AD-A148 785

AD A148785

AD-E401 259

TECHNICAL REPORT ARPAD-TR-84001

DISTRIBUTION OF AVERAGE PARTICLE DIAMETERS FOR THREE LOTS OF NITROGUANIDINE AS MEASURED BY THE FISHER SUB-SIEVE SIZER

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NOVEMBER 1984

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PRODUCT ASSURANCE DIRECTORATE
DOVER, NEW JERSEY

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REPORT DOCUMENTATION PAGE		READ INSTRUCTIONS BEFORE COMPLETING FORM
1. REPORT NUMBER Technical Report ARPAD-TR-84001	2. GOVT ACCESSION NO.	3. RECIPIENT'S CATALOG NUMBER
4. TITLE (and Subtitle) DISTRIBUTION OF AVERAGE PARTICLE DIAMETERS FOR THREE LOTS OF NITROGUANIDINE AS MEASURED BY THE FISHER SUB-SIEVE SIZER		5. TYPE OF REPORT & PERIOD COVERED Final July-Aug 1983
		6. PERFORMING ORG. REPORT NUMBER
7. AUTHOR(s) Eric R. Bixon		8. CONTRACT OR GRANT NUMBER(s)
9. PERFORMING ORGANIZATION NAME AND ADDRESS ARDC, PAD Artillery Systems Div [AMSMC-QAR-R(D)] Dover, NJ 07801-5001		10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS SOW 83G001
11. CONTROLLING OFFICE NAME AND ADDRESS ARDC, TSD STINFO Div (SMCAR-TSS) Dover, NJ 07801-5001		12. REPORT DATE November 1984
		13. NUMBER OF PAGES 34
14. MONITORING AGENCY NAME & ADDRESS(if different from Controlling Office)		15. SECURITY CLASS. (of this report) Unclassified
		15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Fisher sub-sieve sizer	Analysis of variance
Nitroguanidine	Particle size distribution
M30 propellant	Between-drum component of variance
Components of variance	Within-a-drum component of variance
Error variance	Sampling plans

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Three lots of nitroguanidine were sampled extensively and tested with the Fisher sub-sieve sizer (FSSS). The populations of FSSS average particle diameters (APD) were determined for each lot. The components of variance (within-a-drum, between drums, and error variance) were determined for each of the lots with analysis of variance (ANOVA) techniques.

In addition, the FSSS test method itself was subjected to ANOVA techniques to

(cont)

20. ABSTRACT (cont)

determine the components of variance (variance due to technicians, variance due to plug and tube sets, and an estimate of the error variance).

CONTENTS

TABLES

FIGURES

INTRODUCTION

In July 1983, Sunflower Army Ammunition Plant (SFAAP), operated by Hercules Aerospace Division, started manufacture of the first of the three sublots of nitroguanidine (NQ). These sublots were being manufactured in the SFAAP demonstration plant as part of the NQ engineering study. Since the basic goal of the engineering study had been to determine the ballistic effect of NQ particle size on the performance of M30 propellant, the quality assurance effort centered on characterizing as accurately as possible the particle size distribution contained in each sublot [in terms of Fisher sub-sieve sizer (FSSS), average particle diameter (APD) measurements].

QUALITY ASSURANCE SAMPLING PLANS

Preliminary Product Assurance Directorate (PAD) Plan

In March 1983, PAD proposed a sampling plan to ascertain the actual particle size distribution of Fisher sub-sieve values for the NQ lots. The main purpose of the plan was to assure that there would be sufficient sampling to obtain an adequate statistical description of each of the three sublots. This plan stipulated that a single sublot of NQ would consist of about 100 drums and that each drum would contain 50 lb of NQ. Thirty of these drums were to be sampled (sample size to be large enough for three Fisher sub-sieve analyses). Of the 30 drums, 10 were to be sampled in three places:

1. At the top of the barrel
2. At the bottom of the barrel
3. At the middle of the barrel

The samples at the middle and the bottom of the barrels were to be taken with a thief sampler. Single samples were to be taken off the tops of the remaining 20 drums.

Each sample was to be analyzed with the Fisher sub-sieve sizer (FSSS), with triplicate analyses being made of each sample (i.e., the sample was divided into three subsamples and the FSSS test was to be performed on each subsample). After each test, the old subsample was to be discarded and the entire test sequence was to be run on the subsequent subsample.

Adherence to the order of sampling was stressed. The following criteria were given for sampling 100 drums:

1. The first few would be sampled in three places.

2. Once the within-drum component of variance had been established, the sampling could be reduced to one sample from each drum.

3. This would be continued for five to ten drums until the drum-to-drum component of variance had been established.

4. Then every fourth drum would be sampled.

5. Occasionally, a drum could be sampled in three places to confirm that the within-drum component of variance had not changed.

This PAD sampling plan was reviewed by personnel of the Hercules QA Department who then prepared a more detailed sampling plan.

Hercules (SFAAP) Quality Assurance Department Plan

Hercules proposed to implement the PAD sampling plan in the following manner:

For ease of operation, samples would be obtained during the NQ drum packaging operation. The samples were to be obtained by inserting either the sample bag or a long handled plastic cup directly into the product stream between the delumper and the packing drum. Sample size was to be approximately 1/3 to 1/2 the volume of the sample bag, and not less than 1 ounce. Each sample bag was to be identified by lot number, drum number, and location within the drum (bottom, middle, top).

During packaging of the first 500 lb manufactured for each of the three lots, a sample of product stream was to be obtained at 25-lb intervals. This was to be accomplished by sampling material flow into the NQ drums in the following sequence:

Drums no. 1, 3, 5, 7, and 9: obtain sample from bottom, middle, and top of drum.

Drums no. 2, 4, 6, 8, and 10: obtain sample from middle of drum.

Drums no. 25, 40, 55, 70, 85, and 100: obtain sample from bottom, middle, and top of drum.

Drums no. 16, 22, 28, 34, 41, 47, 53, 59, 65, 71, 77, 83, 89, and 95: obtain sample from top of drum.

If the lot size exceeded 100 drums, sampling was to be continued from the top of every sixth drum (drums 101, 107, etc.) until packout had been completed. Also, the last full drum packed was to be sampled.

Discussion

Both The PAD and Hercules (SFAAP) sampling plans were based on 50-lb drums of NQ, the standard amount of NQ which could generally be packed into a drum. Because of the lower bulk density of the Sunflower NQ as compared to NQ from the Cyanamid of Canada, Ltd., it was necessary to pack a smaller amount of material into the volume of a 50-lb drum. It was agreed that 25 lb would be packed into each drum since the propellant manufacturer (Radford) found that quantity to be most convenient. [It should be noted that the bulk density of NQ gets larger as the particle size gets smaller. Thus, large particles will have a bulk density of about 0.2 g/cm^3 while the smaller particles will have a bulk density of about 0.3 g/cm^3.]

The procedure for packing out the drums was to fill them up halfway with NQ, and then pack the material down into the drum with a wooden tamper. (This was a specially designed piece of equipment which basically just consisted of a broom handle mounted perpendicular to a circular piece of plywood which was about the same dimension as the inside of the drum.) After the material had been "tamped" down, additional NQ would be put in the drum until the correct weight (25 lb) had been reached. As a result of using the 25-lb drum, a new sampling plan had to be written to accommodate the increased number of drums.

During manufacture of the sublots, it also became evident that the amount of material required for each lot would not always be 5000 lb; it could vary from as much as 7000 lb for the small and large sublots to about 5000 lb for the medium-size lot. Therefore, to accommodate every possible lot size which might be manufactured, a number of QA plans were developed. These QA plans contained about the same amount of sampling as had been proposed in the Hercules QA plan but were adapted to the various size lots. These final QA plans were the ones used during the packout.

Final Product Assurance Plan

Sampling the 3.5-micron sublot - 7000 lb - 280 drums

Drums no. 1, 3, 5, 7, and 9: obtain sample from bottom, middle, and top of drum.

Drums no. 2, 4, 6, 8, and 10: obtain sample from middle of drum.

Drums no. 25, 76, 127, 178, 229, and 280: obtain sample from bottom, middle, and top of drum.

Drums no. 15, 35, 55, 75, 95, 115, 135, 155, 175, 195, 205, 225, 245, and 270: obtain sample from the top of drum.

Sampling the 5.0-micron sublot - 5000 lb - 200 drums

Drums no. 1, 3, 5, 7, and 9: obtain sample from bottom, middle, and top of drum.

Drums no. 2, 4, 6, 8, and 10: obtain sample from middle of drum.

Drums no. 25, 60, 95, 130, 165, and 200: obtain sample from bottom, middle, and top of drum.

Drums no. 15, 28, 41, 54, 67, 80, 93, 106, 119, 132, 145, 158, 171, and 184: obtain sample from the top of drum.

Sampling the 8.5-micron sublot - 6000 lb - 240 drums

Drums no. 1, 3, 5, 7, and 9: obtain sample from bottom, middle, and top of drum.

Drums no. 2, 4, 6, 8, and 10: obtain sample from middle of drum.

Drums no. 25, 68, 111, 154, 197, and 240: Obtain sample from bottom, middle, and top of drum.

Drums no. 15, 32, 49, 66, 83, 100, 117, 134, 151, 168, 185, 202, 219, and 236: obtain sample from the top of drum.

Sampling Plan for a 6500-lb sublot - 260 drums

Drums no. 1, 3, 5, 7, and 9: obtain sample from bottom, middle, and top of drum.

Drums no. 2, 4, 6, 8, and 10: obtain sample from middle of drum.

Drums no. 25, 72, 119, 166, 213, and 260: obtain sample from bottom, middle, and top of drum.

Drums no. 15, 33, 51, 69, 87, 105, 123, 141, 159, 177, 195, 213, 231, and 249: obtain sample from the top of the drum.

Sampling Plan for a 7500-lb sublot - 300 drums

Drums no. 1, 3, 5, 7, and 9: obtain sample from bottom, middle, and top of drum.

Drums no. 2, 4, 6, 8, and 10: obtain sample from middle of drum.

Drums no. 25, 80, 135, 190, 245, and 300: obtain sample from bottom, middle, and top of drum.

Drums no. 15, 36, 57, 78, 99, 120, 141, 162, 183, 204, 225, 246, 267, and 288: obtain sample from the top of the drum.

For each NQ sublot, six 1/4-lb samples were to be sent to the Large Caliber Weapon Systems Laboratory at ARDC:

1. Two samples taken at the mean of the sublot.

2. Two samples taken at the upper limit of the range of the means of the sublot.

3. Two samples taken at the lower limit of the range of the means of the sublot.

The two 1/4-lb samples were to be obtained by splitting a 1/2-lb sample in half.

One feature of this final QA plan was that it required equal sampling along the lot (that is, every twentieth drum or so) to determine the pure error variance of the test method as well as the drum-to-drum variance. (These data were obtained from all drums which were sampled on the top.) Another feature of the sampling plan was that it allowed for determination of the within-drum variance as well as the between-drum variance from independent data sets (i.e., from drums sampled at the top, middle, and bottom).

EVALUATION OF SOURCES OF ERROR IN THE FSSS TEST PROCEDURE

Variations in some data obtained previously* by Sunflower technicians on a NQ sample were analyzed to evaluate possible sources of error. These data, shown in table 1, evaluate the results of nine technicians using the FSSS. The first data set evaluates two different plugs. The second data set evaluates two different tube sets.

The FSSS is basically an air permeability technique and is utilized in the following manner: The NQ sample is packed into a tube. A set of brass plugs is then put on both sides of the NQ sample. The sample is then packed down to a predetermined porosity. Finally, air is blown through at a fixed flow rate, and the back pressure is measured using a water column. This water column is affixed to a scale and the height of it determines the Fisher sub-sieve value of the sample.

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* Taken from FSSS "round robin" performance at ARRADCOM in 1981.

Table 1. Results (microns) of duplicate and triplicate analyses by multiple technicians using two sets each of plugs and tubes--FSSS test procedure

	Technicians								
Plug set	1	2	3	4	5	6	7	8	9
1	7.5	7.5	6.9	7.43	7.6	7.20	7.0	7.1	7.15
	7.4	7.4	7.0	7.4	7.4	7.15	6.8	6.8	7.20
	8.3	7.1	7.0	7.45	7.3	7.15	6.9	7.2	7.15
2	7.6	7.20	6.8	7.10	7.2	6.6	6.8	6.9	7.0
	7.7	7.15	6.4	7.08	7.3	7.0	6.8	6.9	6.9
	7.6	7.15	6.8	7.05	7.2	7.0	7.0	6.9	6.9
Tube set									
1	7.5	7.6	7.4	7.6	7.6	7.3	7.3	7.1	7.10
	7.45	7.7	8.0	7.7	7.3	7.3	7.0	7.1	7.25
2	8.5	8.5	8.1	8.0	8.3	8.3	7.5	7.6	7.8
	8.5	8.3	7.8	8.0	8.2	8.5	7.7	7.5	7.4

The analysis of variance done on the data is shown in tables 2 and 3.

The components of variance given in tables 2 and 3 can be explained as follows:

1. The error variance of the test is 0.027 or 0.028 µm. The error variance is that variance associated with a single technician's making triplicate determinations on a sample with a given set of tubes and plugs.

2. The variance due to plugs is small at 0.020. It is about two-thirds of the error variance.

3. The variance due to tubes is very large at 0.188. It is approximately six times the error variance.

4. The estimates of the variances due to technicians are 0.052 for the tubes and 0.070 for the plug data. These variances are about three times the error variance.

Table 2. Two-way ANOVA results--technicians versus tubes

Source of variation	Sum of squares (ss)	Degrees of freedom (df)	Mean square (ms)	Test statistic (F)
Tubes	3.4844	1	3.484444	37.2019
Technicians	2.4238	8	0.302969	3.2347
Tubes/technicians interaction	0.7493	8	0.093663	3.4583
Error	0.4875	18	0.027083	
Total	7.1450	35		

The error variance is 0.02708.
The tubes/technicians variance is 0.03329.
The variance due to tubes is 0.18838.
The variance due to the technicians is 0.05233.

Table 3. Two-way ANOVA results--technicians versus plugs

Source of variation	Sum of squares (ss)	Degrees of freedom (df)	Mean square (ms)	Test statistic (F)
Plugs	0.5500	1	0.550046	33.7528
Technicians	3.4856	8	0.435696	26.7359
Plug/technicians interaction	0.1304	8	0.016296	0.5862
Error	1.0009	36	0.027802	
Total	5.1669	53		

The error variance is 0.02780.
The plugs/technicians variance is -0.00384. (Negative components of variance arise strictly from random variation and have no real interpretation. Many authors choose to set them equal to zero.)
The variance due to plugs is 0.01977.
The variance due to the technicians is 0.06990.

Based on these estimates, it was decided to make all measurements on the FSSS with a single tube and a single set of plugs, thereby eliminating the plug and tube variances. Because the number of determinations required by the QA sampling plan for the NQ sublots was extensive, it was not practical to use a single technician. Therefore, technicians could not be eliminated as a source of variance.

SUBLOT MANUFACTURE AND PROCESS SAMPLING

The first sublot to be manufactured was the medium size NQ. Next, the large size was manufactured, and the final manufacturing operation involved production of the small-size NQ particles.

The normal sequence of operations in the manufacture of NQ is that after leaving the pure crystallizer, the NQ crystals get filtered by a rotary drum filter. Knives, actually blades which scrape the filter cake off the rotary drum filter, then scrape off chunks of the NQ filter cake and it is dumped on the dryer. The NQ then proceeds along the dryer which is a long conveyor operation that continuously dries the NQ. The NQ is then fed through the delumper and into the drums.

It was decided to manufacture all the sublots without using the delumper. This was done because it was feared that clumps of wet material might get stuck in the delumper, resulting in a bottleneck in the process as well as a potential hazard. Previous experience in the main plant revealed that if the delumper got stuck, it just kept chewing up the same material. It could then heat up and start to fume, creating a potentially hazardous situation. As a result, it was decided that all these sublots would be packed out, put through the dryer and delumper, and then be packed out again. QA sampling was to be deferred until after the final pack-out.

The result of not using the delumper prior to the first pack-out was basically a lumpy product. In some cases, the moisture content was also too high. The moisture level in a few samples was as high as 48%. (The specification requirement is 0.25%.)

Although the QA sampling was not taken during the manufacturing process, the normal process sampling was still conducted in a routine manner. This sampling amounted to numerous samples being analyzed for NQ concentration, guanidine bisulphate concentration, and also the levels of acid. Also done routinely was a Fisher sub-sieve analysis and a moisture level analysis. Only a single analysis was done using the FSSS. The FSSS and the moisture were run on every fifth drum (or every 125 lb).

Since all three sublots were going to be reworked through the delumper and dryer, it was possible to eliminate unwanted drums from each of the three sublots. The initial FSSS average particle diameters (ADP)--taken prior to the drying and delumping operation--were 3.5, 5.2, and 9.2 microns.

DIFFICULTIES IN THE MANUFACTURING OPERATION

Prior to start of manufacture of the three sublots, all information regarding changing the particle size of the final NQ product had been obtained by taking already manufactured NQ and putting it into solution in the dissolver feed tank. By varying the concentration of NQ in this tank, it was then possible to change the size of the final NQ crystals without any other process changes. (This is essentially a recrystallization process where the dried NQ is redissolved in the dissolver feed tank.)

Regarding these three sublots, the large particles and the medium particles were manufactured by reacting guanidine nitrate with mixed acid to form the NQ. This type of NQ is called "acid" NQ as opposed to recrystallized NQ. During manufacture of the large particles, it became evident that the acid NQ behaved differently from recrystallized NQ as far as the crystal size of the final product. Prior data in manufacturing large-size NQ particles (using recrystallized NQ) had shown that if the NQ concentration in the dissolver feed tank were changed from the 11% or 12% concentration required to make specification grade NQ to about 8%, then large particles of NQ would result. During manufacture of the large-size NQ particles, it became apparent that "acid" NQ did not behave the same as the recrystallized NQ. Even though the concentration in the dissolver feed tank was 8%, only specification grade material was being produced. As a result of this, it was decided to raise the crystallizer temperature and pressure in order to make the large particles. When this was done, the response was very quick. The particle size increased within a number of hours. After a while, the particle sizes were getting too big so the crystallizer temperature was lowered. This resulted in a decrease in the particle size. As a result of this type of overcontrol of the crystallizer temperature, the particles manufactured during this period exhibited a sinusoidal-type variation in the particle size with lows around 8 microns and highs at about 12 microns.

Since it was found that the "acid" NQ behaved differently from the recrystallized NQ, it was decided that the small particle-size NQ should be manufactured with the recrystallization technique. Although the small particles were manufactured from recrystallized NQ, at the maximum vacuum obtainable in the crystallizer (i.e., the crystallizer was operating at the lowest possible temperature), it was still not possible to consistently manufacture 3.00-micron particles. The crystal size varied from 3.00 to 5.00 microns.

One explanation for the difficulty in manufacturing the small particles was that prior to this attempt, the small NQ was manufactured during the winter months when the ambient temperature was very low. As a result of the low temperature of the surroundings, there was virtually no heat transfer from the surroundings to the crystallizer. In the summer months, however, the high temperature of the surroundings (as hot as 105°F) caused a large amount of heat transfer into the crystallizer, making it difficult to keep the temperature (and pressure) low enough to consistently manufacture 3.00-micron NQ.

STATISTICAL ANALYSIS

Sampling was done according to the final quality assurance plan for each of the three sublots. The only outlier which was really uncovered by this sampling plan was in the small sublot. After completion of the sampling procedure, it appeared that drum number 245 had a FSSS of about 5.60 microns. This clearly was not a member of the small population (i.e., the small size NQ had a FSSS APD of about 4.00 microns and a standard deviation of 0.25 microns). The value 5.60 microns is over six standard deviations away from the mean and cannot be considered to be part of the same population. Drums on either side of no. 245 were sampled (nos 244, 246, 243, and 247). Drum number 244 also appeared to have a higher FSSS value than the other drums in the small sublot, so drums 244, 245, and 246 were removed from the sublot. To ascertain the number of drums with high FSSS values in this sublot, an additional random sample of 10 drums was selected and analyzed by the FSSS. Testing of these 10 additional drums did not disclose any additional high FSSS results. It was decided that statistically the sublot should be described as being bimodally distributed; that is, for the most part it was made up of material with a FSSS mean of 4.00 microns and a standard deviation of about 0.25 micron. For a small portion of the lot, there existed another population with a mean of over 5.00 microns. To estimate the percent of defective material in the lot, a percent defective was calculated, based on the number of defective drums found and the total number of drums sampled. Since two defective drums were found in the 39 drums sampled, the percent defective in this sublot was estimated as 5.1.

It is difficult to understand why a sublot should exhibit a bimodal distribution. Certainly, when the NQ comes out of the crystallizer, it is not bimodally distributed. Bimodality of the small distribution was hypothesized as being caused by one of the following:

1. A drum containing some medium size NQ which was accidentally dumped on the dryer, or

2. Some of the material agglomerated in the drums contained a large amount of moisture.

The analysis of variance (ANOVA) results which were obtained from the data on all three sublots is shown in tables 4, 5, 6, and 7. These results have several general features:

1. The magnitude of the F value in each table is indicative of the variation between the drums. Note that the F values are significant for each of the sublots, indicating that there is a significant component of variance between drums for each of the sublots.

2. The components of variance due to the error variance and the variances between drums are determined for each of the sublots. In each case, the variance between drums is larger than the pure error variance. The total variance is equal to the sum of the error variance and the between-drum variance.

Table 4. One-way ANOVA for the defective portion of the small-size sublot

Source of variation	Sum of squares (ss)	Degrees of freedom (df)	Mean square (ms)	Test statistic (F)
Between	0.27909E+00	2	0.13954E+00	0.11972E+02
Within	0.69933E-01	6	0.11656E-01	
Total	0.34902E+00	8	0.43628E-01	

The grand mean of this set of data is 5.4644.
The error variance is 0.01166.
The variance between drums is 0.04363.
The total variance is 0.05429.
The standard deviation of the lot is 0.23299.

Table 5. One-way ANOVA for the large-size sublot

Source of variation	Sum of squares (ss)	Degrees of freedom (df)	Mean square (ms)	Test statistic (F)
Between	0.28420E+02	20	0.14210E+01	0.11814E+02
Within	0.50518E+01	42	0.12028E+00	
Total	0.33472E+02	62	0.53987E+00	

The grand mean of this set of data is 10.0316.
The error variance is 0.12028.
The variance between drums is 0.43357.
The total variance is 0.55385.
The standard deviation of the lot is 0.74421.

Table 6. One-way ANOVA for the medium-size sublot

Source of variation	Sum of squares (ss)	Degrees of freedom (df)	Mean square (ms)	Test statistic (F)
Between	0.16433E+02	20	0.82164E+00	0.19976E+02
Within	0.17275E+01	42	0.41130E-01	
Total	0.18160E+02	62	0.29291E+00	

The grand mean of this set of data is 6.0551.
The error variance is 0.04113.
The variance between drums is 0.26017.
The total variance is 0.30130.
The standard deviation of the lot is 0.54891.

Table 7. One-way ANOVA for the small-size sublot

Source of variation	Sum of squares (ss)	Degrees of freedom (df)	Mean square (ms)	Test statistic (F)
Between	0.61991E+01	32	0.19372E+00	0.82457E+01
Within	0.15506E+01	66	0.23494E-01	
Total	0.77497E+01	98	0.79079E-01	

The grand mean of this set of data is 4.0508.
The error variance is 0.02349.
The variance between drums is 0.05674.
The total variance is 0.08024.
The standard deviation of the lot is 0.28326.

3. The grand mean and the standard deviation are indicated for each of the sublots. The standard deviation is simply the square root of the total variance as presented in these tables. Note that the lot standard deviation increases with the lot particle size.

These results are summarized in table 8. Also shown in this table are the 1st and 99th percentiles of each distribution as predicted by the "t" distribution with the degrees of freedom indicated in the table.

Table 8. Data summary of the sublots

Sublots	% of population	Mean	Standard deviation	1st percentile of the distribution	99th percentile of the distribution	Degrees of freedom
Small	94.9 5.1*	4.05* 5.46	0.283 0.233	3.36 4.40	4.74 6.51	42 3
Medium	100	6.06	0.549	4.69	7.43	23
Large	100	10.03	0.744	8.18	11.87	25

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* Note that the small sublot is bimodally distributed.

Since the small sublot is a bimodal distribution (i.e., composed of two subpopulations), two separate analyses of variance results were generated. The first ANOVA generated (1-way ANOVA for the small size NQ sublot, table 7) represents the bulk of the population (approximately 94.90% as indicated in table 8). The few drums which were running high were removed from the sublot, as previously stated. Three samples were obtained from two of these drums before they were taken out of the small sublot. These results are analyzed using ANOVA and the results are shown in a separate analysis of variance table (table 4). Note that this population has a population mean which is close to the medium-size sublots and a population standard deviation which is similar to the small-size sublots.

As a final check on within-a-drum homogeneity, the drums which were sampled in three places were analyzed using ANOVA with a nested design. These results are shown in tables 9, 10, and 11. This type of ANOVA supplies us with three estimates of the components of variance:

1. A component of variance due to the error of the test method. This variance is often termed the pure error variance. It is basically the pooled variance of all determinations which were made on each sample. It is due to two major factors:

- The error in the test method itself.

- Any difference between the sub-samples taken from the single sample. (This type of error may be reduced by the use of a sample riffler, which divides the single sample taken from the drum into three homogeneous portions. A sample riffler was not used in this study.)

2. A component of variance between samples taken from the same drum. This is termed as the variance within-a-drum and is a measure of within-drum homogeneity (i.e., if the material is completely homogeneous within a drum, then the variation between samples should not show up as being significantly larger than the error variance when measured by an F test).

3. A component of variance between drums.

Table 9. ANOVA using nested design for the small-size sublot

Source of variation	Sum of squares (ss)	Degrees of freedom (df)	Mean square (ms)	Test statistic (F)
Drums	4.9717	9.0000	0.5524	8.2156
Samples	1.3448	20.0000	0.0672	3.4141
Error	1.1817	60.0000	0.0197	

The error variance is 0.01969.
The variance within a drum is 0.01585.
The variance between drums is 0.05391.

Table 10. ANOVA using nested design for the medium-size sublot

Source of variation	Sum of squares (ss)	Degrees of freedom (df)	Mean square (ms)	Test statistic (F)
Drums	4.7367	10.0000	0.4737	2.4862
Samples	4.1915	22.0000	0.1905	5.0275
Error	2.5011	66.0000	0.0379	

The error variance is 0.03790.
The variance within a drum is 0.05088.
The variance between drums is 0.03146.

Table 11. ANOVA using nested design for the large-size sublot

Source of variation	Sum of squares (ss)	Degrees of freedom (df)	Mean square (ms)	Test statistic (F)
Drums	37.3895	10.0000	3.7390	14.4950
Samples	5.6748	22.0000	0.2579	3.3189
Error	5.1296	66.0000	0.0777	

The error variance is 0.07772.
The variance within a drum is 0.06008.
The variance between drums is 0.38678.

The general trend for the magnitude of the different components of variance is that the error variance is generally the smallest. There is a small component of variance due to variation within a drum, and the largest component of variance is due to the differences between drums. In a perfectly homogeneous lot (i.e., where there was not variation within a drum and no difference from drum to drum), the estimates for the components of variance between and within a drum would be zero. Since there are process fluctuations which are significant, the components of variance between and within a drum are not zero.

It is interesting to note that for the case of the medium-size sublot, the largest component of variance was found to be within a drum; that is, the drum-to-drum variation was actually less than the variation observed when the same drum was sampled in different places.

Based on the analysis of variance results obtained using nested classification, the following conclusions were reached:

1. The FSSS method was found to be precise enough to note variations in the final NQ produced within each of the sublots. These variations were found to exist within a drum and between drums, and are variations in excess of the pure "error" variance associated with the FSSS test method itself.

2. The component of variance between drums was approximately equal in magnitude to the error variance for the medium particles; for the large and small particles, however, the component of variance between drums was from 3 to 8 times larger than the pure error variance, indicating that a significant difference between drums exists within each of these two sublots.

A comparison of the ANOVA results for the sublots is shown in table 12. The estimates obtained using 1-way ANOVA are compared with the estimates obtained using a nested design. It is important to note that the ANOVA are based on two essentially different sets of data. The basic statistical quantities which are represented in table 12 (i.e., the mean, error variance, and population variance) are fairly consistent between the two sets of results with the exception of the population variance for the medium-size particles. The estimate of this variance is 0.12024 from the nested data and 0.3013 from the 1-way ANOVA data.

Table 12. Comparison of 1-way ANOVA and nested ANOVA results for population statistics

	1-way ANOVA			Nested ANOVA		
Particles	Mean	Error variance	Population variance	Mean	Error variance	Population variance
Small	4.0508	0.02349	0.0824	3.86	0.01969	0.0895
Medium	6.0551	0.04133	0.30130	5.873	0.03790	0.12024
Large	10.03	0.12028	0.55385	10.11	0.07772	0.52458

The value of the calculated F ratio from these two variances is 2.51. Since $F_{.99}$ (23,33) is equal to 2.48, the difference in the variances is significant.

Because the 1-way ANOVA estimates were obtained from more randomly taken samples than the nested ANOVA estimates, the values for the population mean and standard deviation from the 1-way ANOVA are considered to be more representative of the overall population.

The frequency distributions and histograms for each sublot are shown in tables 13, 14, and 15 and figures 1, 2, and 3. Note the distinct bimodality of the small sublot. The bar at 5.0 microns in the histogram of the small particles is completely missing. The three short bars at the high end of the smalls are representative of the small subpopulation of the smalls. The medium and large histograms appear to be normally distributed. They may be slightly skewed to the low end.

Table 13. Frequency distribution for the small-size sublot

Lower limit	Upper limit	Percent
3.4700	3.6950	8.5714
3.6950	3.9200	24.7619
3.9200	4.1450	27.6190
4.1450	4.3700	19.0476
4.3700	4.5950	8.5714
4.5950	4.8200	5.7143
4.8200	5.0450	0.0000
5.0450	5.2700	1.9048
5.2700	5.4950	1.9048
5.4950	5.7200	1.9048

The upper limit is 5.7200.
The lower limit is 3.4700.

Table 14. Frequency distribution for the medium-size sublot

Lower limit	Upper limit	Percent
5.1700	5.3930	6.3492
5.3930	5.6160	11.1111
5.6160	5.8390	25.3968
5.8390	6.0620	15.8730
6.0620	6.2850	15.8730
6.2850	6.5080	3.1746
6.5080	6.7310	7.9365
6.7310	6.9540	4.7619
6.9540	7.1770	6.3492
7.1770	7.4000	3.1746

The upper limit is 7.4000.
The lower limit is 5.1700.

Table 15. Frequency distribution for the large-size sublot

Lower limit	Upper limit	Percent
8.6000	8.9200	7.9365
8.9200	9.2400	12.6984
9.2400	9.5600	6.3492
9.5600	9.8800	14.2857
9.8800	10.2000	19.0476
10.2000	10.5200	12.6984
10.5200	10.8400	14.2857
10.8400	11.1600	7.9365
11.1600	11.4800	3.1746
11.4800	11.8000	1.5873

The upper limit is 11.8000.
The lower limit is 8.6000.

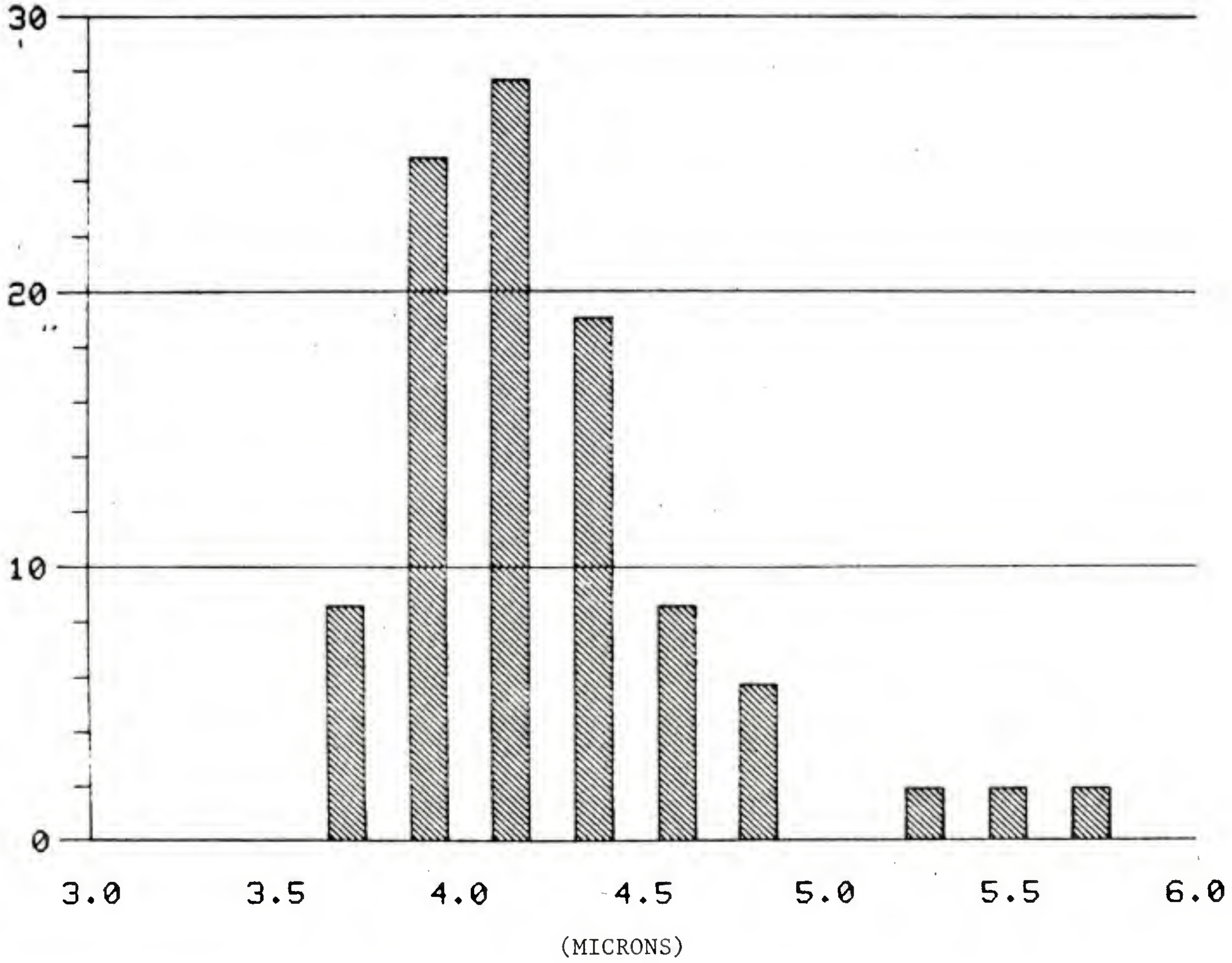


Figure 1. Histogram of the Fisher sub-sieve sizer average particle diameters for the small size sublot

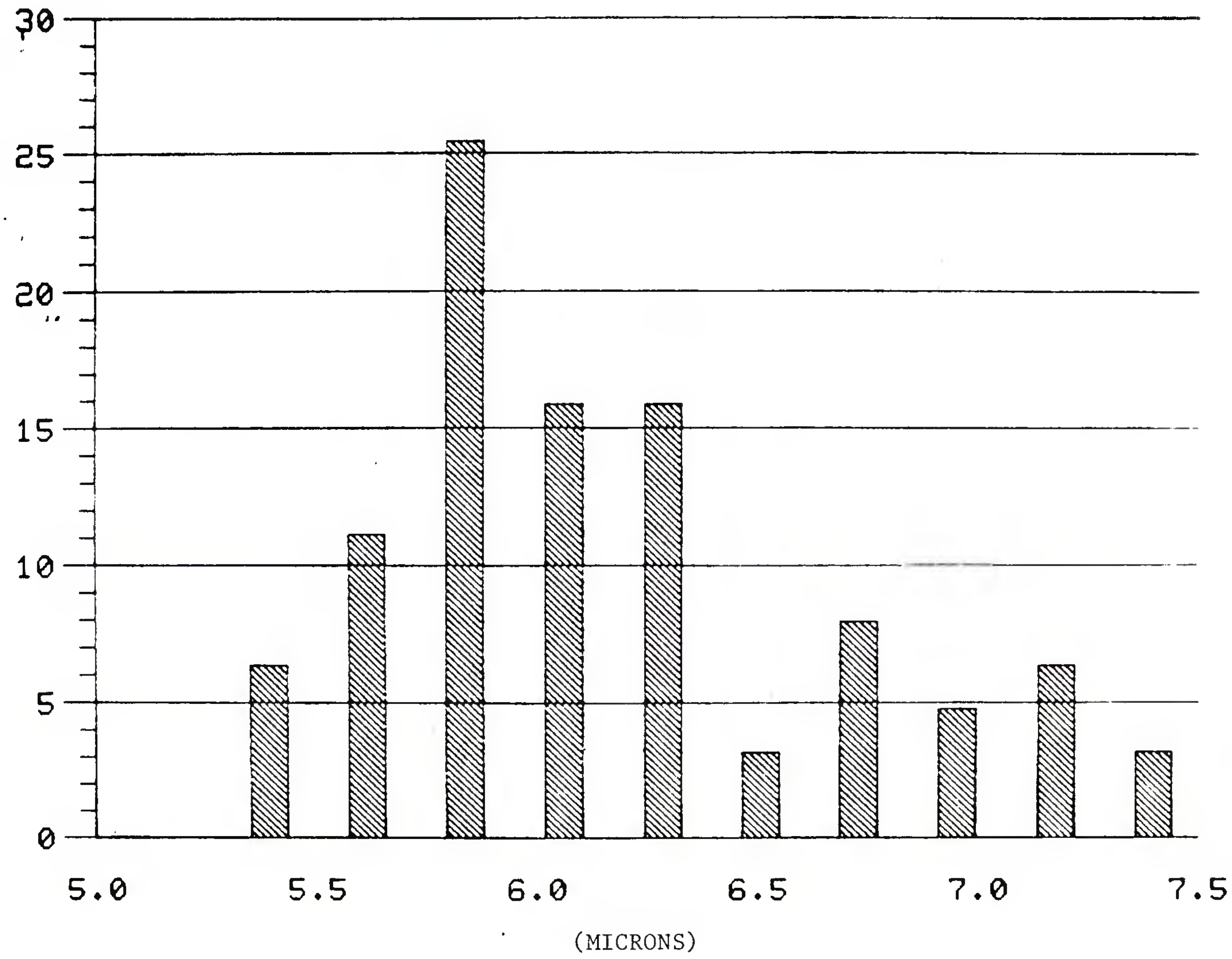


Figure 2. Histogram of the Fisher sub-sieve sizer average particle diameters for the medium size sublot

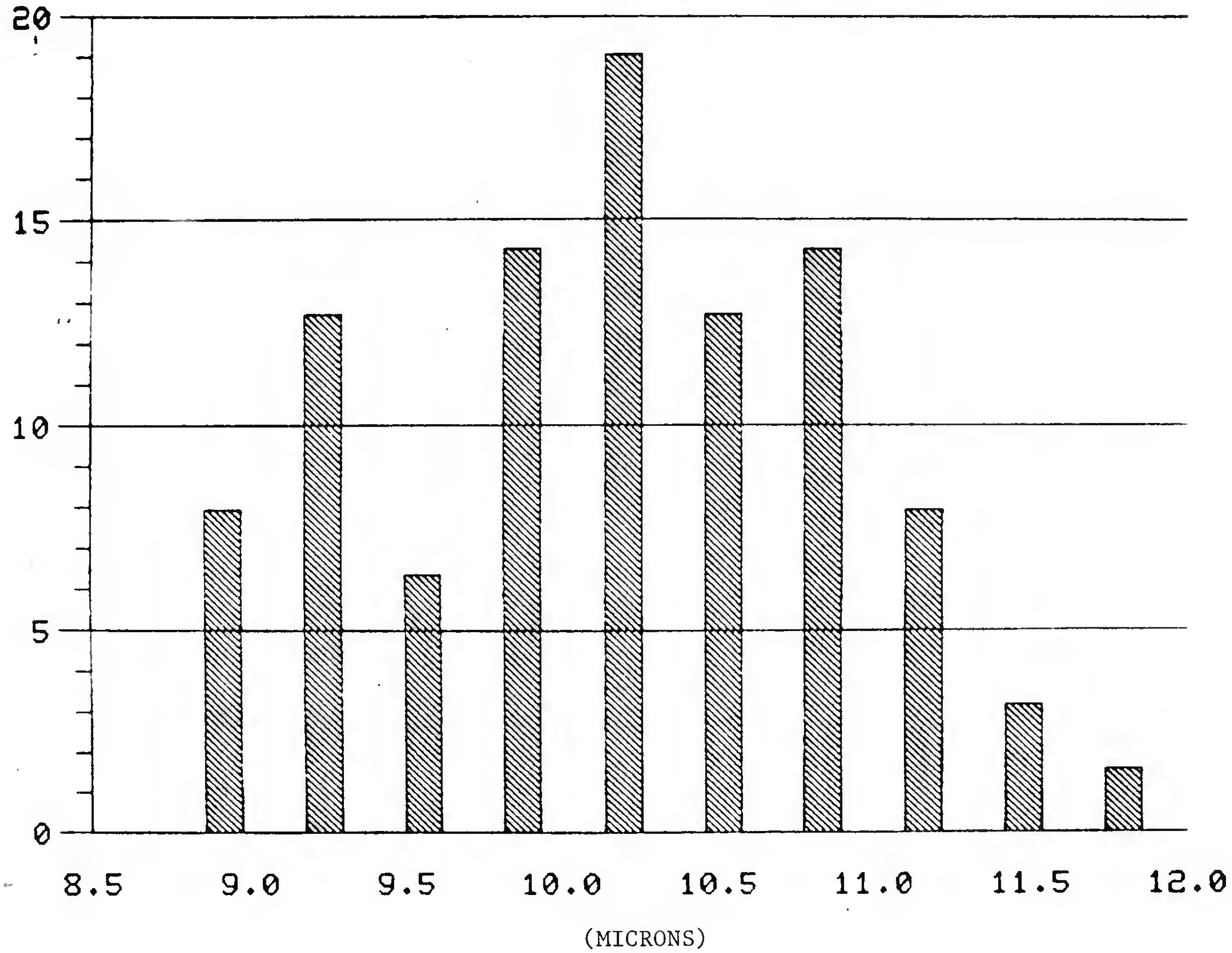


Figure 3. Histogram of the Fisher sub-sieve sizer average particle diameters for the large size sublot

A comparison of the actual sublot particle sizes and the requirements in the scope of work considers the following:

1. The criteria for sublot description as given in the SOW for this engineering study was:

Small Particles	$\overline{X} = 3.00$	$S = 0.50$
Medium Particles	$\overline{X} = 5.00$	$S = 1.00$
Large Particles	$\overline{X} = 8.00$	$S = 1.00$

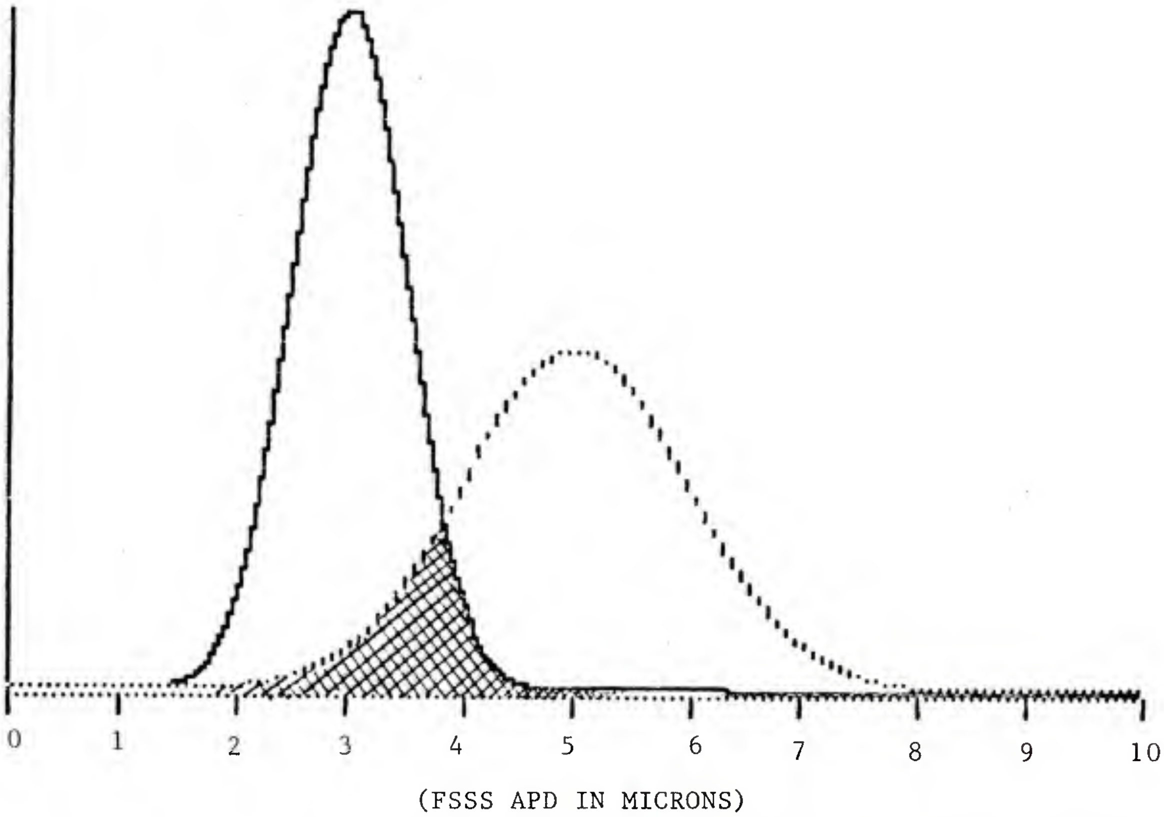
These criteria were based on the fact that three different particle sizes were required for the purposes of this engineering study and for the range of particle sizes which could be produced in the demonstration plant.

2. It became obvious when looking over these requirements that some of the particles in the high end of the small distribution would be the same particle size as the particles in the low end of the medium distribution. The percent of the small and medium distributions which overlapped is shown schematically in figure 4. The method of calculating this overlap is illustrated in figure 5. Basically, the abscissa at the point of intersection of the two distributions was determined. A table of z-scores was then used to evaluate the percent overlap for the distributions.

3. The final value of the percent overlap for the small distribution was determined by linear combination of the results for each of the subpopulations in the smalls; that is, 94.9% of the smalls overlap with 1.57% of the mediums; and 5.1% of the smalls overlap with 39.5% of the mediums. The total overlap is then: [94.9 (1.57) + 5.1 (39.5)]/100 or 3.5%. These results are shown in table 16.

The percent overlap for the actual manufactured sublots, contrasted with the overlap cited in the SOW, is shown in table 17. Note that in each case, the actual overlap is significantly less than that specified in the SOW.

4. Regarding the growth of the particles, it should be noted that prior to delumping and drying, the FSSS values of the small, medium, and large sublots were 3.5, 5.2, and 9.2 microns, respectively. After drying and delumping, the particle sizes were 4.0, 6.0, and 10.0 microns for the small, medium, and large particles, respectively.



The small and the medium particle size distributions as specified in the Scope of Work:

SMALLS: $\bar{X} = 3.00$
$s = 0.5$

MEDIUMS: $\bar{X} = 5.00$
$s = 1.00$

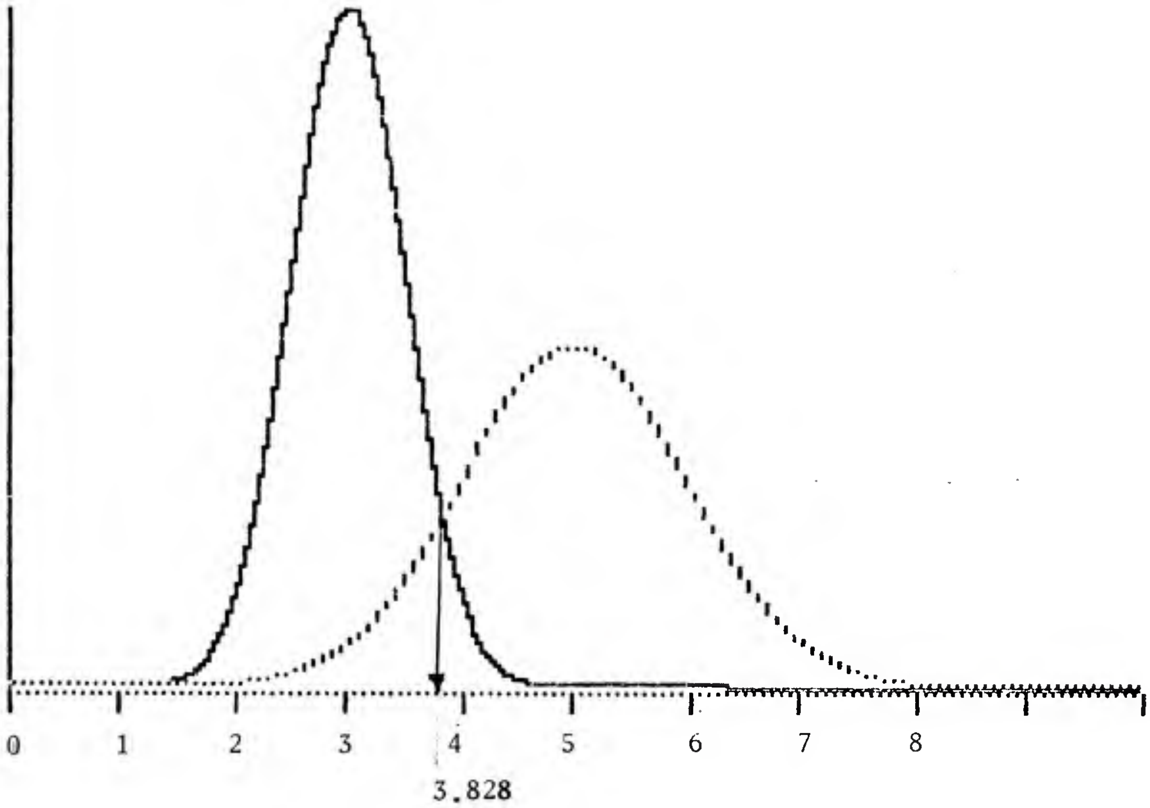
The percent overlap of the two distributions is indicated by the cross-hatched area. This is equal to 16% of the area of either one of the distributions. Therefore:

▨

(1) 16% of the small particles are identical to 16% of the medium particles, or

(2) 16% of the particles in the small population have identical counterparts in the medium population

Figure 4. Percent overlap as specified in the SOW



(FSSS APD IN MICRONS)

Figure 5. Method of obtaining overlap involves determining the value of the abscissa at the point of intersection of the two distributions being considered

Table 16. Percent overlap for several distributions

Distribution 1		Distribution 2			
$\overline{X}$	s	$\overline{X}$	s	Description	% Overlap
3.00	0.50	5.00	1.0	Requirements in SOW for small and medium distributions	16.00
5.00	1.00	8.00	1.0	Requirements in SOW for medium and large lots	13.36
4.05	0.283	6.05	0.55	Actual results for bulk (94.9% of the small distribution) of the small and medium lots	1.57
5.46	0.233	6.05	0.55	Actual results for the small subpopulation (5.1%) which exists in the small and medium lots	39.50
10.03	0.744	6.05	0.55	Actual results for the medium and large lots	0.26

Table 17. Percent overlap between the sublots

Sublots	% overlap permitted in SOW	% actual overlap based on 1-way ANOVA
Small and medium	16.00	3.50
Medium and large	13.36	0.26

CONCLUSIONS

The Fisher sub-sieve sizer test method has been subjected to intense scrutiny regarding sources of variation associated with it. It was determined that the tubes used and the technicians were all major sources of variation in the test method. The plugs used did not appear to be a significant source of variation.

In addition three lots of differing Fisher sub-sieve size average particle diameters have been intensely sampled to provide estimates of the components of variance between and within drums as well as the error variance.

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