

Title	Gel Permeation Chromatography : Band-Broadening and Skewing in High Speed Ge Permeation Chromatography (Special Issue on Polymer Chemistry XII)
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Citation	Bulletin of the Institute for Chemical Research, Kyoto University (1976), 54(2): 100-111
Issue Date	1976-07-20
URL	<a href="http://hdl.handle.net/2433/76654">http://hdl.handle.net/2433/76654</a>
Right	
Type	Departmental Bulletin Paper
Textversion	publisher

## Gel Permeation Chromatography: Band-Broadening and Skewing in High Speed Gel Permeation Chromatography

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*Received March 31, 1976*

A computer simulation of gel permeation chromatographic (GPC) fractionation of polymers was carried out with introducing a simple skewed function as the band-spreading function. With the aid of these results as well as those of actual GPC experiments on narrow distribution polystyrenes, a phenomenological method was proposed for calibrating a GPC unit for band-broadening and skewing phenomena, which one often encounters on operating a high speed GPC. The performance of a high speed GPC was discussed in regard with such phenomena.

### INTRODUCTION

Gel permeation chromatography<sup>1)</sup> (GPC) is now a most routinely used method of determining molecular weight distribution (MWD) of polymers. One of the two recent progresses in this area was the development of GPC gels with small particle size, which led to so-called high speed GPC.<sup>2-4)</sup> The other was the installation of molecular weight (MW) detector which enabled one to monitor MWs of GPC effluents in a continuous fashion.<sup>5,6)</sup> However, even in such GPC units the basic separation mechanism is the same as in any other conventional GPC units: Resulting chromatograms are subject to the dispersion or band-broadening effects due to imperfect resolution of GPC columns.<sup>7-9)</sup> In a previous article<sup>10)</sup> we discussed the dispersion effects on MW-monitor-installed GPC unit on the basis of Tung's phenomenological scheme,<sup>7,8)</sup> which assumes that a pure compound gives a Gaussian shape chromatogram with the dispersion depending on various factors of a GPC unit employed and on its operating conditions.<sup>2-4,12)</sup>

In this study we have examined the effects on high speed GPC in some detail. With such a GPC one often encounters even for pure compounds skewed chromatograms that show significant tailing toward large elution volume side. Accordingly upon making the dispersion correction, Tung's scheme should be modified to take account of band tailing. Here we will discuss this problem. However, we do not intend either to explore the mechanisms of such phenomena or to examine the effects of operating conditions on the extent of dispersion phenomena. We confine ourselves to a phenomenological analysis to establish an adequate method of calibrating GPC unit for such band-broadening and skewing phenomena. Specifically we assume a simple dispersion-correction function, and carry out a computer simulation of the fractionation

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process. These results will be compared with the performance of an actual high speed GPC as well as of a conventional GPC available to us.

## EXPERIMENTAL PROCEDURES

### Computer Simulation Method

The procedures of the simulation are the same as those in our preceding two papers,<sup>10,11</sup> except here we use a skewed correction function instead of a symmetrical Gaussian function employed previously by Tung.<sup>7,8</sup> We assume a  $\log M$  versus elution volume  $v$  (or  $y$ ) calibration with a permeability limit  $v_L$  as

$$v = f(\log M) \quad (1)$$

Using Eq. (1), we hypothetically fractionate a sample with a normalized MWD function  $w(\log M)$  to construct a chromatogram  $F(y_i)\delta y$ , which should be the hypothetical chromatogram obtained if the GPC unit has unlimited resolution but the permeability limit  $y_L$ :

$$F(y_L)\delta y = \sum_{M_j \geq M_L} w(\log M_j)\delta \log M \quad (y \leq y_L) \quad (2a)$$

$$F(y_i)\delta y = \sum_{\delta y} w(\log M_j)\delta \log M = \sum_{\delta y} C_2^{-1} w(\log M_j)\delta y \quad (2b)$$

$$C_2 = (dv/d \log M)_{M=M_j} \quad (\delta y \rightarrow 0) \quad (2c)$$

If and only if the GPC unit has a logarithmic straight line calibration with  $C_2$  being constant for all  $y$  or  $v$  (and has unlimited permeability),  $F(y_i)$  is directly proportional to the MWD function. An experimentally observable chromatogram  $G(v_k)\delta v$  can be constructed from  $F(y_i)\delta y$  by introducing an adequate correlation function  $C(v, y)$ , which was referred to by Tung<sup>7,8</sup> as the instrumental spreading function:

$$G(v_k)\delta v = \sum_i^{all} F(y_i)C(v_k, y_i)\delta y \delta v \quad (3)$$

Obviously if we use a Gaussian function for  $C(v, y)$ :

$$C(v, y) = (h_i/\pi)^{1/2} \exp[-h_i(v_k - y_i)^2] \quad (4)$$

we arrive at Tung's scheme.<sup>7,8</sup> Here we employ a simple two parameter function

$$C(v, y) = N(\alpha_i) X^{\alpha_i} \exp(-\alpha_i X) \quad (5a)$$

$$X = \exp(y_i - v_k) \quad (5b)$$

with  $N(\alpha_i)$  and  $\alpha_i$  being the normalization constant and a parameter representing the extent of skewing, respectively. Admittedly such a choice for chromatograms of pure compounds tested on a high speed GPC was not fully borne out by experiments, but rather was made by a mathematical convenience. In Fig. 1 we compare the two corrections, Eqs. (4) and (5), with corresponding chromatograms of a few narrow distribution polystyrenes. When tested on the high speed GPC, they show certain distortion, which justifies the use of the skewed correction function as a better approximation. Once the chromatogram  $G(v)$  has been constructed by the combination of Eq. (3) with

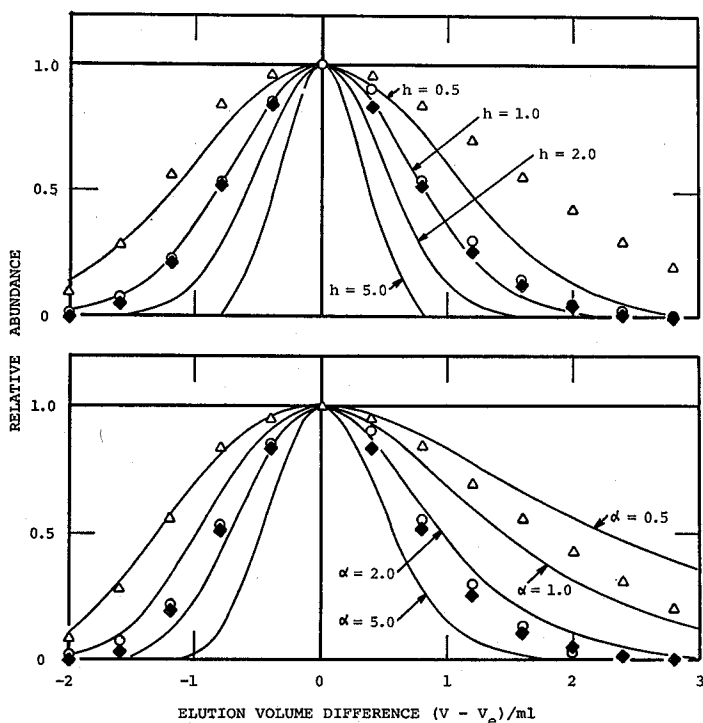


Fig. 1. Properties of Tung's Gaussian spreading function Eq. 4 (above) and present skewed function Eq. 5 (below). Symbols are the chromatograms of standard polystyrenes 11b (○), 4b (◆), and 14b (△) obtained on the high-speed GPC with 4 ml/min flow-rate.

Eq. (4) or with Eq. (5), we can calculate various GPC average MWs, which we call apparent averages,<sup>11,12)</sup> and denote the number average by  $M_n^{app}$ , the weight average by  $M_w^{app}$ , etc.

On carrying out the simulation we need to have two calibrations, *i.e.*,  $\log M$  and  $\alpha$  versus  $v$  calibration (or  $h$  versus  $v$  for the symmetric correction case). For a high speed GPC, both of these are somewhat problematic, as we will come back to these problems later. To establish a method of calibration, we first assume  $\alpha_t (\equiv \alpha)$  be independent of  $v$ , and assume the  $\log M$  versus  $v$  calibration as determined by the conventional elution standard method be valid also. For certain model cases, we further assume two simple two-parameter MWD functions, *i.e.*, the log-normal distribution:

$$w(M) d \log M = (2.3026/\beta\pi)^{1/2} \exp[-(1/\beta^2) \ln^2(M/M_0)] d \log M \quad (6a)$$

$$M_n = M_0 \exp(-\beta^2/4) \quad (6b)$$

$$M_w = M_0 \exp(\beta^2/4) \quad (6c)$$

$$M_w/M_n = Y = \exp(\beta^2/2) \quad (6d)$$

and the Schulz distribution:

$$w(M) \log M = [2.3026 \lambda^{\alpha+1} / \Gamma(\alpha+1)] M^{\alpha+1} \exp(-\lambda M) d \log M \quad (7a)$$

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$$\lambda = \alpha/M_n = (\alpha+1)/M_w = (\alpha+2)/M_z = \dots \quad (7b)$$

$$Y = 1 + 1/\alpha \quad (7c)$$

We examined the shape of  $G(v)$  of such model polymers, assuming adequate  $\alpha$  values and the log  $M$  versus  $v$  relation. Analysis of true and apparent MWs from  $w(M)$  and  $G(v)$ , respectively, provides criteria for establishing the calibration for band-broadening and skewing of a GPC unit.

**Gel Permeation Chromatographic Experiments**

A Waters high speed GPC model ALC/GPC 202/R401 (Water Associates, Milford, Mass.) was employed. Four columns (each 7 mm inner diameter and 30 cm length) of  $\mu$ -styragel® of  $10^6$ ,  $10^5$ ,  $10^4$ , and  $10^3$  Å nominal pore size were used. The carrier solvent was THF, and the flow-rates were 1, 2, and 4 ml/min. At the highest rate only 13 minutes were necessary to complete a run. The total numbers of theoretical plates as determined by acetone were 8,291, 8,395, and 10,936, respectively. The injections were usually 0.3 ml of 0.03 to 0.25% stock solutions. Table I summarizes elution data of standard narrow distribution polystyrenes at the three different rates.

Table I. Peak Elution Volume Data of Narrow Distribution Polystyrene on High Speed GPC Unit

Code	Polystyrene Samples*		Peak Elution Volume $v_e$ (ml)		
	$10^{-4} M_w$	$Y = M_w/M_n$	Flow rate (ml/min)		
			4	2	1
BENZENE	0.0078	1.00	47.0	46.7	46.1
11b	0.40	1.06	39.4	39.1	38.6
8b	1.00	1.04	36.7	36.7	36.1
7b	3.70	<1.06	33.3	33.3	32.9
4b	11.0	<1.06	30.4	30.2	30.0
705	17.9	1.07	29.4	29.2	28.7
3a	41.1	<1.06	27.7	27.4	27.2
13a	67.0	1.15	26.9	26.5	26.3
14b	261.0	1.31	25.0	24.7	24.1
FF35	530	1.1	24.3	23.8	23.7

\* Sample 705 is a National Bureau of Standards (USA) narrow distribution sample NBS 705. Sample FF35 is a Toyo Soda (Tokyo, Japan) high MW, narrow distribution sample, and all others are Pressure Chemical (Pittsburgh, PA.) narrow distribution samples. The MW values are the supplier's designations.

These properties of the high-speed GPC are to be compared with those of a Shimadzu GPC model 1A (Shimadzu Seisakusho, Ltd., Kyoto) used as a model for a conventional GPC unit. Four columns (each 7 mm inner diameter and 120 cm length) of crosslinked polystyrene gels of  $10^6$ ,  $10^5$ ,  $10^5$  and  $10^4$  Å nominal pore size were used. Total void volume of the column system was about 200 ml. Therefore an operation with 1 ml/min flow-rate required nearly 200 minutes to complete a run. The total number of theoretical plates was about 25,700, which was twice better than the high-speed GPC.

## RESULTS AND DISCUSSION

## Evaluation of Skewness Parameter

First we consider a simulation of model GPC experiments to elucidate a method of determining skewness parameter  $\alpha$  as a function of elution volumes. To do this first we need to have  $\log M$  versus  $v$  calibration. For a conventional GPC unit this is usually done with narrow distribution standards by plotting their  $\log$  (nominal weight average value  $M_w$ ) against peak elution volume  $v_e$ . However, a high speed GPC often gives skewed chromatograms even for narrow distribution standards. Therefore, the above procedure might not be legitimate, because the elution-peak MWs might differ greatly from the true MWs of the standard polystyrenes in such skewed chromatograms unless the standards are indeed monodisperse. The extent of such discrepancy is expected to depend on the extent of band broadening and skewing. The two calibrations are closely related with each other: To determine the  $\log M$  versus  $v$  calibration, we need to know the  $\alpha$  versus  $v$  calibration and *vice versa*.

As a working hypothesis we first assumed the MW calibration be given by an adequately drawn smooth curve of  $\log M_w$  versus  $v_e$  plots such as those listed in Table I. Figure 2 shows such a curve for 4 ml/min run. Then using this calibration,

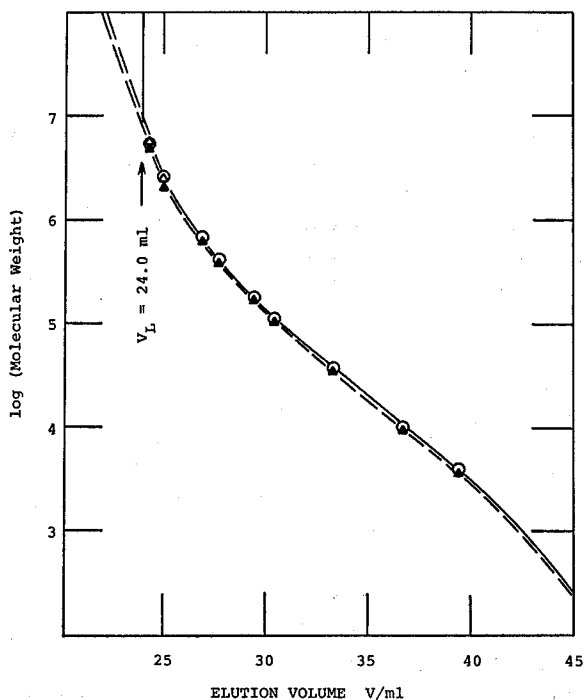


Fig. 2. Logarithmic (molecular weight) versus elution volume calibrations for 4 ml/min flow-rate runs: Solid curve is from  $\log M_w$  versus  $v_e$  plots (O), and broken curve from  $\log M_e$  versus  $v_e$  plots after first iterative simulation ( $\Delta$  for Schulz MWD and  $\blacktriangle$  for log-normal MWD and Schulz MWD, wherever they coincide with each other).

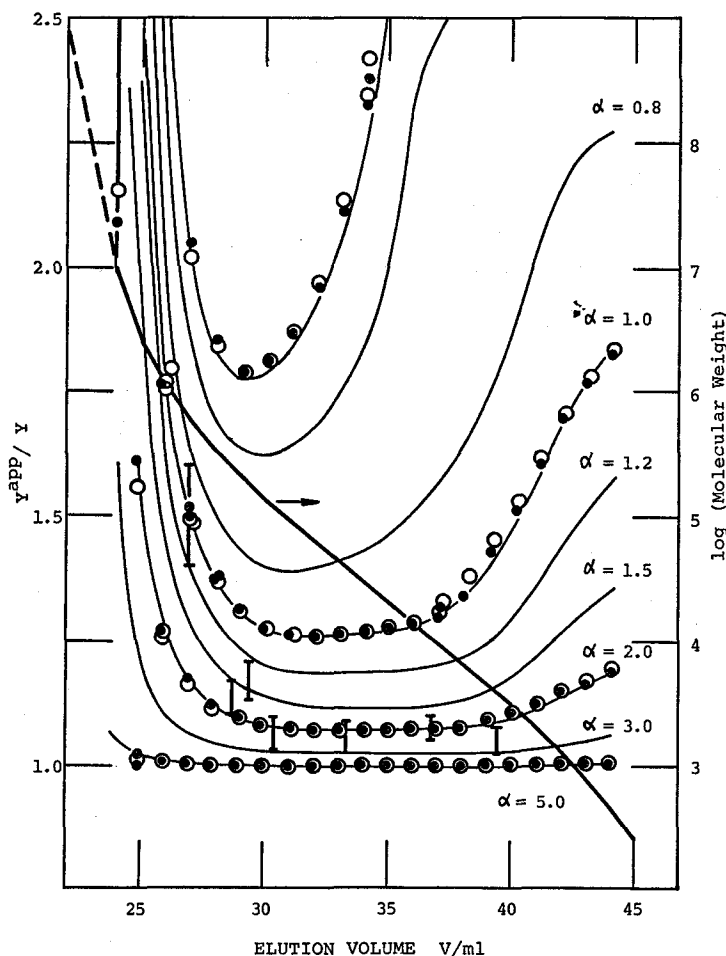


Fig. 3. Plots of  $Y/Y^{app}$  values against peak elution volume  $v_e$  from simulated chromatograms of Schulz type ( $\circ$ ) and log-normal type ( $\bullet$ ) model polymers of narrow distributions ( $Y=1.04\sim 1.15$ ), and of hypothetical monodisperse polymers ( $Y=1.00$ : solid curves), using  $\log M_w$  versus  $v_e$  calibration and given constant  $\alpha$  values as indicated. Half-lines are from experimental chromatograms of standard polystyrenes: Lower ends indicate the values with nominal  $Y$  values, and upper ends those with  $Y=1.00$ .

we calculated various apparent MWs from observed chromatograms of the standard polystyrenes on one hand, and carried out a simulation on model polymers, on the other, with assuming several different  $\alpha$  values. Figure 3 shows examples of  $Y^{app}/Y$  versus  $v_e$  plots from both simulated and actual GPC experiments. Comparing these two results, we could assign  $\alpha$  values and simultaneously estimate peak MW values  $M_e$  adequate to the standard polystyrenes. These  $M_e$  versus  $v_e$  data were used to reconstruct the MW calibration, which is also shown in Fig. 2.

We repeated the above procedures until the calibrations and various average MWs of simulated and actual GPC experiments consistently come to agreement before and after the procedure. To achieve this, only one or two iterations were

sufficient: In fact the original  $\log M_w$  versus  $v_e$  curve was already a good approximation. The shift of only as much as 0.02 logarithmic unit was necessary to obtain the first  $\log M_e$  versus  $v_e$  calibration (see Fig. 2), which was good enough to be employed as the MW calibration. With this calibration, various apparent MWs from experimental and simulated chromatograms were calculated and found to be in satisfactory agreement with each other. These MW values calculated during the second iteration could be used to reassign  $\alpha$  versus  $v_e$  relation (which did not differ from the first one).

By this way we could establish both the  $\log M_e$  and  $\alpha$  versus  $v_e$  relations for the high speed GPC unit for calibrating band broadening and skewing. Figure 4

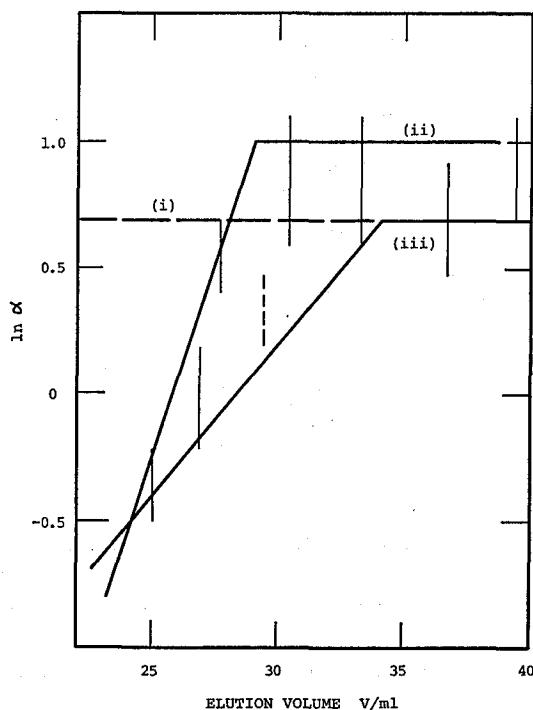


Fig. 4. Plots of  $\alpha$  versus  $v$  relations estimated from the data such as given in Fig. 3. Lines indicate possible choices of  $\alpha$  versus  $v$  relations. See Eqs. 8a-c.

shows the  $\alpha$  versus  $v_e$  relation, for which several choices are possible, because of the ambiguities of experimental data such as nominal  $M_w$  values of the standard polystyrenes, base-line instability of chromatograms, *etc.* Although they are rather arbitrary, the choices are:

(i) Sloppy choice:

$$\alpha = 2.00 \text{ for all } v \quad (8a)$$

(ii) Optimistic choice:

$$\begin{aligned} \alpha &= 2.718 \text{ for } v \geq 29.0 \\ \alpha &= \exp(0.2632v - 6.632) \text{ for } v < 29.0 \end{aligned} \quad (8b)$$



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(iii) Pessimistic choice:

$$\alpha = 2.00 \text{ for } v \geq 34.0$$

$$\alpha = \exp(0.1115v - 3.0983) \text{ for } v < 34.0 \quad (8c)$$

Simulation was carried out using these relations on narrow-MWD low-MW and broad-MWD high MW model polymers of log-normal MWD type. The results are summarized in Table II. We notice that  $M_n^{app}$  values depend significantly on the

Table II. Results of Simulated GPC Experiments on Log Normal Type Model Polymers on High Speed GPC Unit with Flow-Rate 4 ml/min

Type of $\alpha$ vs $v$	Narrow Distribution Polymers			Broad Distribution Polymers		
	$10^{-4}M_n^{app}$	$10^{-4}M_w^{app}$	$Y^{app}$	$10^{-4}M_n^{app}$	$10^{-4}M_w^{app}$	$Y^{app}$
Original Sample	(9.953)	(10.45)	(1.05)	(30.87)	(61.74)	(2.00)
(0) $\alpha = \infty$	9.953	10.45	1.050	30.87	61.74	2.000
(i) $\alpha = 2.00$	8.560	9.896	1.156	25.64	62.96	2.456
(ii) Optimistic	8.948	10.04	1.122	25.64	66.85	2.607
(iii) Pessimistic	7.903	9.645	1.220	20.83	68.27	3.278

specific choice of the  $\alpha$  versus  $v$  relation, while  $M_w^{app}$  values do not. These values are invariably lower than the true values, except for those eluting near the  $v_L$  region. These are of course due to the nature of  $C(v, y)$ , which represents band-tailing toward the larger elution volume side. Comparing the simulated and actual GPC data on the standard polystyrenes, we may conclude that the choice (ii) may be the good approximation.

### Correction for Band-Broadening and Skewing

Employing Eq. (8b) for the  $\alpha$  versus  $v$  calibration, we have examined the performance of the high speed GPC. In Fig. 5 the values of  $Y^{app}/Y$  and  $M_w^{app}/M_w$  are plotted as functions of peak elution volume  $v_e$  for a series of model polymers. The features are essentially similar to those of our previous paper,<sup>11)</sup> in which a Gaussian shape band-spreading function was employed: Namely (i) quantitative interpretation of chromatograms eluting in the region near the  $v_L$  limit is virtually impossible. (ii) The correction was less significant for  $M_w^{app}$  values, but was more so for  $M_n^{app}$  values. (iii) Elution behavior of broad MWD samples are sensitive to the shape of the MWD function especially in the region near the  $v_L$  limit, while those of narrow MWD samples are not necessarily so. In the region where a logarithmic straight line approximation is valid for the MW-calibration and also  $\alpha$  is independent of  $v$ , the correction for the band-broadening and skewing appears to be independent of the MWD of the sample to be treated. This was also true for the band-broadening correction based on Tung's scheme.<sup>7, 8, 11, 13, e, o)</sup> For such a GPC, apparent MWs are treated by the method of Laplace transform as convolutions of  $C(v, y)$  and  $F(y)$ , and therefore the ratios of apparent versus true MWs are independent of the sample's MWD function, which is proportional to  $F(y)$ . To achieve a better result in GPC analysis, one should by all means set up a column system which has a logarithmic

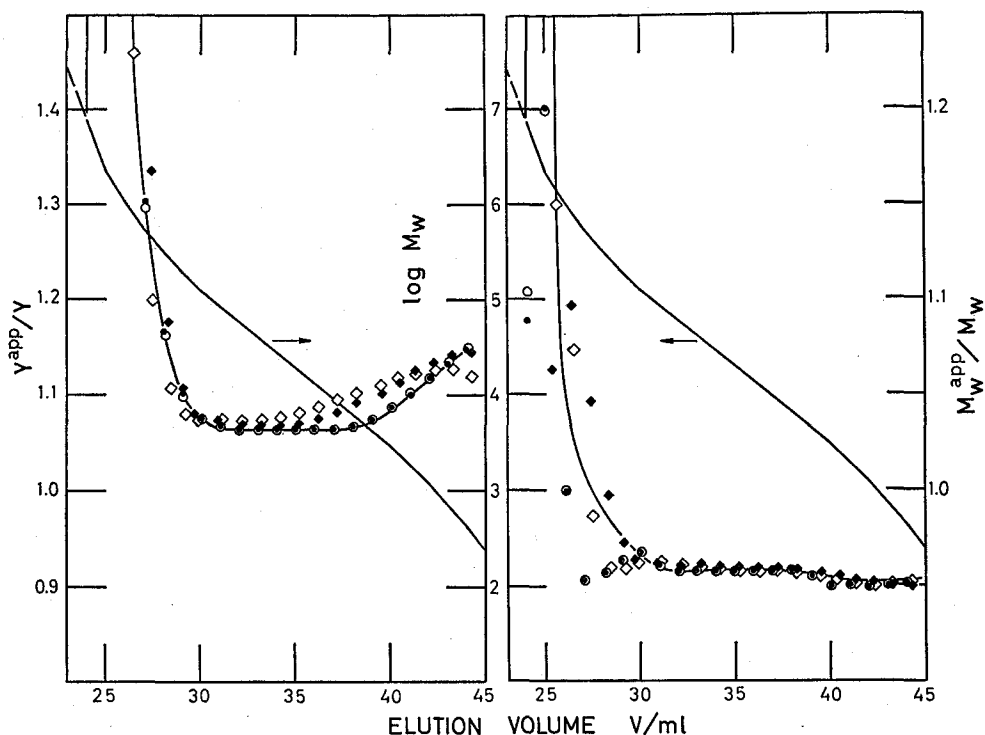


Fig. 5. The performance of the high speed GPC unit (4 ml/min flow rate) as demonstrated by the plots of  $Y^{app}/Y$  (left) and  $M_w^{app}/M_w$  (right) from simulated chromatograms of Schulz type (open marks) and log-normal type (closed marks) model polymers of narrow ( $Y=1.05$ ; circles) and broad ( $Y=2.00$ ; squares) distributions. Solid curves are for hypothetical pure compounds ( $Y=1.00$ ). The simulations were carried out using the first  $\log M_e$  versus  $v_e$  calibration and the Eq. 8b  $\alpha$  versus  $v_e$  relation.

straight line MW calibration in the elution volume range as wide as possible.

Even for a GPC unit which has a distorted MW calibration, the  $Y^{app}/Y$  versus  $v_e$  plots of narrow MWD samples (perhaps  $Y < 1.2$ ) may well approximate those of monodisperse polymers. These standards can then be used to establish the calibrations of both  $\log M$  and  $\alpha$  versus  $v$  relations by the manner as described above. These conclusions may apply for other cases where a different band-spreading function is to be employed. Of course certain other features depend on a specific choice of  $C(v, y)$ : For example, use of a Gaussian function usually predicts larger  $M_w^{app}$  and smaller  $M_n^{app}$  values than the true ones.<sup>7-11,13</sup> Whereas use of the skewed function introduced above predicts smaller  $M_w^{app}$  and much smaller  $M_n^{app}$  values and, consequently, larger  $Y^{app}$  values than the true ones.

Once the  $\log M$  and  $\alpha$  calibrations have been established for a GPC unit, one would hope to use them for deducing true MWDs from experimental chromatograms. To this end several methods<sup>7-9,13</sup> have been proposed for the case where a Gaussian function was used as  $C(v, y)$ . Some of these may be, in principle, applicable to the present case where a skewed function is to be used. However, one should note that what one can obtain after deconvoluting an experimental chromatogram is a hypo-

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thetical chromatogram  $F(v)$  such as defined by Eq. (2). The  $F(v)$  is entirely different from the true MWD, when the sample contains a substantial amount of high MW components that exceed the  $v_L$  limit.<sup>11)</sup> The deconvolution usually demands the full and accurate knowledges of the experimental chromatogram, which are often very difficult to achieve in actual experiments. In that sense a computer simulation experiment, which always provides such knowledges, does not necessarily guarantee the performance of any deconvolution methods when being applied to an actual chromatogram. Because of these reasons, it may not be worthwhile to carry out a tedious deconvolution process to deduce the true MWD. Here we employ a very simple method of evaluating the band-skewing correction: That is, we use the  $Y^{\alpha pp}/Y$ ,  $M_w^{\alpha pp}/M_w$ , etc. values simulated on certain simple model polymers using the log  $M$  and  $\alpha$  calibrations established as above. Table III summarizes the results for a

Table III. Apparent and Corrected MW Data of Two Broad Distribution Polystyrenes Obtained on High Speed GPC (Flow Rate=4 ml/min)

	High Speed GPC Apparent Values	Corrected Values Assuming	
		SCHULZ MWD	LOG NORMAL MWD
RAPRA PS 2 ( $10^{-4} M_w=33.3$ )*			
$v_e$	(28.06)		
$10^{-4} M_n$	11.39	13.40	13.72
$10^{-4} M_w$	29.67	30.61	29.37
Y	2.61	2.28 <sub>4</sub>	2.14 <sub>1</sub>
NBS 706 ( $10^{-4} M_n=12.28$ ; $10^{-4} M_w=25.78$ ; $Y=2.10$ )**			
$v_e$	(28.40)		
$10^{-4} M_n$	11.05	12.74	12.97
$10^{-4} M_w$	25.82	26.93	25.97
Y	2.34	2.11 <sub>4</sub>	2.00 <sub>3</sub>

\* Rubber and Plastics Research Association (Great Britain) polystyrene sample: From light scattering data in benzene and 2-butanone at 30°C measured by H. S.

\*\* National Bureau of Standards (USA) broad MWD standard polystyrene: MW data are NBS specification.

few broad MWD polystyrenes. Apparently these samples are eluted at a critical region near the  $v_L$  limit, *i.e.*, about 28 ml elution volume region, where the MW calibration is highly distorted,  $\alpha$  is sensitive to  $v$ , and therefore the correction factors vary rapidly with  $v$ . Nevertheless, the corrections based on the present scheme appears to be satisfactory or at least leaving only a tolerable discrepancy between the corrected and supposed-to-be true values.

A few other remarks should be added here on the use of a high-speed GPC unit: They are the problems of flow-rate and sample-size dependences of chromatogram shape. In Table I we have seen that the peak elution volume  $v_e$  shifts to a larger  $v$  value as flow-rate increases. A higher speed run results in not only the shift of  $v_e$  but a more significant broadening and tailing (to larger  $v$  side). This problem may be avoided operationally by setting up the MW and  $\alpha$  calibrations for each series or runs of different flow-rate. In fact the procedures mentioned above were applied

to the 1 ml/min and 2 ml/min runs as well. And we found satisfactory results.

However the second problem, *i.e.*, the sample-size dependence appears to be more problematic. Presumably because of the small total volume of a high-speed GPC, overloading effects easily become apparent: Chromatogram shape is quite sensitive to the injection volume, and is somewhat less but still significantly sensitive to the concentration of stock solutions (especially when they are high, say,  $>0.5\%$ ).<sup>14)</sup> Usually a larger sample size results in shifting of chromatogram to larger  $v$  side and more serious tailing. In the above analysis, we have set up a standard working condition for both standard and test samples, and handled their chromatograms as they were. Obviously it is desirable to establish a method of eliminating such a sample-size dependence before applying the calibration procedures such as proposed here. In our preliminary trial we observed that the  $v_0$  shifts to lower  $v$  side more significantly for high MW standards as the sample-size is decreased: The  $v_L$  limit shifts to lower  $v$  side, and the MW calibration becomes closer to a logarithmic straight line.<sup>14,15)</sup> Therefore the decrease in sample-size creates a favorable condition to carry out a quantitative analysis, except that it reduces the detector response which is of course proportional to the sample size. This is particularly important in dealing with broad MWD samples which spread out in the entire  $v$  region. An extensive study on this problem is now in progress. The results will be published elsewhere shortly.

#### ACKNOWLEDGMENT

The computer work was performed with a Facom 230-48 digital computer (Fujitsu Ltd., Tokyo) of Computer Laboratory of this Institute. We thank the staffs of the Laboratory, especially Dr. K. Kajiwara for valuable advices on the computer handling. This work was a part of the presentation given by TK at 1975 GPC seminar held at Pittsburgh, PA., during October 15 to 17, 1975.

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