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A PRODUCTION CONTROL METHOD FOR DETERMINING THE PARTICLE SIZE DISTRIBUTIONS OF THORIUM OXIDE AND THORIUM OXALATE

L. C. Bate
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Abstract

This report describes a simple and rapid analysis method that can be used to estimate particle size distributions in samples of thorium oxalate and thorium oxide. In an analysis, samples are pipeted at predetermined time intervals from a homogeneous mixture of particles falling through a viscous medium. The parameters of Stokes' Law are considered in this analysis method. The natural radioactivity, originating from the decay of thorium and its radioactive daughters, in each aliquot removed during sedimentation is measured by means of a gamma scintillation counter. The weight percent of a fraction containing specific sized particles removed from this mixture is determined by comparing the amount of radioactivity in the aliquot removed with the reference sample of thorium oxalate or oxide being analyzed. Particle size distributions of from 1 to 8 microns can be analyzed by this method.

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A PRODUCTION CONTROL METHOD FOR DETERMINING THE PARTICLE SIZE DISTRIBUTIONS OF THORIUM OXIDE AND THORIUM OXALATE

This simple and rapid analysis method for estimating the particle-size distributions in samples of thorium oxalate and thorium oxide employs a gravity sedimentation technique in which the sample being analyzed is dispersed in a suitable medium and mechanically stirred until the suspension is homogeneous. After the stirring is stopped, the particles are allowed to fall freely. A volumetric pipet mounted in the sedimentation apparatus at a given distance from the top of the liquid is used to pipet samples from the suspension at specific time intervals.

Since the samples of thorium oxalate and thorium oxide are naturally radioactive, it is possible to measure the radioactivity of each aliquot removed from the suspension by means of gamma counting. The amount of radioactivity measured is proportional to the total natural thorium radioactivity in the sample so that the amount of radioactivity observed at any time of sedimentation is proportional to the concentration of particles of a given size (apparent Stokes' diameter) which have fallen in that time.

The method is intended to be used only as a quality control method in the production of thorium oxalate and thorium oxide and not in the assay of the final product. It is complementary to the activation analysis-sedimentation method[2] now being used in more specialized studies of particle-size distribution in samples of thorium oxalate and thorium oxide. At present, the effective particle size distribution range of the pipet method is from 1 to 8 microns.

Principle

The pipet method described by Amstein and Scott[1] has been refined so that the amount of thorium in the aliquot removed from the suspension can easily be determined by measuring the natural radioactive decay products of thorium by means of a gamma scintillation counter. The principles of the refined method involve a mechanical stirring operation to disperse the particles homogeneously in a liquid medium of known viscosity. The particles are allowed to fall freely and at some time of sedimentation, t, an aliquot of the mixture is withdrawn by means of a pipet whose tip is at a depth, h, below the top surface of the liquid medium. (Figure 1) The aliquot withdrawn will be composed of a mixture of particles whose size-distribution can be defined in terms of the time of fall from a given height so that:

(1) the mixture will contain particles that have a sedimentation rate with a time of fall equal to the specified time interval of sedimentation and whose particle size, therefore, is the particle size that is defined for a set of conditions involving a specified time interval of sedimentation and a known distance of fall,

(2) the mixture will also contain a number of particles of smaller size that by virtue of the time interval of sedimentation and distance of fall will be suspended in the liquid medium throughout the area of measurements so that they will be "caught" or picked up in the aliquot of the mixture being analyzed.

The relationship of these principles with the conditions of Stokes' Law make it possible to calculate an effective particle size for a set of conditions involving (1) a specified time interval of sedimentation,

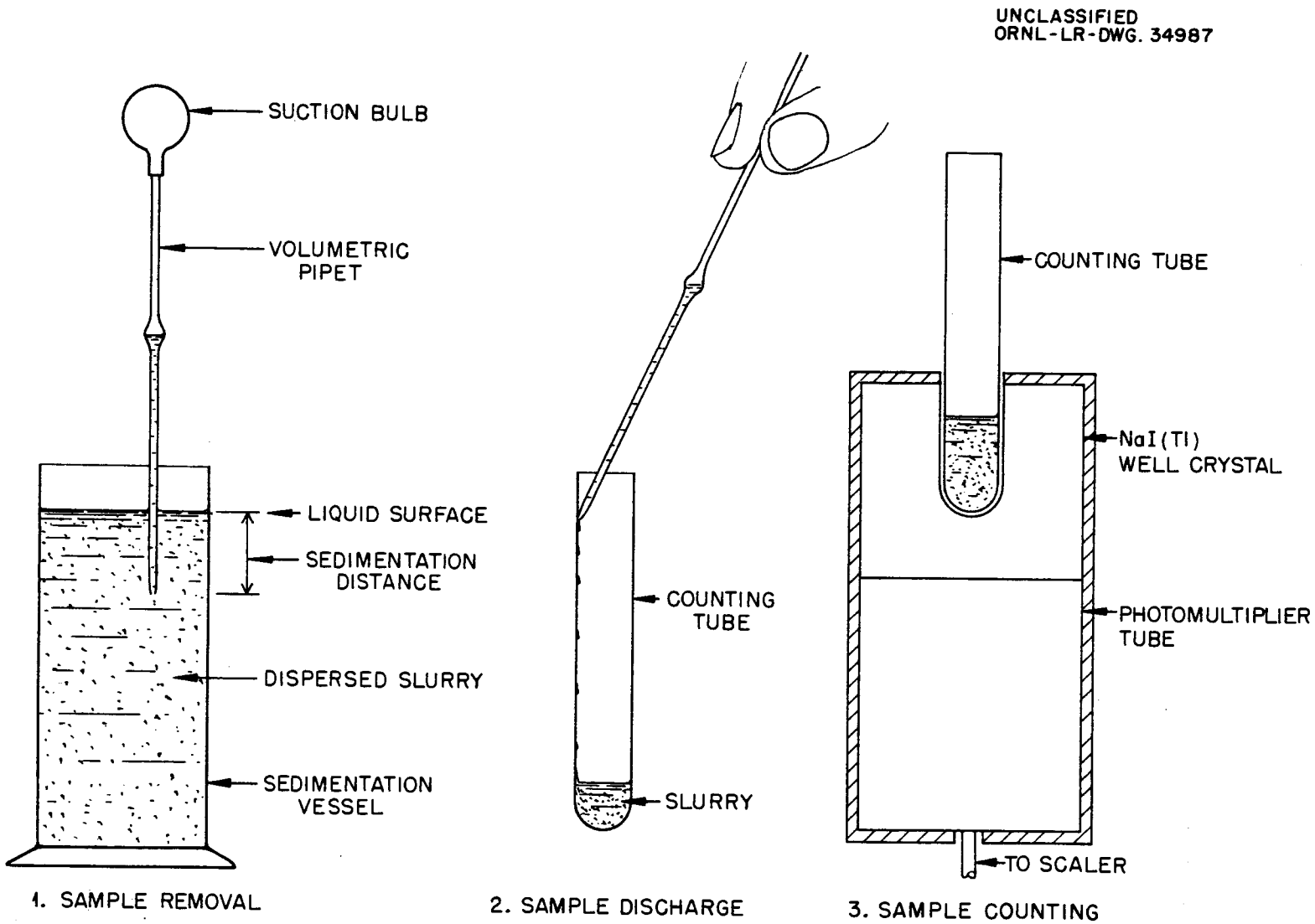

Figure 1. Pipet method for quality control of ThO_2.

(2) the velocity with which a particle of known density will fall, and (3) the viscosity and density of the liquid used as a suspension medium for the dispersed particles. Equation 1, below, mathematically expresses this relationship:

$$d_s = \sqrt{\frac{18hn}{(D_2-D_1)gt}} \qquad (1)$$

where d_s = diameter of particle in cm(micron = 10^{-4} cm),

h = distance below the liquid surface from which the sample is pipeted, cm,

n = viscosity of supporting medium, poises,

D_2 = density of particles, gm/cm^3,

D_1 = density of liquid medium, gm/cm^3,

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

t = time of sedimentation, sec.

A necessary prerequisite of this refined method is that the radioactive particles must be dispersed in a non-radioactive liquid so that when sedimentation takes place and an aliquot is removed from the suspension, the concentration of the particles removed can be determined by a simple, or gross, radioactivity measurement by means of a gamma scintillation counter. The following assumptions are considered in interpreting the data obtained from these radioactivity measurements:

(1) that all of the radioactive particles in the suspension obey Stokes' Law,

(2) that at the time of the start of the analysis, t = o, the radioactive particles are homogeneously suspended in the solution,

(3) that the total radioactivity in an aliquot removed from the suspension and observed by the counter is the sum of the radioactivity of all the various particle sizes (a_1, a_2, a_3, a_n) in that aliquot,

$$A = a_1 + a_2 + a_3 + \text{----------} a_n,$$

(4) that the total amount of radioactivity in an aliquot of the suspension taken at a later time interval of sedimentation and measured by the counter is the sum of the radioactivity of all the particles smaller in size than those observed in the aliquot of the suspension taken at an earlier time interval of sedimentation,

(5) that the total amount of radioactivity in any aliquot removed from the suspension is exactly equal to a fraction of the total radioactivity contributed by all of the particles in the sample being analyzed, and

(6) that a change in the total radioactivity of any aliquot removed from the suspension means that all particles of the next largest diameter have settled to the level of measurement and are removed in the next pipeted aliquot.

Thus, since all of the radioactivity in the suspension is due to radioactive particles, it can be assumed that (1) a particle will contribute an amount of radioactivity to the suspension that is proportional to its mass and (2) that the radioactivity observed by the counter will be due to particles of a given size or smaller, since all particles of the same diameter and density fall with the same constant velocity. This amount of radioactivity will remain constant until all of the particles of this given size have fallen below the level of measurement (in this

instance, the pipet tip). Since this sedimentation function is related to Stokes' Law, the amount of radioactivity at some time interval of sedimentation is proportional to the concentration of the particles in that part of the solution being pipetted and represent a fraction of the total observed radioactivity (or total number of particles in the sample being analyzed) at zero time, the start of the analysis.

Equipment

This method requires the following laboratory equipment:

1. Stirrer, magnetic
2. Stirring bar, magnetic
3. Bottle, 8-ounce, glass, wide mouth
4. Bottle, 40 milliliter, glass sample
5. Block, lucite, 1-inch with holes to hold bottle
6. Pipet, volumetric, 3 milliliters
7. Tube, culture, 18 x 150 mm
8. Holder, culture tube, metal.

The radioactivity measurements are made by placing the culture tube containing the aliquot being analyzed into a gamma scintillation counter.[3] This counter uses a well-type sodium iodide (thallium activated) crystal detector. The radioactivity is measured as the number of gamma counts per minute.

General Procedure of Analysis

Dry and aqueous slurry samples of thorium oxalate and thorium oxide have been analyzed by this method. The general technique of analysis

may be described as a three-step procedure (a) preparation of sample, (b) sedimentation and sampling and (c) measurement of radioactivity and resolution of data.

Thorium oxide samples weighing 3 grams and thorium oxalate samples weighing 6 grams are now being analyzed by this method. The sample is added to 30 milliliters of dispersing agent (0.001 M $Na_4P_2O_7$ in distilled water for ThO_2; methyl alcohol for $Th(C_2O_4)_2$). A 40-milliliter bottle is used to contain the mixture and it is shaken for 30 minutes on a mechanical shaker. After the sample dispersion, the samples are transferred to a wide mouth 8-ounce bottle, and sufficient dispersing agent is added to fill the bottle. A magnetic stirrer is used to stir the dispersed sample until it is homogeneous. After stirring, the sedimentation is started and aliquots of the slurry are pipeted from the bottle at predetermined time intervals. Each aliquot is transferred to a small pyrex culture tube and the gross gamma radioactivity measured in a gamma scintillation counter. Detailed procedures for the analysis of thorium oxide and thorium oxalate are given in Appendix A.

Relationship of Stokes Law and Counting Techniques to Particle Size Analysis

In the method described here, the parameters of Stokes' Law establish one criteria of measurement in that when all other conditions are constant, an effective particle size for a given particulate matter can be calculated. Using the parameters of Stokes' Law for the analysis of thorium oxide, aqueous liquid support medium (0.001 M $Na_4P_2O_7$ and distilled water) have been established and are shown in Table I.

The other criteria, i.e., a radioactivity measurement, provides a means for determining the concentration of particles of a given size that

in their sedimentation obey the parameters of Stokes' Law. This method of determining concentration is simple in that the experimentally determined radioactivity in the aliquot is proportional to the total radioactivity of the sample being analyzed. Thus, a short counting interval is all that is necessary to complete the analysis.

Table I
Particle Size of Thorium Oxide vs. Time of Sedimentation

Effective Particle Size, (micron)	Time*
8	2 min, 31 sec
7	3 min, 17 sec
6	4 min, 28 sec
5	6 min, 24 sec
4	10 min, 3 sec
3.5	13 min, 9 sec
3	17 min, 53 sec
2.5	25 min, 46 sec
2	40 min, 16 sec
1.5	71 min, 3 sec
1	161 min, 3 sec

*The time interval in which particles of the effective size indicated will fall 5 centimeters.

In the analysis of thorium oxalate, a suspending medium of methyl alcohol saturated with sodium pyrophosphate is used. The effective particle sizes for a given time of sedimentation are shown in Table II.

Table II also tabulates data calculated for the dispersion of thorium oxalate in water.

Table II
Particle Size of Thorium Oxalate vs. Time of Sedimentation

Effective Particle Size Microns	Time* For Methyl Alcohol Min	Sec	For Water Hr	Min	Sec
10	2	45		9	2
9	3	23		11	9
8	4	18		14	7
7	5	36		18	27
6	7	38		25	7
5	11	0		36	10
4	17	10		56	30
3.5	22	26		70	28
3.0	30	32		100	27
2.5	43	50		144	30
2.0	68	54		266	0
1.5	122	10		402	40
1.0	275	0	15	24	0

*The time interval in which particles of the effective size indicated will fall 5 centimeters.

A 5-cm fall distance was arbitrarily chosen as the sedimentation distance for all samples in order to minimize the analysis time requirements. The slow sedimentation rate of thorium oxalate in water did not appear practical, and this supporting medium was not used in any of the analyses reported herein.

Data

The correlation of the activation analysis-sedimentation method[2] and this pipet method is good. Since each method is based upon Stokes' Law, any correlation should be relative although the activation analysis sedimentation method will give more particle size data. The data presented in Figures 2 and 3 show the correlation of these methods, and Table III tabulates this data.

Table III
Parameter of Size Analysis of Thorium Oxide by the Pipet and Activation Analysis Sedimentation Method

Sample	Pipet Method		Activation Method	
	d_{50}	σ	d_{50}	σ
A	3.40	1.38	3.67	1.38
B	3.30	1.52	3.65	1.38
C	2.30	1.47	2.65	1.32
D	2.35	1.45	2.68	1.36

where d_{50} = the particle size at 50 percent, and

σ = the particle size (microns) at 87 percent divided by the particle size at 50 percent which is the slope of the curve.

$$\frac{\mu(87\%)}{\mu(50\%)} = \sigma \qquad (2)$$

The data in Table IV and V show the natural radioactivity, particle size, percent undersize and deviation observed during a typical analysis of thorium oxide and thorium oxalate.

Discussion

In order to accept this method as a Stokes' Law relationship, an assumption is made that the particles of thorium oxide and thorium oxalate

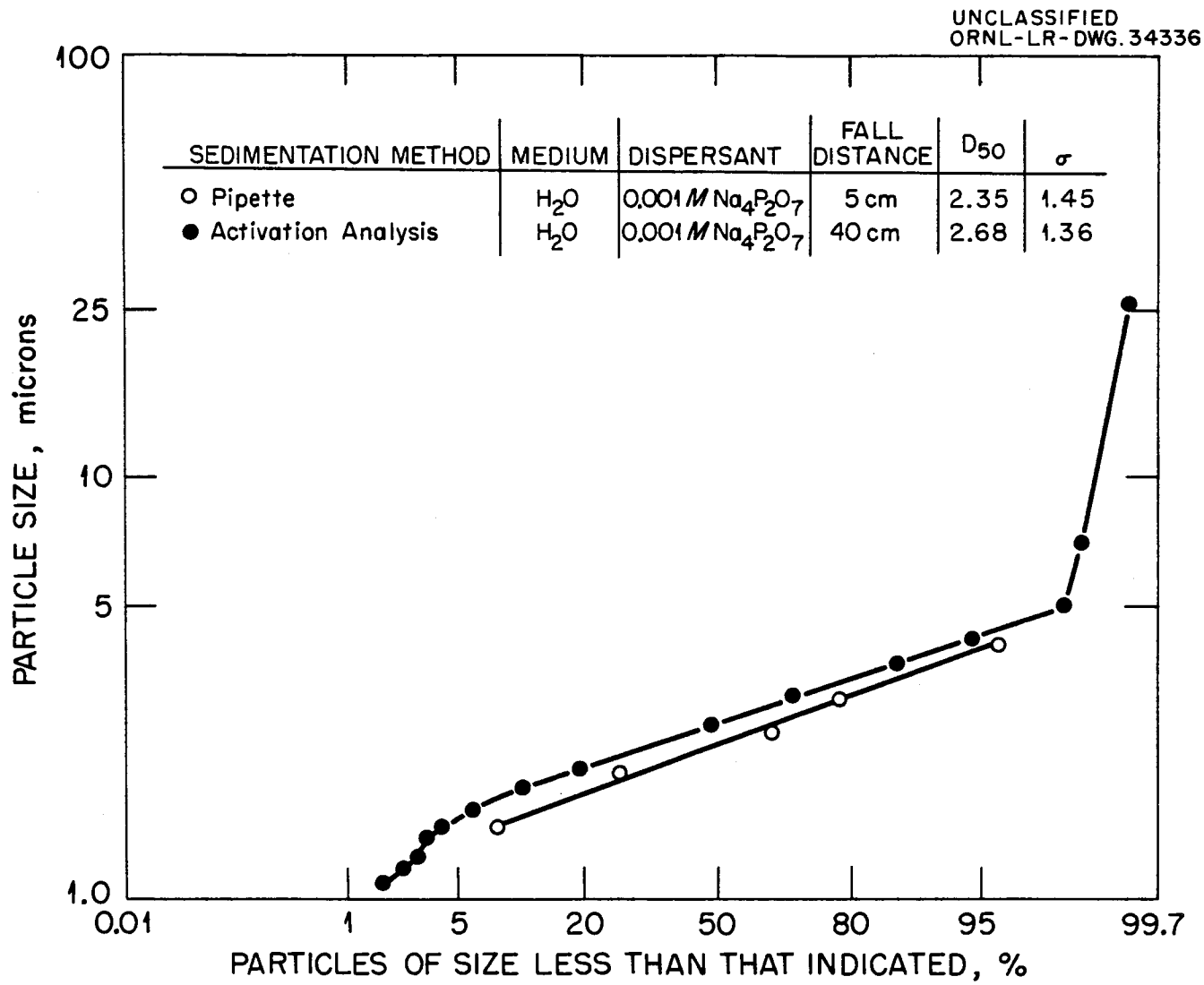

Figure 2. Particle size of ThO_2.

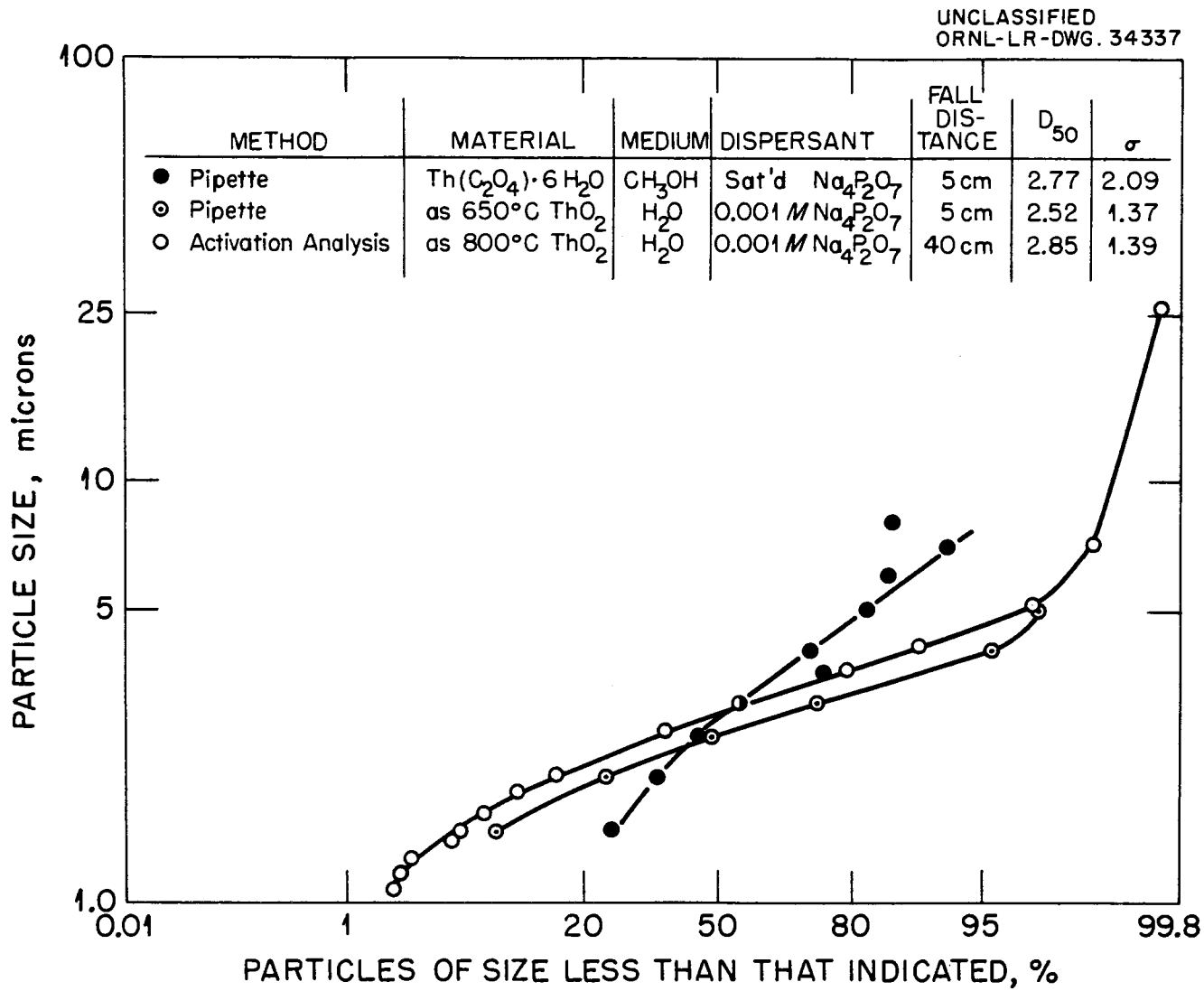

Figure 3. Particle size distribution, sample DT-32.

Table IV
Typical Data Obtained in the Particle Size Analysis of Thorium Oxide by the Pipet-Natural Radioactivity Method

Particle Size, Microns	Counts Corrected for Background, CPM	Percent Undersize
Reference Sample*	1986	100
5	1943	97.8
4	1899	95.6
3	1456	73.3
2.5	986	49.6
2.0	486	24.5
1.5	159	8.0

*This aliquot is taken while the slurry is stirred and homogenous before the start of sedimentation.

Table V
Typical Data Obtained in the Particle Size Analysis of Thorium Oxalate by the Pipet-Natural Radioactivity Method

Particle Size, Microns	Count Corrected for Background, CPM	Percent Undersize
Reference Sample*	1357	100
8	1174	86.5
7	1255	92.4
6	1164	85.8
5	1121	82.6
4	969	71.4
3.5	1014	74.5
3.0	748	55.1
2.5	624	46.0
2.0	486	35.8
1.5	354	26.1

*This aliquot is taken while the slurry is stirred and homogenous before the start of sedimentation.

are spherical in shape. With regard to the radioactivity measurements, it has been assumed that the natural radioactivity in thorium is due to the thoron daughters. The gamma emitters decay through a series of events to become stable lead-208 (see Figure 4). It should be noted, however, that when thorium oxalate is fired to the oxide or when the oxide is fired at higher temperatures, that a loss in radioactivity can result from a loss of thoron. Therefore, depending upon the method of preparation, each batch of thorium oxide will contain a slightly different amount of radioactivity. For example, when thorium oxide is fired, the total radioactivity will grow rapidly (see Figure 5) at first and then assume the natural growth rate. Thus, it must be recognized that this method is dependent upon the natural radioactivity of thorium daughters for the measurement of change in the particle size concentrations as the thorium settles in the supporting medium.

The particle-size distribution analysis of a thorium compound by the use of natural radioactivity is simple and rapid. The gamma scintillation counter measurements require no more than a few minutes, whereas other methods of elemental measurement would require that the weight of thorium be determined by some conventional method after each sample had been dried or dissolved. Such measurements as these could be those involving emission spectroscopy, colorimetry, polarography, etc. Since a minimum of analysis time is required by the method described herein, it is expected that the method could be effectively used as a quality control method in a production area. The data presented elsewhere in this paper substantiates the use of this method in controlling the particle size of thorium compounds whether they are produced either as the oxide or as oxalate.

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Th 90	Th^{232}, Th (thorium) 1.39×10^{10} years		Th^{228}, RdTh (radio-thorium) 1.90 years		
Ac 89	α	Ac^{228}, $MsTh_2$ (meso-thorium 2) 6.13 hours β	α		
Ra 88	Ra^{228}, $MsTh_1$ (meso-thorium 1) 6.7 years β		Ra^{224}, ThX (thorium X) 3.64 days		
Fr 87			α		
Rn 86			Rn^{220}, Tn (thoron) 54.5 seconds		
At 85			α	At^{216} 3×10^{-4} seconds	
Po 84			Po^{216}, ThA (thorium A) 0.158 second	β(0.013%) (?) α	Po^{212}, ThC' (thorium C') 3.0×10^{-7} seconds
Bi 83			α (~100 %)	Bi^{212}, ThC (thorium C) 60.5 minutes β	β (66.3 %) α
Pb 82			Pb^{212}, ThB (thorium B) 10.6 hours β	α (33.7 %)	Pb^{208}, ThD (stable lead isotope)
Tl 81				Tl^{208}, ThC'' (thorium C'') 3.1 minutes β	

Figure 4. The thorium decay series.

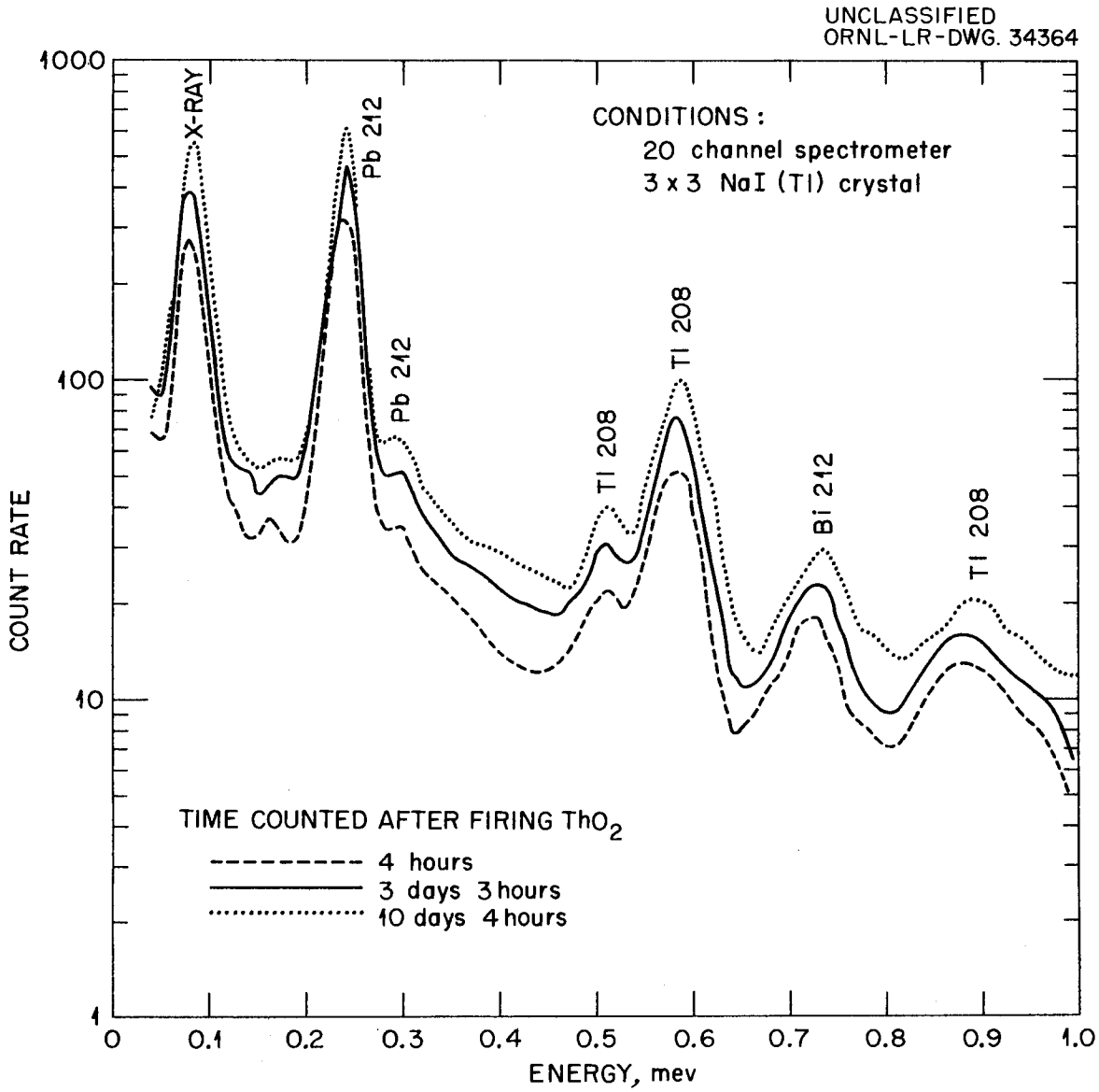

Figure 5. Growth of natural radioactivity in freshly prepared ThC_2.

The results of this investigation have shown that there are a few disadvantages in using natural radioactivity. For instance, a source of error may result during the production of the thorium oxalate from thorium nitrate in that a large portion of a radioactive daughter or daughters may be lost or unequally distributed in the particles. This loss or unequal distribution could account for a variance in radioactivity count rates and result in the presentation of erroneous percent undersize values for any aliquot measured. Another source of error could result from the fact that the gamma energies of the daughter radioactivities vary over a wide energy range. Figure 5 shows that most of the emitted gamma radiations have energies of less than 0.5 Mev. If considerable solids (in this instance, particles) are present in the aliquots measured, a substantial loss of these low-energy radiations could occur since it is difficult to control absorption effects in solid materials. Although each of these conditions appear to be difficult to control, the measurement of a comparator sample containing some portion of the solid or slurry test sample under similar conditions would minimize these effects.

Since the data presented in Table III is expressed as a function of the average particle size (d_{50}) and the slope of the curve, σ, it can be used to show data typical of production control. In our work, the average particle size (d_{50}) obtained by this pipet method when compared with the average particle size obtained by the activation- sedimentation method[2] appeared to be consistently low. The slope of the curve, σ, was also slightly greater. These effects probably result from the disturbing of the slurry when pipetting samples.

Figures 2 and 3 are graphical depictions of observed data. The data in Tables IV and V show that the deviation based upon the radioactivity may be appreciable, but it is well within a 10% limit of error in the analysis of either thorium oxide and on thorium oxalate. Figure 3 also shows the particle-size distribution of a sample of thorium oxalate that has been fired to the oxide and compares this data to that for thorium oxalate.[2] The large change in the slope of the curve for the oxalate sample (apparently due to an increase in particle size) could have resulted from the presence of some oxalic acid in the sample. A study reported elsewhere[4,5] has shown that the size of thorium oxalate particles can increase during their production.

Conclusions

From the data and information presented in this report, it is believed that this method can be used in the production control assay of thorium oxide and thorium oxalate. It is sufficiently rapid so that there is little time delay in the particle-size distribution analysis; data may be furnished in less than four hours after a sample has been received in the analysis laboratory. Although the method has a limited range of particle sizes, i.e., the upper limit is about 8 microns and the lower limit is about 1 micron, smaller sized particles can be measured, if the time of sedimentation is increased. The overall accuracy and precision of the method has been determined as being equal to or less than $\pm$ 10%.

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APPENDIX A

A PIPET METHOD FOR THE PARTICLE-SIZE DISTRIBUTION ANALYSIS OF THORIUM OXIDE

1. Weigh 3 grams of ThO_2 into a 40 ml sample bottle. (NOTE A)
2. Add 20 ml 0.001 M $Na_4P_2O_7$ dispersing agent in distilled H_2O to the bottle.
3. Seal the bottle and then shake it for 30 minutes on a modified Cenco-Meinzer sieve shaker. (NOTE B)
4. After shaking, wash the contents of the sample bottle into a wide mouth 8-oz bottle for the analysis; fill the bottle to its neck with 0.001 M $Na_4P_2O_7$ dispersing solution (see Figure 1 of this report). Place a magnetic stirring bar into the bottle.
5. The pipetting (NOTE C) of duplicate samples of 3 milliliters for reference samples before sedimentation or zero time is accomplished while stirring the sample by means of a magnetic stirrer to insure a homogeneous slurry.
6. Reshake samples and start timer as shaking is stopped.
7. From a depth of 5 cm in the slurry (NOTE D), pipet 3 ml samples at the following times in order to measure the thorium oxide particle sizes indicated. (NOTE E)

Aliquot	Time		Apparent Thorium Oxide Particle Size (micron)
	Minutes	Seconds	
1	2	31	8
2	3	17	7
3	4	28	6
4	6	24	5
5	10	3	4
6	13	9	3.5
7	17	53	3
8	25	46	2.5
9	40	16	2
10	71	3	1.5
11	161	3	1

8. Count each sample in the scintillation counter for 2 minutes. Correct for background (NOTE F).

9. The experimentally determined data for the reference and the aliquot of the unknown sample are used in the following equation:

$$\frac{\text{counts of sample at the given particle size x 100}}{\text{counts of reference samples}} = \%\ \text{undersize}$$

10. The results are reported as percent undersize for a given particle size.

NOTES:

A. This method may also be used for the particle size analysis of thorium oxalate by substituting the medium of $Na_4P_2O_7$ in distilled water for methyl alcohol saturated with $Na_4P_2O_7$ and using 6 grams of thorium oxalate. The following information must be used in pipeting aliquots from the thorium oxalate slurry:

Aliquot	Time		Effective Thorium Oxalate Particle Size, Micron
	Minutes	Seconds	
1	2	45	10.0
2	3	23	9.0
3	4	18	8.0
4	5	36	7.0
5	7	38	6.0
6	11	00	5.0
7	17	10	4.0
8	22	32	3.5
9	30	32	3.0
10	43	50	2.5
11	68	54	2.0
12	122	10	1.5
13	275	00	1.0

B. The sieve shaker is modified by bolting a horizontal rod angled from the corners across center of the shaker. From the horizontal rod

brass adjustable clamps are fastened at an angle of about 30° from vertical. The clamps are adjusted until the sample is level.

C. The pipet must be washed thoroughly to remove all particles and rinsed with water while holding the pipet vertically. Also, a 3-ml pipet is a suitable volume for the radioactivity for measurements.

D. This 5-centimeter depth is critical since the change in concentration of the particles in the solution will be rapid during some portion of the analysis. The pipets are marked for the depth (5 cm) of inserting the pipet into the sedimentation bottle. Hence, they are marked 5 cm from the tip end.

E. A range of particle sizes versus time is given here; however, when the approximate sizes of some of the larger or smaller particle sizes are known, it may be omitted.

F. The absorber must be removed from the crystal to permit the sample tube to enter the well of the NaI crystal. Its removal permits better counting efficiencies for the low energy gamma radiations emitted by the thorium and for the use of large sample tubes. All background radioactivity measurements must be made with the absorber removed.

Distribution

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