Column Fractionation of Polymers.   VII. Computer Program for Determination of Molecular Weight Distributions from Gel Permeation Chromatography*

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Synopsis

Gel permeation chromatography produces a type of differential molecular weight distribution directly and rapidly.   Conversion of these data to conventional molecular weight distributions and plots of distributions is time-consuming.   A computer program is described to perform these operations readily.   Input data from the automated chromatograph, elution volume, and recorder deflection are converted to unit sensitivity and base line corrections applied.   The curve is then numerically integrated and a calibration curve used to convert elution volumes into molecular weights.   Various calibration curves can readily be introduced into the program.   The output, in addition to tabulation of cumulative and differential molecular weight distributions, contains values of $\bar{M}_n$, $\bar{M}_v$, $\bar{M}_w$, $\bar{M}_z$, and $\bar{M}_{z+1}$.   Importantly, a reduced absolute area, i.e., area computed for unit sensitivity on a unit concentration basis, is tabulated.   An additional time-saving eature is the printing out of differential and cumulative molecular weight distribution curves and of a differential histogram.

Introduction

Gel permeation chromatography (GPC) affords a rapid method of obtaining differential molecular weight distributions.[1]   The data from an automated chromatograph[2] consist of a recording of polymer concentration C versus elution volume V.   The concentration is given directly provided that the difference in refractive index between solvent and solution is linear with concentration, a valid assumption at the low concentrations normally encountered.   The elution volume is usually an approximately logarithmic function of the chain length of the polymer molecule.   It is necessary, therefore, to transform these data into a concentration versus molecular weight curve, to convert this to both cumulative and differential distributions, to compute the various molecular weight averages, and to plot the resulting data in some convenient form.   The required computa-

tions are tedious. This paper describes a computer program to perform these operations readily.

Input Data and Computations

The recorder tracing provides the input data, consisting of a tabulation by pairs of peak counts, that is, elution volumes, versus recorder deflection. Readings may be taken at any frequency desired and need not be at uniform intervals. Thus, readings may be more closely spaced in regions of maxima and inflection points. The program will accept up to 200 pairs of points. The initial and final recorder readings at zero concentration define the base line. Other input information includes sample identification, concentration, recorder sensitivity, specification of the lower and upper molecular weight over which distributions are to be computed, the polymer molecular weight per unit chain length, and the exponent ϵ in an applicable Mark-Houwink molecular weight–intrinsic viscosity equation.

Thus, the basic data made available to the program consist of a concentration curve $C(V)$ and a reference or calibration curve $F(V)$, which assumes the standard form $\log L$ versus V, where L is the projected chain length of the polymer peaking at V. The program transforms these data to the O-chart line and removes any sloping base line before making any other computations on the data. Also, the calibration curve is replaced by a curve $G(V) = F(V) + \log M0$, where $M0$ is the molecular weight per Angstrom of projected chain length. Thus, $G(V)$ has the form $\log M$ versus V, where M is the polymer molecular weight. Provision is made for reading $G(V)$ in directly, in case a nonstandard calibration curve is required.

We define the function

$$A(V) = \int_{V_1}^{V} C(\nu)d\nu \Big/ \int_{V_1}^{V_0} C(\nu)d\nu \qquad (1)$$

which is the relative amount of polymer contained in the volume $V_1 - V$. This function is evaluated by a numerical integration subroutine. For output purposes a change of coordinates from V to M is made. This is given by

$$V = G^{-1}(\log M) \qquad (2)$$

where G^{-1} is the function inverse to G. The function printed and plotted as output is

$$a(M) = A(V) = A[G^{-1}(\log M)] \qquad (3)$$

This function gives the relative amount of polymer with molecular weights between M_1 and M, i.e., from the lowest molecular weight up to M and ranges from 0 to 1.

The distribution of this function, i.e., da/dM, is also evaluated and plotted versus M. By the chain rule for derivatives we have

$$\frac{da}{dM} = \frac{dA}{dV}\bigg|_{V_M} \cdot \frac{dG^{-1}}{d\log M} \cdot \frac{d\log M}{dM}$$

$$= \frac{C(V_M)}{\int_{V_1}^{V_0} C(\nu)d\nu} \cdot \frac{1}{(dG/dV)_{V_M}} \cdot \frac{\log e}{M} \qquad (4)$$

where $V_M = G^{-1}(\log M)$. The derivative dG/dV of the standard reference curve was computed externally to the program. Values intermediate to those stored in the program are obtained by linear interpolation. For nonstandard reference curves, the derivative is computed numerically within the program. For this reason, the nonstandard reference curves must be given at equal increments of V.

The moment ratios $\bar{M}_n$, $\bar{M}_v$, $\bar{M}_w$, $\bar{M}_z$, and $\bar{M}_{z+1}$ and also the reduced area α are computed from eqs. (5)–(10).

$$\bar{M}_n = 1 / \int_{M_0}^{M_1} (1/M)(da/dM)dM \qquad (5)$$

$$\bar{M}_v = \left[\int_{M_0}^{M_1} M^\epsilon (da/dM)dM \right]^{1/\epsilon} \qquad (6)$$

$$\bar{M}_w = \int_{M_0}^{M_1} M(da/dM)dM \qquad (7)$$

$$\bar{M}_z = \int_{M_0}^{M_1} M^2(da/dM)dM / \int_{M_0}^{M_1} M(da/dM)dM \qquad (8)$$

$$\bar{M}_{z+1} = \int_{M_0}^{M_1} M^3(da/dM)dM / \int_{M_0}^{M_1} M^2(da/dM)dM \qquad (9)$$

$$\alpha = \int_{V_1}^{V_0} C(\nu)d\nu / (\text{sensitivity·sample concentration}) \qquad (10)$$

Data Presentation

Output from the computer program contains, on the first page, all of the sample identification and the complete input data including the calibration curve and its derivatives and the concentration data both as read and as transformed. The second output sheet is shown in Figure 1. Here in the top line are given the five molecular moment ratios and the reduced area, α. The next two lines show a measure for the inhomogeneity of the polymer under investigation proposed by Schulz:[3]

$$U_n = (\bar{M}_w/\bar{M}_n) - 1 \qquad (11)$$

U_w and U_z are defined correspondingly. In the following lines another quantity is given which represents the absolute width of the polymer dis-

	Number	Viscosity	Weight	Z	Z + 1	Reduced Area
	MN	MV	MW	MZ	M(Z+1)	RED. AREA
	1.455E 05	1.643E 05	1.671E 05	1.890E 05	2.166E 05	9.000E 01
	UN		UW	UZ		
Inhomogeneities	1.482E-01		1.308E-01	1.461E-01		
	SIGMA N		SIGMA W	SIGMA Z		
Standard Deviations	5.603E 04		6.044E 04	7.222E 04		

POL WT	CUM AMT	D AMT/DM	POL WT	CUM AMT	D AMT/CM
1.862E 04	-C.	5.673E-08	1.296E 05	2.418E-01	7.144E-06
2.007E 04	3.909E-05	5.214E-08	1.397E 05	3.190E-01	8.155E-06
2.162E 04	1.563E-04	9.675E-08	1.505E 05	4.109E-01	8.705E-06
2.330E 04	3.522E-04	1.349E-07			8.546E-06
2.510E 04	2.247E-04	1.651E-07			7.701E-06
2.705E 04	9.718E-04	1.907E-07	1.883E 05	7.097E-01	6.318E-06
2.914E 04	1.403E-03	2.205E-07	2.028E 05	7.903E-01	4.749E-06
3.140E 04	1.546E-C3	2.613E-07	2.186E 05	8.535E-01	3.332E-06
3.383E 04	2.637E-03	3.063E-07	2.355E 05	9.004E-01	2.271E-06
3.645E 04	3.496E-03	3.475E-07			1.480E-06
3.928E 04	4.516E-C3	3.719E-07			8.725E-07
4.232E 04	5.668E-C3	3.874E-07	2.946E 05	9.710E-01	4.718E-07
4.560E 04	7.010E-03	4.007E-07	3.174E 05	9.791E-01	2.647E-07
4.913E 04	8.791E-03	5.791E-07	3.420E 05	9.844E-01	1.851E-07
5.294E 04	1.137E-02	7.826E-07	3.685E 05	9.888E-01	1.452E-07
5.704E 04	1.501E-02	9.870E-07			1.092E-07
6.146E 04	1.974E-02	1.153E-06			7.059E-08
6.623E 04	2.552E-02	1.274E-06	4.609E 05	9.970E-01	4.055E-08
7.136E 04	3.233E-02	1.388E-06	4.966E 05	9.980E-01	2.107E-08
7.688E 04	4.045E-02	1.569E-06	5.351E 05	9.986E-01	1.290E-08
8.284E 04	5.065E-02	1.874E-06	5.766E 05	9.991E-01	9.828E-09
8.926E 04	6.388E-02	2.262E-06	6.213E 05	9.995E-01	7.349E-09
9.618E 04	8.1C2E-02	2.729E-06	6.694E 05	9.938E-01	4.486E-09
1.036E 05	1.038E-01	3.452E-06	7.213E 05	9.999E-01	2.081E-09
1.117E 05	1.358E-01	4.560E-06	7.771E 05	1.000E 00	9.434E-14
1.203E 05	1.809E-01	5.874E-06			

Differential Molecular Weight Distribution

Cumulative Molecular Weight Distribution

Molecular Weight
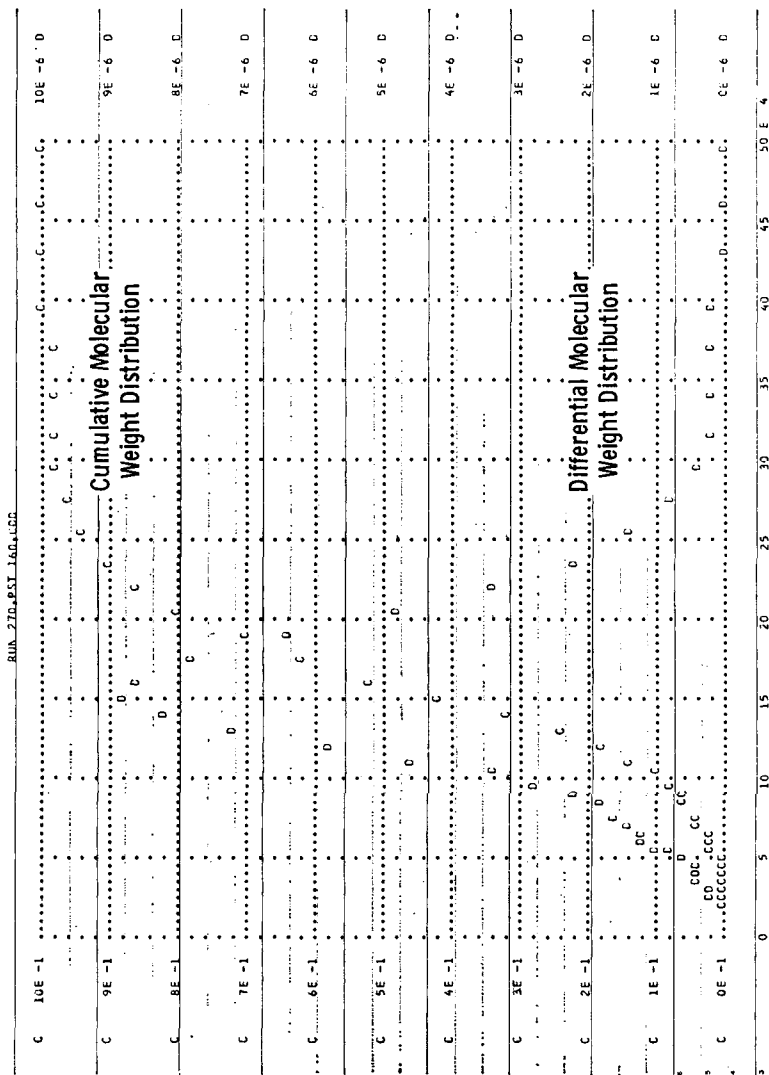
Fig. 1. Sample output of calculations.
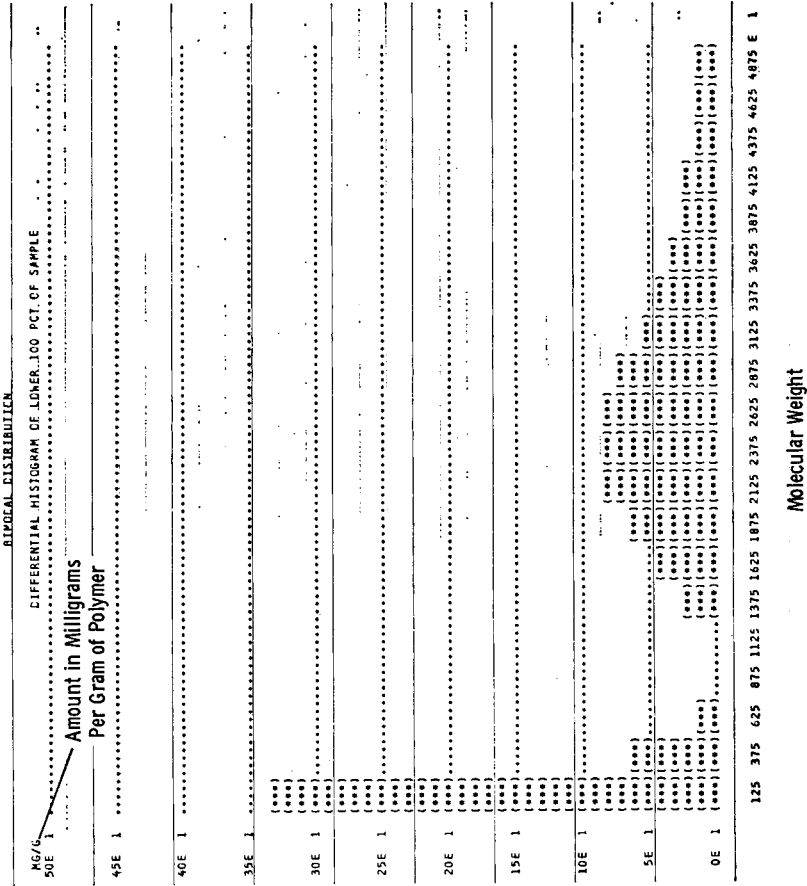
Fig. 2. Sample output of graphs.

Fig. 3. Sample output bimodal distribution, differential histogram.

tribution.[4] Sigma N is the standard deviation of the number distribution of the sample; the other values are defined correspondingly. This is followed by a tabulation of molecular weight, cumulative and differential distributions. Initially, the program terminated at this point. It soon became evident that the limiting step now was plotting the differential and cumulative distribution curves. Therefore, an additional routine was incorporated to produce approximate plots on the printer. A sample of such a plot is shown in Figure 2. Both the cumulative and differential curves are included on a single plot. The user can specify the plot limits. The scales are chosen automatically as 1, 2, or 5 times a power of 10 so as to obtain optimal resolution. The resolution is about 1%, which is adequate for most purposes. Additional plots of the lower ends of the distributions are printed out automatically until sufficient detail is visible around the maximum of the differential curve. The following output pages show a differential histogram of the entire sample (or of at least 90% of it) (Fig. 3). The figure demonstrates that the program is able to compute and plot bimodal distributions. A subsequent graph again shows the details around the maximum of the histogram.

TABLE I
Influence of Number of Points upon Calculation

Number of points	Calculated molecular weight averages					Reduced area α
	$\overline{M}_n$	$\overline{M}_v$	$\overline{M}_w$	$\overline{M}_z$	M_{z+1}	
72	67,420	274,600	305,800	694,700	1,050,000	251.1
54	67,230	274,600	305,900	696,900	1,057,000	251.0
37	67,360	276,100	307,800	704,400	1,071,000	251.3
19	66,930	279,300	311,900	727,000	1,118,000	251.3
10	64,550	287,500	323,600	809,600	1,294,000	251.6
5	57,420	280,900	317,600	825,700	1,340,000	254.3

An important feature of the program is the computation of the viscosity-average molecular weight. The Mark-Houwink exponent included in the input data is that for a polymer–solvent system in which intrinsic viscosity is determined in a separate experiment. This exponent is not necessarily that for the eluting solvent used in the GPC. Agreement between the calculated $\overline{M}_v$ and measured $\overline{M}_v$ ensures proper column calibration and the absence of degradation. A second important control is afforded by the reduced specific area α. For a given polymer–solvent fractionation system, this number should remain constant. By experience it was found that a 10% fluctuation of the data for a polymer-homologous series should be considered normal.

A test was carried out to determine the number of input pairs necessary to define the recorder output sufficiently. The results are shown in Table I. It was found that as little as five pairs, placed properly along the output curve, gave excellent results.

This program was coded in Fortran II for the IBM 7094 computer. Complete program instructions, source deck, and object deck are available on request.

References

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2. L. A. Maley, paper presented to Division of Polymer Chemistry, 148th American Chemical Society Meeting, Chicago, September 1964; *Polymer Preprints*, **5**, No. 2, 712 (1964).
3. G. V. Schulz, *Z. Physik. Chem.*, **B43**, 25 (1939).
4. G. Herdan, *Nature*, **163**, 139 (1949).

Résumé

La chromatographie par perméation sur gel produit un type de distribution différentielle de poids moléculaires directe et rapide. La conversion de ces résultats en distribution conventionnelle de poids moléculaire et les diagrammes de distribution prennent beaucoup de temps. Un programme est décrit en vue de faire ces opérations rapidement. Les données à fournir au départ du chromatographe automatique, le volume d'élution et la déflection de l'enrégistreur sont converties en vue de relier la sensibilité et les corrections des lignes de base appliquées. La courbe est alors intégrée numériquement et la courbe du calibrage utilisée en vue de convertir le volume d'élution en poids moléculaire. Les différentes courbes de calibrage peuvent aisément être introduites dans le programme. Le résultat, outre la tabulation de la distribution de poids moléculaire cumulatif et différentiel contient les valeurs de M_n, M_v, M_w, M_z et M_{z+1}. Une surface absolue réduite, c'ést-à-dire, une surface pour une sensibilité unitaire par unité de base de concentration est également tabulée. Un point important, permettant de réduire le temps est l'impression de courbes de distributions différentielle et cumulative des poids moléculaire et d'obtenir un histogramme différentiel.

Zusammenfassung

Gelpermeationschromatographie liefert direkt und rasch einen Typ einer differentiellen Molekulargewichtsverteilung. Die Umwandlung der Ergebnisse in die konventionellen Molekulargewichtsverteilungen und Verteilungsdiagramme ist zeitraubend. Es wird ein Computerprogramm zur raschen Durchführung dieser Operationen beschrieben. Die Eingabedaten vom automatisierten Chromatographen, das Elutionsvolumen und die Recorderablenkung werden auf Einheitsempfindlichkeit ungewandelt und Basislinienkorrekturen angebracht. Die Kurve wird dann numerisch integriert und eine Eichkurve zur Umwandlung der Elutionsvolumina in Molekulargwichte verwendet. Verschiedenartige Eichkurven können leicht in das Programm eingeführt werden. Der Computer liefert, neben einer Tabellierung der kumulativen und differentiellen Molekulargewichtsverteilung, Werte für M_n, M_v, M_w, M_z und M_{z+1}. Als eine wichtige Grösse wird ein reduzierte absolute Fläche, d.h. eine für Einheitsempfindlichkeit von einer Einheitskonzentrationsgrundlage berechnete Fläche tabelliert. Ein zusätzliches Zeit sparendes Charakteristikum ist das Ausdrucken von differentiellen und kumulativen Molekulargewichtsverteilungskurven und eines Differentialhistogramms.