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Application of GPC to Studies of the Viscose Process. I. Evaluation of the Method*

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Summary

This is the first part in a series of papers describing the application of GPC to studies of the viscose process. In this part the procedures used are described. For these studies THF solutions of nitrocellulose were used. Modifications were made to the standard nitration procedures, resulting in improved efficiency. The importance of sampling homogeneity was studied and precision was obtained. In addition, a computer program to handle the data was developed.

INTRODUCTION

Although chromatography has been used extensively to separate mixtures of organic compounds, only recently has it been used to separate polymers. In conventional liquid–liquid chromatographic systems, the separation is generally based on differences in the chemical affinity of the materials being separated for each of the liquid phases involved in the system. With large polymer molecules, the differences in affinity are so small that efficient separations cannot be achieved.

The idea that separations on the basis of size alone were possible in a chromatographic-type system was first suggested by the observation

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that macromolecules (i.e., cellulose xanthate, lignin sulfonic acid, etc.) were not retained on ion exchange resins (*1*) of the polyvinyl benzene-styrene type even though they had ionic functional groups. Similarly, certain sugars, glycols, and other organic molecules with no ionic groups were held up or completely absorbed in ion exchange columns (*2*). Studies of the relation between the method of preparation of the resin and these phenomena led to the conclusion that small molecules could be retained in the interstitial portion of the resin bead and, conversely, total rejection of the molecule would occur if the molecular dimensions exceeded the dimension of the interstitial portion (*3*).

Experimentation then turned to studies of controlling the pore or interstitial size of polystyrene gels. This can be done by controlling the concentration of diluent during the cross-linking of the resin. By varying the amounts and nature of the diluent, it is possible to produce rigid cross-linked polymers with any desired interstitial dimensions (*4*). Calculated average pore size dimensions on commercially available materials of this type vary from 45 to 10^7 Å. Similar materials can also be prepared from polydextrans, polyacrylamide, etc. These materials will separate macromolecules on the basis of molecular size (*5*).

The mechanism of separation is not entirely clear. There is some evidence of swelling when the resin bead is placed in a solvent. This leads to the title "gel," although in the normal sense of the word it is not a gel. As the liquid phase containing dissolved polymer passes through a column filled with these swollen resin beads, the polymer molecules permeate into those parts of the beads not mechanically barred by size restrictions. The higher molecular weight molecules with their larger dimensions have a greater restriction as to their path, whereas the lower molecular weight molecules can permeate into the beads and are thus "held up" longer on the column. The result is a separation with the higher molecular weight material eluting from the column first. The pattern of retention resembles a logarithmic decay mechanism. For the separation to occur, the "gel" and solvent must be similar in polarity to avoid the possibility of selective association with either phase. Specific strong association between the polymer and the resin beads also must be avoided.

The usual chromatographic column system consists of a series of columns loaded with polymer beads of decreasing interstitial dimensions. Thus in the first column, all of the molecules may permeate into the beads, with the probability that some rejection of the higher

molecular weight molecules occurs. In the next column, total rejection of the highest molecular weight molecules may occur with some rejection of intermediate molecular weights, and so on through the columns. The choice of the proper range of columns depends on the ranges of molecular dimensions being separated.

As in all liquid–liquid chromatographic systems, a suitable detector for the presence and amounts of polymer in the effluent of the column is a problem. One method which has gained wide acceptance uses a differential refractometer. Available commercial units are capable of indicating reproducibly a change in the refractive index of 10^{-7}. Even this remarkable sensitivity is not adequate unless a sufficient difference in refractive index exists between the solvent and solute. The generality which can be made is that a difference of at least 0.1 must exist, a situation which generally can be met with most polymers.

FRACTIONATION OF CELLULOSE

It has long been recognized that a knowledge of the molecular weight distribution is necessary for the complete characterization of cellulose. A large number of attempts have been made to secure this information on various cellulose derivatives. The methods generally have been those of fractionation into fractions of narrower molecular weight distribution, which are then characterized by the available methods, and the construction of the distribution curve using the weight and molecular weight of these fractions. For various reasons which will be discussed later, these results have been unimpressive. Almost all of the work on fractionation methods was done before 1945 with relatively little success. It was realized that a new approach to the problem had to be developed if any progress was to be made, owing to the inadequacies of the existing techniques.

The first major problem encountered with fractionation of cellulose is that it is soluble in a very limited number of solvents, and rapid degradation occurs in most of these. Those in which it is soluble with minimal degradation are complex mixtures—cuene, cadoxene, zincene, ferric tartrate complexes, etc. It is difficult to find cellulose nonsolvents which are miscible with these systems and which will result in a precipitation on a molecular distribution basis. A limited success has been obtained using glycerin or one of the glycols as the nonsolvent, but it is difficult to remove the precipitated fraction due to the high viscosity of the system. Turbidimetric techniques have been unsuc-

cessful because the refractive index of the solvent-nonsolvent mixture is very close to that of cellulose, and it is very difficult to see the precipitated material. Many of the difficulties cited above can be eliminated if a soluble cellulose derivative is used, and most attempts to fractionate cellulose have been made using the nitrate derivative.

The use of the nitrate derivative is justified by the claim that *no* degradation occurs during nitration. This is questionable since the procedures used to study degradation of cellulose are relatively insensitive to small changes, and it is known that almost anything done to cellulose can result in degradation. The operations in the nitration which could lead to degradation are the mechanical opening of the sample and the dilution which occurs during washing to remove the acid.

The procedure for fractionation of cellulose which has gained the widest acceptance is to dissolve cellulose nitrate in ethyl acetate, acetone, or a similar solvent and then fractionate into approximately 30 fractions by precipitation using ethanol or water as the nonsolvent (*6*). As discussed previously, this leads to a series of distributions which are weighed and characterized by measurement of the intrinsic viscosity. These fractions can have a distribution almost as wide as that of the starting material. For this reason, several refractionations are usually run. The validity of the results obtained using this technique (*7*) is questionable. The method will show differences between two extremes, like pulp and a rayon, but is of little value when the differences are small.

Fractional solution techniques have been attempted on cellulose. These techniques, which involve successively leaching with solvents of increasing dissolving power, appear very attractive. Experimentally it has been found that equilibrium is reached very slowly and, in fact, may never be reached. There is no question that better results may be obtained using the fractional precipitation method.

A number of other possible fractionation methods have been considered. These and the techniques of fractional precipitation and solution have been reviewed by Schneider (*8*).

Since the introduction of gel permeation chromatography (GPC) in 1964 (*5*) as a rapid method of fractionating polymers, several papers describing the application of GPC to cellulose derivatives have appeared. Papers by Segal (*9*) and by Rinaudo and Merle (*10*) report the results of studies of nitration methods with the conclusion that the

nitrating acid composition has little or no effect on the GPC fractionation. Detailed studies of calibration methods have been made by Segal (*11*), and Meyerhoff (*12*), and Huang and Jenkins (*13*). The idea of a universal calibration for GPC has received considerable attention, although in 1965 Meyerhoff (*14*) had concluded that the GPC behavior of polymers of different structure cannot be generalized on the basis of chain length. Huang and Jenkins (*13*) prepared samples for GPC calibration by precipitation fractionation of cellulose nitrate and gamma-ray irradiation of wood cellulose. Their calibration curve differed significantly from the curve derived using polystyrene standards.

Applications of GPC to cellulose and cellulose derivatives have been made by Alexander and Muller (*15*), Segal (*16*), Brewer and coworkers (*17*) and Rinaudo and Merle (*10*). In these papers the molecular weight distribution curves for cellulose and cellulose derivatives from different sources have been compared.

The objective of the research reported in this series of papers was to study the changes in the molecular weight distribution during the viscose process and in the use of the products. Therefore the concern was for reproducibility and significance of observed changes in the GPC curves, rather than measurement of the absolute distribution. The need for a data presentation format which was numerical instead of graphical was considered to be of prime importance. In addition, it was also desirable to reduce the personnel time per analysis to as low a level as possible. This paper describes the preparation of cellulose nitrate especially for GPC, an evaluation of the variable in the procedure, and a description of a computer program to handle the data.

EQUIPMENT

A Waters Gel Permeation Chromatograph Model 200 with the automatic sample injector was used for all the studies. Four high resolution columns containing Styragel of porosity 10^6, 10^5, 10^4, and 10^3 Å were used. The eluting solvent was tetrahydrofuran (THF) containing the normal level (0.1%) of stabilizer. The THF was not recycled. Since gelatination occasionally occurs in the sample loops, an extra 7 μ sintered steel filter has been added in the line between the sample loop and the front end of the first column to protect the columns.

METHODS

Nitrating Acid Preparation

The ASTM procedure (*18*) has been modified to eliminate some of the safety hazards, to permit more rapid mixing, and to avoid the preparation of excessive amounts of the acid. The actual procedure used is as follows.

a. The contents of a 1-lb bottle (453 g) of 90% nitric acid are poured carefully into a 2-liter Erlenmeyer flask.

b. The flask is placed in a 3-liter stainless steel beaker, and ice is packed around it.

c. The beaker with the flask is placed on a magnetic stirrer, and a Teflon stirring bar is added.

d. After cooling with stirring for at least 10 min, 187 g of phosphorus pentoxide is added very slowly. This step should take at least 30 min. Be careful not to add any P_2O_5 which shows evidence of being moist.

e. After the P_2O_5 addition is completed, the flask is stirred for at least 1½ hr, adding ice around the flask as necessary.

f. Transfer the nitrating acid to a 1-liter glass-stoppered reagent bottle, and refrigerate until use.

g. This mixture should be used with 48 hr. Any solid separating or noticeable darkening indicates that the acid should be discarded.

Cellulose Sample Preparation

If a pulp sheet is being used, shred or open in a Waring Blendor several grams of sample. If yarn or film, cut into quarter-inch pieces. Powders are used as is. The samples are dried overnight at 50° in small beakers or weighing bottles in an air oven.

Nitration

a. Weigh 50 mg of sample into a 100-ml weighing bottle.

b. Add 25 ml of ice-cold nitrating acid.

c. Place in an ice bath for 60 min.

d. Swirl at 10 min intervals to insure good mixing.

e. Rapidly *but carefully* pour the contents of the weighing bottle into a 60-ml coarse sintered filter funnel, sucking the acid off as rapidly as possible into a 2-liter suction flask.

f. Fill the weighing bottle with cool distilled water, and pour

rapidly over the sample on the filter. Any additional sample adhering to the weighing bottle is rinsed into the funnel with additional water.

g. Wash the sample on the filter with 1 liter of distilled water, adding the water to the funnel with the suction off and then applying a vacuum to the suction flash to remove the water.

h. Place the sample on the sintered glass filter funnel in the oven at 50° and allow it to dry overnight.

i. If yields are desired, a tared filter may be used.

Solution Preparation

Weigh 50 mg of the nitrated cellulose on weighing paper and transfer to a 60-ml glass-stoppered Erlenmeyer flask. Add 50 ml of THF from the storage reservoir of the GPC instrument. For rapid solution, stir on a magnetic stirrer—otherwise allow to dissolve overnight with occasional shaking. Examine the solution for gel particles and discard if further mixing does not result in a good solution. Filter, using the pressure filter apparatus supplied by Waters Associates, and collect the sample in a 60-ml glass-stoppered bottle. Rinse the filter with THF before and after each sample to avoid contamination of samples.

Sample Injection

The syringe is rinsed with a small amount of the sample. Approximately 4 ml of the sample is drawn up into the syringe, and all air bubbles are removed. The solution is injected slowly into the sample loop, displacing the solvent which is in the loop. The 4 ml of sample is sufficient to wash and fill the loop. The sample advance button is pressed, and when the next loop is in position, the next sample is injected. This is continued until all six loops are filled.

STANDARD CURVE

The standard curve used for this study was prepared by nitration and chromatography of a series of pulp, yarn, and Avicel microcrystalline cellulose samples. The elution volume of the peak of the GPC curves for each sample was plotted against log $\overline{DP}$ values obtained on the samples by the viscometric method (ASTM). This curve is reproduced in Fig. 1. It was recognized that the samples were of relatively wide distribution and that this method is not an ideal way to establish the standard curve. Some samples showed evidence of

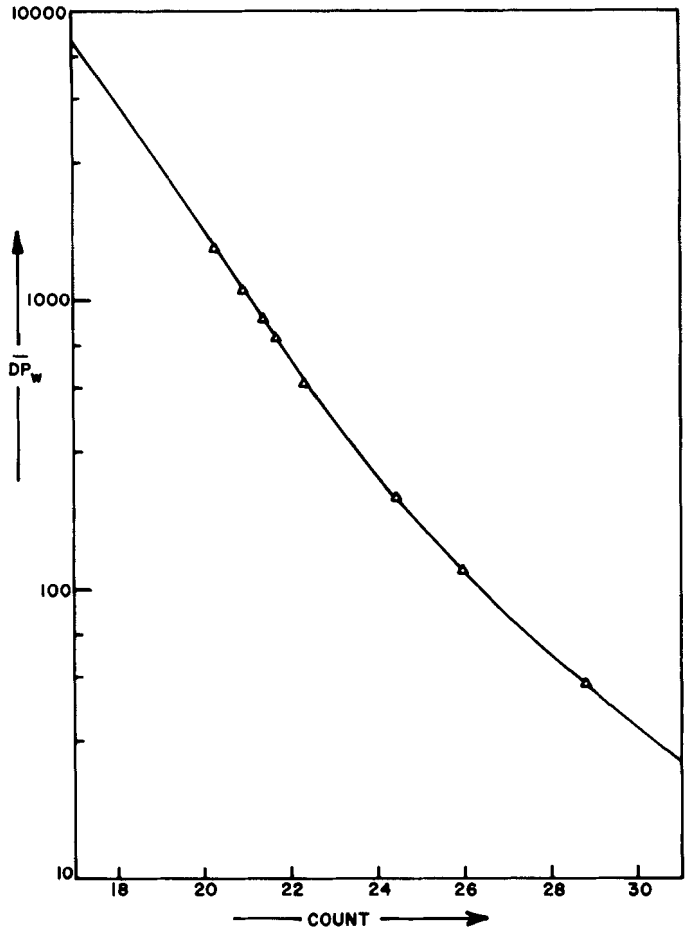

FIG. 1. GPC standard curve for cellulose.

being bimodal, and these values were not considered in plotting the curve. Weight-average DP calculated from GPC curves using this standard curve is in the same order of magnitude as that obtained by the viscometric method (Table 1).

DATA HANDLING

Like any other chromatographic curve representing the separation of a mixture of components, visual comparison of GPC curves is

TABLE 1

Comparison of Weight-Average DP Using GPC and $\overline{DP}$ as Determined Viscometrically

Sample	$\overline{DP}_w$	
	GPC	Viscometric
A	1173	1040
B	1168	1045
C	1046	970
D	1011	890
E	934	755
F	903	740
G	789	660
H	654	600
I	641	535
J	498	350
K	215	245
L	178	200

qualitative. Quantitative information about the molecular weight distribution and any changes that may result during processing can be obtained from a detailed statistical analysis of the curves. This analysis was accomplished using a computer program originally devised by Chevron which has been extensively modified. The parameters calculated include:

the average molecular weights calculated as the first moment, $\mu^{(1)}$, of the particular distribution functions, $N(M)$, $Z(M)$, etc.

$$\mu^{(1)} = \bar{M}_x = \frac{\Sigma N_i M_i^{(x+1)}}{\Sigma N_i M_i^x}$$

when $x = 0$, $\bar{M} = \bar{M}_n$
1, $\bar{M} = \bar{M}_w$
2, $\bar{M} = \bar{M}_z$
3, $\bar{M} = \bar{M}_z + 1$

the polymolecularity functions,

$$U_x = \frac{\bar{M}_{(x+1)}}{\bar{M}_x} - 1$$

and the distribution width indices

$$\sigma_x = \sqrt{M_x M_{(x+1)} - M_x^2}$$

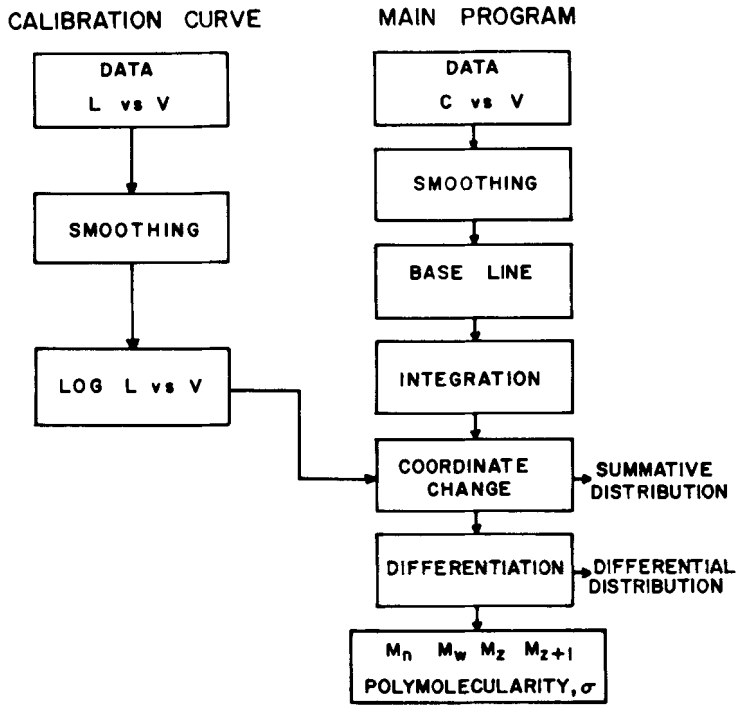

FIG. 2. Schematic of computer program for handling GPC data.

The analysis also included calculation of the integral weight curve and weight and number differential curves for the sample.

The general outline of the program is given in Fig. 2.

Calibration data are entered in a separate program which uses a standard Lagrangian method to smooth the curve, expressing it in the standard form log DP vs. peak elution volume. The compiled data is stored in an out file where it is available for use in the main program.

In the main program, data are entered as the intensity of the curve as a function of the peak elution volume. After smoothing, corrections are made by subtracting the baseline, set as a straight line joining the two extremes of the curve at which points the concentration is zero. These points are also taken as integration limits, and the area beneath the curve is calculated. Coordinates are changed, DP replacing peak elution volume and concentration replacing the intensity. A cumulative distribution curve is then calculated by integration of the curve with the total concentration set at unity. Differentiation of the integral curve yields weight distribution data from which the various

CN. NO. 892
BASELINE SET AT COUNT 38
ALL VALUES AFTER BASE LINE SETTING HAVE BEEN SET AT 0

MN	MV	MW	MZ	M(Z+1)	RED AREA
188.844	336.704	347.291	651.0	1233.4	1.3225

UN	UW	UZ	SIGMA N	SIGMA W	SIGMA Z
0.839	0.874	0.895	173.0	324.7	615.7683

MOL WT	CUM AMT	D AMT/DM	DN/DM
23.1	0.0000	-0.000030	-130.948
26.9	-0.0000	0.000071	264.746
31.4	0.0010	0.000382	1216.623
36.6	0.0041	0.000832	2273.060
42.7	0.0106	0.001259	2948.094
49.8	0.0207	0.001556	3125.874
58.1	0.0345	0.001765	3040.173
67.7	0.0524	0.001950	2880.899
78.9	0.0753	0.002116	2681.682
92.0	0.1039	0.002258	2453.464
107.3	0.1393	0.002389	2227.077
125.1	0.1827	0.002493	1992.946
145.8	0.2347	0.002509	1720.372
170.0	0.2946	0.002436	1432.382
198.3	0.3617	0.002304	1162.274
231.2	0.4351	0.002129	921.058
269.5	0.5129	0.001900	704.755
314.3	0.5921	0.001624	516.719
366.4	0.6698	0.001320	368.377
427.2	0.7406	0.001024	239.799
498.1	0.8044	0.000757	151.954
580.8	0.8565	0.000535	92.055
677.2	0.8996	0.000357	52.652
789.5	0.9311	0.000226	28.661
920.6	0.9544	0.000136	14.754
1073.3	0.9701	0.000079	7.347
1251.4	0.9807	0.000044	3.503
1459.1	0.9874	0.000024	1.624
1701.3	0.9916	0.000012	0.732
1983.6	0.9943	0.000007	0.351
2312.8	0.9961	0.000004	0.193
2696.6	0.9975	0.000003	0.113
3144.1	0.9986	0.000002	0.064
3665.8	0.9994	0.000001	0.030
4274.2	0.9999	0.000000	0.010
4983.4	1.0000	0.000000	0.001
5810.5	1.0000	-0.000000	-0.000
6774.7	1.0000	-0.000000	-0.000
7899.0	1.0000	0.000000	0.000
9209.8	1.0000	0.000000	0.000
10738.1	1.0000	0.000000	0.000
12520.2	1.0000	0.000000	0.000
14597.9	1.0000	0.000000	0.000
17020.4	1.0000	0.000000	0.000

TOTAL NO. OF MOLECULES PR UNIT WT.= 531419.

LINE 100: END OF DATA

FIG. 3. Typical output of GPC program.

average molecular weights are calculated. Distribution width indices and polymolecularities are then calculated. Finally the total number of molecules in unit weight is obtained by integrating the number distribution curve.

Usually the standard calibration data is entered and retained within the saved program. The values of the retention volume are also entered and retained. Thus it is only necessary to enter for each sample, the sample number and the intensity values corresponding to the previously entered peak elution volumes.

An illustration of the typical output is given in Fig. 3. This is a complete statistical description of the DP distribution, cumulative weight, and number differential. Curves can be plotted from the data either manually or by using a standard computer plotting routine.

RESULTS AND DISCUSSION

Homogeneity of Samples

In considering the use of GPC in studies of the viscose process it was recognized that sample uniformity would be a problem. With cellulose, one is dealing with a polymer, the composition of which is determined by the wood source and production conditions.

Usual pulping methods involve as nearly complete dispersion as possible in large quantities of water and extensive mixing prior to laying down the pulp sheet. This would be expected to homogenize the product so that no significant variation exists across the pulp sheet. A commercial pulp sheet was cut into 2-in. squares from which random samples were nitrated and chromatographed. The molecular weight distribution curves from this experiment were laid out on a "mock-up" of the original pulp sheet in the locations from which the samples originated. The results are given in Fig. 4. It can be observed that the changes in distribution within the sheet are probably gradual rather than abrupt (the appearance of the trimodal curve in the middle portion of the sheet has distributions near it, also showing evidence of trimodal distribution. The bimodal nature of the distribution changes gradually, etc.). It should be noted that the $\overline{DP}$ as determined viscosimetrically and the calculated weight-average molecular weight from these GPC curves gave no indication of the degree of nonuniformity in this pulp sheet. These results are given in Table 2. Similar results were obtained on a second pulp sheet. The sampling technique which has been adopted is to take as large a sample as possible, even

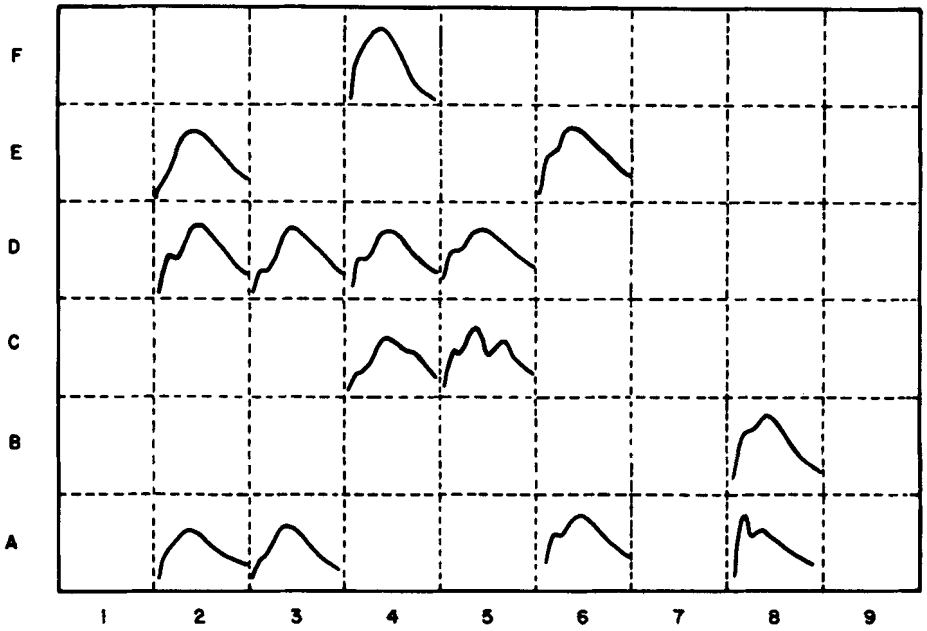

FIG. 4. Differential distribution curves at different points on the pulp sheet. Ordinate is intensity and abscissa is log DP.

TABLE 2

Weight-Average DP and Viscometric $\overline{DP}$ on Individual Segments of Pulp Sheet

$\overline{DP}$	$\overline{DP}_w$
1052	1111
1045	1056
1069	1006
1071	1002
1046	1092
1037	1044
1047	1118
1070	1134
1047	1169
1035	955
	1072
	1114
	1133
	1145

a whole pulp sheet, open it in a Waring Blendor, and then sample from the homogenized sample.

The normal method of baling pulp is to use alternate lots for alternate sheets in the bale. Although no significant differences were observed in the DP distribution between alternate sheets in five bales of different pulps (see Table 3), it is possible that widely different

TABLE 3

DP Distributions in Alternate Sheets in Pulp Bales

Pulp		$\bar{M}_n$	$\bar{M}_w$	$\bar{M}_z$	$\bar{M}_{z+1}$
I	A	306	1118	2056	3045
	B	362	1162	2056	3041
II	A	446	1309	2260	5383
	B	472	1346	2358	3578
III	A	251	1027	2187	3483
	B	261	1006	2189	3624
IV	A	348	1348	2483	3377
	B	355	1417	2527	3490
V	A	303	1243	2317	3305
	B	224	1194	2335	3319
σ between back-to-back sheets		32	34	41	84

distributions could exist in alternate sheets if basic DP were the only factor considered in the blending operation. Consequently this should be considered when sampling from a bale of pulp, i.e., the sample should be taken from pairs of adjacent sheets selected at random. There were significant variations in the molecular weight distribution of pulp lots manufactured over a period of time, as illustrated in Table 4.

The processing used in the manufacture of viscose and in the final

TABLE 4

DP Distributions of Different Pulp Lots from the Same Manufacturer

Variable	Mean	Standard deviation	Standard error	Range
$\bar{M}_n$	536	34	15	86
$\bar{M}_w$	1278	45	20	120
$\bar{M}_z$	2232	125	55	280
$\bar{M}_{z+1}$	3190	251	112	639

product results in drastic changes in the molecular weight distribution of the cellulose. Prior to actual solution of the xanthated crumb, the process is entirely heterogeneous and is particularly subject to nonuniform processing conditions. For example, exposure to oxygen is not uniform during the aging of alkali crumb, temperature variations exist within the steeping tank or aging bins, etc. Consequently the change in distribution will not be uniform throughout the batch. In mixing viscose, however, the distribution nonuniformities are averaged out. These factors must be considered in both experimental design and sampling.

PRECISION OF DATA

The precision of the GPC method when used to determine the molecular weight distribution of cellulose is related to nitration, solution preparation, injection, instrument operation, and data transfer. Each of these variables was considered when establishing the precision of the whole procedure.

Examination of the calculation methods indicated that $\bar{M}_n$ and $\bar{M}_{z+1}$ were most sensitive to small changes in the data at the extreme ends of the GPC curve; $\bar{M}_w$ should be relatively sensitive only to shifts in the maximum peak position and gross changes in the extreme ends of the curve. Precision of these parameters thus represents a reasonable indication of the precision of the whole GPC method.

For the precision study, large samples of commercial pulp and rayon were homogenized, the pulp being opened and mixed in a Waring Blendor and the rayon being cut into quarter-inch pieces with scissors and then blended in the Blendor. Samples of 50 mg were taken from these samples, nitrated, and chromatographed over several weeks time. The data was calculated using the computer program and then statistically analyzed. The data for the two types of samples are compiled in Table 5. There is no significant difference in the precision figures for the two types of samples. Comparison of these data with those obtained by repetitive injections of samples from the same solution suggested that approximately half of this error was related to the analytical sampling, nitration, and solution steps.

The precision figures given in Table 5 indicate that a single sample is adequate if major differences are expected between samples

TABLE 5

Statistical Analysis of GPC Data from Pulp and Rayon Samples

	Variable	Mean	Standard deviation	Standard error	Range
Pulp	$\bar{M}_n$	454	16	5	43
	$\bar{M}_w$	1145	42	13	107
	$\bar{M}_z$	2118	68	22	200
	$\bar{M}_{z+1}$	3050	86	27	256
Rayon	$\bar{M}_n$	293	5	2	14
	$\bar{M}_w$	595	18	7	49
	$\bar{M}_z$	1296	66	27	183
	$\bar{M}_{z+1}$	2357	192	78	541

under study. If only small differences exist, multiple samples must be run, and calculated standard deviations or errors must be used to establish the significance of the differences from the data.

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