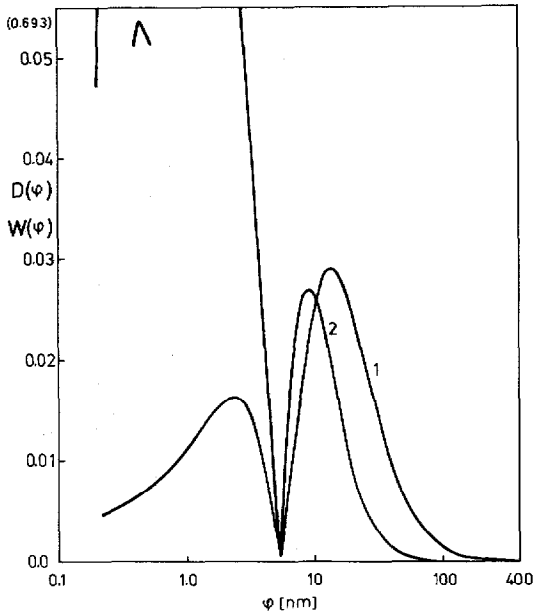
Fig. 4. Calculated $W(\varphi)$ (1) and $D(\varphi)$ (2) distribution curves for Si-200 silica.

Fig. 5. Calculated $W(\varphi)$ (1) and $D(\varphi)$ (2) distribution curves for Si-60 silica (linear φ axis).

however their contribution to the total pore volume remains relatively small, *i.e.*, 4.5 and 4.9%, respectively. Hence, the chromatographic behaviour of the sorbents will be determined mainly by the broader pores, their distributions being represented as smooth asymmetric differential curves in Figs. 2–4.

The numerical characteristics of both the $W(\varphi)$ and the $D(\varphi)$ distributions are presented in Table V together with the specified values of n and h. For all the sorbents, n and h are positive and less than 1 and 2, respectively. Since the last two numbers correspond to a cylindrical pore geometry, it is clear that the average shape of the pores deviates to different extents from the cylinder form. Comparing the values of n and h for each silica, one can see that they nearly satisfy the equation $h = n + 1$, which would hold for strictly cylindrical capillaries. The deviations of up to 3.5% observed appear to be quite acceptable.

As is evident from Table V, the positions of the maxima, $\bar{\varphi}_{W,\max}$ of the calculated $W(\varphi)$ distributions are in excellent agreement with those, $\bar{\varphi}_{W,\max}^{E}$ of the pore-volume distributions determined by nitrogen capillary condensation. This is especially true for Si-60 and Si-100, while for Si-200 the deviation does not exceed 4.5%. A common feature of the $W(\varphi)$ and $D(\varphi)$ distributions for each silica is the lack of coincidence of the respective maxima. As a rule, the $W(\varphi)$ maximum always lies at a greater φ value than that of the corresponding $D(\varphi)$ maximum, *i.e.*, $\bar{\varphi}_{W,\max}$ > $\bar{\varphi}_{D,\max}$. This is quite natural and can easily be explained.

Let us assume that the fraction of pores having diameters φ_j within the range φ_j to $\varphi_j + d\varphi$ is equal to that of the pores of diameters φ_q ranging from φ_q to $\varphi_q + d\varphi$. Moreover, φ_j and φ_q lie on both sides of the position of the $D(\varphi)$ maximum,

TABLE V

NUMERICAL CHARACTERISTICS OF $W(\varphi)$ AND $D(\varphi)$ DISTRIBUTIONS FOR THE SELECTED SILICA GELS

Silica	n	h	$W(\varphi)$ distribution (nm)				$D(\varphi)$ distribution (nm)		
			$\bar{\varphi}_{W,max}^{E}$	$\bar{\varphi}_{W,max}$	$\bar{\varphi}_W$	σ_W	$\bar{\varphi}_{D,max}$	$\bar{\varphi}_D$	σ_D
Si-60	0.645	1.639	6.1	6.0	26.2	29.2	3.6	4.33	5.90
Si-100	0.606	1.633	9.5	9.8	30.6	32.1	5.9	7.58	8.78
Si-200	0.466	1.514	14.0	13.4	32.7	33.2	9.0	11.7	11.2

$\bar{\varphi}_{W,max}^{E}$ = Experimentally determined position of the maximum (by nitrogen capillary condensation); $\bar{\varphi}_{W,max}$ and $\bar{\varphi}_{D,max}$ = positions of the maxima of the calculated distributions; $\bar{\varphi}_W$ and $\bar{\varphi}_D$ = mean values of the pore diameter; σ_W and σ_D standard deviations.

$\bar{\varphi}_{D,max}$, so that $\varphi_j < \bar{\varphi}_{D,max} < \varphi_q$. Then, the overall volume of the φ_q pores will be greater than that of the φ_j pores. On the other hand, if we assume that φ_j and φ_q lie equidistant on both sides of $\bar{\varphi}_{D,max}$ and again $\varphi_j < \bar{\varphi}_{D,max} < \varphi_q$, then, because of the non-symmetrical form of the $D(\varphi)$ distribution, the fraction of the φ_q pores will be greater than that of the φ_j pores, the former having a greater pore-volume contribution than the latter. Under these circumstances the $W(\varphi)$ maximum will lie at a $\bar{\varphi}_{W,max}$ value considerably greater than $\bar{\varphi}_{D,max}$.

Calculated mean φ values, $\bar{\varphi}_W$ and $\bar{\varphi}_D$, as well as the standard deviations, σ_W and σ_D, of the $W(\varphi)$ and the $D(\varphi)$ distributions, are also presented in Table V. In going from Si-60 to Si-200, an increase in the corresponding values is observed, thus indicating a broadening of the pore distributions. A comparison of $\bar{\varphi}_W$ with $\bar{\varphi}_D$ (or of σ_W with σ_D) for each silica gel, however, immediately confirms the difference between the $W(\varphi)$ and the $D(\varphi)$ distributions in Figs. 2–4. In general, the actual pore-size distribution is always narrower than the corresponding pore-volume distribution. According to eqn. 12, this is expected because $W(\varphi)$ is obtained from $D(\varphi)$ by multiplication with φ^{n+1}/J_{n+1}. The latter ratio increases with increasing φ from nearly zero to values greater than unity, thus extending $W(\varphi)$ to a large degree as compared to $D(\varphi)$.

In conclusion, the generalized theoretical approach to the pore-distribution problem described enables the determination of the actual pore-size distribution of solid media, without the need for any model of the pore geometry. The pore-shape index introduced appears to be an averaged quantitative characteristic of the pore form and can be reliably evaluated via the proposed interative procedure. This has been demonstrated with sorbents intended for use in HPLC, whose pore-volume distributions have been calculated from SEC data. From the pore-shape indices, it is found that the geometrical form of the pores can differ from that of cylindrical capilaries. Hence, the commonly accepted model of cylindrical pores cannot always serve as a good approximation of the pore structure of the materials.

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