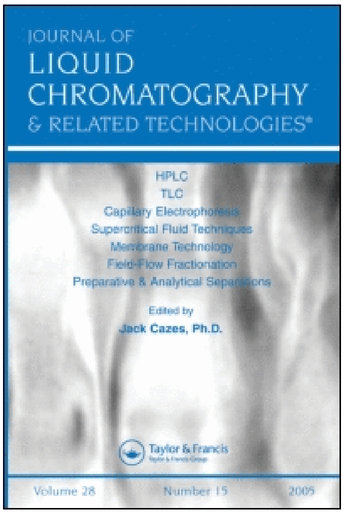

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Remarks on the Calibration of Steric Exclusion Liquid Chromatography by Polymolecular Standards

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REMARKS ON THE CALIBRATION OF STERIC EXCLUSION LIQUID CHROMATOGRAPHY BY POLYMOLECULAR STANDARDS

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ABSTRACT

The relation of polymer molecular characteristics versus chromatographic parameters in steric exlusion liquid chromatography (GPC) was considered as a typical black box problem. Practical problems were discussed for cases of the GPC black box calibration with polymolecular polystyrene standards and of using an improper calibration model. It was concluded that checking the reliability of the GPC black box calibration is of utmost importance especially when narrow calibration standards are not available.

INTRODUCTION

The value of the molecular weight distribution data of polymers evaluated by steric exclusion liquid chromatography (GPC) depends on the sensitivity of the technique in the low and high molecular weight regions and, on the other hand, on the proper solution of the GPC black box problem that is of the reliable mathematical description of the relation of polymer molecular characteristics versus the chromatographic parameters. Proper mathematical description of the GPC separation process of polymers is practically not feasible therefore applications of this technique to establish molecular weight distribution (MWD) curves of polymer samples must be preceded by a solution of the above mentioned black box problem.

The black box symbolizes here processes taking place in the GPC instrument. During the calibration step of the black box input data comprise either values of molecular weights of a set of narrow MWD standards or values of different molecular weight averages of one or more polymolecular standards while chromatograms of the applied standards serve as the output data. Applying the GPC unit for evaluation of MWD curves of polymer samples the input and output data are reversed. Thus in order to correlate properly the input and output data the application of a mathematical model of the black box is required.

The model should encompass mathematical descriptions of the molecular weight, M versus retention volume, V relationship and of the instrumental spreading. With a set of well characterized narrow standards the problem of establishing the V - M relation is a trivial one and only the spreading effects should be properly eliminated. It can not be, however, overstressed that calibrating a GPC unit with characterized polymolecular polymer standards the reliability of the black box mathematical model, i.e.

of the V - M relationship and of the spreading characteristics is of utmost importance. To illustrate this point a mathematical black box model is sought basing on two popular broad MWD polystyrene standards (lustrex and NBS 706 (1)) whose average molecular weights are rather imprecise and, secondly, simulated GPC data are processed with an assumed not correlated black box model.

EXPERIMENTAL

Experimental results obtained for a set of 8 narrow and for a pair of broad polystyrene standards were taken from reference (2). Values of the molecular weight calibration parameters C_1 and C_2 appearing in the model linear relation

$$V = C_1 - C_2 \ln M \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (1)$$

were evaluated either by the least squares method for peak elution volumes and peak molecular weights of the narrow standards or by the iteration method developed for broad standards as described in reference (2). Computer simulations of chromatograms of 4 broad standards evaluated with a linear V - ln M model calibration and assuming infinite column resolution (no spreading effects) were made as described in reference (3).

RESULTS AND DISCUSSION

Evaluation of the GPC black box model based on a pair of broad standards. Values of the calibration paramethers C_1 and C_2 established classically by the least squares method for a set of 8 narrow polystyrene standards as well as values of these parameters calculated for pairs of polymolecular polystyrene standards according to our method in which the spreading effects are numerically eliminated (2) are in Table 1. Using parameters of the evaluated relations percent average molecular weight deviations $\delta\bar{M}$ of the 2 broad polystyrene standards were calculated according to the equation

$$\delta\bar{M} = 100\ (\bar{M}exp - \bar{M}t)\ /\ \bar{M}t \ \ldots\ldots\ldots\ldots \quad (2)$$

where $\bar{M}exp$ may be equal to the number - $\bar{M}n$ or weight - $\bar{M}w$ average molecular weight, respectively as calculated from the GPC data, and the subscript "t" denotes true (supplied) values of the average molecular weights. Values of the symmetrical spreading parameter σ and of the skewing parameter τ were calculated from the following standard relations (4)

$$\sigma = (2\ C_2^2\ \ln X_1)^{1/2} \ \ldots\ldots\ldots\ldots\ldots\ldots \quad (3)$$

$$\tau = C_2\ X_2 \ \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (4)$$

TABLE 1

Molecular weight calibration parameters evaluated for narrow and broad*/ polystyrene standards

No	Type of standards	C_1	C_2
		$cm^3 / 5\ cm^3$	
1 a/	set of 8 narrow	35.077	1.462
2 b/	Pair: lustrex NBS706a	35.437	1.492
3 c/	Pair: lustrex NBS706b	33.735	1.345

*/ Symmetrical spreading is assumed

a/ M peak from 3 550 to 830 000

b/ lustrex: $\overline{M}n$ = 70 000, $\overline{M}w$ = 230 000

NBS706a: $\overline{M}n$ = 136 500, $\overline{M}w$ = 257 800

c/ NBS706b: $\overline{M}w$ = 283 100

where $$X_1 = (\overline{M}n,t / \overline{M}n,exp + \overline{M}w,exp / \overline{M}w,t) / 2$$

and $$X_2 = (\Phi - 1) / (\Phi + 1)$$

$$\Phi = (\overline{M}n,t / \overline{M}n,exp) (\overline{M}w,t / \overline{M}w,exp)$$

Results of the above calculations may be found in Table 2

TABLE 2

Percentage deviations $\delta\overline{M}$ of average molecular weights of broad polystyrene standards and instrumental spreading parameters σ(symmetrical) and τ(skewing) calculated for different variants of the evaluated V - ln M calibration relation

No of cal.eq. from TAB. 1	Polystyren Standard	$\delta\overline{Mn}$	$\delta\overline{Mw}$	σ	10^3 τ
		%		cm^3 / 5 cm^3	
1	lustrex	-2.9	1.7	0,314	9
	NBS706a	-11.9	12.6	0.724	6
	NBS706	-11.9	2.5	0.574	74
2	lustrex	-0.7	0.7	0,177	0.2
	NBS706a	-10.0	11.1	0.687	0.2
3	lustrex	-13.4	15.5	0,722	-0.1
	NBS706b	-14.7	17.2	0.757	-0.1

Parameters of the calibration relation No 1 in Table 1 may be considered as most reliable therefore values of σ and τ calculated with these parameters for the broad standards illustrate correctly the spreading characteristics of the applied instrument. The trouble is that these characteristics depend strongly on the accuracy of values of average molecular weights of the considered standards. When the measured by equilibrium ultracentrifugation $\overline{Mw}$ value of NBS706 standard was taken in the calculations the instrument seemed to have considerable skewing while the light scattering $\overline{Mw}$ value of the same standard did not confirm the existence of skewing effects.

The last result is confirmed, on the other hand, by values of parameters σ and τ calculated for lustrex - the second broad polystyrene standard in case of which $\overline{M}w$ was measured by the light scattering method.

As mentioned above the calibration relations No 2 and No in Table 1 were established with the assumption of symmetrical instrumental spreading. Although values of σ and τ evaluated for calibration No 2 correlate well with this assumption the evident skewiness present in case of calibration No 3 was completely hidden (negligible values of τ). In the last case the wrongly chosen symmetrical instrumental spreading model of the GPC black box strongly influenced values of the V - ln M relation what resulted in much higher values of the symmetrical spreading parameter σ. The described solution example of the GPC black problem may be considered as a typical one since the measurement accuracy of the $\overline{M}w$ value of polymolecular samples is of the order of 5 - 10 % . This is exactly the case with the NBS706 standard where the 2 quoted values of $\overline{M}w$ differ by circa 10 % (288 100 and 257 800). Thus, if an accurate molecular weight calibration curve is to be obtained it is imperative that a reliable spreading characteristics are established. To this end the still best solution is application of a set of narrow standards and checking the instrumental spreading effects with a well molecularly characterized broad standard. In the recent National Bureau of Standards catalog (5) only one value of $\overline{M}_w$ in case of the NBS706 standard is quoted thus avoiding the confusion caused by 2 different values of $\overline{M}_w$ for the same standard.

Using an improper GPC black box model with simulated chromatograms. The simulated GPC chromatograms of 4 polymolecular standards did not involve any spreading effects. When they were used with the GPC black box model comprising the linear V - ln M relation and symmetrical spreading the parameters C_1, C_2 and σ were evaluated for 3 pairs of these standards. The obtained results are in Table 3.

TABLE 3

Molecular weight and symmetrical spreading calibration parameters calculated for pairs of simulated chromatograms with eliminated spreading effects*/

$\overline{M}_w$ of pairs of standards $\overline{M}_w / \overline{M}_n = 2$	C_1	C_2	σ_i	σ_{i+1}
	cm^3 / 5 cm^3			
1 - 2 150 000 2 - 1 300 000	82.61	3.50	2.11	2.19
3 - 13 000 4 - 7 600	75.95	3.00	1.22	0.98
2 - 1 300 000 3 - 13 000	76.51	3.06	2.61	1.10

*/ True values: $C_1 = 77.76$; $C_2 = 3.22$; $\sigma = 0$

After comparing the results in Table 3 with the quoted under the Table true values of the evaluated parameters the simple conclusion is that by using an improper GPC black box model wrong values of the calibration parameters are obtained. In other words - the chosen model supplies non - zero values of all parameters existing in the model. Although the obtained results could have been expected it is usually the case that in practice, by not knowing the proper GPC black box model, the experimenter assumes the simplest one without any evaluation of the source of systematic errors introduced this way into the GPC polymer analyses.

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