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SUBJECT: Determination of Submicron Particle Sizes by an
Activation Analysis - Centrifugation Method

TO: D. G. Thomas

FROM: L. C. Bate and G. W. Leddicotte

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DETERMINATION OF SUBMICRON PARTICLE SIZES BY AN
ACTIVATION ANALYSIS - CENTRIFUGATION METHOD

L. C. Bate
G. W. Leddicotte

The feasibility of determining particle sizes in the submicron range by employing an activation analysis - centrifugation method has been demonstrated. It is believed that this method is now applicable to the analysis of thorium oxide for submicron particles. The same techniques are, in most instances, usable in determining particle sizes in other sample materials.

The information presented in this memorandum will show that particle sizes can routinely be determined in the range of 0.07 micron and that it is possible to use this method in determining particles as small as 0.05 micron. This particular method is rapid and requires only conventional equipment to complete an analysis. The principles of the method and the results obtained in some of the preliminary analyses of thorium oxide are presented below.

Principle

Since particles in the submicron range, suspended in a suitable medium, do not fall or sedimentate according to Stokes' Law, the Stokes'-
(1)
Cunningham correction must be applied. However, when the sedimentation rate is approached by the random variation of the particles, the time required for analysis is very long (a week or more) to determine particles in the range of 0.30 micron or smaller. The use of an external centrifugal
(2)
force in the analysis of particle size has been reported elsewhere. The techniques of this investigation were adaptable for use in the activation analysis - centrifugation method considered here.

The particle size distribution by this method can be calculated from the equation:

$$d_s = \frac{6}{W} \sqrt{\frac{n \ln r/s}{2(D_2 - D_1)T}} \quad (1)$$

where: $W = 2\pi \text{ RPS}$,

d_s = diameter of particle in microns,

W = angular momentum,

r = distance from center of centrifuge to the sampling point, in the supporting medium, (cm),

s = distance from center of centrifuge to the surface of the supporting medium, (cm),

D_2 = specific gravity of particle, grams/cm³,

D_1 = specific gravity of supporting medium, grams/cm³,

T = time (sec),

$\text{RPS} = \frac{\text{RPM}}{60}$ = revolutions per second,

n = viscosity of supporting medium, poises

Since all conditions except time and RPS are constant, then the formula may be reduced to:

$$d_s = \frac{1.655 \times 10^{-2}}{\text{RPS} \sqrt{T}} \quad (2)$$

In this investigation, an International Model 2 centrifuge was used in analysis. Table I shows the particle size in microns with its relationship to the time and the speed (RPM) of the centrifuge.

Table I

The Relationship of the Micron Size of Thorium Oxide to Time and RPM

Total Time		Particle Size in Microns at Centrifuge Speed Equal to					
Min.	Sec.	900 RPM	1280 RPM	1650 RPM	1900 RPM	2350 RPM	2800 RPM
5	300	0.64	0.45	0.35	0.30	0.24	0.20
10	600	0.45	0.32	0.25	0.21	0.17	0.14
20	1200	0.32	0.22	0.17	0.15	0.12	0.10
30	1800	0.26	0.18	0.14	0.12	0.10	0.083
40	2400	0.23	0.16	0.12	0.107	0.086	0.072
50	3000	0.20	0.14	0.11	0.095	0.077	0.064
60	3600	0.18	0.13	0.10	0.087	0.070	0.059
120	7200	0.13	0.092	0.71	0.062	0.050	0.041

Application to the Particle Size Analysis of Thorium Oxide

In the application of this method to the particle size analysis of thorium oxide samples, portions from each sample were "activated" by an irradiation in Hole #10 of the ORNL Graphite Reactor. In this activation, Th^{233} is induced into Th^{232} by the neutron reaction $\text{Th}^{232}(n,\gamma)\text{Th}^{233}$.

Thorium-233 decays with a 23.5 minute half life to its daughter radioactivity,

Pa^{233} .⁽³⁾ Protactinium-233 has a half life of 27.4 days and emits both beta and gamma radiations in its decay. The Pa^{233} gamma radioactivity can be assayed by means of a gamma scintillation counter.

In this study, all the large-sized particles in a sample were determined first by the activation analysis - sedimentation method reported elsewhere.⁽⁴⁾ At a time interval equivalent to the sedimentation of particles having Stokes' diameters of 0.7 micron, the sedimentation analysis was completed and all of the supernatant slurry at and above the collimated slit of the counter was carefully removed by a siphon action. This volume of slurry was shaken to disperse the particles and known aliquots of the slurry transferred to calibrated 100 ml centrifuge tubes. Each sample was then centrifuged for a definite increment of time (see Table I). At

the completion of each centrifugation time, an aliquot of known volume (NOTE a) was pipetted into a counting tube (pyrex culture tube, 15 x 72 mm) for a radioactivity measurement. The volume in the centrifuge tube was kept constant by adding an equal volume of the dispersing agent (in this instance, sodium pyrophosphate) used in the analysis. The radioactivity measurements were made by means of a gamma scintillation counter and the percent undersize concentration of particles of a given size in the slurry calculated.

The samples can be centrifuged at any one of the various speeds shown in Table I. However, in the analyses reported here, the samples were centrifuged at two speeds, 900 RPM and 1900 RPM. Centrifugation at these speeds enabled the analyst to obtain data for varied particle sizes having a constant decreasing size in a minimum amount of time. In our preliminary analyses, the sample that was centrifuged at a speed of 900 RPM was reshaken and then centrifuged at a speed of 1900 RPM; but due to the difficulty in reslurrying the particles, it was decided to use separate portions for each centrifugation speed.

Results Obtained in the Analysis of Thorium Oxide

Tables II and III report the results obtained in the analysis of several samples of thorium oxide by this activation analysis - centrifugation method.

NOTE a: Each aliquot was taken 3 cm. from the bottom of the centrifuge tube so as not to disturb the settled particles. This method will also avoid possible spillage of the sample, since the liquid level is but 3 cm. from top of the centrifuge tube. By following this procedure, the particle-fall distance is 10 centimeters.

Table II

Submicron Particle Size Distribution in Thorium Oxide
(Analysis by an Activation Analysis - Centrifugation Method)

Particle Size, Micron	Percent Undersize	
	Sample 343-2	Sample 343-1
0.38*	10.9	12.9
0.30	5.78	8.29
0.21	4.22	6.67
0.15	2.67	5.26
0.12	2.24	4.59
0.107	1.99	4.14
0.095	1.96	3.84
0.087	1.84	3.78

* Value obtained by sedimentation method; all other values obtained by centrifuge method.

Table III

Reproducibility Study: Submicron Particle Size Distribution
in Thorium Oxide
(Analysis by an Activation Analysis - Centrifugation Method)

Particle Size, Micron	Sample 339-2		Sample 342-1	
	% Undersize**	Deviation	% Undersize**	Deviation
0.70*	--		27.2%	
0.64	--		19.51	± .24
0.45	--		13.94	± .07
0.33*	4.7		--	
0.30	2.07	± .06	8.65	± .04
0.21	1.51	± .02	5.98	± .08
0.15	1.03	± .05	3.70	± .01
0.12	0.93	± .02	--	
0.107	--		2.18	± .13
0.087	--		1.71	± .14

* Value obtained by sedimentation method; all other values obtained by centrifuge method.

** Duplicate portions of sample analyzed by centrifuge method.

A graphical plot of the results obtained for the analysis of these samples by the combined activation analysis - sedimentation - centrifuge method are shown in Figures I, II, III, and IV.

Discussion

a) The data in Table I indicates the relationship of the time and velocity of the centrifuge to give the desired particle size. It is not practical to use a lower angular velocity than 900 RPM because of the heat produced by the built-in variac and apparent deviations in the speed of the centrifuge. When the centrifuge is run at low speeds, it requires a longer time to attain the optimum angular momentum than at higher centrifugation speeds. Also the longer the centrifuge is operated at low speeds, the temperature from induced heat increases and as this increases, the centrifuge speed increases also. This heat effect was observed at a speed of 900 RPM; however, it was negligible if the centrifugation time did not exceed 10 minutes. The optimum angular momentum at higher centrifuge speeds can be reproduced by setting the variac dial on the centrifuge motor to a specific number. The centrifuge was allowed to coast to a stop rather than to be stopped by the attached mechanical brake, because this action prevented any disturbance to the settled particles.

b) When the results of centrifugation from Table II are plotted on log paper vs probability scale, they give the expected continuation of the curve obtained by the sedimentation analysis method. In some thorium oxide samples, this is nearly a straight line (Figures I, II and IV). In another sample (Figure III), the central portion of the curve is nearly horizontal, but the centrifugation data can be plotted as a continuation of the data obtained by the sedimentation method.

c) The data in Table III shows the typical deviations obtained in the analysis of duplicate aliquots from two specific thorium oxide samples. The deviation appears to be due partially to the possible non-uniform mixing of the slurry after its removal from the sedimentation

tube and the technique used in removing a sample aliquot from that portion of the original sample being centrifuged. (See NOTE a above).

d) Centrifugation at high speeds requires approximately one minute to attain full speed and one and a half minutes to stop. Therefore, the measured time interval for centrifugation stated in Table I represents that time when the centrifuge is started and the time at which the centrifuge is turned off. This gives a constant time unit and due to this, no measured time interval of less than five minutes is used. If times of less than five minutes are used, the time to reach full speed is a considerable percent of the total time of centrifugation so that the calculated particle sizes could be in error. In Table I, the total time of centrifugation is given, but in the analysis the measured time is broken into 5 and 10 minute intervals which are added to give total time.

e) The medium used for the centrifugation of particles was 0.005 M $\text{Na}_4\text{P}_2\text{O}_7$ in water. It has been assumed that other dispersant agents would also be adequate.

Conclusions

1) It has been concluded from the data and information presented in this report that the centrifuge method is feasible for use in particle size analysis. Figures I thru IV show that the data obtained in analysis can be plotted as a continuation of the data obtained in the activation analysis - sedimentation analysis method. Also, it is apparent that the reproducibility of data is as good as that observed in the activation analysis - sedimentation method.

2) For the present, samples having less than 10% particles under 0.70 micron remaining in the suspension will not be analyzed unless a specific request is made.

3) The use of a combined activation analysis - sedimentation - centrifuge method of analysis and a choice of sedimentation media (5) now makes it possible to analyze for particle size distributions, particularly in samples of thorium oxide, in the range of ~0.07 micron to 118.0 microns.

4) This method also appears feasible for use in the particle size analysis of sample materials other than thorium oxide. However, it will be necessary to recalculate effective particle size for these materials from the constants given in Equation (1) above.

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