Model analysis of the determination of the Mark–Houwink–Kuhn–Sakurada parameters and molecular weight distribution by means of size exclusion chromatography with dual detection

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The analysis of a polymer obeying the log-normal molecular weight distribution (*MWD*) by means of size exclusion chromatography with dual concentration/light scattering or viscosity detection was theoretically examined. The relations between the theoretical and experimental values of *MWD* parameters and Mark–Houwink–Kuhn–Sakurada constants calculated by comparing viscometric, light scattering and effective linear calibrations to the universal one were calculated as functions of the instrument parameters (interdetector volume and resolution factor). The linearity of calibrations calculated from the dual trace directly or indirectly, by combining with the universal calibration, is preserved.

(Keywords: size exclusion chromatography; dual detection; molecular weight distribution)

INTRODUCTION

Recent effort to improve size exclusion chromatography (s.e.c.) instrumentation and the introduction of computer implemented methods make the experimental work easier and faster[1–5]. This holds true especially with the dual detection—concentration/viscosity or (low angle laser) light scattering[4] (LAL)LS detection. Both combinations may be conveniently used to calibrate the separation system for molecular weight M of an unknown chemically homogeneous polymer.

The evaluation of experimental data including the instrumental corrections is a rather complex task. There are several potential sources of error which may be concealed and even further enhanced by the contemporary 'black box' practice, where the user does not go step by step through the calculations.

The error in the marginal parts of chromatograms, i.e. near the leading and tailing edges, due to noise and/or limited sensitivity of the detectors in regions where the concentration approaches zero has been thoroughly analysed by Procházka and Kratochvíl[6,7]. A convenient way to avoid this error is to find the particular calibration (the dependence $\ln M$ vs. y) for elution volume y in the middle of the chromatogram and to extrapolate it into the uncertain regions of y.

There are two important quantities which decide whether a calibration in the middle of the record is correctly determined: the resolution[8–10] (and the resolution correction) and the interdetector volume[3,11–13] (and its correct determination). The resolution factor h is a measure of the peak broadening and is used for the peak spreading correction. The interdetector volume Δ is not simply the equivalent to the geometric volume of the tubing between detectors because of the flow profiles in the connecting tubing and mixing in the detector cells[14,15], nor is it the distance between the detector signal maxima, at least for a polymer sample; there is a shift due to a change in molecular weight along the chromatographic trace.

There are several methods for determining the interdetector volume. The so-called 'correct' or 'effective' interdetector volume for calculating the molecular weight distribution (*MWD*) is that which provides best agreement of local M average (in the peak region on the retention volume axis) with a narrow standard calibration of the same polymer[15].

A similar statement may, of course, be formulated about the resolution factor h employed in the spreading correction calculations. The actual value may depend even upon the actual correction method. It is clear that, in principle, some h and Δ combination may give correct polydispersity (ratio of the weight-average to the number-average of molecular weight, M_w/M_n) for one sample but to fail for another differing, for example, in polydispersity. If the Mark–Houwink–Kuhn–Sakurada (MHKS) parameters are calculated from the s.e.c. data for an unknown polymer, the error may never be revealed unless a thorough analysis of data based on a series of samples is undertaken.

Our goal is to discuss theoretically the effect of errors in Δ and h on the experimental calibration,

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polymolecularity and MHKS parameters. Analytical formulae will be presented for a polymer obeying the log-normal model *MWD*.

The peak broadening is described by the Tung equation generalized for dual detection[16]

$$S'(V)=\int S(y)\,G(V,y)\,\mathrm{d}y \qquad (1)$$

where S' and S are uncorrected and corrected signals of concentration or molecular weight (either viscosity or LS) detectors and the kernel function is defined according to Tung[8,9] as

$$G(V,y)=\sqrt{(h/\pi)}\exp[-h(V-y)^2] \qquad (2)$$

and V and y are variables denoting elution volume. Tung used y as a variable of theoretical functions and V as a variable of experimental functions; we will follow his convention. We will assume that h is independent of y, which for a narrow-*MWD* polymer is a plausible approximation.

The relation between the concentration chromatogram W and *MWD* (denoted as $w(M)$) is given by[17]

$$W(y)=-BMw(M) \qquad (3)$$

where B is the slope of the *MW* calibration

$$\ln M=A-By \qquad (4)$$

The log-normal *MWD* is given by[18]

$$w(M)=\frac{1}{\beta\sqrt{(\pi)}M\beta}\exp\left[-\frac{1}{\beta^2}\ln^2\frac{M}{M_0}\right] \qquad (5)$$

where

$$\beta=\sqrt{(2\ln M_w/M_n)} \qquad (6)$$

and $M_0=\sqrt{(M_w/M_n)}$ are parameters of the *MWD*. Both theoretical (corresponding to the true *MWD*) and experimental (affected by restricted resolution) chromatograms are Gaussian. The Tung solution[8,9] for the normalized experimental chromatogram may be given in the form

$$W(y)=\frac{B\sqrt{H}}{\beta\sqrt{\pi}}\exp[-HB^2/\beta^2(y-y_0)^2] \qquad (7)$$

where the factor H defined by[19]

$$H=\frac{h(\beta/B)^2}{1+h(\beta/B)^2} \qquad (8)$$

may be taken as a measure of the peak broadening related to the *MWD* width.

THEORY

Calibrations

The effects on the parameters A and B of equation (4) will now be examined: the effect of the restricted resolution of the separation system (characterized by the resolution factor h) and the effect of error δ in the interdetector volume determination. Any of the dependences of $\ln M$ vs. y determined from the dual detection data will be called a 'calibration'.

The effect of resolution. We first discuss the case where the experimental calibrations are computed directly from the dual LS–concentration or viscosity–concentration records and known MHKS constants. A good starting point for the following discussion is the equation[19]

$$A'_h=HA+(1-H)(\ln M_0+a\beta^2/4) \qquad (9)$$

and

$$B'_h=HB \qquad (10)$$

describing the turning of the calibration due to the peak broadening. According to ref. 19 the equations hold for the LS detector with $a=1$ and for the viscometric detector with 'a' being the MHKS exponent. Since, according to equation (8), H is lower than unity, B'_h is lower than B. It is seen that, in this case, the slope of the calibration is decreased due to the restricted column resolution.

Let us consider the case of indirect computation, i.e. if the experimental dependence of $\ln[\eta]$ vs. y is compared to the universal calibration[20] $\ln[\eta]M$ vs. y and the calibration $\ln M$ vs. y is computed. (This option is often contained in software packages, e.g. in that of VISCOTEK Corp. The universal calibration $\ln[\eta]M$ vs. y is usually obtained by calibrating with several narrow *MWD* standards and is therefore considered to be affected neither by the column resolution nor by the error in interdetector volume.) The true and the experimental MHKS constants relate, respectively, the theoretical and the experimental calibration (or viscosity record) to the universal. Considering this and equations (9) and (10) we get for the calibration calculated from the viscometric record and the universal calibration:

$$A''_h=[1+a(1-H)]-a(1-H)(\ln M_0+a\beta^2/4) \qquad (11)$$

and

$$B''_h=B[1+a(1-H)] \qquad (12)$$

Here B''_h is larger than B, i.e. the slope of the experimental calibration is higher than the true one. This behaviour is opposite to that in the above case.

The third calibration which it is necessary to mention is the effective linear one (which is calculated from known M_w, M_n and the experimental chromatogram assumed here to be Gaussian); the constants may be given by[19]

$$A'''=A\sqrt{H}+(1-\sqrt{H})\ln M_0 \qquad (13)$$

and

$$B'''=B\sqrt{H} \qquad (14)$$

Here, as in the first case, the slope is decreased by the effect of the restricted column resolution.

It would of course be possible to compare this calibration to the universal (to get the double-prime constants) but a calibration like this would be of limited use.

The effect of interdetector volume. The error in the interdetector volume Δ will be denoted by δ so that for the experimental value Δ_e we have

$$\Delta_e=\Delta+\delta \qquad (15)$$

For the calibration constants we arrive at

$$A'_\delta=(1+D)A-D\ln M_0-D(1+D/2)a\beta^2/2 \qquad (16)$$

and

$$B'_\delta=(1+D)B \qquad (17)$$

where the dimensionless quantity D is defined by

$$D=\frac{\delta B}{a\ln M_w/M_n} \qquad (18)$$

These equations hold for the LS detection (with $a=1$) and for the viscometric detection with known MHKS constants in the same way as equations (9) and (10).

In the case of the indirect computation, i.e. if universal calibration is involved, we have

$$A''_{\delta}=(1-aD)A+aD\left[\ln M_0+\frac{a\beta^2}{2}\left(1+\frac{D}{2}\right)\right] \qquad (19)$$

and

$$B''_{\delta}=(1-aD)B \qquad (20)$$

From equations (17) and (20) it follows that the slopes of the directly calculated calibrations increase with increasing δ while the slope of indirectly calculated calibrations (via universal calibration) decreases. The situation is similar to the effect of peak spreading.

Mark–Houwink–Kuhn–Sakurada constants

We now discuss the determination of the MHKS constants by combining four different calibrations: universal, UC ($\ln[\eta]M$ vs. y; note that this calibration is supposed to be correct); light scattering, LSC ($\ln M$ vs. y determined from the dual concentration/LS trace); viscometric, VIC ($\ln M$ vs. y determined from the dual concentration/viscometric trace, which corresponds to the $\ln[\eta]$ vs. y dependence through the true MHKS constants); and effective linear, ELC. Combining any two of them, except for the pair ELC and LSC, yields the MHKS constants. Let us take as an example UC

$$\ln[\eta]M=u-u'y \qquad (21)$$

and the viscometric record (which corresponds to VIC)

$$\ln[\eta]=v-v'y \qquad (22)$$

We get for the exponent

$$a=\frac{v'}{u'-v'} \qquad (23)$$

and for the constant

$$\ln K=v+(v-u)a \qquad (24)$$

We may of course make use of more sophisticated (and less graphical) computational methods[21,22] but the physical fact of the relation between the calibrations remains unchanged. A very similar rationale may be followed if the LS detector is employed.

The single-run calibrations are the starting point for the determination of the MHKS parameters at present. In *Table 1* formulae for the apparent or 'experimental' MHKS exponents and constants are summarized as functions of the resolution factor h and the error in the interdetector volume δ. For $h\rightarrow\infty$, i.e. for $H\rightarrow 1$, or for $D\rightarrow 0$, i.e. for $\delta\rightarrow 0$, the experimental MHKS parameters approach the theoretical ones.

Figure 1 demonstrates the single-run-based apparent values of the MHKS exponent a' for a model case of $a=0.5$ and $M_w/M_n=2$. The error is higher in cases of the UC–LSC and UC–VIC combinations than in the cases of the ELC–UC and ELC–VIC combinations. The error is opposite in cases of UC–LSC and UC–VIC (curves 1 and 4, respectively) because the single-prime calibrations (with LSC) turn in the opposite direction to the double-prime ones (based on UC). *Figure 1b* demonstrates the usefulness of the factor H defined by equation (8); the dependences of a' vs. H are almost linear. The factor H comprises both characteristics of the polymer and the separation system. For this reason we suggest that the extent of the instrumental correction should also be expressed in terms of H even in the case of real polymers and separation systems. The same holds for D but here the situation is less involved because of the proportionality $D\sim\delta$.

The experimental determination of the constant K' is more uncertain. We feel that the significance of K' determined from a single s.e.c. run is a supplement to a' determined in the same run rather than a parameter related to the structure of the polymer etc. For this reason we favour dwelling on a' preferably.

Table 1 Apparent MHKS constants K' and exponents a' calculated for the log-normal *MWD* from the true K and a for various combinations of calibrations

Method	a'	$\ln(K'/K)$
Effect of resolution		
UC–LSC	$\frac{a+1}{H}-1$	$-2\frac{(1-H)}{H}(\ln M_0+\beta^2/4)$
UC–ELC	$\frac{a+1}{\sqrt{H}}-1$	$(a+1)\frac{\sqrt{H}-1}{\sqrt{H}}\ln M_0$
UC–VIC	$\frac{aH}{a(1-H)+1}$	$\frac{a(a+1)(1-H)}{a(1-H)+1}$
ELC–VIC	$a\sqrt{H}$	$a[(1-H)(\ln M_0+a\beta^2/4)+\sqrt{H}(\sqrt{H}-1)]$
Effect of interdetector volume		
UC–LSC	$\frac{a+1}{D+1}-1$	$(a+1)\frac{D}{D+1}[\ln M_0-(1+D/2)a\beta^2)a\beta^2/2]$
UC–VIC	$\frac{a(D+1)}{1-aD}$	$\frac{aD(a+1)}{aD-1}[\ln M_0+(1+D/2)a\beta^2/2]$
LS–VIC[a]	$\frac{a(D_V+1)}{1+aD_{LS}}$	$\frac{a}{1+aD_{LS}}\left\{(aD_{LS}-D_V)\ln M_0+\left[D_{LS}\left(1+\frac{aD_{LS}}{2}\right)(1+D_V)-D_V\left(1+\frac{D_V}{2}\right)(1+aD_S)\right]a\beta^2/2\right\}$
ELC–VIC	$a(1+D)$	$-aD[\ln M_0+(1+D/2)a\beta^2/2]$

[a] D_{LS} and D_V are defined for the interdetector volume between the concentration and, respectively, light scattering and viscometric detectors

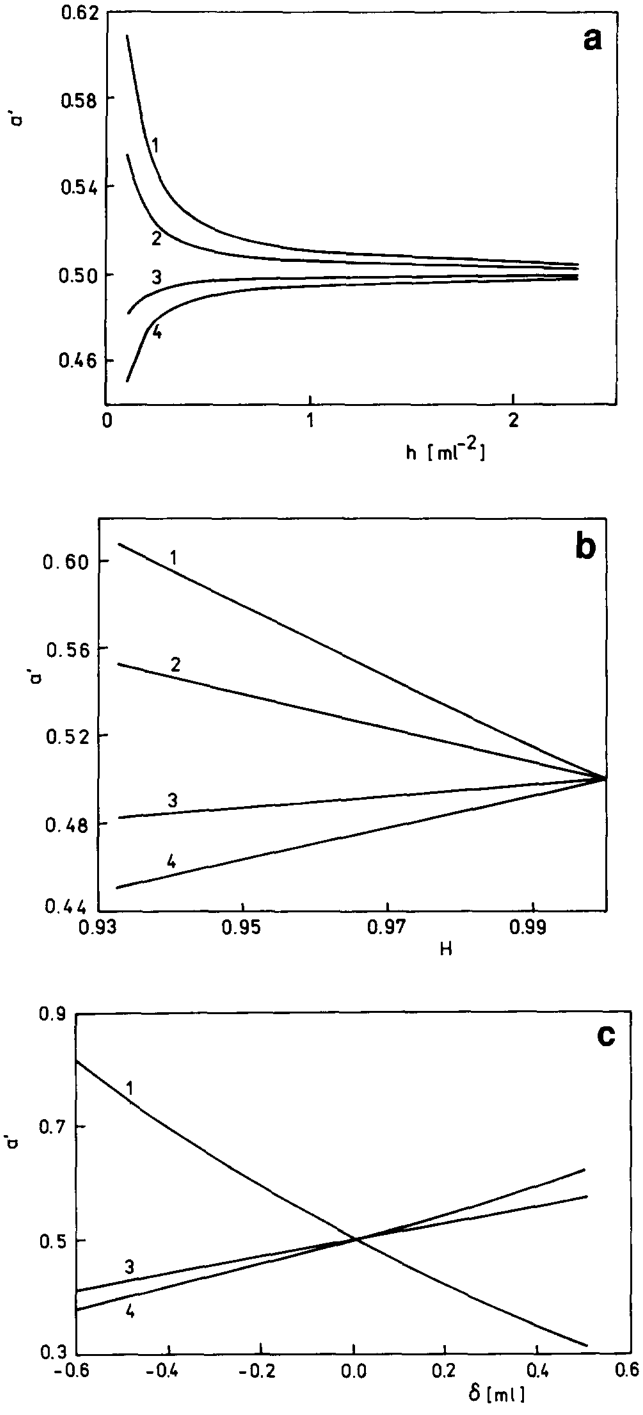

Figure 1 Experimental MHKS exponents a' calculated for a model *MWD* ($a=0.5$; $M_w/M_n=2$) combining different apparent ('experimental') calibrations as functions (a) of the factor h; (b) of the quantity H defined by equation (8); (c) of the factor δ defined by equation (15). The combinations of calibrations for the calculation were: 1, UC–LSC; 2, ELC–UC; 3, ELC–VIC; 4, UC–VIC

The molecular weight distributions

The apparent ('experimental') *MWD* parameters M'_0 and β' are summarized in *Table 2*. *Figure 2* shows some examples of apparent polydispersity $(M_w/M_n)'$ for our model polymer with $a=0.5$ and $M_w/M_n=2$ and the separation system with calibration slope $B=0.1$. The most prominent feature is a high sensitivity of the dual detection methods (LSC–UC and VIC–UC combinations) to the resolution factor h compared to classic analysis of the s.e.c. data based on the conventional calibration. For example, the error of the VIC–UC combination is almost three times higher than in the evaluation according to the calibration, as can be clearly seen from *Figure 2b* where H has been used as ordinate. As in the case of the exponent a' the dependences of $(M_w/M_n)'$ vs. H are practically linear.

As for the effect of the error in the interdetector volume, the dependences of polymolecularity $(M_w/M_n)'$ vs. δ are almost linear too. In the VIC–UC combination, linearity is almost perfect. This may be explained by a partial compensation of the MHKS exponent in the calculation of UC and VIC.

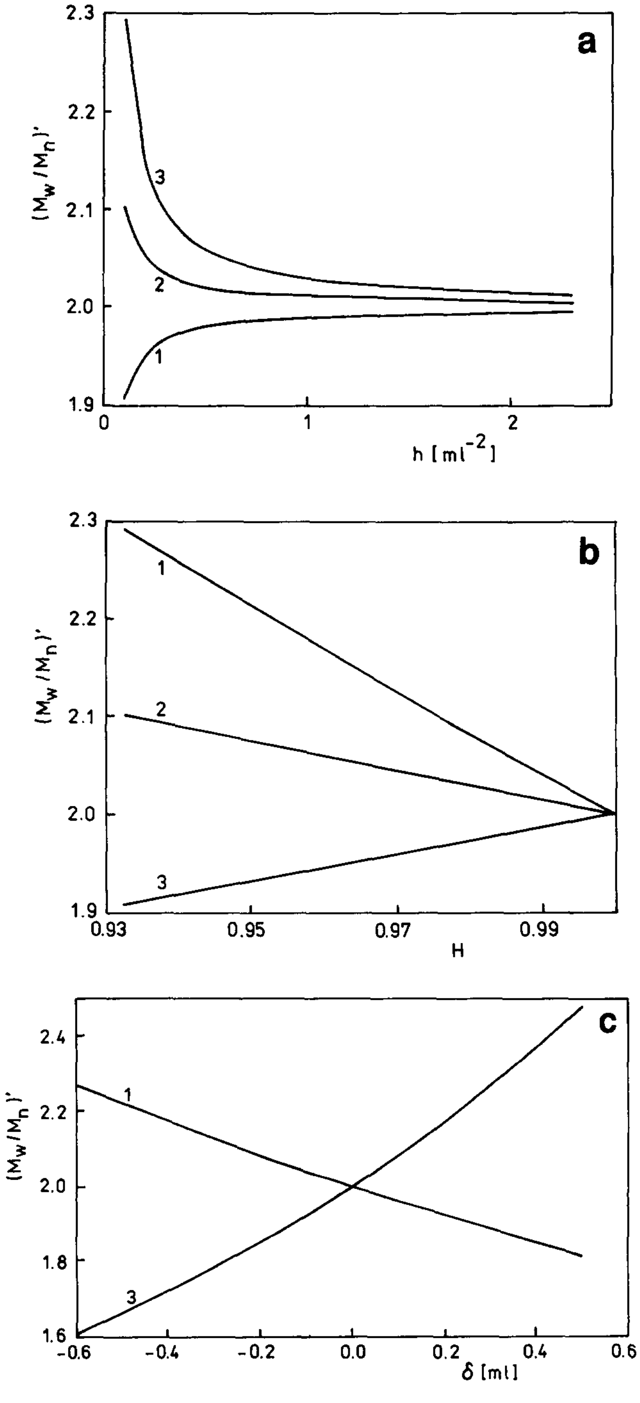

Figure 2 'Experimental' polydispersity $(M_w/M_n)'$ calculated for a model *MWD*. The combinations of calibrations for the calculation were: 1, UC–LS; 2, conventional calibration; 3, UC–VIC. For the *MWD* parameters and for description of abscissa see legend to *Figure 1*

Table 2 Apparent *MWD* parameters β' and M_0' of the log-normal *MWD* defined by β and M_0 as results of the resolution factor h and error in the interdetector volume Δ' for various combinations of calibrations. For the definitions of H and D see equations (8) and (18)

Method	β'/β	$\ln(M_0'/M_0)$
Effect of the resolution		
UC-LS[a]	$\sqrt{H}$	$(1-H)a\beta^2/4$
UC-VIC	$\frac{1+a(1-H)}{\sqrt{H}}$	$-(1-H)a\beta^2/4$
CALIB[b]	$1/\sqrt{H}$	1
Effect of interdetector volume error Δ'		
UC-LSC	$(1+D)$	$-(1+D/2)a\beta^2 D/2$
UC-VIC	$(1-aD)^2$	$(1+D/2)a^2\beta^2 D/2$

[a] Published in ref. 19
[b] Published in refs 8 and 9

Small changes in M_0 (*Table 2*) reflect the shifts due to the calibrations turning around a point, the abscissa of which lies between those of the maxima of the concentration and LS or viscosity traces. (ELC turns around the point which has the same ordinate as the maximum and therefore M_0 does not change at all.)

CONCLUSIONS

The calculations presented display the expected error in the calculation of the MHKS parameters and *MWD* parameters due to the error in the interdetector volume determination and to the restricted resolution power of the separation system if the correction is not performed correctly or at all. It is intended to help in understanding the complexity of the relations between the calibrations and also to familiarize the reader with the tendencies which may occur if different options of commercial software (corresponding to different combinations of calibrations) are taken. If real measurements are undertaken, phenomena such as a different extent of the peak broadening observed in signals of the two detectors, variations in the baseline, etc., may occur. Numerical techniques which are more universal but less graphical have to be used in these cases.

Note added in proof. After this paper was submitted to the editorial board a paper dealing with similar problems was published[23]; we recommend it to the attention of the reader.

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