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PARTICLE SIZE ANALYSIS OF TUNGSTEN METAL POWDER

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H. J. de Bruin

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R. C. Cairns

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Summary

A method of particle size analysis for sub–sieve, tungsten metal powder has been developed using the Andreasen pipette.

Use of ¼ per cent by volume of tungsten powder in demineralised water gives minimum agglomeration. The method is useful for comparing the distribution of different batches of tungsten powder.

No correlation between results from this method and the microscopic counting method used by the suppliers of the powder was found.

CONTENTS

1. INTRODUCTION

Because of work being carried out to simulate uranium sodium systems by pumping suspensions of micron–sized tungsten powder in water, it was necessary to have a method available for the determination of particle size distribution of tungsten powder.

The particle size of tungsten powder formed by hydrogen reduction of the oxide or ammonium paratungstate, is likely to vary considerably from batch to batch, even under apparently identical formation conditions.

The size of the particles depends on factors, such as temperature of the reduction, time of the reduction, history of the original oxide, amount of water vapour in the hydrogen, rate of hydrogen flow, temperature gradient, rate of stoking and thickness of the layer of the material reduced (7). Although the chemical route is different, the particle size of uranium powder formed via the hydride will be determined by much the same variables.

Various grades of tungsten powder are available. The powder being used initially was the H.R.1 grade, produced by Murex Ltd., Rainham, Essex, U.K. It is stated by Murex to have the following analysis:–

Micron size	% by count
1	85
2	13
3	2
occasional particle to 4 micron	

The analysis was obtained by microscopic counting.

It was not convenient to develop a method of counting microscopically, due to the limited facilities available. Also, little success was achieved when an attempt was made to reproduce the counting procedure used by Murex. Attention then turned to sedimentation methods of particle size analysis.

Sedimentation methods depend on Stokes' law:–

$$v = \frac{gd^2(\sigma - \rho)}{18 \quad \mu}$$

where v = terminal velocity, cm/sec.
g = acceleration due to gravity, cm/sec^2.
d = particle diameter, cm.
σ = density of the particle, g/cc.
ρ = density of the fluid, g/cc.
μ = absolute viscosity of the fluid, g/(cm.)(sec.)

For diameters in microns and terminal velocities in cm./min., this reduces to:–

$$d_s = 175\sqrt{\frac{v' \mu}{(\sigma - \rho)}}$$

Use of Stokes' law implies that the particles are spheres, hindered settling and agglomeration do not exist and the flow of the particles through the fluid is streamline. For this later condition the Reynolds number must be less than 0.2 where:-

$$Re = \frac{d \cdot v \cdot \rho}{\mu}$$

In most size analysis work, irregularly shaped particles are encountered. In these cases, the diameter obtained is called the Stokes' diameter, as the irregularly shaped particle settles at a rate equal to that of a sphere, having a diameter equal to the Stokes' diameter.

Many authors have attempted to evaluate the various techniques available for particle size analysis of sub-sieve powders. Heywood (4), after extensive research on the various methods of sedimentation analysis, decided that the pipette sampling method gave the greatest accuracy, combined with reasonable ease of operation and can be applied to the widest range of materials. Heywood recommends the Andreasen pipette, (2), with a suspension of one percent by volume.

Loomis, (8), used the Andreasen pipette for particle size analysis of whiteware clays. He converted the cumulative plots to histograms. Although these histograms are useful for comparative purposes, they lose significance when the cumulative plot is asymptotic to infinity.

Amstein and Scott, (1), used the Andreasen pipette and showed that provided complete dispersion of the powders which they investigated, is obtained, concentrations of up to two percent by volume has no effect on the results. The authors show that sedimentation curves plotted as weight percent undersize versus the logarithm of the Stokes' diameter gives a more symmetrical distribution. This implies that the analysis follows a logarithmic normal-distribution law.

Amstein and Scott do not favour presentation of microscopic counts in the form of histograms, because the graph obtained is not a mathematical function, so that interpolation or smoothing of the experimental points is not possible. Also, a percent by weight distribution is to be preferred to a number distribution. For cases where the frequency distribution is required, it can be obtained from the cumulative plot by differentiation, (6).

Rose, (9), states that although microscopic counting would appear to have the advantage of direct measurement, in practice it has several shortcomings. The particles usually have irregular shapes and it appears that in the matching of circular designs of a graticule to irregularly shaped particles, there is a probability of the occurrence of biased errors. The results can be influenced by fatigue and the general health of the operator. Another error is that due to preferential orientation. It is practically impossible to obtain the dimension of the particle which lies parallel to the optical axis of the microscope.

Jarrett and Heywood, (5), made a comparative test on methods of particle size measurement by sedimentation. With the Andreasen pipette as a standard, comparisons were made between such methods as the hydrometer, divers, manometer and photoextinction. The authors concluded that the Andreasen method is the most accurate.

Bradley and Holmes, (3), have made an exhaustive survey of the literature on all methods of particle size analysis. Sedimentation methods are preferred to microscopic counting by Bradley and Holmes and the authors conclude that the Andreasen pipette method should be used as the standard. It is recommended that a suspension concentration of 0.2-0.4 percent by volume be used.

For the purpose of comparing the particle size distributions of tungsten powder, it was decided to use the Andreasen pipette in this investigation. There is no doubt that the accuracy of the method can be influenced by agglomeration. The investigation carried out was made in an endeavour to eliminate as many of the variables as possible causing agglomeration.

2. APPARATUS AND EXPERIMENTAL PROCEDURE

The conventional Andreasen pipette was used, as shown in figure (1). This consists of a cylinder with a ground-glass socket at the top, into which fits a cone provided with a pipette and a three-way cock arrangement.

The tip of the pipette ends 20 cms. under the liquid level, when the apparatus is properly filled. The cylinder is graduated in centimeters, the zero mark being at the level of the tip of the pipette. The volume of the sample withdrawn is 10 mls. at 20°C, and the sample can be diverted into an external vessel by means of the three-way stop cock.

The entire arrangement was clamped into a thermostatically controlled waterbath. The samples were collected in centrifuge tubes and the tungsten thrown out in an angle-head electrical centrifuge.

The water used was a commercial distilled grade for the initial water runs and demineralised water from run 25 onwards. "Univar" absolute alcohol of 99.5 percent purity was used in the alcohol runs. The tap water contained 40 p.p.m. of total dissolved solids. The glycerol solution was made up from A.R. standard glycerol. The acetone was commercial grade.

The medium was brought up to the experimental temperature by placing it in the waterbath overnight. The concentration of the suspension was calculated on a volume - volume basis. All determinations were carried out at 30°C, except where otherwise specified.

After the tungsten had been added, the suspension was made up to the correct level with the head in position. The head was then removed, replaced by a stopper and the whole shaken by hand for five minutes. A stop watch was started at time zero, which was taken to be the moment that shaking was discontinued. The head was replaced and the apparatus placed in the water bath. At time intervals ranging from minutes to several hours, samples were drawn up into the pipette and discharged into tared centrifuge tubes. The withdrawal time was noted for determinations within the first hour. The settling time in this period was calculated from the time from zero plus half the sampling time. The level of the suspension was determined by calculation.

The sample was centrifuged, decanted and dried in an oven at 110°C. From the weight of tungsten in the tube and the concentration at the start of the run, the percentage by weight of particles that correspond to particles of diameter less than the Stokes' diameter could be calculated.

3. METHOD OF CORRELATION

The results can be plotted on linear ordinates, but in most cases a more normal distribution is obtained by plotting percentage undersize against the logarithm of the Stokes' diameter. This spreads out the finer sizes and eliminates the skewness towards the finer sizes found in linear plots. Semi-logarithmic plots are becoming more normal in sieve analysis.

Histograms are useful in showing results of particle size analysis, but are more often used in the correlation of microscopic counts. Histograms have been used by some authors to show results from the Andreasen pipette, but these can be quite misleading. Care must be taken that the areas on the diagrams are proportional to the group frequencies. The shape of the histograms can vary depending on the class interval used. By judicious choice of the class interval the histogram can be made to be more symmetrical. Histograms also cannot be drawn correctly when the cumulative curve does not cross the 100 percent co-ordinate, as is the case in the present work.

The results of this investigation have been plotted as weight percent undersize versus the logarithm of the Stokes' diameter.

4. RESULTS AND DISCUSSION

The most serious disadvantage of the Andreasen pipette method and indeed any sedimentation method, is that the results can be severely influenced by agglomeration of the particles. Various runs, on the same batch of tungsten, called sample A, were made to determine the most suitable concentration and suspending medium.

(a) Comparison of concentrations

Figure (2) gives a comparison of tungsten concentrations varying from 1 percent to 1/8 percent by volume in distilled water or demineralised water. The 1 percent and 1/2 percent runs show obvious agglomeration, but the 1/4 and 1/8 percent runs confirm each other.

A smooth curve was drawn through the 1/4 and 1/8 percent points and this curve was adopted as the comparison standard. The full curve in each succeeding figure shows this curve.

Figure (3) shows a comparison of concentrations from 1 percent to 1/4 percent by volume in absolute alcohol. The points lie under the full cruve, which indicates that the water runs give less agglomeration. It was noticed that if the tungsten powder was left overnight in the alcohol to attain the bath temperature, considerable agglomeration occurred. These results were non-reproducible, as shown for the 1 percent runs in figure (4).

(b) Influence of de-aerating the suspension

The influence of aeration on the suspension as a cause of agglomeration was studied in several ways:-

(i) Boiling and cooling the suspension and

(ii) Using a suspension at a bath temperature of 85°C.

The results of these runs are shown in figure (5). There is no improvement on the standard curve. The results at 85°C confirm the standard and the results after boiling lie below the standard in run 27, but agree with the standard in run 19.

(c) Comparison of suspending media

Initially qualitative determinations were made to determine the suitability of various suspending media. It was found that non-polar liquids such as benzene or petroleum ether were ineffective, because of flocculation.

Additions of electrolytes such as sodium hexametaphosphate, in as low a concentration as 0.1 percent w/v, also caused immediate settling.

Figure (6) gives a comparison between liquids used in the Andreasen pipette. Smith (10), suggests that metal powders should be degreased before analysis. Runs were made in acetone to determine the effect of degreasing. These results gave no improvement on the standard.

Runs were made to determine the effect of adding a wetting agent to the water. Two drops of Lissapol were added to demineralised water, with no improvement in the distribution.

Runs in 35 percent glycerol solution gave a slight improvement for the coarser sizes, but this was not considered to be significant.

Tap water gave inconsistent results under the standard curve as shown in figure (7). It is likely that this is due to the presence of electrolytes in the tap water.

(d) Comparison of different samples

On the basis of the above, comparisons were made of the seven samples of tungsten in stock, labelled A to G. For each run 1/4 percent by volume of tungsten powder was used in demineralised water. This comparison is shown in Figure (8).

Sample B points approach the sample A standard curve closely. The results for samples C to G generally lie below the standard curve for sizes below four micron and above the standard curve for sizes above four micron. A smooth curve was drawn through the points for samples C to G.

The batches from which samples A and B were taken were purchased at a different time to the batches represented by samples C to G and were no doubt manufactured at different times. Although the differences between the two curves are slight, it is significant that the material was purchased separately.

It is difficult to evaluate a true mean size of particle for comparison of particle sizes. It is not possible to calculate an arithmetic mean from the present results, because of the danger inherent in extrapolating the curves to the 100 percent undersize line.

There appears to be no correlation between the results from this investigation and the results of the microscopic counting as done by Murex Ltd.

5. ACKNOWLEDGMENT

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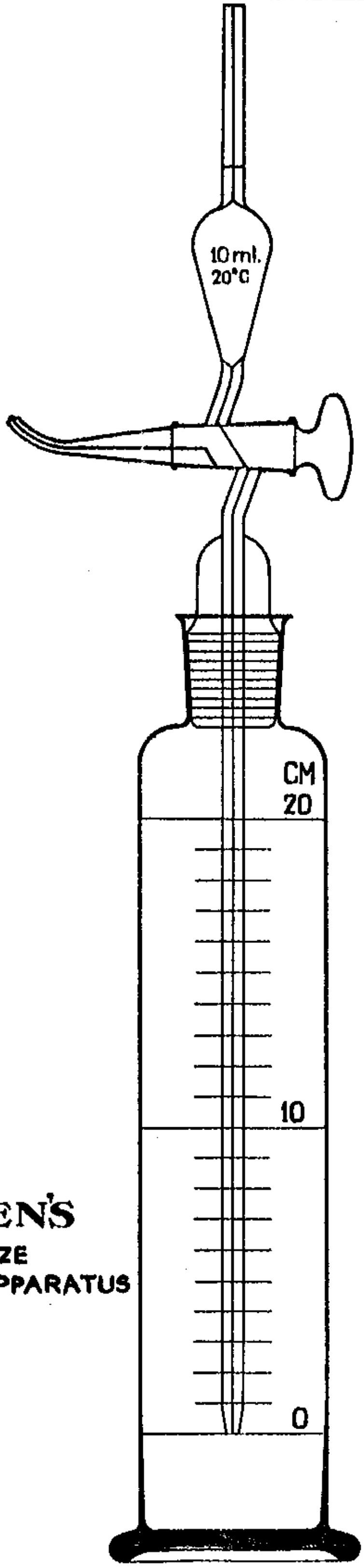


FIGURE 1.

ANDREASEN'S
PARTICLE SIZE
DETERMINATION APPARATUS

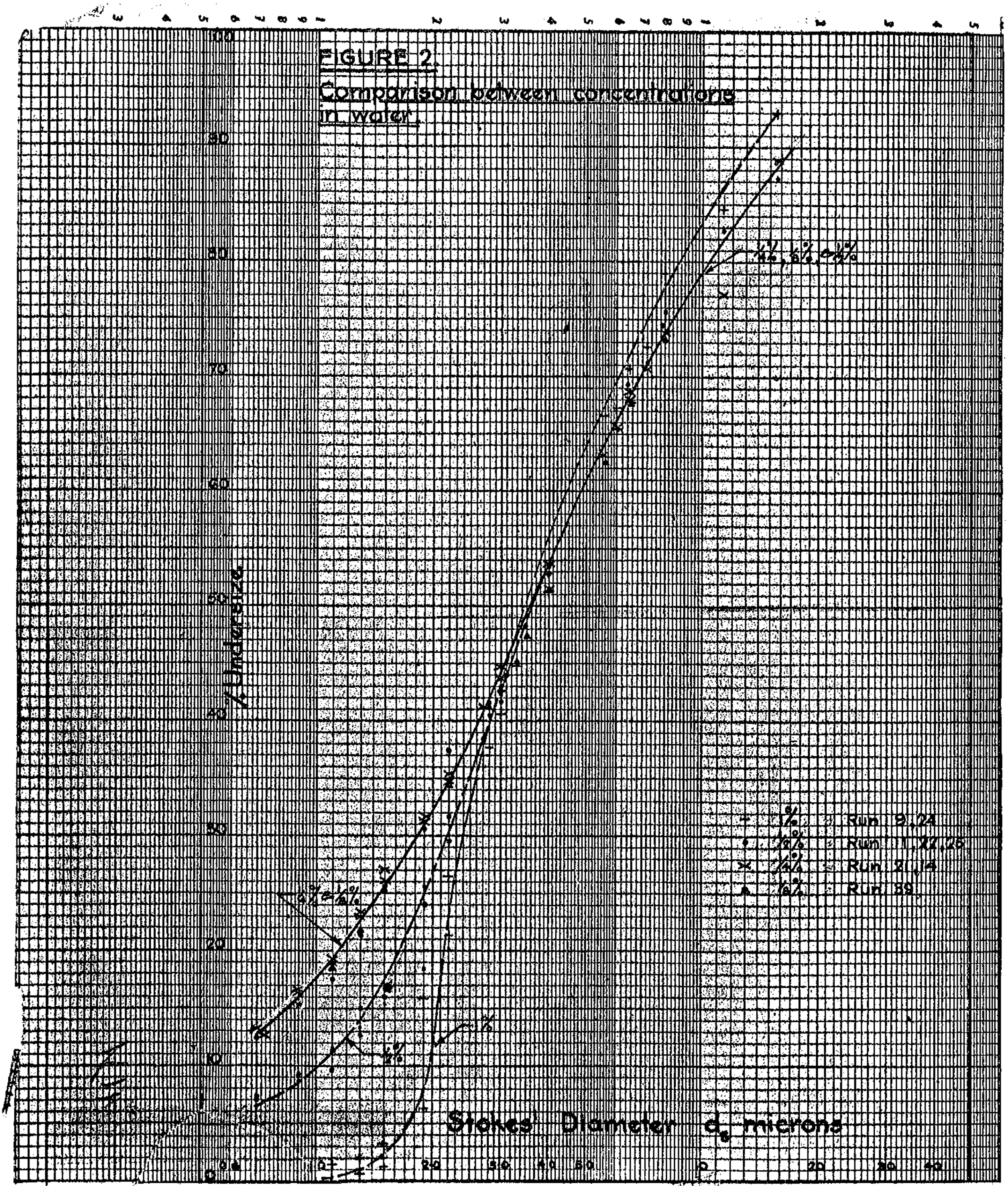


FIGURE 2.
Comparison between concentrations in water.

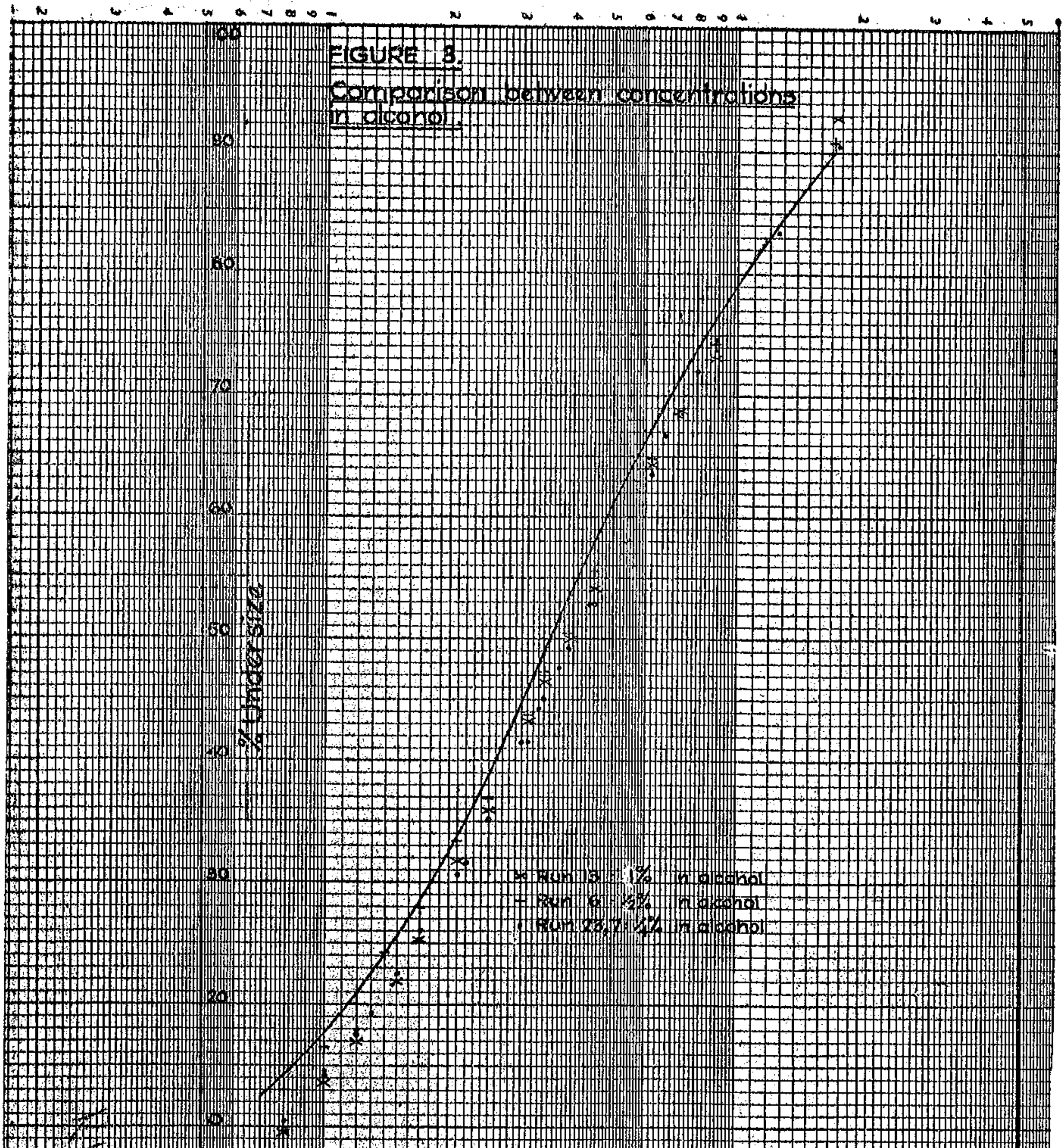


FIGURE 3.
Comparison between concentrations in alcohol.

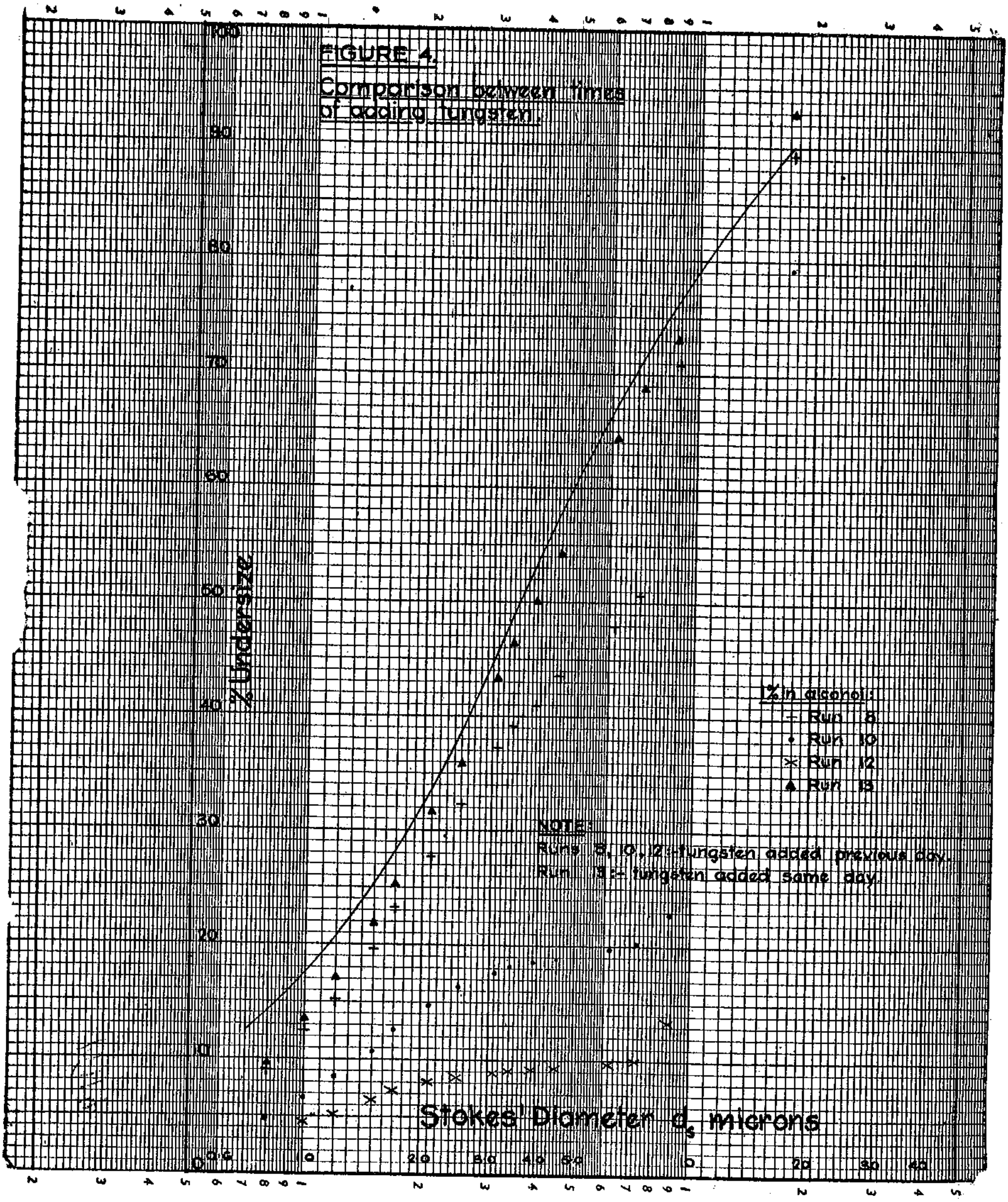


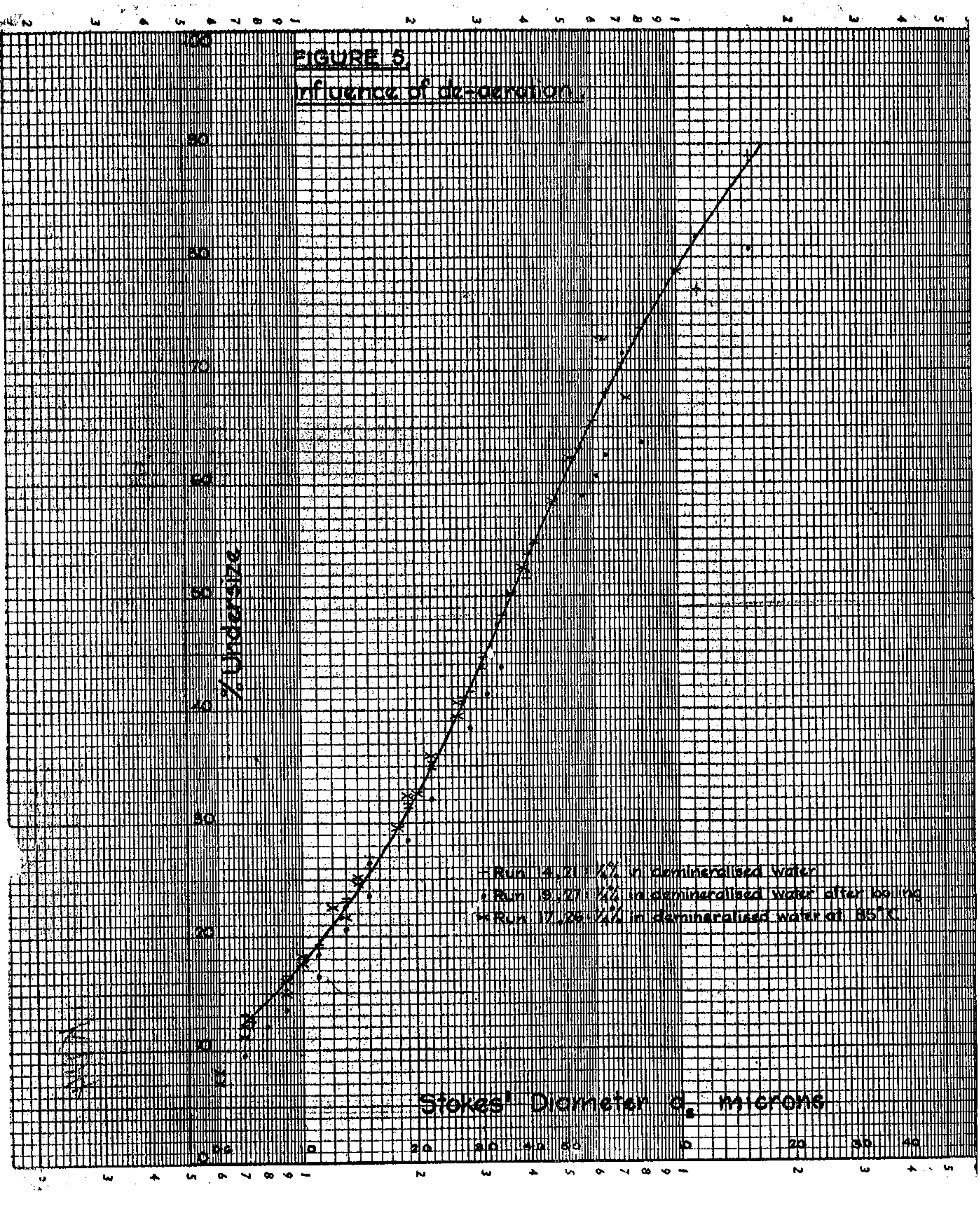
FIGURE 4.

Comparison between times of adding tungsten.

NOTE:

Runs 8, 10, 12:- tungsten added previous day.
Run 13:- tungsten added same day.

FIGURE 5.
Influence of de-aeration.



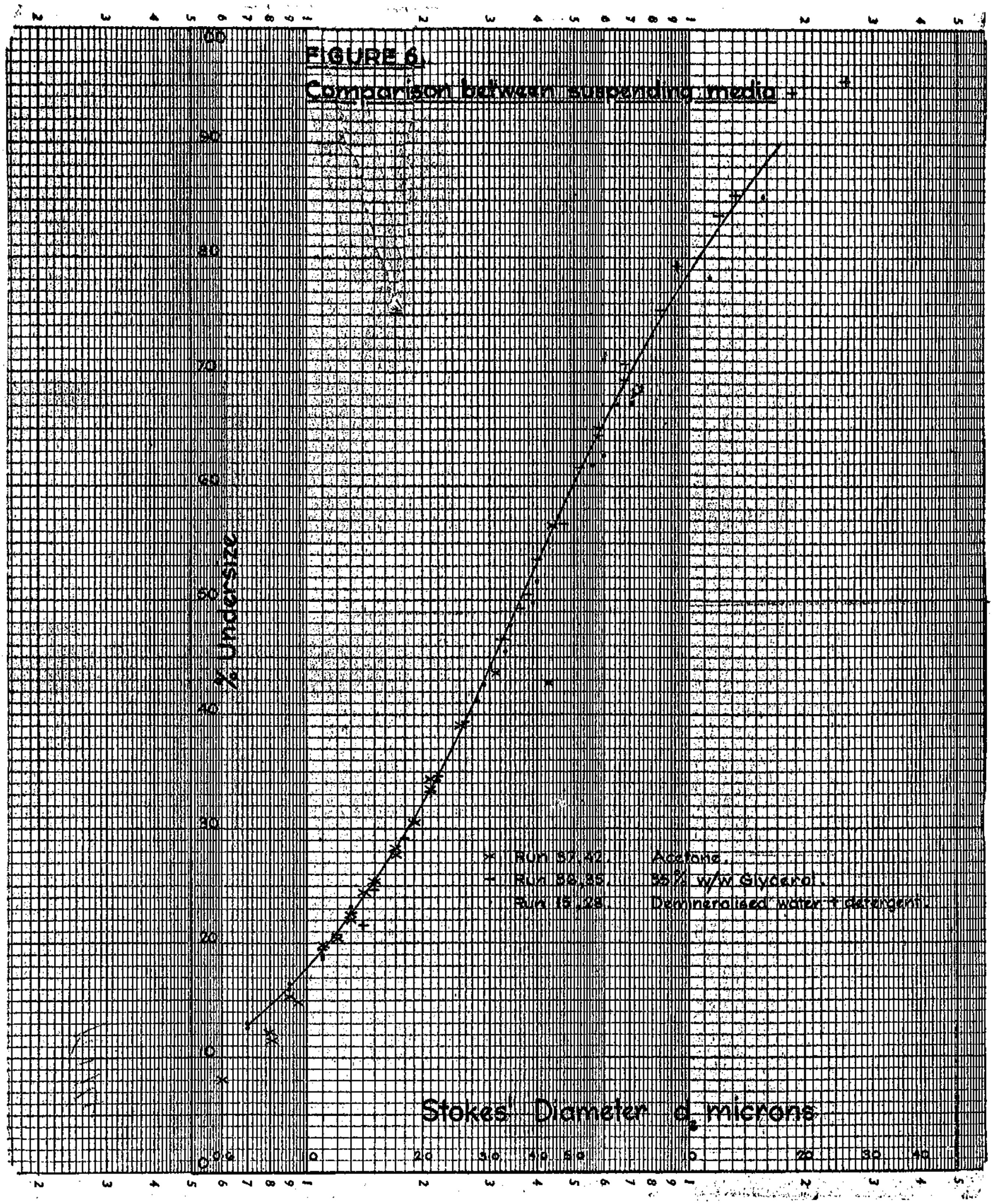


FIGURE 6.

Comparison between suspending media.

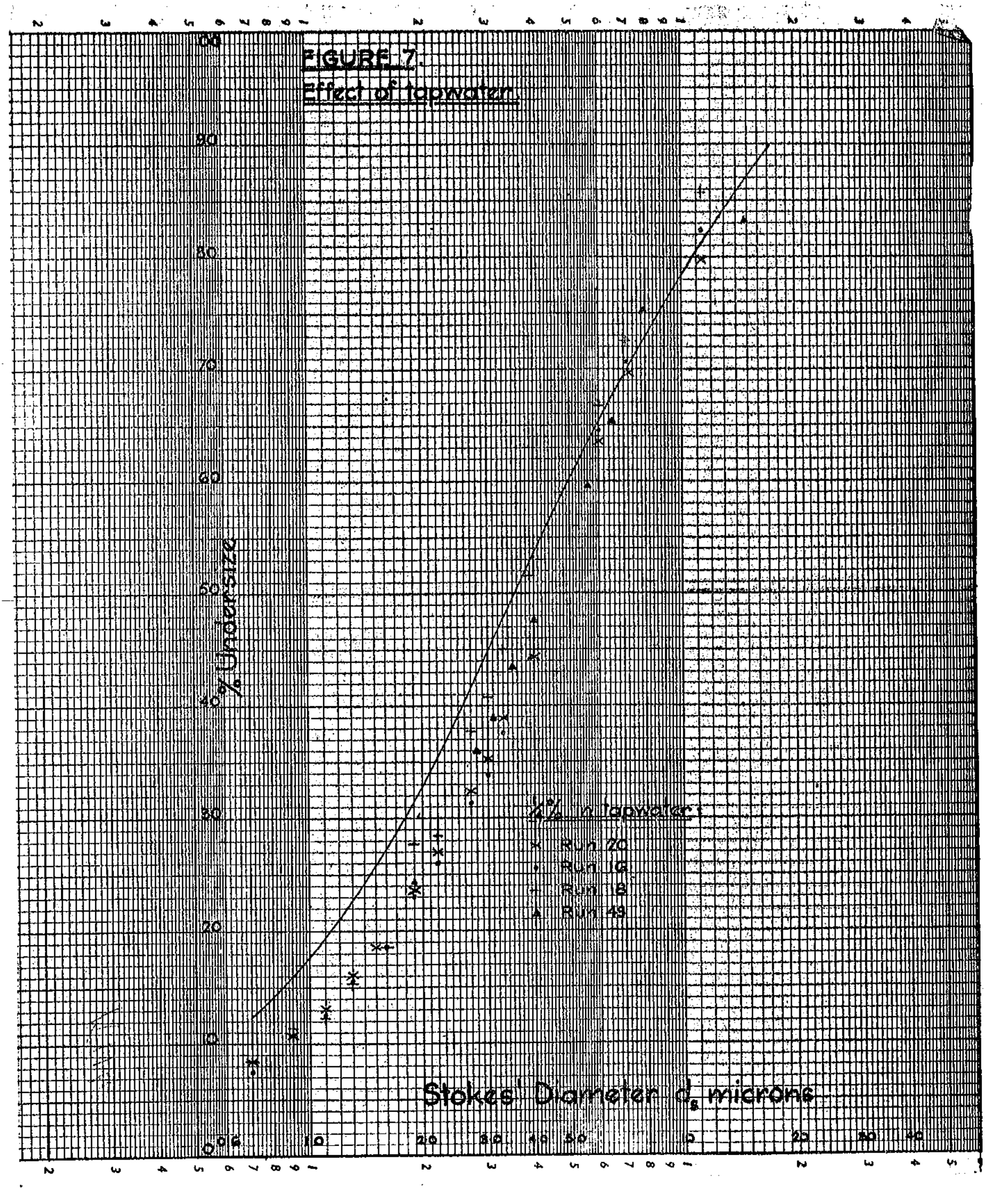


FIGURE 7.

Effect of tapwater.

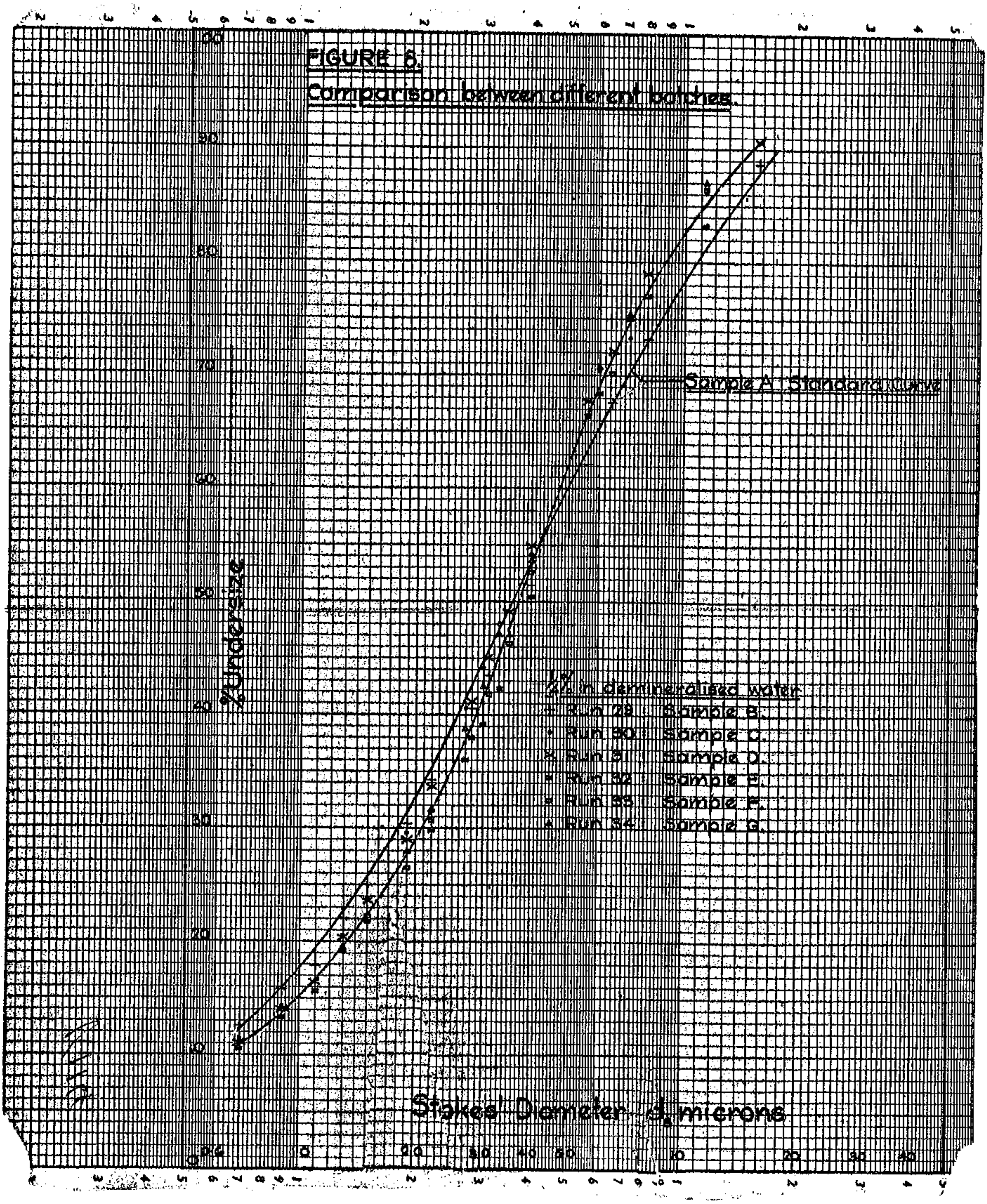


FIGURE 8.

Comparison between different batches.