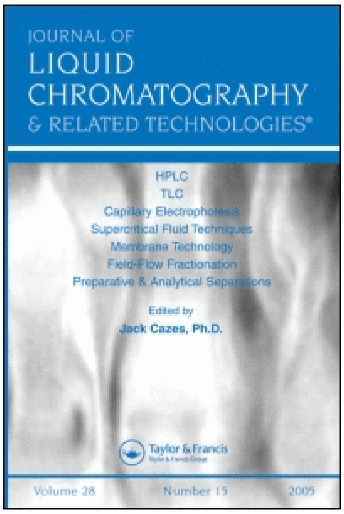

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CHROMATOGRAPHY OF SUSPENSIONS - ANALYTICAL CORRECTIONS FOR AXIAL DISPERSION

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ABSTRACT

An analytical method is proposed to correct the signal from a turbidity detector for axial dispersion in the chromatography of particle suspensions. An earlier analytical method due to Hamielec and Singh[1] is limited to light scattering in the Rayleigh regime. The solution reported herein is derived using the more general Mie light scattering theory and enables the correction of various moments of the particle diameter frequency distribution function. The axial dispersion phenomenon is described by the well known integral equation where the instrumental spreading function is assumed Gaussian. The solution is applicable for both linear and nonlinear particle diameter-retention volume calibration curves.

INTRODUCTION

Chromatography of particle suspensions is a fairly new development. Two complementary approaches exist to the use of flow in packed beds for size separation in the sub-micron range. The technique called hydrodynamic chromatography (HDC) utilizes non-porous packing material. Its complement, liquid exclusion chromatography (LEC) utilizes porous packing material. While other effects are present, size separation in the former depends mainly on the existence of a velocity profile in the capillaries formed by the packing. In the latter case steric exclusion of particles in suspension from the pores of the packing material is a contributing factor. Of more recent origin is the technique known as capillary chromatography (CPC) where size separation beyond the micron range is affected by flow of the particle suspension through an extended capillary tubing.

All these techniques have in common a detection system for monitoring the particle size. The most commonly used detector , though not necessarily the most suitable, is the turbidity detector. Axial dispersion phenomena commonly encountered in chromatographic separations requires the frequency distribution obtained from the detector response to be suitably corrected to account for polydispersity in the detector cell. For a general detector (turbidity detector, refractometer or viscosity-concentration detector), Hamielec and Singh[1] derived correction factors for various diameter averages. However, owing to the restrictive assumption of Rayleigh scattering regime in deriving correction factors for a turbidity detector, their formulae are not applicable for larger particles.

In the present work a turbidity detector in the Mie scattering regime is considered. Moments of the frequency distribution and the number of particles in the detector cell are evaluated as a function of retention volume. This enables all relevant diameter averages for the sample to be calculated.

THEORY

The instrument response F(v) to an input sample W(y) is given by the integral equation:

$$F(v) = \int_0^\infty W(y)\, G(v,y)\, dy \qquad (1)$$

where G(v,y) is the instrumental spreading function which may be approximated by a Gaussian distribution:

$$G(v,y) = \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(- \frac{(v-y)^2}{2\sigma^2}\right) \qquad (2)$$

where σ^2 is the variance of the instrumental spreading function or the single species chromatogram.

Due to column dispersion, the contents of the detector cell at any retention volume, v, is polydisperse and may be considered as made up of all species at retention volume y which are dispersed to v. Accordingly for a turbidity detector the following proportionality holds:

$$W(y)\ G(v,y) \propto N(v,y)\ K(y)\ D^2(y) \quad \text{at retention volume } v \tag{3}$$

where K(y), D(y) and N(v,y) are respectively the extinction coefficient, diameter and number of particles with mean retention volume y at retention volume v. The frequency distribution f(v,D) at v may then be expressed as:

$$f(v,D)\ dD = -\frac{N(v,y)dy}{\int_0^\infty N(v,y)dy} \tag{4}$$

where the negative sign accounts for the negative slope of the particle diameter retention volume calibration curve. From equation (3) it follows that

$$f(v,D)\ dD = -\frac{W(y)\ G(v,y)\ \{K(y)\ D^2(y)\}^{-1}\ dy}{\int_0^\infty W(y)\ G(v,y)\{K(y)\ D^2(y)\}^{-1}\ dy} \tag{5}$$

The number, weight, surface, specific surface, volume and turbidity average diameters of the particles eluting at v may be defined respectively as:

$$D_n(v) = \{\int_0^\infty N(v,y)\ D(y)\ dy\} \Big/ \{\int_0^\infty N(v,y)\ dy\} \tag{6}$$

$$D_w(v) = \{\int_0^\infty N(v,y)\ D^4(y)\ dy\} \Big/ \{\int_0^\infty N(v,y)\ D^3(y)\ dy\} \tag{7}$$

$$D_s(v) = \{\int_0^\infty N(v,y)\ D^2(y)\ dy\}^{\frac{1}{2}} \Big/ \{\int_0^\infty N(v,y)\ dy\}^{\frac{1}{2}} \tag{8}$$

$$D_{ss}(v) = \left\{\int_0^\infty N(v,y)\, D^3(y)\, dy\right\} \Big/ \left\{\int_0^\infty N(v,y)\, D^2(y)\, dy\right\} \qquad (9)$$

$$D_v(v) = \left\{\int_0^\infty N(v,y)\, D^3(y)\, dy\right\}^{1/3} \Big/ \left\{\int_0^\infty N(v,y)\, dy\right\}^{1/3} \qquad (10)$$

$$D_\tau(v) = \left\{\int_0^\infty N(v,y)\, D^6(y)\, dy\right\}^{1/3} \Big/ \left\{\int_0^\infty N(v,y)\, D^3(y)\, dy\right\}^{1/3} \qquad (11)$$

In the above expressions when N(v,y) is replaced by N(v), the number of particles eluting at v, and D(y) in each equation is replaced by the corresponding diameter average, diameter averages for the entire sample are obtained and are denoted respectively by $\bar{D}_n$, $\bar{D}_w$, $\bar{D}_s$, $\bar{D}_{ss}$, $\bar{D}_v$ and $\bar{D}_\tau$. The integrals in the above expressions are all of the form:

$$I(\gamma) = \int_0^\infty W(y)\, G(v,y)\, \{K(y)\, D^2(y)\}^{-1}\, D^\gamma(y)\, dy \qquad (12)$$

so that

$$D_n(v) = I(1)/I(0) \qquad (6a)$$

$$D_w(v) = I(4)/I(3) \qquad (7a)$$

$$D_s(v) = \{I(2)/I(0)\}^{1/2} \qquad (8a)$$

$$D_{ss}(v) = I(3)/\, I(2) \qquad (9a)$$

$$D_v(v) = \{I(3)/I(0)\}^{1/3} \qquad (10a)$$

$$D_\tau(v) = \{I(6)/I(3)\}^{1/3} \qquad (11a)$$

In the absence of an analytical solution, the integral in equation (12) has to be evaluated numerically with W(y), the corrected chromatogram recovered from equation (1) through some suitable numerical procedure such as that due to Ishige[2]. In the following analysis, an analytical solution for equation (12) is developed. The case for a linear and a nonlinear calibration curve are treated separately. Both yield solutions of similar form.

Linear Calibration Curve

For a linear particle diameter retention volume calibration curve D(y) may be written as:

$$D(y) = D_1 \exp(-D_2 y) \tag{13}$$

while $K^{-1}(y)$ may be adequately fitted by an expression of the type:

$$K^{-1}(y) = \sum_{i=1}^{n} \{A_i \exp(B_i\, y)\} \tag{14}$$

The product $\{K(y)\, D^2(y)\}^{-1}\, D^{\gamma}(y)$ is then equivalent to:

$$\{K(y)\, D^2(y)\}^{-1}\, D^{\gamma}(y) = \sum_{i=1}^{n} \{C_i \exp(-E_i\, y)\} \tag{15}$$

where $C_i = A_i\, D_1^{\gamma-2}$ and $E_i = -\{B_i + (2-\gamma)D_2\}$ (16)

Non-Linear Calibration Curve

A nonlinear particle diameter-retention volume calibration curve D(y) may be expressed as

$$D(y) = \sum_{i=1}^{p} D_i \tag{17}$$

where $D_i = D_{i,1} \exp(-D_{i,2}\, y)$

It follows that $D^{\gamma}(y)$ is given by

$$D^{\gamma}(y) = \sum^{m} \frac{\gamma\,!}{\gamma_1\,!\;\gamma_2\,!\;\dots\gamma_p!}\, D_1^{\gamma_1}\, D_2^{\gamma_2} \dots D_p^{\gamma_p} \tag{18}$$

where the sum is taken over all non-negative integers $\gamma_1, \gamma_2, \dots\dots \gamma_p$ for which $\gamma_1 + \gamma_2 \,..\, + \gamma_p = \gamma$. The number of terms in the summation is denoted by m. The product $\{K(y)\, D^2(y)\}^{-1}$ in equation (12) may be represented as:

$$\{K(y)\ D^2(y)\}^{-1} = \sum_{i=1}^{n} \{A_i \exp(B_i\ y)\} \qquad (19)$$

so that $K(y)\ D^{\gamma-2}(y)$ is given by:

$$K(y)\ D^{\gamma-2}(y) = \sum_{i=1}^{m\times n} C_i \exp(-E_i\ y) \qquad (20)$$

where C_i and E_i are related to the coefficients in equations (18) and (19).

Equation (12) may therefore be written as:

$$I(\gamma) = \sum_i C_i \int_0^\infty W(y)\ G(v,y)\ \exp(-E_i\ y)dy \qquad (21)$$

Substitution of the Gaussian form for the instrumental spreading function from equation (2) and simplifying yields:

$$I(\gamma) = \sum_i \left[C_i \exp\{-E_i v + (E_i\sigma)^2/2\} \int_0^\infty W(y) \frac{1}{\sqrt{2\pi\sigma^2}} \exp\left(-\{(v - E_i\sigma^2) - y\}^2/2\sigma^2\right) dy \right] \qquad (22)$$

The integral in the above expression may be recognized as $F(v - E_i\sigma^2)$ by comparison with equations (1) and (2). Therefore,

$$I(\gamma) = \sum_i C_i \exp\{-E_i v + (E_i\sigma)^2/2\}\ F(v - E_i\sigma^2) \qquad (23)$$

Equation (23) can now be used to evaluate the various diameter averages given by equations (6-11a). To evaluate the same for the total sample, one needs to evaluate N(v). From equation (3) it follows that

$$N(v) \propto \int_0^\infty W(y)\ G(v,y)\{K(y)\ D^2(y)\}^{-1}\ dy \qquad (24)$$

or

$$N(v) \propto I(0) \tag{24a}$$

To establish the validity of the above procedure, sample chromatograms were synthesized. The results of calculation of the various diameter averages for two cases are summarised in Table 1, and are compared with values obtained directly from W(y). The latter may be evaluated from the following frequency distribution:

$$f'(D)\,dD = -\frac{N(y)\,dy}{\int_0^\infty N(y)\,dy} = -\frac{W(y)\{K(y)\,D^2(y)\}^{-1}dy}{\int_0^\infty W(y)\{K(y)\,D^2(y)\}^{-1}dy} \tag{25}$$

Good agreement was obtained for the diameter averages calculated both ways. Values of uncorrected diameter averages are also tabulated to indicate the magnitude of axial dispersion corrections. While the corrections for the entries in Table 1, particularly for $\bar{D}_w$, $\bar{D}_{ss}$ and $\bar{D}_\tau$ are relatively small, in practice they are expected to be appreciable[1]. The extinction coefficient data used for the calculations are graphed in Figure 1. It indicates an excellent fit to the data by the expression in equation (14). Figure 2 is a plot of the various diameter averages as a function of retention volume for Case B (Table 1). The particle diameter retention volume calibration curve is also shown for comparison.

CONCLUSION

An analytical method has been developed for determining particle diameter averages corrected for dispersion from the response of a turbidity detector in the Mie scattering regime. The method may be applied with either a linear or a nonlinear particle diameter-retention volume calibration curve. Since Mie theory is applied, this method should find application in analyzing experimental LEC, HDC and CPC chromatograms.

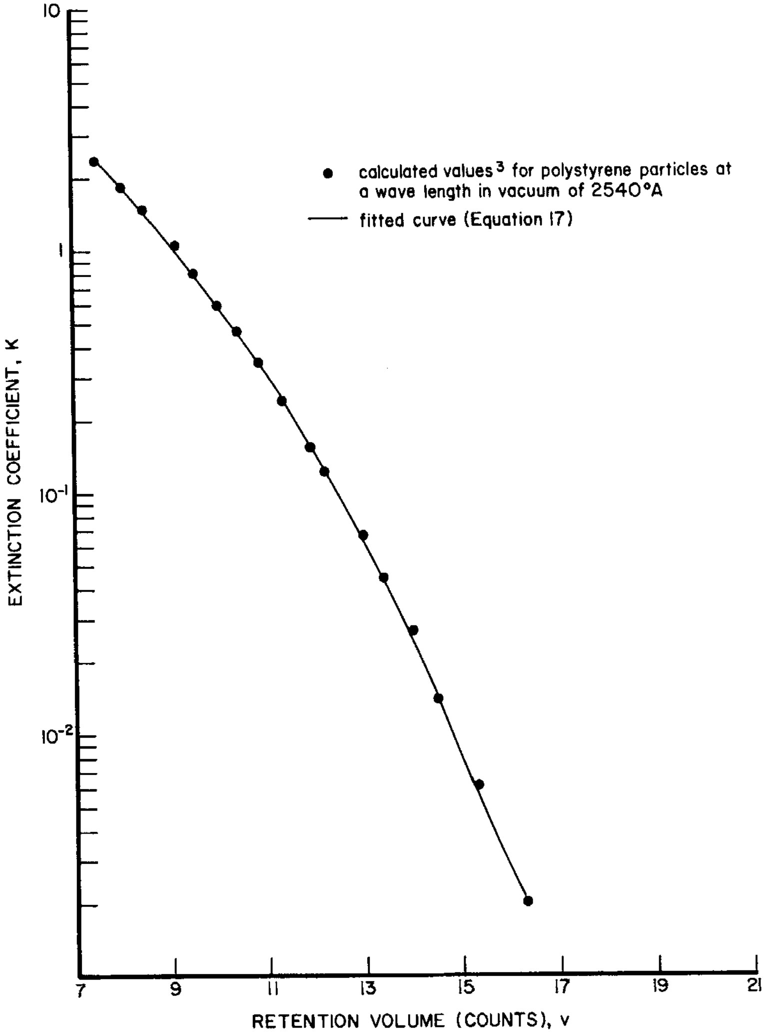

FIGURE 1 Extinction coefficient data for polystyrene particles at a wavelength in vacuum of 2540 °A

For a detector where:

$$W(y)\ G(v,y) \propto N(v,y)\ D^{\alpha}(y) \quad \text{at retention volume } v \qquad (26)$$

(α is a constant equal to 3 for a refractometer or a viscosity concentra-

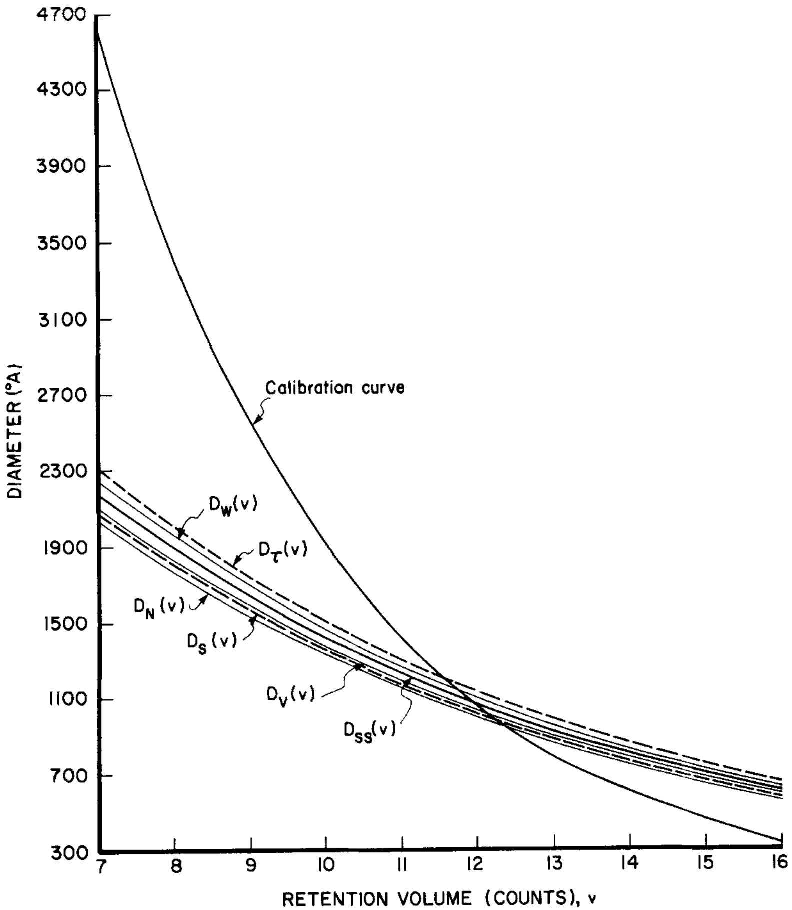

FIGURE 2 Variation of particle diameter averages with retention volume.

tion detector) if D(y) is expressed by equation (17), the integrals involved in calculating the corrected diameter averages are also of the form of equation (21) and may be similarly evaluated.

In conclusion, the proposed method is quite general and may be used to calculate diameter averages corrected for axial dispersion for a general detector.

TABLE 1 Calculation of Particle Diameter Averages.

Calibration Curve (linear)	$D(y) = 36584.0 \exp(-0.295y)$
Extinction Coefficient Fit	$A_1 = 0.2204\times10^{-3}$ $A_1 = 0.4549\times10^{-1}$ $A_3 = 0.5975\times10^{-14}$ $A_4 = -0.8851\times10^{-21}$ $B_1 = 0.8510$ $B_2 = 0.2472$ $B_3 = 2.442$ $B_4 = 3.395$
Instrumental Spreading Function	$\sigma^2 = 0.75$ counts^2

CASE A:

Gaussian W(y) $W(y) = \frac{1}{\sqrt{2\pi\sigma_o^2}} \mathrm{Exp}(-\frac{(y-\bar{y})^2}{2\sigma_o^2})$; $\sigma_o^2 = 0.75$ counts^2 ; $\bar{y} = 11.5$ count

Gaussian F(v) $F(v) = \frac{1}{\sqrt{2\pi\bar{\sigma}^2}} \mathrm{Exp}(-\frac{(v-\bar{v})^2}{2\bar{\sigma}^2})$; $\bar{\sigma}^2 = 1.50$ counts^2 ; $\bar{v} = 11.5$ count

Diameter Averages (°A)	$\bar{D}_n$	$\bar{D}_w$	$\bar{D}_s$	$\bar{D}_{ss}$	$\bar{D}_v$	$\bar{D}_\tau$
Calculated Analytically	932	1145	965	1069	998	1226
Calculated from Equation (25)	731	1145	964	1069	997	1226
Uncorrected	684	1053	734	909	788	1219

CASE B:

$F(v) = 0.3329 \mathrm{Exp}(-4\, \ell n^2 [D(v)/1200])$

W(y) recovered from F(v) using Ishige's[2] Method 2.

Diameter Averages (°A)	$\bar{D}_n$	$\bar{D}_w$	$\bar{D}_s$	$\bar{D}_{ss}$	$\bar{D}_v$	$\bar{D}_\tau$
Calculated Analytically	931	1123	960	1055	991	1195
Calculated from Equation (25)	930	1123	960	1055	990	1195
Uncorrected	683	1032	730	897	782	1187

A copy of the program, deck and listing will be available on request. There is a service charge of $200.

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