

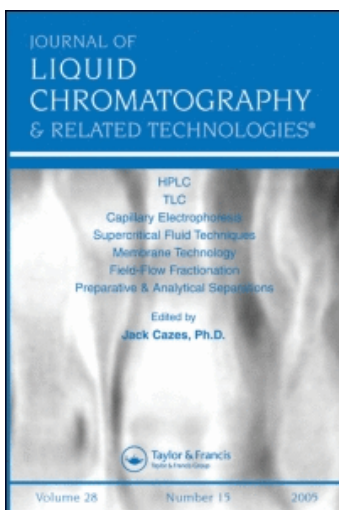
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### Reliability of Chromatographic Results in Determination of Narrow Molecular Weight Distributions of Polymers

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RELIABILITY OF CHROMATOGRAPHIC RESULTS  
IN DETERMINATION OF NARROW MOLECULAR  
WEIGHT DISTRIBUTIONS OF POLYMERS

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ABSTRACT

The influence of the procedure for numerical evaluation of chromatograms on the precision of the calculated molecular parameters of chromatographed polymers and the effect of the precision of the measured physical parameters that determine the resulting chromatogram are studied theoretically in this paper. It is shown by using model log-normal and Poisson molecular weight distributions that molecular parameters and polydispersity of polymers with narrow and ultra-narrow molecular weight distributions in particular can be determined by chromatographic separation methods with high reliability which cannot be obtained when other methods are used.

INTRODUCTION

Size exclusion chromatography (SEC), called alternatively gel permeation chromatography (GPC),

has already become a standard method for characterizing molecular weight distributions (MWD) of polymers. In comparison with classical methods, such as, e.g., precipitation fractionation and subsequent measurement of molecular weights of separated fractions, is manifold more rapid and average molecular weights and MWD are more precise. The precision of 2 - 5 % of molecular weights (1) that is usually obtained is entirely acceptable for the determination of molecular weights and polydispersity values of common polymers. The determination of molecular weights and polydispersity indices,  $I$ , of polymers with narrow and ultra-narrow MWD requires the use of high-efficiency chromatography methods. Thanks to the improvement in the technology of the preparation of columns for SEC, high efficiencies were obtained, and thus it was made possible to obtain in the separation of polymers with narrow MWD results with higher reliability. The invention of field-flow fractionation (FFF) has opened further possibilities of obtaining high selectivity and high resolution in fractionation of polymers (2,3).

As a result of this progress a question appears what are the present possibilities and limits of the determination of accurate and precise values of polydispersity of polymers with narrow and ultra-narrow MWD. If approximately fifteen years ago the separation of polymers into individual mers was practically not obtainable and obtainment of the polydispersity index of fractions,  $I = 1.2$ , by classical methods was considered to be a success, nowadays it is possible to fractionate into individual mers oligomers up to polymeri-

zation degrees ca. 15 - 25 and both to determine analytically and to obtain preparatively fractions with polydispersity values lower than  $I = 1.1$ . The question how real molecular parameters and polydispersity values calculated from experimental chromatographic data of polymers with narrow and ultra-narrow MWD are, has, however, not been studied. For physico-chemical studies of model synthetic polymers and for research of biopolymers in particular, the answer to this question is of fundamental significance.

### THEORETICAL CONSIDERATIONS

Chromatogram  $G(V)$  is a distribution curve in coordinates of the elution volume and of the detector response to an instantaneous concentration of an eluting macromolecular species. The position, the width and the shape of the chromatogram provide the information on average molecular weights and MWD of a polymer sample under separation and on the peak broadening caused by the injection, the columns and the detector. All kinds of the data mentioned above can be obtained by evaluating and interpreting an experimental chromatogram in a suitable manner. Each kind of the information obtained will suffer from the primary error of the measurement of physical quantities in the mentioned coordinates of the chromatogram. Let us notice first the coordinate of the elution volume which can be transformed into the coordinate of the molecular weight by using a calibration (1). The precision of the determination of molecular weights and polydispersity index obtainable by SEC method can be calculated theoretically.

The following relationship holds between the elution time and the partition coefficient

$$V_e = V_0 + K_{SEC} V_i \quad (1)$$

and for the relationship between  $K_{SEC}$  and the ratio of the size of the separated macromolecules of spherical shape to the size of a cylindrical pore it holds that

$$K_{SEC} = (1 - R/r)^2 \quad (2)$$

For the macromolecule the relationship can be written between the radius of an equivalent hydrodynamic sphere and the product of  $[\eta] \cdot M$ , proportional to the hydrodynamic volume,

$$(R/r)^3 = [\eta] \cdot M / ([\eta] \cdot M)_{excl} \quad (3)$$

By substituting from the Mark-Houwink equation

$$[\eta] = K M^a \quad (4)$$

and by rearranging it is obtained

$$(M/M_{excl})^{a+1} = (1 - \sqrt{K_{SEC}})^3 \quad (5)$$

The calibration curve of a system of columns for SEC is usually constructed in the coordinates  $\ln M$  versus  $V_e$  or  $K_{SEC}$ . The maximal selectivity  $d \ln M / d K_{SEC}$  is obtained in the point of inflexion of the calibration curve for which it holds

$$d^2 \ln M / d^2 K_{SEC} = 0 \quad (6)$$

Hence it can be written

$$\begin{aligned} d^2 \ln (M/M_{\text{excl}})^{a+1} / d^2 K_{\text{SEC}} &= \\ &= -1.5 (1 - 0.5 K_{\text{SEC}}^{-0.5}) / (K_{\text{SEC}} - \sqrt{K_{\text{SEC}}})^2 = 0 \quad (7) \end{aligned}$$

The point of inflexion is thus in coordinate  $K_{\text{SEC}} = 0.25$  and the slope of the calibration curve at this point of inflexion is

$$\begin{aligned} d \ln (M/M_{\text{excl}}) / d K_{\text{SEC}} &= \\ &= -1.5 / (K_{\text{SEC}} - \sqrt{K_{\text{SEC}}}) \cdot (a + 1) = \\ &= 6 / (a + 1) \quad (8) \end{aligned}$$

For the obtainable precision of the determination of the molecular weight expressed in terms of per cents of the deviation, % M, which depends on the reproducibility of the elution volume or, more precisely, on the absolute deviation from the correct value,  $\Delta K_{\text{SEC}}$ , it can then be written

$$\% M = \left| 1 - \exp \left( \frac{6 \Delta K_{\text{SEC}}}{a + 1} \right) \right| \times 100 \quad (9)$$

Percentage deviation of polydispersity index, % I, can also be calculated with the aid of Eq. (9). In this case,  $\Delta K_{\text{SEC}}$  has the meaning of the absolute precision of the difference in the partition coefficients that corresponds to the particular value of polydispersity. Table 1 presents the values of % M

TABLE 1

Influence of the Precision of Elution Volume Measurement on the Precision of Molecular Weights and Polydispersity Indices Calculated from SEC Data at the Maximal Selectivity

Precision of elution volume measurement (% rel.)	Precision of calculated molecular parameters		
	% M	% I at I = 1.1	% I at I = 2.0
1.0	7.30	0.095	0.70
0.5	3.60	0.048	0.35
0.1	0.71	0.009	0.07
0.01	0.35	0.005	0.03

and % I calculated theoretically (for two different values of I) for different values of relative errors of retention volumes, which are actually obtainable with respect to the precision of pumps or sensing elements measuring the flow-rate or the volume of the eluent passed.

For instance, if the elution volume is read with the precision of 0.5 %, which is the precision commonly reached with the use of commercial pumps, the obtainable precision of the determination of molecular weights is comparable with the maximal precision of the measurement obtainable by, e.g., light-scattering or osmometry (1). The precision of the determination of polydispersity, I, by means of SEC exceeds the precision obtainable by absolute methods by an order of magnitude (1).

When the obtainable precision of the detector response to the eluting solution of a polymer, i.e., the error of the reading of physical quantity of the other chromatogram coordinate is considered, it is advantageous to start from physical capabilities of the differential refractometer as the most universal detector of the polymer concentration in the eluate. The change in the refractive index of the polymer solution at a given concentration in comparison with the refractive index of the pure solvent will be determined by the relationship

$$\Delta R.I. = \frac{dn}{dc} \times c_I \times \frac{w_I}{w_X} \quad (10)$$

The mean value of the refractive index increment is usually  $dn/dc = 0.1$  (ml/g), the concentration of the polymer solution injected is usually  $c_I = 0.001$  g/ml, and the ratio of the width of the injection to the width of the eluting zone should be  $w_I/w_T = 0.05$  (4). The noise of the base-line of a good quality differential refractometer is  $5 \times 10^{-8}$  units of the refractive index and hence according to Eq. (10) the obtainable precision of the detector response in the vicinity of the maximum of the elution curve is approximately 1 %.

Approximately identical quantitative conclusions are valid for the evaluation of the results of the separations obtained by other methods, particularly by highly efficient FFF method. With FFF Eqs. (1) to (9) are not applicable owing to a sub-



stantially different separation mechanism. Since theoretical relationship between molecular parameters of separated polymers and retentions in FFF is not known, an analogous consideration is based on empirical calibration functions only. But it is possible to take into consideration comparative study of FFF and SEC (3) and fractionation power obtained in FFF (5) and to state on the basis of these results that the precision of the molecular parameters calculated from FFF data, determined by the precision of the coordinate of the elution volume of the fractogram, will be better than in SEC.

The evaluation of MWD, average molecular weights and polydispersity index from chromatograms is carried out by using a numerical calculation. The procedure for numerical processing of experimental chromatograms and the above precision of physical quantities that determine the position, the shape and the width of the chromatogram reflect in the precision of MWD and molecular parameters of polymers under analysis. This problem was already solved partially in the preceding papers (6,7), and will be analyzed in further detail, with particular respect to polymers with narrow and ultra-narrow MWD.

The log-normal distribution, which is a good approximation of SEC chromatograms of polymers with narrow MWD, and the Poisson distribution, which is the most probable distribution of commonly used polystyrene standards prepared by anionic polymerization, will be used for theoretical model calculations.

Molecular weights are calculated from chromatograms according to the following relationship

$$M_w = \frac{\int_0^{+\infty} M W(M) dM}{\int_0^{+\infty} W(M) dM} \quad (11)$$

$$M_n = \frac{\int_0^{+\infty} W(M) dM}{\int_0^{+\infty} M^{-1} W(M) dM} \quad (12)$$

and polydispersity index is calculated according to the relationship

$$I = M_w / M_n \quad (13)$$

The following relationship is valid between the chromatogram (fractogram) and the differential distribution

$$W(M) = G(V) \left( \frac{dV}{dM} \right) \quad (14)$$

The detector response, i.e., the values of  $G(V)$  suffer from the error  $\delta$  discussed in the preceding text. In order to evaluate average molecular weights, Eqs. (11) and (12) can be written in the following forms

$$M_w = \frac{\int_0^{+\infty} M[G(V) \pm \delta] dV}{\int_0^{+\infty} [G(V) \pm \delta] dV} \quad (15)$$

$$M_n = \frac{\int_0^{+\infty} [G(V) \pm \delta] dV}{\int_0^{+\infty} M^{-1} [G(V) \pm \delta] dV} \quad (16)$$

Log-normal weight MWD is defined by the relationship

$$W(\ln M) = \exp[-(\ln M - \ln M_{\max})^2 / 2\sigma^2] / (2\pi\sigma^2)^{1/2} \quad (17)$$

It applies further that

$$M_w = M_{\max} \exp(\sigma^2 / 2) \quad (18)$$

$$M_n = M_{\max} \exp(-\sigma^2 / 2) \quad (19)$$

$$\ln(M_w / M_n) = \sigma^2 \quad (20)$$

Log-normal differential distribution curve of molecular weights is demonstrated schematically in Fig. 1. It is obvious that it holds

$$\ln M = \ln M_{\max} \pm x\sigma \quad (21)$$

TABLE 2

Values of the Multiple of the Standard Deviation, Calculated for Relative Values of  $W(\ln M)$  Function with Regard to the Maximum from Eq. (23)

$W(\ln M)/W(\ln M_{\max})$ (% rel.)	5	2	1	0.5	0.2	0.1
x	2.45	2.80	3.03	3.26	3.53	3.72

It can be written further

$$W(\ln M) / W(\ln M_{\max}) = \exp(-x^2 / 2) \quad (22)$$

If readable level of the ratio  $W(\ln M) / W(\ln M_{\max})$  is adjusted to be equal to an assumed error or to the precision of the reading of the detector response, then the width of the distribution or integration limits can be calculated with respect to the maximum of the distribution curve, in which it makes sense to read  $W(\ln M)$  values according to the modified relationship

$$x = \sqrt{-\ln[W(\ln M) / W(\ln M_{\max})]}^2 \quad (23)$$

Values of  $x$ , i.e., multiples of the standard deviation,  $\sigma$ , (with regard to the maximum of the distribution curve) that define the range of  $W(\ln M)$  values exceeding the level of the adjusted error of the reading are listed in Table 2.

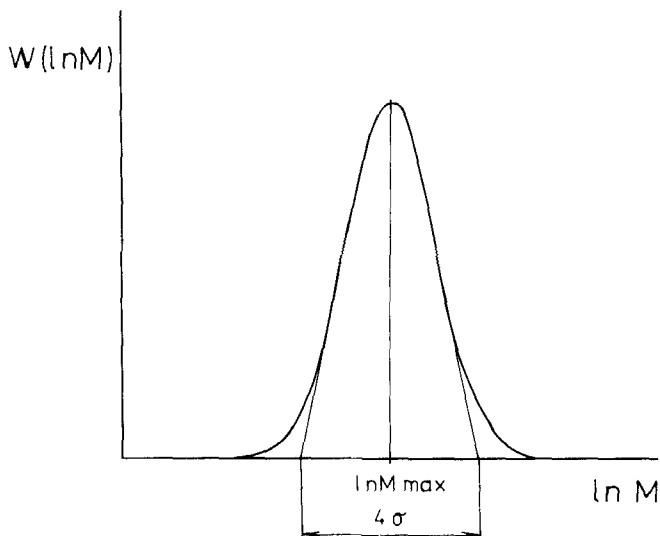


Figure 1. Log-normal distribution curve of molecular weights.

It is obvious that already the range  $\pm 3\sigma$  from the maximum is sufficient for the reading of  $W(\ln M)$  values provided that the precision of the detector response is  $\pm 1\%$  of the  $G(V_{\max})$  value.

Polydispersity index,  $I$ , can be calculated by using Eq. (20), e.g., by graphical evaluation of the  $\sigma$  values. Let us calculate what effect the error of the reading of  $\sigma$  will have on polydispersity. For the ratio of the apparent polydispersity index to the correct polydispersity index it then holds

$$I_a = I (\sigma_a / \sigma)^2 \quad (24)$$

Fig. 2 demonstrates the dependence of the percentage difference between the apparent and the real

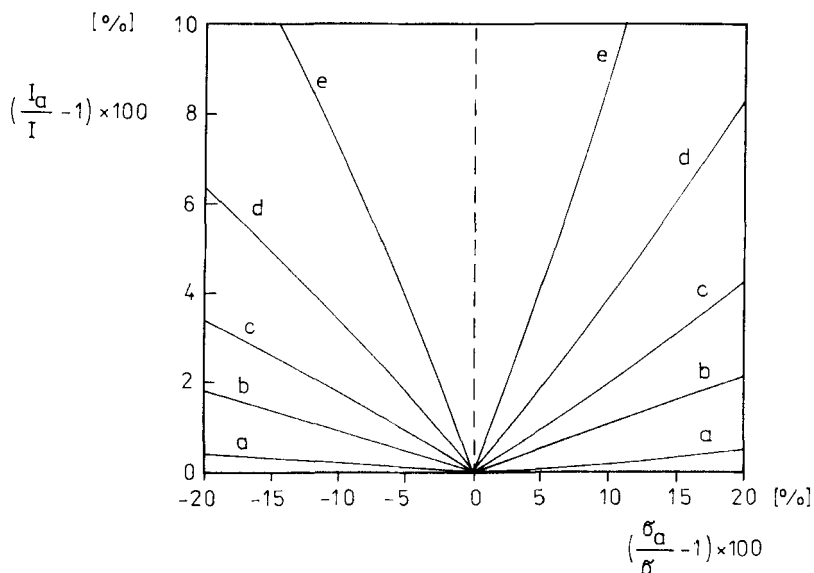


Figure 2. Dependence of the difference between the values of apparent and real polydispersity on the difference between the correct and the apparent values of the read standard deviation of the log-normal molecular weight distribution.

polydispersity values, i.e.,  $(\frac{I_a}{I} - 1) \times 100$  on

the percentage difference between the correct and the apparent values of  $\sigma$ , i.e.,

$$(\frac{\sigma_a}{\sigma} - 1) \times 100.$$

It is obvious from Fig. 2 that for extremely low polydispersity values,  $I = 1.01$ , even the error 20 % rel. of the reading of  $\sigma$  values has practically no effect,  $\sigma$  value can reliably be determined graphically with the precision of ca. 5 % rel., which is the precision satisfactory up to polydispersity values  $I = 1.2$ . For higher polydispersity

values a more precise reading of  $\sigma$  values is desirable.

In practice the distribution function is mostly neither known nor can be predicted and the values of  $M_w$ ,  $M_n$  or  $I$  must be obtained by numerical calculation from an experimental chromatogram. The procedure for the numerical processing of experimental data can influence final results. Important parameters of the numerical calculation which must be taken into consideration are the total width of the interval in which the reading of the peak heights in the chromatogram is taken and the subsequent calculation performed and the density of the chromatogram segmentation or the number of the heights read in the whole width of the chromatogram. These parameters and their influence on the calculated molecular weights were already studied in the earlier papers (6,7), nevertheless for the purpose of the present study it was necessary that general conclusions of the previous study should be given more precision within the interval of narrow MWD.

The calculation was made by using Eqs. (11) to (13) for the log-normal MWD defined by Eq. (17) in the range of polydispersity values  $I = 1.01 - 1.50$ . The results are presented in Table 3. The width of the interval was selected so that it was possible to demonstrate the effect of the interval expansion into the heights range comparable with experimental errors of the detection, as they were calculated in Table 2. The segmentation densities were selected so that the range of two orders of magnitude included all of the practical cases. Number of the points taken for individual cases in

TABLE 3

Dependence of Numerically Calculated Values of Polydispersity of Model log-normal Molecular Weight Distributions on Different Parameters of the Numerical Calculation

Segmentation density $\Delta\sigma$	Deviation of numerically calculated values of polydispersity from the given values %				
	Given value of I				
$\Delta$	1.01	1.05	1.10	1.20	1.50
Interval width $M_{\max} \pm n\sigma$ with $n = 4.0$					
1	-0.0001	-0.0006	-0.0016	-0.0054	-0.0334
0.1	-0.0009	-0.0061	-0.0155	-0.0448	-0.2149
0.01	-0.0011	-0.0071	-0.0182	-0.0521	-0.2456
Interval width $M_{\max} \pm n\sigma$ with $n = 3.5$					
1	-0.0007	-0.0045	-0.0117	-0.0353	-0.1810
0.1	-0.0054	-0.0324	-0.0776	-0.2037	-0.8201
0.01	-0.0063	-0.0374	-0.0889	-0.3212	-0.9157
Interval width $M_{\max} \pm n\sigma$ with $n = 3.0$					
1	-0.0043	-0.0265	-0.0649	-0.1764	-0.7514
0.1	-0.0240	-0.1341	-0.3013	-0.7201	-2.4426
0.01	-0.0271	-0.1508	-0.3369	-0.7983	-2.6658

Table 3 is  $2 \times (n/\Delta) + 1$ , i.e., 9, 81 and 801 points with the interval width  $\pm 4\sigma$ .

The results presented in Table 3 show clearly that for the evaluation of narrow MWD the neglect of the fractions eluting in the interval outside the limits of detectability (1%) has no signi-



TABLE 4

Dependence of Numerically Calculated Values of Polydispersity of Model log-normal Molecular Weight Distributions on the Error of the Reading of the Peak Height from the Base-line

Interval width $M_{\max} - M_{\min}$		Segmentation density $\Delta\sigma$	Error of G(V)	Deviation of numerically calculated values of polydispersity from the given values (%)		
$n_{\min}$	$n_{\max}$	$\Delta$	(%)	Given value of I		
				1.01	1.10	1.50
4.0	4.0	1.0	+1	+0.2033	+2.6222	+22.6088
		0.1	+1	+0.1423	+1.6990	+12.4027
3.0	3.0	1.0	+1	+0.0779	+0.8014	+3.7781
		0.1	+1	+0.0266	+0.2004	-0.1921
		1.0	-1	-0.0915	-0.9996	-5.9769
		0.1	-1	-0.0771	-0.8347	-4.9342
3.0	4.0	1.0	0	-0.0029	-0.0581	-0.7398
		0.1	0	-0.0155	-0.2546	-2.3549
4.0	3.0	1.0	0	-0.0015	-0.0085	-0.0452
		0.1	0	-0.0095	-0.0623	-0.3046

ficant influence. Similarly the segmentation density, provided that it is selected within rational limits, has no significant influence.

In addition, the influence of experimental errors of the detector response, i.e., of G(V) values, was studied with the use of Eqs. (15) and (16). These parameters have not been studied yet. The results of the calculation for the log-normal distribution are presented in Table 4.

The data in Table 4 show that not even systematic errors the magnitude of which is equal to the precision of the reading of G(V) values have any

substantial influence on the calculated polydispersity values, provided that the distributions are calculated in the boundaries within which the reading of  $G(V)$  values has still been reliable. The segmentation density of the whole interval has again only a minor effect. At the same time it is necessary to be aware of the fact that the error of all of the  $G(V)$  values read, either +1 % or -1 %, depending on the actual calculation, demonstrates extreme cases. In practice, this error will fluctuate for various  $G(V)$  values read and it will result in a certain statistical compensation of the set of all of the errors. The extreme cases, as calculated and presented in Table 4, can in practice correspond to a wrong adjustment of the base-line, which can be caused by the noise. In such a case the calculated deviations correspond to the maximal values when the absolute noise level reaches 2 % rel. of the detector response in the chromatogram maximum.

In practical evaluation of the chromatogram, the start and the end of the chromatogram reading need not be at the same distance from the maximum (in the present case judged from the width of the interval in both directions from the maximum), which can be caused by an uncertainty in precise adjustment of the base-line. That is why also this potential influence was evaluated numerically. The results are presented in the second part of Table 4. Even with the difference in the read interval width  $\pm 1\sigma$  both to the right and to the left from the maximum, which exceeds potential errors safely, the values of polydispersity calculated numerically are affected in an entirely negligible manner. For

illustration it is possible to compare analogous values from Table 3.

The Poisson distribution is defined by the relationship

$$N(P-1) = e^{-r} r^{(P-1)} / (P-1)! \\ P = 1, 2, 3 \dots \quad (25)$$

For the weight distribution it then holds

$$W(P) = P \cdot N(P) / P_n \quad (26)$$

For number and weight averages of the polymerization degree and for polydispersity it further holds

$$P_n = \sum_0^{\infty} N(P) \cdot P \quad (27)$$

$$P_w = \sum_0^{\infty} W(P) \cdot P = \left( \sum_0^{\infty} N(P) \cdot P^2 \right) / P_n \quad (28)$$

$$I = P_w / P_n = (r + 1) / r \quad (29)$$

Model Poisson distribution curve of molecular weights is illustrated in Fig. 3. In comparison with the log-normal distribution the Poisson distribution is in coordinates of molecular weights symmetrical enough, and its symmetry increases with increasing value of  $r$ . The log-normal distribution, on the other hand, is strongly asymmetrical in these coordinates; it is symmetrical in the coordinate of the logarithm of molecular weight. The Poisson distribution is,

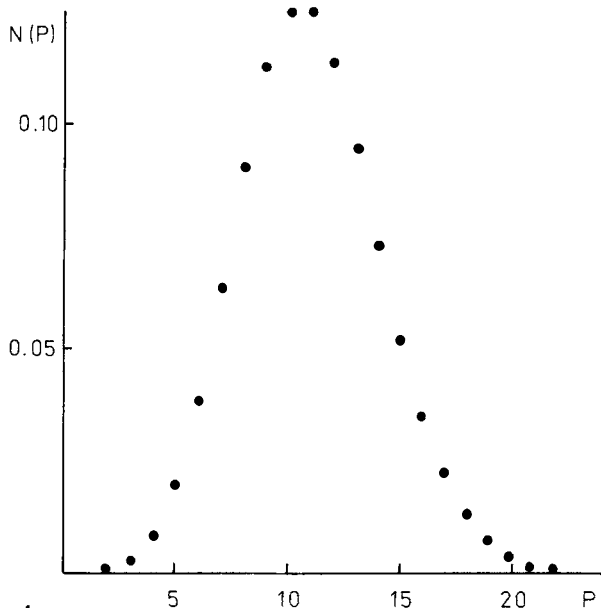


Figure 3. Poisson distribution curve of polymerization degrees. ( $r = 10$ ,  $I_{\text{theor.}} = 1.10$ )

moreover, a distribution function of discrete values of the polymerization degrees, which, understandingly, is a more correct image of physical reality.

The Poisson distribution, defined by Eqs. (25) - (28), was used together with Eqs. (15) and (16) for model calculations analogous to those in the above case of the log-normal distribution. With respect to the character of the Poisson distribution the basic parameters of numerical calculations were selected in a rather different manner. The initial values of parameter,  $r = 10, 30$  and  $100$ , correspond to the values of polydispersity,  $I = 1.10, 1.033$  and  $1.01$ , respectively. The width of the interval of the

TABLE 5

Dependence of Numerically Calculated Values of Polydispersity of Model Poisson Molecular Weight Distributions on the Error of the Reading of the Peak Height from the Base-line

Given value of $r$	Interval width		Error of $N(P)$ (%)	Deviation of numerically calculated from theoretical polydispersity values (%)
	$P_{\min}$	$P_{\max}$		
10	3	21	0	-0.1951
			+0.5	+0.0112
			-0.5	-0.4077
			+1.0	+0.2115
			-1.0	-0.6270
30	16	48	0	-0.0781
			+0.5	-0.0009
			-0.5	-0.1573
			+1.0	+0.0743
			-1.0	-0.2386
100	72	132	0	-0.0226
			+0.5	+0.0026
			-0.5	-0.0485
			+1.0	+0.0271
			-1.0	-0.0750

numerical calculation, i.e., the minimal and the maximal values of the polymerization degree,  $P$ , were selected so that the value of the function in the given point has just exceeded 1 % from the maximal value of  $N(P)$  function. This selection was again taken with respect to the precision of the reading of the peak heights in the chromatogram that is usually reached. In analogy with Eqs. (15) and (16), the effect of systematic errors of the reading of  $N(P)$  values was investigated. The results are summa-

rized in Table 5. The deviations of polydispersity values calculated by the procedure suggested above from the theoretical values calculated according to Eq. (29) are minimal and their expression in terms of per cents in Table 5 demonstrates clearly that with real assumed errors of experimental chromatograms it is possible to reach a high reliability of the calculation of polydispersity values.

### CONCLUSIONS

Numerical calculations of molecular parameters of model log-normal and Poisson molecular weight distributions showed clearly the quantitative extent in which the procedure for the calculation can affect the accuracy and the precision of the result. With the particular method of the calculation the manner in which it is performed does not introduce any significant errors into the result.

By analyzing decisive physico-chemical parameters of separations from the viewpoint of their reproducibility that can be obtained, the limits of reliability of the calculated molecular parameters of polymers with narrow and ultra-narrow MWD were found. It was observed that the existing instrumental and experimental techniques make it possible to determine these parameters with a high precision and reliability. From this viewpoint the chromatographic methods discussed above exceed the potentialities of absolute methods, such as light-scattering, osmometry etc. Molecular parameters and polydispersity of polymers with narrow and ultra-narrow distribu-

tions of molecular weights in particular can be determined entirely reliably, with the precision exceeding by an order of magnitude other methods of characterization that have been used so far.

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### LIST OF SYMBOLS

a            exponent of the Mark-Houwink equation

$c_I$	concentration of injected sample
$G(V)$	chromatogram
$I$	polydispersity index
$K$	constant of the Mark-Houwink equation
$K_{SEC}$	distribution coefficient
$M$	molecular weight
$M_{excl}$	excluded molecular weight
$M_{max}$	molecular weight corresponding to the maximum of the chromatogram
$M_w$	weight average molecular weight
$M_n$	number average molecular weight
$N(P)$	number distribution of polymerization degree
$dn/dc$	refractive index increment
$P$	Polymerization degree
$P_n$	number average polymerization degree
$P_w$	weight average polymerization degree
$R$	radius of equivalent hydrodynamic sphere of the macromolecule
$r$	radius of cylindrical pore
$R.I.$	refractive index
$V_e$	elution volume
$V_i$	total pore volume
$V_o$	total interstitial volume
$W(M)$	weight distribution of molecular weight
$W(P)$	weight distribution of polymerization degree



$w_I$	width of the injection
$w_x$	width of the elution curve
$x$	multiple of standard deviation of the elution curve
$\delta$	error of chromatogram height reading
$[\eta]$	intrinsic viscosity
$\sigma$	standard deviation of the elution curve