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PARTICLE-SIZE DISTRIBUTION OF THORIUM OXIDE BY A CENTRIFUGAL SEDIMENTATION METHOD

O. Menis
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ABSTRACT

A cumulative, centrifugal sedimentation method, which is applicable to the determination of the particle-size distribution of thorium oxide in the particle-size range of 0.1 to 2.0 microns in diameter, is described. This method circumvents the objectionable effects of convection currents and Brownian movement and the inconveniently long sedimentation periods incident to the application of gravitational sedimentation methods to particulate matter less than two microns in diameter. By selection of suitable operating conditions it is possible to accomplish sedimentation in small, cylindrical-shaped cells in 25 minutes or less. Under these selected conditions of sedimentation the particle-size distribution can be obtained from the cumulative sedimentation data by the application of either Oden's method of tangential intercepts orafuncton-plot method. Results by this centrifugal method correlate well with results obtained by different gravitational sedimentation methods for the portion of sample composed of particles greater than two microns in diameter.

PARTICLE-SIZE DISTRIBUTION OF THORIUM OXIDE BY A CENTRIFUGAL SEDIMENTATION METHOD

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INTRODUCTION

Slurries of thorium oxide in aqueous media are under test for use as blankets of fertile material in two-region breeder reactors. Physical properties which may be used for characterization of thorium oxide or correlated with pumping characteristics, settling rates or stability are of special interest and must be determined. One physical property of importance in the characterization of thorium oxide, which is related to the hydrodynamic behavior of slurries, is the size distribution of thorium oxide particles. A gravitational sedimentation method (Andreasen pipet method) was used initially to measure this property of thorium oxide. Samples included thorium oxide that are used for the preparation of slurries and slurries after circulation in test loops. Within the particle-size range, 2 to 10 microns in diameter, for which the Andreasen pipet method is particularly applicable, this method is being used regularly for the measurement of particle-size distribution. For thorium oxide particles less than two microns in diameter, difficulties are encountered in the application of gravitational sedimentation methods. With decreasing particle size, the period of sedimentation becomes excessively long and, furthermore, the effects of convection currents and the Brownian movement become increasingly important and tend to invalidate the test results. A method was, therefore, sought for the determination of the particle-size

distribution of particulate matter less than two microns in diameter which would circumvent the difficulties incident to gravitational sedimentation methods. For this purpose, a centrifugal sedimentation method, which is widely used in the field of colloid chemistry, was utilized. Suitable operating conditions were selected and the method was established to supplement the Andreasen pipet method. By the selection of appropriate operating conditions, the centrifugal method can be used to reduce the time of sedimentation enormously. For instance, thorium oxide particles 0.1 micron in diameter in a xylene medium require four days to fall three cm by gravity sedimentation, whereas, by centrifugal sedimentation at 1,800 rpm, the time can be reduced to about 15 minutes. This reduction in time of sedimentation not only makes it possible to carry out particle distribution measurements for extremely small particles in a reasonable time, but it also reduces errors caused by diffusion and convection.

The centrifugal method, like all sedimentation methods, is based on Stokes' law, which relates the radius of a particle with its limiting velocity of sedimentation according to the following equation,

$$V_o = \frac{2\, g\, r^2\, (\rho - \rho')}{9\, \eta} \qquad (1)$$

V_o = limiting velocity, cm/sec

g = acceleration due to gravity, 980 cm/sec^2

r = radius of particle, cm

ρ = density of particle, g/cm^3

ρ' = density of medium, g/cm^3

η = viscosity of medium, poises

The limiting velocity (V_o), or the constant velocity at which a particle falls through a viscous medium after a short initial period of acceleration, equals h/t where h equals the distance in centimeters through which a particle falls in t seconds. By substituting h/t for V_o and the diameter (D) of the particle for 2r in equation (1) and rearranging, the following form of the Stokes' law equation is obtained:

$$D = \sqrt{\frac{18\,\eta\,h}{(\rho - \rho')\,gt}} \qquad (2)$$

Equation (2) is useful for calculating the particle size from gravitational sedimentation data; however, in applying centrifugal force to increase the rate of sedimentation, the particles no longer fall under the conditions of a constant force of gravitation. The centrifugal force equals $\omega^2 r$ where ω is the angular velocity in radians per second and r is the distance from the axis of rotation; therefore, as the particles move away from the axis of rotation, the centrifugal force increases continuously and the Stokes' law equation no longer applies without modification. Svedberg and Nichols[8] modified the Stokes' law equation to make it applicable to centrifugal sedimentation. For h/g of equation (2) they substituted $\frac{\ln r_2/r_1}{\omega^2}$, where

r_1 = distance from the axis of rotation to the meniscus of the suspension, cm

r_2 = distance from the axis of rotation to some selected point below the meniscus of the suspension, cm

The Svedberg and Nichols equation is

$$D = \sqrt{\frac{18\,\eta \ln r_2/r_1}{(\rho - \rho')\,\omega^2\,t}} \qquad (3)$$

For a fixed set of experimental conditions, equation (3) may be reduced to the form,

$$t = K \frac{1}{D^2}$$

in which the constant, K, combines fixed values for η ρ, ρ', r_1, r_2, and ω. Several factors must be considered in the selection of appropriate values for the variables r_1, r_2, and ω whereby sedimentation will be effected in a convenient time interval without introducing serious errors due to unwarranted approximations. Since the Sverdberg and Nichols equation provides for the change in centrifugal force as a particle moves away from the axis of rotation, this equation may be used to calculate the time required for sedimentation of all particles of a specific size (See Appendix A, Table I); however, the theoretical time of sedimentation calculated by the Svedberg and Nichols equation will not be the same as the measured time because the centrifugal force changes continuously during the acceleration and deceleration intervals. In practice, the time required to accelerate the centrifuge to a selected speed and to decelerate from the selected speed is determined experimentally. Equivalent periods of time for the acceleration and deceleration intervals are then computed. This is accomplished by plotting centrifugal force versus time and graphically intergrating the areas under the portions of the curve corresponding to the acceleration and deceleration intervals. The equivalent time intervals are the periods of time which, at the selected speed, would have been required to settle a particle through the same distance which it settled during the acceleration and deceleration intervals.

The relationship between actual and theoretical time intervals can best be shown as follows:

Let t_a = measured time of acceleration, seconds

t_c = period of time during which centrifuge was operated at a selected, constant speed, seconds

t_d = measured time of deceleration, seconds

t_m = total actual time of centrifugation, measured from the start to the time at which deceleration begins, seconds

t_a', t_d' = equivalent time intervals for acceleration and deceleration, seconds .

t_{th} = theoretical period of time for the sedimentation of a particle of a specific diameter through the distance $r_2 - r_1$ at the selected centrifuge speed, second (calculated by means of equation 3)

$$t_{th} = t_a' + t_c + t_d' \qquad (5)$$

$$t_c = t_{th} - (t_a' + t_d') \qquad (6)$$

$$t_m = t_c + t_a \qquad (7)$$

Actual and equivalent time intervals of acceleration and deceleration for several centrifuge speeds are tabulated in Appendix A, Table II. The theoretical periods of time (t_{th}) required for the sedimentation of particles of thorium oxide ranging from 0.1 to 2 microns in diameter in aqueous and in xylene media at specific centrifugal speeds are also tabulated in Appendix A, Table I. By reference to these tables and application of equations (6) and (7), the actual time intervals of centrifugation, for the particular centrifuge to which these tables apply, can be calculated.

The rate of acceleration and deceleration must also be controlled within specific limits; otherwise tangential forces will lead to the

deposition of particles on the walls of the tube. Berg[2] presents a theoretical treatment of this subject. He concluded that, for small centrifuge tubes suspended 10 cm from the axis of rotation, acceleration must not exceed 100 rpm during the first 10 seconds, after which the centrifuge may be accelerated to any desired speed in an additional 10 seconds. In deceleration, the speed may be reduced to 100 rpm in 10 seconds, after which a minimum of 10 seconds is required to stop the centrifuge completely.

Another factor that must be considered in the selection of operating conditions is the shape and dimensions of the sedimentation cell. Particles moving under a centrifugal force do not follow parallel paths but move radially outwards from the axis of rotation; hence, a sector-shaped cell is required if hindered sedimentation is to be avoided at the walls. Cells of this design have been fabricated and utilized by others.[2,4,7] It has been established, however, that cylindrical shaped cells may be used without introducing significant errors due to hindered settling, if the ratio r_2/r_1 is less than 1.4.[7] In the applications described herein, this condition is fulfilled by making r_1 equal to 8 cm and r_2 equal to 11 cm; the r_2/r_1 ratio is, therefore, 1.38.

The centrifuge was operated at speeds which would produce sedimentation within convenient time intervals, usually within approximately 2 to 25 minutes. For particles of thorium oxide ranging in size from 0.1 to 2 microns in diameter in aqueous or xylene media, with r_1 equal to 8 cm and r_2 equal to 11 cm, the required centrifuge speeds ranged from 300 to 1,800 rpm (See Appendix A, Table I). The conditions of sedimentation were so selected that

the equivalent time intervals for acceleration and deceleration do not represent a major portion of the entire theoretical period.

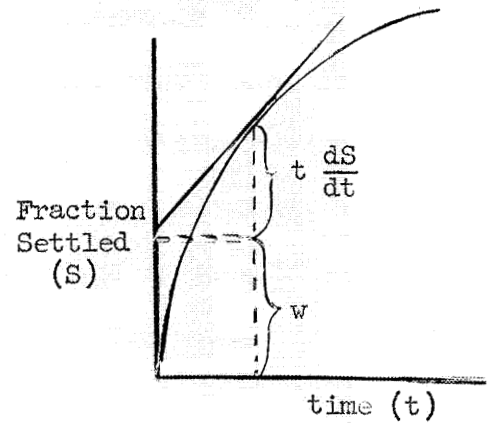
Centrifugal methods, like those of gravitational sedimentation, may be incremental or cumulative. In incremental methods, the concentration of suspended material at some point (or points) below the surface of the suspension is determined after successive intervals of time. By the application of Stokes' law or, if centrifugal force is used, by the Svedberg and Nichols equation, the particle diameters related to these points and time intervals are calculated. In the gravitational method, the measured concentrations, when expressed as percentage of the original concentration, are the weight percentages of the material less than the particular particle sizes which were chosen. This simple relationship does not hold in centrifugal sedimentation.[2,5] The measured concentrations must be corrected to obtain the true particle-size distribution. In cumulative methods, the total amount of the material which has settled below a certain level, within a specific time interval, is determined. This procedure is repeated for succeeding time intervals. From these data and a knowledge of the total amount of solid material initially suspended, the particle-size distribution can be calculated. Both the incremental and cumulative methods have been applied to centrifugal sedimentation. The latter method can be carried out with less exacting measurements of volumes and depths than the former and involves fewer correction calculations; therefore, it has been selected for use in the procedure which is outlined herein.

In the cumulative method, a uniform suspension is centrifuged until all particles of a specific diameter or larger have settled below a certain

level (r_2). The fraction of the material which has settled below the fixed level is then determined. In the present work, the fixed level was taken at 2 mm above the bottom of the centrifuge tube or 3.0 cm below the meniscus(r_1) of the suspension. After centrifugation for a specific period of time, the suspension above the 2-mm level was removed by means of a pipet. The thorium oxide in this suspension and also that remaining in the tube below the 2-mm level was determined by chemical analysis. The thorium oxide in the zone within 2 mm of the bottom of the tube was composed principally of particles which had settled during the centrifugation. Since 1/16 of the suspended material was initially in this zone, however, it was necessary to subtract this amount from the total thorium oxide found in this zone in order to estimate the amount that had entered the zone as a consequence of sedimentation. The solid matter contained in this zone will include not only the particles with diameters equal to or greater than that required to fall 3.0 cm under the conditions of this test but also finer particles which settled from intermediate heights to the 2-mm level during the centrifugation. A correction must be applied for these fine particles before the percentage of the material composed of particles with diameters equal to or greater than the limiting diameter fixed by the experimental conditions can be computed. This may be done by Oden's method of tangential intercepts[1] which applies rigidly to data taken by gravity sedimentation and to centrifugal sedimentation, without significant error, if the operating conditions are such that the variation in centrifugal force throughout the suspension is small and therefore similar to the constant force present in the process of sedimentation by gravitational force. This condition is approached by keeping the

ratio or r_2 to r_1 small. Martin[6] has found that a ratio of 1.5 is acceptable.

Oden's method of tangential intercepts may be explained as follows: when the fraction of the solid material which has settled is plotted versus time,



each point on the curve is related to w by the following equation:

$$w = S - t\,\frac{dS}{dt}\,, \qquad (8)$$

where S is the total fraction deposited at any time t and w is the fraction which consists of particles large enough that they are settled the total distance, $r_2 - r_1$, in time t or less. The term, dS/dt, is the slope (m) of the tangent to the curve and mt is the amount of fine particles which settled from intermediate heights. In practice, the slope of the tangent need not be determined, since the intercept of the tangent with the sediment axis is w, the quantity desired. In centrifugal sedimentation where time is a variable dependent on the angular velocity used, the fraction settled is plotted versus $1/D^2$.

Oden's method is quite satisfactory for determining w for intermediate values of $1/D^2$. For points on the segments of the curve for the fraction settled versus $1/D^2$ which digress only slightly from vertical or horizontal

(initial and terminal segments), it is difficult to construct a tangent accurately Small errors in fixing the slope of the tangent will result in large errors in fixing the position of w; therefore, another method for obtaining w from cumulative sedimentation data was also used. In this method some function of S was plotted versus $1/D^2$ and then w was calculated from the slope of the resulting curve. It was found that when ln 1/1-S was chosen as the function of S, which was plotted versus $1/D^2$, the resulting curve was either a straight line or more nearly approximated a straight line than the curve obtained when S was used. The value of w could be found from the slope (m) of this curve or, if the curve is not linear, of a tangent at any point, $1/D^2$, by the equation

$$w = S - m\left(\frac{1}{D^2}\right)(1 - S) \qquad (9)$$

The difficulty in establishing values of w was thus reduced by the use of this method, since tangents to this curve could be more accurately constructed.

EXPERIMENTAL

Apparatus. An International Clinical centrifuge was used. This centrifuge, which was operated on 115-volt alternating current, was equipped with a 4-place head, taking No. 303 shields. The sedimentation tubes were 2-dram, glass vials, 1.5-cm inside diameter by 6 cm in height, fitted with plastic screw caps. The vials were marked 3.2 cm from the bottom to indicate the height to which they were to be filled. These vials fit closely in the shields. Each vial was suspended in the upper section of its shield by the cap which exceeded the shield in diameter. The calibration mark which

indicated the position of the meniscus of the suspension was 8 cm from the axis of rotation when the vials assumed a horizontal position during centrifugation. The distance from the meniscus to a level 2 mm from the bottom of the vial was considered to be the sedimentation distance; therefore the distance from the axis of rotation to the level at which the particles were settled was 11 cm and r_2/r_1 (equation 3) equaled 11/8 or 1.38.

The speed of the centrifuge was indicated continuously by a tachometer generator (Weston Model 774, Type A-3) which was attached to the lid of the centrifuge and coupled to an extension of the centrifuge motor shaft by means of a V-notch contact. The DC-voltage output of this tachometer, which was proportional to the speed, was measured by means of a Weston, 3-range, DC voltmeter. A stroboscope (General Radio Strobotac, Model 631 BL) was used as a standard speed indicator to calibrate the tachometer; by this means the output of the tachometer generator was found to be 4.12 volts per 100 rpm. (A hand tachometer was also tested and found to be much less satisfactory than the tachometer-generator because it produced a variable drag which greatly affected the speed of the centrifuge.)

The speed of the centrifuge was regulated by means of a Powerstat variable transformer which was substituted for the rheostat control, built into the base of the centrifuge. By means of this arrangement, marked variations in the temperature of the bowl due to heat dissipation from the rheostat were prevented. The Powerstat was connected to the centrifuge motor in such a manner as to supply variable current rather than the customary variable voltage. By the use of this control, together with a voltage regulator (Sola 120 volt-amp, constant voltage transformer), the

the stability and reproducibility of the centrifuge speed was improved over that attainable by use of the rheostat provided with the centrifuge.

A Thompson electric stop clock was used to measure the time of centrifugation.

A 5-ml transfer pipet was used to remove the suspension above the 2-mm level after the centrifugation was completed. The pipet was attached to a ring stand by means of a clamp. A No. 18 hypodermic needle was attached to the pipet by means of a short piece of rubber tubing. The tip of the needle was bent at a right angle to reduce disturbance of the sediment while the supernatant suspension was being removed. A 5-ml hypodermic syringe, connected to the pipet with rubber tubing, was used to draw up the suspensions.

Operational Technique. Approximately 0.5 g of sample (dry thorium oxide or thorium oxide slurry) was added to 100 ml of the aqueous medium or the dry oxide was added to 100 ml of xylene that contained 0.2 ml of oleic acid. In either case, the suspension was dispersed by agitation in a Waring blender for three minutes or by shaking for several hours with a mechanical shaker (Burrell, wrist-action Model BT). Before placement of a portion of the suspension in the centrifuge tube, the suspension was shaken by hand to insure that the portion removed was representative. Approximately 5 ml of the suspension was then removed by means of a pipet with a large tip opening, after which a sufficient volume of the suspension was added to a sedimentation tube to fill the tube to the 3.2-cm calibration mark. The sedimentation tube was capped, shaken vigorously, and then placed in a centrifuge shield. A similar tube, filled to the calibration mark with water, was placed in the opposite shield to balance the centrifuge. The centrifuge lid was then closed, thus engaging the tachometer, following

which the centrifuge was started immediately at a predetermined setting of the Powerstat which was slightly in excess of that required to attain the maximum speed desired. At the same time, the electric timer was started. After acceleration to the desired speed, the Powerstat setting was reduced slightly to the setting necessary to maintain the selected speed. During the centrifugation it was occasionally necessary to adjust the Powerstat slightly to maintain a constant speed. After the time necessary to settle particles of a specific size had elapsed, the Powerstat control was turned back to a position slightly below the predetermined minimum setting at which the centrifuge will operate. The deceleration was, therefore, carried out with a small current going through the centrifuge motor which was sufficient to prevent an extremely rapid rate of deceleration and also gave a very slow terminal deceleration.

After the centrifuge had stopped, the tube containing the suspension was quickly but carefully removed, uncapped, and then placed in a clamp below the pipet. The tube was then raised slowly until the tip of the hypodermic needle attached to the pipet was 2 mm from the bottom of the tube. By means of the attached syringe, the suspension above the 2-mm level was drawn up into the pipet, without distributing the settled material on the bottom of the tube; thus, the sample was separated into settled and unsettled portions. The centrifugation procedure was repeated on separate aliquants at appropriate speeds and time intervals for at least five different particle sizes ranging from 0.1 to 2 microns in diameter. If practical, data were obtained for at least two particle sizes larger and two smaller than the mean particle size.

The amount of thorium oxide in each portion was determined by the use of a spectrophotometric method in which Thoron was used as the chromogenic reagent.(9) The thorium oxide in aqueous suspensions was dissolved in a mixture of nitric and perchloric acid to which a drop of 1:10 hydrofluoric acid was added. If the suspending medium was xylene, the xylene was removed by evaporation prior to dissolution of the thorium oxide by the acid treatment. The acid solution was diluted to a specific volume from which an aliquot was withdrawn for the determination of thorium.

Calculation of Distribution. From the amount of thorium found, the fraction of the sample settled in each case is calculated in the following manner.

Let M = quantity of ThO_2 found below the 2-mm level, mg

N = quantity of ThO_2 found in the portion withdrawn from above the 2-mm level, mg

P = quantity of ThO_2 initially present below the 2-mm level, $1/16\ (N + M)$, mg

S = fraction of ThO_2 settled below the 2-mm level

w = fraction of sample composed of particles with diameters equal to or greater than the limiting diameter (D) which settled below the 2-mm level

D = limiting diameter (diameter of particle that settled 3 cm during centrifugation under the specific operating conditions)

Then $$S = \frac{M - P}{N + M - P}$$

If Oden's method of tangential intercepts is used to determine w, plot S as the ordinate versus $1/D^2$, for the values of S which were found for the different selected values of D. Draw a tangent to the curve at specific values for $1/D^2$. The intercept of the tangent with the ordinate axis is equal to w.

If the function method is used to determine w, plot ln 1/1-S versus $1/D^2$; then determine the slope (m) of this curve (if a straight line) or of tangents to this curve at the different selected values for $1/D^2$. Then calculate w by means of the equation

$$w = S - m\left(\frac{1}{D^2}\right)(1 - S)$$

Finally

100 w = per cent of total solids composed of particles with diameters equal to or greater than D

100 (1 - w) = per cent undersize

The particle-size distribution is ordinarily presented graphically by plotting the limiting diameters (D), as the ordinate, versus per cent undersize, as the abscissa, on log-probability graph paper (See Appendix, Figures 3, 4, 5).

Description of the ThO_2 Samples Used as Typical Samples. The following samples, received from the Reactor Experimental Engineering Division, were chosen as typical samples for illustrating the application of this centrifugal sedimentation method for particle-size determinations.

Sample	Code		Description
A	CS-21	(LO-2)	Thorium oxide prepared by Lindsay Chemical Company by ignition of thorium oxalate to 800°C. This sample had also been circulated as a water slurry in C-loop for 30 hours.
B	LO-7-RS-A	(LO-7)	Thorium oxide prepared by Lindsay Chemical Company by ignition of thorium oxalate to 800°C. This sample had also been dispersed in water by a Day Rapisonic Homogenizer.
C	S-5		Thorium oxide prepared by ignition of thorium formate to 650°C. This sample had also been circulated as a water slurry in S-loop (Run 49) for 1500 hours, a sodium silicate solution added and the slurry autoclaved at 250°C.

DISCUSSION

The centrifugal sedimentation method described in a preceding section has been applied to the evaluation of the particle-size distribution of thorium oxide in a variety of samples. The majority consisted of aqueous slurries containing small amounts of stabilizing agents (sulfate, silicate, or pyrophosphate) in which the oxide had been subjected to the forces encountered during rapid circulation in test loops under high pressure and at elevated temperatures. A number of samples of thorium oxide degraded by means of devices such as micropulverizers, homogenizers or colloid mills were also subjected to examination. The centrifugal method has been found to be particularly useful for the determination of the particle size of fractions less than two microns in diameter; in many cases, this fraction encompassed 70 to 90 per cent of the sample.

The two variables commonly used to fix the limiting diameter of particles settled were sedimentation time and centrifugal speed. The entire range of limiting particle size from 0.1 to 2 microns was covered by selection of centrifugal speeds within the range, 300 to 1,800 rpm, and sedimentation times from 2 to 25 minutes. With slight changes in r_1 and r_2, and a moderate increase in centrifugal speed, the particle-size range can be extended to 0.03 micron, if desired, without increasing the sedimentation interval to more than one hour.

Gravitational methods were used for the fraction which contained the particulate matter larger than two microns in diameter. Typical test results are presented graphically in the Appendix, Figures 3, 4, 5, as log-probability curves. A log-normal distribution is indicated by a

linear graph.[3] Distribution data for a particular sample by the gravitational and centrifugal methods do not over-lap appreciably because each technique was applied to different size ranges. The fact, however, that the distribution data by both methods plot as a straight line is indicative of the high degree of correlation attained. In Figure 3, data for the particle-size distribution for throium oxide which was determined by the centrifugal method and that which was obtained by a gravitational method, utilizing an activation analysis technique,[5] are plotted as a log-probability curve. The dispersing medium used for both methods was 0.001 M $Na_4P_2O_7$. In this case, a straight line can be drawn from which no point digresses by more than four per cent.

In Figure 4, the particle-size distribution of a thorium oxide, as determined by the centrifugal method and also by two different gravitational methods, is presented graphically. Three different dispersing media were used. The test results by the Andreasen pipet method indicate that the thorium oxide was slightly more finely divided in 0.001 M $Na_4P_2O_7$ than in xylene that contains a small amount of oleic acid. Yet the points do not digress widely from a straight line; this indicates that the particle-size distribution is log normal and that the dispersion was not greatly affected either by the method used or by the medium in which the test was made.

With some samples of thorium oxide, however, the medium in which the thorium oxide was dispersed affected the dispersion to a marked degree. This is illustrated by the data presented in Table IX and Figure 5. The thorium oxide used in these tests had been degraded by circulation for 1,500 hours in a test loop. Sodium silicate had been added to the aqueous slurry. Test data from centrifugal sedimentation tests made either in

0.005 M sulfuric acid or 0.001 M solutions of $Na_4P_2O_7$, indicate that almost all the thorium oxide was dispersed as particles within the range, 0.1 to 0.5 microns. When the centrifugal method was used with xylene as the dispersing medium, the particle-size distribution was quite different. The fraction less than 0.1 micron in diameter increased to 30 per cent; at the same time, the fraction consisting of particles larger than 0.5 microns in diameter increased to approximately 20 per cent. The distribution as determined in a xylene medium by a gravitational sedimentation, using the Andreasen pipet or the Wagner turbidimeter,(10) correlates well with the data by centrifugal sedimentation in the same medium. From the particle-size distribution in a 0.005 M solution of $Na_4P_2O_7$, as determined by activation analysis, it is indicated that the dispersion was somewhat less in this medium than it was in xylene.

In the application of the cumulative centrifugal sedimentation method, the total solid material which settled is determined. As previously discussed, the fraction of the total solids settled which consist of particles larger than a specific diameter (fixed by the operating conditions used) is then determined by one of two methods; namely, Oden's tangential intercept method and the function method. A comparison of the particle-size distribution as determined by the two methods is presented in Table VI. Duplicate tests were made (A and B) in which the fraction settled for different limiting diameters was found to differ by no more than three per cent. The average values of the per cent settled were computed and, from these results, the particle-size distribution, expressed as cumulative weight per cent undersize, was computed by the intercept and by the function method. The results obtained by the two methods agree, in all cases, within five per cent.

CONCLUSION

The cumulative, centrifugal sedimentation method is applicable to the determination of the particle-size distribution of thorium oxide in the particle-size range, 0.1 to 2 microns in diameter. The results by this method correlate well, in general, with results obtained by gravitational sedimentation methods (Andreasen pipet, turbidimetric and activation analysis) for the portion of sample composed of particulate matter greater than two microns in diameter.

In interpreting the data obtained by the cumulative centrifugal method, either Oden's method of tangential intercepts or a function method can be used. For practical purposes, the results are equally reliable.

In the majority of tests made, thorium oxide was found to exhibit no significant difference in particle-size distribution when the sedimentation tests were made in different dispersing media; however, this was not always the case since, with some samples, the particle-size distribution varied appreciably in different dispersing media.

ACKNOWLEDGEMENT

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APPENDIX

A. Equations for Calculating Centrifugal Sedimentation Time

1. Aqueous medium

$$D = \sqrt{\frac{18 \times 10^8 \, \eta \ln r_2/r_1}{(\rho - \rho')\omega^2 t}}$$

Equation (3)
(Svedberg and Nichols Equation)

or

$$t = \frac{18 \times 10^8 \, \eta \ln r_2/r_1}{(\rho - \rho')\omega^2 D^2}$$

when D = diameter, microns

η = 0.009 (25°C), poise

ρ = 9.8, g/cm^3

ρ' = 1.0, g/cm^3

r_1 = 8 cm

r_2 = 11 cm

t = time, seconds

ω = angular velocity, radians/second

then

$$t = \frac{18 \times 10^8 \times 0.009 \times \ln 11/8}{(9.8 - 1.0)\omega^2 D^2} = \frac{5.86 \times 10^5}{\omega^2 D^2}$$

when rpm = centrifuge speed, revolutions/minute

$$\omega = \frac{2\pi(\text{rpm})}{60}$$

then

$$t = \frac{5.34 \times 10^7}{(\text{rpm})^2 D^2} \qquad (10)$$

2. Xylene medium

When η = 0.006 (25°C), poise

ρ = 9.8, g/cm^3

ρ' = 0.9, g/cm^3

$$t = \frac{18 \times 10^8 \times 0.006 \times \ln 11/8}{(9.8 - 0.9)\omega^2 D^2} = \frac{3.86 \times 10^5}{\omega^2 D^2} = \frac{3.52 \times 10^7}{(\text{rpm})^2 D^2} \qquad (11)$$

Table I

Centrifugal Sedimentation Time for Thorium Oxide

Diameter, Microns	Speed, rpm	Sedimentation Time, Seconds: In H_2O		In Xylene	
		t_{th} (a)	t_m (b)	t_{th} (c)	t_m (b)
2.0	300	148	156	98	106
1.5		264	272	174	182
1.0		594	602	392	400
0.5	600	594	606	392	404
.3	1200	412	420	272	280
.25		594	602	392	400
.2		928	936	613	621
.15	1800	730	734	483	487
.1		1,640	1,644	1,087	1,091

(a) Time calculated by equation (10).
(b) Time corrected for acceleration and deceleration periods, $t_m = t_{th} - (t_a' + t_d') + t_a$. See Table II and explanation on page 5.
(c) Time calculated by equation (11).

Table II

Corrections of Centrifuging Time for Periods of Acceleration and Deceleration

Speed, rpm	Acceleration Time, Seconds		Deceleration Time, Seconds	
	t_a	t_a'	t_d	t_d'
300	60	35	65	17
600	50	27	70	11
1200	50	31	75	11
1800	30	17	80	9

Note: t_a, t_d, - actual measured acceleration and deceleration times, respectively.
t_a', t_d' - equivalent acceleration and deceleration times, respectively. (See page 4 for definition of terms.)

B. Example of the Calculation of Particle-Size Distribution from Centrifugal Sedimentation Data

Table III

Determination of Amount of ThO_2 in Sediment and Supernatant Portions

ThO_2 - Sample C - Dispersed in Xylene

Conditions

ThO_2, dissolved in HNO_3, $HClO_4$ and HF
Method, Spectrophotometric Thoron for Th
Final volume, V_f, ml, 50
Wavelength, mμ, 545
Light path, cm, 1
Factor, F, (μg ThO_2/ml per absorbancy unit) 16.4
Total ThO_2, mg, $\frac{F \times Z \times A}{1,000}$

Test A	Limiting Diameter, μ	Volume, ml	Aliquot, ml	Dilution, Z	A	ThO_2 mg
Supernatant Portion	1.00	100	1	5,000	0.245	20.1
	0.50				.209	17.2
	.30		2	2,500	.341	14.0
	.25				.275	11.3
	.20		5	1,000	.570	9.4
	.15	25	1	1,250	.350	7.2
	.10		2	625	.278	2.9
Sediment	1.00	100	5	1,000	.403	6.6
	0.50		2	2,500	.227	9.3
	.30		1	5,000	.154	12.6
	.25				.179	14.7
	.20				.202	16.6
	.15				.232	19.0
	.10				.290	23.8
Test B						
Supernatant Portion	1.00	100	1	5,000	0.261	21.4
	0.50				.208	17.1
	.30		2	2,500	.345	14.2
	.25				.295	12.1
	.20		5	1,000	.590	9.7
	.15	25	1	1,250	.330	6.8
	.10		2	625	.282	2.9
Sediment	1.00	100	5	1,000	.401	6.6
	0.50		2	2,500	.217	8.9
	.30		1	5,000	.155	12.7
	.25				.175	14.4
	.20				.206	16.9
	.15				.240	19.7
	.10				.295	24.2

Table IV

Calculation of the Fraction of the ThO_2 Settled (Sample C)

Test	Limiting Diameter, μ	Supernatant, N, mg	Sediment: Uncorrected, M, mg	Sediment: Corrected[a], M - P, mg	Total, N + M - P, mg	Fraction Settled[b]
A	1.00	20.1	6.6	4.9	25.0	0.20
	0.50	17.2	9.3	7.6	24.8	.31
	.30	14.0	12.6	10.9	24.9	.44
	.25	11.3	14.7	13.1	24.4	.54
	.20	9.4	16.6	15.0	24.4	.61
	.15	7.2	19.0	17.4	24.6	.71
	.10	2.9	23.8	22.1	25.0	.88
B	1.00	21.4	6.6	4.9	26.3	0.19
	0.50	17.1	8.9	7.3	24.4	.30
	.30	14.2	12.7	11.0	25.2	.44
	.25	12.1	14.4	12.7	24.8	.51
	.20	9.7	16.9	15.2	24.9	.61
	.15	6.8	19.7	18.0	24.8	.73
	.10	2.9	24.2	22.5	25.4	.89

(a) Sediment corrected for ThO_2 initially below the 2-mm level is M - P, when P is 1/16 (N + M).

(b) (M - P)/(N + M - P).

(See page 14 for definition of terms)

C. Empirical Function Method of Determining Particle-Size Distribution From Sedimentation Data

$$w = S - 1/D^2 \left(\frac{dS}{d\ 1/D^2}\right) \qquad \text{(Oden's Tangential Intercept Eq.)} \qquad (12)$$

Plot ln $1/1-S$ instead of S vs $1/D^2$; if a straight line is obtained the equation for the line is:

$$\ln \frac{1}{1-S} = m(1/D^2)$$

$$\frac{1}{1-S} = e^{m(1/D^2)}$$

$$1-S = e^{-m(1/D^2)}$$

$$S = 1-e^{-m(1/D^2)}$$

by differentiation, $dS/d(1/D^2) = me^{-m(1/D^2)}$

then, by substitution, equation 12 becomes $w = S-(1/D^2)me^{-m(1/D^2)}$

or $w = S-m(1/D^2)(1-S)$

w can therefore be calculated by the above equation, using the graphically determined slope (m) of the line obtained from the plot of ln $1/(1-S)$ vs $1/D^2$. If the plot does not result in a straight line, the slope of the tangent to the line at a point corresponding to $1/D^2$ is used as (m).

Table V

Particle-Size Distribution From Fraction Settled as Calculated by the Function Method

(Sample C)

Limiting Diameter, D, μ	$1/D^2$ [a]	Fraction Settled, S	1-S	$\frac{1}{1-S}$	$\ln \frac{1}{1-S}$
1.00	1.00	0.20	0.80	1.25	0.223
0.50	4.00	.31	.69	1.45	.371
.30	11.1	.44	.56	1.79	.582
.25	16.0	.53	.47	2.13	.725
.20	25.0	.61	.39	2.56	.940
.15	44.5	.72	.28	3.57	1.27
.10	100	.89	.11	9.10	2.21

D, μ	Slope [b], m	$m(1/D^2)$	$m(1/D^2)(1-S)$	$S - m(1/D^2)(1-S)$	Cumulative Per Cent
1.00	0.085	0.085	0.068	0.13	87
0.50	.044	.176	.121	.19	81
.30	.028	.311	.174	.27	73
.25	.024	.384	.177	.35	65
.20	.021	.525	.205	.40	60
.15	.018	.800	.224	.50	50
.10	.016	1.60	.176	.71	29

(a) $1/D^2$ is used instead of time, because time is a variable dependent on the angular velocity.

(b) From slope of curve in Figure 2.

D. Comparison of Intercept and Function Methods

Table VI

Comparison of Particle-Size Distribution by Two Methods of Calculation

(Sample C)

D, μ	Fraction Settled[a] Test A	Test B	Av.	Tangential[b] Intercept	Cumulative Per Cent Method: Intercept	Function[c]	Difference
1.00	0.20	0.19	0.20	0.15	85	87	- 2
0.50	.31	.30	.31	.20	80	81	- 1
.30	.44	.44	.44	.28	72	73	- 1
.25	.54	.51	.53	.35	65	65	0
.20	.61	.61	.61	.45	55	60	- 5
.15	.71	.73	.72	.53	47	50	- 3
.10	.88	.89	.89	.66	34	29	+ 5

(a) Table IV

(b) Figure 1

(c) Table V

E. Comparison of Particle-Size Distribution Data

Table VII

Comparison of Particle-Size Distribution by a Centrifugal and Gravitational Method[a]

Dispersing Medium: $Na_4P_2O_7$, 0.001 M
ThO_2: Sample A

Limiting Particle Diameter, μ	Cumulative Per Cent		
	Centrifugal		Gravitational
	Intercept	Function	Activation Analysis
3.0			94
2.0	87	92	90
1.0	68	70	77
0.7			60
.5	48	48	
.3	37	36	
.25	32	32	
.2	27	27	

(a) See Figure 3

Table VIII

Comparison of Centrifugal and Gravitational Methods Using Various Dispersing Media[a]

ThO_2: Sample A

Limiting Particle Diameter, μ	Cumulative Per Cent			
		Gravitational		
	Centrifugal	Andreasen		Activation
	Xylene	Xylene	0.001 M $Na_4P_2O_7$	0.005 M $Na_4P_2O_7$
15				97
10				94
7		83	91	88
5		77	83	80
3		57	62	61
2	49	40	48	47
1.5	33	28	41	35
1.0	20			20
0.7				12
0.5	8			
0.2	1			

(a) See Figure 4

Table IX

Comparison of Centrifugal and Gravitation Methods Using Various Dispersing Media[a]

ThO_2: Sample C

Limiting Particle Diameter, μ	Cumulative Per Cent					
	Centrifugal			Gravitational		
	H_2SO_4, 0.005 M	$Na_4P_2O_7$, 0.001 M	Xylene	Andreason Xylene	Turbidimetric Xylene	Activation $Na_4P_2O_7$, 0.005 M
10				100		97
5				99	100	96
2				95	95	91
1	98	100	87	92	90	82
0.7						73
.5	92	99	81	78	67	
.3	75	89	73			
.25	66	80	65			
.20	47	61	60			
.15	21	30	50			
.10	3	3	29			

(a) See Figure 5

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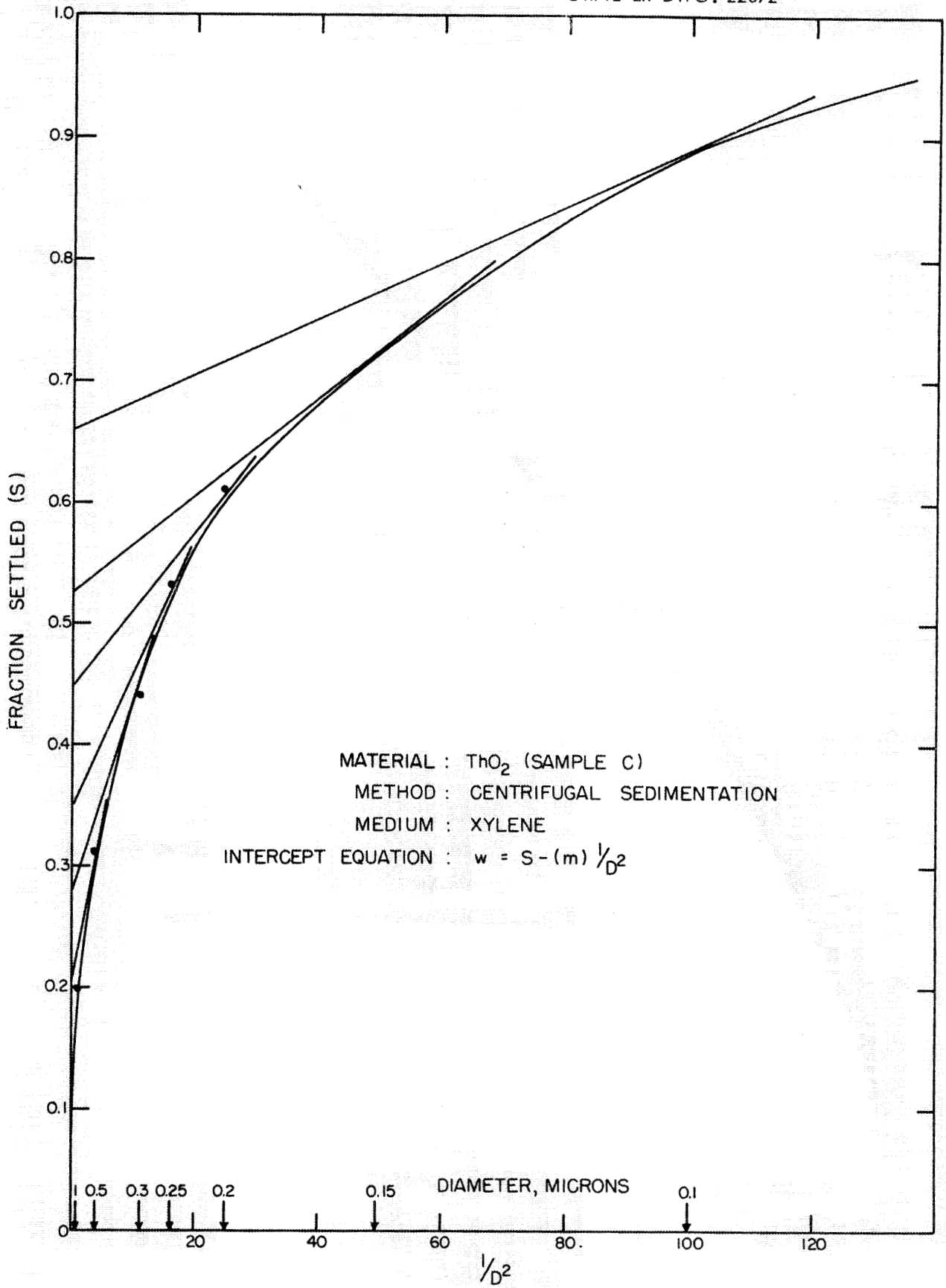

FIGURE I. TANGENTIAL INTERCEPT METHOD FOR DETERMINING PARTICLE-SIZE DISTRIBUTION FROM SEDIMENTATION DATA

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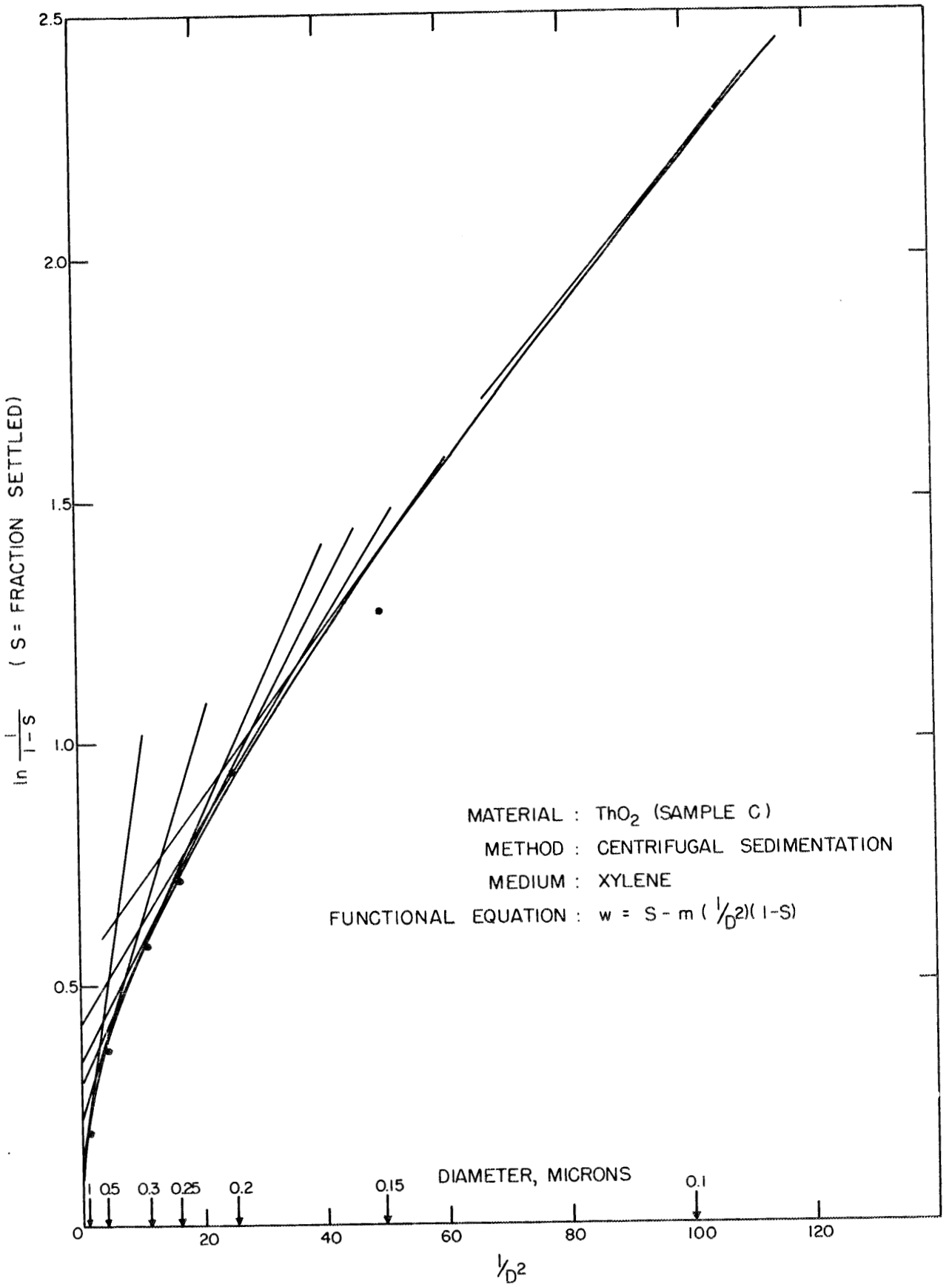

FIGURE 2. EMPIRICAL FUNCTION METHOD FOR DETERMINING PARTICLE-SIZE DISTRIBUTION FROM SEDIMENTATION DATA

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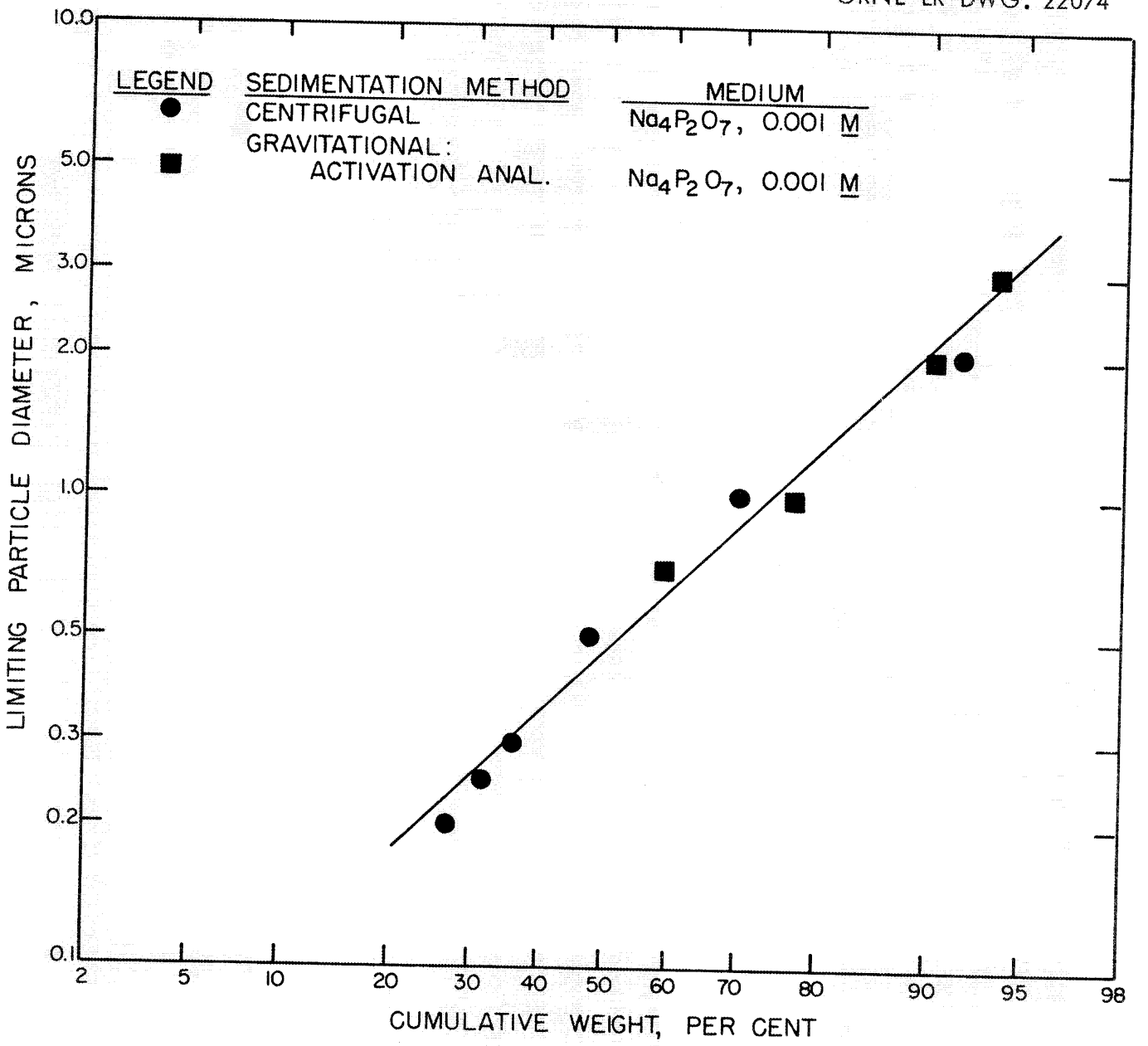

FIGURE 3. PARTICLE-SIZE DISTRIBUTION OF THORIUM OXIDE (SAMPLE A) COMPARISON OF A CENTRIFUGAL AND A GRAVITATIONAL METHOD

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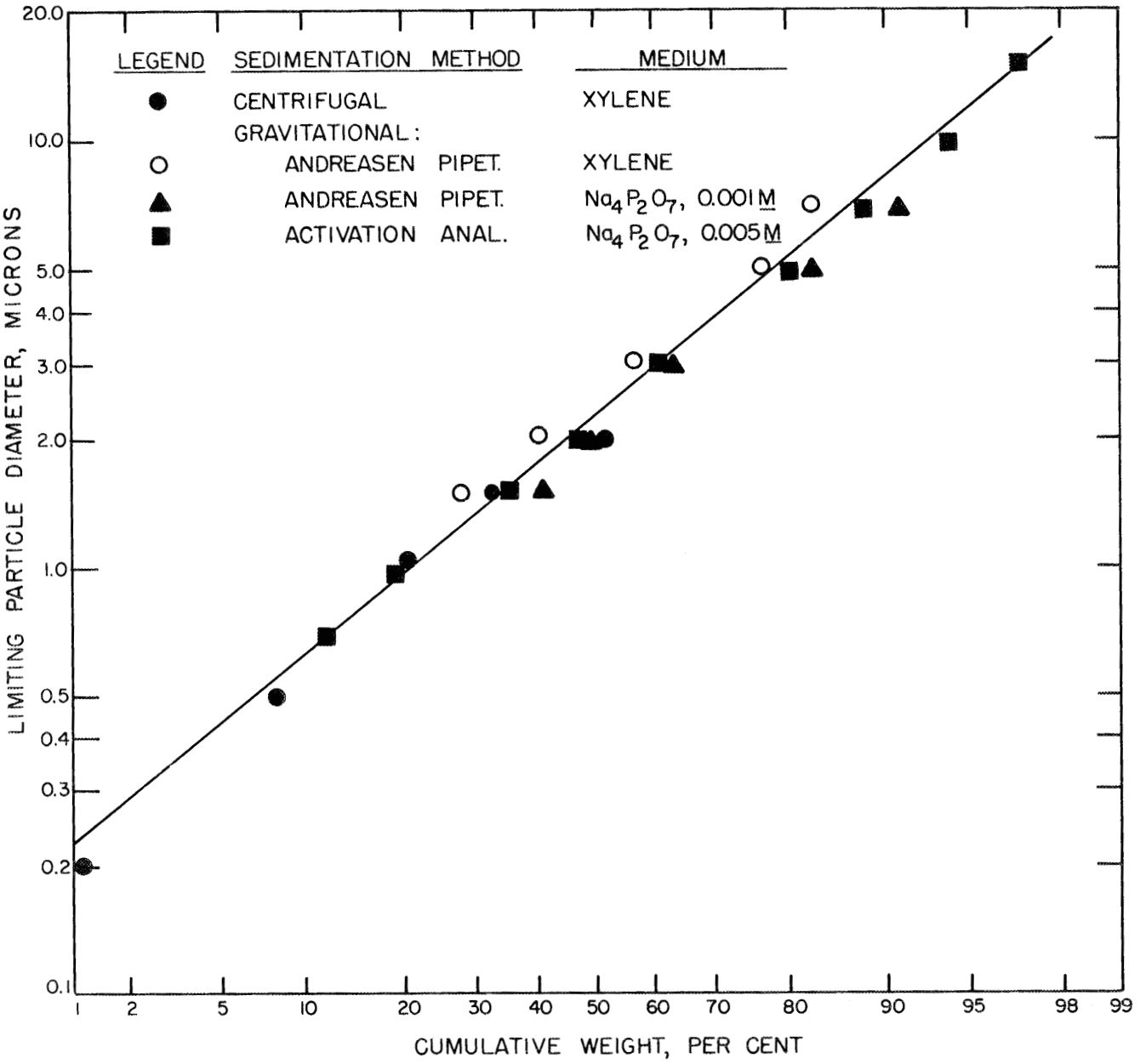

FIGURE 4. PARTICLE-SIZE DISTRIBUTION OF THORIUM OXIDE (SAMPLE B) COMPARISON OF CENTRIFUGAL AND GRAVITATIONAL METHODS USING VARIOUS DISPERSING MEDIA

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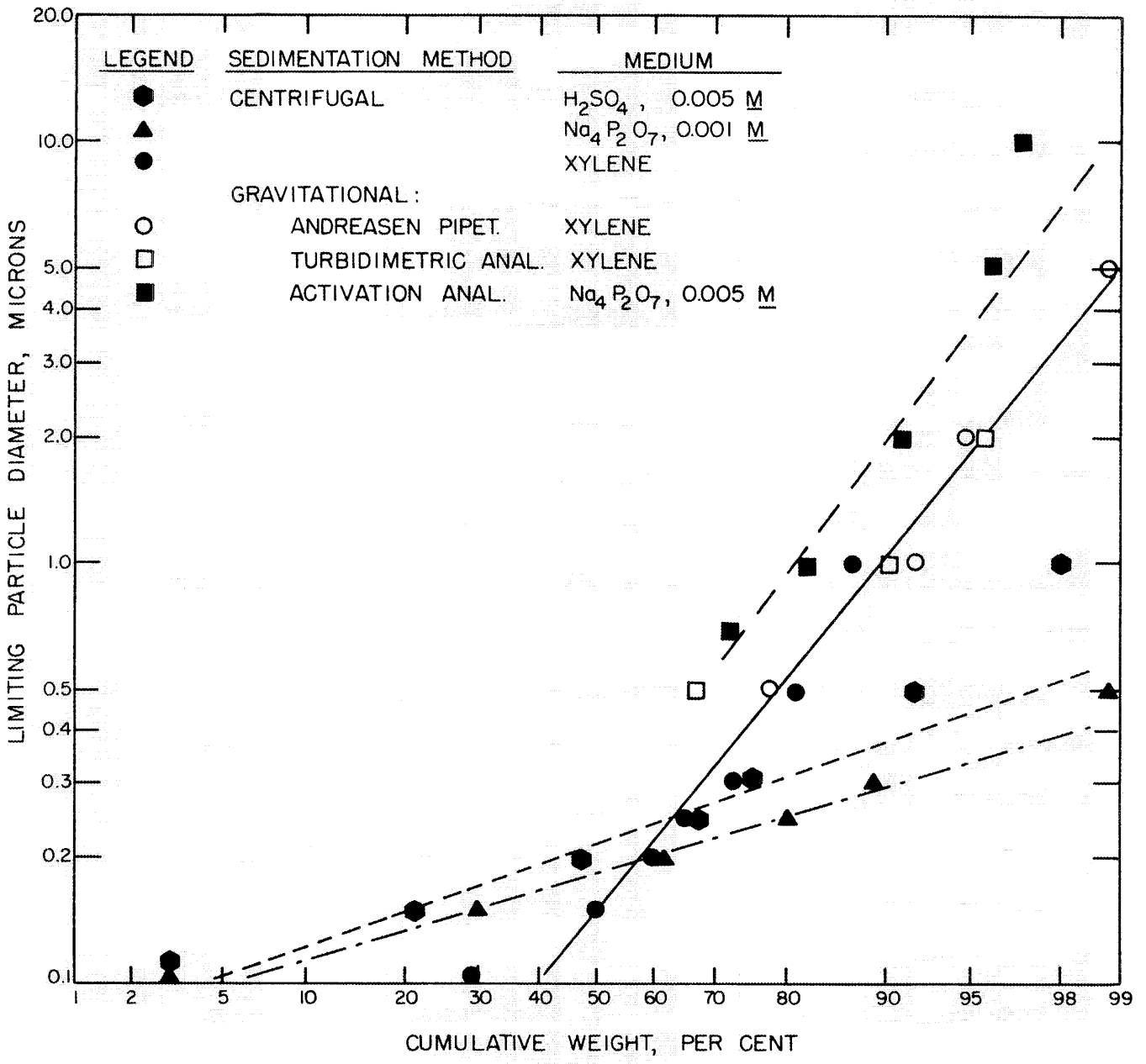

FIGURE 5. PARTICLE-SIZE DISTRIBUTION OF THORIUM OXIDE (SAMPLE C) COMPARISON OF CENTRIFUGAL AND GRAVITATIONAL METHODS USING VARIOUS DISPERSING MEDIA

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