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Accurate Calibration of a Gel-Permeation Chromatograph by Use of Broad Molecular Weight Distribution Standards

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ABSTRACT

Two methods for developing GPC calibration parameters for any polymer are described and compared. The first method assumes a quadratic calibration curve of the form log $M = C_1 + C_2V + C_3V^2$, where V is the retention volume, and utilizes molecular weight averages of a polymer standard combined with nonlinear regression analysis to determine values of the constants C_1, C_2, and C_3. No reference to a standard polystyrene curve is necessary. The second method assumes the validity of the universal calibration technique in which the calibration curve of any polymer can be determined with reference to a standard polystyrene curve provided representative Mark-Houwink parameters are available. The chromatographic data is used to determine these parameters for any polymer. Results of applying both procedures to polystyrene, polybutadiene, poly(methyl methacrylate), and poly(vinyl chloride) are presented and show that in most instances the second method is simpler to apply and more accurate.

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INTRODUCTION

The introduction of modern high-speed packings for the practice of gel-permeation chromatography (GPC) has virtually eliminated the need for axial broadening corrections of the chromatograms [1]. However, the improved resolution so gained has highlighted the need for accurate calibration of the columns.

Since the mechanism of GPC involves separation by size rather than by molecular weight, calibration curves based solely on polystyrene standards are not applicable for use directly with other polymers due to the difference in the hydrodynamic volume of polymers with different chemical structures. Attempts to rectify this problem have included the "Q" factor method [2], and the universal calibration method [3]. The first of these methods is simple to apply but has many shortcomings while the second is more accurate, provided reliable estimates of the Mark-Houwink parameters of the polymer of interest are known.

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Methods based on secondary standards, i. e., polymers with a broad MW distribution but with known MW averages, were first used by Hamielec [4]. In this procedure a linear calibration curve of the form

$$\log M = C_1 + C_2 V$$

was assumed, and the constants C_1 and C_2 derived from the gel-permeation chromatogram of the standard polymer by a standard Rosenbrock two parameter search method. Loy [5] introduced a simpler and consequently more accurate method to obtain the constants C_1 and C_2 by a technique in which each constant was determined separately. Both methods however rely on the calibration curve being linear which for most systems is not the case over the total MW range.

We decided to examine whether a calibration curve of the form given in Eq. (1) may be more appropriate to our GPC system.

$$\ln M = C_1 + C_2 V + C_3 V^2 \qquad (1)$$

If this calibration curve is appropriate, then the estimate for weight average molecular weight is given by Eq. (2):

$$\overline{M}_W = \Sigma W_i \exp\{C_1 + C_2 V_i + C_3 V_i^2\} \qquad (2)$$

where W_i is the weight fraction of polymer eluting at volume V_i

The estimate for the number-average molecular weight is given by Eq. (3):

$$M_n = 1/\Sigma W_i/\exp\{C_1 + C_2V_i + C_3V_i^2\} \tag{3}$$

The estimate for the polydispersity index then becomes

$$\mathrm{PDI} = \overline{M}_w/\overline{M}_n$$

$$= \Sigma W_i \exp\{C_2V_i + C_3V_i^2\} \Sigma W_i \exp - \{C_2V_i + C_3V_i^2\}$$

Thus if we know $\overline{M}_n$ and $\overline{M}_w$ for the secondary standard we can find the optimum values C_2 and C_3 by minimizing the objective function shown by Eq. (4):

$$F = [(\overline{M}_W/\overline{M}_n) - \Sigma W_i \exp\{C_2V_i + C_3V_i^2\} \Sigma W_i \exp - - \{C_2V_i + C_3V_i^2\}]^2 \tag{4}$$

using a two-variable Rosenbrock search. The parameter C_1 is then obtained by an iteration procedure.

If the correct value for C_1 is $C_1 + \delta C_1$, then

$$\overline{M}_w = \Sigma W_i \exp\{C_1 + \delta C_1 + C_2V_i + C_3V_i^2\}$$

$$= \exp\{\delta C_1\} \Sigma W_i \exp\{C_1 + C_2V_i + C_3V_i^2\}$$

Thus $\delta C_1 = \ln (\overline{M}_{w(\text{actual})}/\overline{M}_{w(\text{estimated})}$

$\overline{M}_{w(\text{est})}$ is obtained from Eq. (2) with an initial guess at C_1. The procedure is then repeated with the new value of C_1 until δC_1 is smaller than some arbitrary small value.

To overcome the disadvantage of the universal calibration method, in that reliable Mark-Houwink parameters of the polymer of interest must be known, Mahabadi and O'Driscoll [6] utilized a secondary standard to determine these parameters directly from the chromatogram. They used a search method to minimize the function shown in Eq. (5) to calculate an optimum value of α_2, the Mark-Houwink exponent, of the polymer of interest.

$$F_1 = \{n\}^{\overline{M}}{}_n/K_1 - [\Sigma(W_iM_{i_1}{}^{\beta\alpha_2})/\Sigma(W_i/M_{i_1}{}^{\beta})] \tag{5}$$

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where K_1 is the Mark-Houwink constant for polystyrene

$$\beta = (\alpha_1 + 1)/(\alpha_2 + 1)$$

α_1, α_2 being the Mark-Houwink exponents for polystyrene and the polymer sample, respectively; K_2 is then calculated from the appropriate Mark-Houwink equation.

A recent publication [7] has investigated the use of this technique over a narrow MW range.

This work extends the previous work [7] with regard to using the universal calibration method of Mahabadi and O'Driscoll over a wider MW range and also looks at the method proposed above in the utilization of a quadratic calibration curve.

EXPERIMENTAL

The GPC used was as described previously [7].

Standard polystyrene (PS) polybutadiene, (PB), polyisoprene (PI) and poly(methyl methacrylate) (PMMA) were prepared in our laboratories by anionic polymerization techniques. Poly(vinyl chloride) (PVC) and PB secondary standards were also obtained from ICI (Aust.) and Phillips Chemicals, respectively.

Number-average molecular weights were determined on a Mechrolab Model 501 automatic membrane osmometer in toluene at 303°K.

Viscosity-average molecular weights were obtained by conventional dilution viscometry in an automatic viscometer. Since the polymers produced by anionic polymerization had a narrow MW distribution as measured by GPC, the viscosity-average molecular weight was used as an approximation for the weight-average molecular weight in the various calibration calculations.

RESULTS AND DISCUSSION

Quadratic Calibration Curve

The results of using this technique have been collected in Table 1 for the PVC and PS standards. With the PS samples we were also able to compare the parameters obtained for the quadratic calibration curve with those obtained by fitting the data from a normal PS calibration curve to a quadratic function. Thus by the search technique the values obtained after 11 cycles were

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TABLE 1. GPC Data of Poly(vinyl Chloride) and Polystyrene Standards (Quadratic Form of Calibration Curve is Assumed)

	Laboratory or manufacturer's data		GPC Data	
Polymer	M_w × 10^3	M_n × 10^3	M_w × 10^3	M_n × 10^3
Poly(vinyl chloride)	68.6	25.5	73	32
	118	41	176	53
	140	55	212	103
	200	64	375	126
Polystyrene	7.3	5	8	7
	25	23	21	18
	150	137	88	75
	412	345	275	187

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$C_1 = 8.25$

$C_2 = 0.015$

$C_3 = -0.0023$

which at first glance seem to compare favorably with those obtained by the normal PS calibration procedure, viz., $C_1 = 7.118$, $C_2 = 0.0138$ $C_3 = 0.001997$. However as the function is logarithmic, these small differences are quite significant as can be seen from Table 1, where the MW averages obtained by this technique show considerable deviation from those obtained by the classical techniques.

Universal Calibration Method

The results obtained by the technique of Mahabadi and O'Driscoll based on the universal calibration method have been collected in Table 2. For each polymer type, the lowest MW standard was used to determine the Mark-Houwink parameters K and α for that polymer, and these values were then used in the subsequent calculations.

TABLE 2. GPC Data of Laboratory Standards (Calibration According to Method of Mahabadi and O'Driscoll)

Polymer	$\overline{M}_v \times 10^3$ (viscometry)	$\overline{M}_n \times 10^3$ (membrane osmometry)	$\overline{M}_v \times 10^3$ (GPC)	$\overline{M}_n \times 10^3$ (GPC)
Polybutadiene	18.5	16.1	18.5	16.0
	175	137	192	142
	272	206	312	243
	610	479	720	513
Polyisoprene	12.2	10.8	12.2	10.7
	148	127	153	125
	473	402	527	412
Poly(methyl methacrylate)	7.5	5.8	7.7	5.7
	60	33.2	61	34.5
	102	80.3	85	67
	475	307	405	279

The agreement between the GPC results and those obtained by the classical techniques is excellent for the low MW standards, but the differences increase with increasing MW. However, the agreement remains excellent when one takes into consideration the errors inherent in the methods used to calibrate the standards in the first place.

CONCLUSIONS

The method of Mahabadi and O'Driscoll in the calibration of GPC columns with broad MW distribution standards has been shown to be accurate over a wide range of molecular weights for a variety of polymer types.

Search techniques for the determination of calibration line constants other than those in which a linear calibration line can be assumed have been shown to be not reliable enough to justify the large amount of effort used in their determination.

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REFERENCES

[1] R. P. Chaplin and W. Ching, Chromatographia, in press.
[2] L. E. Maley, J. Polym. Sci. C, 8, 253 (1965).
[3] Z. Grubisic, P. Rempp, and H. Benoit, J. Polym. Sci. B, 5, 753 (1967).
[4] S. T. Balke, A. W. Hamielec, and B. P. LeClair, Ind. Eng. Chem. Prod. Res. Develop., 8, 54 (1969).
[5] B. R. Loy, J. Polym. Sci. Polym. Chem. Ed., 14, 2321 (1976).
[6] H. K. Mahabadi and K. F. O'Driscoll, J. Appl. Polym. Sci., 21, 1283 (1977).
[7] R. P. Chaplin, J. K. Haken, and J. J. Paddon, J. Chromat., in press.

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