

*A New Method of Determining the Distribution Curve of
Polydisperse Colloidal Systems.*

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PART I.—THEORY OF THE METHOD.

I. *Introduction.*

No quantitative method has been developed for the complete determination of the distribution curve of polydisperse systems containing all sizes of particles of colloidal dimensions. Certain of the methods used in the mechanical analysis of soils could, with sufficiently accurate temperature control and refinement of detail, enable the distribution curve to be constructed as far down as particles of equivalent diameter $200\ m\mu$, but, owing to the slow rate of settling of such particles in water under gravity, the estimations would take several weeks to carry out. These methods are very ably discussed by F. V. von Hahn in a recent monograph.* The special problems of the mechanical analysis of soils have been critically reviewed by M. Köhn.†

The force acting on particles in suspension can be enormously increased by the use of the centrifuge, which has been developed by Svedberg so successfully that even large molecules, such as those of the proteins, can be made to sediment with appreciable velocity. The range of forces available is therefore ample for the study of polydisperse systems.

In the centrifuge, the time t taken for a spherical particle of radius r and density D to travel from x_1 to x_2 (these distances being measured from the axis of rotation) in a liquid of density d and viscosity η is given by

$$\ln \frac{x_2}{x_1} = \frac{2}{9} \frac{r^2}{\eta} (D - d) \omega^2 t, \quad (1)$$

where ω is the angular velocity. If N is the number of revolutions per second, we have, on evaluating the constants,

$$\log_{10} \frac{x_2}{x_1} = 3.81 \frac{r^2}{\eta} (D - d) N^2 t. \quad (2)$$

* 'Die Dispensoidanalyse,' Dresden (1928).

† 'Landw. Jahrb.,' vol. 67, p. 485 (1928).

The force on the particles increases with their distance from the axis, so that during sedimentation they are continuously accelerated. This has the effect of establishing a variation in concentration for each size of particle, the concentration increasing as we approach the axis of rotation, with, of course, the sudden drop to zero at the point corresponding to the distance the particles under consideration have moved from the surface of the liquid. Thus it is impossible to obtain a representative sample of the particles smaller than a given equivalent diameter by withdrawing a quantity of the liquid at the calculated depth, as is done in the case of the pipette method with gravity sedimentation. This method is therefore inapplicable to the case of the centrifuge.

A possible method of using the centrifuge would be to collect and weigh the sediment obtained after the time calculated for a given size of particle to traverse the whole column of liquid. This would be analogous to Odén's method of obtaining a distribution curve in the case of gravity separation.* The calculations involved would, however, be even more complex because of the unequal concentration set up in the tube by the centrifugal force. The use of the elaborate Odén-Keen balance† involves second differentials, and apparently the centrifugal method would involve third differentials with a corresponding reduction in accuracy the more marked because, in place of a continuous record, only a few points on the curve could be obtained experimentally.

The calculations could all be avoided if the sediment were redispersed and the centrifuging repeated time after time until all the particles were removed. Even qualitatively this method is only to be used as a last resort, because of the great number of repetitions needed for a clean separation. The classic experiments of Perrin on gamboge suspensions show clearly what must be expected from this method. In attempting to fractionate kaolin by this method the author carried out 13 successive treatments without removing all the smaller particles. Quantitatively there are slight losses in material at each step, and these become serious before the final separation has been attained.

The above considerations apply with equal weight to another type of machine in increasing use, particularly amongst soil investigators, namely, the Sharples supercentrifuge. In this machine, which works on the principle of a cream separator, the liquid is kept in rotation by the steel cylinder up which it is passed, and the solid is deposited on the inner wall of the cylinder. The

* Fisher and Odén, 'Proc. Roy. Soc. Edin.', vol. 44, p. 98 (1924).

† 'Roy. Soc. Proc.', A, vol. 106, p. 33 (1924).

velocity of the liquid and of the cylinder can be chosen so that the liquid which is led off at the top contains only particles of less than the chosen equivalent diameter. The material deposited inside the cylinder contains, as in the ordinary centrifuge, all sizes of particles, but the proportion of the smaller particles present will be even higher. This is due to the small radius of the cylinder which causes an extreme variation of the force acting on the particles, from zero along the axis to a very high value at the surface of the cylinder. The speed of rotation of the latter may be as high as 40,000 revolutions per minute. Under these conditions, in order to effect a clean separation by the super-centrifuge, an even larger number of successive treatments would be required than in the case of the ordinary tube centrifuge. It cannot, therefore, be used for quantitative mechanical analysis.

II. *Description of the New Method.*

A. *General Considerations.*—The ideal way of carrying out a mechanical analysis, either by the centrifuge or by gravity, would be to allow all particles of different sizes to move from the same plane, at a given time. They should move into the pure dispersion medium at their varying characteristic speeds with the largest particles in front and the smallest ones behind. The largest particles would reach the bottom of the vessel first. Any given equivalent diameter could be chosen and the time calculated for particles of this size to travel from the top of the column to the bottom, and when this time had elapsed the sediment would contain only particles larger than this and the supernatant liquid only the particles smaller. Removal of the sediment or of the top liquid would result in a quantitative fractionation in one operation. In practice this ideal can be nearly approached by starting with a thin layer of the poly-disperse system on top of a column of the dispersion medium. Since, however, the systems considered are denser than pure water, a stable layer cannot be obtained unless the lower column has some indifferent substance dissolved in it to raise its density above that of the suspension. Cane sugar and urea are two suitable substances. They are extremely soluble, and moderately concentrated solutions have a higher density than most suspensions. Although it is not possible to work with a layer of suspension infinitely thin, its thickness can be reduced in comparison with that of the whole column until the required accuracy is attained. In this case the sediment collected at the bottom of the column will contain all particles greater than r , where r corresponds to the movement through the total liquid column, and the supernatant liquid will contain all particles less than r_0 , where r_0 corresponds to the passage through

the lower column only. Thus both sediment and supernatant liquid will contain particles in the range r to r_0 . The problem, then, is so to choose the lower liquid and the dimensions of the two columns, that the range of overlapping r to r_0 is as small as is consistent with accuracy in other respects.

B. *Gravity Separations*.—It has not been found possible, so far, to apply these principles with any accuracy to the case of sedimentation under gravity. There are two main difficulties. The first is, that the boundary between the upper and lower liquids does not remain sharp. Owing to slight variations in temperature or concentration the upper liquid sends down "streamers" of suspension into the heavier liquid below. These may cause an error of several per cent. Secondly, the sediment is very loosely packed and it is not possible to separate quantitatively the supernatant liquid from it.

C. *Centrifugal Separation*.—The use of the high-speed centrifuge overcomes both these difficulties. The boundary between the two liquids actually becomes more sharply defined as centrifuging proceeds, and even if "streamer" formation has begun, the liquid of lower density moves rapidly back into place under its action. Experiments with coloured aqueous solutions overlying sugar solutions are most illuminating in showing the state of the boundary and its improvement with continued centrifuging. The second difficulty also disappears. The sediment generally adheres so well to the glass bottom of the centrifuge tube that the supernatant liquid can be quantitatively poured off without any special precautions. The sediment can be quantitatively washed out of the tube by a stream of water from a wash bottle.

The formation of the one layer above the other is very easily effected by the use of a pipette with the tip bent horizontally. The tip should be held against the wall of the tube on the surface of the heavier liquid and should be raised gradually as it empties so that the tip always remains in the upper surface. With a little practice a very sharp boundary can be established. It deteriorates on standing, and the tubes should be centrifuged as soon as possible after filling, although an interval of 10 minutes does not seriously affect the result.

(i) *Theoretical Development*.—In the centrifuge tube shown in the figure the thickness of the layer of clay suspension is $x_2 - x_1$ and that of the lower liquid $x_3 - x_2$, where x_1 , x_2 and x_3 represent distances from the axis of rotation. The lower liquid has a density d_2 and viscosity η_2 . At a speed of N revolutions per second the time taken for a particle of radius r and density D to travel from x_1 to x_2 is

$$t_1 = \frac{\log(x_2/x_1) \eta_1}{3.81 r^2 N^2 (D - d_1)}, \quad (3)$$

and from x_2 to x_3 it is

$$t_2 = \frac{\log(x_3/x_2) \eta_2}{3 \cdot 81 r^2 N^2 (D - d_2)}. \quad (4)$$

The total time

$$t = \frac{1}{3 \cdot 81 r^2 N^2} \left\{ \frac{\eta_1 \log x_2/x_1}{D - d_1} + \frac{\eta_2 \log x_3/x_2}{D - d_2} \right\}. \quad (5)$$

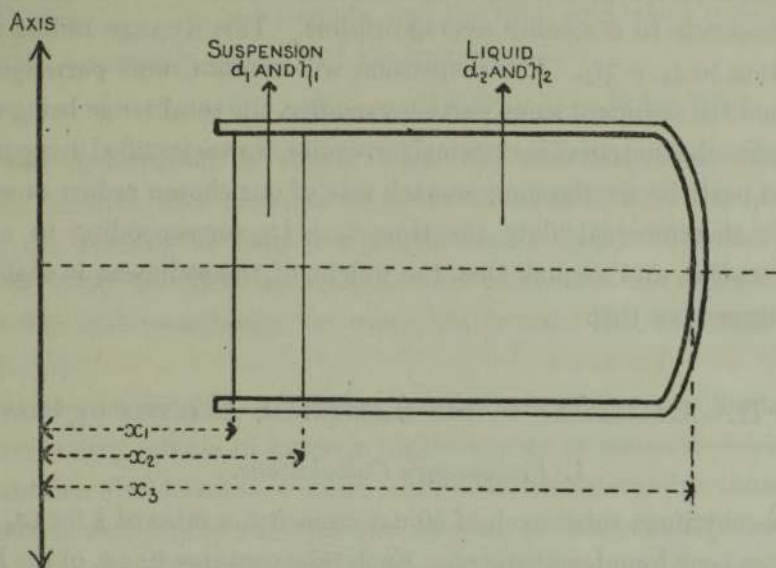


FIG. 1.

In this time t particles of radius r and all larger particles will be at the bottom of the tube. But there will also be some particles of radius less than r which have traversed distances between $x_3 - x_1$ and $x_2 - x_1$ in the time t , amongst the sediment. The smallest of these will have traversed $x_3 - x_2$ only. Let its radius be r_0 . Then from (4) and (5)

$$\frac{r^2}{r_0^2} = \frac{\log x_2/x_1}{\log x_3/x_2} \cdot \frac{\eta_1}{\eta_2} \cdot \frac{D - d_2}{D - d_1} + 1. \quad (6)$$

For accurate results this ratio should be as near unity as possible, that is, the first term on the right-hand side should be made small. Taking the various factors in turn, we should have $\log x_3/x_2 > \log x_2/x_1$. This is readily secured by making $x_2 - x_1$ small compared with $x_3 - x_2$. In order to obtain weighable amounts of sediment and using 50 c.c. centrifuge tubes, we cannot make $x_2 - x_1$ much less than 1/10th of $x_3 - x_2$. The author finds a ratio of 1 : 4 convenient (see below). The second factor η_1/η_2 can easily be reduced to $\frac{1}{2}$ or less by the use of sugar solutions with relative viscosities between 2 and 3. In this respect sugar is superior to urea. Finally $(D - d_2)/(D - d_1)$ will only be very slightly

greater than unity for dilute suspensions. Thus we can, without difficulty, reduce r^2/r_0^2 to 1.10 — 1.20, *i.e.*, r/r_0 to 1.05 — 1.10.

If in carrying out a mechanical analysis we choose a radius such that all particles larger will have settled through the whole combined column, we have a number of smaller particles in the sediment corresponding to the range $r - r_0$. The sediment is heavier than it should be, and the fraction reported really corresponds to a smaller average radius. This average radius is that corresponding to $t_2 + \frac{1}{2}t_1$. The suspension will contain some particles larger than this and the sediment some particles smaller, the total range being $r_0 - r$. Unless the distribution curve is extremely irregular, we are justified in considering the mass of particles overlapping on each side of our chosen radius as sensibly equal. We therefore calculate the time $t_2 + \frac{1}{2}t_1$ corresponding to a given equivalent radius, and assume that the weight of the sediment is that of the particles larger than this.

PART II.—APPLICATION TO THE MECHANICAL ANALYSIS OF CLAYS.

I. Preliminary Calculations.

With six centrifuge tubes each of 50 c.c. capacity, a ratio of $\frac{1}{4}$ for $(x_2 - x_1)/(x_3 - x_2)$ has been found convenient. Each tube contains 40 c.c. of the heavier lower liquid and 10 c.c. of the clay suspension, so that 60 c.c. of clay suspension can be treated as one operation. With a 0.5–1.0 per cent. clay suspension the fractions obtained are suitable for weighing. The tubes are marked at x_2 for convenience in filling. The actual dimensions are $x_1 = 5.65$ cm., $x_2 = 7.2$ cm., and $x_3 = 13.5$ cm. in the machine as used at present; thus $\log x_2/x_1 = 0.1050$ and $\log x_3/x_2 = 0.2728$.

The centrifuge used could be run at speeds varying from 2300 to 3900 revolutions per minute. The lowest speed was suitable for the separation of the fractions 1μ to 0.5μ , and the highest one for the finer fractions. When running the centrifuge at the lowest speed a correction had to be applied to the calculated value of $\frac{1}{2}t_1 + t_2$, due to the inequality of the acceleration and retardation which occupied an appreciable proportion of the time. The only time which can be controlled with accuracy is that which elapses from first switching on the electric motor to switching it off again. Starting at $t = 0$, let the centrifuge reach its steady velocity after a seconds, let it be switched off after b seconds and finally come to rest after c seconds. The force on a particle varies as the square of the speed, so that from $t = 0$ to $t = a$ seconds the average effect is given by the root-mean-square of the speeds measured at equal time intervals.

Thus the total effect is equivalent to $(b - a)$ seconds at the steady maximum speed, plus a seconds at the R.M.S. speed during acceleration, plus $(c - b)$ seconds at the R.M.S. speed during retardation. If these R.M.S. speeds are N_a and N_r revolutions per second,

$$\text{total equivalent time} = b - a + a \cdot N_a^2/N^2 + (c - b) N_r^2/N^2.$$

Now the measured time is b seconds, and the total equivalent time is $t_2 + \frac{1}{2}t_1$, so that the magnitude and sign of the correction is

$$b - (t_2 + \frac{1}{2}t_1) = a - a \cdot N_a^2/N^2 - (c - b) N_r^2/N^2.$$

Since the acceleration is slower than the retardation the correction is generally positive, and amounts to 40 to 60 seconds with the centrifuge in present use running at 2500 revolutions steady speed. For the maximum speed of 3500 to 3900 revolutions the correction is negligible, as the acceleration and retardation are more nearly alike and the total times are much longer.

The choice of suitable substances for the lower layer was limited to non-electrolytes very soluble in water, a high viscosity at moderate concentrations being another desideratum. Cane sugar was very naturally chosen; it can be obtained sufficiently pure for the purpose as lump sugar, although it is advisable to filter the concentrated solution before use. A stock solution of 450 gm. per litre was made up and diluted twice, or four times, for use in the centrifuge. The dilution was necessary because at 450 gm. per litre a slow partial coagulation of the clay could be observed in certain cases. No coagulation takes place at dilutions of $\times 2$ and $\times 4$, and the potential of the particles is only slightly reduced thereby, even in the case of the sensitive hydrogen clays. The dilution $\times 4$ is only used for the finest fractions so as to reduce the time of centrifuging by decreasing the viscosity of the lower liquid. The accuracy is also reduced somewhat owing to the increase in the ratio r/r_0 which is about 1.09 for dilution $\times 2$ and 1.13 for dilution $\times 4$. Urea has also been successfully used for the lower liquid. Even at 450 gm. per litre it does not appear to cause much coagulation. The densities and viscosities of the various solutions used are given in Table I. The density and viscosity of the clay layer are taken as those of water. For this reason the concentration should not be much above 0.5 per cent. if accuracy is to be attained, and even for qualitative work not above 1 per cent.

The times calculated for each size of particle can now be tabulated. Since both the speed of the centrifuge and the temperature are variable (the former owing to variations in bearing friction and motor power), the complete tables

Table I.

Substance.	Concentration in grams per litre.	Approximate density.	Viscosity at 15° C.	Viscosity at 20° C.
Cane sugar	450	1.170	0.0601	0.0541
	225	1.085	0.0226	0.0194
	112.5	1.042	0.0155	0.0135
Urea	450	1.112	0.0166	0.0151
	225	1.056	0.0129	0.0118
Water	—	1.000	0.0114	0.0101

are arranged so that the correct values of $t_2 + \frac{1}{2}t_1$ can be obtained by interpolation. As an example, Table II gives the complete data for the separation of particles of equivalent diameter 0.5μ , using sugar solution with 225 gm. per litre as lower liquid. In Table III the data at 20° C. for all the fractions

Table II.—Times taken for the Separation of all Particles greater than 0.5μ for various temperatures and speeds. Density of clay = 2.65.

Speed. Revolutions per minute.	Temperature.	t_1 .	t_2 .	$\frac{1}{2}t_1 + t_2$.
	° C.	secs.	secs.	min. secs.
2500	15	180	1001	19 41
2500	20	154	869	17 3
2700	15	155	871	17 6
2700	20	132	742	14 34
2900	15	133	747	14 40
2900	20	116	641	12 37

Correction for acceleration and retardation = + 49 seconds.

Table III.—Times taken for the Separation of Particles of various sizes at 20° C. Density of clay = 2.65.

Equivalent diameter.	Lower liquid.	Speed.	$\frac{1}{2}t_1 + t_2$.	r/r_0 .
$m \mu$.	gm. per litre.	r.p.m.	h. min. sec.	
500	Sugar 225	2700	0 14 34	1.09
200	Sugar 225	2700	1 19 47	1.09
200	Urea 450	2700	1 4 50	1.12
100	Sugar 225	3700	2 59 40	1.09
100	Urea 450	3700	2 18 20	1.12
50	Sugar 112.5	3700	8 0 0	1.13
50	Urea 225	3700	7 10 50	1.15

readily separated by this method in a reasonable time are collected. The correction is not included.

So far experiments have not been carried down to equivalent diameters less than $50\text{ m}\mu$, although by using a centrifuge of higher speed it should just be possible to get down to $20\text{ m}\mu$ in a working day. If reasonably large quantities of clay are to be qualitatively fractioned by this method the lower limit of $100\text{ m}\mu$ is most convenient with the present machine.

II. *Alternative Methods and Details of Technique.*

The quantitative mechanical analysis as described above is best referred to an ignited basis because of the traces of sugar or urea present in the sediment. If necessary this could be washed out by suspending in water, precipitating with a few drops of acid and washing by decantation, and the precipitated clay could then be dried at any desired temperature.

It can either be combined with an ordinary mechanical analysis by the pipette method or applied to the whole fraction less than $2\ \mu$ or less than $1\ \mu$ separated by decantation. Since the coarsest fraction determinable with accuracy by the centrifuge is $0.5\ \mu$ the total fraction less than $1\ \mu$ should be determined by the pipette method. In this way the whole range $2\ \mu$ – $50\text{ m}\mu$ or even $2\ \mu$ – $20\text{ m}\mu$ can be quantitatively fractionated in as many steps as required. Sufficient of the whole clay fraction for the centrifugal analysis can be obtained by sampling repeatedly at 10 cm. with 8-hour intervals. If the mechanical analysis by the pipette method is being carried out in quadruplicate two such repetitions will suffice. The 160 c.c. of clay obtained can be diluted to 320 c.c. with advantage if the soil contains 40 per cent. or more of the clay fraction so that four fractionations by the centrifuge can be carried out. The author usually takes the ranges $2\ \mu$ – $500\text{ m}\mu$, $2\ \mu$ – $200\text{ m}\mu$, $2\ \mu$ – $100\text{ m}\mu$, and $2\ \mu$ – $50\text{ m}\mu$ for successive treatments, the fraction $2\ \mu$ – $1\ \mu$ being obtained by the pipette method on the total soil residues in the sedimentation cylinders (10 cm. in 32 hours at 18° C.). The individual fractions are then calculated by difference.

In comparing different clays it is necessary to use the correct value for the density. This is easily determined on the total fraction less than $2\ \mu$ with the pycnometer, and the assumption must then be made that all the fractions have the same density. The extent to which this assumption is valid is being examined.

III. *Results Obtained.*

If the above considerations are valid, then, provided there is no coagulation of the clay, the same result should be obtained with different liquids. The

fact that duplicate estimations carried out with the same liquid at different temperatures agree well is hardly a sufficiently drastic test. We require to know also in what cases the lower liquid may cause coagulation and how that coagulation affects the different sizes of particles present.

(A) The agreement between duplicates carried out at different temperatures with the same liquid is within 1.5 per cent.

For the fraction $1 \mu - 0.46 \mu$ a sample of Putnam clay gave 11.4 and 10.7 per cent. respectively calculated on the original soil, or 19.0 and 17.8 per cent. calculated on the clay fraction.

For the same fraction in the case of bentonite values of 33.8, 33.1 and 32.6 per cent. were obtained calculated in material less than 1μ , or 34.8, 34.1 and 33.6 per cent. calculated on the total clay fraction.

(B) For a well-dispersed clay the effect of dilution below 1 per cent. is negligible.

The bentonite used for (A) above had been prepared by neutralising a well-washed hydrogen bentonite with NaOH to a p_H of 9. As used above the concentration was 0.985 gm. per 100 c.c., and the mean value for the fraction $1 \mu - 0.46 \mu$ was 33.2. On dilution $\times 4$ it was 32.0, which in view of the small amount ignited (0.0472 gm.) may be considered a satisfactory agreement.

(C) Comparison of different lower liquids.

Table IV shows the values obtained for urea and sugar solutions in the case of the bentonite suspension used in (A). The equivalent diameters do not correspond exactly with those of Table III, due to a miscalculation of the times taken for centrifuging.

Table IV.—Comparison of Sugar and Urea Solutions as Lower Liquids.
Bentonite concentration = 0.985 gm. per 100 c.c. Total Fraction less than 1μ .

Lower liquid.		Fraction.	Percentage of fraction.	Percentage of total bentonite.
	gm. per litre			
Urea	450	$1 \mu - 460 m\mu$	36.5	31.0
Sugar	225	$1 \mu - 460 m\mu$	33.2	28.2
Urea	450	$1 \mu - 230 m\mu$	48.3	41.0
Sugar	225	$1 \mu - 230 m\mu$	46.9	39.8
Urea	225	$1 \mu - 115 m\mu$	61.4	52.1
Sugar	112.5	$1 \mu - 115 m\mu$	60.1	51.0
		Less than $115 m\mu$	39.9	33.9

It would appear from the above that urea solutions with 450 gm. per litre are somewhat too concentrated. They apparently cause a slight coagulation of the coarser particles. It will be shown in the next section that partial coagulation may affect the various sizes of particles differently. That sugar solutions with 450 gm. per litre are too concentrated is shown by the fact that for the fraction $1\ \mu - 0.5\ \mu$ the values obtained were 6.6, 4.9 and 5.0 per cent. higher respectively than those with 20 per cent. sugar for the three methods of dispersion of bentonite given below in Table V. The results with diluted sugar solutions have shown that so long as the clay is suitably dispersed and diluted they may be relied upon. Cataphoresis measurements have shown that the potential of the double layer is only reduced a little by 20 per cent. sugar solutions (this is true both for hydrogen and sodium clays), and an ultra-microscopic count on a clay fraction suspended in water and in 20 per cent. sugar solution gave the same number of particles in each case. It does not follow, however, that 20 per cent. sugar solutions will have no action on concentrated clay suspensions, which are much more sensitive than dilute ones. In these cases macroscopic observations in test tubes may give little information because, as will be shown below, clays may undergo very large changes in degree of dispersion without any flocculation being noticed.

(D) Influence of the method of dispersion.

Three complete mechanical analyses of bentonite were carried out. In the first, 20 gr. material was simply dispersed in 1 litre of water. Since the bentonite used was a sodium-calcium clay, the sodium largely predominating, a high degree of dispersion was attained. The water-soluble material (mainly gypsum) was determined on a separate sample. In the second the procedure recommended by the International Society of Soil Science, namely, treatment with N/5 HCl, washing, and dispersion with ammonia, was used, but instead of 0.3N.NH₃, only 0.06N.NH₃ was used. In the third the International method was followed exactly. The results are given in Table V on an ignited basis. The International method gives the lowest result both for the total clay fraction and for the finest fraction less than 115 $m\mu$. None of these methods gives as high a value for the finest fraction as that given in Table IV, namely, 33.9 per cent., which was obtained on dispersion of the pure sodium clay.

For comparison the results of the mechanical analysis of Putnam clay, using dispersion by the International method (0.3 N.NH₃) are given in Table VI. The finest Putnam clay fractions are evidently better dispersed by the International method than the corresponding fractions in the case of bentonite.

It is evident that clays are much more sensitive to alkalis than has hitherto

Table V.—Influence of the Method of Dispersion on the Mechanical Analysis of Bentonite.

Fraction.	Equivalent diameter.	Dispersion medium.		
		Water.	0.06 N. NH_3 .	0.3 N. NH_3 .
Fine sand	0.2 — 0.02 mm.	4.8	3.7	3.6
Silt	0.02 — 0.002 mm.	10.8	22.7	28.0
Clay	Less than 2 μ	83.7	67.9	61.9
	2 μ — 1 μ	1.3	13.2	10.0
	1 μ — 460 $m\mu$	35.6	26.7	26.5
	460 $m\mu$ — 230 $m\mu$	3.5	6.4	5.7
	230 $m\mu$ — 115 $m\mu$	21.3	5.9	11.4
	Less than 115 $m\mu$	22.0	15.7	8.3
Soluble	(Water) 1.5	(HCl) 5.7	(HCl) 6.2

Table VI.—Mechanical Analysis of Putnam Clay.

Fraction.	Equivalent diameter.	Percentage.
Coarse sand	2 mm. — 0.2 mm.	0.0
Fine sand	0.2 mm. — 0.02 mm.	14.8
Silt	0.02 mm. — 0.002 mm.	26.8
Clay	Less than 2 μ	60.1
	2 μ — 1 μ	1.7
	1 μ — 0.46 μ	10.6
	0.46 μ — 0.23 μ	10.3
	0.23 μ — 0.11 μ	11.7
	0.11 μ — 0.07 μ	14.7
	Less than 70 $m\mu$	10.1
Soluble in N/5 HCl	1.6

been supposed, and that they can undergo partial coagulation without the total clay percentage being much altered. It is proposed to make an extended study of these phenomena using the new centrifuge method. It will be assumed, unless there is evidence to the contrary, that clays which have been electrolysed and then brought to a p_H of 8-9 by the addition of sodium or potassium hydroxide, are, at a sufficient dilution, in a state of maximum dispersion. It is known that under such conditions the potential of the double layer reaches a maximum value and that excess of alkali causes a marked decrease.*

* Private communication from Prof. R. Bradfield.

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Summary.

1. The various methods of applying the centrifuge to the quantitative mechanical analysis of continuously polydisperse systems are discussed. The existing methods are shown to be, at best, highly inconvenient, laborious and inaccurate.

2. A new method of using the high-speed laboratory centrifuge is worked out in detail and is shown to be applicable within the range $2 \mu - 20 m\mu$. Its accuracy is capable of considerable variation to suit different needs.

3. The accuracy of the new method under conditions suited to clays has been tested and it has been found reliable to about 1 per cent., which is comparable with the accuracy of existing methods for fractions greater than 2μ .

4. The variations in the degree of dispersion of bentonite under different conditions have been investigated as an example of the application of the new method to clay problems.

The Time Course of the Heat Effects in Rapid Chemical Changes.

Part I.—Apparatus and Methods.

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Introduction.

Continuous flow calorimetry has now been in use for upwards of 30 years, having been adopted in the first instance by Callendar and Barnes* for determination both of the specific heat of water at various temperatures and of J , the mechanical equivalent of heat. The principle of the method is simply that the fluid, upon which calorimetric observations are to be made, is driven continuously through a tube, and at a definite point or part of the tube acquires a certain amount of heat (by electric heating, mixture with another fluid or otherwise). The amount of heat in question is determined by noting the temperature of the moving fluid just before it reaches the heating zone, the temperature of the moving fluid just after it has passed the heating zone and M , the volume of fluid moving through the tube per second.

* 'Phil. Trans.,' A, vol. 199, p. 55 (1902).