

An Analytical Solution to Tung's Axial Dispersion Equation. Applications in Gel Permeation Chromatography

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INTRODUCTION

Tung's axial dispersion equation was recently solved analytically by Hamielec and Ray¹ using the method of molecular weight averages (an appropriate name coined by Provder and Rosen²). This paper discusses applications of our method to a variety of problems in gel permeation chromatography (GPC). Included are recent applications developed by Provder and Rosen² where a general instrumental spreading function was used to correct molecular weight averages. Other applications to be discussed include the development of a criterion for the evaluation of column resolution and equations which may be used to interpret data obtained by GPC in recycle mode.

THEORY AND APPLICATIONS

General Axial Dispersion Equation after Tung³

We can consider the permeation process to cause a series of eluent volume delays, one for each molecular size. In this manner we can separate the permeation process, of which $W(y)$, the corrected chromatogram, is a consequence, from the dispersion process and treat the latter separately.

We now treat the input to that part of the GPC system which is responsible for axial dispersion as some arbitrary function, $W(y)$. The impulse due to molecular species of characteristic volume y equals

$$W(y)\delta(v - y)dy.$$

The response of the GPC to this particular impulse will be equal to

$$W(y)G(v - y)dy.$$

The total response at eluent volume v will be

$$F(v) = \int_{-\infty}^{\infty} W(y)G(v - y)dy. \quad (1)$$

We are assuming here that the shape of the response for all species is of the same form and equal to $G(v - y)$. Equation (1) is a general form of Tung's

axial dispersion equation. The expression $G(v - y)$ might have the rather general form⁴

$$G(v - y) = \phi(v - y) \exp \{-h(v - y)^2\} \quad (2)$$

where h , the resolution factor, equals $1/(2\mu_2)$ where μ_2 is the variance about the mean eluent volume y .

For the special case of a Gaussian instrumental spreading function,

$$\phi(v - y) = \left(\frac{h}{\pi}\right)^{1/2}$$

Method of Molecular Weight Averages¹

Tung's general axial dispersion equation may be considered the convolution integral of the bilateral LaPlace transformation, and hence

$$\bar{F}(s) = \bar{G}(s)\bar{W}(s) \quad (3)$$

where

$$\bar{F}(s) = \int_{-\infty}^{\infty} F(v) \exp \{-sv\} dv,$$

$$\bar{G}(s) = \int_{-\infty}^{\infty} G(v) \exp \{-sv\} dv,$$

$$\bar{W}(s) = \int_{-\infty}^{\infty} W(v) \exp \{-sv\} dv.$$

The ratios of corrected to uncorrected molecular weight averages may be expressed as

$$\frac{M_K(t)}{M_K(\infty)} = \frac{\left[\int_{-\infty}^{\infty} W(v)M(v)^{K-1}dv \right] / \left[\int_{-\infty}^{\infty} W(v)M(v)^{K-2}dv \right]}{\left[\int_{-\infty}^{\infty} F(v)M(v)^{K-1}dv \right] / \left[\int_{-\infty}^{\infty} F(v)M(v)^{K-2}dv \right]} \quad (4)$$

where $K = 1, 2, 3, 4$ correspond to number, weight, Z , and $Z + 1$ average molecular weights, respectively. A similar expression may be written for intrinsic viscosity²:

$$\frac{[\eta](t)}{[\eta](\infty)} = \frac{\int_{-\infty}^{\infty} W(v)M^a(v)dv}{\int_{-\infty}^{\infty} F(v)M^a(v)dv} \quad (5)$$

where a is the exponent in the Mark-Houwink intrinsic viscosity-molecular weight expression.

Linear Molecular Weight Calibration Curve

For calibration curves which are linear over the elution volume range of interest,

$$M(v) = D_1 \exp \{-D_2v\} \quad (6)$$

where $D_1, D_2, >0$. Substituting eq. (6) into (4) and (5) and applying eq. (3) yields

$$\frac{M_K(t)}{M_K(\infty)} = \frac{\bar{G}[(K - 2)D_2]}{\bar{G}[(K - 1)D_2]} \tag{7}$$

$$\frac{[\eta](t)}{[\eta](\infty)} = \frac{1}{\bar{G}[aD_2]} \tag{8}$$

Nonlinear Molecular Weight Calibration Curve

If the nonlinear part of the calibration curve can be expressed as

$$M^\alpha(v) = C(1,\alpha)y + C(2,\alpha)y^2 + \dots \tag{9}$$

where $y = \exp \{-D_\alpha v\}$; $\alpha = -1, a, 1, 2, 3, \dots$; and $C(1,\alpha), C(2,\alpha), \dots$ and D_α are constants, then the corrected molecular weight averages and intrinsic viscosity may be expressed as

$$M_1(t) = \frac{1}{\left[\sum_{i=1}^N C(i, -1) \bar{F}(iD_{-1}) / \bar{G}(iD_{-1}) \right]} \tag{10}$$

$$M_2(t) = \left[\sum_{i=1}^N C(i, 1) \bar{F}(iD_1) / \bar{G}(iD_1) \right] \tag{11}$$

$$M_K(t) = \frac{\left[\sum_{i=1}^N C(i, K - 1) \bar{F}(iD_{K-1}) / \bar{G}(iD_{K-1}) \right]}{\left[\sum_{i=1}^N C(i, K - 2) \bar{F}(iD_{K-2}) / \bar{G}(iD_{K-2}) \right]} \tag{12}$$

$$[\eta](t) = \left[\sum_{i=1}^N C(i, a) \bar{F}(iD_a) / \bar{G}(iD_a) \right] \tag{13}$$

where N is the number of terms in eq. (9), $D_0 = 0$ and $\sum_{i=1}^N C(i, 0) = 1$.

Linear Calibration Curve and Gaussian Instrumental Spreading Function

For the special case of a linear calibration curve and a Gaussian instrumental spreading function, correction equations for the molecular weight averages and the intrinsic viscosity become

$$\bar{F}(s) = \bar{W}(s) \exp \{s^2/4h\} \tag{14}$$

$$\frac{M_K(t)}{M_K(\infty)} = \exp \{(3 - 2K)D_2^2/4h\} \tag{15}$$

$$\frac{[\eta](t)}{[\eta](\infty)} = \exp \{-a^2D_2^2/4h\} \tag{16}$$

where D_2 is the slope of the molecular weight calibration curve (see eq. (6)).

Linear Calibration Curve and General Instrumental Spreading Function

Provdor and Rosen² have proposed the use of a general statistical shape function to describe instrumental spreading. This function, which accounts for deviation from the Gaussian shape, has the form

$$G(v) = \phi(v) + \sum_{n=3}^{\infty} (-1)^n \frac{A_n}{n!} \frac{\phi^n(v)}{(\sqrt{2h})^n} \quad (17)$$

where $\phi(v) = (h/\pi)^{1/2} \exp(-hv^2)$ and $\phi^n(v)$ denotes its n th-order derivatives.

The coefficients A_n are functions of μ_n , the n th-order moments about the mean eluent volume, μ_1 , of the observed GPC chromatogram normalized. The coefficients are related to the moments as

$$A_3 = \frac{\mu_3}{\mu_2^{3/2}} \quad (18)$$

$$A_4 = \left(\frac{\mu_4}{\mu_2^2} \right) - 3 \quad (19)$$

and, as before, the variance is related to the resolution factor as $\mu_2 = 1/2h$.

The coefficient A_3 or μ_3 provides a measure of skewness. When A_3 is positive, the chromatogram is skewed to higher elution volumes with a lowering of the number- and weight-average molecular weights. When A_3 is negative, the opposite is true. Similar behavior is found with the skewing factor, SK , in the equations of Balke and Hamielec.⁵ Finite values of A_4 give a symmetrical distribution but provide a measure of deviation from the Gaussian shape. Provdor and Rosen² neglected coefficients A_5 , A_7 , A_8 , \dots and set A_6 equal to $10A_3^2$. This gives a model with three parameters, h , μ_3 , and μ_4 . These parameters can be determined using calibration standards. Provdor and Rosen suggested the use of number- and weight-average molecular weights and intrinsic viscosity. Calibration procedures with the general shape function will be discussed later.

Provdor and Rosen applied the method of molecular weight averages using the general shape function to obtain equations for corrected molecular weight averages and intrinsic viscosity. Unfortunately they made a small error in the development. Many of the equations presented in their paper are therefore incorrect. Only the corrected equations will be given in this paper. These results follow:

$$\bar{G}(s) = \exp\{s^2/4h\} \left\{ 1 + \sum_{n=3}^{\infty} \frac{A_n}{n!} \left(\frac{-s}{\sqrt{2h}} \right)^n \right\}. \quad (20)$$

It follows therefore that

$$\frac{M_K(t)}{M_K(\infty)} = \exp\left\{ \frac{-(2K-3)D_2^2}{4h} \right\} \frac{\left\{ 1 + \sum_{n=3}^{\infty} (A_n/n!) \left[\frac{-(K-2)D_2}{\sqrt{2h}} \right]^n \right\}}{\left\{ 1 + \sum_{n=3}^{\infty} (A_n/n!) \left[\frac{-(K-1)D_2}{\sqrt{2h}} \right]^n \right\}} \quad (21)$$

$$\frac{[\eta](t)}{[\eta](\infty)} = \exp \left\{ \frac{-a^2 D_2^2}{4h} \right\} \frac{\{1\}}{\left\{ 1 + \sum_{n=3}^{\infty} (A_n/n!) [(-aD_2)/(\sqrt{2}h)]^n \right\}} \quad (22)$$

Using the truncated form where $A_5 = 0$, $A_6 = 10A_3^2$, $A_7 = 0$, $A_8 = 0$, ... and introducing the moments, one obtains for number- and weight-average molecular weights and intrinsic viscosity the following equations:

$$\frac{M_n(t)}{M_n(\infty)} = \exp \{ D_2^2/4h \} \left\{ 1 + \frac{D_2^3 \mu_3}{6} + \frac{D_2^4}{24} \left(\mu_4 - \frac{3}{4h^2} \right) + \frac{D_2^6 \mu_3^2}{72} \right\} \quad (23)$$

$$\frac{M_w(t)}{M_w(\infty)} = \exp \{ -D_2^2/4h \} / \left\{ 1 - \frac{D_2^3 \mu_3}{6} + \frac{D_2^4}{24} \left(\mu_4 - \frac{3}{4h^2} \right) + \frac{D_2^6 \mu_3^2}{72} \right\} \quad (24)$$

$$\frac{[\eta](t)}{[\eta](\infty)} = \exp \{ -a^2 D_2^2/4h \} / \left\{ 1 - \frac{a^3 D_2^3 \mu_3}{6} + \frac{a^4 D_2^4}{24} \left(\mu_4 - \frac{3}{4h^2} \right) + \frac{a_6 D_2^6 \mu_3^2}{72} \right\} \quad (25)$$

The use of calibration standards (not necessarily of small polydispersity) with known number- and weight-average molecular weights and intrinsic viscosity and eqs. (23), (24), and (25) permits the evaluation of h , μ_3 , and μ_4 over the range of eluent volumes of interest. Provder and Rosen² have done this with polystyrene and poly(vinyl chloride) standards. They also set $\mu_4 = 0$ and used the combinations M_n - M_w and M_n - $[\eta]$ to determine h and μ_3 . The moment μ_4 affects M_n and M_w in essentially the same manner as h . Therefore, setting $\mu_4 = 0$ has the effect of lowering h but changing μ_3 insignificantly. The information M_n , M_w , and $[\eta]$ for calibration standards therefore appears to be insufficient to establish whether μ_4 is significant or not. Corrected M_n , M_w , and $[\eta]$ appear to be equally good when μ_4 is set equal to zero. For a nonlinear molecular weight calibration curve substitute equation (20) into equations (12) and (13).

Finding the Differential Molecular Weight Distribution (DMWD)

To find the corrected DMWD, one must establish the proper instrumental spreading function, determine by calibration numerical values for the parameters of the spreading function, and then solve Tung's axial dispersion equation.

The most difficult step is to establish the proper instrumental spreading function. To emphasize this difficulty, we will present an example using data provided by Provder and Rosen.² Refer to their example 184-212 where the following parameters were determined by matching M_n , M_w , and $[\eta]$ for polystyrene calibration standards: (i) $h = 0.796$, $\mu_3 = 0.891$, $\mu_4 = 0$ { M_n , M_w }; (ii) $h = 0.788$, $\mu_3 = 0.891$, $\mu_4 = 1.0$ { M_n , M_w , $[\eta]$ }.

The following corrections are obtained for (i) where $\mu_4 = 0$:

$$\frac{M_1(t)}{M_1(\infty)} = 1.039 \exp \{D_2^2/4h\}$$

$$\frac{M_2(t)}{M_2(\infty)} = 1.063 \exp \{-D_2^2/4h\}$$

$$\frac{M_3(t)}{M_3(\infty)} = 1.900 \exp \{-3D_2^2/4h\}$$

$$\frac{M_4(t)}{M_4(\infty)} = -1.688 \exp \{-5D_2^2/4h\}$$

An impossible situation. The instrumental spreading function is obviously inadequate. The corrected chromatogram would have negative heights.

And for the second set (ii) where $\mu_4 = 1.0$ we obtain

$$\frac{M_1(t)}{M_1(\infty)} = 1.049 \exp \{D_2^2/4h\}$$

$$\frac{M_2(t)}{M_2(\infty)} = 1.052 \exp \{-D_2^2/4h\}$$

$$\frac{M_3(t)}{M_3(\infty)} = 1.398 \exp \{-3D_2^2/4h\}$$

$$\frac{M_4(t)}{M_4(\infty)} = 1.071 \exp \{-5D_2^2/4h\}$$

$$\frac{M_5(t)}{M_5(\infty)} = 0.275 \exp \{-7D_2^2/4h\}$$

$$\frac{M_6(t)}{M_6(\infty)} = 0.1860 \exp \{-9D_2^2/4h\}$$

We will refer to these results in the discussions to follow.

Gaussian Instrumental Spreading Function

For the case cited, the corrections for the number- and weight-average molecular weights (corrections for deviation of instrumental spreading function from Gaussian shape) are about 5%. One might therefore expect that the use of a Gaussian instrumental spreading function would permit one to find the corrected DMWD with little error. An examination of the corrections for the higher averages, however, suggests that this may indeed not be the case. For this argument we are of course assuming that the general shape function is valid in this instance. The use of a Gaussian instrumental spreading function for the solution of Tung's axial dispersion equation would give a corrected DMWD with correct M_n and M_w , but with incorrect M_z and higher molecular weight averages. But then how can we be sure that the general instrumental spreading function as used in this example is indeed the correct one? This point will now be discussed under the following heading.

Non-Gaussian Instrumental Spreading Function

The recommended method² of finding the appropriate instrumental spreading function is to use standards of known $\{M_n, M_w, [\eta]\}$, $\{M_n, M_w\}$, or $\{M_n, [\eta]\}$ to evaluate the h , μ_3 , and μ_4 parameters in the function (in the latter two cases μ_4 is set equal to zero). This has already been done, see examples (i) and (ii). An examination of the corrections for deviations from the Gaussian shape indicates a great difference between the two instrumental spreading functions (one found setting $\mu_4 = 0$ and the other with $\mu_4 = 1.0$). A negative correction for the former results in a negative value for $M_4(t)$ and indicates that the corrected DMWD would have some negative heights, see example (i). This situation is obviously not possible, ruling out the possibility that the associated instrumental spreading function is a good one. However, it should be pointed out that the set of parameters $h = 0.796$, $\mu_3 = 0.891$, $\mu_4 = 0$, gives satisfactory corrections to M_n , M_w , and $[\eta]$. This information is therefore insufficient to assess the validity of the correction to M_z and higher average molecular weights. The corrections to M_z are very different, one being 1.9 and the other 1.4. Which of these is correct we do not know. Probably, on the basis of no negative heights in the corrected DMWD, the value 1.4 is closer to the truth. It is becoming clear that, to calibrate the GPC so that one obtains a corrected DMWD with many of its higher molecular weight averages accurate, one must use standards whose higher molecular weight averages are known. An alternative procedure would be to use truly monodispersed standards, measure the response, and calculate the moments directly. These unfortunately are not available at the present time.

It seems that we have no ready means of establishing the validity of an instrumental spreading function. The best we can do at present is to calibrate for M_n , M_w , and $[\eta]$.

A Criterion for Resolution in GPC: Gaussian Instrumental Spreading Function

Referring to eq. (15),

$$\frac{M_K(t)}{M_K(\infty)} = \exp \{ (3 - 2K)D_2^2/4h \}, \quad (15)$$

it is apparent that, to minimize the correction for imperfect resolution, one should choose a single column or column combination for which $D_2^2/4h$ is as small as possible. That is, the slope of the molecular weight calibration curve should be as small and the resolution factor as large as possible (variance of single species chromatogram as small as possible). Another interesting observation which may not have been obvious is the fact that greater resolution power is necessary for the higher molecular weight averages. For example, for a single value of $D_2^2/4h$, the correction for imperfect resolution is approximately the same for M_n and M_w , but increases rather rapidly for M_z and higher averages. When discussing resolution, one

should therefore specify the average molecular weight in question. The fact that D_2 , the slope of the calibration curve, and h , the resolution factor, in general vary with molecular weight is consistent with the observation that a column may give good separation at an intermediate molecular weight but may be entirely inadequate for higher molecular weights. At the high end and similarly at the low end of the molecular weight spectrum, D_2 , the slope of the calibration curve, increases very rapidly resulting in poor resolution and a large correction.

The greatest benefit of eq. (15) is its applicability to broad as well as narrow MWD standards of any shape. It permits the resolution power to be measured for the polymer in question with a once-through technique. The molecular weight calibration curve must of course be available. The polymer sample (not necessarily having a narrow DMWD) is injected to find either $M_n(\infty)$ or $M_w(\infty)$. Having knowledge of its true number- or weight-average molecular weight is sufficient to evaluate $D_2^2/4h$ with eq. (15).

Let us therefore define a specific resolution factor $R_s(K, M_0)$ as follows:

$$R_s(K, M_0) = \frac{(-1)^{K+1} 4h}{(2K - 3)D_2^2} \quad (26)$$

where $K = 1, 2, 3, \dots$ and M_0 is the molecular weight at the peak eluent volume. Column or column combination resolution may be considered perfect when $R_s(K, M_0) > 100$. The subscripts K, M_0 are used to emphasize the need to specify the particular molecular weight average and the molecular weight at the peak eluent volume.

To show that eq. (26) is consistent with present practice, we will show that under limiting conditions it is equivalent to a form after Bly.⁶ Bly proposed the following expression:

$$R_s^1 = \frac{2(V_2 - V_1)}{(W_1 + W_2)(\ln M_1 - \ln M_2)} \quad (27)$$

where V_1 and V_2 are eluent volumes of species 1 and 2 and W_1 and W_2 are the associated peak widths (width of the baseline of the curve between two tangents drawn on the points of inflexion of the curve and extended to the baseline) and M_1 and M_2 are the associated molecular weights.

Assuming the species are neighbors and the molecular weight calibration curve is linear in the vicinity $W = W_1 = W_2$, then

$$\ln M_1 - \ln M_2 = D_2(V_2 - V_1)$$

$$R_s^1 = \frac{1}{D_2 W}$$

For Gaussian distribution $W = 4\mu_2^{1/2} = (8/h)^{1/2}$,

$$R_s^1 = \frac{h^{1/2}}{\sqrt{8}D_2} \quad (28)$$

For $K = 1$ or 2 ,

$$R_s(1, M_0) = R_s(2, M_0) = \frac{4h}{D_2^2} = 32(R_s^1)^2.$$

Hence, Bly's expression is consistent with eqs. (15) and (26) in the limit of monodisperse standards. The use of Bly's eq. (27) with polymer standards that are not truly monodisperse would of course introduce an error. This limitation does not exist with the use of eq. (15). If essentially monodisperse standards were available, h could be measured directly with a once-through technique. A knowledge of M_n and M_w or M_n and $[\eta]$ would then permit one to calculate D_2 as well with eq. (15).

Non-Gaussian Instrumental Spreading Function

The principal use of an expression for resolution such as eq. (26) is probably to evaluate gels, column geometry, and packing procedures. Skewing of single species chromatograms is largely due to column overloading (see Fig. 12, in Hamielec)⁷. A satisfactory column or column combination may give highly skewed chromatograms when operated in an overloaded manner. It is true that the resolution factor h and the slope of the molecular weight calibration curve, D_2 , do depend somewhat on polymer loading but not nearly to the same extent as does skewing. The resolution factor also depends upon flow rate. The dependence of μ_4 on gel, column geometry, packing procedure, and GPC operation is not understood at this time.

For practical purposes it is recommended that eq. (26) be used to evaluate the resolution of a single column or column combination. The resolution factor h should be evaluated using correction equations with μ_4 set equal to zero.

GPC Operation in Recycle Mode

There appears to be a great deal of interest developing in the possible use of recycle to obtain increased resolution with GPC.

We will now formulate some equations which apply to both narrow and broad DMWD polymers being analyzed by GPC in recycle mode. We assume that the molecular weight calibration curve is linear and that the instrumental spreading function is Gaussian. As the path length of gel is increased, separation increases with a resultant reduction in polymer loading at any point in the column. Therefore, even though deviations from the Gaussian shape may be significant for one or two passes through the column or column combination, one would expect these deviations to become negligible with increasing number of passes. On this basis it is reasonable to assume a Gaussian spreading function. Errors that might be introduced for small number of passes will be discussed later.

If D_2 is the slope of the molecular weight calibration curve for one pass ($n = 1$), the slope after n passes will be D_2/n . The next question to answer

is, how does the resolution factor (or variance due to axial dispersion) vary with number of passes? For $n = 1$,

$$\frac{1}{h_1} = \frac{1}{h} + \frac{1}{h_0}$$

where h_1 is the resolution factor after one recycle pass, h_0 is due to constant extra column spreading and is independent of n , and h is due to column spreading including the passage of the sample through the pump for one pass.

$$\text{For } n = n, \frac{1}{h_n} = \frac{n}{h} + \frac{1}{h_0}$$

Neglecting $1/h_0$ and rewriting eq. (15) for recycle mode, we obtain

$$\frac{M_K(t)}{M_K(\infty)} = \exp\left(\frac{1}{n} (3 - 2K) D_2^2/4h\right). \quad (15a)$$

With increasing n , the correction for imperfect resolution decreases and in the limit of $1/n = 0$ becomes zero.

Equation (15a) will now be used to develop an extrapolation technique which will permit one to obtain $M_K(t)$ using a finite number of recycle passes. Taking logarithms, one obtains

$$\ln M_K(\infty) = -(3 - 2K) (D_2^2/4h) \frac{1}{n} + \ln M_K(t). \quad (15b)$$

For each pass through the detector, a new response is measured and $M_K(\infty)$ calculated. A plot of $\ln M_K(\infty)$ versus $1/n$ should yield a straight line with intercept $\ln M_K(t)$, the desired quantity. A similar equation may be written for the polydispersity:

$$\ln P(\infty) = (D_2^2/2h) \frac{1}{n} + \ln P(t). \quad (15c)$$

A similar extrapolation technique could be used to find the true polydispersity, $P(t)$. For a small number of passes one might find deviations from a straight line. These would probably be due to deviation from the Gaussian shape for the instrumental spreading function and to h_0 .

SUMMARY

Equations developed for correcting M_n , M_w , and $[\eta]$ for imperfect resolution are generally satisfactory. Choosing the appropriate instrumental spreading function is however a very difficult task. There is need for further research on this problem, in particular with polymer standards for which the DMWD or even M_z is known (in addition to M_n and M_w).

A criterion for resolution in GPC which is based on a solution of Tung's axial dispersion equation has been proposed.

The operation of GPC in recycle mode appears very promising. Equations have been developed to interpret data obtained in this operational mode. It is probable that a great deal of work will be done in this area in the very near future.

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