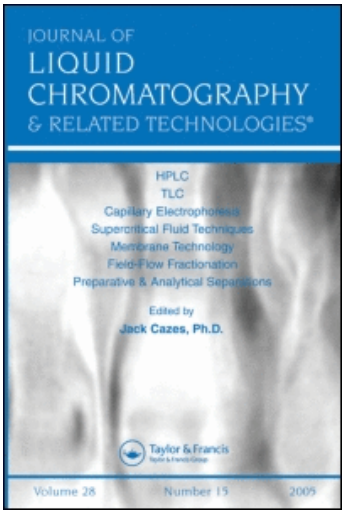


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# Size Exclusion Chromatography (SEC) of Complex Polymers - Generalized Analytical Corrections for Imperfect Resolution

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# SIZE EXCLUSION CHROMATOGRAPHY (SEC) OF COMPLEX POLYMERS - GENERALIZED ANALYTICAL CORRECTIONS FOR IMPERFECT RESOLUTION

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## ABSTRACT

Herein is reported generalized analytical solutions which permit correction for imperfect resolution when the molecular weight calibration curve is nonlinear and the variance of single-species chromatograms changes significantly with molecular size of the polymer solute. Two kinds of generalized analytical solutions have been obtained. One is a solution of Tung's integral equation for the corrected chromatogram or the molecular weight distribution and the other is a solution for the corrected molecular weight averages of the whole polymer. Also discussed is the use of local corrections for imperfect resolution across the chromatogram with detectors such as the low angle laser light scattering spectrophotometer (LALLS) when used with micro and macropackings.

## INTRODUCTION

To date, analytical solutions for Tung's integral equation for the corrected chromatogram have not been reported. Many numerical techniques have been proposed and evaluated and the better of these include the iterative method of Ishige et al. (1), the method of Chang and Huang (2) and more recently the method proposed by Vozka and Kubin (3). Analytical solutions for Tung's integral equation for the molecular weight averages were first published by Hamielec and Ray (4) for the case of a uniform Gaussian instrumental spreading function.

Provder and Rosen (5) generalized these solutions to include a uniform non-Gaussian instrumental function. Both of these analytical solutions are limited to a SEC operation where the molecular weight calibration curve is linear and the variance of single-species chromatograms is independent of molecular size of the polymer solute. The solutions to be presented herein are analytical and account for non-linear molecular weight calibration curve and non-uniform instrumental spreading function with the variance of single-species chromatograms varying with molecular size of the polymer solute. The limiting factor which remains is that the instrumental spreading function is Gaussian.



## THEORY

Tung's integral equation which follows is the starting point for all rigorous methods of correction for imperfect resolution.

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

F(v) is the detector response or chromatogram at retention volume v. The kernel G(v,y) is called the instrumental spreading function and is the normalized detector response for a single species with mean retention volume y. W(y)dy is the area of the detector response for a single species with mean retention volume in the range, y-y+dy. W(y) is the detector response or chromatogram corrected for peak broadening. Species with the same mean retention volume may, in certain circumstances, have different molecular weights and compositions and possibly significantly different instrumental spreading functions as with complex polymers, those having variable long chain branching frequency and copolymers with variable composition. In these instances equation (1) would not be valid and a more complex form involving

multiple integrals would have to be used. Until there is experimental evidence to the contrary, it will be assumed that equation (1) is valid under all circumstances of GPC operation.

We now define a distribution function W(v,y), where W(v,y)dvdy is the area under the detector response in the retention volume range, v-v+dv due to polymer solute species with mean retention volume in the range, y-y+dy. Let us investigate the following properties of W(v,y)

$$W(v,y) = W(y)\, G(v,y) \tag{2a}$$

$$\int_0^\infty W(v,y)dy = F(v) \tag{2b}$$

$$\int_0^\infty W(v,y)dv = W(y) \tag{3}$$

It is clear from equation (3) that a knowledge of W(v,y) permits a simple direct integration to obtain W(y), the chromatogram corrected for peak broadening. At a particular retention volume, v, W(v,y) gives the distribution of polymer molecular sizes in the detector cell. A detector system which could provide a measure of W(v,y), would provide a direct instrumental means of measuring W(y). This possibility will be discussed later. We will now consider the special case where the instrumental spreading function G(v,y) is Gaussian with variance which depends on the size of the polymer solute and where the slope of the molecular weight calibration curve varies with retention volume. For this situation Tung's integral equation takes the form:

$$F(v) = \frac{1}{\sqrt{2\pi\sigma(v)^2}} \int_0^\infty W(y) \exp\left\{ -(v-y)^2/2\sigma(v)^2 \right\} dy \tag{1a}$$

The use of $\sigma(v)^2$ rather than $\sigma(y)^2$ is an approximation which should be valid when peak broadening is not excessive. In this case,

$$W(v,y) = \frac{W(y)}{\sqrt{2\pi\sigma(v)^2}} \exp\left( -(v-y)^2/2\sigma(v)^2 \right) \quad (2c)$$

Let us now derive an expression for $\bar{M}_W(v, uc)$ which is the weight average molecular wieght of the contents of the detector cell. The LALLS detector system would measure this molecular weight average.

$$\bar{M}_W(v,uc) = \int_0^\infty M(y)\, W(v,y)dy \Big/ \int_0^\infty W(v,y)dy \quad (4)$$

where

$$M(y) = D_1(v) \exp(-D_2(v)y)$$

Local linearization is being employed to account for a nonlinear molecular wieght calibration curve. Substituting for W(v,y) and with some algebraic manipulation one obtains

$$\bar{M}_W(v,uc) = \frac{M(v)\exp\{ (D_2(v)\sigma(v))^2/2 \}}{F(v)\sqrt{2\pi\sigma(v)^2}} \int_0^\infty W(y)\exp - \{\frac{\left(v-D_2(v)\sigma(v)^2-y\right)^2}{2\sigma(v)^2}\}dy \quad (6)$$

Comparing the integrals in equations (1a) and (6) it is clear that

$$\frac{\bar{M}_W(v,uc)}{M(v)} = \frac{F(v-D_2(v)\sigma(v)^2)}{F(v)} \exp\{(D_2(v)\sigma(v))^2/2\} \quad (7)$$

The weight-average molecular weight of the whole polymer corrected for imperfect resolution is given by (7,8)

$$\bar{M}_W(c) = \int_0^\infty F(v)\, \bar{M}_W(v,uc)dv \Big/ \int_0^\infty F(v)dv \quad (8a)$$

$$= \int_0^\infty M(v)F(v-D_2(v)\sigma(v)^2) \exp\{(D_2(v)\sigma(v))^2/2\}dv \Big/ \int_0^\infty F(v)dv \quad (8b)$$

This is an extension of the original analytical solution after Hamielec and Ray (4) for variable variance of the single-species chromatograms

and for a nonlinear molecular weight calibration curve. In a similar manner correction equations for other molecular weight averages and intrinsic viscosity may be derived and these follow (7,8).

$$\frac{\bar{M}_K(v,uc)}{M(v)} = \frac{F\left(v-(K-1)D_2(v)\sigma(v)^2\right)}{F\left(v-(K-2)D_2(v)\sigma(v)^2\right)} \exp\left\{\frac{(2K-3)}{2}\left(D_2(v)\sigma(v)\right)^2\right\} \tag{9}$$

$$\frac{[\eta](v,uc)}{[\eta](v)} = \frac{F\left(v-aD_2(v)\sigma(v)^2\right)}{F(v)} \exp\left\{\left(aD_2(v)\sigma(v)\right)^2/_2\right\} \tag{10}$$

$$\bar{M}_K(c) = \int_0^\infty F(v)\bar{M}_K{}^{K-1}(v,uc)dv \;/\; \int_0^\infty F(v)\bar{M}_K{}^{K-2}(v,uc)dv \tag{11}$$

$$[\eta](c) = \int_0^\infty F(v)[\eta](v,uc)dv \;/\; \int_0^\infty F(v)dv \tag{12}$$

where for $K = 1$, $\bar{M}_1(c) = \bar{M}_N(c)$ and $\bar{M}_1(v,uc) = \bar{M}_N(v,uc)$

$K = 2$, $\bar{M}_2(c) = \bar{M}_W(c)$ and $\bar{M}_2(v,uc) = \bar{M}_W(v,uc)$, and so on.

Equations (9)-(12) may be used to calculate whole polymer molecular weight averages and intrinsic viscosity corrected for imperfect resolution when the variance of single-species chromatograms and the slope of the molecular weight calibration curve vary with retention volume.

We will now derive an analytical solution for W(y), the chromatogram corrected for peak broadening. We approximate W(v,y) with the form

$$W(v,y) = \frac{F(v)}{\sqrt{2\pi\bar{\sigma}(v)^2}} \exp\left\{-\left(y-\bar{y}(v)\right)^2 / 2\bar{\sigma}(v)^2\right\} \tag{13}$$

An examination of equation (2a) might suggest that the shape of W(v,y) depends on the shape of W(y). This is true up to a point. However, for a particular retention volume, v, the range of y which is significant

may only include a small portion of W(y). The corrected chromatogram is then given by

$$W(y) = \int_0^\infty \frac{F(v)\ \exp\left[-(y - \bar{y}(v))^2 / 2\bar{\sigma}(v)^2\right]}{\sqrt{2\pi\bar{\sigma}(v)^2}}\, dv \qquad (14a)$$

or more directly in this case by

$$W(v) = F(v)\ \left[\sigma(v)/\bar{\sigma}(v)\right]\ \exp\left\{-(v-\bar{y}(v))^2/2\bar{\sigma}(v)^2\right\} \qquad (14b)$$

A detector system which could say measure $\bar{M}_N(v,uc)$ and $\bar{M}_W(v,uc)$ would also provide a measure of $\bar{y}(v)$ and $\bar{\sigma}(v)^2$. The LALLS detector system which gives a measure of $\bar{M}_W(v,uc)$ with the additional assumption that $\bar{y}(v) = v$ would provide a measure of $\bar{\sigma}(v)^2$. This would in effect with the use of equation (14), provide a direct measure of W(y). For the case of a Gaussian instrumental spreading function it can readily be shown using equations (9) and (13) that

$$\bar{y}(v) = v + \frac{1}{D_2(v)}\, \ell n\, \frac{F\left(v+D_2(v)\ \sigma(v)^2\right)}{\sqrt{F\left(v-D_2(v)\ \sigma(v)^2\right)\ F\left(v+D_2(v)\ \sigma(v)^2\right)}} \qquad (15)$$

$$\bar{\sigma}(v)^2 = \sigma(v)^2 + \frac{1}{D_2^2(v)}\, \ell n\, \frac{F\left(v-D_2(v)\ \sigma(v)^2\right)\ F\left(v+D_2(v)\ \sigma(v)^2\right)}{F(v)^2} \qquad (16)$$

It can readily be shown with a Taylor series expansion accurate to second order that

$$\bar{y}(v) = v + \sigma(v)^2\, \frac{F'(v)}{F(v)} \qquad (15a)$$

$$\bar{\sigma}(v)^2 = \sigma(v)^2 + \sigma(v)^4\, \left(\frac{F''(v)}{F(v)} - \left(\frac{F'(v)}{F(v)}\right)^2\right) \qquad (16a)$$

The expansion properly eliminates the dependence on $D_2(v)$. For computational reasons it is easier to employ equations (15) and (16)

with any convenient value for $D_2(v)$. To solve for W(y) one must have values for $\sigma(v)^2$. These may be found by standard calibration techniques. The use of equations derived above to correct the chromatogram and whole polymer molecular weight averages will be illustrated under Results and Discussion.

We will now derive equations which will permit the investigation of the magnitude of corrections for imperfect resolution for the weight average molecular weight of the detector cell contents ($\bar{M}_W(v,uc)/M(v)$) for both micro and macropackings. Micropackings with particles of about 5-15 microns give small peak broadening (small $\sigma(v)^2$) and small peak separation (large $D_2(v)$). Macropackings with particles of about 30-60 microns give large peak broadening (large $\sigma(v)^2$) and large peak separation (small $D_2(v)$). An examination of equation (7) might suggest that the correction for imperfect resolution in the detector cell would be smaller for micropackings that for macropackings due to the $\sigma(v)^2$ term in $F(v-D_2(v)\sigma(v)^2)$. To investigate this further we will begin with a polymer sample which has the most probable distribution and then assume that it is analyzed with an SEC with micropacking and then with macropacking. The MWD of the sample is given

$$W(M) = \frac{M}{\bar{M}_N^2} \exp\{ - M/\bar{M}_N \} \qquad (17)$$

with $\bar{M}_N = 2 \times 10^5$ and $\bar{M}_W = 4 \times 10^5$

For convenience we will assume that the molecular weight calibration curve is linear and given by

$$M = D_1 \exp(-D_2 v) \qquad (18)$$

The associated chromatogram is given by

TABLE 1

Parameters Employed in Equations (6), (18) and (19) for Micro and Macropackings

| Micropacking | Macropacking |
|---|---|
| $D_2 = 0.357\ ml^{-1}$ | $D_2 = 8.62 \times 10^{-2} ml^{-1}$ |
| $\sigma = 0.70$ ml | $\sigma = 2.90$ ml |
| $D_2\sigma = 0.25$ | $D_2\sigma = 0.25$ |
| $D_2\sigma^2 = 0.1750$ ml | $D_2\sigma^2 = 0.725$ |

$$W(v) = \frac{D_2 D_1^2}{\bar{M}_N^2} \exp(-2D_2 v) \exp\left\{ -\left(\frac{D_1}{\bar{M}_N}\right) \exp(-D_2 v) \right\} \qquad (19)$$

We will consider relatively small corrections for peak broadening and since we have a relatively broad MWD, we will set $F(v) \simeq W(v)$. The parameters in these equations employed for micro and macropackings are given in Table 1. Again for convenience it is assumed that the variance does not vary with retention volume. The results of this comparison will be given under Results and Discussion.

## RESULTS AND DISCUSSION

We will begin with a discussion of corrections for imperfect resolution for the LALLS detector system and compare the magnitude of these corrections for micro and macropackings. Table 2 shows the corrections required for typical micro and macropackings. It is clear that the magnitude of the corrections are about the same for both micro and macropackings. Apparently the smaller $D_2(v)\sigma(v)^2$ obtained with micropackings are compensated for my the narrower and steeper chromato-

TABLE 2

Corrections for Imperfect Resolution with the LALLS Detector System

| Micropacking | | | Macropacking | | |
|---|---|---|---|---|---|
| v(ml) | $F(v)x10^3$ | $\bar{M}_w(v,uc)/M(v)$ | v(ml) | $F(v)x10^3$ | $\bar{M}_w(v,uc)/M(v)$ |
| 27 | 16.0 | 0.745 | 56 | 3.6 | 0.740 |
| 28 | 64.0 | 0.853 | 60 | 14.4 | 0.846 |
| 29 | 136.3 | 0.937 | 64 | 31.2 | 0.930 |
| 30 | 186.6 | 1.002 | 68 | 44.1 | 0.995 |
| 31 | 187.7 | 1.055 | 72 | 46.1 | 1.041 |
| 32 | 152.1 | 1.084 | 76 | 38.9 | 1.077 |
| 33 | 105.9 | 1.109 | 80 | 28.2 | 1.105 |
| 34 | 66.4 | 1.127 | 84 | 18.4 | 1.122 |
| 35 | 38.6 | 1.139 | 88 | 11.1 | 1.134 |
| 36 | 21.3 | 1.153 | 92 | 6.3 | 1.147 |



gram. It is remarkable that the correction $\bar{M}_w(v,uc)/M(v)$ at the high molecular weight end of the chromatogram is as much as 25% even though the correction to the whole polymer $\bar{M}_w$ is only about 3%. In other words corrections for imperfect resolution are a must when employing the LALLS detector system if quantitative estimates of the molecular weight calibration curve M(v) are to be made.

We will now present an example of the application of equation (14) to solve for the chromatogram W(v) corrected for peak broadening for a situation where the variance of single-species chromatogram varies somewhat with retention volume (or molecular size). We will then use the same chromatograms F(v) and W(v) and use a nonlinear molecular weight calibration curve to solve for the corrected molecular weight averages. One approach is to integrate W(v) directly and the other is to use equations (9) and (11) to generate the molecular weight averages corrected for imperfect resolution.

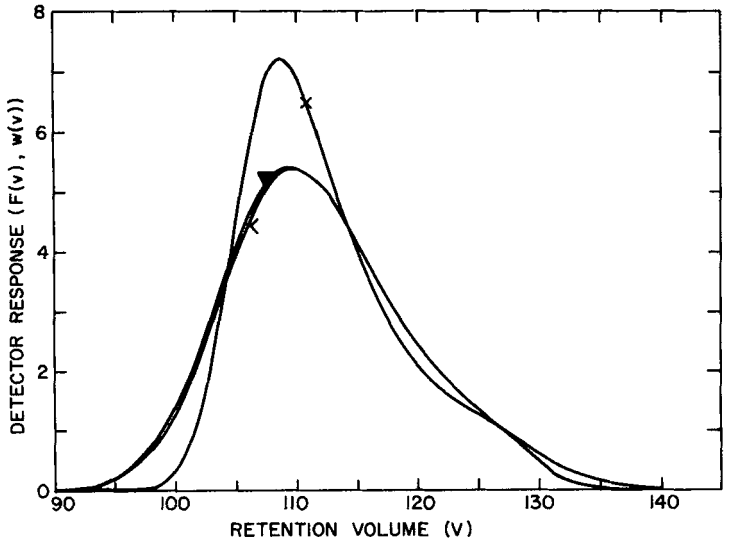


FIGURE 1. Analytical solution of Tung's Integral Equation - A Comparison of the Uncorrected Chromatogram F(v) with the Corrected Chromatogram W(v) and with W(v) Rebroadened.

| | | Variance ($ml^2$) | Retention Volume (ml) |
|---|---|---|---|
| X | W(v) | | |
| ▼ | F(v) | | |
| < | W(v) Rebroadened | 16.0 | 90-100 |
| | | 17.0 | 102 |
| | | 18.0 | 104-125 |
| | | 16.7 | 127.5 |
| | | 16.2 | 130 |
| | | 16.0 | 132-147 |

TABLE 3

Molecular Weight Averages Corrected for Imperfect Resolution

| Method | $\bar{M}_N(c)$ | $\bar{M}_W(c)$ | $\bar{M}_Z(c)$ |
|---|---|---|---|
| W(v) | $1.44 \times 10^6$ | $1.54 \times 10^6$ | $1.65 \times 10^6$ |
| Equations (9) and (11) | $1.41 \times 10^6$ | $1.57 \times 10^6$ | $1.64 \times 10^6$ |

Figure 1 shows F(v), W(v) and W(v) rebroadened and illustrates the application of equation (14). The variances of single-species chromatograms employed are shown in the caption.

Table 3 shows the corrected molecular weight averages with the molecular weight calibration curve given by equation (20)

$$\ell n\ M = 27.43 - 0.1922v + 6.62 \times 10^{-4}\ v^2 \qquad (20)$$

The agreement between F(v) and rebroadened W(v) shown in Figure 1 is excellent confirming the applicability of equation (14) and the proposed analytical solution of Tung's integral equation. The agreement between corrected molecular weight averages shown in Table 3 also confirms the validity of the proposed method of correcting whole polymer molecular weight averages when the variance and slope of the molecular weight calibration curve vary with retention volume.



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