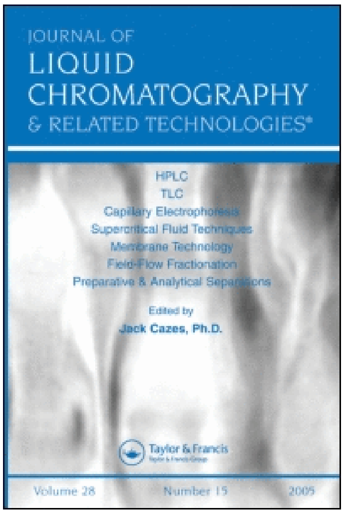

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Hydrodynamic and Size Exclusion Chromatography of Particle Suspensions - A Review

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HYDRODYNAMIC AND SIZE EXCLUSION CHROMATOGRAPHY OF PARTICLE SUSPENSIONS - A REVIEW

by

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ABSTRACT

Particle chromatography using packed beds has attracted considerable attention in recent years. While, size separation in hydrodynamic chromatography (HDC) occurs in the interstitial voids of a nonporous packed bed, separation in size exclusion chromatography (SEC), which involves the use of a porous packed bed, results predominantly from the selective permeation of particles in the pores. In this paper, the developments in the understanding of these processes are critically examined and shortcomings of present theory are pointed out. Signal detection and methods of chromatogram interpretation are reviewed.

INTRODUCTION

Chromatographic separation of colloidal particles using packed beds is approximately ten years old. Though, vast strides have been made in the understanding of the separation process, some basic problems still remain, pertaining particularly to the

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holdup of colloid particles in the packed beds and the excessive broadening of colloid peaks. While, understandably, the earlier works were mainly qualitative, adequate theory now exists to enable quantitative particle size measurement. A number of applications have been reported which demonstrate the considerable ease, rapidity and reliability of chromatographic techniques. These include detection of particle agglomeration[1,2], measurement of particle growth kinetics[1,3,4], swelling effects[2], etc.

In this paper, we critically review the theoretical and experimental developments as regards colloidal separations in packed beds. New insight is provided and future research thrust is suggested to resolve present bottle-necks.

REVIEW OF EXPERIMENTAL INVESTIGATIONS

Hydrodynamic chromatography (HDC) is a technique originally developed by Small[1] to effect colloidal size separation in nonporous packed beds. It is only fair to point out that, similar developments using porous beds appeared not as an extension of HDC but through an independent study by Krebs and Wunderlich[5], three years prior to Small's published work. Undoubtedly, later works using porous beds were immensely facilitated by Small's observations of HDC behaviour. Studies on HDC have since been actively pursued by Stoisits et al[6] and McHugh and co-workers[7,8,9] whose major contribution is the development of a theory to explain colloid migration. Size exclusion chromatography (SEC) which utilises porous beds, is capable of increased resolution compared to HDC, provided the packing is judiciously chosen. It is not surprising, therefore, that it has received considerable attention in recent years.

We now, briefly, discuss the experimental developments in HDC and SEC. Since, similar observations have been made in both, the principal results of these investigations are briefly summarised at the end of the discussion.

A. HYDRODYNAMIC CHROMATOGRAPHY

Hydrodynamic chromatography is based on Small's discovery that, the rate of colloid transport through a nonporous packed bed depends on the size of the colloid, the size of the particulate material that constitutes the packed bed, and the flowrate and composition of the eluant. The rate of migration of a colloid may be conveniently expressed by a dimensionless quantity, the R_F number. It is the rate of migration of a colloid peak relative to a marker species.

Figures 1 and 2 show R_F data measured by Small as a function of the particle diameter of polystyrene latices; the parameters in the respective plots are the packing size and the ionic strength of the eluant. Significantly, R_F is always greater than unity, i.e., particles move faster through the bed than the eluant. The

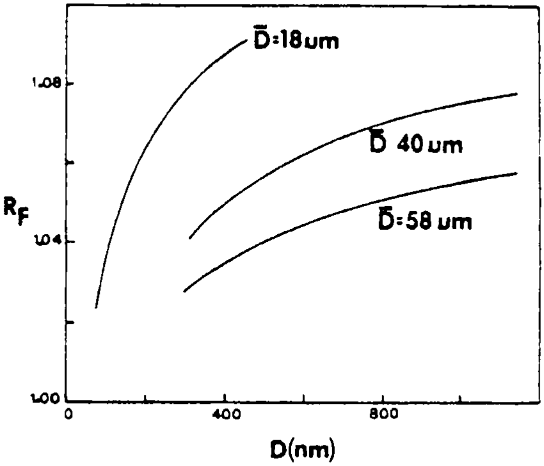

FIGURE 1: The dependence of R_F on latex particle diameter and packing diameter $\bar{D}$.

data are easily understood if the packed bed is viewed as a system of parallel capillaries. Depending on the ionic strength of the eluant, the colloidal forces can either enhance or hinder the average velocity of the particle. Decreasing the ionic strength, increases the volume of the relatively slow moving fluid in the vicinity of the capillary wall from which particles are effectively excluded. Obviously, larger particles are excluded to a greater extent. Consequently, the mean velocity of the particle exceeds that of the fluid; the factor increases with the ratio of particle size to capillary radius (or packing diameter). At high ionic strength, van der Waals forces cause the larger particles to spend a greater fraction of their time in the sluggish wall regions, so that the R_F dependence on particle size may reverse.

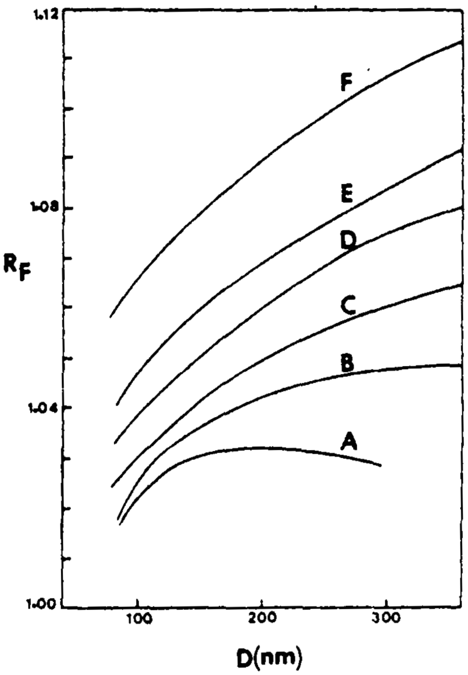

FIGURE 2: The effect of the ionic strength of the eluant on the R_F of polystyrene latices. Eluant concentration moles per liter of NaCl. A, 1.76 x 10^{-1}; B, 9 x 10^{-2}; C, 2.96 x 10^{-2}; D, 4.6 x 10^{-3}; E, 1.7 x 10^{-3}; F, 4.25 x 10^{-4}.

The experimental observations of Small were subsequently confirmed by McHugh et al[7]. Additionally, the peak variance has been shown to be a decreasing function of particle size[10].

B. SIZE EXCLUSION CHROMATOGRAPHY

Krebs and Wunderlich[5] were the first to report a separation of polymethyl methacrylate and polystyrene latices using silica gel having very large pores (500-50,000 °A). This was followed by the work of Gaylor and James[11] who fractionated polymeric latices and inorganic colloidal silica, using columns packed with porous glass and water compatible polymeric porous gels. Coll and Fague[12,13] experimenting with porous glass packing (CPG, 500-3000°A pore size), found it necessary to add electrolyte as well as surfactant to the aqueous eluant. In the absence of electrolyte, the colloids could not sample the pore volume. Peak broadening was observed to be more extensive than in size exclusion chromatography of polymer molecules.

Hamielec and Singh[14] presented the first comprehensive theoretical and experimental investigation of SEC. Using porous glass and silica packing (100-30,000 °A pore size), they established at low ionic strength, the universality of the particle diameter-retention volume calibration curve. The slope of the calibration curve was essentially independent of the eluant flowrate; however, it became smaller (corresponding to a better resolution) with a reduction in packing size. The effects of the mobile phase flowrate and latex particle size on peak variance are shown in Table 1. Analytical expressions were derived to correct measured diameter averages for imperfect resolution.

Nagy[10,15] investigated the chromatography of polystyrene latices using porous glass packing materials (CPG 500-10,000 °A and Fractosil 25,000 °A pore size). In a distinct departure from previous practice, only emulsifier (ionic) was added to the

TABLE 1

Peak Broadening Data for Polystyrene Latices Measured by Hamielec and Singh[14]

Eluant Flowrate (mℓ/min)	Chromatogram Variance (mℓ^2)		
	PS 1000 °A	PS 2340 °A	PS 3120 °A
0.94	23.09	20.66	19.39
2.58	29.75	28.69	27.88
7.50	34.47	32.89	29.34

aqueous eluant, resulting in significantly reduced material loss within the packed bed. While the ionic strength effects observed with the Fractosil system were similar to those in HDC and may be explained analogously, R_F factors in general were comparatively higher due to partial accessibility of the pores to the diffusing colloids (a marker species is, however, able to sample the entire pore volume).

Johnston et al[16] recently reported the feasibility of chromatographing polystyrene latices using porous CPG columns (1000 and 3000°A pore size). A reduction in packing size caused a small increase in R_F, while, significantly increasing sample loss. In general, the peak variance increased with particle size, attained a maximum and then started to decrease, analogous to the behaviour of polymer molecules (the data in Table 1 shows only the decreasing trend). An attempt was made to correlate the statistical properties of the chromatograms of narrow distribution latices with their mean retention volumes. Such an attempt is valid, provided the latices are sufficiently narrow to permit equating their spreading functions with the corresponding measured chromatograms. This condition is not fulfilled for the Dow latices used, as can easily be demonstrated theoretically[17].

Husain et al[18] also examined the chromatography of polystyrene latices using porous CPG columns (1000, 2000 and 3000 °A pore size). They advocated the merits of calibrating columns individually to weed out those with inadequate peak resolution and significant particle holdup. Common with previous observations, the extent of skewing in the chromatograms of narrow distribution latices was observed to increase with particle size.

Kirkland[19] investigated the properties of small porous silica microspheres (less than 10 μ compared with approximately 35 μ CPG packing size, pore size less than 75 nm) and superficially porous particles (solid core, porous crust, packing size less than 25 μ) for characterizing inorganic silica sols in the range 1-50 nm. Columns using both types of packing materials exhibited high resolution because of rapid equilibration of slowly diffusing colloids with the pores. The effect of flowrate on peak broadening and the role of ionic strength in colloid separation were observed to be similar to those in earlier studies.

A brief summary of the main results of the above investigations is now given under three classifications: peak separation, peak broadening and material loss.

Peak Separation

1. The particle diameter-retention volume calibration curve, in general, is composed of two linear segments: a segment at low retention volumes, beyond the exclusion limit of the porous packing, corresponds to HDC size separation, while, a segment at high retention volumes corresponds to SEC size separation.
2. The calibration curve is insensitive to flowrate variations.
3. Increasing the ionic strength of the aqueous eluant causes a shift in the calibration curve to high retention volumes due to increased accessibility of the column voids. At low ionic strength, a universal calibration is obtained.
4. Reducing the packing size improves peak separation.
5. SEC is not limited by a minimum particle size. However, the effectiveness of separation in HDC decreases as the ratio of particle to capillary diameter approaches zero.

Peak Broadening

1. In general, peak variance increases with colloid size, reaches a maximum and then starts to decrease as the exclusion limit of the porous column is approached. In HDC, it decreases with increasing particle size.
2. An increase in flowrate causes increased peak broadening in SEC. In HDC, the effect is not known.
3. In SEC, dispersion increases at higher ionic strength due to increased pore permeability. A similar effect may be

expected in HDC; however, no experimental data have been reported.

4. The chromatograms of narrow distribution particle standards are generally skewed.

Material Loss

1. Increasing the electrolyte concentration of the eluant decreases sample recovery. However, if the ionic strength is adjusted by addition of an ionic emulsifier (within limits), material loss is reduced.
2. Sample loss increases with colloid size.
3. Reduction in the size of the packing, enhances material loss.

While factors governing peak separation are fairly well understood, those that affect peak broadening and particularly sample recovery are not. A systematic study to determine the roles of colloid composition, packing type, pore size, operating temperature etc. is required to acquire a better understanding of these phenomena.

DETECTION OF COLLOIDAL PARTICLES

One of the most widely used detector in the chromatography of colloidal particles is the turbidity detector. Depending on the wavelength, the resulting signal is due either to a combination of scattering and chemical absorption or principally due to scattering. Differential refractometry has some inherent drawbacks in its application to particle chromatography and has been used much less extensively. Both modes of detection are now briefly examined.

A. TURBIDIMETRIC DETECTION

The turbidity of very small particles (small relative to the wavelength of light) is proportional to the sixth power of the particle diameter while, for larger particles, the dependence is lower. As a consequence, the small particle signal is relatively weak, though it can be augmented by using shorter wavelengths. However, for obtaining particle size distributions, the relative signal rather than the absolute signal is of interest. Calculations by Silebi and McHugh[9] indicate that, a change of wavelength or refractive index ratio (colloid to medium) has a small influence on the relative signal for nonabsorbing particles. However, the relative signal is considerably improved at absorption wavelengths due to a significant enhancement in the extinction coefficient of small particles. These theoretical deductions were experimentally substantiated by Nagy[10,15] using polystyrene latices.

Appreciable error may result "if instruments which are perfectly suitable for ordinary absorption measurements are used for turbidity measurements without proper modifications and precautions"[20]. While such errors were believed to be negligible by earlier workers[9], their existence was unequivocally demonstrated by Husain et al[18] who compared the detector response to a suspension of polystyrene spheres with the response to a solution of sodium dichromate. Furthermore, they showed that, impurities (such as residual styrene monomer in polystyrene particles) and additives (such as emulsifier) may cause the measured extinction coefficient to differ from theoretical calculations based on Mie theory. The discrepancy may theoretically be accounted for by employing an effective imaginary refractive index ratio[10,15].

B. DIFFERENTIAL REFRACTOMETRY DETECTION

Based on Mie theory, Zimm and Dandliker[21] derived a general refractive index expression given by

$$\frac{dn_s}{dc} = \frac{3n_m}{2\,\alpha^3 \rho_p} \mathrm{Re}\{ \sum_{n=1}^{\infty} \frac{2n+1}{2n(n+1)} (a_n - b_n) \} \qquad (1)$$

where c is the weight concentration in gms/cm^3, ρ_p is the particle density, α is a dimensionless size parameter ($\alpha = \pi D/\lambda$, where D and λ are respectively, the particle diameter and wavelength in the medium), n_m and n_s are the refractive indices of the medium and dispersion, respectively, and a_n and b_n are functions of α and m (m is the refractive index ratio of particle to medium). The above equation does not contain the restriction that α be small. In the limit as $\alpha \to 0$, it reduces to

$$\frac{dn_s}{dc} = \frac{3\,n_m}{2\rho_p}\,\frac{(m^2 - 1)}{(m^2 + 2)} \qquad (2)$$

In accordance with equations (1) and (2), dn_s/dc is expected to be independent of c and at small values of α, to be independent of α as well.

Measurements by Silebi and McHugh[9] show a surprising agreement of measured data with equation (2) for polystyrene latices as large as 350 nm. Subsequent data (measured by Nagy[10]) from the same laboratory indicate that, dn_s/dc reverses in sign with increasing particle size; its implication is that the signal is null for some intermediate particle size. Coll and Fague[13] observed that dn_s/dc was independent of c for a given latex, though its value increased linearly with particle diameter. Neither Nagy nor Coll and Fague were able to explain their results satisfactorily. Interpretation of their data is complicated due to the use of a broad wavelength source.

It is the authors' opinion that, these seemingly conflicting data are in fact consistent with the Zimm and Dandliker equation. Calculations indicate that, depending on the values of m and α, dn_s/dc may either increase with particle size or decrease and eventually change sign[21,22]

Differential refractometry shows a less dramatic dependence on particle size than turbidimetry of nonabsorbing particles. The advantage is, however, negated by the requirement of a higher sample concentration compared to the amount necessary for a photometric detection. This is due to the limited sensitivity of available differential refractometers. With the advent of more sensitive detectors, this drawback will likely be overcome.

THEORETICAL ANALYSIS OF PEAK SEPARATION

A theoretical analysis of peak separation and broadening provides an insight into the causes of imperfect resolution in chromatographic processes. While theory adequately predicts peak separation in HDC, a similar comprehensive treatment is lacking for SEC. Attempt to predict peak broadening has at best been dismal[10]. Now, let us briefly examine the theories proposed to explain peak separation in HDC and SEC.

A. HYDRODYNAMIC CHROMATOGRAPHY

Two approaches have been taken to model the role of colloidal forces in HDC. The capillary model, first proposed by Small[1] and developed in several sources since[6,7,8,23], considers the interstitial space as a system of inter-connecting parallel capillaries of equal radii. In the second approach proposed by Buffham, the speed of a chromatographic transient is calculated from the behaviour of a colloidal suspension in equilibrium in the vicinity of a plane interface. Buffham's theory yields results independent of the geometry of the particulate material constituting the HDC colum.

According to the capillary model, the average velocity of the particle is calculated by weighting the local particle velocity, $v_{pz}(r)$ with the concentration at that position (the radial concentration distribution may be shown to be a Boltzmann), to give

$$\bar{v}_p = \frac{\int_0^{R-a} v_{pz}(r) \exp[-\phi(r)/\kappa T] r \, dr}{\int_0^{R-a} \exp[-\phi(r)/\kappa T] r \, dr} \qquad (3)$$

where the upper integration limit accounts for the inability of a particle to approach the capillary wall closer than its radius, a. $v_{pz}(r)$ is given by a modified Poiseuille equation which takes the wall effect into account. The interaction energy term, $\phi(r)$ is the superposition of the double layer repulsive and van der Walls attractive potentials. The average velocity of an ionic marker, $\bar{v}_m$ is obtained by taking the limit of the above integrals as the particle radius tends to zero. R_F is then calculated from its definition

$$R_F = \bar{v}_p/\bar{v}_m \qquad (4)$$

The corresponding expression for R_F derived by Buffham is given by

$$R_F = \frac{V}{A} \frac{1}{\int_0^{\infty} \exp[-\phi(h)/\kappa T] dh} \qquad (5)$$

where V is the volume of the mobile phase and A is the surface area of the packing. In the above equation, the R_F dependence on packing diameter is manifested by the presence of A.

Both theories adequately predict the variation of R_F with particle diameter over a wide range of ionic strength. Unlike the capillary model, equation (5) predicts an increase in R_F with hydraulic radius (V/A) or packing diameter, contrary to the observed dependence. This marks the distinct failing of the equilibrium approach.

B. SIZE EXCLUSION CHROMATOGRAPHY

Due to the complex flow pattern in a porous packed bed, the attendant difficulty in predicting the migration rate of a colloid is obvious. Nagy[10,15] attempted to simplify this problem by using very large pores relative to the colloid sizes being separated. Their analysis, therefore, assumes that all particles enter the pores and accordingly, describes one extreme of SEC where all species permeate the porous matrix. A flow-through bank model was considered (see Figure 3). The spaces between the banks have zero volume and serve as a mixing region for altering particle trajectories. The probability of a particle entering a tube at the start of a bank is assumed equal to the ratio of flow through all such tubes to the total flowrate through all tubes in the bank. The principal result of their analysis predicts that

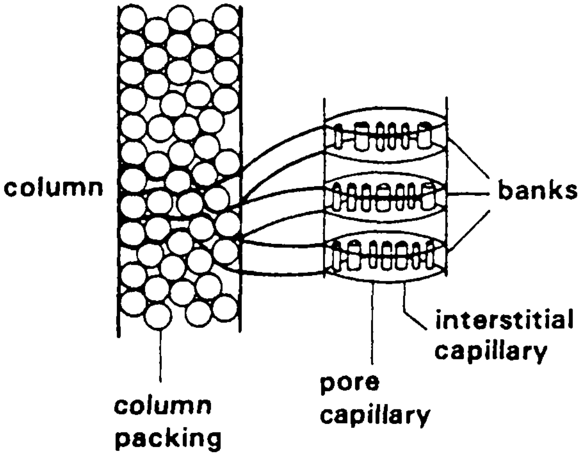

FIGURE 3: A bank model of a SEC column.

$$\frac{1}{R_F} = \frac{(V_{pc}/V)}{R_{F,pc}} + \frac{(V_{ic}/V)}{R_{F,ic}} \qquad (6)$$

where $R_{F,ic}$ and $R_{F,pc}$, the separation factors corresponding to the interstices and pores respectively, are calculated as before. V_{pc}, V_{ic} and V represent the pore volume, interstitial volume and total void volume, respectively.

Now, it is shown that the result in equation (6) may be obtained using a simpler model, which regards the column voids as a system of parallel capillaries of the interstitial and pore type (no mixing region is considered and capillaries are continuous across the length of the column). The peak retention volume of the colloid peak, V_p is given by

$$V_p = n_{pc} Q_{pc} \bar{t}_{pc} + n_{ic} Q_{ic} \bar{t}_{ic} \qquad (7)$$

where n, Q and $\bar{t}$ denote tube number, flowrate and average residence time, respectively. It follows, therefore, that

$$1/R_F = (n_{pc} Q_{pc} \bar{t}_{pc} + n_{ic} Q_{ic} \bar{t}_{ic})/V_m \tag{8}$$

where V_m, the retention volume of a marker peak, is equal to V. If the length of the column is L and cross-sectional area of a capillary, A, then

$$\begin{aligned} 1/R_F &= L/V_m \, [n_{pc} Q_{pc}/(\bar{v}_p)_{pc} + n_{ic} Q_{ic}/(\bar{v}_p)_{ic}] \\ &= L/V_m \, [n_{pc} A_{pc} (\bar{v}_m/\bar{v}_p)_{pc} + n_{ic} A_{ic} (\bar{v}_m/\bar{v}_p)_{ic}] \\ &= (n_{pc} A_{pc} L/V_m)/R_{F,pc} + (n_{ic} A_{ic} L/V_m)/R_{F,ic} \\ &= (V_{pc}/V)/R_{F,pc} + (V_{ic}/V)/R_{F,ic} \end{aligned}$$

The derived result is identical to equation (6). The apparent equivalence of the two models is a direct consequence of assigning, in the bank model, the probability that a particle travels through a given tube. Therefore, it is not surprising for calculations based on equation (6) to agree rather poorly with experimental data since, the equivalent model (which allows no fluid intermixing) considered here, is hardly representative of the flow process in a packed column.

Nagy cites several reasons, chief among which is the slow diffusion coefficient of colloids, to justify the use of a flow model as opposed to a diffusion model. As pointed out by Small[24], separation by flow seems unlikely, since very little fluid would flow through the extremely fine pores of the packing, when the much less restricted pathway around the particles is available to it. We suggest that, since the equilibrium theory for HDC is essentially independent of the complex flow geometry, it may be possible to extend the treatment to predict colloid behaviour in SEC.

CALCULATION OF PARTICLE SIZE DISTRIBUTIONS

Axial dispersion is a serious imperfection in the analysis of particle sizes by chromatography. It causes the elution of a single species to occur over a range of retention volumes. Interpretation of a chromatogram must, therefore, account for this spreading. It involves an evaluation of instrumental spreading, and correction of the detector response to obtain the true concentrations of the component species. The measured chromatogram, F(v) is related to the true chromatogram, W(y) by

$$F(v) = \int_0^\infty W(y)\, G(v-y)\, dy \tag{9}$$

where G(v-y) is the normalized spreading function (uniform) of a species with mean retention volume, y. When detection is turbidimetric, both F(v) and W(y) represent turbidities while, in the case of differential refractometry, they represent refractive index increments.

Equation (9) may be solved both numerically and analytically. Numerically, it is solved either for G(v-y)[25] (when F(v) and W(y) are known) or, as is the more usual situation, the integral equation is solved for W(y) (when F(v) and G(v-y) are known), which may then be converted into a particle size distribution. In contrast, analytical solutions enable the direct calculation of moments of the size distribution function; the size distribution itself is not obtained. Both methods of solution are now briefly discussed.

A. NUMERICAL SOLUTION OF AXIAL DISPERSION EQUATION

Several numerical methods have been reported in the literature for the solution of the integral equation. These have been reviewed by Friis and Hamielec[26] and more recently evaluated by Silebi and McHugh[9] for their application to particle chromatography. They conclude that a method due to Ishige et al[27] performs better than other available methods. A principle drawback of the method, however, is its tendency to overestimate the count of small particles in a polydispersed population. Modifications of Ishige's algorithm fail to overcome this defect[17]. Unless a more effective method is developed for calculating W(y), it is preferable to apply analytical methods to obtain size information.

TABLE 2

A Comparison of the Analytical Methods for Solving the Integral Equation

Attributes	Method* 1 Hamielec and Singh[14]	 2 Husain et al.[28]	 3 Husain et al.[29]
1. Calibration curve	Linear	Nonlinear	Nonlinear
2. Spreading function	Eqn.(10) or Provder and Rosen's[30] shape function	Eqn.(10)	Eqn.(10) or Provder and Rosen's[30] shape function
3. Light scattering theory which may be applied	Rayleigh	Mie	Mie
4. Chemical absorption may be present in tubidimetric detection.	No	Yes	Yes
5. Diameter averages are calculated as a function of retention volume	No	Yes	No

* The refractive index detector (dn_s/dc = constant) can be treated using all the above methods. However, Method 3 is most general.

B. ANALYTICAL SOLUTION OF AXIAL DISPERSION EQUATION

Three analytical methods for solving the integral equation have been reported[14,28,29]. Their main features are compared in Table 2. It is important to realise that, the solution derived for a Gaussian spreading function, $G_o(v-y)$ is equally applicable to a whole family of functions of the form

$$G(v,y) = G_o(v-y)\,\psi(y) \qquad (10)$$

where $\psi(y)$ is an unspecified function of y. (This can easily be demonstrated by substituting equation (10) in equation (21) of Reference 28). This considerably extends the applicability of the solution for a Gaussian spreading function to an infinite set of non-Gaussian, non-uniform functions. The analytical solution is given in terms of a single adjustable parameter. In some practical situations, the spreading function may not be representable by equation (10); this may be inferred from the difficulty of obtaining meaningful diameter averages from chromatograms of narrow particle standards. In such a situation, it is desirable to consider the general shape function proposed by Provder and Rosen[30].

RECOMMENDATIONS

There is a need for new packings specifically designed for SEC to minimise particle loss and peak broadening. The optimum packing particle is probably one with a solid core and superficial surface pores. Factors affecting particle loss both in HDC as well as in SEC need to be better understood.

A multiple wavelength UV/Visible light turbidity detector has been theoretically evaluated and found to have reasonable promise as an analytical tool for particle size measurement[31]. Likewise, IR detection has been shown to have some useful features[10]. An experimental investigation of both these detectors is desirable. Also, more sensitive refractometers with a monochromatic light source should be evaluated.

The theory of HDC should be extended to investigate the possibility of predicting the chromatogram shape. The corresponding development of a theory of SEC, to adequately predict peak separation as well as peak shape, may be facilitated by the use of model porous spheres.

The numerical treatment of chromatographic data is rather inadequate. It is desirable to develop new improved methods for recovery of W(y).

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