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## EFFECT OF OPERATING PARAMETERS ON POLYMER MOLECULAR WEIGHT ACCURACY WITH TIME-DELAY, EXPONENTIAL-DECAY THERMAL FIELD FLOW FRACTIONATION

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### SUMMARY

Previous studies have demonstrated the advantages of determining polymer molecular weight distributions (MWD) by time-delay, exponential-decay thermal field flow fractionation (TDE-TFFF). The method is especially promising for characterizing the MWD of fragile, ultra-high-molecular-weight (MW) polymers. With this method, high-resolution separations are carried out by imposing a thermal gradient across a flowing mobile liquid phase in a thin channel formed with parallel plates. The TDE-TFFF technique permits highly reproducible MW measurements to be made without frequent recalibration. This study examines the effect of important operating parameters, flow-rate and time-delay/decay time constant  $\tau$  values, on the accuracy of MW measurements by TDE-TFFF. Separation resolution and molecular-weight accuracy are increased in TDE-TFFF by operating at longer  $\tau$  values and higher flow-rates. Nomographs are given that allow the selection of optimum operating parameters using results from a preliminary separation.

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### INTRODUCTION

A wide range of organic-soluble polymers<sup>1-5</sup> and certain water-soluble polymers<sup>6</sup> can be characterized by thermal field flow fractionation (TFFF). This method uses a temperature gradient across a thin, open channel formed by parallel plates to separate materials on the basis of molecular weight (MW) differences<sup>7,8</sup>. As result of the temperature difference between the two plates, sample components are pushed against an accumulation wall. Higher MW components that are pushed closer to this wall are intercepted by slower flowstreams of the essentially laminar flow profile formed between the two plates, and elute after the lower MW components that are carried away by faster flowstreams. Compared to the widely used method of polymer characterization by size-exclusion chromatography (SEC), TFFF provides higher resolution for better MW accuracy and superior capability for characterizing ultra-high MW polymers<sup>5</sup>.

A useful technique for characterizing polymers by TFFF involves programming a temperature gradient ( $\Delta T$ ) decrease during the separation, so that a wide MW

range can be covered during a single experiment. A convenient programming method involves maintaining a constant temperature differential  $\Delta T$  for a time  $\tau$  after injecting the sample, after which  $\Delta T$  is exponentially decreased, also with a time constant  $\tau$ . This approach, called time-delay, exponential-decay TFFF (or TDE-TFFF), results in a linear plot of  $\log MW$  versus retention time  $t_R$  that provides convenient and accurate calibrations over a wide MW range<sup>4</sup>. Previous studies have demonstrated that the TDE-TFFF method is capable of reproducing number- and weight-average MW values for polymers within 3% (1  $\sigma$ ) without the need for frequent recalibration<sup>5</sup>. This method also has been used with a continuous viscosity detector to produce unique intrinsic viscosity distributions that closely correlate with polymer end-use and solution properties<sup>9</sup>.

The object of this study was to determine the effect of major operating variables on the accuracy of MW values that are measured by TDE-TFFF. Such information should assist in defining experimental conditions for conveniently determining accurate molecular weight distribution (MWD) values for polymer samples.

## THEORY

The basis for solute retention in TFFF has previously been established<sup>1,7</sup>. With TDE-TFFF, the MW-retention relationship can be expressed as<sup>4</sup>:

$$\ln M = (1/\alpha) \ln \{(2.2 b \tau F)/[D_T V_0 (\Delta T)_0]\} + (t_R/\alpha\tau) \quad (1)$$

where  $M$  is the molecular weight (g/mol),  $\alpha$  (a constant describing polymer conformation) is  $\approx 0.6$  for random-coil polymers,  $b$  is a channel constant,  $\tau$  is the exponential delay/decay time constant,  $F$  is the flow-rate (ml/min),  $D_T$  is the thermal diffusion coefficient (apparently independent of polymer molecular weight  $M$ ),  $V_0$  is the channel dead volume (ml),  $(\Delta T)_0$  is the initial temperature difference between the hot and cold plates ( $^{\circ}\text{C}$ ), and  $t_R$  is the retention time (min) of the solute. Eqn. 1 predicts that sample analysis time is primarily controlled by  $\tau$ . Flow-rate exhibits less influence on retention, as does  $(\Delta T)_0$ . The level of the latter often is dictated by the retention needed to separate the lowest MW component in the sample from the channel dead-volume peak at  $V_0$ . As a result,  $(\Delta T)_0$  often is not an experimental variable used in optimizing a particular TDE-TFFF measurement.

Resolution and the ultimate MW accuracy of the measurement are also functions of the operating variables in a separation, as predicted by<sup>10</sup>,

$$R_{sp} = 0.58 \alpha\tau/\sigma \quad (2)$$

$$M_w^* = e^{\frac{1}{2}(\sigma/\alpha\tau)^2} - 1 \quad (3a)$$

$$M_n^* = e^{-\frac{1}{2}(\sigma/\alpha\tau)^2} - 1 \quad (3b)$$

where, the specific resolution value  $R_{sp}$  represents the usual chromatographic resolution for a pair of bands having a decade of MW difference, and the band standard deviation  $\sigma$  is the square root of the band variance contribution resulting from instrumental band broadening. The MW accuracy parameters  $M_w^*$  and  $M_n^*$  describe

the expected errors in the calculated  $M_w$  and  $M_n$  values as the result of instrumental band broadening.

Eqns. 2 and 3 describe the influence of the exponential time delay/decay  $\tau$  value and flow-rate on band broadening, and their resultant effect on MW accuracy<sup>10</sup>. Therefore, information on the level of effect of these variables in experimental situations is needed to anticipate errors in MW measurements that can be expected under particular operating conditions.

The effect of operating variables on TDE-TFFF retention can be predicted from the relationship in eqn. 1. The change in retention time with change in  $\tau$  is described by,

$$\Delta t_R = t_{R1}[(\tau_2/\tau_1) - 1] - \tau_2 \ln(\tau_2/\tau_1) \quad (4)$$

where  $\Delta t_R = (t_{R2} - t_{R1})$  is the change in retention time,  $t_{R1}$  is the retention time of the initial experiment,  $t_{R2}$  is the retention time of the proposed experiment,  $\tau_1$  is the exponential time delay/decay constant for the initial experiment, and  $\tau_2$  is the exponential time delay/decay constant for the proposed experiment. This expression is useful in application studies to determine the change in time of a separation when the  $\tau$  value is varied, or conversely, after a preliminary separation with an initial  $\tau_1$  value, to predict the  $\tau_2$  value that will result in desired separation time. For example, if a TDE-TFFF separation was carried out with an initial  $\tau_1$  value of 20.0 min and showed an initial retention time  $t_{R1}$  of 60 min, eqn. 4 predicts that if a new value  $\tau_2$  of 25.0 min is used, the change in the retention time of the peak would be,

$$\Delta t_R = 60[(25/20) - 1] - 25 \ln(25/20) = 9.4 \text{ min}$$

Thus, the new retention time for the larger  $\tau$  value would be  $60 + 9.4 = 69.4$  min.

Similarly, the effect of a flow-rate change on TDE-TFFF retention is predicted by,

$$\Delta t_R = -\tau \ln(F_2/F_1) \quad (5)$$

or in another form,

$$F_2 = F_1 e^{-\Delta t_R/\tau} \quad (5a)$$

Fig. 1 shows a nomograph that can be used to predict the separation time change for a desired flow-rate change, or the flow-rate change required for a particular separation time change. This nomograph relates the change in analysis time to the initial/proposed flow-rate ratio for a range of exponential delay/decay  $\tau$  values. For example, this nomograph can be used to predict the change in TDE-TFFF analysis time with flow-rate change. If the flow-rate in a  $\tau = 20$  min separation is changed from ( $F_1$ ) 0.15 ml/min to ( $F_2$ ) 0.67 ml/min, the resulting  $F_1/F_2$  ratio (0.22) in the Fig. 1 nomograph indicates a 30-min decrease in analysis time (as illustrated by the black circle in the figure).

An analogous relationship exists for the effect of changing the initial channel

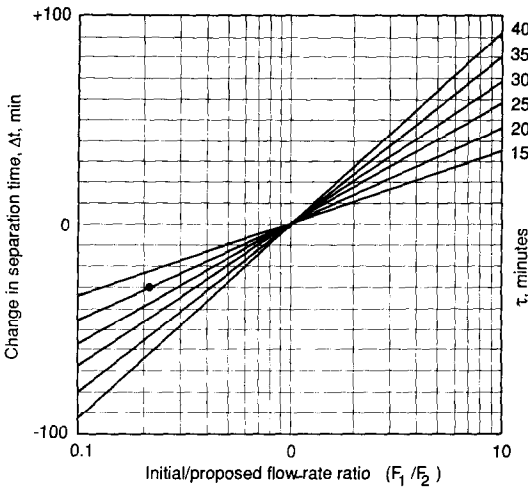


Fig. 1. Nomograph for variation in TDE-TFFF analysis time for change in the initial/proposed flow-rate ratio.

block temperature difference  $(\Delta T)_0$  on solute retention time in TDE-TFFF. This relationship can be expressed as,

$$\Delta t_R = -\tau \ln[(\Delta T_0)_1/(\Delta T_0)_2] \tag{6}$$

or, alternatively,

$$(\Delta T_0)_2 = (\Delta T_0)_1 e^{\Delta t_R/\tau} \tag{6a}$$

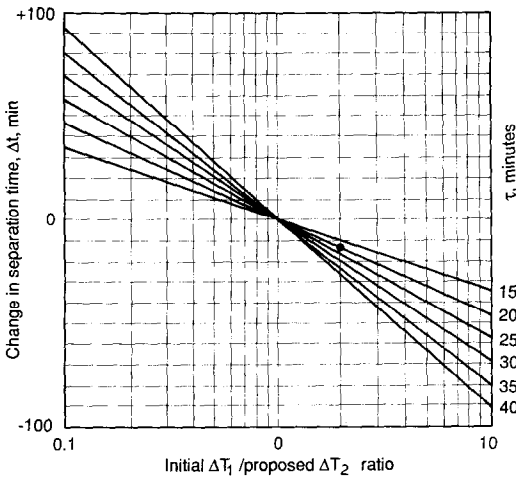


Fig. 2. Nomograph for variation in TDE-TFFF analysis time for change in the initial  $(\Delta T)_0$ /proposed  $(\Delta T)_0$  ratio.

Shown in Fig. 2 is a nomograph describing the effect of varying  $(\Delta T)_0$  to produce a change in TDE-TFFF separation time. For example, when the initial temperature difference  $(\Delta T_0)_1$  of 80°C is changed to a proposed temperature  $(\Delta T_0)_2$  of 40.0°C (ratio = 2.00), the nomograph in Fig. 2 indicates a decrease in analysis time of 13.9 min (as indicated by the black circle in the figure).

#### EXPERIMENTAL

The apparatus used in this study has been previously described<sup>4-6</sup>. TDE-TFFF separations were performed using the following conditions: channel thickness, 132  $\mu\text{m}$ ; initial hot block temperature, 90°C; cold block temperature, 20°C; mobile phase, dioxane; sample, 25  $\mu\text{l}$ , 1 mg/ml of each standard; UV detector, 260 nm. HPLC-grade dioxane was from American Burdick and Jackson (Muskegon, MI, U.S.A.). Polymer standards were obtained from Polymer Labs. (Amherst, MA, U.S.A.).

Peak analysis measurements were conducted with a new software program called THEOPS written in Fortran 77 on a Hewlett-Packard 1000 Series computer<sup>11</sup>. Separation data were collected on a Hewlett-Packard LAS data handling system. Polymer MW calculations were carried out with the software previously described<sup>5</sup>.

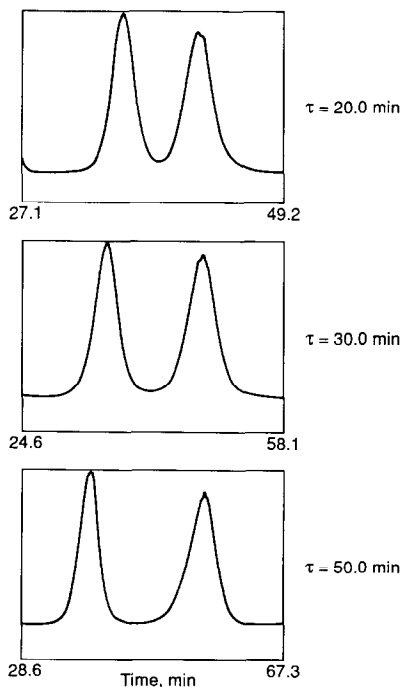


Fig. 3. Effect of exponential time-delay, time-decay  $\tau$  values on separation resolution. Narrow MW polystyrene standards; initial hot block temperature, 90°C; cold block temperature, 20°C; exponential time-delay, time-decay constant,  $\tau$ , as shown; dioxane carrier flow-rate, 0.15 ml/min; sample, 25  $\mu\text{l}$ , 1 mg/ml each; UV detector, 260 nm.

## RESULTS AND DISCUSSION

*Effect of  $\tau$* 

Eqn. 2 predicts that separation resolution should increase as the  $\tau$  value used for the TDE-TFFF separation is increased. Therefore, the effect of increasing  $\tau$  should be to increase the accuracy of MW measurements as a result of decreasing the effects of instrumental band broadening. Fig. 3 shows the increasing resolution for MW 194 000 and 1 000 000 polystyrene standards with increasing  $\tau$  values.

However, peak width or the variance of the peak can also be affected by the extent that individual components making up the polymer standard are resolved by the separation method. Since TFFF is a high-resolution method, capable of higher resolution than SEC<sup>4,5</sup>, the end effect is that apparent band broadening can be mainly a method-resolution effect, rather than instrumental band-broadening effects. If this

TABLE I  
EFFECT OF  $\tau$  VALUES ON PEAK VARIANCE AND SHAPE

<i>Polystyrene standards</i>								
$\tau$ (min)	194K		515K		1000K		1850K	
	Variance <sup>a</sup>	Skew <sup>b</sup>	Variance	Skew	Variance	Skew	Variance	Skew
20	7.45	0.03	8.41	-0.42	11.42	0.50	9.55	0.24
25	9.76	0.06	9.39	-0.12	14.79	0.56	14.13	-0.30
Repeat	9.66	0.09	-	-	12.79	0.27	-	-
Repeat	9.62	0.14	-	-	13.58	0.43	-	-
30	11.85	-0.10	14.22	0.60	15.51	-0.19	17.70	-0.04
40	18.57	-0.20	18.82	-0.26	22.98	-0.40	29.55	-0.21
50	18.93	-0.19	24.13	-0.17	35.79	-0.71	40.00	-0.25

<sup>a</sup>Variance in min<sup>2</sup>.

<sup>b</sup>Mathematical peak skew from ref. 11.

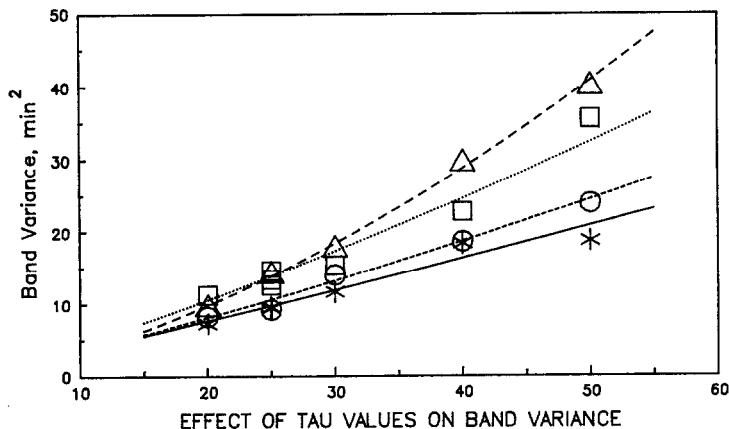


Fig. 4. Effect of exponential time-delay, time-decay  $\tau$  values on band variance. Conditions as in Fig. 3 (\* 194K; (○) 515K; (□) 1000K; (△) 1850K.

is the case, it would be expected that as resolution is increased by increasing  $\tau$  values, the variance of the bands actually should increase (rather than the intuitively expected decrease) as larger  $\tau$  values are used in the separation. This trend is borne out by the data in Table I with narrow MW polystyrene standards.

As the separation  $\tau$  value is increased, the measured peak variance values also increase as a result of greater resolution of the individual constituents in the polystyrene standards. This trend is graphically shown in Fig. 4, where the increase in band variance with increasing  $\tau$  values is almost linear, with plots for the higher MW components showing a steeper slope. This latter trend could be due to the higher resolution that TDE-TFFF exhibits for higher MW (more strongly retained) components (smaller impact of instrumental band broadening.) A less likely explanation is the larger polydispersity of the higher MW standards, resulting in broader bands because of larger resolution of the individual components as resolution is increased (larger  $\tau$  values).

The effect of increasing resolution by increasing the  $\tau$  values is also illustrated by the data for band skew in Table I. The general trend is a decrease of the mathematical band skew values as resolution is increased (increase in  $\tau$ ). The tendency of the data to slightly negative values (slight frontal band skew) with  $\tau$  increase could be due to the natural MW distribution of the sample towards the low MW end—as resolution increases, the instrumental band broadening is decreased so that the true MWD is now more apparent.

The effect of increasing the separation  $\tau$  values on measured molecular weights is also shown in Table II, which contains calculated MW values for four narrow MW polystyrene standards. As the separation  $\tau$  value was increased (increased resolution), calculated  $M_w$  values generally decreased, indicating increased accuracy due to the decreased effects of instrumental band broadening. Note that instrumental band broadening generally tends to increase measured  $M_w$  values as a result of the positive bias that is given to the features of the distribution curve from which values are calculated<sup>5</sup>.

Because of the bias of the level of resolution on measured  $M_w$  values, the influence of  $\tau$  values is especially reflected in calculated polydispersity values  $d$ , as shown in Table II. As  $\tau$  is increased (increased resolution), the calculated polydispersity values decrease. The “true” polydispersity values for these standards probably still are not approached by the conditions of these experiments. Other TFFF studies have shown that these ionic-polymerized polymers have polydispersities of  $< 1.01$  (ref. 12).

### *Flow-rate effects*

Eqn. 1 predicts that a plot of  $\log MW$  versus retention time  $t_R$  obtained with a particular  $\tau$  value should produce a straight-line (except at  $t_R$  values approaching the channel dead volume  $V_0$ ). Also predicted by eqn. 1 is that a change in flow-rate should result in a change in the intercept of this straight-line plot, but no change in its slope. This effect was verified in previous work<sup>4</sup>, and is further confirmed by the data in Fig. 5. Here, as the flow-rate is increased from 0.1 to 0.4 ml/min, the intercept increases and the absolute level of MW accessible during the experiment also increases, as predicted by Eqn. 4. For example, at 0.4 ml/min it can be anticipated that polystyrenes in the  $5 \cdot 10^4$ – $3 \cdot 10^6$  MW range could be accessed and measured under these particular operating conditions.

TABLE II  
EFFECT OF  $\tau$  ON MOLECULAR WEIGHT

$\tau$	194K				515K				1000K				1850K			
	$M_w^a$	$M_n^b$	$d^c$	$d$	$M_w$	$M_n$	$d$	$d$	$M_w$	$M_n$	$d$	$d$	$M_w$	$M_n$	$d$	$d$
20	199 000	189 000	1.05	1.08	513 000	491 000	1.08	1.08	1 060 000	977 000	1.09	1.09	1 910 000	1 770 000	1.08	1.08
25	196 000	184 000	1.06	1.15	550 000	479 000	1.15	1.15	1 020 000	964 000	1.07	1.07	1 940 000	1 830 000	1.06	1.06
Repeat	205 000	191 000	1.07	1.06	549 000	517 000	1.06	1.06	1 070 000	976 000	1.10	1.10	1 860 000	1 770 000	1.05	1.05
30	200 000	188 000	1.06	1.06	552 000	520 000	1.06	1.06	991 000	941 000	1.05	1.05	1 820 000	1 710 000	1.06	1.06
40	195 000	184 000	1.06	1.06	537 000	507 000	1.06	1.06	997 000	945 000	1.03	1.03	1 860 000	1 770 000	1.06	1.06
50	190 000	181 000	1.05	1.04	522 000	504 000	1.04	1.04	973 000	927 000	1.05	1.05	1 807 000	1 770 000	1.06	1.06

<sup>a</sup> $M_w$  = weight-average molecular weight.

<sup>b</sup> $M_n$  = number-average molecular weight.

<sup>c</sup> $d$  = polydispersity,  $M_w/M_n$ .



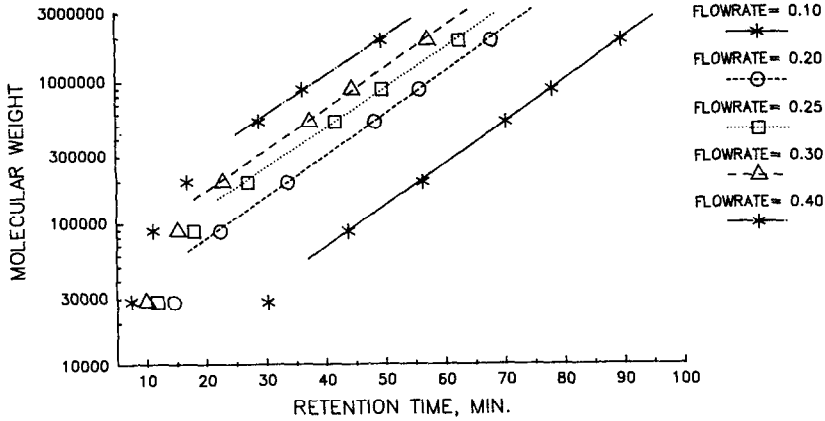


Fig. 5. Effect of flow-rate on TDE-TFFF calibration plots. Conditions as in Fig. 3, except flow-rates as shown.

Flow-rate and the initial temperature differential  $(\Delta T)_0$  both can influence separation resolution and significantly affect the accuracy of molecular weights determined by TDE-TFFF. Flow-rate is often of more concern, since the level of  $(\Delta T)_0$  usually is dictated by the range of molecular weights in the sample, and normally is not a parameter that is changed after the desired resolution from the channel dead-time peak is established. Intuitively, one would expect that increasing the flow-rate,  $F$ ,

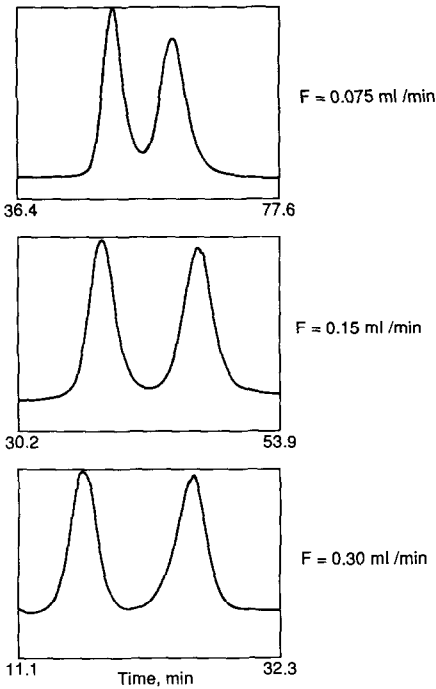


Fig. 6. Effect of flow-rate on separation resolution in TDE-TFFF. Conditions as in Fig. 3, except flow-rates as shown;  $\tau = 25.0 \text{ min}$ .

TABLE III  
EFFECT OF FLOW-RATE ON BAND VARIANCE AND SHAPE

Flow-rate (ml/min)	194K			515K			1000K			1850K		
	$\sigma_t^a$	$\sigma_v^b$	Skew	$\sigma_t$	$\sigma_v$	Skew	$\sigma_t$	$\sigma_v$	Skew	$\sigma_t$	$\sigma_v$	Skew
0.075	3.57	0.268	0.39	3.25	0.244	0.44	4.73	0.355	0.54	4.22	0.316	-0.34
0.10	3.24	0.324	0.19	3.49	0.349	0.43	3.99	0.399	0.00	4.30	0.430	0.40
0.15	3.10	0.466	0.09	3.06	0.459	0.12	3.49	0.523	0.27	3.76	0.564	-0.30
Repeat	3.10	0.465	0.14	—	—	—	3.69	0.553	0.43	—	—	—
0.20	3.23	0.645	-0.30	3.04	0.609	-0.07	3.17	0.633	0.09	3.53	0.704	0.23
0.30	2.94	0.882	-0.26	3.71	1.11	-0.91	3.66	1.10	-0.94	3.46	1.04	0.24
0.40	2.41	0.963	-0.05	3.93	1.57	-0.27	4.00	1.60	-0.89	3.63	1.45	0.00

<sup>a</sup>Standard deviation, min.

<sup>b</sup>Standard deviation, ml.

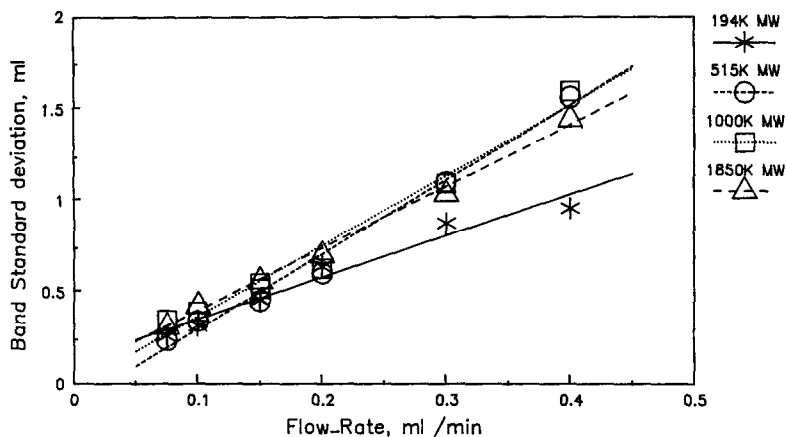


Fig. 7. Effect of flow-rate on band volume standard deviation. Conditions as in Fig. 3, except  $\tau = 25.0$  min, flow-rates as shown.

would decrease resolution because of added band broadening caused by resistance to mass transfer effects. However, as illustrated in Fig. 6, increasing  $F$  (constant  $\tau$ ) actually increases resolution in TDE-TFFF. The reason for this is that at higher flow-rates, solutes under a higher thermal-gradient field elute earlier from the channel, staying closer, on average, to the accumulation wall. This results in shorter distances for diffusion-limited mass-transfer contributions to band broadening within the channel; less-than-expected band broadening at higher flow-rates is observed, and higher resolution results. This same effect has been predicted and experimentally observed in exponential time-delay, time-decay sedimentation FFF<sup>13</sup>.

The unique increase in resolution in TDE-TFFF with increased flow-rate is also shown by the data in Table III. As illustrated by the plot in Fig. 7, the standard deviation of the bands in volume units show the usual increase with increased flow-rate because of resistance to mass transfer effects, as previously described<sup>8</sup>. The in-

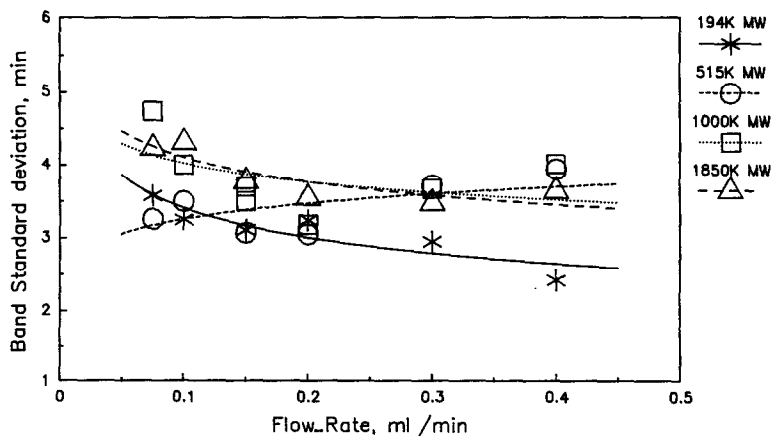


Fig. 8. Effect of flow-rate on band time standard deviation. Conditions as in Fig. 3, except  $\tau = 25.0$  min, flow-rates as shown.

TABLE IV  
EFFECT OF FLOW-RATE ON MOLECULAR WEIGHT

Polystyrene standards

Flow-rate (ml/min)	194K				1000K				515K				1850K			
	$M_w^a$	$M_n^b$	$d^c$	$M_w$	$M_n$	$d$	$M_w$	$M_n$	$d$	$M_w$	$M_n$	$d$	$M_w$	$M_n$	$d$	
0.075	213 000	195 000	1.09	536 000	494 000	1.09	1 260 000	1 010 000	1.24	2 220 000	1 860 000	1.19	2 220 000	1 860 000	1.19	
0.10	194 000	190 000	1.02	564 000	502 000	1.13	1 000 000	919 000	1.09	1 980 000	1 830 000	1.09	1 980 000	1 830 000	1.09	
0.15	196 000	184 000	1.06	550 000	479 000	1.15	1 020 000	964 000	1.07	1 940 000	1 830 000	1.06	1 940 000	1 830 000	1.06	
Repeat	205 000	191 000	1.07	549 000	517 000	1.06	1 070 000	976 000	1.10	1 860 000	1 770 000	1.05	1 860 000	1 770 000	1.05	
Repeat	212 000	200 000	1.06	—	—	—	1 060 000	1 000 000	1.07	—	—	—	—	—	—	
0.20	199 000	183 000	1.09	559 000	512 000	1.09	998 000	949 000	1.05	1 960 000	1 810 000	1.08	1 960 000	1 810 000	1.08	
0.30	191 000	179 000	1.07	511 000	475 000	1.08	953 000	908 000	1.05	1 940 000	1 800 000	1.08	1 940 000	1 800 000	1.08	
0.40	196 000	177 000	1.11	540 000	482 000	1.12	940 000	885 000	1.06	1 910 000	1 750 000	1.09	1 910 000	1 750 000	1.09	

<sup>a</sup>  $M_w$  = weight-average molecular weight.

<sup>b</sup>  $M_n$  = number-average molecular weight.

<sup>c</sup>  $d$  = polydispersity,  $M_w/M_n$ .

crease in band volume is somewhat less for the smaller MW 194 000 polystyrene standard because of the larger solute diffusion coefficient. The increased band volumes for the higher MW components in Fig. 7 is a combination of poorer diffusion (poorer mass transfer) and larger sample polydispersity effects. On the other hand, as shown in Fig. 8, the band standard deviation in time units decreases with increasing flow-rate, verifying the increased time-based resolution seen in Fig. 6.

The effect of flow-rate on band skew shown in Table III is variable, and no significant trend is apparent.

The effect of flow-rate on the calculated molecular weights for polystyrene standards is shown in Table IV. The data indicate that satisfactorily accurate MW values for polymers can be obtained over a wide range of flow-rates. However, as discussed earlier, separations performed by TDE-TFFF at higher flow-rates provide somewhat higher resolution and more accurate MW measurements. Note that the concentration of eluting species is decreased at higher flow-rates because of increased band volumes (Fig. 8); increasing the flow-rate reduces the detector/background noise ratio and decreases the precision of the MW measurement. Therefore, a compromise of flow-rate and other operating parameters often is indicated.

As expected, polydispersity values at higher flow-rates are generally smaller as a result of better resolution and reduced instrumental band broadening.

## CONCLUSIONS

Nomographs relating retention to the exponential time-delay, time-decay constant  $\tau$  values and flow-rate levels are useful in arriving at practical operating conditions for MW measurements by TDE-TFFF. Most-accurate MW and polydispersity measurements are obtained with conditions for highest resolution with TDE-TFFF: large  $\tau$  values and high flow-rates. However, in most practical situations, a compromise is often in order, since large  $\tau$  values mean long analysis times. With the channel thickness and apparatus used in this study, it appears that a flow-rate of 0.15–0.2 ml/min and a  $\tau$  value of about 25 min represent a reasonable compromise between MW accuracy, precision and sample detectability. However, other studies<sup>1,2</sup> suggest that thinner channels will permit higher resolution, improved sample detectability and faster analyses by using smaller  $\tau$  values.

## ACKNOWLEDGEMENT

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