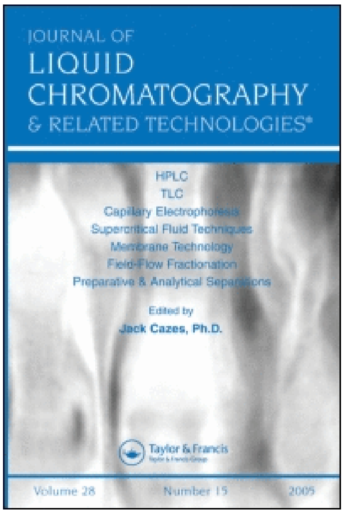

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A STATISTICAL EVALUATION OF METHODS OF CHROMATOGRAM INTERPRETATION-GPC

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ABSTRACT

Herein is reported a statistical evaluation of two common methods of determining the molecular weight calibration curve using broad molecular weight distribution standards. A Monte-Carlo simulation technique was employed to investigate and compare error propagation in these methods. It has been common practice to evaluate methods of chromatogram interpretation on an entirely theoretical basis without consideration of error propagation in the calculation procedures employed in the various methods. It is possible for a method which has a sounder theoretical basis to give less reliable results because of excessive error propagation. A statistical evaluation of error propagation also identifies the steps in calculation procedures where serious error propagation occurs leading perhaps to alternate and improved calculation paths.

The analysis of several sources of error is presented in detail including propagation errors due to errors in the molecular weight averages of the broad molecular weight distribution standards and chromatogram replication error.

INTRODUCTION

In much of the literature published in the polymer field, little attention is given to the errors in the results of analysis by GPC. The majority of results for polymer samples are reported only as $\bar{M}_N$, $\bar{M}_W$ and polydispersity with no confidence interval quoted on these values.

One reason for this neglect is the complexity of the problem A standard or series of standards is first used to obtain a molecular weight calibration curve followed by the use of this curve to establish the $\bar{M}_N$, $\bar{M}_W$ values for the polymer sample under consideration.

In almost all cases, only broad molecular weight standards are available. As a result, the calibration curve is obtained by complex formulae involving integration. The analysis of the unknown is also carried out by these complex formulae which may even include a non-linear correction factor for axial dispersion. As a result, standard statistical techniques for estimating the error in the results due to errors in input parameters become impractical.

It is the purpose of this report to present a reasonably simple method for estimating the error magnitudes of the results due to input errors, and also to determine to some extent which input parameters are most important. The analysis technique used involved a Monte-Carlo type simulation and will be discussed in more detail later.

Two simple methods for GPC analysis by broad standards were considered in this paper. The first was the linear effective calibration method developed by Balke, Hamielec et al(1) normally referred to as the Hamielec method. The second method examined was a modified form of the Hamielec method called GPCV2 which corrects for axial dispersion to present a true molecular weight calibration curve. The GPCV2 method was developed by Yau et al(2) and will be referred to as the Yau method in this paper.

THEORY

The two techniques investigated both assume a linear calibration curve of the form $\log M_v = \log D_1 - D_2 v$ (or $M_v = D_1 e^{-D_2 v}$) where D_1 is related to the intercept of the curve, D_2 is related to the slope of the calibration curve and M_v is the molecular weight of the polymer eluting at retention volume v. The general equations for number and weight average molecular weights are expressed by equations (1) and (2), where the W_v points represent the normalized chromatogram of the polymer corrected for axial dispersion.

$$\overline{M}_W(t) = \Sigma\ W_v M_v = \Sigma\ W_v D_1 e^{-D_2 v} \tag{1}$$

$$\overline{M}_N(t) = \frac{1}{\Sigma\ W_v/M_v} = \frac{D_1}{\Sigma\ W_v e^{D_2 v}} \tag{2}$$

In Hamielec's method, the original chromatogram uncorrected for axial dispersion, F_v, is used in place of W_v. The D_1, D_2 values then are not the true values but are "effective" values called D_1', D_2'. Thus, in Hamielecs method, equations (1) and (2) become;

$$\overline{M}_W(t) = \Sigma\ F_v D_1' e^{-D_2' v} \tag{3}$$

$$\overline{M}_N(t) = \frac{D_1'}{\Sigma\ F_v e^{D_2' v}} \tag{4}$$

The value of D_1' and D_2' are found using the broad standard. In order to calculate these values, equations (3) and (4) are combined and equations (5) and (6) are used.

$$\frac{\overline{M}_W(t)}{\overline{M}_N(t)} = \{\Sigma\ F_v e^{-D_2' v}\}\ \{\Sigma\ F_v e^{D_2' v}\} \tag{5}$$

$$\overline{M}_W(t) = D_1'\ \Sigma\ F_v e^{-D_2' v} \tag{6}$$

The standard is assumed to have "known" $\overline{M}_W(t)$ and $\overline{M}_N(t)$ values and these are used with its chromatogram F_v in equation (5) to find D_2' by a single-variable search technique. With D_2' known, equation (6) is used to calculate the value of D_1'. When an unknown polymer sample is then analyzed, these values along with F_v for the sample are used in equations (3) and (4) to calculate $\overline{M}_W(t)$ and $\overline{M}_N(t)$ for the polymer sample.

The Yau method proposes to calculate the true values D_1, D_2 by the same general technique by including a correction factor for axial dispersion (h) in the calculations. The modified equations for this system are given in equations (7), (8) and (9).

$$\bar{M}_W(t) = e^{-D_2^2/4h} \Sigma F_v D_1 e^{-D_2 v} \tag{7}$$

$$\bar{M}\ (t) = \frac{D_1 e^{D_2^2/4h}}{\Sigma F_v e^{D_2 v}} \tag{8}$$

$$\frac{\bar{M}_W(t)}{\bar{M}_N(t)} = e^{-D_2^2/2h} \{\Sigma F_v e^{-D_2 v}\} \{\Sigma F_v e^{D_2 v}\} \tag{9}$$

In these equations, $h = \frac{1}{2} \sigma^{-2}$ where σ^{-2} is the variance about the mean of a single species chromatogram. It must be determined beforehand by the analysis of a narrow standard.

These equations are handled in the same general fashion as in the Hamielec method. Equation (9) and F_v for the standard and an estimated h value are used to evaluate D_2 via a single variable search method, followed by the use of equation (7) or (8) to evaluate D_1. The unknown polymer is then analyzed by finding F_v and using D_1, D_2 and h in equations (7) and (8) to calculate $\bar{M}_W(t)$ and $\bar{M}_N(t)$.

Note that there is very little difference between the two methods except for the non-linear correction term $E = \exp(D_2^2/4h)$. However, depending upon the extent of dispersion, it may help to eliminate some of the bias in the Hamielec method (present when the dispersion is large), or it may cause more severe propagation of the sources of experimental error.

The ultimate test of any method of analysis must consist of assessing how well it minimizes both the bias and the variance to error propagation, these two factors often having to be traded off against one another.

SOURCES OF ERROR

In using the two GPC methods discussed, several sources of error appear in the combined calibration and analysis of unknown technique. These errors shall be discussed in turn.

i) Skewing

It is possible that the columns used lead to skewing, hence non-Gaussian chromatograms, which is not accounted for.

ii) Mismatched Standard and Sample Distributions

The standard and the unknown may differ in their distributions. This may show up as a differing amount of narrowness, a difference in the elution volume range at which the majority of polymer is observed or even that parts of the chromatogram for the unknown may lie outside the calibration curve produced by the standard. Yau et al(2) have suggested that the Hamielec method does not provide accurate results if the standard and unknown do differ in their distribution.

iii) Characterization of the Standard

During the development of the calibration curve, the $\overline{M}_N$, $\overline{M}_W$ values for the standard are assumed known from some other technique such as osmometry for $\overline{M}_N$ and light scattering for $\overline{M}_W$. However, these values will have error associated with them, perhaps as high as 10%, due to experimental error in the methods.(3,4)

iv) Replication Errors

The GPC chromatograms which are produced are not necessarily exactly the same from one analysis to the next. This could be due to environmental change such as a change in temperature or perhaps a change in the packing material with time. This leads to replication errors which affect both the replication of the standard and the unknown polymer chromatograms.

v) Dispersion Factor

Specifically for the Yau et al method it is possible that there are errors present in the value of h which is evaluated using narrow polymer standards. This could be due either to experimental error or due to lack of narrow standard for the polymer being analyzed. In the second case, this necessitates either estimating h from narrow polystyrene standards or making a reasonable guess of the value, both of which may cause significant errors perhaps as high as 50%.

Note that the effects of errors due to types (i) to (iv) may also be a function of the true h value in the Yau method. The correction factor used introduces non-linearity as discussed previously, and the degree of non-linearity may then depend to some extent on the value of h.

METHOD OF ANALYSIS

The basic idea of a Monte-Carlo simulation is to assume a polymer standard and some polymer samples with truly known properties ($\overline{M}_N$, $\overline{M}_W$) and with chromatograms F_V obtained from a GPC with no measurement error and a known dispersion factor h.

Simulated errors of a magnitude expected to occur in practice are then added to these true quantities ($\overline{M}_N$ and $\overline{M}_W$ of the standard F_V of the sample and the dispersion parameter h), and the effect that these errors have on the estimated final properties ($\overline{M}_N$, $\overline{M}_W$, $P=\overline{M}_W/\overline{M}_N$) of the sample is observed. A reasonably large number (50 in our analysis) of such simulations using different random errors are usually performed in order to get an estimate of the distribution of the results about the known true values which were used to generate them.

Any method of analysis will usually result in two types of error. A bias (a difference between the mean of the results obtained by the analysis and the true value) will usually be present due to the non-linearities of the methods and the approximations made in developing the theory. This has usually been the only factor looked at in discussions on various methods of testing GPC data. However, equally important is the error variance of the estimated properties. This source of variation results from the propagation of the various sources of random measurement errors into the final results. A convenient measure of the total effect of these two sources of error is the Mean Square Error (MSE) defined as the expected deviation between the estimated property (y_i) obtained by a given method and its true value μ, that is

$$\mathrm{MSE} = E(y_i - \mu)^2 \tag{10}$$

It is easily shown that this MSE can be expressed as the sum

$$\mathrm{MSE} = E(y_i - \bar{y})^2 + E(\bar{y} - \mu)^2$$

$$= (\text{error variance}) + (\text{bias})^2 \tag{11}$$

where $\bar{y}$ is the mean of the distribution of values y_i of the property.

Obviously one should compare methods by looking at their relative MSE's and not just at the bias components of them. Methods which serve to reduce the bias component of error (such as Yau et al's modification of Hamielec et al's method) may in fact increase the propagation error component. Such a situation is depicted in Fig. 1.

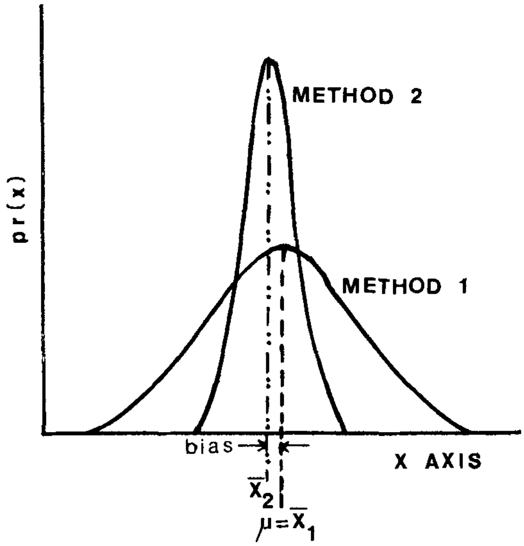

Figure 1: Comparison of two hypothetical GPC analysis methods. Method 1 may be more accurate for calculating true mean (i.e. no bias) at expense of larger variance than method 2.

In order to select a realistic "known" situation on which to base our simulation study and to obtain realistic estimates of measurement and replication errors, we made use of the extensive GPC data obtained by Garcia(5) on acrylonitrile polymers. The standard was a 94% acrylonitrile - 6% styrene copolymer provided by Monsanto with $\bar{M}_N$ = 38,800 (estimated using osmometry) and $\bar{M}_W$ = 117,000 (estimated using light scattering techniques). The unknown polymer samples consisted of 100% acrylonitrile polymer produced under a variety of conditions (varying temperature, initiator levels and conversions). A total of 100 chromatograms including a considerable number of replicates were available for evaluation of distributional shapes and replicate variations.

A number of distribution models were fitted to the chromatograms of both the standard and samples. As a result of this a Weibull distribution was used in the subsequent studies to represent the chromatograms of the standard and a Gamma distribution was used for the sample chromatograms. These were truncated after 60 points (in steps of .5 mℓ from starting elution volume) to avoid the problems inherent with infinite tailed distributions.

SIMULATION RESULTS

In order to evaluate the effect of each source of error (section 3) on the results of analyzing the GPC data by the two methods, a set of Monte-Carlo simulations were performed assuming only one source of error in each case. A final more realistic simulation in which all sources of error were simultaneously present was then performed. These are discussed in turn.

i) Skewing

The sample and standard chromatograms used in this study are skewed to the right as is the usual situation. Neither the Hamielec nor the Yau methods take such skewing into account and therefore they will both suffer from some biasing of the results.

ii) Mismatched Standard and Sample Distributions

As mentioned previously, Yau et al have shown that the bias component of the error in Hamielec's method depends to some extent on the chromatograms of the standard and sample being similar. In order to ensure that such a component of error is present in our analysis samples having chromatograms considerably different from that of the standard were used. (see Fig. 2). This pronounced difference should serve to inflate the bias component of the MSE of the estimates obtained by Hamielec's method.

iii) Errors in Characterizing the Standard

In evaluating the parameters of the calibration curve (D_1' and D_2' in Hamielec's method and D_1 and D_2 in Yau's) using equations (5), (6) or (7), (8), (9) respectively, it is assumed that the values of the number and weight average molecular weights for the standard are known. In fact, the errors inherent in obtaining these estimates for a broad standard by such usual methods as osmometry and light scattering would appear to be in the order of up to 10%(3,4). A conservative error of 6% (standard

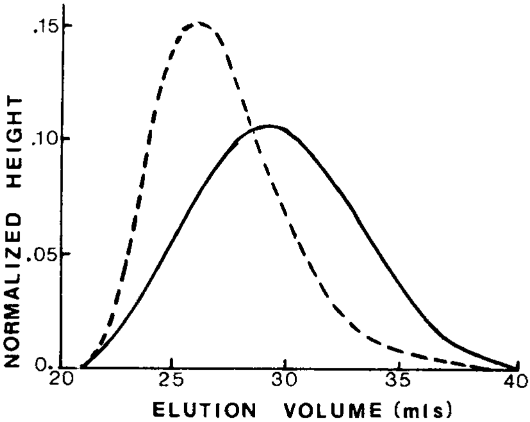

Figure 2: Comparison of chromatogram of standard and chromatogram of sample (standard —; sample --)

deviation) was therefore used in the studies reported here. Other simulations using 3% and 9% errors in the standard's molecular weights showed that the resulting propagation of error into the final estimates of the sample molecular weights simply varied linearly with the standard's errors.

To investigate the propagation of these errors in analysis of the standard a Monte-Carlo simulation was carried out in the following manner. Taking $\overline{M}_N$ = 38,800 and $\overline{M}_W$ = 117,000 (Monsanto values) to be the true molecular weight averages of the standard, a simulated pair ($\overline{M}_{N_{ST.}}$, $\overline{M}_{W_{ST.}}$) was obtained by adding random normal deviates (uncorrelated with σ = 6%) to the true values. Values of the calibration constants (D_1' and D_2' or D_1 and D_2) were then calculated using this simulated pair which were then used to obtain $\overline{M}_N$, $\overline{M}_W$ and polydispersity(P) estimates for the sample by both Hamielec's and Yau's method. No other sources of error were introduced. (ie. the chromatograms F_V and the dispersion factor h were assumed determined without error). This process was repeated 50 times to provide a sampling distribution for these estimates (for a given value of h).

Since the results will be dependent upon the amount of dispersion in the columns the entire simulation was then redone for 12 different values of dispersion as simulated by using 12 different values of the dispersion factor h in generating the data. (with h values of .05, .1, .15, .2, .25, .3, .5, .6, .7, .9, 1.38, 3.0)

The propagation error variances (VAR) and the mean square errors (MSE) of the sample $\overline{M}_N$, $\overline{M}_W$ and P were calculated in the following manner.

$$\mathrm{VAR}(y) = \frac{1}{49} \sum_{t=1}^{50} (y_i - \bar{y})^2 \tag{12}$$

$$\mathrm{MSE}(y) = \frac{1}{50} \sum_{t=1}^{50} (y_i - \mu)^2 \tag{13}$$

where $\bar{y}$ is the average of the sample property and μ is the true mean.

Since the same standard and sample chromatograms were used for the different assumed values of dispersion the true averages μ corresponding to each value of h were calculated using the dispersion correction $E(t) = \exp(+D_2^2/4h)$ with no errors at all assumed. These are shown in Table 1 for sample B7-5

Note that the molecular weight averages increase as h decreases until very small h values when there is a dramatic decrease. This indicates that the low molecular weight tail is being corrected first and only for very low h does the high molecular weight section become affected. Also, as h decreases, the percent correction for $\overline{M}_N$ (due to E(t)) differs from the correction for $\overline{M}_W$ (which is 1/E(t)). This could result in a very strong non-linear effect for small h especially in the polydispersity.

TABLE 1

True Values for Samples B7-5 as Function of h Value

h Value	$\overline{M}_N(t) \times 10^{-5}$	$\overline{M}_W(t) \times 10^{-6}$	$\overline{P}_t = \overline{M}_W/\overline{M}_N$	E(t)*
.05	3.24	1.52	4.69	31.46
.1	11.16	2.25	2.01	1.52
.15	10.35	2.16	2.09	1.25
.2	9.98	2.12	2.13	1.16
.25	9.77	2.10	2.15	1.12
.3	9.64	2.09	2.17	1.10
.5	9.40	2.06	2.20	1.05
.6	9.34	2.06	2.20	1.04
.7	9.30	2.05	2.21	1.04
.9	9.25	2.05	2.22	1.03
1.38	9.19	2.04	2.22	1.02
3.0	9.12	2.04	2.23	1.01
100,000	9.07	2.03	2.24	1.00

*$E(t) = e^{+D_2^2/4h}$ which represents the size of the correction made for axial dispersion. ie. 1.10 represents a 10% change in Hamielec's value.

In Fig. 3 the propagation error standard deviations (PE) and the root mean square error (RMSE) expressed as percentages of the true means, that is $(\sqrt{VAR}/\mu)*100$. and $(\sqrt{MSE}/\mu)*100$ respectively are plotted for the $\overline{M}_N$, $\overline{M}_W$ and P values obtained from the 50 simulation results using both methods of analysis.

The propagation error standard deviations for Hamielec's method was always slightly lower than those for Yau's but due to the bias component in the former method the RMSE's were always slightly larger. Since the correction factor, E(t), would not perfectly correct for dispersion in practice even if h were exactly known, the RMSE plots in Fig. 3 may be too low for Yau's method.

From Fig. 3, we see that there is less than a 1% difference in RMSE between these two methods for dispersion factors h greater than .5 for $\overline{M}_N$ difference (correction of about 5%), or .2 for $\overline{M}_W$

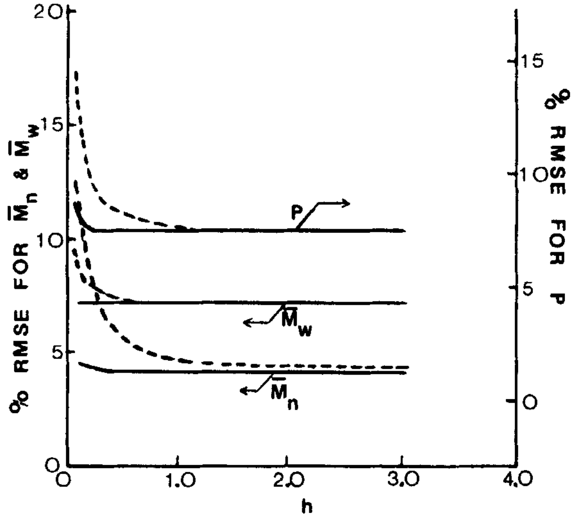

Figure 3: % RMSE curves for sample $\overline{M}_N$, $\overline{M}_W$ and polydispersity, P, resulting from 6% errors in $\overline{M}_N$ and $\overline{M}_W$ of the standard (Yau —; Hamielec --)

and P differences (correction of about 16%). Below these values, the RMSE difference becomes appreciably greater due to the increased bias in Hamielec's method when dispersion is large.

As far as the error magnitudes are concerned, Fig. 3 illustrates that 6% errors in $\bar{M}_{W_{ST}}$ and $\bar{M}_{N_{ST}}$ yield 4 to 5% errors in $\bar{M}_N$ and 7 to 8% errors in $\bar{M}_W$ and P for the sample.

This study also found that errors in $\bar{M}_N$ for the sample were most sensitive to errors in $\bar{M}_{N_{ST}}$, errors in $\bar{M}_W$ for the sample were most sensitive to errors in $\bar{M}_{W_{ST}}$ while errors in P for the sample were essentially equally affected by errors in $\bar{M}_{N_{ST}}$ and $\bar{M}_{W_{ST}}$.

iv) Errors in Replication of the Chromatograms

To characterize the type of replication errors inherent in the chromatograms of a sample injected a number of different times, truncated Gamma distributions were fitted to the replicate chromatograms obtained in Garcia's work.(5) The average distribution parameters (θ,r) obtained on three different replicated samples (with 4 replicates each) and the estimates of pooled variances (S_θ^2, S_r^2) and covariance ($S_{r\theta}^2$) of these parameters are given in Table II.

To evaluate the propagation effect of these chromatogram replication errors on the variance of the estimated sample molecular weight averages, the following procedure was followed. A set of 50 bivariate, normally distributed random deviates was generated with variance and covariances of the distribution parameters equal to those in Table 2. These were then added to the mean values of $\hat{\theta}$ and $\hat{r}$ for sample B7-5 (see Fig. 2) and a simulated set of 50 Gamma distributions were generated to represent 50 replicates of a sample chromatogram. Assuming that $\bar{M}_{N_{ST}}$ and $\bar{M}_{W_{ST}}$ were known without error, and the dispersion factor h also known, the calibration constants were obtained. For each simulated sample chromatogram the molecular weights and polydispersity were

TABLE 2

Samples Chosen for Study

Sample No.	Conditions	Parameter Estimates	Pooled Variances and Covariance	Correlation Parameter ρ
B7-5	X = .93 $[I]_o$ = .2 wt% T = 60°C	$\hat{\theta}$ = .774 $\hat{r}$ = 4.74	S_θ^2 = .0067 S_r^2 = .0953 $S_{r\theta}^2$ = .0138	.54
B8-1	X = .12 $[I]_o$ = .025 wt% T = 60°C	$\hat{\theta}$ = .755 $\hat{r}$ = 4.98		
H1-4	X = .98 $[I]_o$ = .05 wt% T = 80°C	$\hat{\theta}$ = .737 $\hat{r}$ = 4.63		

calculated. This was repeated for all 12 h values stated previously.

Fig. 4,5, and 6 display the RMSE and $\sqrt{VAR/\mu}$ values (PE) of $\overline{M}_N$ $\overline{M}_W$ and P respectively for the two methods. It can be seen that the RMSE for Hamielec's method is always less than the corresponding RMSE for Yau's method. In fact, for values of h below 1.0, the RMSE by Hamielec's method was even below the propagation error standard deviation for Yau's values. It is also interesting to note that a bias develops in Yau's method due to the nonlinear correction factor as illustrated by the difference between the propagation error variance curve and the RMSE curve for Yau, but this is only around a 1% difference at most and is fairly negligible.

The error magnitudes of the three properties differed markedly. For $\overline{M}_N$, the RMSE values were around 16 to 18% of μ for most h values. For $\overline{M}_W$, the error values were 13 to 15% while for polydispersity the RMSE values were normally only 9 to 10%. It

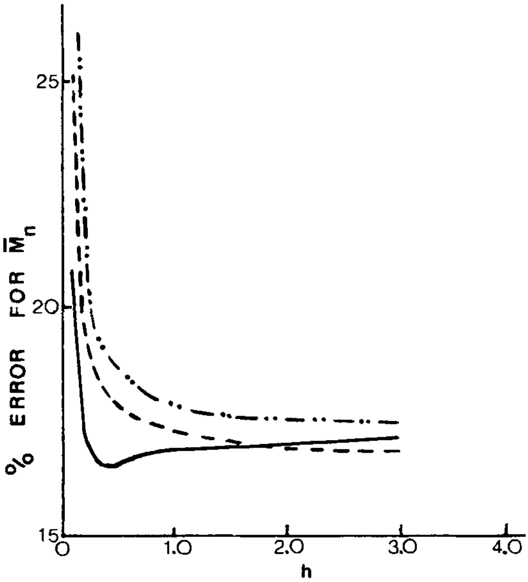

Figure 4: % error curves due to errors in replication for sample M_N (Hamielec RMSE —; PE for Yau --; Yau RMSE -••-••)

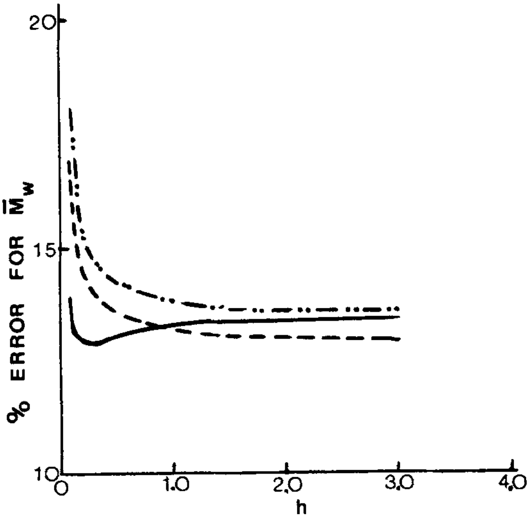

Figure 5: % error curves due to errors in replication for sample M_W (Hamielec RMSE —; PE for Yau --; Yau RMSE -••-••)

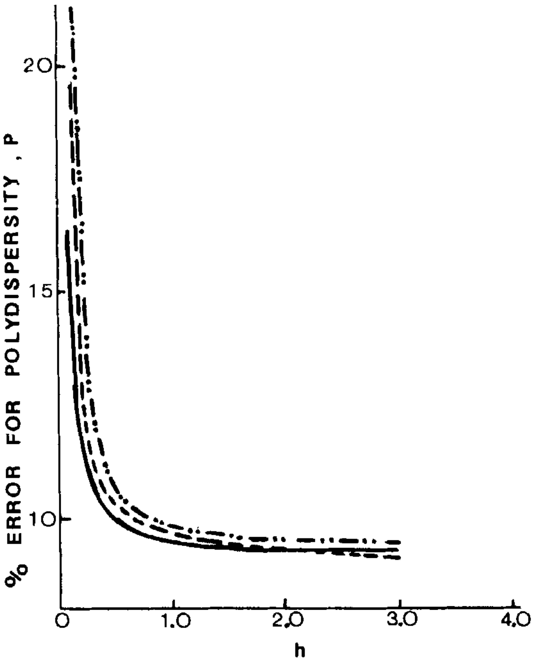

Figure 6: % error curves due to errors in replication for sample polydispersity (Hamielec RMSE —; PE for Yau --; Yau RMSE -••-••)

is also worth noting that for low h values (below .9) that errors in the replication of chromatograms cause more problems in Yau's method as shown by the very rapid exponential rise at low h values for RMSE.

v) Errors in Dispersion Factor

Due to the absence of narrow standards for a given polymer, either a narrow polystyrene standard is used to determine h or else an estimate is made. There is therefore a chance of large errors in h occurring, perhaps 50% or higher as stated earlier.

To examine the error propagation due to this source, a Monte-Carlo simulation was carried out as follows. For each of the 12 h values given earlier, a set of 50 random normal deviates with mean zero and σ_h = 1,2,3,6 or 9% of the given h were generated and added to the h value. For each of these, assuming $\bar{M}_{N_{ST}}$, $\bar{M}_{W_{ST}}$ as known, the calibration constants were calculated and then used to determine $\bar{M}_N$, $\bar{M}_W$ and P for the sample assuming no errors in the chromatograms. This provided sampling distributions for a given h and σ_h which were then analyzed as in the study of errors in the standard molecular weights.

To examine values of σ_h = 25, 50 or 100% of a given h, a slight alteration was necessary to prevent h from being negative. To handle these cases, random normal deviates of sufficient σ were introduced into $\ell n(h)$ to yield a set of 50 h values with the desired σ_h but all non-zero. The calculation procedure was then the same as for the normal set of h values.

Fig. 7,8, and 9 display the RMSE values for $\bar{M}_N$, $\bar{M}_W$ and P for the sample respectively for Hamielec's method as well as for Yau's

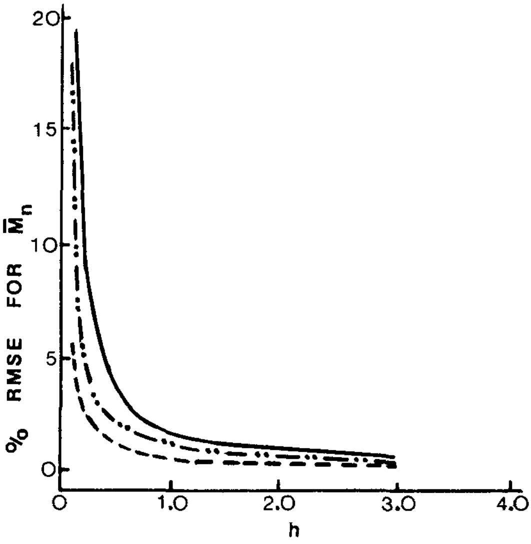

Figure 7: % RMSE curves due to errors in h for sample $\bar{M}_N$ (Hamielec RMSE —; Yau RMSE for 25% error in h ---; Yau RMSE for 50% error in h -••-••)

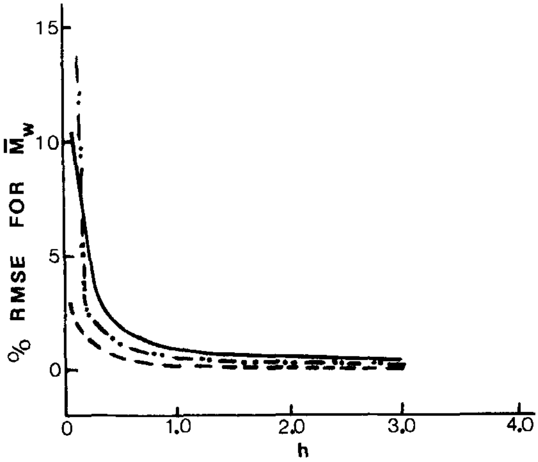

Figure 8: % RMSE curves due to errors in h for sample $\bar{M}_W$ (Hamielec RMSE ——; Yau RMSE for 25% error in h ---; Yau RMSE for 50% error in h -••-••)

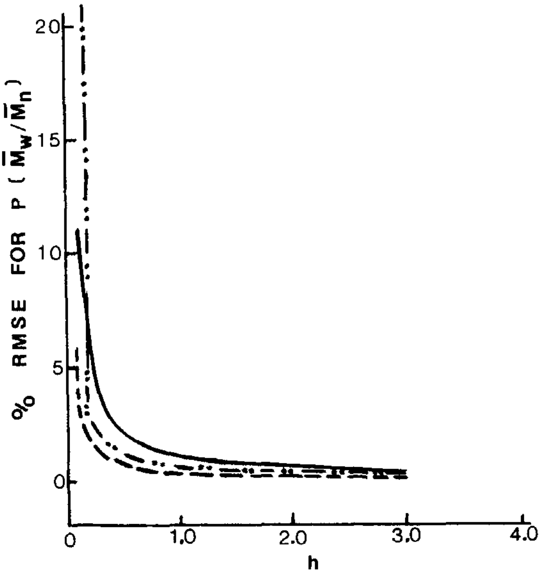

Figure 9: % RMSE curves due to errors in h for sample polydispersity (Hamielec RMSE ——; Yau RMSE for 25% error in h ---; Yau RMSE for 50% error in h -••-••)

method for values of σ_h = 25 and 50% of the h value. It is apparent that unless σ_h = 50% or more and h is less than .2 that RMSE for Yau's method is less than the RMSE for Hamielec's method.

Also, even for σ_h as high as 50%, for all h above .4 the RMSE values are always below 4% of μ and as such it would seem that changes in h are fairly insignificant.

This study also found that σ_h had to be around 60% or greater for most h values before RMSE for Yau would be larger than RMSE for Hamielec.

COMBINATION OF ALL SOURCES OF ERROR

To make final conclusions and comparisons, a Monte-Carlo simulation was carried out using all the sources of error together and was carried out as follows.

A vector of parameters was defined as $(\bar{M}_{N_{ST}}, \bar{M}_{W_{ST}}, h, \hat{\theta}, \hat{r})$ which were the parameters which the individual error analyses examined. Three sets of 50 random normal deviates were produced and added to the first three elements of the vector such that $\sigma_{\bar{M}_{N_{ST}}}$ = 6%, $\sigma_{\bar{M}_{W_{ST}}}$ = 6% and σ_h = 10% (and also σ_h = 100% using variation in ℓn h). Also, a bivariate set of parameters $(\hat{\theta}, \hat{r})$ were produced as discussed previously. For each vector, the first three values were used to calculate the calibration parameters which were then used to calculate $\bar{M}_N$, $\bar{M}_W$ and P for the sample produced by generating the chromatogram with the parameter values $\hat{\theta}$ and $\hat{r}$. The propagation error variance and RMSE value were arrived at as before with the procedure being repeated for all the h values for this study.

The results are shown in Fig. 10,11 and 12 for $\bar{M}_N$, $\bar{M}_W$ and P for the sample respectively. Again the RMSE for Hamielec's method is always below the RMSE for Yau's method. Also, it is apparent that changing the σ_h from 10% to 100% changes the RMSE values by less than 1% for all h values above .4, thus indicating the small effect errors in h have on the total error in this analyses.

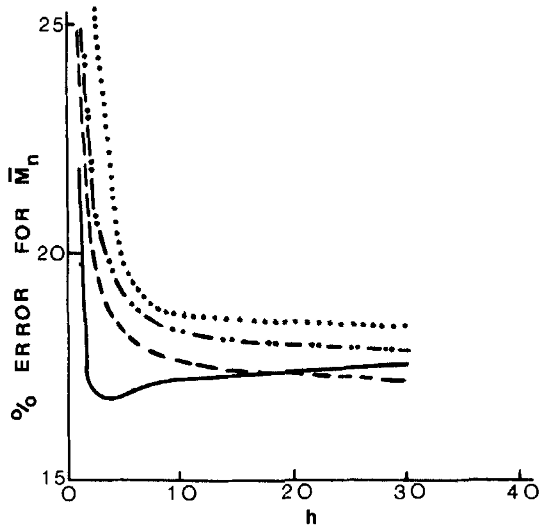

Figure 10: % error due to including all errors (comprising 6% error in M_N and M_W of standard, replication error and 10% or 100% errors in h) for sample $\overline{M}_N$ (Hamielec RMSE ——; PE for Yau with 10% error in h --; Yau RMSE with 10% error in h -••-••, Yau RMSE with 100% error in h ••••)

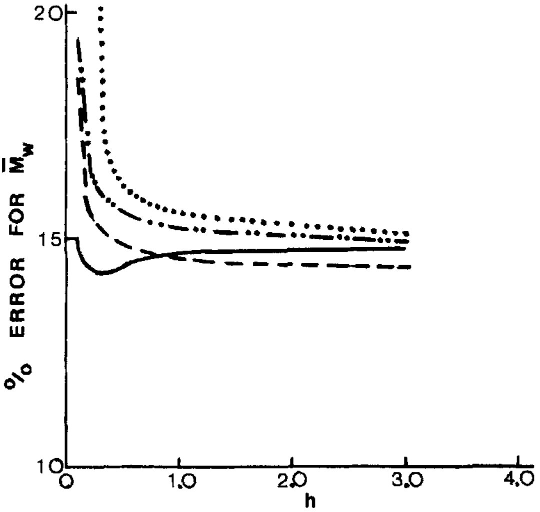

Figure 11: % error due to including all errors for sample $\overline{M}_W$ (Hamielec RMSE ——; PE for Yau with 10% error in h --; Yau RMSE with 10% error in h -••-••, Yau RMSE with 100% error in h ••••)

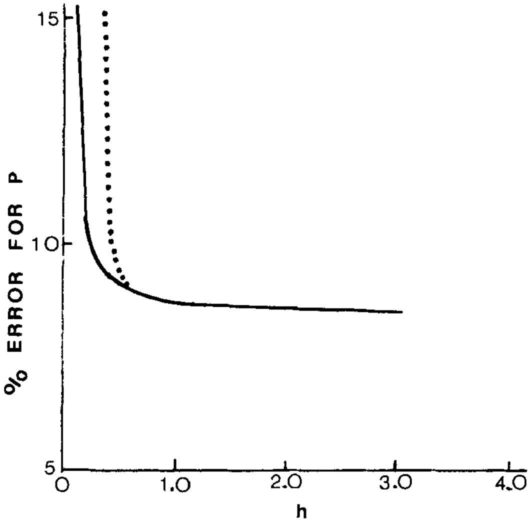

Figure 12: % error due to including all errors for sample polydispersity (Hamielec RMSE —; PE for Yau with 10% error in h --; Yau RMSE with 10% error in h -••-••, Yau RMSE with 100% error in h ••••)

The magnitudes of the errors vary widely. For $\overline{M}_N$, it is 17 to 19% for h above .5, for $\overline{M}_W$ it is 14 to 16% for h above .5, while for P it is 8 to 10% for the same h range.

Fig. 13 shows the various error results for the total source of error study as well as for the individual contributions for $\overline{M}_N$ for the sample. It is fairly obvious that the dominant effect in producing the total error is the error due to replication errors since the replication error curves lie so close to the total error curves. It would therefore appear that to reduce the final error in the results it is most profitable to try and achieve reproducability in the analysis.

CONCLUSIONS

Although one must be cautious in trying to generalize the results of a simulation study such as this, that has been performed

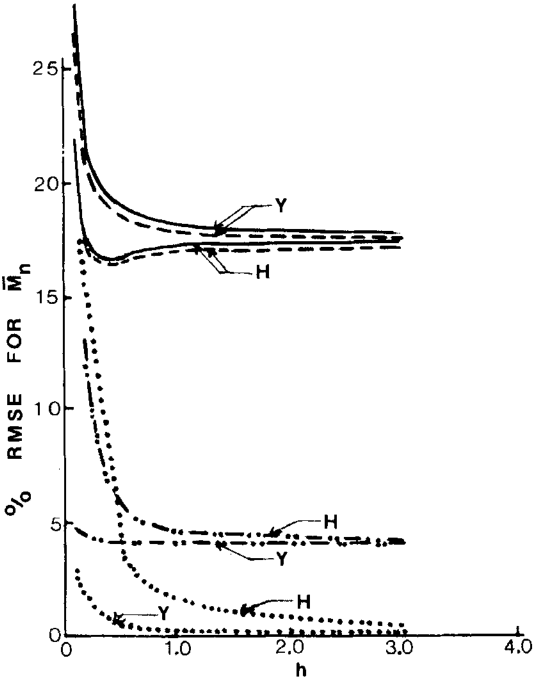

Figure 13: Comparison of RMSE magnitudes for the various errors for sample $\overline{M}_N$ where H = Hamielec, Y = Yau. (All errors included —; replication errors only ---; 6% errors in the standard $\overline{M}_N$ and $\overline{M}_W$ -••-••; RMSE for 50% errors in h study •••••)

on a particular system, a number of interesting points have become apparent.

In the total error analysis, it was found that errors of around 15% to 20% in the estimated sample values of $\overline{M}_N$ and $\overline{M}_W$ and around 10% in the polydisperisity (P) of a sample could easily result from small errors inherent in the characterization of the properties of the standard and from chromatogram reproducibility errors. The latter type of error was found to be the most important.

In comparing the linear effective calibration method of analysis proposed by Balke, Hamielec, et al(1) with Yau's modification of it(2), it was found that the correction for bias provided for in the latter method was often negated by increased propagation of experimental errors in this method. In fact, in terms of mean squared error, which includes both the contributions due to bias and to propagation of experimental errors, the simpler Hamielec method was usually as good as or better than Yau's modification of it.

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