

DETERMINATION OF THE MARK-HOUWINK CONSTANTS BY GEL PERMEATION CHROMATOGRAPHY WITH CORRECTION FOR LONGITUDINAL SPREADING

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The determination of the Mark-Houwink constants using gel permeation chromatography data, based on a known universal calibration dependence and the recorded chromatograms of one or several characterized polydisperse polymer samples, has been modified by including correction factors for the longitudinal spreading. Verification by means of artificial, computer-generated chromatograms shows that the new procedure considerably raises the accuracy and reliability of the results obtained.

To evaluate gel permeation chromatography (GPC) data in terms of the molar mass averages (number average M_n , mass average M_w etc.) and of molar mass distribution, it is necessary to know the relation between the elution volume, v , and the molar mass, M , for the column system used. This calibration curve is best determined by measuring the retention volumes of a number of characterized polymer fractions with narrow distribution which span a sufficiently wide range of molar masses. Since, however, the quantity which governs retention in GPC is the effective hydrodynamic volume^{1,2} which for polymer coils is given not only by the length (molar mass), but depends also on the chain flexibility and on the interaction between segments and solvent molecules, the calibration dependences of the given column are generally different for the individual polymers. Usually, however, no high-quality and well characterized fractions are available for the analyzed polymer, with the exception of polystyrene, for which there exists a number of commercially available and satisfactory calibration standards.

In this situation the column can be calibrated by polystyrene standards and the so-called universal calibration dependence¹

$$\ln(M \cdot [\eta]) = f_u(v) \quad (1)$$

is found, where the intrinsic viscosity, $[\eta]$, of polystyrene fractions is either measured directly, or calculated from the Mark-Houwink equation

$$[\eta]_s = K_s \cdot M^{a_s} \quad (2)$$

(the index refers to the calibration standard, usually polystyrene), using known molar mass values and the reported constants K_s, α_s valid for the mobile phase used. The function of elution volume f_u is usually assumed in the form of a polynomial, and coefficients at the individual powers of v are determined by regression analysis. The universal calibration dependence $f_u(v)$ is then recalculated to the actual calibration curve $f(v)$ valid for the given polymer by means of the relation

$$\ln M_p = f(v) = f_u(v)/(\alpha_p + 1) - \ln K_p/(\alpha_p + 1), \quad (3)$$

in which K_p, α_p are the Mark-Houwink constants for the analyzed polymer.

A situation often arises, however, where this procedure cannot be employed, because the constants K_p, α_p are not known for the given polymer in the mobile phase used. Their determination by means of the classical procedure is a very laborious process, where the polymer sample is fractionated and each fraction is characterized by measuring the intrinsic viscosity and molar mass by some absolute method.

If one or several unfractionated samples of the analyzed polymer are at disposal, for which at least two molecular characteristics are known (M_n, M_w or $[\eta]$), such information — along with the recorded chromatograms — is sufficient for the determination of the constants K_p, α_p , necessary for the recalculation of the universal calibration dependence by means of Eq. (3), on the basis of a procedure suggested by Weiss and Cohn-Ginsberg³, which can be described by the following scheme. According to Eq. (3) the molar mass M_p can be written as a function of the elution volume, v , by using the known universal dependence $f_u(v)$ and the (still unknown) constants K_p and α_p ,

$$M_p(v) = \exp [f_u(v)/(\alpha_p + 1)]/K_p^{1/(\alpha_p + 1)}. \quad (4)$$

(As only the constants K_p and α_p are used below, the index is dropped for the sake of simplicity.) For the number and mass average we have, then,

$$M_n = \left\{ \int_0^\infty M^{-1} f_w(M) dM \right\}^{-1} = K^{-1/(1+\alpha)} / \int \exp \left[-\frac{f_u(v)}{\alpha + 1} \right] g(v) dv, \quad (5)$$

$$M_w = \int_0^\infty M f_w(M) dM = K^{-1/(1+\alpha)} \cdot \int \exp \left[\frac{f_u(v)}{1 + \alpha} \right] g(v) dv; \quad (6)$$

similarly, for the intrinsic viscosity,

$$[\eta] = K^{1/(1+\alpha)} \int \exp \left[\frac{\alpha f_u(v)}{\alpha + 1} \right] g(v) dv. \quad (7)$$

In deriving expressions (5)–(7) we used Eq. (4) together with the relation between the molar mass distribution, $f_w(M)$, and the chromatogram corrected for axial spreading, $w(v)$:

$$f_w(M) dM = -w(v) dv ; \quad (8)$$

it is assumed that for the employed polymer samples with broad distribution the corrected chromatogram w can be replaced by the experimentally available, uncorrected chromatogram $g(v)$ with sufficient accuracy. The sought constants K , α may now be found by solving two of Eqs (5)–(7), inserting into the respective left-hand sides the two experimentally determined characteristics. The solution is considerably simplified by forming combinations of M_n , M_w , and $[\eta]$ such that the parameter K is cancelled; the following equations are suitable for this purpose:

$$[\eta] \cdot M_n = \frac{\int \exp [\alpha f_u(v)/(\alpha + 1)] g(v) dv}{\int \exp [-f_u(v)/(\alpha + 1)] g(v) dv} , \quad (9)$$

$$\frac{M_w}{M_n} = \int \exp \left[-\frac{f_u(v)}{\alpha + 1} \right] g(v) dv \cdot \int \exp \left[\frac{f_u(v)}{\alpha + 1} \right] g(v) dv . \quad (10)$$

Finally, if the intrinsic viscosities $[\eta]_1$ and $[\eta]_2$ of two polydisperse samples are known, we can write

$$\frac{[\eta]_1}{[\eta]_2} = \frac{\int \exp [\alpha f_u(v)/(\alpha + 1)] g_1(v) dv}{\int \exp [\alpha f_u(v)/(\alpha + 1)] g_2(v) dv} , \quad (11)$$

where $g_i(v)$ ($i = 1, 2$) is the measured chromatogram of the i -th sample. Depending on the combination of characteristics available, one of Eqs (9)–(11) is solved for α , and K is subsequently determined by direct substitution of α into the respective Eq. (5), (6) or (7), as the case may be.

The method in several modifications has been verified on a number of polymers⁴⁻¹⁴. The authors agree that although a considerable scatter is observed in the Mark–Houwink constants calculated in this way from chromatograms of different polymer samples, a high K value is always accompanied by a low value of the exponent, α , so that the molar masses of test polymers, calculated from their chromatograms using the recalculated calibration dependence (3), are in a satisfactory agreement with the results obtained by absolute methods.

One part of such variability in the values of Mark-Houwink constants must be attributed to errors in input data (experimental chromatograms $g(v)$, universal calibration dependence $f_u(v)$, and the initial molecular characteristics M_n , M_w , $[\eta]$), but replacement of the corrected chromatogram w by the uncorrected function $g(v)$ certainly plays a role as well (cf.¹³). However, the column system was calibrated by means of good primary standards; therefore, it would be possible, in principle, to employ one of the reported procedures¹⁵⁻¹⁸ for determining the spreading factor, $h(v)$, from their chromatograms, and to substitute into Eqs (9)–(11), instead of $g(v)$, the corrected chromatograms $w(v)$ obtained by solving the Tung integral equation¹⁹

$$g(v) = \int_{-\infty}^{\infty} \sqrt{\left(\frac{h(y)}{\pi}\right)} \exp[-h(y)(v-y)^2] w(y) dy. \quad (12)$$

As effective methods developed for solving Eq. (12) are often rather involved and would render the procedure very cumbersome, the Weiss and Cohn-Ginsberg procedure has been improved in this study by considering the imperfect resolution of real columns in GPC, *i.e.*, by including the appropriate correction factors. Modified forms of Eqs (9)–(11) have been derived which can be solved for correct α (and subsequently K) values unaffected by axial dispersion.

THEORETICAL

Let it be assumed, for the sake of simplicity, that the observed universal calibration dependence of the column is linear,

$$\ln(M \cdot [\eta]) = f_u(v) = A_u - B_u v; \quad (13)$$

hence, the real calibration curve valid for the analyzed polymer may also be written in a linear form,

$$\ln M = f(v) = A - Bv, \quad (14)$$

$$A = (\alpha + 1)^{-1} (A_u - \ln K), \quad (14a)$$

$$B = B_u / (\alpha + 1), \quad (14b)$$

where K and α are the sought Mark-Houwink constants.

If we want to introduce correction factors for axial spreading into Eqs (5) and (6), it is sufficient to bear in mind that their right-hand sides define uncorrected (*i.e.*, calculated from the experimental chromatogram $g(v)$) values of the number (Eq. (5)) and mass (Eq. (6)) average molar mass, $M_n^{(u)}$ and $M_w^{(u)}$; these can be corrected for imperfect resolution of GPC columns by multiplying by the appropriate correction

factors in the sense of the equations

$$M_n = M_n^{(u)} \exp(B^2/4h), \quad (15a)$$

$$M_w = M_w^{(u)} \exp(-B^2/4h), \quad (15b)$$

derived by Hamielec and Ray²⁰; it is assumed that the spreading factor h has been determined in advance from chromatograms of primary calibration standards along with the determination of the universal calibration curve (if h depends on the elution volume, we substitute a value corresponding either to the maximum or to the centroid²¹ of the chromatogram of the characterized polymer sample under consideration). The still unknown quantity B is replaced by the known slope of the universal calibration B_u using expression (14b); by dividing Eqs (5), (6), a modified form of relation (10) is obtained:

$$M_w/M_n = \exp[-B_u^2/2h(\alpha + 1)^2] \int \exp\left[\frac{f_u(v)}{\alpha + 1}\right] g(v) dv \cdot \int \exp\left[-\frac{f_u(v)}{\alpha + 1}\right] g(v) dv. \quad (16)$$

Solving this equation, we obtain α which is no longer affected by the axial spreading.

To correct for axial spreading also Eqs (9) or (11), one should first derive a correction factor analogous to expressions (15) also for the intrinsic viscosity. For a polydisperse sample we have

$$[\eta] = K \int_0^\infty M^\alpha f_w(M) dM, \quad (17)$$

where α , K are constants of Eq. (2) for the analyzed polymer. Using Eqs (8) and (14), this may be rewritten to

$$[\eta] = K \int_0^\infty M^\alpha w(v) dv = K \int \exp[\alpha(A - Bv)] w(v) dv. \quad (18)$$

If the corrected chromatogram in the exact expression (18) is replaced by the experimentally accessible quantity $g(v)$, an analogous equation is obtained,

$$[\eta]^{(u)} = K \int \exp[\alpha(A - Bv)] g(v) dv, \quad (19)$$

which defines the intrinsic viscosity $[\eta]^{(u)}$ calculated from the chromatogram $g(v)$, and thus not corrected for the effect of axial spreading. By means of the Tung integral equation, the latter relation can be rewritten to

$$\begin{aligned}
 [\eta]^{(w)} &= K \int \exp [\alpha(A - Bv)] \left\{ \int \sqrt{\frac{h}{\pi}} \exp [-h(v - y)^2] w(y) dy \right\} dv = \\
 &= K \sqrt{\frac{h}{\pi}} \int w(y) dy \int \exp [\alpha(A - Bv) - h(v - y)^2] dv = K \sqrt{\frac{h}{\pi}} \int w(y) I(y) dy, \quad (20)
 \end{aligned}$$

where we have introduced

$$I(y) = \int \exp [\alpha(A - Bv) - h(v - y)^2] dv. \quad (20a)$$

The integral in the last formula can be evaluated analytically; we have

$$I(y) = \sqrt{\frac{\pi}{h}} \exp \left[\alpha(A - By) + \frac{\alpha^2 B^2}{4h} \right], \quad (20b)$$

so that

$$[\eta]^{(w)} = K \exp (\alpha^2 B^2 / 4h) \int w(y) \exp [\alpha(A - By)] dy, \quad (21)$$

or, with respect to Eq. (18),

$$[\eta] = [\eta]^{(w)} \exp \left(- \frac{\alpha^2 B^2}{4h} \right), \quad (22)$$

which is an expression analogous to relations (15) and allows us to correct the intrinsic viscosity calculated from the experimental chromatogram for the effect of axial spreading.

Similarly to the preceding procedure, we replace the unknown slope B of the actual calibration dependence by B_u using expressions (14b), and obtain finally the sought modification of Eq. (7):

$$[\eta] = K^{1/(1+\alpha)} \exp \left[- \frac{\alpha^2 B_u^2}{4h(\alpha + 1)^2} \right] \int \exp \left[\frac{\alpha f_u(v)}{\alpha + 1} \right] g(v) dv. \quad (23)$$

The modified form of Eq. (9) needed for the calculation of the exponent α corrected for the effect of axial spreading from the combination $M_n[\eta]$ then is

$$[\eta] \cdot M_n = \exp \left(- \frac{B_u^2}{4h} \frac{1 - \alpha}{1 + \alpha} \right) \frac{\int \exp [\alpha f_u(v) / (\alpha + 1)] g(v) dv}{\int \exp [-f_u(v) / (\alpha + 1)] g(v) dv}. \quad (24)$$

It is important to bear in mind that when the ratio of two intrinsic viscosities in the sense of expression (11) is used, the correction factor for the intrinsic viscosity cancels, provided the spreading factor is independent of the elution volume; in the opposite case we obtain the following modified form of Eq. (11):

$$\frac{[\eta]_1}{[\eta]_2} = \exp \left[- \frac{\alpha^2 B_u^2}{4(\alpha + 1)^2} \left(\frac{1}{\bar{h}_1} - \frac{1}{\bar{h}_2} \right) \right] \frac{\int \exp [\alpha f_u(v)/(\alpha + 1)] g_1(v) dv}{\int \exp [\alpha f_u(v)/(\alpha + 1)] g_2(v) dv}, \quad (25)$$

where \bar{h}_1 , \bar{h}_2 are the mean values of the spreading factor valid in the respective intervals of elution volume spanned by the first and the second chromatogram.

RESULTS AND DISCUSSION

To avoid the effect of errors in the input data, the new method was tested on artificial, computer-generated chromatograms. Table I summarizes the number average molar masses and polydispersity indices of eight "polymer samples" for which uncorrected chromatograms were generated by a procedure described earlier^{18,22}, under the assumption that their distribution $f_w(M)$ obeys the Schulz-Zimm model function with two adjustable parameters a , b . The actual calibration dependence was chosen in the linear form

$$\ln M = f(v) = A - Bv = 24.47905 - 0.3097v \quad (26)$$

and the dependence of the spreading factor on the elution volume was described by the equation

$$h(v) = -0.93102 + 0.0254v - 0.000073v^2. \quad (27)$$

From the selected values of Mark-Houwink constants ($K = 1.44 \cdot 10^{-4}$, $\alpha = 0.65$),

TABLE I

Average molar masses of samples used in generation of model chromatograms. Calibration linear, $\ln M = 24.47905 - 0.3097v$; $h(v) = -0.93102 + 0.0254v - 7 \cdot 10^{-5}v^2$

Sample No	1	2	3	4	5	6	7	8
$M_n \cdot 10^{-4}$	5	10	40	80	5	10	40	80
M_w/M_n	2	2	2	2	1.5	1.5	1.5	1.5

the intrinsic viscosity was calculated for each sample by means of the relation

$$[\eta] = K \int M^\alpha f_w(M) dM = (K/a^\alpha) \Gamma(b + \alpha + 1) / \Gamma(b + 1), \quad (28)$$

where $b = (M_w/M_n - 1)^{-1}$, $a = b/M_n$. The constants of the universal calibration dependence, A_u, B_u , were determined by transforming Eq. (26) using expressions (14).

The M_n and M_w values from Table I, the intrinsic viscosity values calculated from expression (28), the generated uncorrected chromatograms $g(v)$ for the individual samples and the constants A_u, B_u of the universal calibration dependence were then used as input data for the individual programs which calculated α by the method of interval halving in the range $0.5 \leq \alpha \leq 1.0$ using either Eqs (9)–(11) or (16), (24) and (25). The mean value calculated from (27) for the range of the elution volume spanned by the chromatogram of the sample under consideration was substituted for the spreading factor h . As soon as the optimal α was found, the program determined the corresponding constant K as the average from two values obtained by direct substitution of α into equations defining the two molecular characteristics used ($M_n, M_w, [\eta]$, or $[\eta]_1$ and $[\eta]_2$, as the case may be). In the calculation of K without correction for axial spreading Eqs (9)–(11) were used directly. When using the modified equations (16), (24), (25), the respective correction factor had to be considered also in the determination of K ; e.g., K was determined from M_n by means of the relation

$$K^{1/(1+\alpha)} = \frac{1}{M_n} \frac{\exp [B_u^2/4h(1 + \alpha)^2]}{\int \exp [-f_u(v)/(1 + \alpha)] g(v) dv} \quad (29)$$

which can be readily derived by combining Eqs (5), (15a), and (14b).

The results of the calculations are summarized in Tables II, III, and IV as the relative deviations of K and α , recovered from the individual combinations of experimentally available quantities, from the true values $K = 1.44 \cdot 10^{-4}$, $\alpha = 0.65$, using either the original procedure without correction (i.e., from Eqs (9)–(11)) or the modified method with correction factors according to Eqs (16), (24), and (25).

In all cases the new procedure leads to a pronounced decrease in the error of the calculated values of Mark-Houwink constants. Data in Tables II, III also show that the errors δK and $\delta \alpha$ in the uncorrected constants increase with increasing average molar mass of the polymer standard, in agreement with the fact that the assumed dependence of the spreading factor on the elution volume as described by Eq. (27) has resulted in a considerably lower separation efficiency in the range of high M values (cf. Table II); here, too, the new procedure can improve considerably the

results obtained, as can be seen from the fact that no observable dependence on the sample molar mass is reflected in the values of $\delta\alpha^*$ and δK^* in Table II.

The results summarized in Table IV (as well as additional values not given in the Table and calculated from other combinations of two polymer samples with known

TABLE II

Error in Mark-Houwink constants recovered on the basis of the combination $[\eta]$. M_n without correction (δK , $\delta\alpha$, from Eq. (9)) and with correction for axial spreading (δK^* , $\delta\alpha^*$, from Eq. (24)).

The symbol \bar{h} denotes the mean spreading factor. Mean error is defined as $\sum_{i=1}^8 |\delta_i|/8$

Sample	\bar{h}	δK , %	$\delta\alpha$, %	δK^* , %	$\delta\alpha^*$, %
1	0.360	-37.0	5.3	9.1	-1.3
2	0.319	-40.6	5.6	12.2	-1.6
3	0.249	-49.8	6.5	21.2	-2.5
4	0.225	-56.3	7.4	14.3	-1.9
5	0.353	-54.3	9.8	9.2	-1.3
6	0.312	-59.7	10.7	12.3	-1.6
7	0.235	-69.8	12.5	25.3	-2.8
8	0.212	-75.2	13.7	12.1	-1.6
Mean error:		55.3	8.9	14.5	1.8

TABLE III

Error in Mark-Houwink constants recovered on the basis of the combination M_w/M_n without correction (δK , $\delta\alpha$, from Eq. (10)) and with correction for axial spreading (δK^* , $\delta\alpha^*$, from Eq. (16))

Sample	δK , %	$\delta\alpha$, %	δK^* , %	$\delta\alpha^*$, %
1	-82.9	24.9	-17.6	2.9
2	-88.4	28.5	-23.8	3.8
3	-96.7	40.2	-53.9	9.5
4	-98.6	48.2	-72.7	14.9
5	-97.0	42.0	-21.5	3.5
6	-97.2	47.4	-25.9	4.1
7	- ^a	- ^a	-54.5 ^b	9.5 ^b
8	- ^a	- ^a	-82.4 ^b	19.7 ^b
Mean error:	93.5	38.5	33.9	6.5

^a The program did not find α in the interval $\langle 0.5, 1.0 \rangle$. ^b Not included in the mean.

TABLE IV

Error (percent) in Mark-Houwink constants recovered from the combination of two chromatograms of samples with known intrinsic viscosities without correction (δK , $\delta\alpha$, from Eq. (11)) and with correction for axial spreading (δK^* , $\delta\alpha^*$, from Eq. (25))

Chromatogram of sample															
2		3		5				8							
δK	$\delta\alpha$	δK^*	$\delta\alpha^*$	δK	$\delta\alpha$	δK^*	$\delta\alpha^*$	δK	$\delta\alpha$	δK^*	$\delta\alpha^*$				
Along with chromatogram No 2															
—	—	—	—	23	-3.4	8.4	-1.9	6.6	-1.6	1.7	-1.0	26.3	-3.7	5.1	-1.6
Along with chromatogram No 3															
23.2	-3.4	8.4	-1.9	—	—	—	—	16.6	-2.8	5.7	-1.6	41.2	-4.9	-4.0	-0.7
Along with chromatogram No 5															
6.6	-1.6	1.7	-1.0	16.6	-2.8	5.7	-1.6	—	—	—	—	19.3	-3.1	2.6	-1.3
Along with chromatogram No 8															
26.3	-3.7	5.1	-1.6	41.2	-4.9	4.0	-0.7	19.3	-3.1	2.6	-1.3	—	—	—	—
Mean error															
18.7	2.9	5.1	1.5	26.9	3.7	6.0	1.4	14.2	2.5	3.3	1.3	29.9	3.9	3.9	1.2

intrinsic viscosity values) suggest that the error in the recovered values of the Mark-Houwink constants increases if the average molar mass values (and thus also the intrinsic viscosities) of both samples are close to each other (*cf.* the combination of samples 2 and 3, Table IV). Hence, in the determination of the Mark-Houwink constants by means of Eq. (11) or the modified Eq. (25), it is desirable, in order to obtain reliable results, to choose both polymers with the largest possible difference in the intrinsic viscosity values.

It can be seen, by comparing data in the Tables, that the smallest error in the calculated K and α values is obtained by employing the procedure in which chromatograms of two polymer samples with known $[\eta]$ are used (Eq. (11) or (25)), while the least favourable results are obtained by using the combination M_w/M_n . This is easy to understand, bearing in mind the numerical values of the respective correction factors. Thus, *e.g.*, for the combination of polymers 5 and 8 the corresponding correction factor in Eq. (25), $\exp\{-[\alpha^2 B_u^2/4(\alpha + 1)^2](1/\bar{h}_5 - 1/\bar{h}_8)\}$, is 0.983; basically, this value is given only by the difference between the reciprocal values of the spreading factors for these two polymers. The correction factor in Eq. (24), $\exp[-B_u^2(1 - \alpha)/4h(1 + \alpha)]$, becomes 0.962 for sample 5 and 0.937 for sample 8, while the correction factor in Eq. (16), $\exp[-B_u^2/2h(\alpha + 1)^2]$, already differs very much from unity and becomes 0.873 for sample 5 and 0.797 for sample 8. Using experiments with real polymer samples, Dobbin and coworkers¹¹ found earlier that the procedure of determination of K and α by means of Eq. (11) gave the most reliable results.

It may be summarized, therefore, that if two polymer samples with sufficiently different intrinsic viscosity values are available, the latter procedure should be given preference. If only one secondary standard is at disposal, the combination $M_n[\eta]$ should be used; the ratio M_w/M_n cannot be recommended, because it is most affected by the effect of the imperfect resolving power of real columns.

It is always advisable to evaluate the chromatograms — along with the determination of universal calibration dependence — also in terms of the spreading factor and of its dependence (if any) on the elution volume. In the calculation of the Mark-Houwink constants, the modified equations (16), (24) or (25) ought to be used, as this greatly raises the reliability of the results obtained.

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