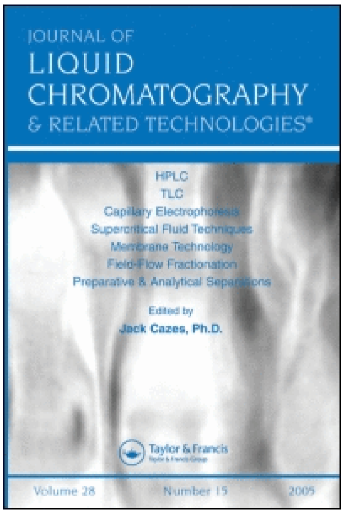

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CALIBRATION OF SEPARATION AND INSTRUMENTAL PEAK BROADENING IN SEC COUPLED WITH LIGHT SCATTERING OF SIMPLE POLYMERS

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ABSTRACT

A recently developed procedure for calibration of separation and instrumental peak broadening in SEC was used for a comparative study of separation and axial dispersion of polystyrene, poly(methyl methacrylate) and poly(vinylchloride). The influence of the uncertainty in the volume lag between the concentration and LALLS detectors upon peak broadening was investigated and a new procedure for the determination of the lag was proposed. The applicability of the universal calibration concept was tested; all the polymers have been found to match a single universal calibration function. Polystyrene and poly(methyl methacrylate) also coincided very well with respect to the instrumental spreading, but for poly(vinylchloride) spreading was found to be a function of polymer concentration.

Dedicated to Prof. J. Schurz on the occasion of his 65th birthsday

TABLE 1

Production of Thermoplastics in Western Europe
1988 (1000 tons/a)

Simple polymers	69%	Complex Polymers	31%
PVC	5100	LDPE	4960
PP	2950	LLDPE	500
HDPE	2550	SAN, ASA	285
EPS	493	PP-Compounds	160
PMMA	5	RF-PP	6
PC	198	POLYMER BLENDS	
POM	89	PC/ABS, PPO/PS	
PPO	89	PP/EPDM, PC/PBTP	
PA	650	PBTP/PETP...	150
PTFE	12		
PETP,PBTB	328		
	14266		6526

INTRODUCTION

Simple polymers, i.e., linear homopolymers at present still represent about 70% of the total mass of thermoplastics produced in Western Europe (Table 1).

Despite their technical importance and structural simplicity, reliable and accurate determination of the molecular mass distribution of these polymers on an absolute scale by SEC is not yet accomplished in conventional measurements, since it requires a precise calibration of separation and instrumental peak broadening. Experimental evaluation of instrumental peak broadening in particular is a troublesome task, since truly monodisperse standards of synthetic polymers are not available. Furthermore, many recommended procedures such as the reverse flow technique (1), recycling methods (2) or complex calibration methods with samples of known molar mass distribution (MMD) (3) are too tedious to become general practice. Recent developments therefore have intensified the use of online molecular mass detection for calibration of instrumental peak broadening (4 - 7). Using polystyrene standards and a multimodal polystyrene sample with broad MMD, the application of an improved computational procedure for simultaneous calibration of separation and instrumental peak broadening has recently been presented (8). In this paper this procedure is used in a comparative study of separation and instrumental peak broadening of polystyrene, poly(methyl methacrylate) and poly(vinylchloride) to gain further experience on the general validity of this method.

MATERIALS

Samples of polystyrene standards were obtained from Polymer Laboratories Ltd. (Church Stretton, Shropshire, UK). Poly(methyl methacrylate) (PMMA) and poly(vinylchloride) (PVC) standards were obtained from Polymer Standards Service GmbH. (Mainz, F.R.G.). Nominal molecular weight averages of the samples are summarized in table 2. Tetrahydrofurane (THF) anal. grade (Merck, Darmstadt, F.R.G.) was used as supplied. PS and PVC samples were dissolved during 24 h at ambient temperature; for PMMA samples the temperature of 50 °C was used.

METHODS

Apparatus

The measurements were carried out at ambient temperature on a high-performance SEC system consisting

TABLE 2

Peak molecular weight ($M_p = \sqrt{M_w * M_n}$) and polydispersity (M_w/M_n) of polystyrene (PS), poly(vinylchloride) (PVC) and poly(methyl methacrylate) (PMMA) standards as given by the suppliers and the composition of a broad multimodal PS mixture

Code	M_p	M_w/M_n	Composition of PS-7 M_p	weight%
PS-1	9000	1.04	PS injection molding	
PS-2	34500	1.05	grade	64.7
PS-3	68000	1.06	68000	4.6
PS-4	170000	1.04	110000	9.2
PS-5	500000	1.08	170000	5.3
PS-6	1130000	1.06	390000	3.4
PS-7	mixture		670000	9.1
			1130000	3.7

Code	M_p	M_w/M_n	Code	M_p	M_w/M_n
PMMA-1	34400	1.04	PVC-1	12900	1.16
PMMA-2	73000	1.04	PVC-2	19100	1.25
PMMA-3	145000	1.05	PVC-3	34400	1.15
PMMA-4	245000	1.03	PVC-4	45900	1.14
PMMA-5	570000	1.03	PVC-5	68900	1.12
			PVC-6	87800	1.16

of the following components: HPLC-pump Modell 510 (Waters Associates, Milford, MA, USA), an injection valve with 25 μl loop (Knauer, Berlin, F.R.G.), PL mixed gel column (Polymer Laboratories Ltd., Church Stretton, Shropshire, UK) of 60 cm length and 10 μm particle diameter. Two detectors - a low angle laser light scattering (LALLS) photometer, (KMX6, LDC/Milton Roy, Hasselroth, F.R.G.) and a differential refractometer detector (Multiref 902, Optilab, Vällingsby, Sweden) - were connected in series. Specific refractive index increments of the different polymers were taken from the literature (PS, dn/dc = 0.185 ml/g; PMMA, dn/dc = 0.083 ml/g; PVC, dn/dc = 0.104 ml/g) (9). The effective flow rate (1.07 ml/min) was checked by weighing the eluent.

Data Acquisition and Evaluation

SEC/LALLS data were collected by a personal computer (IBM PC-XT), equipped with a 4 channel high speed data acquisiton system of 12 bit resolution. The concentration signal S(v) was normalized with respect to the area $e(v) = S(v)/\int S(v)\,dv$. The LALLS signal E(v) was normalized so that $E(v)/e(v) = M_w(v)$ and $\int E(v)\,dv = M_w$, where $M_w(v)$ is the instantaneous weight average molecular mass in the detector cell. Computer programs for data acquisition and interactive processing of the SEC data, including graphical selection of baseline, integration limits and calculation of the 'eluogram' e(v) and transformed scattering signal E(v) were developed in our laboratory.

Calibration of Separation and Peak Broadening

The theoretical approach to the evaluation of the axial dispersion in SEC is based on the equations of Tung (10), Berger (11), and Yau (12). On the basis of a linear calibration function $\ln M(v) = A - B*v$, which is very often realized with modern mixed bed columns, and assuming the axial dispersion function to be a Gaussian with variance σ^2, two basic equations relating the true calibration function M(v), the dispersion parameter σ and the SEC/LALLS signals e(v) and E(v) have been derived:

$$E(v) = e(v-B\sigma^2) * \exp(B^2\sigma^2/2) * \exp(A - Bv) \qquad [1]$$

$$e(v) = E(v+B\sigma^2) * \frac{\exp(B^2\sigma^2)}{\exp(A - Bv)} \qquad [2]$$

For details concerning the derivation of eq. [1] and [2] we refer to (7,8). Both equations are equivalent. A new computational procedure for solving these equations for the unknown coefficients of M(v) and σ by nonlinear regression has been presented recently (8). This procedure allows one to evaluate σ when the true M(v)-function is known, or to calculate the coefficients of the linear calibration function in case of known σ. With broad and narrow samples the values of A,B and σ can be calculated by an iterative procedure without a priori knowledge of M(v). Figure 1 shows the eluograms e(v), the light scattering functions E(v), and the $M_w(v)$-functions for PS-5 and PS-7. The effective calibration line $M_w(v)$ of the narrow sample PS-5 deviates from the classical calibration line (squares in fig. 1) much more than those of PS-7. Starting values for the coefficients A and B were obtained from $M_w(v)$ of the broad sample PS-7, since the function $M_w(v)$ of a broad distribution sample is generally very close to the true M(v), as proved by model calculations (13). E(v) of the narrow sample was calculated from the measured e(v) on the basis of eq.[1] using A and B from $M_w(v)$ of PS-7; σ was then varied until the best fit between the calculated and measured E(v) was obtained. E(v) of the broad sample PS-7 was treated in a similar way, now

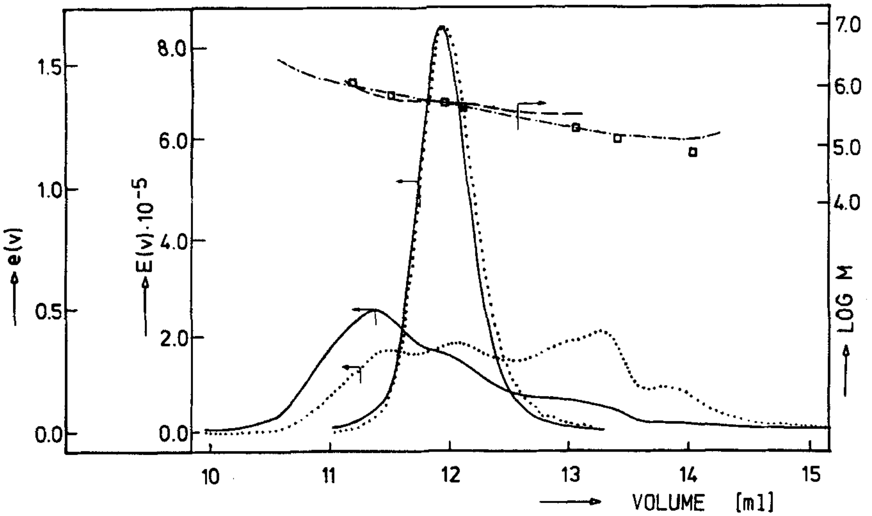

FIGURE 1 Eluogram e(v) (•••), light scattering function E(v) (——) and effective calibration lines $M_w(v)$ (—•—) of narrow polystyrene standard PS-5 and broad mixture PS-7 (for composition cf. table 2); (□) points from calibration with narrow standards

optimizing for A and B. This procedure results in an increase of the slope of $M_w(v)$ of PS-7. After 3 - 4 repetitions of these steps, $M_w(v)$ of PS-7 converged to M(v) whilst A, B and σ became constant within the precision of measurement.

For narrow samples of PMMA (14) and PVC (15), another calibration method was adopted using this evaluation procedure. Starting from the measured $M_w(v)$-function and assuming different σ values, different calibration lines M(v) were calculated. This apparent M(v)-functions intersect within a very small domain (± 2% in M, ± 0.2% in v). Although these crosspoints do

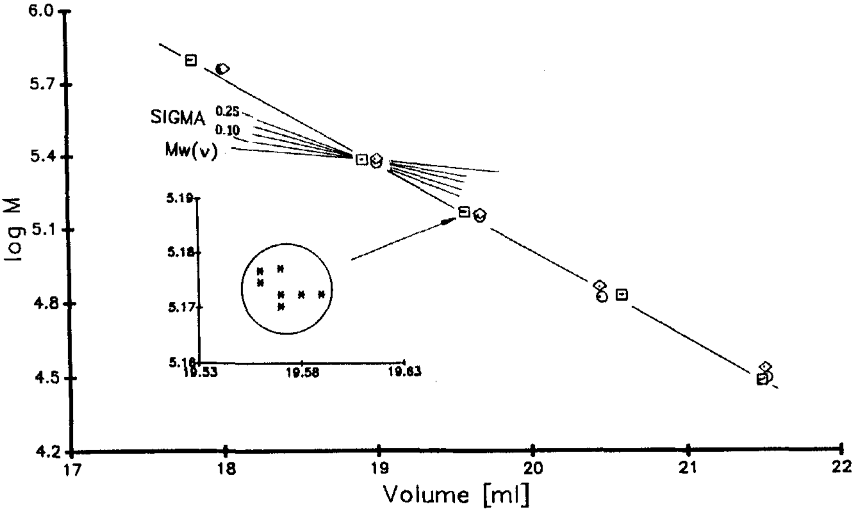

FIGURE 2 Calibration for PMMA by different methods; ◇ M_p from suppliers data; ○ M_p from SEC/LALLS online; □ crosspoints of apparent M(v)-functions (cf. text)

not coincide with points from classical calibration carried out both with the suppliers data and our own SEC/LALLS measurements of weight and number average molecular weight (uncorrected for peak broadening), the agreement of the calibration line is very good, as seen clearly in figure 2.

Determination of Detector Lag

Data evaluation from SEC/LALLS online requires a precise determination of the volume lag between the two detectors connected in series, since this parameter influences the slope of the molecular mass function $M_w(v)$ and consequently the value of σ. This was

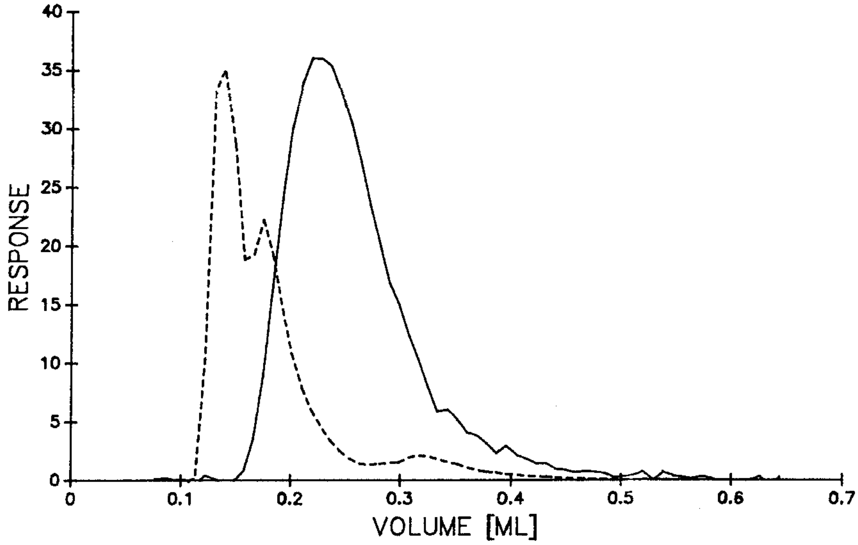

FIGURE 3a Concentration (——) and LALLS (•••) signals from a SEC/LALLS run without columns inserted

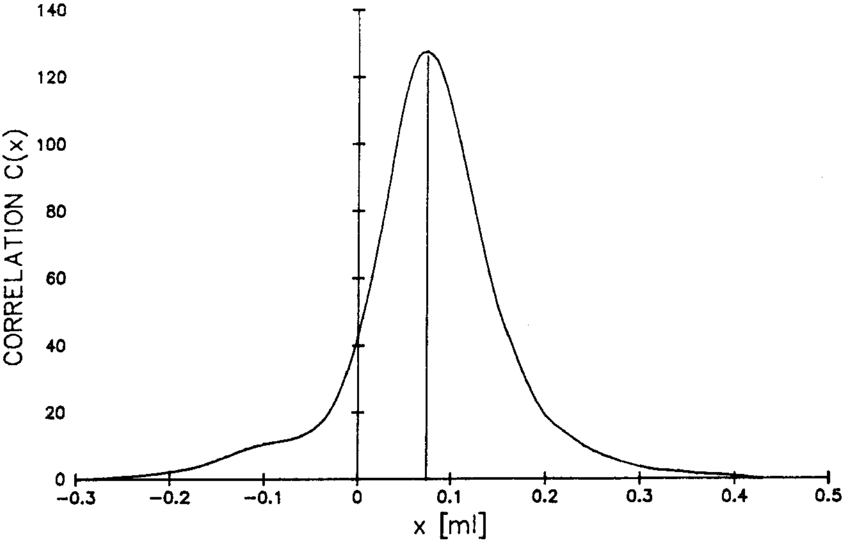

FIGURE 3b Determination of the detector lag from the maximum of the crosscorrelation function of the signals in figure 3

accomplished by crosscorrelation of concentration and light scattering signal from chromatographic runs without columns inserted,

$$C(x) = \int e(v) * E(v-x)\, dv$$

The lag value results from the maximum of the correlation function. The reproducibility of that method (±5μl) appeared to be superior to any other method tested in our laboratory. Figures 3a and 3b show typical SEC/LALLS signals and the calculated correlation function.

RESULTS AND DISCUSSION

In figure 4 the product of peak molecular weight M_p and limiting viscosity number $[\eta]$, measured by means of an Ubbelohde viscometer at 25 °C, is plotted versus the retention volume v. According to the approach suggested by Benoit et al. (16), all polymers match into a single universal calibration function if the molecular separation is controlled by hydrodynamic volume only. We see that the concept of universal calibration is realized reasonably well for PS, PMMA and PVC, when the following parameters of the Staudinger-Mark-Houwink equation are used:

$K = 1.6*10^{-4}$ dl/g, $a = 0.706$ for PS (17),
$K = 1.6*10^{-4}$ dl/g, $a = 0.770$ for PVC (18),
$K = 1.3*10^{-4}$ dl/g, $a = 0.688$ for PMMA (19),

A comparative investigation of PS, PMMA, and PVC concerning peak broadening has been performed on the same SEC column. Summing up numerous experiments, the

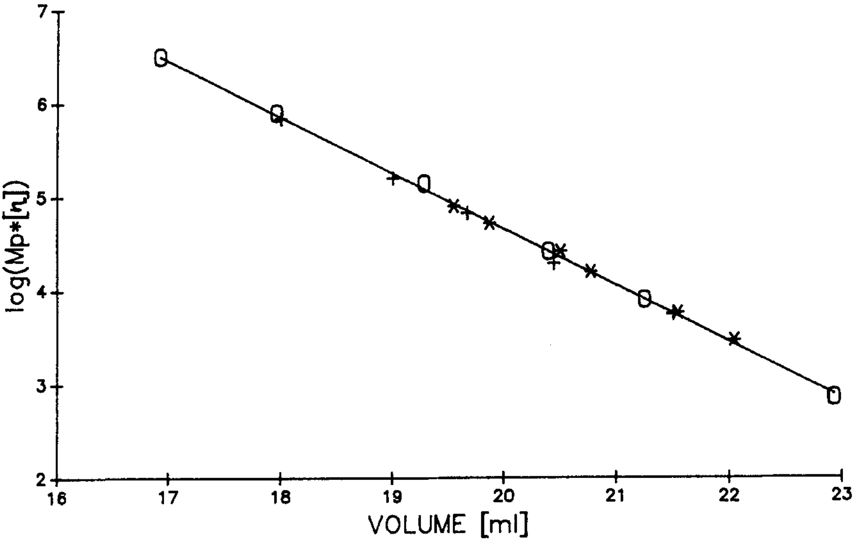

FIGURE 4 Universal calibration plot of PS (o), PMMA (+) and PVC (*) samples in THF

dependence of the peak broadening parameter σ on the elution volume is shown in figure 5. As can be seen, the data for PMMA and PS decrease with elution volume. According to the theoretical approach of Cheng, Wang and Zhao (20)

$$V_{max} = V_o + 1 / (k*B) ,$$

where k is a constant close to 1, V_o is the exclusion limit and B = the slope of M(v), the maximum V_{max} of σ is expected to lie between 13.5 and 15.0 ml. However, for PVC the σ values have been found to depend on concentration. At a high PVC concentration (2 mg/ml, x in fig. 5), σ increases with elution volume. Only when the injected concentrations are less than 1 mg/ml

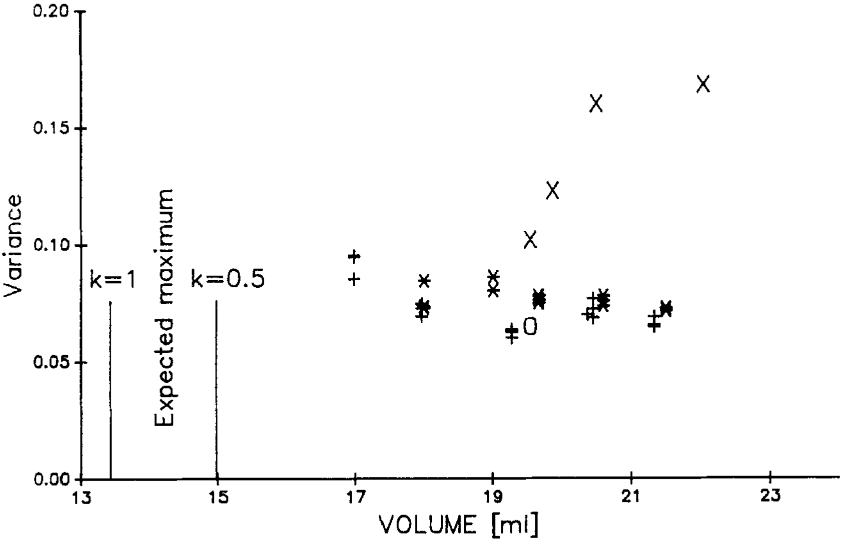

FIGURE 5 Variance σ^2 of the spreading function of PS (+), PMMA (*) and PVC (o,x) samples; (o) PVC conc. < 1.0 mg/ml, (x) PVC conc. > 2.0 mg/ml

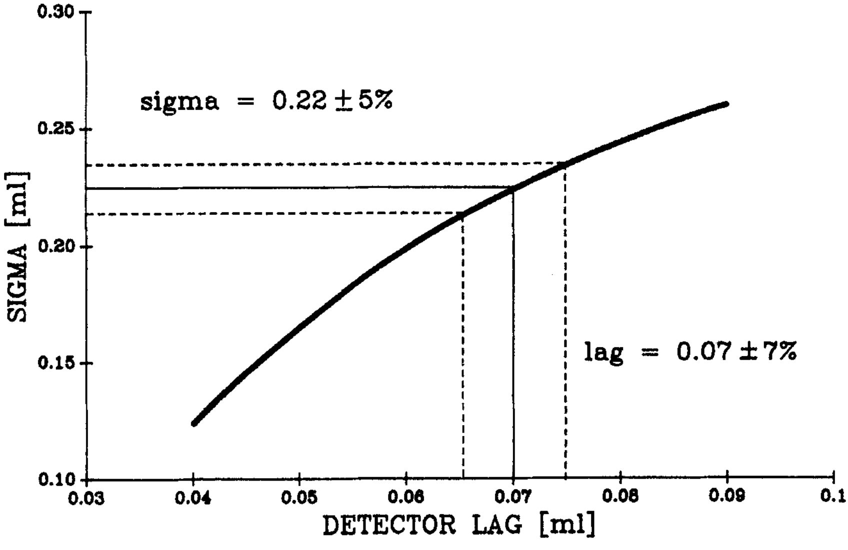

FIGURE 6 Effect of the precision of detector lag determination on the spreading factor calculated from SEC/LALLS.

(o in fig. 5) the value of σ becomes comparable with that for PS or PMMA. The fact that the PVC samples coincide quite well with PS and PMMA in the universal calibration plot but differ so much with regard to peak broadening is surprising. This phenomenon must be further studied and no explanation can be presented at this time.

To evaluate the influence of the precision of detector lag determination upon the peak broadening parameter calculated from SEC/LALLS, σ was determined for a wide range of detector lags. The functional dependence of the σ parameter on the detector lag is shown in figure 6. Taking the standard error for the determination of the lag (±7%) an uncertainity of ±5% in the calculated dispersion parameter will result. Since the reproducibility of peakdispersion from SEC/LALLS is about ± 15%, the precision of the lag appears to be sufficient for the applicability of the method.

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