Centrifugal sedimentation methods of particle size determination

8.1 Introduction

Gravitational sedimentation particle size measurement techniques are of limited value for particles smaller than about a micron due to the long settling times required. In addition, gravitational sedimentation devices generate inaccurate data due to the effect of convection, thermal diffusion and Brownian motion. Centrifuging the suspension in order to speed up the settling process reduces these errors. As with gravitational sedimentation, various options are available (Table 8.1). These may be categorized as:

- variable time (t varies, all other parameters remain constant);
- variable measurement radius (r varies, all other parameters remain constant);
- variable surface radius (S varies, all other parameters remain constant);
- combinations of these variables e.g. variable time and height {t and (r/S) vary, all other parameters remain constant}.

Centrifugal techniques may be classified as incremental or cumulative, homogeneous or line-start. Incremental, line-start techniques are restricted to photocentrifuges and the attenuation has to be corrected for the breakdown in the laws of geometric optics unless the data are being used solely for comparison purposes. This correction can be considerable for powders having a wide size range, for example a 0.10 \( \mu m \) particle may cut off less than a tenth of the light that one would expect from its geometric size whereas a 1 \( \mu m \) particle may cut off more than one would expect.
Table 8.1 Commercial sedimentation particle size analyzers

<table>
<thead>
<tr>
<th>Homogeneous, incremental centrifugal sedimentation</th>
<th>Homogeneous, cumulative centrifugal sedimentation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Simcar centrifuge</td>
<td>Alpine centrifuge</td>
</tr>
<tr>
<td>Ladal pipette centrifuge</td>
<td>Hosokawa Mikropul</td>
</tr>
<tr>
<td>Ladal x-ray centrifuge</td>
<td>Sedimentputer</td>
</tr>
<tr>
<td>Brookhaven scanning x-ray centrifuge</td>
<td></td>
</tr>
<tr>
<td>Brookhaven BI-DCP, disc photocentrifuge</td>
<td></td>
</tr>
<tr>
<td>Kaye disc photocentrifuge</td>
<td></td>
</tr>
<tr>
<td>Coulter photofuge</td>
<td></td>
</tr>
<tr>
<td>Technnord photocentrifuge</td>
<td></td>
</tr>
<tr>
<td>Horiba cuvette photocentrifuges</td>
<td></td>
</tr>
<tr>
<td>LUM Lumifuge 114</td>
<td></td>
</tr>
<tr>
<td>Seishin cuvette photocentrifuge</td>
<td></td>
</tr>
<tr>
<td>Shimadzu cuvette photocentrifuge</td>
<td></td>
</tr>
</tbody>
</table>

A further problem arises, due to the presence of a range of particle sizes in the light beam at any one time, so that, even excluding extinction coefficient problems, the response may not be proportional to the projected area of the particles.

In homogeneous, incremental, centrifugal techniques, (Figure 8.1) matters are also more complex than for homogeneous, incremental, gravitational sedimentation. The particles move in radial paths, hence the number of particles smaller than Stokes diameter entering the measurement zone is less than the number leaving, so that the measured concentration of these particles is smaller than their original concentration.

In this presentation, some of the methods for centrifugal sedimentation particle size analysis in current use are described. Although operating procedures are not covered here, it is stressed that two factors, more than anything else, lead to incorrect analyses. The first is incorrect sampling, since analyses are carried out on from a tenth of a gram up to a few grams and these samples must be representative of the bulk for the analyses to be meaningful. The second is dispersion; it has been said rightly that the most important factor in obtaining accurate sedimentation data is dispersion – the second most important factor is dispersion and the third is also dispersion!
8.2 Stokes' equation for centrifugal sedimentation

8.2.1 General theory

A particle settling in a centrifugal field is acted upon by a drag force and a centrifugal force. The force balance in the laminar flow region is given by:

$$ \frac{\pi}{6} \left( \rho_s - \rho_f \right) d_v^3 \frac{d^2r}{dt^2} = \frac{\pi}{6} \left( \rho_s - \rho_f \right) d_v^3 \omega^2 r - 3\pi d_d \eta \frac{dr}{dt} $$

where:

- \( r \) = radial distance from the axis of the centrifuge to the particle;
- \( dr/dt \) = outward velocity of the particle;
- \( \rho_s, \rho_f \) = density of the particle and suspension medium respectively;
- \( \eta \) = coefficient of viscosity of the medium;
- \( d_v \) = volume diameter of the particle;
- \( d_d \) = drag diameter of the particle;
- \( \omega \) = speed of rotation of the centrifuge in rad.s\(^{-1}\).

At the terminal velocity, the outward radial acceleration, \( d^2r/dt^2 = 0 \) so that this equation becomes:

$$ 3\pi d_d \eta \frac{dr}{dt} = \frac{\pi}{6} \left( \rho_s - \rho_f \right) d_v^3 \omega^2 r $$
Centrifugal sedimentation methods 395

\[
\frac{dr}{dt} = u_c = \frac{(\rho_s - \rho_f) d_{St}^2 \omega^2 r}{18 \eta}
\]  

(8.2)

Thus, the settling velocity is not constant as in gravitational sedimentation but increases with increasing radius. Comparing with Stokes equation for gravitational settling (settling velocity under gravity = \( u_{St} \)):

\[
u_c = \frac{\omega^2 r}{g} u_{St} = Gu_{St}
\]  

(8.3)

\( G \), the separation factor, is a measure of the increased rate of settling in a centrifugal field. Rewriting equation (8.2) in integral form:

\[
\int_{r=S}^{r} \frac{dr}{r} = \frac{(\rho_s - \rho_f) d_{St}^2 \omega^2}{18 \eta} \int_{0}^{t} dt
\]

\[
\ln \frac{r}{S} = \frac{(\rho_s - \rho_f) d_{St}^2 \omega^2 t}{18 \eta}
\]

\[
d_{St} = \sqrt{\frac{18 \eta \ln (r/S)}{(\rho_s - \rho_f) \omega^2 t}}
\]  

(8.4)

\( t \) is the time for a particle of Stokes diameter \( d_{St} \) to settle from the surface of the fill liquid at radius \( S \) to measurement radius \( r \) which, for cumulative techniques, is equal to \( R \), the distance from the axis to the inside radius of the centrifuge.

8.3 Homogeneous, incremental, centrifugal sedimentation

8.3.1 General theory

The largest particle, of Stokes diameter \( d_{St} \), present in the measurement zone at time \( t \) and radius \( r \) will have originated from the surface at radius \( S \).
From equation (8.4) the following relationship holds:

\[ \frac{r}{S} = \exp \left( \frac{(\rho_s - \rho_f) d_{Si}^2 \omega^2 t}{18\eta} \right) \]  

(8.5)

\[ \frac{r}{S} = \exp \left( kd_{Si}^2 t \right) \]

where

\[ k = \frac{(\rho_s - \rho_f) \omega^2}{18\eta} \]

Particles in the measurement zone of size \( d_i \) will have originated from radius \( r_i \) where \( r > r_i > S \) and:

\[ \frac{r}{r_i} = \exp \left( kd_i^2 t \right) \]  

(8.6)

The particles originally at radius \( r_i \), in an annular element of thickness \( \Delta r \), move in diverging (radial) paths and at radius \( r \) occupy an annular element of thickness \( \Delta r \). There will be a fall in the concentration of particles of this size in the measurement zone therefore, since the same number of particles will occupy a greater volume. The fractional increase in volume is given by:

\[ \frac{r\Delta r}{r_i\Delta r_i} = \left( \frac{r}{r_i} \right)^2 \]  

(8.7)

since, from equation (8.6), \( \Delta r/\Delta r_i = r/r_i \).

For a polydisperse system, with a weight fraction of \( f(d)dd \) in the size range \( d \) to \( d + dd \), the fractional concentration \( dQ \) of this weight fraction at \( r \) is given by:

\[ dQ = \left( \frac{r_i}{r} \right)^2 f(d)dd \]
Hence, the mass undersize \( d_{Sl} \) is:

\[
Q(d_{Sl}) = \int_{d=0}^{d_{Sl}} \left( \frac{r}{r} \right)^2 f(d) \, dd
\]

(8.8)

Combining with equation (8.6) gives:

\[
Q(d_{Sl}) = \int_{d_i=0}^{d_{Sl}} \exp \left( -2k d_i^2 t \right) f(d) \, dd
\]

(8.9)

Substituting for \( k \) from equation (8.5):

\[
Q(d_{Sl}) = \int_{d_i=0}^{d_{Sl}} \exp \left[ -2 \left( \frac{d_i}{d_{Sl}} \right)^2 \ln \left( \frac{r}{S} \right) \right] f(d) \, dd
\]

(8.10)

Various solutions to these equations have been proposed:

- In the variable time method the concentration is measured as a function of \( t' = \omega^2 t \) and all other variables are kept constant.
- In the variable height method the concentration is measured as a function of \( (r/S) \) and all other variables are kept constant.
- For scanning systems (variable time and height) both \( \omega^2 t \) and \( r \) vary and in pipette withdrawal systems \( \omega^2 t \) and \( S \) vary.

### 8.4 Variable time method (\( r \) and \( S \) constant, \( t \) variable)

#### 8.4.1 General theory

Differentiation of equation (8.9) gives:

\[
\frac{dQ}{dd} = \exp \left( -2k d^2 t \right) f(d)
\]

(8.11)

where \( f(d) = \frac{dF(d)}{dd} \).
The boundary conditions are that $Q = 1$ when $i = 0$ for all $r_i$, i.e. initially the concentration is the same throughout the suspension: $Q = 0$ when $r = S$ for $t > 0$, i.e. the surface concentration falls to zero on start-up; with the additional condition that $F(d) = 0$ when $d = 0$. Thus:

$$F(d_s) = \int_{0}^{Q_s} \exp\left(2kd^2t\right)dQ$$

$$F(d_s) = \int_{0}^{Q_s} \left(\frac{r_s}{S}\right)^2 dQ$$

(8.12)

d$_s$ is the diameter of the particle that settles from the surface, radius S, to the measurement radius $r$ in time $t$. The expression was first developed by Berg [1] and later by Kamack [2]. Berg solved equation (8.12) graphically by plotting $(r/S)^2$ against $Q$ and determining the area under the curve, deriving the following formulae:

$$\int_{d=0}^{d_s} F(d)dd = c_x + \frac{y}{4a} 5c_x - 4F\left(\frac{d}{2}\right) \text{ for } x < \frac{a}{5}$$

(8.13)

$$\int_{d=0}^{d_s} F(d)dd = c_x \left(1 + \frac{2x}{3S}\right) \text{ for } c_x < 0.15$$

(8.14)

where $r = S + x$ and $c_x$ is the concentration at radius $x$ at the time required for a particle of diameter $d_m$ to fall from the surface to measurement radius $x$. These equations are applicable for powders having a wide size range, losing accuracy for monodisperse powders where volume concentration changes rapidly with changing $r$. Equation (8.13) is used for the calculation of the smallest $F(d)$, that is the smallest $c_x$, and equation (8.14) for higher values of $F(d)$. $F(d) = 0$ when $d = 0$, hence $F(d/2)$ may be estimated by joining $F(d)$ to 0 for a small value of $d$ since most functions are linear towards the origin. The $F(d)$ curve is then built up step-by-step. Berg determined concentration using pipette withdrawal or small divers.
Kamack offered the following solution to equation (8.12). If $Q$ is plotted as a function of $y_i = \left(\frac{r_i}{S}\right)^2$ with $t' = \omega^2 t$ as parameter, a family of curves is obtained whose shape depends on the particle size distribution function. The boundary conditions are that $Q = 1$ when $t' = 0$ for all $r_i$ (i.e. the suspension is initially homogeneous) and $Q = 0$ for $r_i = S$ when $t' > 0$ (i.e. the surface region is particle free as soon as the centrifuge bowl spins). Hence all the curves, except for $t' > 0$, pass through the point $Q = 0$, $r_i = S$, and they will all be asymptotic to the line $t' = 0$, which has the equation $Q = 1$. Furthermore, from equation (8.12), the areas under the curves are each equal to $F(d_{Sl})$.

Let $Q_1$ be the smallest experimentally determined concentration so that $t_1 > t_2 > t_r$ and let $Q$ be determined at a fixed sampling distance $r$ for various values of $t$. Then one point is known on each curve in addition to the common point $y = 1$, $Q = 0$. Such a set of points is illustrated by the black circles in Figure 8.2. To each point corresponds a known value of $d_{Sl}$ obtained from equation (8.4). Further, the area included between each curve, the concentration axis and the ordinates $Q = 0$ and $Q_{Sl}$ is equal to $F(d_{Sl})$. Thus $F(d_{Sl})$ is approximated by the trapezoidal rule for, first of all,

![Figure 8.2](image-url)
400 Powder sampling and particle size determination

$F_1 = 0.5(1 + y)Q_1$. Now considering the curve for $l_2$, a point can be found on it corresponding to $d_1$, i.e. a point such that the area under the curve up to this point is $F_1$, which is now known.

If the ordinate at this point is called $y_{1,2}$ and the abscissa $F_{1,2}$ then, by equation (8.4):

$$d_1 = \sqrt{\frac{9\eta \ln y_{1,2}}{(\rho_s - \rho_f)\omega^2 t_2}}$$
$$d_2 = \sqrt{\frac{9\eta \ln y}{(\rho_s - \rho_f)\omega^2 t_2}}$$

so that $y_{1,2} = y^{(d_1/d_2)^2}$ where $y = (r/S)^2$

Equating areas:

$$(1 + y)Q_1 = (1 + y_{1,2})Q_{1,2} = 2F_1$$

so both $y_{1,2}$ and $Q_{1,2}$ are known.

Applying the trapezoidal rule:

$$F_2 - F_1 = \frac{1}{2} \left( y + y_{1,2} \right) \left( Q_2 - Q_{1,2} \right)$$

Substituting for $Q_{1,2}$ from equation (8.16):

$$F_2 = \frac{1}{2} \left( y + y_{1,2} \right) Q_2 + \left[ 1 - \frac{y + y_{1,2}}{1 + y_{1,2}} \right] F_1$$

Proceeding in a like manner gives the general formulae:

$$F_n - F_{n-1} = \frac{1}{2} \left( y + y_{n-1,n} \right) \left( Q_n - Q_{n-1,n} \right)$$

and so on. By considering this series of equations with successive elimination of the $Q$ functions, there is obtained a general equation in recursive form:
where \( y'_{j,i} = y \left( \frac{d_j}{d_i} \right)^2 \) 

\[
d_n = \sqrt{\frac{9\eta l n y}{(\rho_s - \rho_f) y_n}}
\]

\( i = 1, 2, 3, \ldots, m; \ y_{0,1} = 1 \)

Equations (8.21) are a set of linear equations which express the desired values of \( F_i \) explicitly in terms of the measured values of \( Q_i \). The coefficients of the equations depend upon the values of \( d_i \) (corresponding to the value of \( t_i' \) ) at which the concentrations are measured; more exactly, the coefficients depend on the ratios of the values of \( d_i \) as shown in equation (8.22). Consequently, if the values of \( d_i \) are chosen in a geometric sequence when carrying out a particle size analyses, the coefficients are considerably easier to calculate and the equations themselves are also simplified. A ratio of \( \sqrt{2} \) is recommended. The coefficients depend also on the values of \( y \) that is, the dimensions of the centrifuge bowl employed.

The modified form of equation (8.21) for experimental points in a 2:1 progression in time giving a \( \sqrt{2}:1 \) progression in diameter is:

\[
F_i = \frac{1}{2} y_B Q_i + \sum_{j=1}^{i-1} \left[ \frac{y_B}{y^2 + y^{2(1-j)}} - \frac{y_B}{y^2 + A} \right] F_j
\]

where \( A = 1 \) for \( j = 1 \), \( A = y^{\frac{1}{2}} \) for \( j \neq 1 \) and \( y_B = y + \frac{1}{2} \)

When \( i = 1 \), \( F_1 = \frac{1}{2} (1 + y) Q_1 \)
When \( i = 2 \), \( F_2 = \frac{1}{2} \left( y + y^2 \right) Q_2 + \left[ \frac{y + y^2}{y^4 + y^2} - \frac{y + y^2}{y^2 + 1} \right] F_1 \)

And so on.

In a later paper Kamack [3] replaced his earlier approximate solution with an exact solution which is equally practical to use and which has more accuracy and generality. Starting with equation (8.11) he derived the exact solution:

\[
F(d_{S_1}) = \exp \left[ -2 \ln \left( \frac{r}{S} \right) Q(d_{S_1}) \right] - \int_0^\infty h(x)Q(d_{S_1} \exp(-x))dx \tag{8.25}
\]

in which \( h(x) \) is a function which depends on the ratio \( r/S \) and \( \alpha = \ln(d/d_{S_1}) \). For full details readers should refer to the original paper.

It is preferable, when using the Kamack equation, to smooth out the experimental data. This can be done manually by plotting \( Q \) against \( d_{S_1} \) on log-probability paper or using a smoothing equation during computer data collection.

Alternative solutions to equation (8.9) are available if the shape of the distribution curve is assumed. Svarovsky and Friedova [4] assumed a fit by the 3-parameter equation of Harris [5] the parameters being found by means of a curve-fitting technique applied to the measured concentrations. This method is applicable to variable height, variable time and variable height and time. The main disadvantage of this method is that it is unsuitable for multi-modal distributions.

Svarovsky and Svarovska [6] derived an alternative version of equation (8.25) and later [7,8] developed a new data analyzer for data evaluation. Their equation was:

\[
F(T) = e^{a} \left[ C(T) - \int_T^\infty H(Z)C(\frac{Te^{-Z}}{Z})dZ \right] \tag{8.26}
\]

where \( Z = \ln(t/T) \); \( t \) is time as a variable, \( T \) is the time at which a measurement is made.

\( a = 2\ln(r/S) \)
Centrifugal sedimentation methods

\[ H(Z) = K(Z) - \int_{-\infty}^{Z} K(Z'-Z)H(Z')dZ' \]

For \( Z \geq 0 \)

\[ K(Z) = a \exp(a)(-Z - a \exp(-Z)) \]

and \( K(Z) = 0 \) for \( Z < 0 \)

Function \( H(Z) \) is a convolution integral which is readily computed digitally for different values of \( a \) and then used in equation (8.26) for evaluation.

Alex [9] suggested iteration by Neumann's series, Langarm approximations or substitution of polynomial functions for the distribution curves in order to solve the problem. Lloyd et al. [10] suggested a complicated solution involving high order differentials; they also speculated on the 'on-line' evaluation of experimental data. Truly on-line evaluation is, however, impossible and only a delayed quasi-on-line evaluation can be performed [11].

8.4.2 The Simcar pipette disc centrifuge (\( r \) constant, \( S \) assumed constant, \( t \) variable)

The Simcar centrifuge was developed by Slater and Cohen [12] to conform with Kamack's theory and was, in essence, a centrifugal version of the gravitational pipette. One problem with this instrument was the amount of suspension required so that the liquid level did not alter appreciably during an analysis (about 2.5 liter of liquid containing about 5 g of powder). The amount removed at each withdrawal was about 40 ml but variable, hence the error due to assuming a constant liquid level, \( S \), increased as more samples were withdrawn.

Since no correction was available for the fall in surface with each extraction, it was inadvisable to withdraw more than four samples in each analysis. The analysis was carried out in duplicate to give eight points on the distribution curve so that a single evaluation from about 5 \( \mu \)m to 0.2 \( \mu \)m took up to a full day.

Concentrations were determined by drying and weighing. Using the modified equation to take into account the changing liquid level and a more reproducible withdrawal volume would allow more data points to be taken in a single run.
8.4.3 Worked example

(a) Determination of F factors for a centrifuge without scanning

Centrifuge dimensions: $R = 8$ cm, $h = 0.70$ cm, $r = 7$ cm. Hence, for a fill volume of 100 cm$^3$, $S = 4.304$ cm. Applying equations (8.22) and (8.23) gives the following $y_{ij}$ values for a 2:1 progression in time:

Table 8.2 $y_{ij}$ values for a centrifuge operating under fixed radii conditions

<table>
<thead>
<tr>
<th></th>
<th>$y$</th>
<th>$y_{1,2}$</th>
<th>$y_{2,3}$</th>
<th>$y_{3,4}$</th>
<th>$y_{4,5}$</th>
<th>$y_{5,6}$</th>
<th>$y_{6,7}$</th>
<th>$y_{7,8}$</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>2.645</td>
<td>1.626</td>
<td>1.275</td>
<td>1.129</td>
<td>1.063</td>
<td>1.031</td>
<td>1.015</td>
<td>1.008</td>
</tr>
</tbody>
</table>

i.e. $y_{1,2} = y^{1/2}$, $y_{2,3} = y^{1/4}$ and so on. From these $y_{ij}$ values the following $F_i$ values are determined:

Table 8.3 $F_i$ values for a centrifuge operating under fixed radii conditions

\[
\begin{align*}
F_1 &= 1.823Q_1 \\
F_2 &= 2.136Q_2 - 0.626F_1 \\
&= 1.823Q_2 - 1.141Q_1 \\
F_3 &= 2.136Q_3 - 1.008Q_2 - 0.200Q_1 \\
F_4 &= 2.136Q_4 - 1.008Q_3 - 0.174Q_2 - 0.023Q_1 \\
F_5 &= 2.136Q_5 - 1.008Q_4 - 0.174Q_3 + 0.021Q_2 + 0.046Q_1 \\
F_6 &= 2.136Q_6 - 1.008Q_5 - 0.174Q_4 + 0.021Q_3 + 0.021Q_2 + 0.001Q_1 \\
F_i &= 2.136Q_i - 1.008Q_{i-1} - 0.174Q_{i-2} + 0.021Q_{i-3} + 0.021Q_{i-4} + \ldots \\
\end{align*}
\]

Particle size is determined using equation (8.23) and measured concentration is converted to mass undersize using equation (8.21). The results are presented in Table (8.4).

Material: quartz $\rho_s = 2650$ kg m$^{-3}$ $\rho_f = 1000$ kg m$^{-3}$

$N = 1500$ rpm ($\omega = 50\pi$ rad s$^{-1}$) $\eta = 0.001$ Pa s

\[
\bar{d}_i = \left[ \frac{9 \times 0.001 \times \ln\left( \frac{7}{4.304} \right)^2}{(2650 - 1000) \times (50\pi)^2 t_i} \right] d_i = 1.893 / \sqrt{T_i}
\]
Table 8.4 Mass percentage undersize determination for homogeneous, incremental centrifuge technique (variable time method)

<table>
<thead>
<tr>
<th>$i$</th>
<th>Time ($T$) (min)</th>
<th>Size ($d_{sl}$) ($\mu$m)</th>
<th>Measured (% conc. ($Q$))</th>
<th>Mass % undersize ($F$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>256</td>
<td>0.118</td>
<td>256</td>
<td>6.9</td>
</tr>
<tr>
<td>2</td>
<td>128</td>
<td>0.167</td>
<td>128</td>
<td>18.7</td>
</tr>
<tr>
<td>3</td>
<td>64</td>
<td>0.237</td>
<td>64</td>
<td>34.5</td>
</tr>
<tr>
<td>4</td>
<td>32</td>
<td>0.335</td>
<td>32</td>
<td>65.5</td>
</tr>
<tr>
<td>5</td>
<td>16</td>
<td>0.473</td>
<td>16</td>
<td>88.4</td>
</tr>
<tr>
<td>6</td>
<td>8</td>
<td>0.669</td>
<td>78.2</td>
<td>97.3</td>
</tr>
<tr>
<td>7</td>
<td>4</td>
<td>0.947</td>
<td>87.9</td>
<td>99.4</td>
</tr>
<tr>
<td>8</td>
<td>2</td>
<td>1.339</td>
<td>93.6</td>
<td>100.0</td>
</tr>
<tr>
<td>9</td>
<td>1</td>
<td>1.893</td>
<td>96.7</td>
<td>100.0</td>
</tr>
</tbody>
</table>

Table 8.5 $Q_{ij}$ values for homogeneous, incremental centrifuge technique (variable time method) with measurement times in a 2:1 progression

| $Q_{1,2}$ | 5.3 |
| $Q_{1,3}$ | 6.1 |
| $Q_{1,4}$ | 6.5 |
| $Q_{1,5}$ | 6.7 |
| $Q_{1,6}$ | 6.8 |
| $Q_{1,7}$ | 6.9 |
| $Q_{1,8}$ | 6.9 |
| $Q_{1,9}$ | 6.9 |
| $Q_{1,10}$ | 6.9 |
| $Q_{1}$ | 3.8 |
| $F_{1}$ | 6.9 |
| $Q_{6,7}$ | 86.9 |
| $Q_{6,8}$ | 91.8 |
| $Q_{6,9}$ | 94.4 |
| $Q_{6,10}$ | 95.9 |
| $Q_{6}$ | 78.2 |
| $F_{6}$ | 97.3 |
| $Q_{2,3}$ | 14.2 |
| $Q_{2,4}$ | 16.3 |
| $Q_{2,5}$ | 17.5 |
| $Q_{2,6}$ | 18.1 |
| $Q_{2,7}$ | 18.4 |
| $Q_{2,8}$ | 18.6 |
| $Q_{2,9}$ | 18.7 |
| $Q_{2,10}$ | 18.7 |
| $Q_{3,4}$ | 27.2 |
| $Q_{3,5}$ | 30.6 |
| $Q_{3,6}$ | 32.4 |
| $Q_{3,7}$ | 33.5 |
| $Q_{3,8}$ | 34.0 |
| $Q_{3,9}$ | 34.1 |
| $Q_{3,10}$ | 34.4 |
| $Q_{4,5}$ | 51.9 |
| $Q_{4,6}$ | 58.2 |
| $Q_{4,7}$ | 61.8 |
| $Q_{4,8}$ | 63.6 |
| $Q_{4,9}$ | 64.5 |
| $Q_{4,10}$ | 65.0 |
| $Q_{5,6}$ | 74.2 |
| $Q_{5,7}$ | 80.9 |
| $Q_{5,8}$ | 84.7 |
| $Q_{5,9}$ | 86.6 |
| $Q_{5,10}$ | 87.6 |
| $Q_{6}$ | 87.9 |
| $F_{6}$ | 99.4 |
8.4.4 The Ladal x-ray disc centrifuge (r constant, S constant, t variable)

This is an extension of the Allen and Svarovsky [13] x-ray gravitational sedimentometer. The x-rays are generated by an isotope source and, after passing through the suspension, they are detected by a scintillation counter. The signal from the counter passes to a pre-amplifier, and thence to a ratemeter, and a trace is recorded by a pen recorder.

The attenuation of the x-ray beam is proportional to the mass concentration at the measurement radius that has to be converted to the size distribution using the Kamack equation. A size range of about 8:1 is covered in about an hour.

8.4.5 Discussion of the Kamack equation

The Kamack treatment builds up the concentration gradients within the centrifuge for each of the measurement times. The $Q_{ij}$ values (Table 8.5) may be determined using equation 8.19 and, in combination with the $y_{ij}$ values, generate the concentration gradients.

In Figure 8.2 the black circles are the measured concentrations at a fixed measurement and surface radius and the white circles give the calculated concentration gradient for $i = 7$.

In essence we are building up the concentration gradient between the measurement radius and the surface for each measurement time. For example, at $i = 2$ the concentration at the measurement radius is 3.8% and, from the first measurement we deduce that the concentration at a radius $y$, $Q_{1,2}$, is 5.3%. In figure (8.2) the concentration gradient for $i = 7$ is displayed as an example.

8.5 Variable time and height method (S constant, both r and t vary)

8.5.1 Stokes diameter determination.

The approximation due to Kamack can be modified, for the scanning mode of operation, by replacing the constant $(r/S)$ with the variable $(r_i/S)$ where $r_i$ is the position of the source and detector at time $t$ i.e. equation (8.4) becomes:
\[ d_{St,i} = \sqrt{\frac{9\eta \ln y_i}{\sqrt{(\rho_s - \rho_f)}}} \omega^2 t_i \]  

(8.27)

where \( y_i = (r_i/S)^2 \) and \( d_{St,i} \) is the largest particle present at the measurement radius \( r_i \) at time \( t \).

8.5.2 Mass frequency undersize determination.

Equation (8.12) becomes:

\[ F(d_{St}) = \int_0^Q \exp(2kd^2t) dQ \]

i.e.,

\[ F_i(d_{St}) = \int_0^Q \left( \frac{r_i}{S} \right)^2 dQ \]  

(8.28)

modifying equation (8.21) to:

\[ F_i = \frac{1}{2} \left( y_i + y_{i-1,i} \right) Q_i + \sum_{j=1}^{i-1} \left( \frac{y_i + y_{i-1,i}}{y_{j+1,i} + y_{j,i}} - \frac{y_i + y_{i-1,i}}{y_{j,i} + y_{j-1,i}} \right) F_j \]

where \( y_i = \left( \frac{r_i}{S_i} \right)^2 \) and \( y_{j,i} = \left( \frac{d_{j,i}}{d_i} \right)^2 \)

\[ i = 1, 2, 3, ..., m; \quad y_{0,i} = 1 \]  

(8.29)

8.5.3 DuPont/Brookhaven scanning x-ray disc centrifugal sedimentometer (Bl-XDC) (S constant, r variable, t variable)

This instrument was developed as a centrifugal version of the Allen and Svarovsky’s [13] x-ray gravitational sedimentometer in order to reduce the analysis time and measure down to smaller sizes [14,15]. The x-rays are generated by an air cooled low power x-ray tube and, after passing through the suspension, they are detected by a scintillation counter. The signal is
then processed to generate the size distribution. The attenuation is proportional to the mass concentration at the measurement radius, which has to be converted to the size distribution using the Kamack equation. A size range of about 8:1 is covered in about an hour.

This instrument was designed [16] to fill a need for fast, reproducible sedimentation analyses in the sub-micron size range. The heart of the instrument is a hollow, x-ray transparent, disc which, under normal operating conditions, contains 20 ml of suspension at a concentration of around 0.2% by volume. The centrifuge speed is selectable in the range 750 to 6000 rpm. The default condition is for the source and detector to remain stationary for 1 minute at a radial position of 48.00 mm and then to scan towards the surface. Total run time is normally 8 min.

A commercial version is available from Brookhaven as the BI-XDC (Figure 8.17). The instrument can operate in the gravitational or centrifugal mode and the analyses can be blended to cover a total size range of 0.05 \( \mu \text{m} \) to over 100 \( \mu \text{m} \). A size range of 15:1 is covered in a standard 8 min analysis. Weiner et. al. [17] describe its application to accelerated size analyses down to 10 nm.

A computer controlled particle size measurement device with very high resolution was presented by Foerderreuther [18] based on the Brookhaven optical and x-ray disc centrifuges.

8.5.4 Worked example

(a) Determination of \( F \) factors for a centrifuge with scanning

Hyperbolic scan - The analyzer is scanning upwards, at a varying rate, from an initial radius of 7 cm to just below the surface at \( S = 4.304 \text{ cm} \) so that the following relationship holds:

\[
0.24
\]

\begin{align*}
18.7
\end{align*}

\( t \) in seconds, \( r_j \) in \( \mu \text{m} \).

The hyperbolic scan gives similar resolution at all sizes hence is preferable for centrifugal particle size analysis.

\[
S = 4.304 \text{ cm} \quad \rho_s = 2650 \text{ kg m}^{-3}
\]
\[
\eta = 0.001 \text{ Pa s} \quad \rho_f = 1000 \text{ kg m}^{-3} \quad N = 1500 \text{ rpm} (\omega = 50\pi \text{ rad s}^{-1})
\]
From equation (8.15)
\[ y = \left(\frac{7}{4.304}\right)^2 = 2.645 \]

From equation (8.27):
\[ d_{St,i} = \sqrt{\frac{18 \times 0.001 \times \ln(r_i/4.304)}{4130 \times (50\pi)^2 \times t_i}} \]

where \( y_i = (r_i/S)^2 \)

Applying equation (8.29):
\[
\begin{align*}
F_1 &= 1.020Q_1 \\
F_2 &= 1.065Q_2 - 0.059F_1 \\
F_3 &= 1.138Q_3 - 0.105F_2 - 0.030F_1 \\
F_4 &= 1.235Q_4 - 0.155F_3 - 0.061F_2 - 0.017F_1 \\
F_5 &= 1.367Q_5 - 0.227F_4 - 0.094F_3 - 0.035F_2 - 0.010F_1 \\
F_6 &= 1.563Q_6 - 0.356F_5 - 0.132F_4 - 0.051F_3 - 0.0109F_2 - 0.005F_1 \\
F_7 &= 1.940Q_7 - 0.683F_6 - 0.169F_5 - 0.057F_4 - 0.021F_3 - 0.008F_2 - 0.002F_1 \\
\end{align*}
\]

Thus the \( F \) values as given in Table (8.6) and the \( y_i \) values given in Table (8.7) can be determined.

**Table 8.6 Centrifuge particle size analysis, homogeneous mode with scanning**

<table>
<thead>
<tr>
<th>(i)</th>
<th>Time ( T ) (secs.)</th>
<th>Radius ( r_i ) (( \mu )m)</th>
<th>Stokes diameter ( d_{st,i} ) (( \mu )m)</th>
<th>Measured concentration ( Q_i ) (%)</th>
<th>Percentage undersize ( F_i ) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>7</td>
<td>60</td>
<td>7</td>
<td>1.893</td>
<td>95.6</td>
<td>99.9</td>
</tr>
<tr>
<td>6</td>
<td>120</td>
<td>5.927</td>
<td>1.086</td>
<td>88.6</td>
<td>97.2</td>
</tr>
<tr>
<td>5</td>
<td>180</td>
<td>5.377</td>
<td>0.740</td>
<td>75.7</td>
<td>87.0</td>
</tr>
<tr>
<td>4</td>
<td>240</td>
<td>5.019</td>
<td>0.532</td>
<td>55.8</td>
<td>62.6</td>
</tr>
<tr>
<td>3</td>
<td>300</td>
<td>4.757</td>
<td>0.384</td>
<td>32.5</td>
<td>35.7</td>
</tr>
<tr>
<td>2</td>
<td>360</td>
<td>4.553</td>
<td>0.263</td>
<td>11.5</td>
<td>12.2</td>
</tr>
<tr>
<td>1</td>
<td>420</td>
<td>4.388</td>
<td>0.143</td>
<td>0.9</td>
<td>0.92</td>
</tr>
</tbody>
</table>
Applying equation (8.28) to the \( y_i \) values given in Table 8.5, the following \( y_{ij} \) values are determined:

Table 8.7 \( y_{ij} \) for centrifuge particle size analysis, homogeneous mode with scanning

<table>
<thead>
<tr>
<th>( y_1 )</th>
<th>( y_2 )</th>
<th>( y_3 )</th>
<th>( y_4 )</th>
<th>( y_5 )</th>
<th>( y_6 )</th>
<th>( y_7 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.038</td>
<td>1.119</td>
<td>1.222</td>
<td>1.360</td>
<td>1.561</td>
<td>1.896</td>
<td></td>
</tr>
<tr>
<td>( y_{1.2} )</td>
<td>1.011</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( y_{1.3} )</td>
<td>1.005</td>
<td>( y_{2.3} )</td>
<td>1.054</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>( y_{1.4} )</td>
<td>1.003</td>
<td>( y_{2.4} )</td>
<td>1.028</td>
<td>( y_{3.4} )</td>
<td>1.110</td>
<td></td>
</tr>
<tr>
<td>( y_{1.5} )</td>
<td>1.001</td>
<td>( y_{2.5} )</td>
<td>1.014</td>
<td>( y_{3.5} )</td>
<td>1.055</td>
<td>( y_{4.5} )</td>
</tr>
<tr>
<td>( y_{1.6} )</td>
<td>1.001</td>
<td>( y_{2.6} )</td>
<td>1.007</td>
<td>( y_{3.6} )</td>
<td>1.025</td>
<td>( y_{4.6} )</td>
</tr>
<tr>
<td>( y_{1.7} )</td>
<td>1.000</td>
<td>( y_{2.7} )</td>
<td>1.002</td>
<td>( y_{3.7} )</td>
<td>1.008</td>
<td>( y_{4.7} )</td>
</tr>
</tbody>
</table>

8.6. Variable inner radius (Both \( S \) and \( t \) vary, \( r \) remains constant)

8.6.1 Stokes diameter determination

Let the time of the first withdrawal be \( t_1 \); the largest particle present in the withdrawn sample at this time will have fallen from the surface at radius \( S \) to the measurement zone at radius \( r \). Equation (8.6) will apply and may be written:

\[
d_i^2 t_1 = k \ln \frac{r}{S}
\]

(8.30)

The liquid level will then fall to \( S_1 \) where:

\[
S_1^2 - S^2 = \frac{v}{\pi h}
\]

(8.31)

where \( v \) is the volume extracted (10 cm\(^3\)) and \( h \) is the thickness of the centrifuge bowl (1.02 cm). The fall in the inner radius can therefore be determined:

\[
\Delta S = S_1 - S
\]

(8.32)
Let the time for the second withdrawal be $t_2$; the largest particle present in the withdrawn sample will have fallen from $x_{1,2}$ to $x_{1,2}'$ in time $t_1$, a distance $\Delta x_{1,2}$ due to the withdrawal of the first sample and from $x_{1,2} + \Delta x_{1,2}$ to $r$ in a time $t_2 - t_1$.

Hence:

$$d_2^2 t_1 = k \ln \frac{x_{1,2}}{S} \quad (8.33)$$

$$d_2^2 (t_2 - t_1) = k \ln \frac{r}{x_{1,2} + \Delta x_{1,2}} \quad (8.34)$$

Adding equations (8.33) and (8.34) gives:

$$d_2^2 t_2 = k \ln \frac{r}{S \left(1 + \frac{\Delta x_{1,2}}{x_{1,2}}\right)^{-1}} \quad (8.35)$$

For the third withdrawal; in time $t_1$ particles of size $d_3$ will fall from the surface at radius $S$ to $x_{1,3}$, hence:

$$d_3^2 t_1 = k \ln \frac{x_{1,3}}{S} \quad (8.36)$$

These particles will then fall a distance $\Delta x_{1,3}$ due to the withdrawal of the first sample where, from equation (8.31):

$$\left(x_{1,3} - \Delta x_{1,3}\right)^2 - x_{1,3}^2 = 3.1207 \quad (8.37)$$

In the next time increment, particles of size $d_3$ will fall from radius $x_{1,3} + \Delta x_{1,3}$ to radius $x_{2,3}$ hence:

$$d_3^2 (t_2 - t_1) = k \ln \frac{x_{2,3}}{x_{2,3} + \Delta x_{2,3}} \quad (8.38)$$
These particles will then fall a distance $\Delta x_{2,3}$ due to the withdrawal of the second sample where:

$$\left( x_{2,3} - \Delta x_{2,3} \right)^2 - x_{2,3}^2 = 3.1207 \quad (8.39)$$

and

$$d_3^2 (t_3 - t_1) = k \ln \frac{r}{x_{2,3} + \Delta x_{2,3}} \quad (8.40)$$

Adding equations (8.36), (8.38) and (8.40) gives:

$$d_3^2 t_3 = k \ln \frac{r}{S} \left[ \left( 1 + \frac{\Delta x_{1,3}}{x_{1,3}} \right)^{-1} \left( 1 + \frac{\Delta x_{2,3}}{x_{2,3}} \right)^{-1} \right] \quad (8.41)$$

The bracketed terms are the correction terms for the fall in level due to each extraction. Repeating this gives, for the $n$th withdrawal:

$$d_n^2 t_n = k \ln \frac{r}{S} \left[ \left( 1 + \frac{\Delta x_{1,n}}{x_{1,n}} \right)^{-1} \left( 1 + \frac{\Delta x_{2,n}}{x_{2,n}} \right)^{-1} \cdots \left( 1 + \frac{\Delta x_{n-1,n}}{x_{n-1,n}} \right)^{-1} \right] \quad (8.42)$$

This differs from the variable time equation in that the Stokes diameter reduces more rapidly thus, effectively, making this technique into a scanning technique.

**8.6.2 Ladal pipette disc centrifuge**

The Ladal pipette centrifuge was developed as a centrifugal version of the Andreasen gravitational pipette [11]. This pipette centrifuge (Figure 8.3) was designed by Allen and Svarovsky [19] to operate with a reduced volume of suspension (150 ml), as compared to the Simcar. The modified Kamack equation, given above, was derived to correct for the changing surface radius as samples were extracted. One of the consequences of this fall in surface radius with time, is a reduction in the measurement time down to about an hour. At 500 rpm the measured size range for quartz is
approximately 8 μm to 0.8 μm in 1 h and these sizes are halved if the speed is doubled.

8.6.3 Worked example

(a) Determination of ratio of Stokes diameters for constant r, variable S and t.

Using a feed volume of 150 cm$^3$ gives $S = 4.146$ cm; hence equation (8.33) becomes:

$$d_h = \frac{t}{\ln(7/4.146)}$$

letting $(k/t_1)$ be equal to 1.91 makes $d_1 = \text{unity}$.

Second extraction, for withdrawals in a 2:1 progression in time, $(t_2=2t_1)$

Equation (8.33) gives:  

$$d_2^2 = 1.91\ln(x_{12}/4.146)$$

Fig. 8.3 Line diagram of the Ladal pipette centrifuge.
Equation (8.34) gives: \[ d_2^2 = 1.91 \ln\left[\frac{7}{(x_{12} + \Delta x_{12})}\right] \]

Hence \[ x_{1,2}^2 + x_{1,2}\Delta x_{1,2} = 29.022 \]

and from equation (8.31): \[ (x_{1,2} + \Delta x_{1,2})^2 - x_{1,2}^2 = 3.1207 \]

Solving simultaneously gives \[ x_{1,2} = 5.244 \] and \[ \Delta x_{1,2} = 0.2896 \]; hence \[ d_2 = 0.670 \]. Assuming that this progression in sizes continues then \[ d_3 = 0.670^2 - 0.449 \]. Substituting this value in equation (8.36) gives:

\[ x_{1,3} = 4.146 \exp\left(\frac{0.449^2}{1.91}\right) \]
\[ x_{1,3} = 4.608 \]

Substituting in equation (8.37): \[ \Delta x_{1,3} = 0.327 \]

From equation (8.38):
\[ x_{2,3} = 4.935 \exp\left(\frac{0.449^2}{1.91}\right) \]
\[ x_{2,3} = 5.484 \]

From equation (8.39): \[ \Delta x_{2,3} = 0.278 \]; Substituting these values into equation (8.41) gives a more accurate value for \( d_3 \), \( t_3 = 4t_1 \).

\[
d_3^2 = \frac{1.91}{4} \ln\left( \frac{7}{4.146} \left(1 + \frac{0.327}{4.608}\right)^{-1} \left(1 + \frac{0.278}{5.484}\right)^{-1} \right)
\]
\[ d_3 = 0.440 \]

This iteration is repeated until the assumed value and the derived value are sensibly equal. The derived diameter ratios are shown in Table 8.8.

**Table 8.8** Ratio of particle sizes for extraction in a 2:1 progression in time

<table>
<thead>
<tr>
<th>Ratio of times</th>
<th>1</th>
<th>2</th>
<th>4</th>
<th>8</th>
<th>16</th>
<th>32</th>
<th>64</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ratio of sizes</td>
<td>1</td>
<td>0.670</td>
<td>0.438</td>
<td>0.282</td>
<td>0.179</td>
<td>0.112</td>
<td>0.070</td>
</tr>
</tbody>
</table>
8.6.4 Mass frequency undersize determination

Let the final sample withdrawn be of concentration $Q_1$ and let the surface be at $S_1$ immediately prior to this withdrawal, then:

\[
F_i = \frac{1}{2}(1 + y_1)Q_1
\]  
(8.43)

where:  
\[
y_1 = \left(\frac{r}{S_1}\right)^2
\]  
(8.44)

\[
F_i = \frac{1}{2}(1 + y_{1,2})Q_{1,2}
\]  
(8.45)

and:  
\[
y_{1,2} = y_2\left(\frac{d_1}{d_2}\right)^2
\]  
(8.46)

Hence, by the trapezoidal rule:

\[
F_2 - F_1 = \frac{1}{2}\left(y_2 + y_{1,2}\right)(Q_2 - Q_{1,2})
\]

where  
\[
y_2 = \left(\frac{r}{S_2}\right)^2
\]

Substituting for $Q_{1,2}$ gives:

\[
F_2 = \frac{1}{2}\left(y_2 + y_{1,2}\right)Q_2 + \left[1 - \frac{y_2 + y_{1,2}}{1 + y_{1,2}}\right]F_1
\]  
(8.47)

Proceeding in a like manner gives the general formula:

\[
F_n - F_{n-1} = \frac{1}{2}\left(y_n + y_{n-1,n}\right)(Q_n + Q_{n-1,n})
\]
By successively eliminating the \( Q \) functions, this gives a general equation in recursive form as before:

\[
F_i = \frac{1}{2} \left( y_i + y_{i-1,i} \right) Q_i + \sum_{j=1}^{i-1} \left[ \frac{y_i + y_{i-1,i} - y_j - y_{j-1,i}}{y_{j+1,i} + y_{j,i} - y_{j-1,i} + y_{j-1,i}} \right] F_j \tag{8.48}
\]

\[
y_i = \left( \frac{r}{S_i} \right)^2 \quad \text{and} \quad y_{i-1,i} = \frac{y_i}{d_i}
\]

A numerical solution is given below for a feed volume of 150 cm\(^3\) and a 2:1 progression in time. \( y_{j,i} \) values are given in Table (8.5) and these are inserted into the general equation to give the \( F \) values presented in Table 8.9. The dimensions of the centrifuge bowl are such that \( y_i = 1.364 \).

**Table 8.9 Tabulated \( y_{i,j} \) values for a pipette centrifuge**

| \( y_{1,2} \) | 1.1654 |
| \( y_{1,3} \) | 1.0793 |
| \( y_{1,4} \) | 1.0391 |
| \( y_{1,5} \) | 1.0195 |
| \( y_{1,6} \) | 1.0099 |
| \( y_{1,7} \) | 1.0053 |
| \( y_{2,3} \) | 1.2216 |
| \( y_{2,4} \) | 1.1057 |
| \( y_{2,5} \) | 1.0519 |
| \( y_{2,6} \) | 1.0263 |
| \( y_{2,7} \) | 1.0140 |
| \( y_{3,4} \) | 1.2863 |
| \( y_{3,5} \) | 1.1352 |
| \( y_{3,6} \) | 1.0632 |
| \( y_{3,7} \) | 1.0353 |
| \( y_{4,5} \) | 1.3616 |
| \( y_{4,6} \) | 1.1715 |
| \( y_{4,7} \) | 1.0882 |
| \( y_{5,6} \) | 1.460 |
| \( y_{5,7} \) | 1.224 |
| \( y_{6,7} \) | 1.601 |

Calculation of \( F \) values; using a feed volume of 150 cm\(^3\) as before.

Equation (8.43) gives

\[
F_1 = \frac{1}{2} \left( 1 + 1.364 \right) Q_1
\]

\[
F_1 = 1.182 Q_1
\]

Equation (8.47) gives

\[
F_2 = \frac{1}{2} \left( 1.494 + 1.1654 \right) Q_2 + \left[ 1 - \frac{2.6596}{2.1654} \right] F_1
\]
Equation (8.48) gives:

\[ F_3 = \frac{1}{2} (1.651 + 1.222) Q_3 + \left[ 1 - \frac{2.873}{2.302} \right] F_2 + \left[ \frac{2.873}{2.302} - \frac{2.873}{2.079} \right] F_1 \]

\[ F_3 = 1.4366Q_3 - 0.249F_2 - 0.133F_1 \]

and so on, giving the general equations for the conditions \( i = 7, V = 150 \text{ cm}^3 \) presented in Table 8.10. An alternative approach to the procedure outlined above has been presented by Dumm and Hogg [20].

**Table 8.10** Table of \( F \) values for a pipette withdrawal centrifuge

<table>
<thead>
<tr>
<th>( F_i )</th>
<th>( F_1 )</th>
<th>( F_2 )</th>
<th>( F_3 )</th>
<th>( F_4 )</th>
<th>( F_5 )</th>
<th>( F_6 )</th>
<th>( F_7 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>( F_1 )</td>
<td>1.1822Q_1</td>
<td>1.330Q_2 - 0.228F_1</td>
<td>1.4366Q_3 - 0.2486F_2 - 0.133F_1</td>
<td>1.5658Q_4 - 0.3093F_3 - 0.1509F_2 - 0.0757F_1</td>
<td>1.7255Q_5 - 0.3836F_4 - 0.1950F_3 - 0.0877F_2 - 0.0427F_1</td>
<td>1.9373Q_6 - 0.4713F_5 - 0.2595F_4 - 0.1200F_3 - 0.0521F_2 - 0.0249F_1</td>
<td>2.2255Q_7 - 0.5755F_6 - 0.3489F_5 - 0.1717F_4 - 0.0760F_3 - 0.0323F_2 - 0.0153F_1</td>
</tr>
</tbody>
</table>

### 8.7 Photocentrifuges

#### 8.7.1 Introduction

In the photocentrifuge method the concentration of a suspension is monitored using a light beam. The light can come from either a white light source (an incandescent bulb) or a monochromatic coherent source (a laser) and the detector may be either a photodiode or photomultiplier. The signal from the detector is usually digitized and converted to a size distribution via a computer.

Photocentrifuges are available in both disc and cuvette configuration. The former are normally used in the line-start mode and the latter in the homogeneous mode. The line-start mode has a much higher resolution.
than the homogeneous mode so that multimodal distributions are closely defined. The homogeneous mode can be run using a gradient procedure, with acceleration over time, which greatly speeds up the analysis. Both modes suffer the disadvantage that the laws of geometric optics do not apply, and the correction required can introduce large errors, especially with size distributions having a wide size range. For the examination of paint pigments, end-use properties may be more closely related to the attenuation curve than the derived size distribution. It is therefore arguable that the measured relationship between attenuation and Stokes diameter should be used to define the powder rather than size distribution.

8.7.2 Disc photocentrifuges.

The first disc photocentrifuge was developed by Kaye [21]. In this instrument, concentration changes within a suspension are followed using a white light beam. The instrument is usually used in the line-start mode and intuitively, one would expect that attenuation would be proportional to the projected area of the particles in the beam so that the curve of attenuation against Stokes diameter would be a differential surface distribution. However, Treasure [22] derived a relationship which showed that the attenuation, due to the finite width of the light beam, was proportional to the volume (mass) of particles in the beam [23,24]. In the line-start mode it is necessary to use a spin liquid that is denser than the suspension, otherwise the suspension can break through the interface and settle en-masse in a phenomenon known as streaming. In order to eliminate this effect a buffer layer technique is often used (Figure 8.4).

Fig. 8.4 The line-start technique.
The spin liquid may consist of 15 ml of 10% aqueous glycerol on which is floated 0.5 ml of water. For a more viscous suspension the concentration of glycerol can be increased. It is however necessary that the buffer layer be less dense than the fill liquid so that inversion does not occur. An interface forms between the two liquids and this may be broken up by a momentary change in the speed of the centrifuge although this is not always necessary to eliminate streaming. Typically, 0.25 ml of dilute suspension is then introduced; this tends to break through the air-water interface and spread out on the diffuse interface between the buffer liquid and the spin liquid, which is the starting radius for the subsequent sedimentation process [25]. If streaming persists it may be eliminated by using much smaller volumes of buffer liquid and suspension, e.g. 0.1 ml. Coll and Searles [26] used 20 ml of sucrose solution topped by 1 ml of n-dodecane to prevent evaporation. Several injections of 0.25 ml of colloid sample, \( \approx (001\%) \) concentration, were then injected through the oil layer.

In the external gradient method, a hypodermic syringe is used to form the gradient. For spin conditions requiring 15 ml of aqueous spin liquid exactly 15 ml are drawn into a 25 ml syringe. Air bubbles are expelled and, with the needle pointing down, an additional 1 ml of methanol is drawn in and the entire volume injected into the disc. Finally 1 ml of a suspension containing \(< 0.5\%\) by volume solids in an 80:20 water/methanol solution are added. An application of this technique is described by Devon et. al. [27]. A density method with correction for light scattering has also been published [28].

It must be stressed that the raw curves are not size distributions and calibration is required to convert to absolute values [29]. The importance of the correction for the breakdown in the laws of geometric optics is stressed by Weiner et. al. [30] who show excellent agreement between theory and experiment when this is done correctly. They also use the Brookhaven disc photocentrifuge to characterize ASTM carbon blacks.[31] This method has been used to characterize void-containing latex particles [32]. Commercial instruments are available from Joyce-Loebl, CPS Instruments and Brookhaven.

8.7.3 Homogeneous mode

This is the preferred mode with cuvettes; it is still however necessary to correct for radial dilution effects.
(a) Stokes diameter determination

For a constant (centrifuge) speed operation equation (8.4) is applied. In the gradient mode (centrifuge speed increasing with time in order to speed up the analysis) \( \omega \) is replaced by an expression relating centrifuge speed with time.

(b) Mass frequency undersize determination

The light cut off by particles in the light beam is related to the concentration by the equation:

\[
\ln \frac{I_0}{I} = b \sum_{r=\min}^{r=St} K_r n_r d_r^2
\]

(8.49)

where

- \( I_0 \) is the intensity of the emergent light beam when no particles are present
- \( I \) is the intensity of the light beam at time \( t \) after the start of sedimentation
- \( b \) is a constant depending on the dimensions of the light beam, the geometry of the system and the shape of the particles
- \( n_r \) is the number of particles in the beam of diameter \( d_r \)
- \( d_{St} \) is the diameter of the largest particle in the light beam
- \( K_r \) is the extinction coefficient for a particle of diameter \( d_r \)

Kamack's equation is applied with the assumption that the attenuation is proportional to the product of the extinction coefficient and the cross-sectional area of the particles in the beam i.e. \( \ln(I_0/I) \) is replaced by the optical density \( D \) where:

\[
D = \log \frac{I_0}{I}
\]

The data are then converted to a mass distribution by summating the product of \( D \) and \( d_{St} \).
8.7.4 Worked example assuming that the conditions in section 8.4.3 applies for a centrifuge without scanning

Material: titanium dioxide
Initial concentration 3.48 g in 100 cm³
Density of powder \( \rho_s = 4125 \text{ kg m}^{-3} \)
Density of liquid \( \rho_l = 1000 \text{ kg m}^{-3} \)
Liquid viscosity \( \eta = 0.000891 \text{ Pa s} \)
Centrifuge speed \( N = 3000 \text{ rpm} = 314 \text{ rad s}^{-1} \)

Table 8.11 Conversion of attenuation of homogeneous centrifuge into a cumulative surface undersize distribution assuming constant extinction and shape coefficients

<table>
<thead>
<tr>
<th>(i)</th>
<th>(T) min.</th>
<th>(I)</th>
<th>log((I_0/I))</th>
<th>log((I_0/I))</th>
<th>Stokes diameter (D_i(\mu m))</th>
<th>Surface (%) undersize (F_i(S))</th>
</tr>
</thead>
<tbody>
<tr>
<td>8</td>
<td>0</td>
<td>15.0</td>
<td>0.778</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>1</td>
<td>17.2</td>
<td>0.719</td>
<td>92.4</td>
<td>0.65</td>
<td>99.7</td>
</tr>
<tr>
<td>6</td>
<td>2</td>
<td>20.2</td>
<td>0.648</td>
<td>83.3</td>
<td>0.46</td>
<td>98.3</td>
</tr>
<tr>
<td>5</td>
<td>4</td>
<td>25.9</td>
<td>0.541</td>
<td>69.5</td>
<td>0.325</td>
<td>92.3</td>
</tr>
<tr>
<td>4</td>
<td>8</td>
<td>36.6</td>
<td>0.391</td>
<td>50.3</td>
<td>0.23</td>
<td>75.5</td>
</tr>
<tr>
<td>3</td>
<td>16</td>
<td>53.4</td>
<td>0.227</td>
<td>29.2</td>
<td>0.163</td>
<td>48.8</td>
</tr>
<tr>
<td>2</td>
<td>32</td>
<td>71.7</td>
<td>0.099</td>
<td>12.7</td>
<td>0.115</td>
<td>22.6</td>
</tr>
<tr>
<td>1</td>
<td>64</td>
<td>83.8</td>
<td>0.031</td>
<td>4.0</td>
<td>0.081</td>
<td>7.3</td>
</tr>
<tr>
<td></td>
<td>90.0</td>
<td></td>
<td></td>
<td>0</td>
<td>0.058</td>
<td>0</td>
</tr>
</tbody>
</table>

From Stokes equation, at \( T = 1 \) min.:

\[
d_1 = \sqrt{\frac{18 \times 0.000891 \ln(7/4.304)}{3125 \times 314^2 \times 60}} = 0.65 \mu m
\]
Table 8.12 Conversion of cumulative undersize distribution by surface into a cumulative undersize distribution by mass

<table>
<thead>
<tr>
<th>Relative surface</th>
<th>Mean diameter</th>
<th>Stokes diameter</th>
<th>Mass % undersize.</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta S$</td>
<td>$\bar{d}$</td>
<td>$\Sigma \Delta S \bar{d}$</td>
<td>$d_i$ (μm)</td>
</tr>
<tr>
<td>0.3</td>
<td>0.784</td>
<td>20.964</td>
<td>0.65</td>
</tr>
<tr>
<td>1.4</td>
<td>0.56</td>
<td>14.790</td>
<td>0.46</td>
</tr>
<tr>
<td>6.0</td>
<td>0.392</td>
<td>9.922</td>
<td>0.325</td>
</tr>
<tr>
<td>16.8</td>
<td>0.278</td>
<td>6.113</td>
<td>0.23</td>
</tr>
<tr>
<td>26.7</td>
<td>0.197</td>
<td>3.034</td>
<td>0.163</td>
</tr>
<tr>
<td>26.2</td>
<td>0.139</td>
<td>1.111</td>
<td>0.115</td>
</tr>
<tr>
<td>15.3</td>
<td>0.098</td>
<td>0.278</td>
<td>0.081</td>
</tr>
<tr>
<td>7.3</td>
<td>0.070</td>
<td>0.050</td>
<td>0.058</td>
</tr>
<tr>
<td></td>
<td>0.00</td>
<td>0.00</td>
<td>0.00</td>
</tr>
</tbody>
</table>

8.8 Line-start incremental centrifugal sedimentation

8.8.1 Line-start, incremental centrifugal technique

In the line-start technique the centrifuge disc is filled with clear liquid and allowed to attain its running speed. A small volume of buffer liquid is then introduced. The suspension is then introduced at time $t = 0$. The start radius is assumed to be at the mid-point of the suspension radius.

(a) Stokes diameter determination

Since all the particles emanate from the same starting point, the Stokes diameter is determined using equation (8.4) with $r$ as the measurement radius and $S$ as the midpoint of the suspension layer.

(b) Mass frequency undersize determination

There is some disagreement as to whether the optical attenuation using the line-start technique is proportional to surface or volume distribution or whether it varies in a complex manner with $d_{Sr}$. The consensus is that a volume relationship applies.

A wedge shaped detector window (with radial sides, circular inner and outer sides), centered on $r$ and spanning $r_1$ to $r_2$ where $r_2 > r_1$, will view an
annular section of the disc. At time $t = 0$ there is only clear liquid in the window. As time progresses, the largest particles present in the suspension will enter the window and at time $t$ the diameter of the particles at the center of the window will be:

$$d_{St} = \sqrt[1/(\gamma - \pi)]{\frac{\ln \frac{r}{S}}{t}}$$  \hspace{1cm} (8.50)

The suspension in the window will contain particles with diameters in the size range $d_1 = d_{St}(1 - \beta)$ to $d_2 = d_{St}(1 + \theta)$ where $d_1$ is the diameter of the particle just entering the window and $d_2$ the diameter of the particle just leaving it:

$$d_1 = d_{St}(1 + \theta) = \sqrt[1/(\gamma - \pi)]{\frac{\ln \frac{r_1}{S}}{t}} \quad d_2 = d_{St}(1 - \beta) = \sqrt[1/(\gamma - \pi)]{\frac{\ln \frac{r_2}{S}}{t}}$$  \hspace{1cm} (8.51)

If we substitute to eliminate $d_{St}$ we find that $\beta$ and $\theta$ are dependent only on geometric factors and not on material properties.

$$\theta = 1 - \frac{\ln (r_1 / S)}{\ln (r / S)} \quad \beta = \frac{\ln (r_2 / S)}{\ln (r / S)} - 1$$  \hspace{1cm} (8.52)

If the detector window is fixed, both $r_1$ and $r_2$ will remain constant during a run, so that $\beta$ and $\theta$ will be constants independent of time. Note that while the ratio of $d_1/d_2$ remains constant with time the difference between $d_1$ and $d_2$ decreases since the value of $d_{St}$ decreases with time:

$$d_2 - d_1 = d_{St}(\theta + \beta)$$  \hspace{1cm} (8.53)

i.e. the difference is proportional to the Stokes diameter].

The optical density is proportional to $n_c d_r^3$ since the range of summation of equation (8.53) is proportional to $d_{St}$.

$$D = K_{St} n_{St} d_{St}^3$$  \hspace{1cm} (8.54)
Fig. 8.5 Elemental area under attenuation curve for photocentrifuge in line-start mode.

Fig. 8.6 Converting the line-start attenuation curve into a mass frequency curve
The elemental area under the experimental curve of attenuation \((D)\) versus time \((t)\) (Figure 8.5) is given by:

\[
\Delta A = \sum_{t_1}^{t_2} D_i dt
\]  

(8.55)

Since \(t \propto 1/d^2\); from equation (8.54) the elemental area under the attenuation curve becomes:

\[
\Delta A = \int_{(1-\beta)d_{st}}^{(1+\theta)d_{st}} n(d_{st}) d^3 d_{st} (\frac{dd_{st}}{d^3_{st}})
\]

(8.56)

the relative number of particles in the size range \(d_1\) to \(d_2\)

\[
\Delta A = \int_{(1-\beta)d_{st}}^{(1+\theta)d_{st}} n(d_{st}) d_{st}
\]  

(8.56)

Multiplying each ordinate by \(d^2_{st}\) or \(d^3_{st}\) gives the area or volume of distribution. A full solution is generated if the extinction factor is introduced into the equation.

Alternatively the recorder trace of attenuation against time can be converted to attenuation against Stokes diameter and then normalized, i.e. the area under the curve is made equal to 100 (Figure 8.6). It is assumed that this curve is the mass frequency distribution \((dW/dd_{st}\) versus \(d_{st}\)) uncorrected for the breakdown in the law of geometric optics. The normalized curve of the product of \(dW/dd_{st}\) and extinction coefficient is the corrected distribution. This has the effect, in the above example, of reducing the measured median size of titanium dioxide from 0.49 \(\mu m\) to 0.45 \(\mu m\).

8.8.2 Discussion of line-start theory

Although equation (8.56) is the recommended one for the line-start technique [33] there is considerable disagreement as to whether it is correct and it is often assumed that the attenuation is proportional to
projected area rather than particle volume. An alternative treatment, in agreement with the volume proportionality, is presented below.

The number fraction of particles in the field of view is given by:

$$n(d_{St}) = \sum_{r=(1-\beta)}^{r=(1+\theta)} f(n)dd_{St,r}$$  \hspace{1cm} \text{(8.57)}$$

where $f(n) = dN/dd_{St}$

Treasure assumed that the relative number concentration in the light beam, centered on $d_{St}$ may be expressed by the linear function $n(d_{St}) = f + g(d_{St})$. Thus the total cross-sectional area of particles in the beam is proportional to:

$$\Delta A = \int_{(1-\beta)d_{St}}^{(1+\theta)d_{St}} \left\{ f + g \left( \frac{d}{d_{St}} \right) \right\} d^2dd$$ \hspace{1cm} \text{(8.58)}$$

The solution to this integral, if higher order terms are neglected, gives the proportionality:

$$D \propto (\theta + \beta)(f + g)d_{St}^3$$

$$D \propto (f + g)d_{St}^3$$ \hspace{1cm} \text{(8.59)}$$

since $(\theta + \beta)$ is a constant. The optical density of the suspension is therefore proportional to the total particle volume in the beam as before i.e.

$$D \propto K_{St}n(d_{St})d_{St}^3$$ \hspace{1cm} \text{(8.60)}$$

Other published solutions state that the amount of light cut off is proportional to particle volume [34,35] for line-start and to particle surface for homogeneous mode.
Nelson et. al. [36] challenged these derivations. Using a general series expansion, they stated that the solution to equation (8.53) takes the form

\[ f(d) = (\beta + \theta) \sum f_j d_{St}^{j+1} \]  

(8.61)

Thus, the fraction of particles in the field of view varies in a complex fashion with \( d_{St} \).

The conclusion drawn from equation (8.56) is at odds with published data on polystyrene lattices and silver bromide, in which a volume proportionality is found [37,38]. However these distributions were narrow, and with narrow distributions the difference between volume and surface distributions is small. The conclusion is also at variance with data published on BCR 66 quartz powder, ranging in size from 0.3 to 3 \( \mu \)m. In this case, the median for the attenuation curve was 1.52 \( \mu \)m which reduced to 1.14 \( \mu \)m with extinction factor correction [39] and a correction of this magnitude could hide the effect.

Centrifugal photosedimentation yields an attenuation curve; particles at the fine end of the distribution, at say 0.1 \( \mu \)m, obscuring the light by perhaps one twentieth of their geometric area whereas at the coarse end, say 1 \( \mu \)m, the ratio can be greater than two. The correction for extinction coefficient modifies the shape of the curve considerably, making decisions as to correct theory to apply difficult. The unmodified attenuation curve may be more relevant to end-use properties, for hiding power of pigments for example, than the derived size distribution. Since the introduction of a correction for extinction coefficient has such an enormous effect on the shape of the distribution curve for wide distributions the correction should be applied with caution.

Putman et. al. [40] used a CONTIN-based approach towards data analysis of photosedimentometry using the Shimadzu SA-CP2-10 to accurately determine size distributions. Contin is a mathematical FORTRAN IV program, which analyzes an experimental signal consisting of a sum of exponential curves, and determines its individual functions each with a weight.
8.8.3 BI-DCP disc (photo)centrifuge particle size analyzer

The technology that Brookhaven developed for the x-ray centrifuge has been transferred to their photocentrifuge (Figure 8.7). The revised software is for analysis by the homogeneous start technique plus a scanning head detector.

The high-resolution line-start technique can be used, but this is not amenable to scanning since the low concentrations necessarily employed generate a noisy baseline. An additional benefit of the new software is that it allows for particles whose density is lower than that of the surrounding liquid, thus making it suitable for emulsion sizing.
**Fig. 8.8** Block diagram of the Horiba cuvette photocentrifuge.

### 8.9 Cuvette photocentrifuges

In these instruments (Figure 8.8) the disc is replaced with a rectangular cell containing a homogeneous suspension. Unless corrections are applied for radial dilution effects and the breakdown in the laws of geometric optics, the derived data are suitable only for comparison purposes. For example, a 50:50 mixture of 0.25 and 0.60 μm spherical silica particles was recorded as 54.4:45.6 with no correction for radial dilution, and this increased to 70:30 without extinction coefficient correction with the smaller particles grossly under-counted. A computer program to correct for the light scattering of small particles reduces these errors [41].

Bowen *et. al.* [42] report on a method of programming the Horiba CAPA-700 to generate accurate sub-μm measurement of alumina and quartz powders. Using the manufacturer’s correction for light scattering was found unsatisfactory. It was also found that the light scattering correction was strongly affected by the shape of the particles [43].

An alternative procedure is to use several wavelengths and deconvolute the resulting set of linear equations that develop in order to find the size distribution. This procedure was applied by Niemann and Weichert who used a modified Phillips-Twomey algorithm [44,45]. Their photo-
centrifuge used white light from a short arc xenon high-pressure lamp. Two light beams are generated, one passing through the suspension at a depth of 2 mm and the other at a depth of 20 mm. Four cuvettes are used, two containing clear liquid and two containing suspension. The light beams are collected with fiber optic guides after passing through the cuvettes and then separated into four wavelengths. Additional photodetectors monitor the intensity of the lamp at the same four wavelengths. The speed of the wheel accelerates continuously over 20 minutes to a final speed of 3,000 rpm and maintained at this speed until all the particles have settled. This system enables a broad size distribution from below 0.05 μm to 10 μm (e.g. quartz in water) to be analyzed in 30 minutes.

Instruments are available from Horiba, Seishin, Shimadzu and LUM. They can be run in the gravitational, centrifugal, gravitational followed by centrifugal or gradient mode. In the gradient mode, the centrifuge accelerates over the analysis time to reduce the measurement time. The simpler instruments operate at constant speed and an analysis can take 45 min, which can be reduced to a few minutes in the more sophisticated versions.

Horiba CAPA-700 covers the size range 0.01 to 300 μm, automatically selecting the best of five operating conditions, involving the three modes enumerated above, at centrifuge speeds from 300 to 10,000 rpm.

Horiba CAPA-300 is a more economical version covering the size range 0.04 to 300 μm.

Seishin offer three versions of their micron photo-sizers covering the size range 0.1 to 500 μm, the SKC-2000, the SKC-3000 and the SKC-5000.

Shimadzu SA-CP3 operates at 120, 240 or 480 rpm and in any of four modes to cover the size range 0.02 to 150 μm.

Shimadzu SA-CP4 operates in the range 500 to 11,000 rpm to cover the size range 0.01 to 500 μm.

L.U.M. LUMiFuge™ 114 (Laboratory, Environmental, Medical Diagnostics & Technology) is a photocentrifuge covering the size range 0.1 to 300 μm with a sample volume of 0.1 to 2ml. No sample pre-dilution is required and eight simultaneous analyses can be carried out. The photocentrifuge operates in the gradient mode with at speeds accelerating from 300 to 3000rpm.
8.10 Homogeneous, cumulative, centrifugal sedimentation

The shape of the centrifuge tube is immaterial for instruments operating in the incremental mode but the shape is important for instruments operating in the cumulative mode since particles travel in radial paths.

The disadvantages of cylindrical tubes are that sedimenting particles strike the walls of the tube, agglomerate with other particles on the walls and reach the bottom more quickly than freely sedimenting particles. The oblique force of the suspension on the walls also set up convection currents within the suspension. The advantages of cylindrical tubes instead of sector or conoidal-shaped tubes (Figure 8.9) is that they are easier to construct and may be used in ordinary laboratory centrifuges.

8.10.1 General theory

Equation (8.6) may be written (for \( r_i = S \) and \( r = R \)):

\[
S = R \exp\left(-kd^2t\right)
\]  
(8.62)

At time \( t \), all particles greater than \( d_{S_i} \) will have reached the bottom of the container (\( r = R \)). In addition, partial sedimentation will have taken place for particles smaller than \( d_{S_t} \). For each of these smaller sizes, a starting point \( x_0 \) exists, beyond which all the smaller particles will have reached \( R \) where, from equation (8.62):

\[
x_0 = R \exp\left(-kd^2t\right)
\]  
(8.63)
The volume fraction of suspension lying between $R$ and $x_0$ for shallow bowl or flat sector shaped tubes is equal to:

$$\frac{R^2 - x_0^2}{R^2 - S^2} = \frac{R^2}{R^2 - S^2} \left[ 1 - \exp(-2k_d^2 t) \right]$$

(8.64)

If the particle size distribution is defined such that the weight fraction in the size range $d$ to $d+\delta d$ is $f(d)\delta d$ then the weight of particles with diameters greater than $d_{S_1}$ that have completely settled is:

$$W = \int_{d_{S_1}}^{\infty} f(d)\delta d$$

(8.65)

The weight fraction of particles smaller than $d_{S_1}$ which have completely settled is:

$$W_{u} = \frac{R^2}{R^2 - S^2} \int_{0}^{d_{S_1}} \left[ 1 - \exp(-2k_d^2 t) \right] f(d)\delta d$$

(8.66)

The total weight fraction deposited is:

$$P = W + \frac{R^2}{R^2 - S^2} \int_{0}^{d_{S_1}} \left[ 1 - \exp(-2k_d^2 t) \right] f(d)\delta d$$

(8.67)

The weight fraction oversize can be determined if the weight fraction deposited is measured for different values of the variables $S$, $R$ and $t$.

Similarly, the weight fraction of particles still in suspension at time $t$ will consist of particles smaller than $d_{S_1}$ that have originated in the volume between the surface $S$ and radius $x_0$.

By comparison with equations (8.66) and (8.67) this fraction is:

$$1 - P = \frac{R^2}{R^2 - S^2} \int_{0}^{d_{S_1}} \left[ \exp(-2k_d^2 t) - \exp(-2k_d^2 t_{S_1}) \right] f(d)\delta d$$
\[ 1 - P = \frac{1}{1 - \exp(-a)} \int_0^{d_{St}} \left[ \exp\left(-\frac{ad^2}{d_{St}^2}\right) - \exp(-a) \right] f(d)dd \quad (8.68) \]

where \( a = 2 \log \left( \frac{R}{S} \right) \)

### 8.11 Variable time method (variation of \( P \) with \( t \))

Romwalter and Vendl [46] derived a solution to equation (8.67) by differentiating with respect to time and substituting back in the original equation. Brown [47] drew attention to an error in their derivation and stated that an exact solution for the distribution function appeared to be difficult, if not impossible, to obtain by the above method.

The following solutions were derived by Robison and Martin [48,49] who used sector-shaped tubes. Their analyses agreed closely with those obtained using the variable height method.

\[ \int_0^{d_{St}} f(d)dd = 1 - \left[ \frac{M(6 - M)}{8} P + \frac{Md_{St}}{8} \frac{dP}{dd} + \frac{M(M - 2)(M - 4)}{8} I(d_{St}) \right] \quad (8.69) \]

where \( I(d_{St}) = \frac{1}{d^{M}} \int_0^{d_{St}} Pd^{M-1}dd \)

and \( M = \frac{4\left(R^2 - S^2\right)}{S^2 \ln(R/S)} \)

An exact solution to equation (8.67), as given by Kamack [50], is as follows:

\[ F(d_{St}) = \left( \frac{\exp(a) - 1}{a} \right) \left( q(d_{St}) - \int_0^{\infty} h_1(x)q\left\{ d_{St} \exp(-x) \right\} \right) \quad (8.70) \]

where \( q(d) = p(d) + \frac{d}{2} \frac{dP}{dd} \)

and \( h_1(x) = h(x) \exp(-2x) \)
434 Powder sampling and particle size determination

\[ x = \ln \left( \frac{d_{st}}{d} \right) \]

and the 'resolvent kernel' \( h(x) \) is a function that depends on the apparatus constant.

Muschelknautz [51,52] designed a centrifuge in which the displacement of two diametrically opposed bodies floating in a dispersion was measured. The bodies are fixed on a common rod and are immersed at different depths in two chambers. The differential force yields the size distribution directly. Sokalov et al. [53] described a centrifugal sedimentometer with a float measurement system.

8.12 Sedimentation distance small compared with distance from centrifuge axis

The simplest procedure with a homogeneous, centrifugal system is to make \( r-S \) small compared with \( S \) and assume that the particles fall with constant velocity.

Equation (8.2) becomes:

\[ u_c = \frac{(\rho_s - \rho_f) d_{st}^2}{18\eta} \omega^2 \left( \frac{r + S}{2} \right) \]  

(8.71)

This approach has been used by several investigators and applies to the Alpine sedimentation centrifuge and the Mikropul.

8.12.1 Hosokawa Mikropul Sedimentputer

The Hosokawa Mikropul Sedimentputer [54-56] has a sealed suspension in a cell that is rotated. As the particles settle, out the center of gravity changes, which creates an inbalance that causes the cell to vibrate (Figure 8.10). By detecting the amplitude and angular velocity of the vibration, the size distribution is obtained.

Muschelknautz designed a centrifuge in which the displacement of two diametrically opposed bodies floating in a dispersion was measured [57-60]. The bodies are fixed on a common rod and are immersed at different depths in two chambers. The differential force yields the size distribution.
Fig. 8.10 The Mikropul Sedimentputer. (a) Schematic of the system. (b) The settling of particles causes the center of gravity to shift.

8.12.2 Alpine long-arm centrifuge

The Alpine sedimentation centrifuge is a long-arm centrifuge of diameter 400 mm with a 50 mm high measuring cell. The rate at which sediment settles out is determined by measuring pressure changes at the bottom of the cell using a diaphragm arrangement.

8.13 Variable inner radius (variation of \( P \) with \( S \))

Brown [61] avoided the complications arising from the differentiation of equation (8.66) with respect to time by considering the fraction sedimented in a given time interval with the centrifuge tubes filled with suspension to a series of levels. On increasing \( S \) an increasingly large fraction of suspended particles will be deposited in a given time. Equation (8.67) may be written:
\[ P = W + \frac{R^2}{R^2 - S^2} I \]  

(8.72)

Differentiating equation (8.72) with respect to \( S \), keeping \( R \) and \( I \) constant, and substituting back for \( P - W \), gives:

\[ \left( \frac{\delta P}{\delta S} \right)_{R,I} = \frac{2R^2S}{(R^2 - S^2)^2} I \]

Substituting for \( I \) from equation (8.72) gives:

\[ P = W + \frac{R^2 - S^2}{S} \frac{\delta P}{\delta S} \]

(8.73)

Thus, a rigorous solution is obtained by keeping \( R \) and \( I \) constant, and determining the weight fraction deposited for varying heights of suspension. Just as in gravitational sedimentation, second derivatives of the fraction sedimented are required in order to obtain the distribution. In order to obtain \( F(d_{sl}) \) in terms of the second derivatives of \( P \), it is necessary to differentiate equations (8.61) and (8.66) with respect to \( S \), eliminating \( d_{sl}d_{sl}/dS \) from the two resulting equations.

\[ \left( \frac{\delta d_{sl}}{\delta S} \right)_{R,I} = \frac{d_{sl}}{2S \ln(R/S)} \]

(8.74)

giving, in combination with the differential of equation (8.66):

\[ \frac{f(d_{sl}) \delta d_{sl}}{\delta S} = \frac{\ln(R/S)}{2S} \left[ \frac{R^2 + 3S^2 \delta P}{S \delta S} - \frac{(R^2 - S^2) \delta^2 P}{\delta S^2} \right] \]

(8.75)

Combining these two equations gives:

\[ F(d_{sl}) \delta d_{sl} = \frac{\ln(R/S)}{d_{sl}} \left[ \frac{R^2 + 3S^2 \delta P}{S \delta S} - \frac{(R^2 - S^2) \delta^2 P}{\delta S^2} \right] \]

(8.76)
Similarly, the distribution function may be derived in terms of \( \frac{\delta P}{\delta t} \) and \( \frac{\delta^2 P}{\delta S \delta t} \) by differentiating equations (8.63) and (8.67) with respect to time:

\[
F(d_{sl}) = \frac{2t}{ds_t} \frac{\delta P}{\delta t} - \frac{R^2 - S^2}{2S} \frac{\delta^2 P}{\delta S \delta t}
\]  

(8.77)

Three distinct methods are therefore available for calculating the mass distribution of particles in suspension for a series of sector-shaped tubes filled to a series of levels. First, the mass fraction of particles larger than a known diameter may be calculated from equation (8.77) and the distribution function determined from the slope of the cumulative mass deposited against \( S \). Secondly, the distribution function may be calculated directly in terms of the first and second derivatives of the fraction sedimented with respect to the length of the column of suspension centrifuged by use of equation (8.77). Thirdly, from the sedimentation-time curve at a series of levels, the distribution functions may be calculated by the use of equation (8.77).

8.13.1 Alternative theory (variation of \( P \) with \( S \))

An alternative approach is given by Murley [62] as follows:

If the inner radius of the centrifuging suspension is decreased by a small amount \( \delta S \), then the extra weight of sample introduced into the centrifuge is \( 2\pi STc \delta S \), \( T \) is the thickness of the suspension in an axial direction and \( c \) is the weight of solid per unit volume of suspension. For this extra amount of material added, all that with a particle size less than \( d_{sl} \) will reach the collecting plane at \( R \) and all that with a particle size greater than \( d_{sl} \) will be at a smaller radius than \( R \) at the end of the running time \( t \). The extra weight of sample deposited at radius \( R \) due to this change in radius \( S \) of the top surface of the sample is therefore:

\[
\Delta P = -2\pi STc \int_{d_{sl}}^{\infty} f(d) dd \delta S
\]  

(8.78)

The negative sign occurs because the added layer causes a decrease in \( S \). This equation applies to an apparatus where the liquid is run off and the deposited layer is retained for analysis. In the type of apparatus where the
overlying liquid is removed for estimation of the weight of solids the following equation is applicable:

\[ \Delta P = -2\pi STc8S \int_{d_{S1}}^{0} f(d)dd \]  \hspace{1cm} (8.79)

By plotting \( P \) against \( S \) and finding the slope of the curve, \( f(d)dd \) may be evaluated. Equations (8.78) and (8.79) can also be derived by differentiating equation (8.69) which may be written:

\[ P = \left\{ 1 - \int_{0}^{d_{S1}} f(d)dd \right\} + \frac{R^2}{R^2 - S^2} \int_{0}^{d_{S1}} \left\{ 1 - \exp(-2kd^2l) \right\} f(d)dd \]  \hspace{1cm} (8.80)

\[ 1 - P = \frac{1}{R^2 - S^2} \int_{0}^{d_{S1}} \left\{ R^2 \exp(-2kd^2l) - S^2 \right\} f(d)dd \]  \hspace{1cm} (8.81)

where \( 1 - P \) is the mass fraction still in suspension. The mass fraction of powder that has been sedimented is \( P \) where \( P = \pi(R^2 - S^2)Tc(1-P) \), i.e.

\[ P = \pi Tc \int_{0}^{d_{S1}} \left[ R^2 \exp(-2kd^2l) - S^2 \right] f(d)dd \]  \hspace{1cm} (8.82)

Differentiating this with respect to \( S \) leads directly to equation (8.65).

8.14 Variable outer radius (variation of \( P \) with \( R \))

Donaghue and Bostock [63] differentiated equation (8.68) with respect to \( R \), giving:

\[ \int_{0}^{d_{S1}} f(d)dd = P + R \left( \frac{R^2 - S^2}{2S^2} \right) \frac{dP}{dR} \]  \hspace{1cm} (8.83)

Slope measurements of the \( P-R \) curve permit calculation of the mass fraction oversize.

The apparatus developed for this determination consisted of a stepped centrifuge so that the suspension is contained in a space consisting of a
number of rings, each of which has the same inner radius \( S \), but progressively larger outer radii \( R \) from top to bottom. Particles are deposited on detachable surfaces that are removed and dried before weighing, the supernatant being removed before the centrifuge is stopped.

The advantage of this instrument, over the Simcar which was developed later, was that six points on the distribution curve were determined simultaneously. The main disadvantage, which prevented the centrifuge from being accepted, was loss of sediment due to movement of supernatant liquid during its withdrawal.

![Fig. 8.11 MSA special centrifuge tube.](image)

**8.15 Line-start cumulative centrifugal sedimentation**

**8.15.1 MSA analyzer**

The MSA analyzer (Figure 8.11) operates in this mode [64]. Objections that can be leveled at this technique are:

- The amount of deposited sediment is determined by its height and, since the settled volume is not independent of size, errors are introduced.

The lower part of the sedimentation cell has sloping walls, hence some particles adhere to this section and others slide down the sloping walls into the measurement zone, so that large particles are frequently found at a level where only small particles should be present.

**8.16 Particle size analysis using non-invasive dielectric sensors**

The use of capacitance measurement is based upon the principle that the concentration changes as particles settle through a suspension and will alter the effective dielectric constant between the sensing electrodes. A complete capacitance transducer consists of capacitance sensing electrodes together with capacitance sensing electronics, which is essentially a capacitance to voltage converter.
The analyzer described by Simons and Williams [65] consisted of an array of eight pairs of capacitance electrodes mounted vertically down the side of a sedimentation tube of length 26 cm and diameter 2.5 cm. The electrodes were embedded in acrylic and flush mounted to the inside wall of the tube.

Soda glass spheres at a volume concentration of 1.65%, in size ranges from 20 to 60 μm and 2 to 18 μm, gave results comparable with Andreasen and Elzone.

**Fig. 8.12** Diagrammatic section of the Hauser-Lynn centrifuge

**8.17 Supercentrifuge**

The supercentrifuge rotates at speeds between 8000 and 50 000 rpm and may be used to determine the size distribution of particles too small to be analyzed with conventional centrifuges.

Several ways of using Hauser's [66,67] supercentrifuge (Figure 8.12) for particle size analysis have been described. The usual procedure involves successive fractionation of the suspension and weighing of the fractions collected on a removable liner on the bowl [68-70].
Centrifugal sedimentation methods

suspension is fed into the bottom of the bowl and the particles move in a spiral path until they reach the wall. The liquid is then discharged in an annular layer over the overflow dam wall.

If \( Q \) is the rate of flow of the suspension that causes a particle of diameter \( D \) to be deposited at a height \( h \) above the feed inlet, it can be shown that [67].

\[
Q = khD^2
\]  

(8.84)

If the removable liner is divided into identical strips, dried and weighed, the weight deposited on each strip may be used to find the size distribution [71]. The constant \( k \) may be evaluated from curves given by Hauser and Lynn [72] or a nomograph developed by Saunders [73] may be used.

This method of determining size distributions cannot be recommended for routine analyses and a method developed by Bradley is to be preferred [74]. This method is applicable to the Sharples supercentrifuge.

If \( D_m \) is the diameter of the smallest particle retained in the centrifuge, it can be shown that:

\[
P = W + \int_{0}^{d_S} \frac{R^2 - x_0^2}{R^2 - S^2} f(d) dd
\]

(8.85)

This is identical to equation (8.65), but the relationship between \( x_0 \) and \( D \) is more complicated than for a centrifuge without flow.

Bradley derives the empirical solution for the Sharples supercentrifuge as:

\[
\frac{(\rho_s - \rho_f) \omega^2 d^2}{18Q} = 4.1 \times 10^{-3} x_0^{-1.2}
\]

(8.86)

This gives, for the supercentrifuge as well as for batch centrifuges:

\[
W = P - \frac{R^2 - S^2}{2S} dP
\]

(8.87)

which is the same as equation 8.72.
Hence, the weight fraction oversize is calculable by measurement of $P$ for different values of $S$ at constant $W$ and $Q$. The quickest analytical procedure is to calculate $P$ from gravimetric or chemical analysis of feed and overflow suspensions. Choice of flowrate and speed can be made in accordance with prior knowledge of approximate size and use of derived theoretical expressions, or by trial and error to establish the rate at which $P$ approaches unity with maximum $S$.

The main disadvantages of the technique are the need for large samples and the uncertainty of end effects in the bowl. A big advantage is the ability to use an item of standard equipment without modification for a size below the range of most of the specially designed centrifuges.

8.18 Ultracentrifuge

The rotor of the ultracentrifuge is spun at speeds of up to 60 000 rpm in a vacuum to minimize air drag [75-77]. It may be used, therefore, to measure the size distribution of very fine particles. McCormick [78], for example, describes its use for determining the size distribution of polystyrene ($0.088 < d < 0.511$) $\mu$m and Brodnyan [79] uses it for determining emulsion particle size. It has also been used in combination with light scattering for polymer size distribution determination [80].

In a round-robin test series Mueller [81] found the ultracentrifuge to be the most satisfactory size analysis method for the sub-$\mu$m range; a sample containing nine monodisperse components with 10% diameter difference being resolved.

An analytical ultra-centrifugation technique has been used in combination with a scanning optical absorption system for particle size distribution determination. The system was demonstrated for colloidal platinum (0.4 to 2) nm and unstabilized zinc (4-9) nm during particle growth [82]. A review of examples of colloid analysis of nanosize particles by ultracentrifugation with a focus on multicomponent mixtures has been published [83].

This is claimed to be the first fractionating analytical technique with almost atomic resolution.

8.19 Conclusions

Sedimentation techniques are widely used for particle size analysis since the determined size distribution relates to unit operations such as classification. The distribution also relates to many end-use properties
such as the hiding power and gloss of pigments. Thermal diffusion limits the use of gravity sedimentation to powders containing a limited amount of sub-micron material, but the technique is extended into the sub-micron size range with the use of centrifuges.

Gravitational and centrifugal sedimentation using a pipette is attractive due to its versatility and low capital cost, but the analysis requires a skilled operator and is time consuming.

Mass distributions are also determinable using x-ray systems that are available as gravity and centrifugal sedimentometers. These are essential where speed and running costs are more important than capital costs.

Photosedimentometers are also available for gravitational and centrifugal sedimentation. Centrifugal photosedimentometers are available with disc and cuvette cells. The former are usually used in line-start mode which gives high resolution, whereas the latter operate in the homogeneous mode. These instruments need to be calibrated, or corrected, for the breakdown in the laws of geometric optics. The modified distribution greatly alters the raw curve for sub-micron powders with a wide size range, thus limiting the accuracy of this technique. Accuracy is not always important; detecting changes which may affect powder handling or final product may be all that is necessary.

References

5  Harris, C.C. (1969), *AMIE Trans.*, 244, 187,402
7  Svarovsky, L. and Svarovska, J. (1975), *J. Phys E*, 9, 959-962,402
8  Svarovsky, L. and Svarovska, J. (1976), *Dechema Monogram*, Nürnberg, Nos. 1589-1615, 279-292,402
9  Alex, W. (1972), *Dissertation*, Univ. Karlsruhe, Germany,403
444  Powder sampling and particle size determination

18 Foerderreuther, H. (1998), GT. Lahor-Faschz, 42(3), 234, Ger., 408
21 Kaye, B. H. (1962), British Patent 895 222, 418
Centrifugal sedimentation methods

53 Sokolov, V et al. (1975), *Zh. Prike. Khim.*, (Leningrad), 48(7), 1651,434
54 Kaya, N., Yokoyama, T. and Arakawa, M. (1986), *Kona*, No 4, 82,434
446 Powder sampling and particle size determination

64 ASTM C678-75 (Reapproved 1991), Standard test method for determination of particle size of alumina or quartz using centrifugal sedimentation.


69 McIntosh, J. and Seibie, F.E. (1940), Br. J. Exp. Path., 21, 143.


77 Alexander, J. ed. (1926), Colloid Chem., Chemical Catalogue Co., NY Ch. 6 by T. Svedberg.


