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DENSIMETRIC DETECTION IN GEL PERMEATION CHROMATOGRAPHY

VII. CALCULATION OF MOLECULAR WEIGHT DISTRIBUTIONS USING A PROGRAMMABLE POCKET CALCULATOR

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SUMMARY

It is shown that the measurement of density (mass per unit volume) according to the mechanical oscillator method can be used with advantage for detection in high-performance gel chromatography. The digital signals obtained from such an instrument are inherently integrated over each measuring interval, hence calculation of molecular weight averages from the raw data can be done very easily by means of a programmable pocket calculator. The program described in this paper has been written for the HP 34C; it includes compensation for flow-rate changes and baseline drift and accepts a sufficiently large number of data points. The performance of the method was tested by arranging a photometer and the density detector in series in the eluent stream from a gel permeation chromatographic column.

INTRODUCTION

Gel permeation chromatography (GPC) is a powerful tool in the characterization of polymers with respect to their molecular weight distribution (MWD): qualitatively, the comparison of chromatograms shows differences in the MWD of polymer samples; quantitatively, it allows the simultaneous determination of the mass and number average, M_w and M_n, molecular weights from one single chromatogram. If GPC is used as a quantitative method, one must keep in mind possible sources of error, estimate their influence on the results and try to minimize their effects, as has been pointed out by several authors[1–3]. Some problems can be avoided if the measurement of density (mass per unit volume) according to the mechanical oscillator method[4] is used for detection, as will be shown in this paper. In this case, molecular weight averages can be calculated very easily and with good accuracy by means of a programmable pocket calculator. To elucidate the scope and limitation of this method, the various sources of errors in GPC will first be discussed.

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Errors due to the separation system

The first group of errors includes those arising from adsorption and partition mechanisms besides the steric exclusion process[1], concentration effects (leading to distorted chromatographic peaks[5–7]) and peak dispersion due to diffusion phenomena in the separation columns, detector(s) and in the capillary connections between them[1–3,5–8].

While one can mostly avoid the first two error sources by choosing a suitable solvent and column set and keeping the sample concentration low enough, peak dispersion cannot be completely avoided. Depending on the quality of the separation system, there are three possible cases[1]:

(1) Peak spreading may be neglected; the chromatogram can be converted directly into the MWD.

(2) Peak spreading is small, but not negligible: one can use a manual method for correcting the molecular weight averages, for example the ASTM standard method D 3593-77[1]; corrections to each molecular weight in the MWD are beyond the scope of this approach.

(3) Correction of more significant peak spreading is somewhat problematic and generally requires a computer[9–13], which is, however, no substitute for a good separation system.

It is clear, that the accuracy demanded of the molecular weight averages determines the limits in these three cases. If appropriate chromatographic equipment is used, a manual method will be sufficient for many purposes, such as comparing different samples of a polymer (as long as the same column set is used).

Let us consider the separation system to be perfect: there will still remain several sources of error, which are now discussed.

Errors in data acquisition and treatment

The first critical point is the accurate determination of elution volumes. Letot *et al.*[2] demonstrated that calculation of elution volumes from elution times is superior to direct volume measurement (by a siphon volume counter), since modern high-performance liquid chromatographic (HPLC) pumps afford sufficiently constant flow-rates (at least within the time required for an average chromatogram). Long-term changes of flow-rate can be corrected by an internal standard method[15,16]:

$$V_e = T_e V_{st}^{cal}/T_{st} \tag{1}$$

where T_e = elution time corresponding to elution volume V_e, T_{st} = actual elution time of internal standard, and V_{st}^{cal} = elution volume of internal standard in calibration runs.

The subsequent transformation of elution volumes, V_e, into molecular weights requires a reliable calibration curve, which can be obtained by various methods[1,17–20]. The most popular approach is the peak position calibration (using narrow MWD standards). If the relationship of peak retention volumes to molecular weights can be represented by

$$\ln M = a - bV_e \tag{2}$$

which can be achieved by choosing an appropriate column set[21], a and b can be calculated using a least squares method. (Also calibration with broad MWD standards, such as GPCV2 and GPCV3, generally assumes a linear approximation of the GPC calibration curve.)

For the calculation of M_w and M_n the chromatogram has to be divided into small slices (usually of equal volume intervals), which implicitly involves two assumptions: each fraction is considered to consist of molecules of the same molecular mass; and the area of each slice is approximated by a rectangle. The problems arising from this procedure have been discussed by Füzes[22], who pointed out that neglection of small amounts of polymer at both sides of the peak results in serious errors in M_w and M_n; large deviations from the correct values may occur especially if the number of data points is too small, the MWD is broad and the signal-to-noise ratio of the detector is poor. Moreover, a drift of the baseline may cause serious errors, unless it is compensated. Another source of error, which is very often neglected, arises from the calculation of molecular weight averages using:

$$M_w = \Sigma\ (h_i M_i)/\Sigma\ h_i \tag{3}$$

$$M_n = \Sigma\ h_i/\Sigma\ (h_i/M_i) \tag{4}$$

This is only justified if the response factor of the detector is independent of concentration and molecular weight. (The latter may not be fulfilled especially in the low-molecular-weight region[23].) Furthermore, the graphical determination of the height, h_i, of each slice and the corresponding molecular weight, M_i, from the recorder trace can lead to erroneous results, if a manual method is used for the calculation of molecular weight averages.

Considering all these problems, the use of a density meter according to the mechanical oscillator method[4] as a detector in GPC offers considerable advantages:

(1) As we have shown previously[24], the density of a polymer solution represents its concentration within a sufficiently wide concentration range. Depending on the type of polymer, the response factors are constant even at rather low molecular weights (mostly down to $1 \cdot 10^3$–$3 \cdot 10^3$, sometimes even lower).

(2) The signals from such an instrument are inherently integrated over each measuring interval, thus no approximation is required.

(3) Elution times are determined with high accuracy and can be printed together with the detector response, thus no graphical determination is necessary.

Detection by measurement of density

In a previous paper[25] we gave a detailed description of the densimetric detector, hence its working principle is here only briefly mentioned. Density measurement according to the mechanical oscillator method is based on the determination of the period of an oscillating, U-shaped tube filled with the sample[4]. A small density change, $\Delta\rho$, will cause a change, ΔT, in the period, T_0

$$\Delta\rho = 2A \cdot T_0 \cdot \Delta T \tag{5}$$

wherein A is a constant for each individual oscillator. The concentration, c_i, of a solute is given by

$$c_i = \frac{\Delta\rho}{1 - \rho_0 \bar{V}_i^*} \tag{6}$$

where ρ_0 is the density of the pure solvent and $\bar{V}_i^*$ is the (apparent) partial specific volume of the solute.

To achieve the required high sensitivity, it is necessary to use a reference cell for compensation of temperature variations

$$n_1 T_1 = n_2 T_2 \cdot \frac{n_1 T_1'}{n_2 T_2'} \tag{7}$$

where T_1, T_2 are the periods of oscillation of the cells at a given temperature, θ; T_1', T_2' are the periods of oscillation of the cells at $\theta + \Delta\theta$ and n_1, n_2 are the number of periods per measuring interval. In this manner baseline stability can be drastically improved, baseline drift due to temperature variations being eliminated. In order to avoid an increase of baseline noise resulting from the division of T_1' by T_2', a sliding average is used for T_2'; thus a considerable reduction of noise is achieved for the reference signal, and the signal-to-noise ratio of the compensated signal becomes comparable to that obtained from the measuring cell without compensation.

With $n_1 = 1000$ a resolution in density of $2.5 \cdot 10^{-7}$ g/cm^3 is achieved at measuring intervals of 4.5 sec, corresponding to 75 μl at a flow-rate of 1.00 ml/min.in *ca.* 1 · Chromatograms are registered by a x,t-recorder and by a matrix printer, as is shown in Fig. 1. From these data molecular weight averages can be calculated very easily, as will now be shown.

Calculation of molecular weight averages

Manual data reduction from a gel chromatogram is rather laborious, but it can be facilitated by the use of a programmable pocket calculator, as Navas[26] has recently shown. There are, however, several objections to his program (which was written for the HP 29C): it does not accept a sufficient number of data points; its use is rather inconvenient and the cumulative distribution is calculated beginning from the high-molecular-weight end of the chromatogram, which is unusual.

We have now developed a new program, designed especially for use with the densimetric detector. It has been written for the HP 34C; a BASIC version for use with other calculators is in preparation. The present program uses a linear calibration (eqn. 2), and enables the correction of elution volumes by an internal standard method (eqn. 1) and of baseline drift. Molecular weight averages are calculated using eqns. 3 and 4, which is acceptable in the case of densimetric detection even in the low-molecular-weight region.

Because the measuring intervals of the densimetric detector are constant within *ca.* $1 \cdot 10^{-3}$%, only the first elution time has to be entered; subsequent values are calculated by a subroutine and displayed before entering the corresponding detector

386	09:04	Z3	22596695	618213496
387	09:08	Z3	22596696	640810192
388	09:13	Z3	22596695	663406887
389	09:17	Z3	22596695	686003582
390	09:22	Z3	22596697	708600279
391	09:26	Z3	22596694	731196973
392	09:31	Z3	22596694	753793667
393	09:35	Z3	22596695	776390362
394	09:40	Z3	22596695	798987057
395	09:44	Z3	22596696	821583753
396	09:49	Z3	22596695	844180448
397	09:53	Z3	22596695	866777143
398	09:58	Z3	22596694	889373837
399	10:02	Z3	22596696	911970533
400	10:07	Z3	22596699	934567232
401	10:11	Z3	22596701	957163933
402	10:16	Z3	22596710	979760643
403	10:20	Z3	22596719	002357362
404	10:25	Z3	22596732	024954094
405	10:29	Z3	22596749	047550843
406	10:34	Z3	22596768	070147611
407	10:39	Z3	22596787	092744398
408	10:43	Z3	22596805	115341203
409	10:48	Z3	22596824	137938027
410	10:52	Z3	22596837	160534864
411	10:57	Z3	22596847	183131711
412	11:01	Z3	22596856	205728567
413	11:06	Z3	22596861	228325428
414	11:10	Z3	22596864	250922292
415	11:15	Z3	22596862	273519154
416	11:19	Z3	22596859	296116013
417	11:24	Z3	22596852	318712865
418	11:28	Z3	22596845	341309710
419	11:33	Z3	22596836	363906546
420	11:37	Z3	22596826	386503372
421	11:42	Z3	22596811	409100183
422	11:46	Z3	22596798	431696981
423	11:51	Z3	22596781	454293762
424	11:55	Z3	22596770	476890532
425	12:00	Z3	22596756	499487288
426	12:04	Z3	22596743	522084031
427	12:09	Z3	22596733	544680764
428	12:13	Z3	22596725	567277489
429	12:18	Z3	22596716	589874205
430	12:22	Z3	22596711	612470916
431	12:27	Z3	22596708	635067624
432	12:32	Z3	22596703	657664327
433	12:36	Z3	22596702	680261029
434	12:41	Z3	22596699	702857728
435	12:45	Z3	22596698	725454426
436	12:50	Z3	22596697	748051123
437	12:54	Z3	22596697	770647820
438	12:59	Z3	22596696	793244516

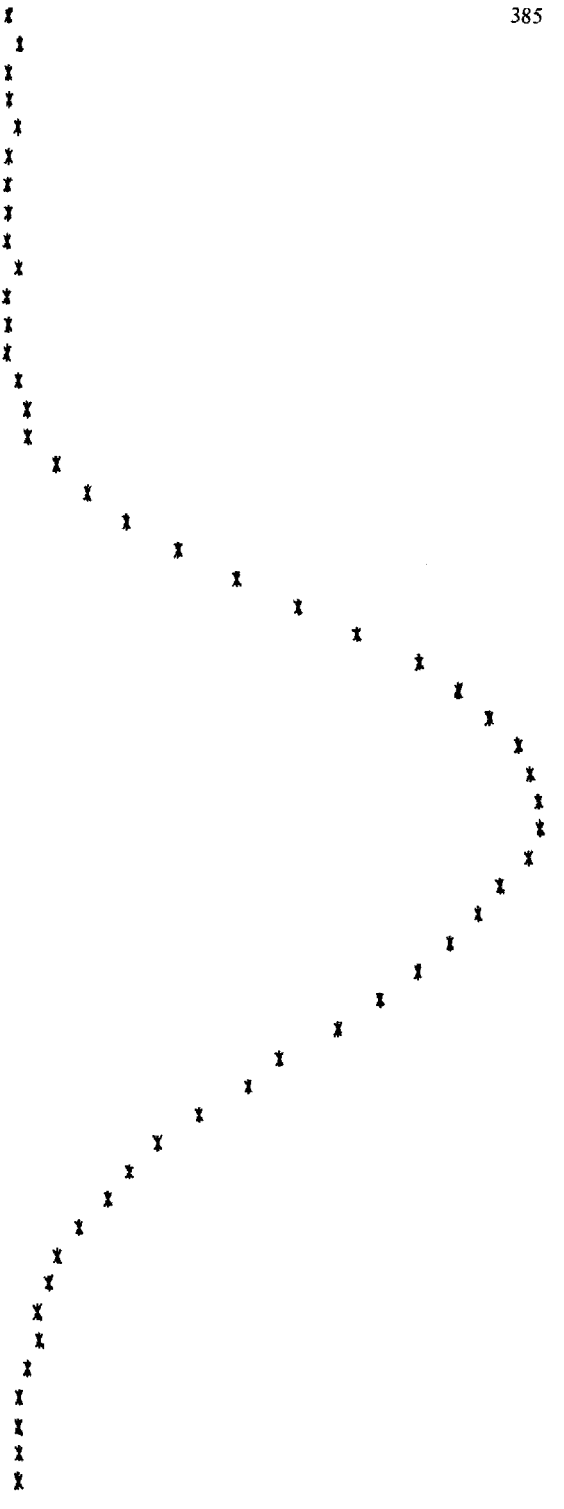

Fig. 1. Chromatogram of polystyrene batch 60422 (Pressure Chem.) with densimetric detection. Sample: PS 9000. Chromatographic conditions as in Fig. 2. Measuring intervals: 4.5 sec. Resolution: $2.5 \cdot 10^{-7}$ g/cm³. Plotted curve: $6.25 \cdot 10^{-5}$ g/cm³ full scale. The values in the five columns are as follows: number of measuring interval; elution time, t_i (min/sec); working mode (Z3 means compensated signal); detector response, x_i; summation of x_i values, I_i.

response, x_i. For the sake of convenience, only the last three digits, r_i, of x_i have to be entered, the base $B = x_i - r_i$ being entered into a memory register before commencing the program, as well as the calibration parameters, a and b. Baseline drift can be compensated by

$$h_i = r_i - \bar{r}_0 + i \cdot \frac{\bar{r}_0 - \bar{r}'_0}{N + 1} \tag{8}$$

where $\bar{r}, \bar{r}'_0$ are the average r values before and after the peak, respectively, and N is the number of data points within the peak.

The peak area A ($= \Sigma h_i$) is determined from the I_i values in column 5 of Fig. 1 before entering the first r_i:

$$A = I_N - I_0 - N\left(B + \frac{\bar{r}_0 + \bar{r}'_0}{2}\right) \tag{9}$$

TABLE I

MOLECULAR WEIGHT PROGRAM (FOR HP 34C)

Step/Key entry	*Step/Key entry*	*Step/Key entry*	*Step/Key entry*
001 h LBL A	031 h LBL 1	061 h LST x	091 1
002 f fix 2	032 RCL 8	062 RCL .0	092 0
003 f CLEAR Σ	033 RCL 9	063 —	093 0
004 STO .0	034 +	064 RCL .2	094 ×
005 R/S	035 5	065 1	095 R/S
006 g → H	036 EEX	066 +	096 CLX
007 ÷	037 1	067 ÷	097 RCL 1
008 STO .1	038 0	068 h LST x	098 f fix 0
009 R/S	039 ÷	069 RCL f I	099 R/S
010 —	040 g → H	070 —	100 x ⇄ y
011 CHS	041 STO + 0	071 ×	101 ×
012 STO.2	042 RCL 0	072 +	102 STO + 3
013 STO f I	043 RCL .1	073 R/S	103 h LST x
014 R/S	044 ×	074 ENTER	104 RCL 1
015 —	045 RCL 7	075 ENTER	105 ÷
016 CHS	046 ×	076 STO + 2	106 STO + 4
017 RCL 9	047 RCL 6	077 RCL 5	107 g DSE
018 RCL .0	048 +	078 ÷	108 GTO 1
019 +	049 g e^x	079 1	109 RCL 3
020 2	050 STO I	080 0	110 RCL 2
021 ÷	051 RCL 0	081 0	111 ÷
022 RCL 8	052 f h → MS	082 ×	112 R/S
023 +	053 f fix 4	083 R/S	113 h LST x
024 RCL .2	054 ENTER	084 CLX	114 RCL 4
025 ×	055 R/S	085 RCL 5	115 ÷
026 —	056 x = y	086 RCL 2	116 R/S
027 STO 5	057 R/S	087 —	117 ÷
028 R/S	058 f fix 2	088 +	118 f fix 2
029 g → H	059 RCL 9	089 RCL 5	119 h RTN
030 STO 0	060 —	090 ÷	

TABLE II

INSTRUCTIONS FOR USE OF THE MOLECULAR WEIGHT PROGRAM

Instruction	*Input*	*Key*	*Output*
Enter a in R_6	a	STO 6	a
Enter $-b$ in R_7	$-b$	STO 7	$-b$
Enter B in R_8	B	STO 8	B
Calculate $\bar{r}_0$, enter $\bar{r}_0$ in R_9		STO 9	$\bar{r}_0$
Calculate $\bar{r}_0'$			$\bar{r}_0'$
Press A to initiate the program		A	$\bar{r}_0'$
Enter elution volume of standard in calibration	V_{st}^{cal}	ENTER	V_{st}^{cal}
Enter actual elution time of standard (min, sec)	T_{st}	R/S	Flow rate (ml/h)
Enter number of last interval before the peak/ (column 1 of Fig. 1)	n_0	ENTER	n_0
Enter number of last interval within the peak/ (column 1 of Fig. 1)	n_N	R/S	N
Enter corresponding I_0 (column 5 of Fig. 1)	I_0	ENTER	I_0
Enter I_N (column 5 of Fig. 1)	I_N	R/S	A
Enter t_0 (last t before the peak)	t_0	R/S	t_1
Beginning of the subroutine:			
When t_i is displayed, enter corresponding r_i	r_i	R/S	h_i
(if no r_i has been entered, the		R/S	% polymer
program stops and displays t_i again)		R/S	% cumul.
		R/S	M_i
End of loop: next t_i displayed		R/S	next t_i
When $i = N$, the program starts calculating M_w,M_n and M_w/M_n		R/S	M_w
		R/S	M_n
		R/S	M_w/M_n

where I_0 is the last value of I before the peak and I_N is the last value of I within the peak.

Thus a loop can be used to calculate the elution time, elution volume, the corresponding molecular weight M_i, the height h_i of each slice, the weight fraction w_i (or % polymer) and the cumulative distribution (% cumul.). By this procedure the program accepts a much larger number of data points than one will ever need (up to 9999). The program keystrokes to be entered with the calculator set to the PROGRAM mode (PRGM) are listed in Table I.

Before initiating the program, the calibration parameters a and b and the base B have to be entered into the memory registers 6–8, and remain there as long as the same column set and solvent is used. For each individual chromatogram, the average $\bar{r}_0$ has to be calculated and entered into memory register 9, $\bar{r}_0'$ (if $\bar{r}_0 \neq \bar{r}_0'$) is calculated and the program is initiated with $\bar{r}_0'$ in the x-register (with the calculator set to the RUN mode).

Instructions for the use of the program are given in Table II.

EXPERIMENTAL

The performance of the density detector and the program was tested by a dual-detector method: use of a UV-photometer and the density detector in series

eliminated errors due to the separation columns, thus any differences in M_w/M_n should originate from the detectors or the connections between them.

Molecular weight averages were calculated from the density values by the program described, and from the UV-trace by a conventional method (using the same elution volume intervals as in densimetric detection).

The chromatographic apparatus consisted of a LDC Constametric II G pump, two column sets (PL-Microgel, 500–1000 Å, and two Waters Bondagel E 125), an UV–VIS photometer LDC Spectromonitor II and our density detector (as described previously[25]) connected to a three-channel recorder (LINEAR) and a matrix printer (Epson MX 80). The solvent used was tetrahydrofuran (THF) (p.a., Merck). Polystyrene standards (Waters, Milford, MA and Pressure Chem., Pittsburgh, PA, U.S.A.) were used as received. The chromatographic conditions were as follows: flow-rate 1.00 ml/min; sample concentration, 0.1–0.5% (w/v); injected volume, 50 μl; resolution of the density detector, $2.5 \cdot 10^{-7}$ g/cm^3, measuring intervals 4.5 sec.

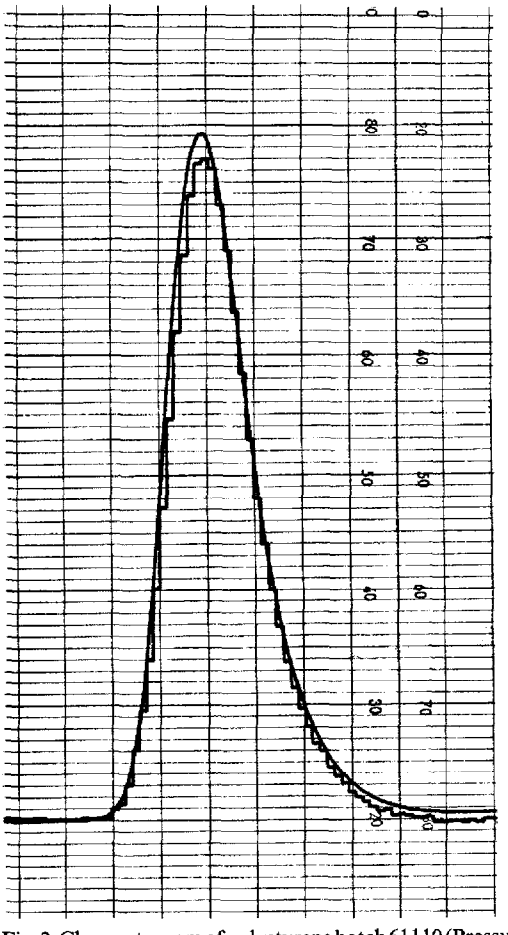

Fig. 2. Chromatogram of polystyrene batch 61110 (Pressure Chem.) with photometric (smooth curve) and densimetric detection. Column: PL-Microgel, 500–1000 Å. Eluent: THF, 1.00 ml/min. Sample injected: 50 μl, $\approx$0.5% (w/v). UV detection: 260 nm, E = 1.28 full scale. Densimetric detection: measuring intervals 4.5 sec, $1.25 \cdot 10^{-4}$ g/cm^3 full scale; recorder speed 2 cm/min.

RESULTS AND DISCUSSION

Comparison of the recorder traces from the photometric and densimetric detection shows very good agreement of the elution curves (Fig. 2). Calculation of molecular weight distributions from the chromatograms yields very similar results, as is shown in Table III.

TABLE III

MOLECULAR WEIGHT DISTRIBUTION OF POLYSTYRENE 3600 (PRESSURE CHEM.), AS OBTAINED FROM DENSIMETRIC AND PHOTOMETRIC DETECTION (PL-MICROGEL, 500–1000 Å)

a = 17.37856487; b = 0.742162000; B = 22,596,000; $\bar{r}_0$ = 697.25 ± 1.14; $\bar{r}_0'$ = 696.14 ± 1.07; Flow-rate = 59.98 ml/h; A = 3717.20.

t_i (min:sec)	From density meter				From photometer		
	h_i	% pol.	% cum.	M_i	h_i	% pol.	% cum.
11:28	9.78	0.26	100.00	7163	3	0.20	100.00
11:32	16.81	0.45	99.74	6774	7	0.46	99.80
11:37	28.85	0.78	99.28	6406	9	0.59	99.34
11:41	45.88	1.23	98.51	6057	16	1.05	98.75
11:46	70.91	1.91	97.27	5728	24	1.57	97.71
11:50	101.94	2.74	95.37	5417	37	2.42	96.13
11:55	137.97	3.71	92.62	5122	51	3.34	93.71
11:59	174.00	4.68	88.91	4844	68	4.46	90.37
12:04	211.04	5.68	84.23	4581	86	5.64	85.91
12:08	239.07	6.43	78.55	4332	103	6.75	80.28
12:13	261.10	7.02	72.12	4096	114	7.47	73.53
12:17	271.13	7.29	65.10	3874	121	7.93	66.06
12:22	270.16	7.27	57.80	3663	122	7.99	58.13
12:26	261.19	7.03	50.54	3464	119	7.80	50.13
12:31	243.23	6.54	43.51	3276	109	7.14	42.33
12:35	220.26	5.93	36.97	3098	88	5.77	35.19
12:40	196.29	5.28	31.04	2929	80	5.24	29.42
12:44	170.32	4.58	25.76	2770	69	4.52	24.18
12:49	143.35	3.86	21.18	2620	56	3.67	19.66
12:53	120.38	3.24	17.32	2477	49	3.21	15.99
12:58	100.42	2.70	14.08	2342	38	2.49	12.78
13:02	84.45	2.27	11.38	2215	30	1.97	10.29
13:07	69.48	1.87	9.11	2095	24	1.57	8.32
13:11	56.51	1.52	7.24	1981	21	1.38	6.75
13:16	47.54	1.28	5.72	1873	17	1.11	5.37
13:21	37.57	1.01	4.44	1771	14	0.92	4.26
13:25	30.61	0.82	3.43	1675	12	0.79	3.34
13:30	27.64	0.74	2.61	1584	9	0.59	2.56
13:34	18.67	0.50	1.86	1498	8	0.52	1.97
13:39	14.70	0.40	1.36	1417	7	0.46	1.44
13:43	12.73	0.34	0.97	1340	6	0.39	0.98
13:48	9.76	0.26	0.62	1267	4	0.26	0.59
13:52	7.80	0.21	0.36	1198	3	0.20	0.33
13:57	5.83	0.16	0.15	1133	2	0.13	0.13
	M_w = 3603				M_w = 3597		
	M_n = 3238				M_n = 3256		
	M_w/M_n = 1.11				M_w/M_n = 1.10		

TABLE IV

MOLECULAR WEIGHT AVERAGES OF POLYSTYRENES I–III CALCULATED FROM CHROMATOGRAMS OBTAINED FROM TWO DIFFERENT COLUMN SETS WITH DENSIMETRIC AND PHOTOMETRIC DETECTION

Polystyrenes: I, Standard No. 25168 (Waters), M_w = 20,800, M_n = 20,200, M_w/M_n = 1.03; II, Batch 60422 (Pressure Chem.), $M\eta$ = 9177 ± 5%, M_n = 9168 ± 5%, GPC: M_w = 9966, M_n = 9569, M_w/M_n = 1.04; III, Batch 61110 (Pressure Chem.), $M\eta$ (molecular weight by intrinsic viscosity) = 3600 ± 5%, M_n = 3570 ± 5%, GPC: $M_w/M_n \leq 1.06$.

Polymer	*Column set*	*Detector*	M_w	M_n	M_w/M_n
I	Microgel 500–1000 Å	Density	20,176	19,098	1.06
I	Microgel 500–1000 Å	UV	20,193	19,277	1.05
II	Microgel 500–1000 Å	Density	8984	7863	1.14
II	Microgel 500–1000 Å	UV	8658	7670	1.13
III	Microgel 500–1000 Å	Density	3603	3238	1.11
III	Microgel 500–1000 Å	UV	3577	3256	1.10
III	2x Bondagel E 125	Density	3504	3163	1.11
III	2x Bondagel E 125	UV	3460	3169	1.09

The determination of molecular weight averages of various polystyrenes using two different column sets gave very similar values of M_w/M_n for both detectors, as is seen in Table IV. Compared with reported values they are generally too high, most probably resulting from the separation column, which was, however, not the subject of our investigations.

The small differences in the values of M_w/M_n obtained from photometric and densimetric detection, respectively, could be explained by diffusion phenomena in the capillary connections between the detectors. This was confirmed by arranging the photometer behind the density detector: in this case the values of M_w/M_n obtained from the photometer were slightly higher than those from the density meter.

CONCLUSIONS

Densimetric detection fulfils the demands of high-performance GPC and offers some advantages. The response represents the integral concentration of eluted substance within each measuring interval, thus no partial integration is required. The printed, digital raw data can be used for the calculation of molecular weight distributions by a computer or, as an inexpensive alternative, by a programmable pocket calculator, which will be sufficient in many cases. For this purpose, a convenient program has been developed, which comprises algorithms for compensation of baseline drift and flow-rate changes and accepts a sufficiently large number of data points. The time required for calculation of molecular weight distribution and average molecular weights from the set of data in Table III is about 20 min; if peak spreading is corrected using the ASTM standard method D 3595-77, molecular weight averages can be calculated with good accuracy from the raw data within less than half an hour. The use of a programmable pocket calculator for data reduction is thus a feasible and inexpensive method, which can be applied in many cases.

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