AN IMPROVED SEDIMENTATION METHOD FOR THE DETERMINATION OF PARTICLE SIZES, USING AN AUTOMATIC RECORDER.

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The " sedimentation tube " method of determining the size distribution of particles in suspension consists in allowing the particles to sediment in a vertical tube which is provided with an open capillary side tube containing a suitable index liquid. The passage of particles past the orifice of the side tube (upwards or downwards as the case may be) produces, in the liquid contained in the main tube above this junction, a decrease in density proportional to the mass of particles sedimented. This change is recorded by a downward movement of the index liquid, and by determining the latter movement as a function of time, an accumulation curve may be plotted, whence the size distribution of the particles is calculable by use of Stokes' law.

Such a sedimentation tube was first used by Wiegner,[1] and modified by Ostwald and Hahn.[2] It was considerably improved by Kelley,[3] who bent the side tube, at a point nearly level with the surface of the suspension, into a nearly horizontal position. In this way, the movement of the meniscus is considerably magnified. A similar tube, adapted for systems in which the disperse phase is lighter than the medium, was used by Kraemer and Stamm.[4] Lambert and Wightman [5] described a means of recording the movement of the index photographically, and the present paper relates to improvements in the technique and theory of this method. All these experiments refer to suspensions in aqueous media.

The Sedimentation Tube.

The principal difficulty attending the use of a tube of this type is in obtaining free movement of the index. Previous workers have used water, or an aqueous solution of low surface tension, as the index liquid, but the difficulty of eliminating sticking with a water meniscus is well known, and considerable improvement has been effected by the writer by employing benzene. For this purpose a side tube is used, having the form shown in Fig. 1. The tube is in two sections, the joint being sealed by a short piece of rubber pressure tubing. The capillary attached to the vertical tube A is filled with dispersion medium (water or solution), while the index tube proper (B) contains benzene. The boundary between the liquids is in a wide cylindrical bulb C such that, for a movement of the index meniscus over its whole range, the movement of the boundary is accommodated within the cylindrical portion of the bulb. Since only *changes* in hydrostatic pressure are involved, the exact position of the boundary, when the tube is set up, is immaterial.

[1] Wiegner, *Landw. Versuchsstat.*, **91**, 41, 1919.
[2] Ostwald and Hahn. *Kolloid-Z.*, **30**, 62, 1922.
[3] Kelley, *Ind. Eng. Chem.*, **16**, 928, 1924.
[4] Kraemer and Stamm, *J. Amer. Chem. Soc.*, **46**, 2709, 1924.
[5] Lambert and Wightman, *J. Opt. Soc. Amer.*, **11**, 393, 1925.

The side tube is provided with a bulb D containing benzene, in order to minimise evaporation from the index meniscus. For a similar purpose the vertical tube A is provided with a special cap F, as described by Kelley. This has a small vent and incorporates a reservoir for the appropriate liquid. The tube illustrated is adapted for a rising disperse phase (after Kraemer and Stamm), and principal dimensions of the writer's example are given in the diagram. The capillary tube has a bore 2 mm. in diameter.

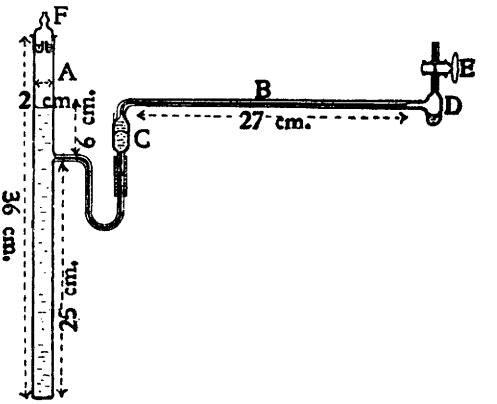

FIG. 1.—Sedimentation tube.

The components of the apparatus are cleansed separately in chromic acid mixture and washed with distilled water before use. The detachable side tube is then washed with alcohol or acetone and dried by drawing air through it. By careful suction and manipulation of the tap E, the tube B and upper portion of the bulb C are filled with benzene, the lower portion of C with solution; during this operation benzene is drawn over into the bulb D. With the tap closed, the side arm is attached to the main tube as shown; by manipulation of E the liquid is allowed to run back until it reaches the vertical tube. In order to avoid air bubbles, the bore at the lower end of the detachable side tube is bell-mouthed. The benzene level is maintained near the top by allowing sufficient liquid to run back from the reservoir C.

The apparatus is then fixed in position in the thermostat, and allowed to reach temperature equilibrium. The suspension, previously brought to the correct temperature, is run into the vertical tube to a suitable height, E is opened, and recording is begun.

With an aqueous liquid as the index, trouble due to sticking was experienced, and the movement exhibited considerable lag, but with benzene sticking is eliminated, and the index is much more mobile (see later).

The Recorder.

The recording camera is essentially similar to that described by Lambert and Wightman.[5] It comprises a box containing three rollers, whose axes are parallel to the side tube, arranged approximately in a vertical plane (see Fig. 2). Bromide paper from the bottom roller R_1 passes over the top roller R_2, which is an idler, and is wound on to the middle roller R_3. A light source placed vertically above the tube is illuminated periodically for a suitable fraction of time, and the optical action of the tube is such that an image of the liquid column is projected on to the sensitive paper through a slit on the top of the box. The record thus obtained gives the position of the index as a function of time. Measurements on the record are based on a reference line obtained by fixing a piece of fine wire across the slit at the lower end. The action of the camera is automatic.

An improved method of operating the camera has been described by the writer in a separate paper.[6] The motor for winding the exposed paper comes into operation only after an exposure has been made, for sufficient time to bring a new portion of paper into the field. In consequence a wide range of exposure frequencies may be provided, the apparatus described allowing of intervals of 1, 10, 20, 30, or 60 minutes between exposures. The frequency of exposures is varied according to the rapidity of sedimentation, and even during a single "run" may be decreased as the movement slows down.

The apparatus is set up in a light-tight air thermostat regulated to within 0·1° C. of the desired temperature (25° C. in this case), and the arrangement adopted by the writer is shown in Fig. 2. The baseboard A carries a vertical pillar B, to which the sedimentation tube is attached,

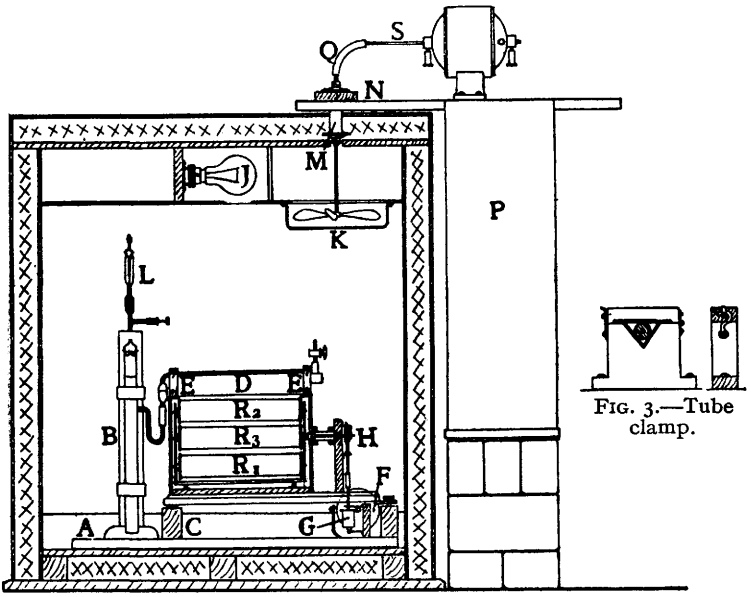

FIG. 2.—Arrangement of sedimentation apparatus.

FIG. 3.—Tube clamp.

and transverse blocks C on which rest (in slight depressions) the levelling screws of the camera D. The side arm of the sedimentation tube is supported in two wooden V-blocks E, which are fastened to the camera box. These blocks are lined with felt and have a hinged clamping member secured by a hook, the whole being made to fit the tube, without shake but without strain. (See Fig. 3.) Similar blocks are used to hold the vertical tube to the pillar. By this means the tube may be placed in position quickly and reproducibly. The rubber joint in the side arm enables the latter to be set at any convenient angle by adjustment of the camera alone, since the tube is attached to the camera and is always parallel to it. This direct attachment is made practicable by the discontinuous action of the camera, for since the winding motor is in operation for only a few seconds after each exposure, the vibration is negligible.

[6] Sumner, *J. Scientific Instruments*, **8**, 104, 1931.

The front of the camera is detachable, and the rollers are mounted in a frame which slides into the box between guides. Attachment of the middle roller to the winding shaft is by means of a dog clutch. The driving motor F is fastened to the floor of the thermostat, and drives the roller through two consecutive worm gears. The first gear G is mounted below the camera stand, similarly to the motor (the baseboard A being cut to accommodate it), and the second gear H is arranged on the stand itself. Details of the arrangement are given in the previous paper.

The illuminant is a 60-watt gas-filled lamp J, enclosed in a box which has a slit about 2 mm. wide, parallel to the side tube. The filament of the lamp is transverse to the slit, so that an approximation to a point source is obtained; this gives a sharp image. The slit is long enough for the whole length of the tube to be illuminated. The side tube is so disposed in relation to the paper and illuminant as to give the best image, this position being found by experiment. The duration of each exposure is 1½ seconds. With benzene the image is less intense than with water, but there is sufficient contrast for measurement. The paper used is Wellington Platino-Matt, single weight, 10 inches wide.

The thermostat comprises a lagged, double-walled box fitted with partitions so as to form a flue at the back, communicating with a warm air chamber at the top. Air is drawn into the flue at the bottom, which is open to the main enclosure, and passes across the heater, which consists of a grid of nichrome wire arranged in the flue. The warm air rises into the top compartment, whence it is driven downwards into the experimental enclosure by a fan K working just below an opening in the partition. A positive air circulation is thus maintained. The thermo-regulator L is supported at the rear of the pillar B; for temperature control an improved circuit, described elsewhere by the writer,[7] is used. The fan bearing is a cycle hub M attached to a board N, which is arranged just clear of the top of the thermostat. N in turn is carried from a resilient structure P built alongside the thermostat. The flexible drive Q from the extended motor shaft S consists of rubber pressure tubing. In this arrangement no part of the fan system is directly attached to the thermostat, and vibration is minimised.

Calibration.

The relation between the position of the index meniscus and the mass of particles sedimented is obtained by calibration, following the method of Lambert and Wightman. The vertical tube is filled with pure dispersion medium (water or solution), until the index stands near the upper limit of the range, and the recorder is started, exposures being made once per minute. Successive portions of liquid are then withdrawn in a weighed pipette of suitable form, and determined by weighing, until the index reaches the lower limit of the range. Time is given after each withdrawal for equilibrium to be regained.

The record so obtained shows the relation between displacements of the index, *on the paper*, and changes in hydrostatic pressure; also the speed with which equilibrium is regained. The desired relation with the mass of particles sedimented, which is derived at length by Lambert and Wightman, may be obtained very simply as follows.

[7] Sumner, *ibid.*, **7**, 398, 1930.

The movement due to a given decrease in hydrostatic pressure is entirely independent of how the change is produced. If, therefore, a displacement between two given points is produced (*a*) by withdrawal of δW gms. of water, (*b*) by sedimentation of δP gms. of particles, these two changes are equivalent. Let ρ_p, ρ_w be the densities of particles and medium respectively, A the cross-section of the main tube. In sedimentation, $\delta P/\rho_p$ c.c. of particles are replaced by the same volume of medium; the corresponding change in pressure is therefore $\delta P/A\rho_p$ $(\rho_p - \rho_w)$ gms. per sq. cm. Hence we have

$$\frac{\delta P}{A\rho_p}(\rho_p - \rho_w) = \frac{\delta W}{A}$$

or

$$\delta P = \delta W\left(\frac{\rho_p}{\rho_p - \rho_w}\right) \quad . \quad . \quad . \quad (1)$$

From the record and weighings a calibration curve may be plotted by means of this relation, giving δP as a function of the recorded length. With a uniform straight tube, if there were no parallax error this relation would be linear. In view of the error a slight curvature is to be expected, but with the particular tube described, it is found that no appreciable deviation from a straight line occurs.

In the experiments described by Lambert and Wightman, each sedimentation experiment is accompanied by a calibration. In a series of consecutive experiments, this is unnecessarily tedious, as it is found that the position of the apparatus is reproducible within the accuracy of experiment. It is therefore sufficient to use the same curve for a number of experiments, although it is advisable to check the calibration from time to time. A composite curve may be derived from a number of independent calibrations, which are arranged to overlap so as to obtain values at more points in the range of movement than is possible in a single experiment. The separate curves are compared by measuring values against l on a common graph, a "best curve" may be drawn, the value of dP/dl at various values of l. By plotting these dP/dl δP over any range being obtained by integration of the area under the curve.

Correction Due to Viscosity.

As has been pointed out by Lambert and Wightman, there is a lag in the movement of the index, due to its viscosity. The method of correction described, however, is not strictly accurate, and a simpler method is due to the writer.

Considering the calibration curve, let . . . l_0, l_0, l_1, l_2 . . . l_n . . . l, l, . . . be the lengths of column at successive minutes, l_0 and l being the equilibrium values before and after the withdrawal of δW gms. of solution. In the interval l_n to l_{n+1}, the mean effective pressure P will be proportional to $\frac{1}{2}(l_n + l_{n+1}) - l$, and the velocity will be $(l_n - l_{n+1})$ per minute. We have then

$$(l_n - l_{n+1}) \propto P/X,$$

where P/X is the effective pressure gradient. X will vary with the position of the index meniscus; for a small movement it will be sensibly constant, and

$$(l_n - l_{n+1}) = \frac{1}{k}[\tfrac{1}{2}(l_n + l_{n+1}) - l] \quad . \quad . \quad . \quad (2)$$

where k is constant. k may be evaluated by plotting $(l_n - l_{n+1})$ against $\left(\frac{l_n + l_{n+1}}{2} - l\right)$ for successive points. Since it involves X, some variation over the range of the index tube is to be expected.

Multiplying across by k and adding $\frac{1}{2}(l_n - l_{n+1})$ to both sides, we get

$$(k + \tfrac{1}{2})(l_n - l_{n+1}) = l_n - l \quad . \quad . \quad . \quad (3)$$

This is equivalent to the relation used by Lambert and Wightman. It is not permissible, however, to assume that it holds also for the sedimentation values, as is done by these authors. During sedimentation, the point of equilibrium for the index is moving continuously, and at any instant the lag of the meniscus behind its true position will be such that the pressure difference, due to the lag, suffices to impart to the liquid its observed velocity. Let l_n, l_{n+1} be the observed lengths of column at successive minutes, and l'_n, l'_{n+1} the corresponding true values. The mean lag of the meniscus in the interval will be $\frac{1}{2}(l_n + l_{n+1}) - \frac{1}{2}(l'_n + l'_{n+1})$, the observed velocity $(l_n - l_{n+1})$ per minute. Then we have

$$k(l_n - l_{n+1}) = \tfrac{1}{2}(l_n + l_{n+1}) - \tfrac{1}{2}(l'_n + l'_{n+1}). \quad . \quad . \quad . \quad (4)$$

That is, the mean lag is equal to k times the distance moved in the minute, *i.e.*, to the distance moved in k minutes if the speed is uniform over this range of time. This will be true at the beginning of the experiment, where also the error is most significant, since the movement is most rapid, and if k is small, it will hold closely for other points also. In other words, the meniscus should have reached its observed position k minutes before it actually does so. Applying this principle to the whole curve, it is evident that the corrected curve may be obtained from the observed curve by keeping the lengths unaltered and decreasing the time values by k minutes.

The significance of this correction depends on the rate of sedimentation; in all cases, however, it is offset by the fact that zero time on the record does not, in general, correspond with the actual beginning of sedimentation, but with some later time, depending on the time of pouring the suspension into the main tube. It may be assumed that the process of sedimentation starts when agitation of the suspension ceases. If, therefore, conditions are arranged so that pouring of the suspension into the tube is completed approximately k minutes before the first exposure occurs, the record itself will have a lag practically equal to that of the meniscus. The error in taking the record without correction then becomes negligible. With the writer's apparatus, it is found that k is of the same order over the whole range of the index tube, so that this is valid for the complete record. The first reading on the record may be unreliable, but the correct value is readily obtained by extrapolation.

In the apparatus described, using benzene as the index liquid, a new equilibrium in a calibration is nearly reached within one minute of withdrawing a quantity of solution, so that from (3), k is of the order $\frac{1}{2}$. With water, a new equilibrium had not been reached in five minutes after withdrawal. This difference is greater than can be attributed to the higher viscous resistance with water, and was probably due to surface tension effects, since sticking trouble was experienced also. Owing to the low surface tension of benzene, and the solvent action of the liquid on grease, trouble of this kind is not encountered in the

improved apparatus. A record of the meniscus in a steady state shows quite slight random variations about a mean position.

If to both sides of (4) we add $\frac{1}{2}(l_n - l_{n+1}) + \frac{1}{2}(l'_n - l'_{n+1})$, which is equal to $(l_n - l_{n+1})$ if the speed is uniform, we obtain

$$(k + 1)(l_n - l_{n+1}) = l_n - l'_{n+1} \quad . \quad . \quad . \quad (5)$$

which differs from the expression

$$(k + \tfrac{1}{2})(l_n - l_{n+1}) = l_n - l'_{n+1} \quad . \quad . \quad . \quad (6)$$

used when applying (3) to the sedimentation values, as suggested by Lambert and Wightman. The latter correction is too small by

$$\tfrac{1}{2}(l_n - l_{n+1}).$$

Derivation of Distribution Curve.

A curve showing the mass distribution of the particles over the range of sizes may be derived as follows. Let P be the total mass of particles which have passed the orifice in time t from the beginning of sedimentation. If h is the maximum distance to be traversed by the particles (*i.e.*, the distance of the orifice from the upper or lower surface of the liquid, according as $(\rho_p - \rho_w)$ is positive or negative), then after time t all particles having velocities greater than h/t will have settled out completely; let the total mass of such particles be S. Then it may be shown readily that

$$S = P - t\frac{dP}{dt} \quad . \quad . \quad . \quad . \quad (7)$$

The sedimentation record (in conjunction with the calibration curve) gives the (P, t) curve, and from this the values of S at various t values may be obtained by drawing tangents to the curve at the appropriate points. The intercept cut off the P axis by a tangent is evidently $\left(P - t\frac{dP}{dt}\right)$, which is equal to S by equation (7). This method is described by Svedberg.[8]

If r is the radius of particles having the velocity h/t, we have by Stokes' law

$$h/t = \frac{2}{9}g\left(\frac{\rho_p - \rho_w}{\eta}\right)r^2 \quad . \quad . \quad . \quad . \quad (8)$$

or

$$r^2 = \frac{9}{2} \cdot \frac{h\eta}{g(\rho_p - \rho_w)} \cdot \frac{1}{t} = \frac{c}{t} \quad . \quad . \quad . \quad (9)$$

where η is the viscosity of the medium and g the gravity constant.

A curve may be plotted, having either S or dS/dr as ordinate and r as abscissa, by deriving S or δS from the (P, t) curve as described, and the corresponding r and δr values by use of equation (8). dS/dr is taken as the value of $\delta S/\delta r$ at the middle of the interval. Previous workers have used the values corresponding to equal intervals of *time*, but a considerable saving in calculation, in the case of the differential curve, is achieved by working in terms of equal intervals of *radius*. The times corresponding to δr, $2\delta r$ . . . $n\delta r$ . . . are calculated from equation (8), and tangents to the (P, t) curve are drawn at the calculated points. The $\delta S/\delta r$ values may be plotted against r as before, or the δS values read off may be

[8] Svedberg, *Colloid Chemistry*, 1928, p. 176 *et seq.*

plotted against $n(=r/\delta r)$. In either case integration of the area under the curve gives S over the range in question; the latter method is, however, less laborious.

It is convenient in many cases to use the fraction S/S_∞, where S_∞ is the quantity corresponding with complete sedimentation. If the calibration curve of the apparatus is linear to within a sufficient degree of accuracy, S/S_∞ is equal to the ratio of the corresponding lengths of column. In such a case, it is unnecessary to use the calibration at all; the curve is plotted in terms of length instead of mass. Where this does not hold, or where the mass of particles is wanted, the calibration must be used.

It is to be noticed that no correction is necessary for a *uniform* downward drift of the index, due to evaporation. The effect of this is to increase the apparent values of P and $t\frac{dP}{dt}$ by equal amounts, so that the derived S values are independent of the error. Such a slight drift is actually observed.

This method was developed in the "Thomas Graham" Colloid Research Laboratory in the Victoria University of Manchester. Thanks are due to Mr. D. C. Henry, director of this laboratory, for facilities afforded, and also to the Department of Scientific and Industrial Research for a Senior Research Award.

Summary.

An improved technique, developed from the method of Lambert and Wightman, is described, for applying an automatic recording camera to the determination of particle sizes by a sedimentation tube method. Special features include a tube arranged for the use of benzene as the index liquid, a new design of discontinuous recording camera, and a simple method of correcting for the effect of viscosity in the index tube. Simplified means of deriving the calibration equation and of deducing the size distribution from the experimental record, are also given.