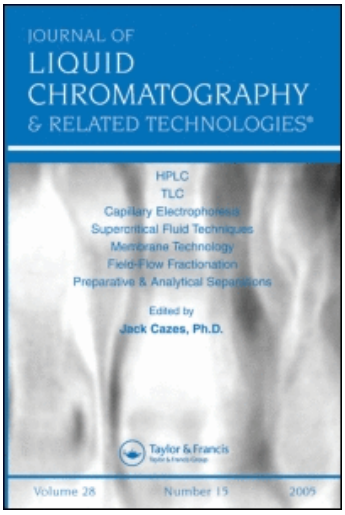

Journal of Liquid Chromatography & Related Technologies
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713597273

Fractionating Power in Sedimentation Field-Flow Fractionation with Linear and Parabolic Field Decay Programming

P. Stephen Williams[a]; J. Calvin Giddings[a]; Ronald Beckett[b]
[a] Department of Chemistry, University of Utah Salt Lake City, Utah [b] Water Studies Centre Chisholm Institute of Technology Caulfield East, Victoria, Australia

To cite this Article Williams, P. Stephen , Giddings, J. Calvin and Beckett, Ronald(1987) 'Fractionating Power in Sedimentation Field-Flow Fractionation with Linear and Parabolic Field Decay Programming', Journal of Liquid Chromatography & Related Technologies, 10: 8, 1961 — 1998
To link to this Article: DOI: 10.1080/01483918708066808
URL: http://dx.doi.org/10.1080/01483918708066808

JOURNAL OF LIQUID CHROMATOGRAPHY, 10(8&9), 1961-1998 (1987)

FRACTIONATING POWER IN SEDIMENTATION FIELD-FLOW FRACTIONATION WITH LINEAR AND PARABOLIC FIELD DECAY PROGRAMMING

P. Stephen Williams[1], J. Calvin Giddings[1]*, and Ronald Beckett[2]

[1]*Department of Chemistry*
University of Utah
Salt Lake City, Utah 84112
[2]*Water Studies Centre*
Chisholm Institute of Technology
Caulfield East, Victoria, Australia 3145

ABSTRACT

Following an earlier treatment of exponentially programmed field decay in field-flow fractionation (FFF), expressions have been derived for retention time and fractionating power F_d for linear and two types of parabolic programmed field decay. The particular case of sedimentation FFF has been considered and plots of both retention time and F_d as functions of particle diameter are generated by computer in order to illustrate the influence of the various experimental parameters. Approximate analytical expressions have been derived for retention time and F_d in each case, and from these the means of calculating both the initial field strength and the program time necessary to obtain a desired level of F_d at some particular particle size have been obtained. Finally the special properties and possible uses of these programs have been discussed.

INTRODUCTION

Field-flow fractionation (FFF) is a chromatographic-like technique exhibiting high resolving power for the separation and characterization of macromolecules, colloids, and fine particles (1). The process is carried out in a thin uniform flow channel devoid of packing. Retention is induced by the application of a perpendicular field or gradient rather than by a stationary phase. The simplicity of the channel leads to exact equations relating molecular weight, particle diameter, and other sample properties to observed values of the elution volume. Thus in many cases the characterization of complex macromolecular materials can be achieved without calibration.

For macromolecular and colloidal materials spanning a broad particle size or mass range, it has been found desirable to program certain FFF parameters in order to reduce the time needed to proceed through the particle mass or size range (2-9). Most commonly the field strength has been chosen for programming because this parameter is subject to exacting control over a broad range. Field programming is especially important for the subtechnique sedimentation FFF because otherwise the high selectivity of this technique tends to distribute particles too widely over the elution range. Programming serves as a means for focusing diverse particle sizes into a reasonable experimental range of elution times.

In an earlier paper (10) we established a theoretical foundation for describing resolving power for field-flow fractionation systems subject to programming. This was achieved by first formulating an index F_d, termed the fractionating power, which, unlike most other indices, is a continuous mathematically describable function of particle diameter (or mass) and of experimental parameters. We then derived a general equation which contained time-based integrals extending over retention and band broadening parameters; these can be integrated and turned into explicit and functional equations for specific program forms. The example chosen to illustrate our theory was that of exponential

field decay programmed sedimentation FFF. This programming form was chosen because it has been subject to a number of studies and used for a variety of applications, particularly by Kirkland and Yau (7-9). We therefore examined this programming system in detail, showing the dependence of F_d on lag time, flow velocity, program speed, initial field strength, particle density, and channel thickness. We also developed some practical guidelines for the application of this form of programming to the characterization of particle size distribution, in which a fixed level of resolution, represented by F_d, is required.

While exponential field decay has proven to be an effective programming mode for sedimentation FFF, no studies have been done to show how this case compares with many other possible modes of programming in terms of providing desired resolution levels over specified particle diameter ranges. Indeed, such a study would be difficult without the basic work of the previous paper in which the fractionating power F_d is formulated as an objective measure of resolving capabilities. Accordingly, in this paper we develop the theory and accompanying plots necessary to show the behavior of sedimentation FFF systems subject to linear field decay programming and two forms of parabolic field decay programming. With each of these cases we have included an arbitrary time lag period t_1 in which the field strength is held constant prior to the initiation of programming. In each of the program types the field strength S reaches zero in a finite time t_p after the field decay begins. This contrasts with exponential field decay in which S remains finite until the program is arbitrarily terminated. The time-dependent behavior of S for these programming forms is illustrated in Figure 1. We note that the earliest work on FFF programming (2,3) utilized linear and parabolic field programming.

GENERAL THEORY

Our criterion of resolution is the fractionating power F_d, which is defined by

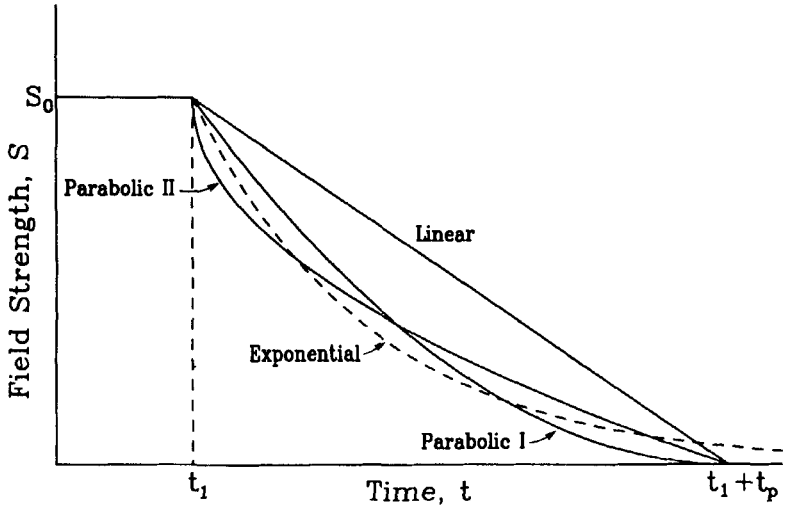

FIGURE 1. Illustration of the dependence of field strength S on time for the three field decay program types considered here (solid lines) and for exponential field decay with $\tau' = t_p/3$ (dashed line).

$$F_d = \frac{R_s}{\delta d/d} = \frac{d}{4\sigma_t}\frac{\delta t_r}{\delta d} \qquad (1)$$

where R_s is the resolution achieved between two close-lying particles whose diameters differ by the small increment δd. Thus F_d is a kind of specific resolution, ideally (but not practically) equal to the resolution of two particles differing by a factor of 2 in diameter d. The second form of eq 1 shows the relationship of F_d to band broadening, represented by the standard deviation in time σ_t of an emerging thin band of uniform particles and the increase δt_r in retention time associated with the increment δd.

To make clear the necessity of dealing with small particle diameter increments δd for a rigorous and unambiguous formulation of F_d, we show F_d below as the limiting form of eq 1 as δd approaches zero

$$F_d = \frac{d}{4\sigma_t}\frac{dt_r}{dd} = \frac{t_r}{4\sigma_t}\frac{d \ln t_r}{d \ln d} = \frac{t_r}{4\sigma_t} S_d \qquad (2)$$

This equation shows that F_d is simply related to retention time t_r, peak width parameter σ_t, and the diameter-based selectivity S_d, defined as d ln t_r/d ln d.

Retention time t_r must be obtained from the basic integral equation for programming (2)

$$L = \int_o^{t_r} R\langle v\rangle \, dt \qquad (3)$$

applicable to both field and flow programming. With field programming the mean flow velocity <v> is held constant and therefore comes out of the integral. We then have

$$\frac{L}{\langle v\rangle} = t^o = \int_o^{t_r} R \, dt \qquad (4)$$

where the channel length L divided by <v> is equal to the channel void time t^o, which equals the time necessary to elute a non-retained marker peak. The integral now extends only over retention ratio R, which in each case varies in a specified manner with time as a result of the variable field strength.

The band width parameter σ_t must be expressed in terms of plate height H, which also varies with field strength. Because of this variation, the general equation for σ_t involves the integration of H over channel coordinate z or an integration of H combined with some other terms over the residence time t in the channel as shown by the expressions (10)

$$\sigma_t = \frac{\left(\int_o^L H \, dz\right)^{1/2}}{R_r\langle v\rangle} = \frac{\left[\int_o^{t_r} (H/\langle v\rangle) R \, dt\right]^{1/2}}{R_r} \qquad (5)$$

where R_r is equal to the retention ratio at the time of elution. To evaluate these integrals we use the well-established form of H (1,11)

$$H = \frac{\chi w^2 \langle v \rangle}{D} \tag{6}$$

in which w is the channel thickness, D the particle diffusion coefficient, and χ a nonequilibrium coefficient that varies strongly but in a complex manner with retention ratio R (11). The substitution of eq 6 into 5 yields

$$\sigma_t = \frac{w}{D^{1/2} R_r} \left(\int_0^{t_r} \chi R \, dt \right)^{1/2} \tag{7}$$

The evaluation of eqs 4 and 7 requires an explicit form of the time dependence of χ and R. The variation of these parameters is tied to the time dependence of the field strength S, namely S(t), which depends on the programming mode. There are very good approximate expressions for both R and χ relating each to retention parameter λ, which is in turn directly influenced by the field strength. For R we have

$$R = 6\lambda(1 - 2\lambda) \tag{8}$$

which is accurate to within 0.37% up to $\lambda = 0.15$, and for χ we have

$$\chi = \frac{24\lambda^3(1 - 10\lambda + 28\lambda^2)}{(1 - 2\lambda)} \tag{9}$$

which is accurate to within 6.2% up to $\lambda = 0.15$. Retention parameter λ for spherical particles is related to field strength S via the equation

$$\lambda = \frac{\Lambda}{Swd^n} \tag{10}$$

where w is the channel thickness, d is the particle diameter, and n is a number (generally an integer) dependent on the field type (e.g., n = 3 for sedimentation FFF and n = 1 for flow FFF). The constant Λ may be shown (12) to be given by

$$\Lambda = \frac{kTd^n}{(F/S)} = \frac{kTd^n}{\phi} \qquad (11)$$

where k is the Boltzmann constant, T is the system temperature, F is the force exerted by the field on a particle of diameter d, and $\phi = F/S$ is the field-particle interaction parameter which for sedimentation FFF is equivalent to the effective particle mass, i.e.

$$\phi = \frac{\pi}{6} d^3 \Delta\rho \qquad (12)$$

As mentioned above, n = 3 for sedimentation FFF and it follows from eqs 11 and 12 that

$$\Lambda = \frac{6kT}{\pi\Delta\rho} \qquad (13)$$

The particle diffusion coefficients are given by the Stokes-Einstein equation

$$D = \frac{kT}{3\pi\eta d} \qquad (14)$$

ISOCRATIC ELUTION

Following the initiation of flow there is an optional hold period, of arbitrary duration t_1, common to each of the programs, during which the field is maintained at its initial strength S_o. We shall consider the isocratic elution of components within this period before proceeding with the derivation of equations for retention and fractionating power for those components eluted under the various field decay programs.

Retention time is given simply by

$$t_r = \frac{t^o}{R_o} = \frac{t^o}{6\lambda_o(1 - 2\lambda_o)} \tag{15}$$

where R_o is the retention ratio for the component at the initial field strength S_o, and λ_o is the value of the retention parameter λ under the same conditions and is obtainable using eq 10. Substituting for λ_o with eq 10, differentiating with respect to d, and replacing λ_o gives us

$$\frac{dt_r}{dd} = \frac{nt^o}{d} \frac{(1 - 4\lambda_o)}{6\lambda_o(1 - 2\lambda_o)^2} \tag{16}$$

An expression for σ_t is obtained by substituting for R and χ in eq 7 using eqs 8 and 9, respectively

$$\sigma_t = \frac{2wt_r^{1/2}}{D^{1/2}} \frac{\lambda_o(1 - 10\lambda_o + 28\lambda_o^2)^{1/2}}{(1 - 2\lambda_o)} \tag{17}$$

Finally, substitution of eqs 15, 16 and 17 into eq 2 gives an expression for F_d

$$F_d = \frac{n}{24w} \left(\frac{3}{2}Dt^o\right)^{1/2} \frac{(1 - 4\lambda_o)}{\lambda_o^{3/2}(1 - 2\lambda_o)^{1/2}(1 - 10\lambda_o + 28\lambda_o^2)^{1/2}} \tag{18}$$

LINEAR FIELD DECAY WITH TIME LAG

Following the initial hold or "time lag" period t_1, the field is assumed to decay linearly to zero over a programmed time period t_p, according to the equation

$$S(t) = S_o\left(1 - \frac{(t - t_1)}{t_p}\right) = S_o\left(\frac{t_p + t_1 - t}{t_p}\right) \tag{19}$$

where S(t) is the field strength at time t where $t \geq t_1$ (see Figure 1).

Consider the elution of some component for which $t_r > t_1$. From eq 4 we have

$$t^o = \int_o^{t_1} R_o \, dt + \int_{t_1}^{t_r} R \, dt \tag{20}$$

From eqs 10 and 19 we see that the retention factor λ varies with time as follows

$$\lambda = \frac{\lambda_o t_p}{(t_p + t_1 - t)} \tag{21}$$

Substituting R from eq 8 into eq 20 and then using eq 21 for λ we obtain

$$t^o = R_o t_1 + 6\lambda_o t_p \int_{t_1}^{t_r} \frac{dt}{(t_p + t_1 - t)} - 12\lambda_o^2 t_p^2 \int_{t_1}^{t_r} \frac{dt}{(t_p + t_1 - t)^2} \tag{22}$$

Evaluating the integrals and rearranging gives us the equation

$$\ln\left(\frac{t_p + t_1 - t_r}{t_p}\right) + 2\lambda_o\left(\frac{t_p}{t_p + t_1 - t_r}\right) + \frac{t^o}{6\lambda_o t_p} - \frac{t_1}{t_p} - 2\lambda_o\left(1 - \frac{t_1}{t_p}\right) = 0 \tag{23}$$

This may be treated as an equation in the variable $x = (t_p + t_1 - t_r)/t_p$ and solved numerically using the Newton-Raphson iteration.

We write

$$f(x) = \ln(x) + \frac{2\lambda_o}{x} + \frac{t^o}{6\lambda_o t_p} - \frac{t_1}{t_p} - 2\lambda_o\left(1 - \frac{t_1}{t_p}\right) \qquad (24)$$

The first differential of f(x) with respect to x is then

$$f'(x) = \frac{1}{x} - \frac{2\lambda_o}{x^2} \qquad (25)$$

The iteration which converges on the solution for f(x) = 0 is given by

$$x_{new} = x - \frac{f(x)}{f'(x)} \qquad (26)$$

Due to the nature of the approximation used for R (given by eq 8) there cannot be a meaningful solution corresponding to $\lambda_r > 0.5$, i.e. retention time must not be so long that the retention factor λ is allowed to exceed 0.5 before elution is realized. We see from eq 21 that it is therefore necessary that

$$t_r \leq t_1 + t_p(1 - 2\lambda_o) \qquad (27)$$

This in turn correponds to the condition

$$x \geq 2\lambda_o \qquad (28)$$

A suitable test for the existence of a meaningful solution may therefore be written as

$$\ln(2\lambda_o) + \frac{t^o}{6\lambda_o t_p} + (1 - 2\lambda_o)\left(1 - \frac{t_1}{t_p}\right) \leq 0 \qquad (29)$$

We can substitute for λ_o in eq 23 using eq 10 and differentiate with respect to d. On replacing λ_o, making the substitution $x = \lambda_o/\lambda_r$ and rearranging we obtain

$$\frac{dt_r}{dd} = \frac{n}{R_r d}\{t^o - 12t_1\lambda_o^2 - 12t_p\lambda_o(\lambda_r - \lambda_o)\} \quad (30)$$

The standard deviation in retention time is obtained by solving the integral of eq 7. Substituting for R and χ using eqs 8 and 9, respectively, and for λ using eq 21, with subsequent integration results in

$$\sigma_t = \frac{12w}{D^{1/2}R_r}\{t_1\lambda_o^4(1 - 10\lambda_o + 28\lambda_o^2)$$

$$+ t_p\lambda_o\lambda_r^3(\frac{1}{3} - \frac{5}{2}\lambda_r + \frac{28}{5}\lambda_r^2) - t_p\lambda_o^4(\frac{1}{3} - \frac{5}{2}\lambda_o + \frac{28}{5}\lambda_o^2)\}^{1/2} \quad (31)$$

Substituting for dt_r/dd and σ_t in eq 2 gives us an expression for F_d

$$F_d = \frac{nD^{1/2}}{48w}\{t^o - 12t_1\lambda_o^2 - 12t_p\lambda_o(\lambda_r - \lambda_o)\}\cdot$$

$$\{t_1\lambda_o^4(1 - 10\lambda_o + 28\lambda_o^2) + t_p\lambda_o\lambda_r^3(\frac{1}{3} - \frac{5}{2}\lambda_r + \frac{28}{5}\lambda_r^2)$$

$$- t_p\lambda_o^4(\frac{1}{3} - \frac{5}{2}\lambda_o + \frac{28}{5}\lambda_o^2)\}^{-1/2} \quad (32)$$

We are able to make various approximations given the condition $\lambda_o < \lambda_r << 1$. For example, eq 23 reduces to

$$\ln(\frac{t_p + t_1 - t_r}{t_p}) = \frac{t_1}{t_p} - \frac{t^o}{6\lambda_o t_p} \quad (33)$$

so that

$$\lambda_r = \lambda_o \exp(\frac{t^o}{6\lambda_o t_p} - \frac{t_1}{t_p}) \quad (34)$$

and

$$t_r = t_1 + t_p\{1 - \exp(\frac{t_1}{t_p} - \frac{t^o}{6\lambda_o t_p})\} \quad (35)$$

Similarly, eq 32 reduces to

$$F_d = \frac{nD^{1/2}t^o}{48w}\left(\frac{t_p\lambda_o\lambda_r^3}{3}\right)^{-1/2} \quad (36)$$

Substituting for λ_r using eq 34 then gives us

$$F_d = \frac{n(3Dt^o)^{1/2}}{48w\lambda_o^2}\left(\frac{t^o}{t_p}\right)^{1/2} \exp\left(\frac{6\lambda_o t_1 - t^o}{4\lambda_o t_p}\right) \quad (37)$$

As discussed later the linear decay program is not suited to the analysis or characterization of wide particle size ranges. However, it has the potential to effect extremely high fractionating power over narrow ranges of d. It is therefore of interest to derive equations for t_p/t^o and S_o which will give rise to some maximum F_d, $F_d(max)$, at some particle diameter of particular interest, d_m. The maximum F_d is realized when $dF_d/dd = 0$. Differentiating eq 37 with respect to d yields

$$\frac{dF_d}{dd} = \frac{n(3Dt^o)^{1/2}}{48w\lambda_o^2}\left(\frac{t^o}{t_p}\right)^{1/2} \exp\left(\frac{6t_1\lambda_o - t^o}{4t_p\lambda_o}\right)\left(\frac{2n - \frac{1}{2}}{d} - \frac{nt^o}{4t_p\lambda_o d}\right) \quad (38)$$

At this point we shall restrict ourselves to consideration only of sedimentation FFF for which n = 3. It is apparent from eq 38 that the maximum F_d is predicted for particles for which

$$\lambda_o = \frac{3}{22}\frac{t^o}{t_p} \quad (39)$$

Substituting this back into eq 37 and substituting for D using eq 14, we get

$$F_d(max) = \frac{1}{16w}\left(\frac{22}{3}\right)^2\left(\frac{kTt^o}{\pi\eta d_m}\right)^{1/2}\left(\frac{t_p}{t^o}\right)^{3/2}\exp\left(\frac{3}{2}\frac{t_1}{t_p} - \frac{11}{6}\right) \qquad (40)$$

For $t_1 = 0$ we can rearrange this to an equation for determining the required t_p/t^o

$$\frac{t_p}{t^o} = 1.51\left(\frac{\pi\eta d_m}{kTt^o}\right)^{1/3}\left(wF_d(max)\right)^{2/3} \qquad (41)$$

From eqs 10, 13, and 39 we obtain the equation for the required S_o

$$S_o = \frac{44kT}{\pi\Delta\rho w d_m^3}\frac{t_p}{t^o} \qquad (42)$$

From eqs 34 and 39 we see that for $t_1 = 0$, $\lambda_r/\lambda_o = 3.39$ for the particle size giving rise to $F_d(max)$.

PARABOLIC FIELD DECAY WITH TIME LAG: TYPE I

In this case, following the initial hold period t_1, the field decays according to the parabolic equation

$$S(t) = S_o\left(1 - \frac{(t - t_1)^2}{t_p}\right) = S_o\left(\frac{t_p + t_1 - t}{t_p}\right)^2 \qquad (43)$$

The directrix of this parabolic field program is parallel to the time axis so that at the time $t = t_1 + t_p$, when the field strength has decayed to zero, the slope of the plot of field strength as a function of time is also zero (see Figure 1). Retention time is again found as the solution to eq 20 but here the retention factor λ is given by

$$\lambda = \lambda_o\left(\frac{t_p}{t_p + t_1 - t}\right)^2 \qquad (44)$$

Substituting in eq 20 for R via eq 8 and in turn for λ via eq 44 yields

$$t^o = R_o t_1 + 6\lambda_o t_p^2 \int_{t_1}^{t_r} \frac{dt}{(t_p + t_1 - t)^2}$$

$$- 12\lambda_o^2 t_p^4 \int_{t_1}^{t_r} \frac{dt}{(t_p + t_1 - t)^4} \qquad (45)$$

Solving the integrals and rearranging gives us the equation

$$\frac{2\lambda_o t_p^3}{(t_p + t_1 - t_r)^3} - \frac{3t_p}{(t_p + t_1 - t_r)} + \frac{t^o}{2\lambda_o t_p}$$

$$+ 3\left(1 - \frac{t_1}{t_p}\right) - 2\lambda_o\left(1 - \frac{3t_1}{t_p}\right) = 0 \qquad (46)$$

Again, we can treat this as an equation in $x = (t_p + t_1 - t_r)/t_p$ and solve via the Newton-Raphson method. Here

$$f(x) = \frac{2\lambda_o}{x^3} - \frac{3}{x} + \frac{t^o}{2\lambda_o t_p} + 3\left(1 - \frac{t_1}{t_p}\right) - 2\lambda_o\left(1 - \frac{3t_1}{t_p}\right) \qquad (47)$$

and

$$f'(x) = - \frac{6\lambda_o}{x^4} + \frac{3}{x^2} \qquad (48)$$

The iteration is again given by eq 26. As for the case of linear decay, the existence of a meaningful solution must be tested for before carrying out the iteration. The requirement for λ not to exceed 0.5 translates to

$$t_r \leq t_1 + t_p\left(1 - (2\lambda_o)^{1/2}\right) \qquad (49)$$

which in turn corresponds to

$$x \geq (2\lambda_o)^{1/2} \tag{50}$$

It follows that a suitable test for the existence of a meaningful solution may be written as

$$-\frac{2}{(2\lambda_o)^{1/2}} + \frac{t^o}{2\lambda_o t_p} + 3\left(1 - \frac{t_1}{t_p}\right) - 2\lambda_o\left(1 - \frac{3t_1}{t_p}\right) \leq 0 \tag{51}$$

We can differentiate eq 46 with respect to d, substituting for λ_o using eq 10. Reintroducing λ_o, making the substitution $x = (\lambda_o/\lambda_r)^{1/2}$, and rearranging we obtain

$$\frac{dt_r}{dd} = \frac{n}{R_r d}\{t^o - 12t_1\lambda_o^2 - 4t_p[(\lambda_o\lambda_r^3)^{1/2} - \lambda_o^2]\} \tag{52}$$

Solving the integral in eq 7 with λ given by eq 44 results in

$$\sigma_t = \frac{12w}{D^{1/2}R_r}\{t_1\lambda_o^4(1 - 10\lambda_o + 28\lambda_o^2) + t_p\lambda_o^{1/2}\lambda_r^{7/2}\left(\frac{1}{7} - \frac{10}{9}\lambda_r + \frac{28}{11}\lambda_r^2\right) - t_p\lambda_o^4\left(\frac{1}{7} - \frac{10}{9}\lambda_o + \frac{28}{11}\lambda_o^2\right)\}^{1/2} \tag{53}$$

Then combining eqs 2, 52 and 53 results in the following expression for F_d

$$F_d = \frac{nD^{1/2}}{48w}\{t^o - 12t_1\lambda_o^2 - 4t_p[(\lambda_o\lambda_r^3)^{1/2} - \lambda_o^2]\} \cdot \{t_1\lambda_o^4(1 - 10\lambda_o + 28\lambda_o^2) + t_p\lambda_o^{1/2}\lambda_r^{7/2}\left(\frac{1}{7} - \frac{10}{9}\lambda_r + \frac{28}{11}\lambda_r^2\right) - t_p\lambda_o^4\left(\frac{1}{7} - \frac{10}{9}\lambda_o + \frac{28}{11}\lambda_o^2\right)\}^{-1/2} \tag{54}$$

We can again derive simplified results which will be valid when $\lambda_o < \lambda_r << 1$. Equation 46 reduces to

$$\frac{t_p}{(t_p + t_1 - t_r)} = \frac{t^o}{6\lambda_o t_p} - \frac{t_1}{t_p} + 1 \tag{55}$$

It follows that

$$\lambda_r = \lambda_o\left(\frac{t^o}{6\lambda_o t_p} - \frac{t_1}{t_p} + 1\right)^2 \tag{56}$$

and

$$t_r = t_1 + t_p\left(1 - \frac{6\lambda_o t_p}{t^o - 6\lambda_o t_1 + 6\lambda_o t_p}\right) \tag{57}$$

Equation 54 similarly reduces to

$$F_d = \frac{nD^{1/2}t^o}{48w}\left(\frac{7}{t_p\lambda_o^{1/2}\lambda_r^{7/2}}\right)^{1/2} \tag{58}$$

which in turn, when eq 56 is substituted for λ_r, reduces to

$$F_d = \frac{n(7Dt^o)^{1/2}}{48w\lambda_o^2}\left(\frac{t^o}{t_r}\right)^{1/2}\left(\frac{t^o}{6\lambda_o t_p} - \frac{t_1}{t_p} + 1\right)^{-7/2} \tag{59}$$

We can derive guideline equations for t_p/t^o and S_o in a manner similar to that employed for linear field decay. Differentiating eq 59 with respect to d yields

$$\frac{dF_d}{dd} = \frac{n(7Dt^o)^{1/2}}{48w\lambda_o^2}\left(\frac{t^o}{t_p}\right)^{1/2}\left(1 - \frac{t_1}{t_p} + \frac{t^o}{6\lambda_o t_p}\right)^{-7/2} \cdot$$

$$\left\{\frac{(2n - \frac{1}{2})}{d} - \frac{7n}{2d}\frac{t^o}{6\lambda_o t_p}\left(1 - \frac{t_1}{t_p} + \frac{t^o}{6\lambda_o t_p}\right)^{-1}\right\} \tag{60}$$

Again restricting our consideration to sedimentation FFF we deduce from eq 60 that the maximum F_d is given when

$$\lambda_o = \frac{5}{33}\frac{t^o}{(t_p - t_1)} \tag{61}$$

Substituting λ_o back into eq 59 and using eq 14 for D gives

$$F_d(max) = \frac{1}{16w}\left(\frac{33}{5}\right)^2\left(\frac{10}{21}\right)^{7/2}\left(\frac{7kTt^o}{3\pi\eta d_m}\right)^{1/2}\left(\frac{t_p}{t^o}\right)^{3/2}\left(\frac{t_p}{t_p - t_1}\right)^{7/2} \tag{62}$$

Again, if we assume $t_1 = 0$, we can rearrange this to an equation for the required t_p/t^o for specified values of d_m and $F_d(max)$

$$\frac{t_p}{t^o} = 2.18\left(\frac{\pi\eta d_m}{kTt^o}\right)^{1/3}\left(wF_d(max)\right)^{2/3} \tag{63}$$

We obtain the equation for the required S_o from eqs 10, 13 and 61

$$S_o = \frac{198kT}{5\pi\Delta\rho w d_m^3}\frac{t_p}{t^o} \tag{64}$$

From eqs 56 and 61 we see that when $t_1 = 0$, $\lambda_r/\lambda_o = 4.41$ for the particle size corresponding to the maximum F_d.

PARABOLIC FIELD DECAY WITH TIME LAG: TYPE II

We shall now consider the field to decay according to the following parabolic equation

$$S(t) = S_o\left(1 - \left(\frac{t - t_1}{t_p}\right)^{1/2}\right) = S_o\left(\frac{t_p^{1/2} - (t - t_1)^{1/2}}{t_p^{1/2}}\right) \tag{65}$$

In this case the directrix of the field program lies parallel to the field strength axis; thus the initial slope of the plot of

field strength against time (at time $t = t_1$) is instantaneously infinite (see Figure 1). Here the slope approaches $-S_o/2t_p$ as field strength approaches zero at time $t = t_1 + t_p$, i.e., half the constant slope of the linear program. We now have the retention factor λ given by

$$\lambda = \lambda_o\left(\frac{t_p^{1/2}}{t_p^{1/2} - (t - t_1)^{1/2}}\right) \tag{66}$$

Combining eqs 8, 20, and 66 gives us

$$t^o = R_o t_1 + 6\lambda_o t_p^{1/2} \int_{t_1}^{t_r} \frac{dt}{\left(t_p^{1/2} - (t - t_1)^{1/2}\right)}$$

$$- 12\lambda_o^2 t_p \int_{t_1}^{t_r} \frac{dt}{\left(t_p^{1/2} - (t - t_1)^{1/2}\right)^2} \tag{67}$$

Solving the integrals and rearranging yields

$$(1 + 2\lambda_o)\ \ln\left(\frac{t_p^{1/2} - (t_r - t_1)^{1/2}}{t_p^{1/2}}\right)$$

$$+ \frac{2\lambda_o t_p^{1/2}}{t_p^{1/2} - (t_r - t_1)^{1/2}} - \frac{t_p^{1/2} - (t_r - t_1)^{1/2}}{t_p^{1/2}}$$

$$+ \frac{t^o}{12\lambda_o t_p} + 1 - \frac{t_1}{2t_p} - \lambda_o\left(2 - \frac{t_1}{t_p}\right) = 0 \tag{68}$$

Again the Newton-Raphson method is ideally suited to solve for t_r. Treating eq 68 as an equation in $x = \left(t_p^{1/2} - (t_r - t_1)^{1/2}\right)/t_p^{1/2}$, we have

$$f(x) = (1 + 2\lambda_o)\ \ln(x) + \frac{2\lambda_o}{x} - x + \frac{t^o}{12\lambda_o t_p}$$

$$+ 1 - \frac{t_1}{2t_p} - \lambda_o(2 - \frac{t_1}{t_p}) \qquad (69)$$

and

$$f'(x) = \frac{(1 + 2\lambda_o)}{x} - \frac{2\lambda_o}{x^2} - 1 \qquad (70)$$

The iteration which converges on the solution for $f(x) = 0$ is given by eq 26. Again it is essential to test for the existence of a meaningful solution; this is again governed by the condition $\lambda_r \leq 0.5$ which corresponds to

$$t_r \leq t_1 + t_p(1 - 2\lambda_o)^2 \qquad (71)$$

This in turn is equivalent to

$$x \geq 2\lambda_o \qquad (72)$$

and a suitable test may be written

$$(1 + 2\lambda_o)\ \ln(2\lambda_o) + (2 - \frac{t_1}{2t_p})(1 - 2\lambda_o) + \frac{t^o}{12\lambda_o t_p} \leq 0 \qquad (73)$$

Differentiating eq 68 with respect to d, making the substitution $x = \lambda_o/\lambda_r$, and rearranging gives us the following expression for dt_r/dd.

$$\frac{dt_r}{dd} = \frac{n}{R_r d}\{t^o - 12t_1\lambda_o^2 - 24t_p\lambda_o[\lambda_r - \lambda_o + \lambda_o\ \ln(\lambda_o/\lambda_r)]\} \qquad (74)$$

Solving the integral in eq 7 with λ being given by eq 66 results in

$$\sigma_t = \frac{12w}{D^{1/2}R_r}\{t_1\lambda_o^4(1 - 10\lambda_o + 28\lambda_o^2) + t_p\lambda_o^4(\frac{1}{3} - \frac{5}{3}\lambda_o + \frac{16}{5}\lambda_o^2)$$

$$- t_p\lambda_o^2\lambda_r^2(1 - \frac{20}{3}\lambda_r + 16\lambda_r^2)$$

$$+ t_p\lambda_o\lambda_r^3(\frac{2}{3} - 5\lambda_r + \frac{64}{5}\lambda_r^2)\}^{1/2} \quad (75)$$

Substituting the dt_r/dd from eq 74 and σ_t from eq 75 into eq 2 gives us

$$F_d = \frac{nD^{1/2}}{48w}\{t^o - 12t_1\lambda_o^2 - 24t_p\lambda_o(\lambda_r - \lambda_o + \lambda_o \ln(\lambda_o/\lambda_r))\}\cdot$$

$$\{t_1\lambda_o^4(1 - 10\lambda_o + 28\lambda_o^2) + t_p\lambda_o^4(\frac{1}{3} - \frac{5}{3}\lambda_o + \frac{16}{5}\lambda_o^2)$$

$$- t_p\lambda_o^2\lambda_r^2(1 - \frac{20}{3}\lambda_r + 16\lambda_r^2)$$

$$+ t_p\lambda_o\lambda_r^3(\frac{2}{3} - 5\lambda_r + \frac{64}{5}\lambda_r^2)\}^{-1/2} \quad (76)$$

If we now assume that the condition $\lambda_o < \lambda_r << 1$ holds then eq 68 reduces to

$$\ln(\frac{\lambda_r}{\lambda_o}) + \frac{\lambda_o}{\lambda_r} = \frac{t^o}{12\lambda_o t_p} - \frac{t_1}{2t_p} + 1 \quad (77)$$

We cannot solve this analytically for λ_r but we note that for $\lambda_o << \lambda_r$

$$\frac{\lambda_r}{\lambda_o} \simeq \exp(\frac{t^o}{12\lambda_o t_p} - \frac{t_1}{2t_p} + 1) \quad (78)$$

This expression for λ_r/λ_o may be taken as a first approximation to which we can apply a correction corresponding to just one iteration of the Newton-Raphson type. We thereby obtain

$$\frac{\lambda_r}{\lambda_o} \simeq \exp\left(\frac{t^o}{12\lambda_o t_p} - \frac{t_1}{2t_p} + 1\right) - 1 \qquad (79)$$

This approximation is accurate to within 2.2% for $\lambda_r/\lambda_o \geq 5$. The error rises to 6.2% when $\lambda_r/\lambda_o = 3$, but nevertheless we can expect sufficient accuracy for the elution of all but the smallest particles. It follows that

$$t_r \simeq t_1 + t_p \left[\frac{\exp\left(\frac{t^o}{12\lambda_o t_p} - \frac{t_1}{2t_p} + 1\right) - 2}{\exp\left(\frac{t^o}{12\lambda_o t_p} - \frac{t_1}{2t_p} + 1\right) - 1} \right]^2 \qquad (80)$$

When $\lambda_o < \lambda_r << 1$, eq 76 reduces to the form

$$F_d \simeq \frac{n(Dt^o)^{1/2}}{48w\lambda_o^2} \left(\frac{t^o}{t_p}\right)^{1/2} \frac{\lambda_o}{\lambda_r} \left\{\frac{2}{3}\frac{\lambda_r}{\lambda_o} - 1\right\}^{-1/2} \qquad (81)$$

and when λ_r/λ_o is replaced by eq 79

$$F_d \simeq \frac{n(Dt^o)^{1/2}}{48w\lambda_o^2} \left(\frac{t^o}{t_p}\right)^{1/2} \left\{\exp\left(\frac{t^o}{12\lambda_o t_p} - \frac{t_1}{2t_p} + 1\right) - 1\right\}^{-1}$$

$$\left\{\frac{2}{3}\exp\left(\frac{t^o}{12\lambda_o t_p} - \frac{t_1}{2t_p} + 1\right) - \frac{5}{3}\right\}^{-1/2} \qquad (82)$$

In order to determine $F_d(\max)$ and the corresponding particle diameter d_m, we differentiate eq 81 with respect to d and set the result to zero

$$\frac{dF_d}{dd} = \frac{n(Dt^o)^{1/2}}{48w\lambda_o^2} \left(\frac{t^o}{t_p}\right)^{1/2} \left\{\frac{2}{3}\left(\frac{\lambda_r}{\lambda_o}\right)^3 - \left(\frac{\lambda_r}{\lambda_o}\right)^2\right\}^{-1/2}$$

$$\left[\frac{(2n - \frac{1}{2})}{d} - \frac{d(\lambda_r/\lambda_o)}{dd} \frac{\left(\frac{\lambda_r}{\lambda_o} - 1\right)}{\left(\frac{2}{3}\left(\frac{\lambda_r}{\lambda_o}\right)^2 - \left(\frac{\lambda_r}{\lambda_o}\right)\right)} \right] \qquad (83)$$

The maximum in F_d is therefore given when

$$\frac{d(\lambda_r/\lambda_o)}{dd} \frac{(\frac{\lambda_r}{\lambda_o} - 1)}{(\frac{2}{3}(\frac{\lambda_r}{\lambda_o})^2 - (\frac{\lambda_r}{\lambda_o}))} = \frac{2n - \frac{1}{2}}{d} \tag{84}$$

The differential of (λ_r/λ_o) with respect to d is obtained by differentiating eq 77 rather than the more approximate eq 78. After rearranging we obtain

$$\frac{d(\lambda_r/\lambda_o)}{dd} = \frac{n}{d} \frac{t^o}{12\lambda_o t_p} (\frac{\lambda_r}{\lambda_o})^2 (\frac{\lambda_r}{\lambda_o} - 1)^{-1} \tag{85}$$

Substitution of this into eq 84 yields the result

$$\frac{\lambda_o}{\lambda_r} = \frac{2}{3} - \frac{n}{(2n - \frac{1}{2})} \frac{t^o}{12\lambda_o t_p} \tag{86}$$

We can now equate this with our approximate expression for λ_r/λ_o (eq 79). For sedimentation FFF where n ◻ 3 and for $t_1 = 0$ we obtain by numerical means the result

$$\lambda_o = \frac{t^o}{10.8t_p} \tag{87}$$

Substituting for λ_o in eq 86 and subsequently for λ_r/λ_o and λ_o in eq 81 gives

$$F_d(max) = 0.767 \frac{(D_m t^o)^{1/2}}{w} (\frac{t_p}{t^o})^{3/2} \tag{88}$$

where D_m is the diffusion coefficient for the particle size giving rise to the maximum in F_d. Substituting for D_m using eq 14 and rearranging gives an equation for the required t_p/t^o

$$\frac{t_p}{t^o} = 1.72 \left(\frac{\pi\eta d_m}{kTt^o}\right)^{1/3} \left(wF_d(max)\right)^{2/3} \quad (89)$$

Combining eqs 87, 10, and 13 gives us an equation for the required initial field strength S_o

$$S_o = \frac{64.8kT}{\pi\Delta\rho w d_m^3} \frac{t_p}{t^o} \quad (90)$$

Incidentally, we see from eqs 87 and 79 that at $F_d(max)$, $\lambda_r/\lambda_o \approx 5.7$. We can therefore expect eqs 88, 89, and 90 to be acceptably accurate.

COMPUTATION

Computer programs were written in FORTRAN 77 to carry out the calculation of retention and fractionating power for each of the field decay programs discussed. These programs were implemented on a DEC 20 computer. In every case the range of particle diameter to be considered was divided into a large number of small increments. Calculations started at the lowest discrete particle size. Retention time was first determined for isocratic elution at the initial field strength according to eq 15, and if this did not exceed the hold time t_1 the fractionating power was determined using eq 18. When a particle size was encountered for which retention time calculated under initial isocratic conditions exceeded time t_1, then it was recognized that that size, and all larger particles would be eluted during the subsequent programmed field decay.

The three field decay programs each required numerical solution for retention time. In each case the root of some function in x was required, the retention time then being obtained from the root. For a particle which elutes just after t_1 the solution for x is just less than unity; since the iterative procedure requires an initial estimate to the solution, this was conveniently set to

unity. Iteration was continued until the relative difference between the results of consecutive iterations was less than 10^{-6}. For the remaining discrete particle sizes the initial estimate was simply the solution for x for the previous particle size. Provision of such a good estimate minimized the number of iterations required for convergence. In fact the programs requiring iterative solutions for retention time were only marginally slower than the wholely analytic calculations for simple exponential field decay (10). The existence of a solution was always tested for before starting the iterative procedure.

The approximate expressions for R and χ used in the various derivations deteriorate rapidly in accuracy for $\lambda > 0.15$. The deterioration is particularly rapid for χ. Calculation and plotting of retention time and F_d were carried out only for those particles for which $\lambda_o \leq \lambda_r \leq 0.15$. We can therefore be confident of the validity of all tabulated and plotted results.

RESULTS AND DISCUSSION

Although the equations derived for retention time and F_d are general we have here restricted our consideration to the subtechnique of sedimentation FFF. In order to demonstrate and compare the different field decay programs, we have developed sets of F_d versus d and t_r versus d plots corresponding to the variation of certain program parameters. In all such diagrams solid lines represent plots of F_d (referred to the left hand vertical axis) against particle diameter d and broken lines represent plots of retention time t_r (referred to the right hand vertical axis) versus d.

For the three programs, we have chosen to illustrate the effect on F_d and t_r of varying the initial field strength S_o. In addition, the effect of the program time relative to nonretained peak time (t_p/t^o) is examined.

In the interest of simplicity the initial hold time t_1 was set to zero for all plots discussed. In fact t_1 has little effect

on F_d in the case of the linear and parabolic programs until it approaches the magnitude of t_p.

Typical values are assigned to the remaining parameters and these remain unchanged for all plots. However, we can deduce the effect of their variation by considering the various equations derived for t_r and F_d.

The nonretained peak time t^o was held at 50 sec. We can see from eqs 15, 23, 46, and 68 that for some initial field strength S_o, if program time constants (t_1 and t_p) are held constant relative to t^o then retention time will also be constant relative to t^o no matter how the latter varies; thus retention times are directly related to t^o. Similarly, under the same provisions, F_d is proportional to the square root of t^o (see eqs 18, 32, 54, and 76).

Fluid viscosity η was set at 0.01 poise corresponding to an aqueous phase at 293 K. Provided the effects of secondary relaxation are negligible (13,14), and of course sufficient time is allowed for primary relaxation, the fluid viscosity will have no effect on retention. Since particle diffusion coefficient D is inversely dependent on η we see by inspection of the expressions derived for fractionating power (in particular, eqs 18, 32, 54, and 76) that F_d is inversely proportional to $\eta^{1/2}$.

A density difference, $\Delta\rho$, between the particles and fluid of 1.5 g/ml was considered. This corresponds to an aqueous suspension of silica particles. We see from eqs 10, 11, and 12 how $\Delta\rho$ influences the retention factor λ through the particle-field interaction parameter ϕ in sedimentation FFF, which is to be considered here. It is apparent that λ is inversely dependent on the product $S\Delta\rho$. It follows that the effects of variation of $\Delta\rho$ will exactly parallel those for the variation of S_o; this deduction is equally valid for retention and for fractionating power.

The channel thickness w was fixed at 0.0125 cm, a value at the lower extreme for experimental channels used in sedimentation FFF. Channel thickness influences retention factor λ in the same

way as $\Delta\rho$ (see eq 10). It follows that the variation of w has a parallel effect to the variation of S_o (and $\Delta\rho$); this will include any shifts in the maxima of F_d together with the accompanying change in the magnitude of F_d. However, as may be deduced from inspection of the expressions derived for F_d, there is an additional inverse dependence of F_d on w.

Finally a system temperature of 293 K was assumed. From eqs 10 and 11 we see that λ is directly proportional to temperature. Therefore varation of the reciprocal of temperature has a parallel effect to variation of S_o. In addition, F_d is dependent on the square root of D and consequently on $(T/\eta)^{1/2}$. This second dependence will tend to predominate. For example, a rise in temperature of just 10°C, from 20° to 30°C, for an aqueous phase raises $(T/\eta)^{1/2}$ by 14%. Generally then increased temperatures are desired, so far as they do not lead to practical difficulties such as vaporization of the fluid or leakage at seals.

The results for the linear and two parabolic programs have many features in common and may therefore be discussed together. These results are illustrated by Figures 2 and 3 for the linear program and Figures 4-7 for the two parabolic programs. Figures 2, 4 and 6 show the effects of variation of the initial field strength S_o on retention time and F_d for the linear, parabolic type I, and parabolic type II programs, respectively. The value of t_p/t^o was held at 50 for all these plots, and t_1/t^o at zero. The field therefore decays to zero in time t_p, or since t^o = 50 s, in 41.67 min. The retention time plots therefore have a natural cut-off very close to 41.67 min. As the field strength approaches zero, particles remaining in the channel are swept to the outlet as their corresponding retention factors R and λ increase. This accounts for the tendency of the retention time plots to level out near the limit close to t_p. The ultimate limit will of course be equal to $(t_p + t^o)$. The retention time plots terminate when λ_r is predicted to reach a value of 0.15 for reasons explained earlier. In practice we expect the plots of retention time versus particle diameter to continue as close to horizontal lines.

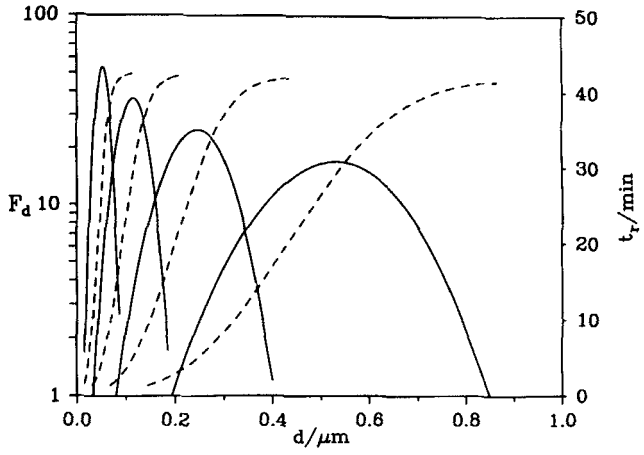

FIGURE 2. Illustration of the influence of S_o on F_d and retention time t_r with linear field decay program. Full lines represent plots of F_d and broken lines plots of t_r (referred to righthand axis). Reading from left to right for both F_d and t_r curves, S_o = 10,000, 1000, 100, and 10 gravities. For all plots t_1 = 0, t_p/t^o = 50, t^o = 50 s, w = 0.0125 cm, Δp = 1.5 g/ml, η = 0.01 poise, and T = 293 K.

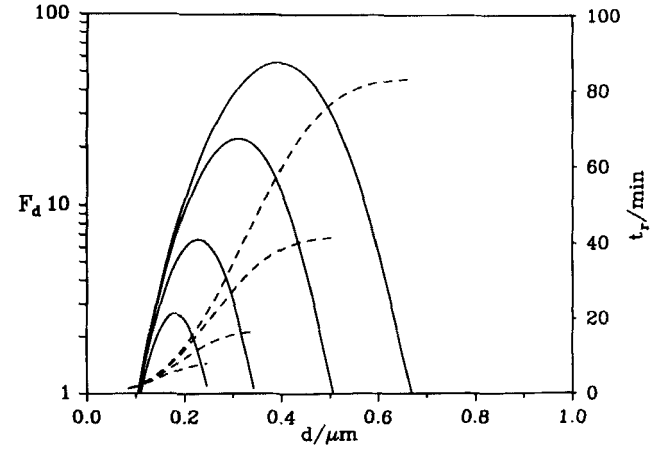

FIGURE 3. Illustration of the influence of t_p/t^o on F_d and t_r with linear field decay program. Reading from bottom to top for both F_d (full) and t_r (broken) curves, t_p/t^o = 10, 20, 50, and 100. For all plots S_o = 50 g; other parameters as for Figure 2.

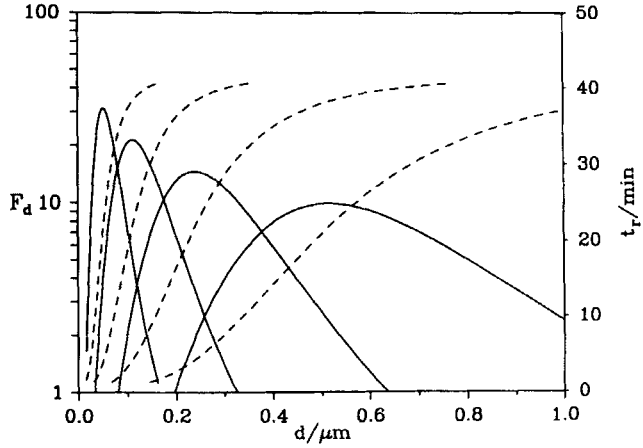

FIGURE 4. Illustration of the influence of S_o on F_d and t_r with parabolic type I field decay program. Reading from left to right for both F_d (full) and t_r (broken) curves, S_o = 10,000, 1000, 100, and 10 g; other parameters as for Figure 2.

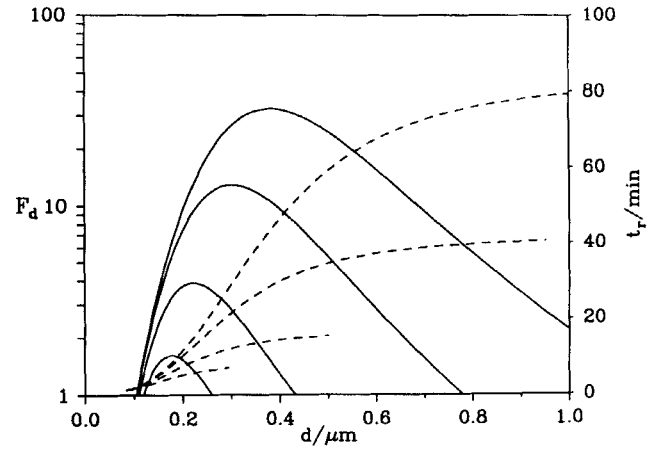

FIGURE 5. Illustration of the influence of t_p/t^o with parabolic type I field decay program. Reading from bottom to top for both F_d (full) and t_r (broken) curves, t_p/t^o = 10, 20, 50, and 100. For all plots S_o = 50 g; other parameters as for Figure 2.

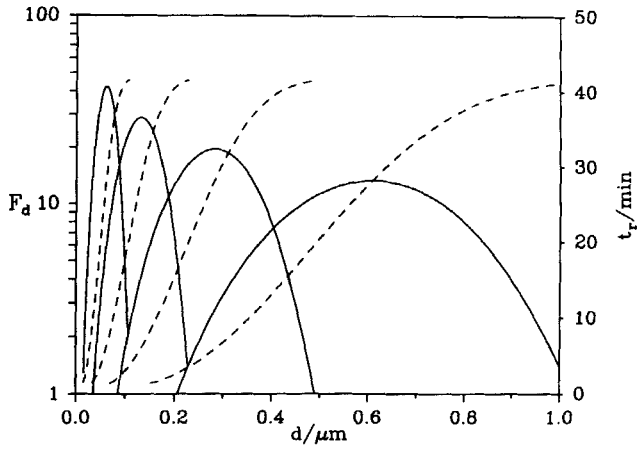

FIGURE 6. Illustration of the influence of S_o on F_d and t_r with parabolic type II field decay program. Reading from left to right for both F_d (full) and t_r (broken) curves, S_o = 10,000, 1000, 100, and 10 g; other parameters as for Figure 2.

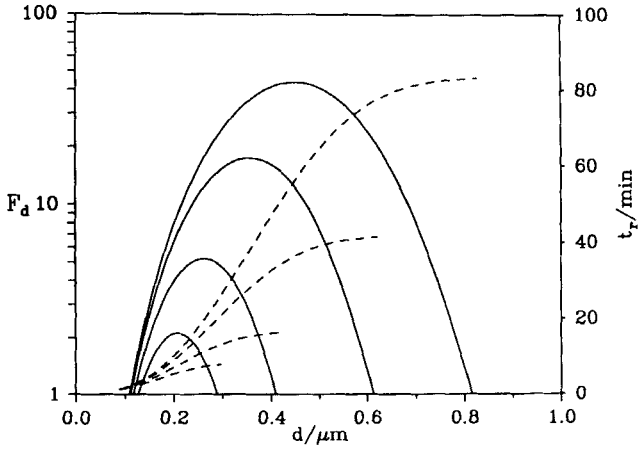

FIGURE 7. Illustration of the influence of t_p/t^o with parabolic type II field decay program. Reading from bottom to top for both F_d (full) and t_r (broken) curves, t_p/t^o = 10, 20, 50, and 100. For all plots S_o = 50 g; other parameters as for Figure 2.

With regard to the plots of F_d, we see a rapid increase in F_d with d as the particles become large enough to be significantly retained at the initial field strength S_o. The increase is so rapid that we chose to use a logarithmic scale in F_d to better illustrate the results. We see a progression towards larger particles for this steep rise in F_d as the initial field strength is lowered.

Following the maximum in the F_d curve, there is a fairly rapid decline in F_d (although less rapid for the parabolic type I program where the decay is less abrupt towards the end of the program) as field strength decays to zero. For Figures 2, 4 and 6, as stated above, both t_p/t^o and t^o are held constant. Thus t_p is constant. Therefore the rate of field decay at any particular time is directly proportional to the initial field strength. The larger particles will start to migrate at a significant velocity only when the field has decayed to a sufficiently low level. It follows that the decline in F_d from this "threshold" level is more rapid for the higher initial field strengths because relatively less time remains for the field to decay to zero. Consequently we see a progression towards a lower cut-off in d as S_o is increased. The net result is a progression of the maximum in F_d towards smaller particle diameter as S_o is increased.

We can combine eqs 42, 64, and 90 to obtain an expression for the particle diameter corresponding to the maximum in F_d

$$d_m = \left(\frac{c_1 kT}{\pi \Delta\rho w S_o} \frac{t_p}{t^o}\right)^{1/3} \tag{91}$$

where c_1 is 44.0 for the linear program, and 39.6 and 64.8 for the types I and II parabolic programs, respectively. The substitution of this d_m into eqs 40, 62 and 88 results in expressions for $F_d(max)$ having the common form

$$F_d(max) = \frac{c_2}{w} \left(\frac{kT}{\pi}\right)^{1/3} \left(\frac{t^o}{\eta}\right)^{1/2} (\Delta\rho w S_o)^{1/6} \left(\frac{t_p}{t^o}\right)^{4/3} \tag{92}$$

where c_2 is 0.286 for the linear, 0.168 for the type I parabolic and 0.221 for the type II parabolic program.

From eq 91 we see that the position of the maximum in F_d is dependent on $(S_o/(t_p/t^o))^{-1/3}$ while we know that the rate of field decay at any particular time is directly proportional to $S_o/(t_p/t^o)$. Figures 3, 5 and 7 show the effect of variation of t_p/t^o at constant S_o. We see a progression of the maximum in F_d towards higher d as t_p/t^o is increased, consistent with eq 91. At the same time we see an increase in $F_d(max)$ with t_p/t^o, consistent with eq 92. Again we see the cut-off in the plots of t_r close to the respective values of t_p when λ_r is predicted to attain a value of 0.15.

Examination of Figures 2 to 7 reveals a difference in the variation of F_d with d as predicted for the three programs. The linear program produces plots where F_d rises to a maximum and returns to a relatively low level over the narrowest range of d (for a given d_m and $F_d(max)$). The type II parabolic program produces plots of F_d which rise and fall a little less rapidly so that the band of d for which F_d exceeds some chosen level is slightly wider. The widest bands are predicted for the type I parabolic program. This is as might be expected since the field decay is much more gradual as it approaches zero. This allows relatively more time for larger particles to migrate through the channel before the field decays to zero.

We can obtain expressions for $F_d/F_d(max)$ as a function of d/d_m for each of the programs as follows. We shall assume zero t_1 in the interests of simplicity. For the linear program eq 37 gives a good approximation for F_d when $d \geq d_m$. We can obtain an expression for $F_d/F_d(max)$ directly from this, remembering that $\lambda_{o,m}/\lambda_o = (d/d_m)^3$, $D/D_m = (d_m/d)^{1/2}$ (the subscript m referring to particles giving rise to the maximum F_d), and that λ_o for particles of diameter d_m is given by eq 39. We get

$$\frac{F_d}{F_d(max)} = \left(\frac{d}{d_m}\right)^{11/2} \exp\left(\frac{11}{6} - \frac{11}{6}\left(\frac{d}{d_m}\right)^3\right)$$

$$= \left\{\left(\frac{d}{d_m}\right)^3 \exp\left(1 - \left(\frac{d}{d_m}\right)^3\right)\right\}^{11/6} \quad (93)$$

From eqs 32 and 34 we can obtain a better approximate expression for F_d which is good for a wider range of d extending to $d < d_m$, although not for $d \ll d_m$. When $t_1 = 0$ we get

$$F_d = \frac{(3Dt^o)^{1/2}}{16w\lambda_o^2}\left(\frac{t^o}{t_p}\right)^{1/2}\left[\exp\left(\frac{t^o}{2\lambda_o t_p}\right) - 1\right]^{-1/2} \quad (94)$$

In the same way that eq 93 was derived we obtain from eq 94 an improved expression for $F_d/F_d(max)$

$$\frac{F_d}{F_d(max)} = \left(\frac{d}{d_m}\right)^{11/2} \exp(11/6)\left\{\exp\left(\frac{11}{3}\left(\frac{d}{d_m}\right)^3\right) - 1\right\}^{-1/2} \quad (95)$$

For the type I parabolic program we can obtain an expression for F_d from eqs 54 and 56 which is reasonably good for a fairly wide range of d extending into the region of $d < d_m$. For $t_1 = 0$ we obtain the equation

$$F_d = \frac{(7Dt^o)^{1/2}}{16w\lambda_o^2}\left(\frac{t^o}{t_p}\right)^{1/2}\left\{\left(\frac{t^o}{6\lambda_o t_p} + 1\right)^7 - 1\right\}^{-1/2} \quad (96)$$

From eqs 61 and 96 we in turn obtain

$$\frac{F_d}{F_d(max)} = \left(\frac{d}{d_m}\right)^{11/2}\left\{\frac{(2.1)^7 - 1}{\left(1.1(d/d_m)^3 + 1\right)^7 - 1}\right\}^{1/2} \quad (97)$$

In the case of the type II parabolic program we are limited by the accuracy of our approximate expression for λ_r/λ_o given by eq 79. Therefore any expression we derive for $F_d/F_d(max)$ using eq

79 will be acceptably accurate only when λ_r/λ_o is greater than around 3. From eqs 79 and 87, assuming $t_1 = 0$, we see that

$$\frac{\lambda_r}{\lambda_o} \simeq \exp\left[0.900\left(\frac{d}{d_m}\right)^3 + 1\right] - 1 \qquad (98)$$

It is apparent from eq 98 that λ_r/λ_o falls below 3 when $d/d_m = 0.75$. We can derive an expression for $F_d/F_d(\max)$ from eqs 81 and 98

$$\frac{F_d}{F_d(\max)} = \left(\frac{d}{d_m}\right)^{11/2} \frac{[\exp(1.90) - 1][2\exp(1.90) - 5]^{1/2}}{[\exp[0.900(d/d_m)^3 + 1] - 1][2\exp[0.900(d/d_m)^3 + 1] - 5]^{1/2}} \qquad (99)$$

This expression proved to be accurate to within 6.3% down to $d/d_m = 0.80$. In this region the expression underestimates the true F_d. The expression is not considered accurate enough however to predict d/d_m, with $d < d_m$, for a given $F_d/F_d(\max)$.

In Table 1 we list values of d/d_m corresponding to the minimum and maximum of the range of d for which $F_d/F_d(\max)$ exceeds certain fixed levels with the three program types (only the upper limit to the range is given for the type II parabolic program). The listed values of d/d_m were obtained by numerical means via eqs 95, 97, and 99. Although the lower limits for d/d_m are not tabulated for the type II parabolic program, we see from our results that the values obtained in practice are a little lower than the corresponding limits for the type I program. This may be explained by the fact that for a given d_m and $F_d(\max)$ the initial field strength must be higher for the type II than for the type I parabolic programs.

TABLE 1

Table of the upper and lower limits to the range of d/d_m for which $F_d/F_{d(max)}$ exceeds various levels for linear, type I parabolic, and type II parabolic decay programs.

	Linear		Parabolic I		Parabolic II	
	d/d_m		d/d_m		d/d_m	
$F_d/F_{d(max)}$	Lower	Upper	Lower	Upper	Lower	Upper
0.9	0.863	1.115	0.841	1.177	-	1.154
0.8	0.810	1.165	0.777	1.272	-	1.217
0.7	0.764	1.208	0.724	1.360	-	1.269
0.6	0.720	1.248	0.677	1.450	-	1.319
0.5	0.676	1.288	0.631	1.549	-	1.368
0.4	0.629	1.331	0.584	1.664	-	1.420
0.3	0.577	1.379	0.532	1.809	-	1.477
0.2	0.514	1.437	0.472	2.014	-	1.546
0.1	0.426	1.520	0.389	2.380	-	1.645

Finally we note that for both exponentially programmed FFF (10) and isocratic FFF the speed of analysis at some desired level of F_d is governed by the nonretained time t^o. Fast analysis is favored by the lowering of t^o. Such action leads to a requirement for increased t_p/t^o and S^o for a given $F_d(max)$ and d_m (see eqs 41 and 42; 63 and 64; and 89 and 90). The advantages of faster analysis may be considered to outweigh the disadvantages of higher initial field strength and higher flowrate. Of course in practice there must be some compromise when a limit to either field strength or flowrate (or their combination) is imposed.

CONCLUSION

The linear and parabolic decay programs are shown by the above to be unsuited to the characterization of samples of extremely wide size or mass range. However, if interest is focused in some narrower size or mass range, then the programs described

here would be highly suitable. They would yield the required resolution in the range of interest and provide some less detailed information outside that range for monitoring or scouting. The desired information would emerge more rapidly than with programs (such as exponential) having broader F_d curves because for these additional time is needed to generate excess F_d values. Situations where such characteristics may be desirable include process control where speed is highly important and the examination of biological samples where particular species or fragments are of interest. Not only could a pair of sample components of very similar size or mass be efficiently separated, but a program such as those discussed would be well suited to the sharp division of some polydisperse or complex sample into two fractions at some well-defined size or mass.

ACKNOWLEDGMENT

This work was supported by Grant No. GM10851-29 from the National Institutes of Health.

TABLE OF SYMBOLS

c_1	coefficient in general expression for d_m (eq 91)
c_2	coefficient in general expression for $F_d(\max)$ (eq 92)
d	particle diameter
d_m	d corresponding to the maximum in F_d curve, $F_d(\max)$
D	particle diffusion coefficient
D_m	D for particle of diameter d_m
F	force exerted on a particle by the applied field
F_d	diameter-based fractionating power
$F_d(\max)$	the maximum in F_d for a set of experimental parameters
H	theoretical plate height
k	Boltzmann constant
L	channel length
n	exponent of d in relation between λ and d (eq 13)

R	retention ratio
R_o	R at initial field strength S_o
R_r	R at point of elution
R_s	resolution
S	field strength
$S(t)$	S at time t
S_o	initial field strength
S_d	diameter-based selectivity
t	time measured from start of a run
t^o	void time
t_1	lag time before start of field decay
t_p	program time, time from start of field decay to the extrapolation to zero field strength
t_r	retention time
T	absolute temperature
$\langle v \rangle$	mean fluid velocity
w	channel thickness
x	equal to λ_o/λ_r for a particular d
z	distance along channel measured from inlet
δd	small change in particle diameter
δt_r	small difference in retention time corresponding to δd
$\Delta\rho$	particle-fluid density difference
η	fluid viscosity
λ	retention parameter
λ_o	retention parameter at initial field strength S_o
$\lambda_{o,m}$	λ_o for the particle diameter giving rise to $F_d(max)$
λ_r	λ at the point of elution
Λ	constant given by eq 14
σ_t	standard deviation in retention time
ϕ	field-particle interaction parameter
χ	nonequilibrium coefficient in plate height equation (eq 6)

REFERENCES

1. Giddings, J.C., Field-Flow Fractionation, Sep. Sci. Technol., 19, 831, 1984.

2. Yang, F.J.F., Myers, M.N., and Giddings, J.C., Programmed Sedimentation Field-Flow Fractionation, Anal. Chem., 46, 1924, 1974.

3. Giddings, J.C., Smith, L.K., and Myers, M.N., Programmed Thermal Field-Flow Fractionation, Anal. Chem., 48, 1587, 1976.

4. Giddings, J.C., Caldwell, K.D., Moellmer, J.F., Dickinson, T.H., Myers, M.N., and Martin, M., Flow Programmed Field-Flow Fractionation, Anal. Chem. 51, 30, 1979.

5. Giddings, J.C., and Caldwell, K.D., Field-Flow Fractionation: Choices in Programmed and Nonprogrammed Operation, Anal. Chem., 56, 2093, 1984.

6. Wahlund, K.-G., Winegarner, H.S., Caldwell, K.D., and Giddings, J.C., Improved Flow Field-Flow Fractionation System Applied to Water-Soluble Polymers: Programming, Outlet Stream Splitting, and Flow Optimization, Anal. Chem., 58, 573, 1986.

7. Yau, W.W., and Kirkland, J.J., Retention Characteristics of Time-Delayed Exponential Field-Programmed Sedimentation Field Flow Fractionation, Sep. Sci. Technol., 16, 577, 1981.

8. Kirkland, J.J., Rementer, S.W., Yau, W.W., Time-Delayed Exponential Field-Programmed Sedimentation Field Flow Fractionation for Particle-Size-Distribution Analyses, Anal. Chem., 53, 1730, 1981.

9. Kirkland, J.J., Yau, W.W., Sedimentation Field Flow Fractionation, Science, 218, 121, 1982.

10. Giddings, J.C., Williams, P.S., and Beckett, R., Fractionating Power in Programmed Field-Flow Fractionation: Exponential Sedimentation Field Decay, Anal. Chem., in press.

11. Giddings, J.C., Yoon, Y.H., Caldwell, K.D., Myers, M.N., and Hovingh, M.E., Nonequilibrium Plate Height for Field-Flow Fractionation in Ideal Parallel Plate Columns, Sep. Sci., 10, 447, 1975.

12. Giddings, J.C., Myers, M.N., Caldwell, K.D., and Fisher, S.R., in Methods of Biochemical Analysis, Vol. 26, Glick, D., Ed., Wiley, New York, 1980, p. 79.

13. Yau, W.W., Kirkland, J.J., Nonequilibrium Effects in Sedimentation Field Flow Fractionation, Anal. Chem., 56, 1461, 1984.

14. Giddings, J.C., Simplified Nonequilibrium Theory of Secondary Relaxation Effects in Programmed Field-Flow Fractionation, Anal. Chem., 58, 735, 1986.