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RAPID METHODS TO ESTIMATE THE MOLECULAR WEIGHT DISTRIBUTIONS OF POLYMERS

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the University of Cincinnati, Cincinnati, Ohio;
Richard G. Griskey and Siu-Yuen Fok, authors).

NOTICES

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FOREWORD

This report was prepared by the University of Cincinnati, Cincinnati, Ohio, under USAF Contract No. AF 33(616)-7450. The contract was initiated under Project No. 7360, "The Chemistry and Physics of Materials," Task No. 736005, "Analytical Research on Experimental Organic and Inorganic Materials." The work was administered under the direction of the Directorate of Materials and Processes, Deputy for Technology, Aeronautical Systems Division, Wright-Patterson Air Force Base, Ohio. Mr. Freeman F. Bentley was the project engineer.

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The authors wish to thank the E. I. DuPont De Nemours and Company for the generous gift of Nylon samples.

ABSTRACT

A comparative study of three rapid, inexpensive methods for determination of polymer molecular weight distribution was carried out on 66 nylon samples. The methods were cumulative precipitation fractionation, swelling and turbidimetric titration.

The most rapid and precise of these was found to be turbidimetric titration.

This technical documentary report has been reviewed and is approved.

Freeman F. Bentley

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Chief, Analytical Branch
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and Processes

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RAPID METHODS TO ESTIMATE THE MOLECULAR WEIGHT DISTRIBUTIONS OF POLYMERS

by

Richard G. Griskey and Siu-Yuen Fok

INTRODUCTION

All polymers, excepting some natural ones, consist of many molecular species covering a broad spectrum of sizes. Actually, then, polymers are usually molecular mixtures rather than chemical individuals.

This peculiarity means that polymers of identical average molecular weights can actually be quite different structurally. These differences can result in altered properties which cannot be predetermined unless the molecular weight distributions are known.

Several methods can be used to determine polymer molecular weight distributions (i.e. fractionation, sedimentation). Unfortunately, these techniques are generally time consuming and expensive. Furthermore, one of the most widely used techniques, sedimentation, is practical only for very high molecular weight polymers. Hence, rapid, precise, inexpensive methods having more general applicability are clearly needed.

A literature survey indicated that three such techniques had been proposed and studied to varying extents. These methods were cumulative precipitation fractionation (1, 2), swelling (3, 4), and turbidimetric titration (5, 6, 7, 8, 9, 10, 11, 12, 13, 14).

There had, however, been no study that compared the three techniques. Furthermore, the polymers that had been studied were all of fairly high molecular weight.

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It was therefore decided to undertake the present investigation first to compare the techniques and second to extend their use to polymers that could not be effectively studied by sedimentation.

Theory

A. General

The more rigorous methods of molecular weight distribution determination are treated in a number of sources.

Discussion of the use of sedimentation and ultracentrifugation can be found in various references (15, 16, 17, 18, 19, 20).

The same holds true for fractionation (1, 2, 21, 22, 23, 24, 25, 26, 27, 28, 29). One of these (1) outlines a technique, cumulative precipitation fractionation, that is of particular interest since it is fairly rapid and simple. It will be discussed in some detail.

B. Cumulative Precipitation Fractionation

Spencer (1) suggested a molecular weight distribution determination based on the relation of polymer molecular weight to solubility.

The method consisted of making up a dilute polymer solution, placing equal amounts in several containers and then adding different amounts of a precipitant to each container. In essence, a series of small scale fractional precipitations would be carried out.

Supernatant liquids would then be drawn off and the precipitates dried and weighed. An average molecular weight of each sample would then be determined.

If it was assumed that all the polymer above a certain molecular weight M_s was in the precipitate, then, all of the polymer below M_s would be in the liquid.

Hence,

weight fraction = C = $\int_{M_s}^{\infty} M_s\ W(M)\ dM.$

Where , W(M) is the normalized weight distribution.

Then, the weight average molecular weight of the fraction is

$$\overline{M_w} = \frac{1}{c} \int_{M_s}^{\infty} M_s\ M \cdot W(M)\ dM$$

Solving for M_s,

$$M_s = \frac{d(C \cdot M_c)}{dc}$$

Thus, if $C \cdot M_{cw}$ is plotted versus C it is possible to determine the M_s values corresponding to the various C'S. Further, if (1-C) is plotted against M_s the integral weight distribution curve would be obtained.

A similar analysis could be carried out for the number average molecular weight simply by substituting M_{cn} and N(M) for the M_{cw} and W(M) respectively.

C. Swelling

A considerable amount of time could be saved if in a fractionation the necessity for separating a precipitate from its supernatant liquid, drying and weighing it could be eliminated.

Boyer (3, 4) in essence, proposes a method for accomplishing this and in so doing, suggests a rapid method of molecular weight distribution determination.

Again, a dilute polymer solution was prepared and added in equal amounts to a series of vessels. In this particular case the vessels were equipped with calibrated tips. Next, a precipitant is added to the vessels in amounts varying over the precipitation range. It is then possible to measure the amount of polymer precipitate in each of the vessels by reading the calibrated tips. A plot of the amount of precipitate versus amount of non solvent added yields a curve that can be converted to a cumulative weight distribution curve.

The conversion is accomplished by making use of two relations. The first is due to Schulz (30) and relates γ (volume of non solvent added) to M (polymer precipitate molecular weight).

$$\gamma = \alpha + \frac{\beta}{M^m}$$

This indicates that increasing amount of non solvent brings about a lower molecular weight polymer solution.

Boyer (3) proposes a second relation

$$\gamma = \alpha + \frac{\sigma}{S^s}$$

That shows the dependence of S, swelling ratio (CC swollen gel/gram polymer) on solvent composition.

Knowledge of these relations make it possible to convert the plot of gel volume versus amount non solvent to a curve of grams of polymer versus molecular weight.

This could be accomplished in the following manner -- a given value of γ yields a M and S value. If the volume of gel corresponding to γ is divided by S then a polymer weight is obtained. Additionally a corresponding M value is determined. This would lead to a plot of polymer weight versus molecular weight and ultimately to a cumulative weight distribution curve.

D. Turbidimetric Titration

Adams and Powers (5) and Morey and Tamblyn (6) have made use of light scattering as a means of circumventing the time consuming operations associated with fractionation.

As a non solvent is added to a polymer solution increasing amounts of material will precipitate. At the same time the solution's optical density will increase. Hence, optical density is related to the amount of polymer precipitated.

It is also known that increasing amounts of non solvent addition will result in the precipitation of larger amounts of lower molecular weight material. If this principle, and the one related to optical density are combined we have a method for determining a curve related to a cumulative weight molecular weight distribution.

Actually, the plot should be $\left[\log\left(\frac{I_o}{I}\right)\right]\frac{V}{V_o}$ versus percent non solvent. Where,

I_o = percent transmittance before precipitation commences.

V_o = volume percent of non solvent before precipitation commences.

I = percent transmittance at any given percent of non solvent.

V = any given percent of non solvent.

However, for low concentrations $V = V_o$, and $\log\left[\frac{I_o}{I}\right]$ is nearly the same as $\left[\log\left(\frac{I_o}{I}\right)\right]\frac{V}{V_o}$. Thus, a plot of $\log\left[\frac{I_o}{I}\right]$ versus percent non solvent is adequate to describe a relative molecular weight distribution.

A number of investigators other than those mentioned previously have also studied this technique (7, 8, 9, 10, 11, 12, 13, 14).

Apparatus and Experimental Procedure

A. Introduction

In general, the devices required for the rapid estimates of polymer molecular weight distributions were simple and inexpensive. The techniques, themselves, were also relatively simple when compared to the more rigorous determinations such as sedimentation.

A complete summary for each technique follows.

B. Cumulative Precipitation Fractionation

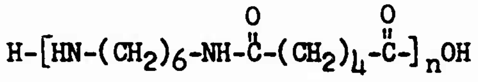
A series of 150 ml weighing bottles were used as fractionation vessels. Formic acid (90%; specific gravity 1.2) was the solvent -- distilled water the non solvent.

Initially, 20 ml of a dilute 66 nylon solution (1 gram solute per 100 ml solvent) was placed in each vessel. Non solvent was then added at a rate of 20 ml per hour to the first vessel until a definite change in turbidity was noted. The solution was stirred continuously at a rate of 200 rpm from the start of the addition of non solvent. Stirring was continued for 30 minutes after the turbidity change.

Essentially the same procedure was followed for the remaining vessels. The only differences being that incremental amounts of non solvent were added to the second and succeeding vessels and that stirring times after completion of non solvent addition were increased incrementally by 15 minutes for each vessel.

When the stirring was completed the vessels were placed in a constant temperature bath for a 24 hour period. Then they were withdrawn and the supernatant liquid was removed with the aid of a water suction flask. The precipitates were then dried and weighed. Next, their average molecular weights were determined.

End group measurement was initially the technique used for this determination. The theory involved is simple and straightforward. 66 Nylon has the structure shown below



$$H\text{-}[HN\text{-}(CH_2)_6\text{-}NH\text{-}\overset{\overset{O}{\|}}{C}\text{-}(CH_2)_4\text{-}\overset{\overset{O}{\|}}{C}\text{-}]_nOH$$

Hence, there is an amine and carboxyl end on each molecule. If the total number of ends could then be determined a measure of molecular weight would be possible.

This can be obtained from the equation

$\bar{M}n$ = number average molecular weight

$$\bar{M}n = \frac{2 \times 10^6}{\text{total equivalent ends}/10^6 \text{ grams}}$$

The ends are obtained by an appropriate analysis and calculated from the equation

$$\text{Ends, equivalents}/10^6 \text{ grams} = \frac{\text{net titer} \times N(\text{titrant}) \times 10^3}{\text{grams of sample}}$$

Total ends were found by multiplying the amine ends by a factor of two. The method of Waltz and Taylor (31) was used to determine the amine ends.

Basically, the method consists of a conductometric titration. The equipment used for the determination consisted of a conductance cell with two electrodes of 3 cm^2 area set 1 cm apart, a 110 volt, 60 cycles, resistance bridge and suitable burettes.

The first step was to determine the basic character of the solvent (a mixture of phenol, ethanol, and water) used for 66 nylon. A blank was prepared which consisted of 5 ml of phenol, 2.5 ml of 95% ethanol and 1 ml of water. It was then titrated with 0.001N hydrochloric acid. Resistance values were read after every 0.2 ml addition of the acid. The reciprocal of these values, conductance, was then plotted against the ml of acid added. A discontinuity in the plot indicated the end point of the titration.

Essentially the same procedure was followed for the determination of the amine ends. A 0.2 gram of 66 nylon was first dissolved in 2.5 ml of warm phenol. Then after three of four hours, 2.5 ml of 95% ethanol and one ml of water were added. A titration with 0.01N HCl followed as outlined above.

Waltz and Taylor (31) recommended a much larger sample size (2-3 grams) than was used in the present study. However, it was found that the smaller sample size yielded equivalent results (see Table 1 below).

Table 1

Equivalence of Large and Small Sample Sizes

Sample Code	Sample Size (gms)	Mn
1	0.2	16,700
1	3	16,650

An alternate method of determining fraction average molecular weights - intrinsic viscosity - was also considered.

The method used was that described by Sorensen and Campbell (32) and Taylor (33). It consists of measuring the relative times of flow of a polymer solution and a solvent respectively in a suitable pipette viscometer (one in which solvent flow time is between 100 and 200 seconds). The ratio of the flow times is then defined as the relative viscosity.

$$\eta \text{ rel} = \frac{\text{solution flow time}}{\text{solvent flow time}}$$

Intrinsic viscosity, (η) is defined as

$$(\eta) = \lim_{C \to 0} \frac{(\text{ rel} - 1)}{C}$$

Where C = concentration of the solution.

A number 100 Cannon-Fenske pipette was used for the determinations.

C. Swelling

The apparatus for the swelling measurements consisted of a series of Imhoff cones (Figure 1A). Each of the cones has a volume of one liter and a calibrated tip.

The procedure was similar to that outline by Boyer (3, 4). A dilute solution (0.25 to 1.00 $\frac{\text{grams solute}}{\text{100 grams solvent}}$) of 66 nylon in 90% formic acid was prepared. About 20 ml of the solution was then pipetted to a 100 ml beaker. Non solvent (water) was added from a burette at a rate of 10 ml per hour with a stirring rate of 200 rpm until a definite turbidity was observed. Stirring was continued for an additional half hour. Then, the solution was transferred to the first Imhoff cone which was immersed in water bath 2 or $3^{\circ}C$ below room temperature.

A second portion of the solution was then transferred to a beaker. The amount of non solvent used to obtain turbidity with the first sample is then added at the same rate with a 200 rpm stirring rate. A twenty minute period of stirring without addition follows. Then, an additional amount of non solvent is added. Stirring is continued for a half hour followed by transfer to the second Imhoff cone.

This procedure was followed with succeeding samples until all eight cones contained solutions. After a 24 hour waiting period the precipitate volumes were observed.

D. Turbidimetric Titration

A modified Beckman model B spectrophotometer was used for the turbidimetric titration study (Figure 1B). A 150 ml beaker painted black except for two small windows was used for the solution container. The beaker was placed inside the spectrophotometer chamber and positioned so that the light source and receiver were in line with the windows. The chamber lid was replaced with a wooden one painted black to eliminate reflection. Holes were cut into the lid to permit insertion of glass tubing and a stirrer. The tubing was attached to a fractionating funnel.

The windows on the beaker were designed so that the solution level was at least 1 cm above them. This was done to prevent the glass stirrer from affecting the light transmittance.

Turbidimetric titration has been described in several literature sources (5, 6, 7, 8, 9, 10, 11, 12, 13, 14). Basically, the technique used in this investigation differs in that no specially constructed light scattering device is used but rather an ordinary spectrophotometer. Another difference is that previous investigators have studied polymers of much greater molecular weights than 66 nylon.

Initially, a dilute solution of 66 nylon was prepared (concentration of 0.0625 gram solute per 100 mls. solvent). Then about 40 ml was pipetted into the sample container which was properly positioned in the spectrophotometer chamber.

The spectrophotometer was set up for green light (λ = 5200Å). This particular wavelength was chosen because it was recommended by Gooberman (10) who noted that it gave the best compromise between sharpness and sensitivity.

Non solvent addition then commenced. The rate was 1 ml per 35 seconds. Addition rate was controlled by a system of two stopcocks, one in the glass tubing and the other in the fractionating funnel. The solution was stirred continuously at a rate of 200 rpm. Just before the appearance of the cloud point (initial turbidity observed) the spectrophotometer needle was adjusted to read 100% transmittance. Readings of transmittance were then taken every 10 seconds until they leveled off. These data then gave a tabulation of transmittance versus non solvent addition because of the constant rate of addition of water.

Results

A. Cumulative Precipitation Fractionation

Initially, a fractionation was attempted in the manner described by Spencer (1). It was found, however, that the amounts of precipitate obtained were not large enough to yield precise results.

The main difficulty was that all of the fractions obtained were 95% or higher of the total amount of polymer present. This meant that only a limited description of the molecular weight distribution could be obtained.

Results of four such fractionations are shown in Figures 2 and 3. In Figure 2 weight 0/0 precipitated is plotted against $\bar{M}n$ as determined by end group measurement. Weight 0/0 precipitated is plotted against (η) in Figure 3.

As can be seen the data scatter somewhat in both cases. However, both figures give the same overall indication - namely, that polymer sample 1 has a larger amount of higher molecular weight species than does sample 2. This is not surprising, because whole polymer 1 had a higher average molecular weight than did whole polymer sample 2.

The use of this technique is not recommended because it not only gives a limited description of the polymer molecular weight distribution but also because it involves a prohibitive amount of laboratory work.

It did, however, serve a particularly useful purpose in this investigation since it established relative differences in the polymer molecular weight distributions of polymers 1 and 2.

B. Swelling

As was indicated earlier, the swelling studies were carried out using a battery of eight Imhoff cones. This was done in accordance with a suggestion of Boyer's (4). Actually, Boyer used only one flask in his study which extended the experimental time to about ten days. He indicated that use of more flasks would possibly reduce the experimental time.

This meant that an experimental technique had to be developed and optimized since no previous study had used a battery of flasks.

First, the concentrations of the solutions to be used had to be determined. In this particular case there were two limiting factors which fixed the range of concentrations that could be used. These were availability of solvent (90% formic acid) and the limited volumes that could be read from the cones' calibrated tips. The range of concentrations fixed by these two factors was from 0.25 to 1.00% (grams polymer/100 ml solvent).

A variable that definitely had to be established was the time necessary to define the swelling curve. It was found that such curves could be established in about 24 hours. A comparison between measurements made in both 24 and 48 hour periods is shown in Figure (4). Longer times yielded essentially the same curves. Actually it was found that a relative difference between samples could be indicated in as little as 18 hours. However, 24 hours was the shortest time for which a time-independent swelling curve could be determined.

It was also found that stirring rate is a critical factor in studies of this type. A rate of 200 rpm was found to be optimum for this particular system. It is suggested that careful consideration be given to this factor in any future studies.

Although Boyer (4) indicated that temperature control was probably important, he did not consider this in his study. Data was found to scatter badly without temperature control in the present study. As a result a bath was used to eliminate any such fluctuations.

When the technique had been finally developed and optimized consideration was given to the validity of the results.

Studies of the behavior of swelling ratio and precipitate molecular weight with increasing amount of non solvent were carried out simultaneously with the swelling experiments. This was done so that the relations of these entities to the amount of non solvent could be determined. Figures 5 and 6 show the results of this work.

An analysis of the swelling curves shown in Figure 7 was then carried out using Figures 5 and 6. This enabled the determination of amount of precipitate corresponding to each amount of non solvent added together with the corresponding molecular weight.

There is also additional substantiating evidence. Boyer (4) in his study pointed out that the plot of ml of precipitate versus of non solvent is in itself related to a differential weight distribution curve. A copy of a schematic drawing from his paper is shown in Figure 8. In this plot he depicts three swelling curves -- one for a fraction of high molecular weight (A in Figure 8), another for a normal polymer (B in Figure 8) and still another for a polymer having a larger amount of low molecular weight species than the others.

Comparison of this schematic with Figure 7 clearly indicates that sample 1 has more higher molecular weight species present than does sample 2.

Also, if we plot the slope of the cumulative swelling curve against the percent non solvent added (Figure 4), we will get a comparative distribution curve (Figure 9), which shows that sample 1 has more higher molecular weight species present than does sample 2.

Swelling studies were also carried out for other polymer samples. These data are shown in Figures 10 and 11. Data for two different polymers are given in each of the two figures. Actually, the sample labeled with the same number, i.e., 3 and 3A differ only in that they are different portions of the same blend.

This means that a comparison between the similarly numbered samples data points should indicate the precision of the swelling technique with respect to intra-blend variations. Figure 10, which compares samples 3 and 4 indicates that the intra-blend precision is quite good. However, Figure 11 seems to contradict this conclusion since considerable scatter is apparent.

There is a plausible explanation for this. All of the sample used in this study contain titanium dioxide, which is used as a delustrant for 66 nylon. The percentage by weight in samples 1 and 2 was about 0.05%, in samples 3 and 4 about 0.30% and in samples 5 and 6 (which have considerable scatter) about 2.00%. It therefore appears that when considerable titanium dioxide is present, swelling is not a precise technique. This is due probably to variation in the amount of titanium dioxide present from sample to sample.

C. Turbidimetric Titration

Initially, a 0.25% concentration was used for the samples in the turbidimetric titration study. It was found, however, that a less concentrated solution (0.0625%) yielded more complete data (see Figures 12 and 13).

Additional amounts of the same polymer samples tested in the swelling studies were used for the turbidimetric titrations. This was done so that the turbidimetric titration data could be evaluated by using the data from the swelling studies.

Results from the turbidimetric titrations are shown in Figures 12 to 18.

If we compare these data to the results of the swelling studies we see that excellent correspondence is obtained. For example, polymer sample 1 has a larger amount of high molecular weight species than does polymer sample 2 according to Figures 13 and 14. This checks with the results pertaining to samples 1 and 2 from the swelling studies. It also is consistent with the indication obtained in the cumulative precipitation fractionation.

Again, if we plot the slope of the cumulative distribution curve against the percent non solvent (Figures 13 and 14) we get a comparative distribution curve of samples 1 and 2. It is clear that these curves agree with those of Figure 9.

The same holds true for samples 3 and 4 (sample 4 having more high molecular weight species by both methods) and also for samples 5 and 6 (sample 5 having more high molecular weight species than sample 6 by both methods).

It also can be seen that intra-blend or batch precision is also quite good for turbidimetric titration since the data points for additional samples show little scatter.

One particular point of interest regarding turbidimetric titration was its speed -- requiring only forty-five minutes to determine a complete curve.

Conclusions

The following conclusions have been reached in the present investigation.

1. 66 nylon end group measurements can be made with as little as 0.2 grams of polymer.
2. A successful technique has been developed for swelling studies using a battery of precipitation flasks rather than just a single vessel.
3. Temperature control and stirring were found to have an important bearing on swelling studies.
4. A turbidimetric titration technique using an ordinary Beckman B spectrophotometer has been developed.
5. Three candidate techniques -- cumulative precipitation fractionation, swelling and turbidimetric titration were found to give essentially equivalent results for relative molecular weight distribution measurements.
6. Cumulative precipitation fractionation is not as suitable as the other techniques since it is time consuming and gives only a limited description of the polymer molecular weight distributions.
7. Both swelling and turbidimetric titration provide rapid, precise methods for estimating the molecular weight distribution of a polymer having a low average molecular weight (25,000 or less).
8. Turbidimetric titration is recommended as the technique to be used since it is much more rapid (45 minutes) than swelling (18 to 24 hrs.).

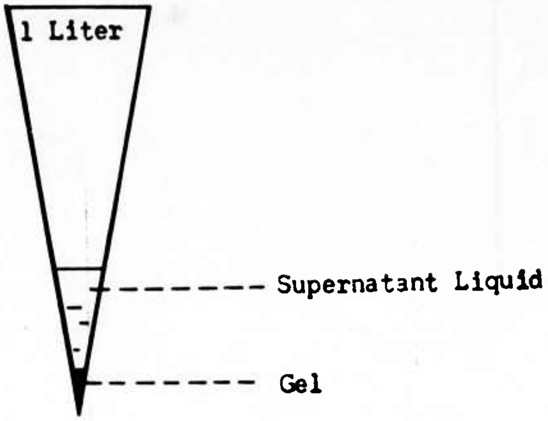


Figure 1 A. Imhoff Cone

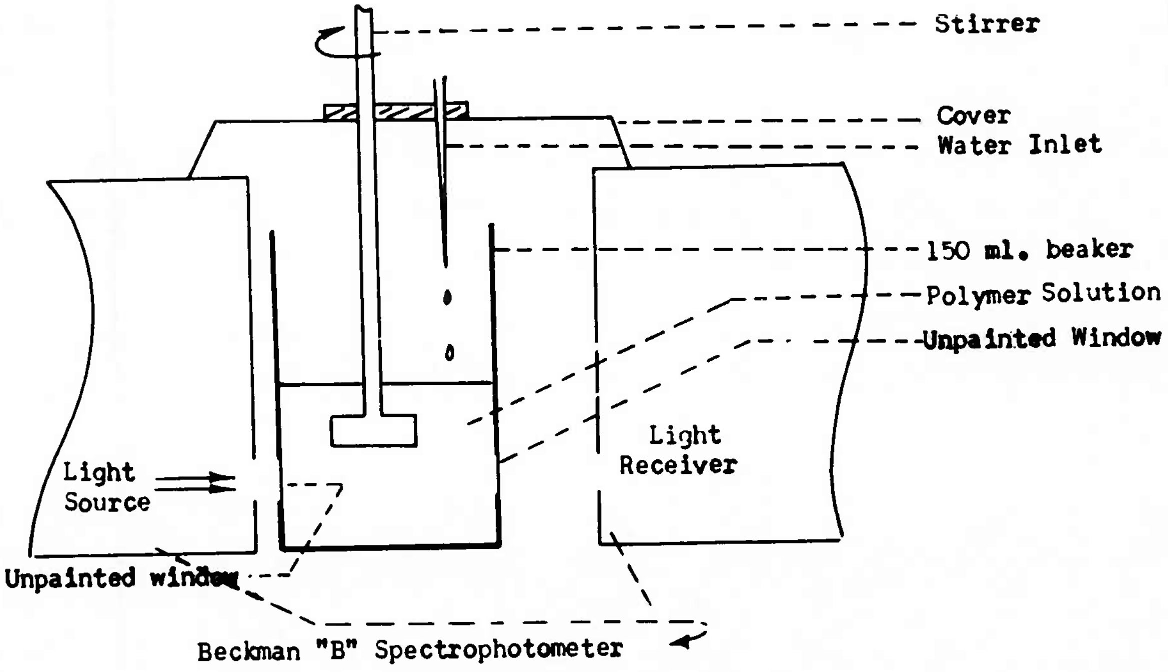


Figure 1 B. Apparatus for Turbidimetric Titration

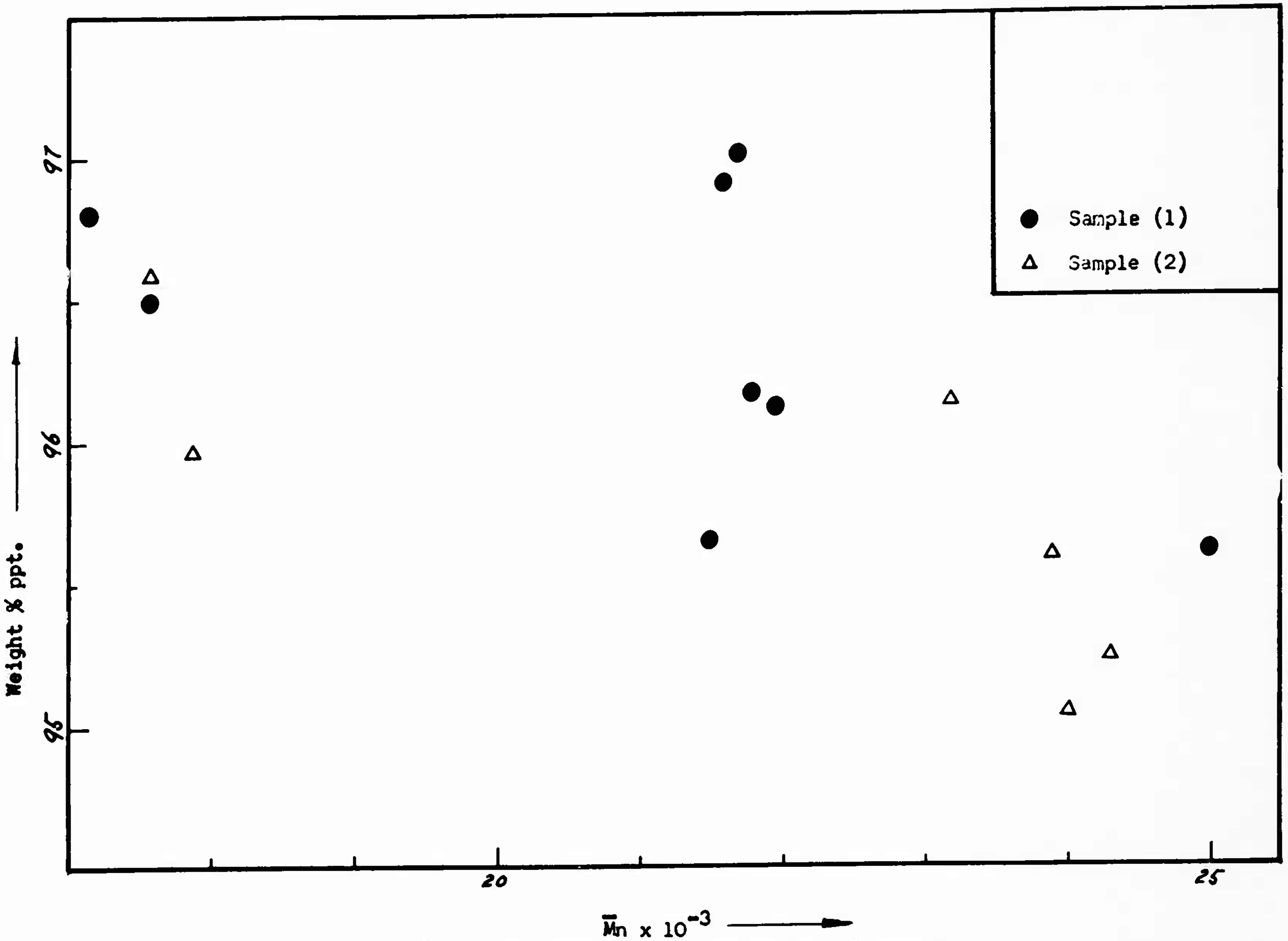


Figure 2. Cumulative Precipitation Fractionation

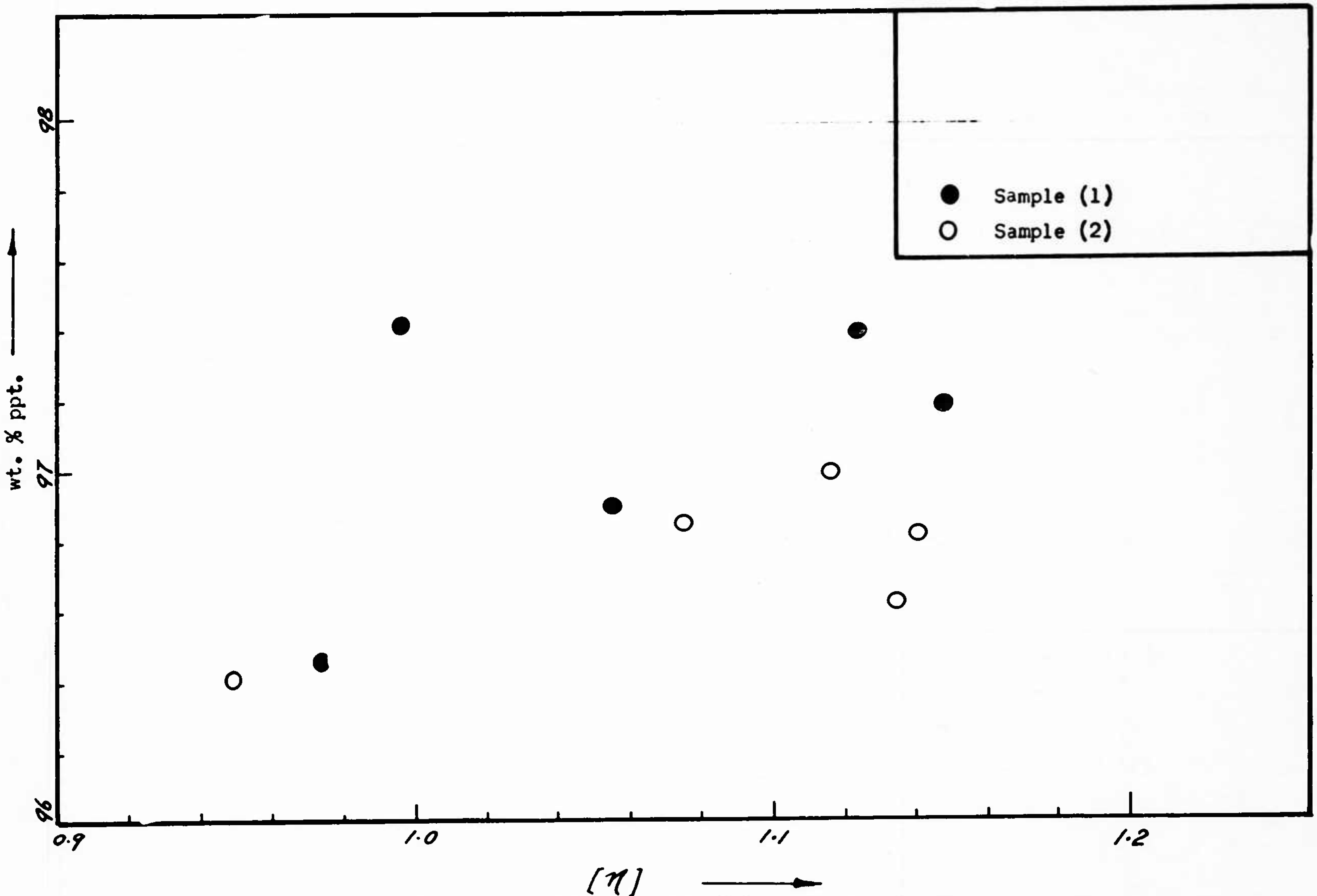


Figure 3. Cumulative Precipitation Fractionation

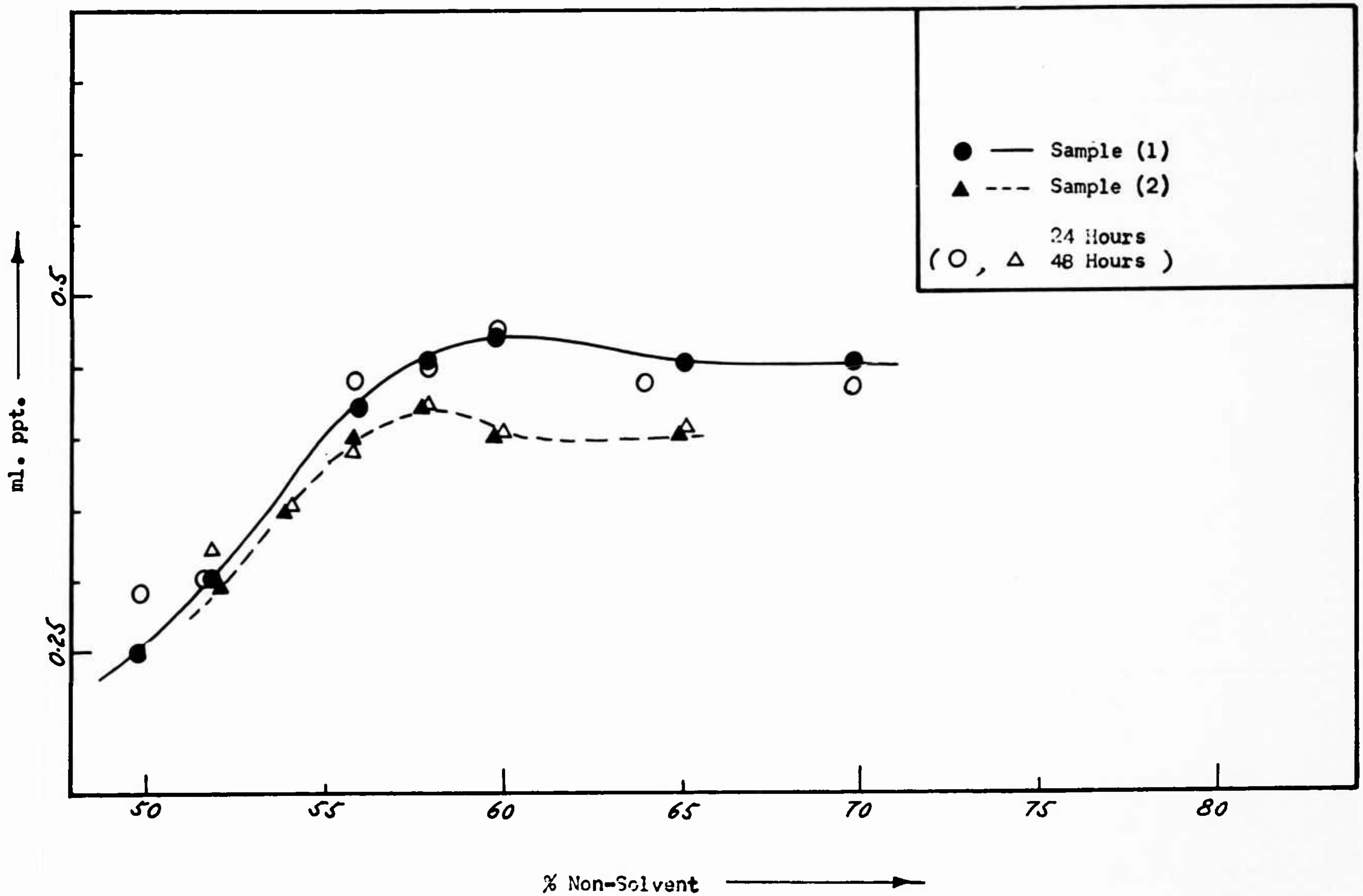


Figure 4. Swelling - 0.25 $\frac{\text{Gr. solute}}{\text{100 ml. solvent}}$

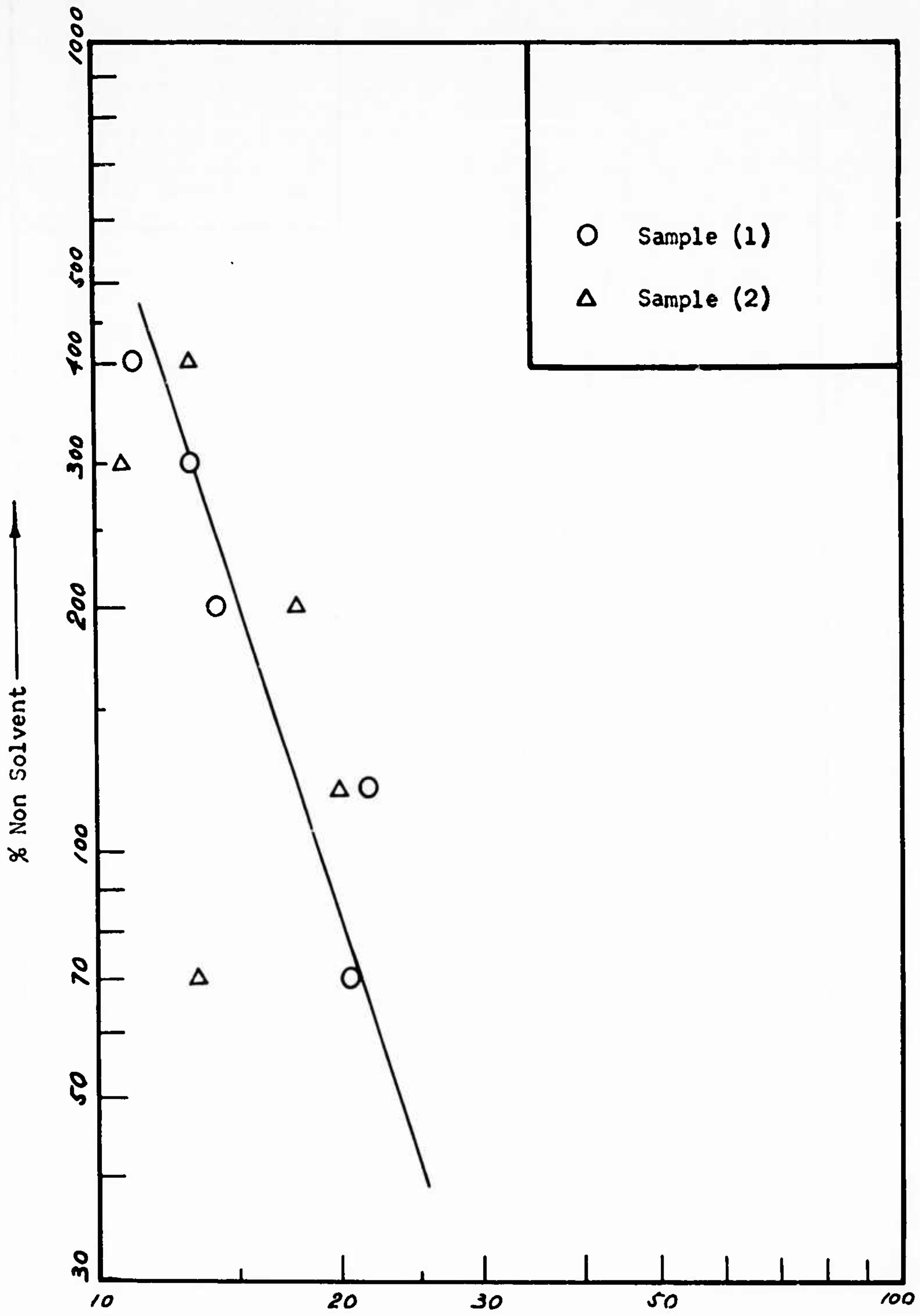


Figure 5. Swelling Ratio ML/GM

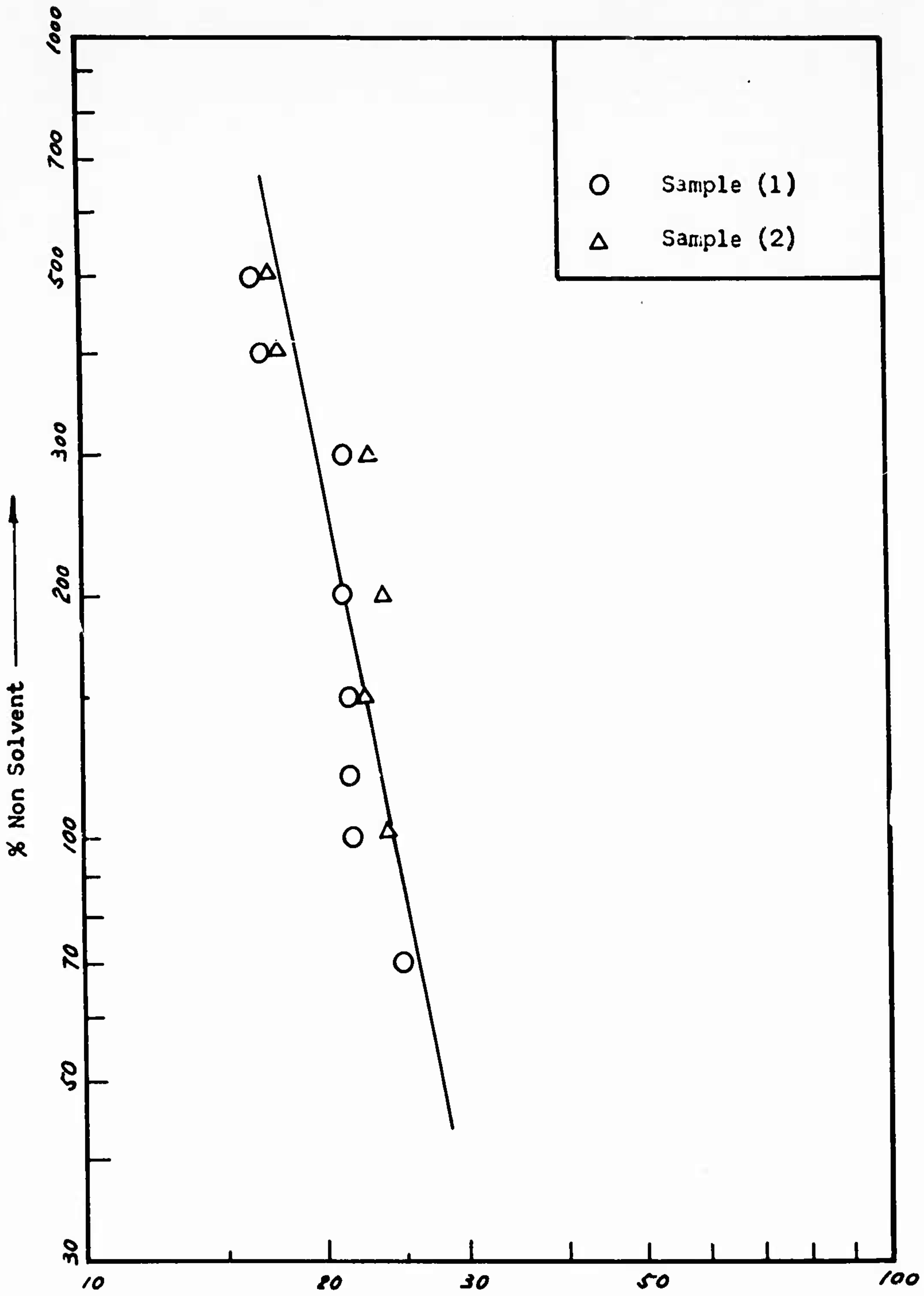


Figure 6. Percent Non Solvent Relating to $\overline{M}n \times 10^{-3}$ →

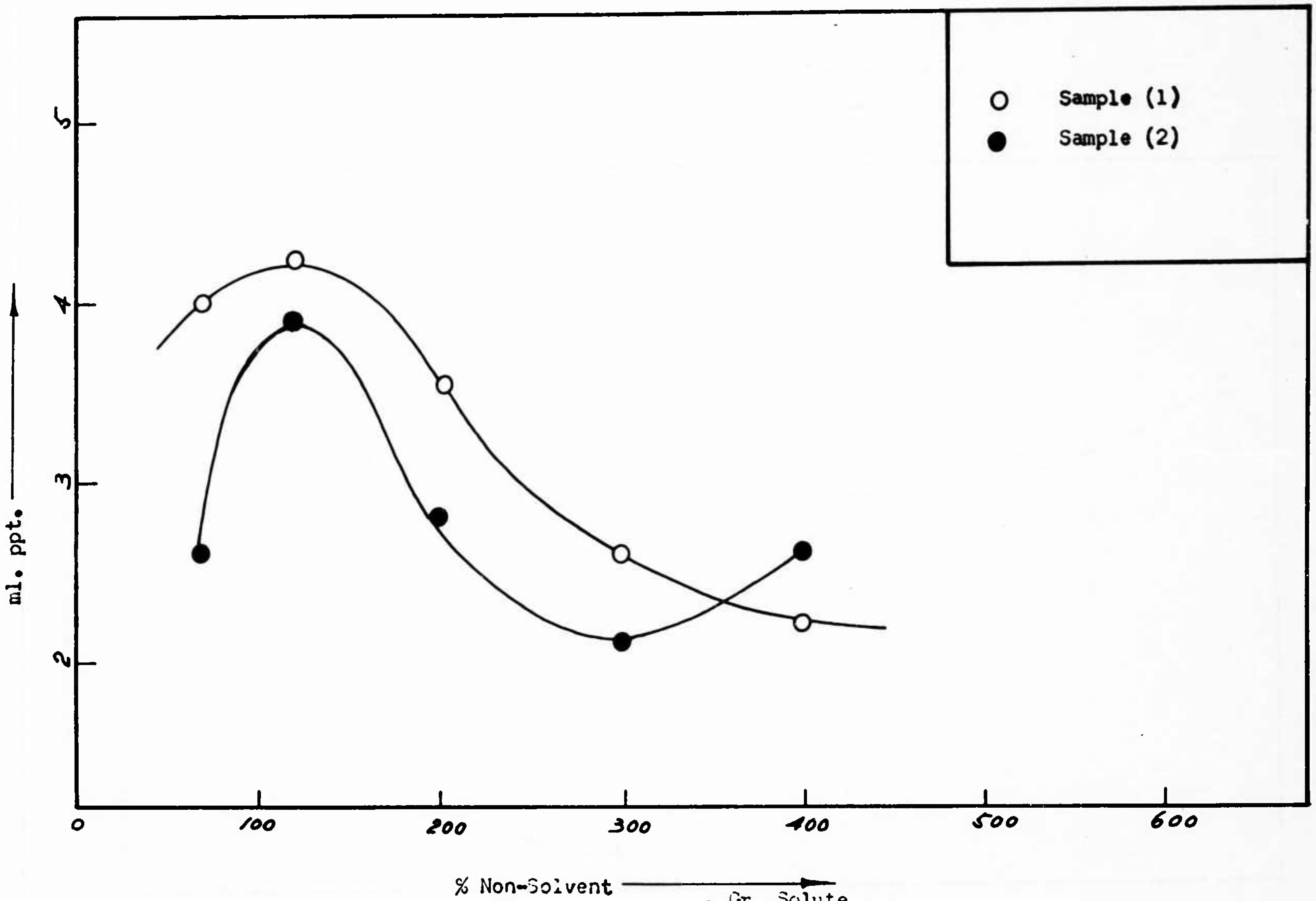


Figure 7. Swelling - 1 $\frac{\text{Gr. Solute}}{\text{100 ml. Solvent}}$

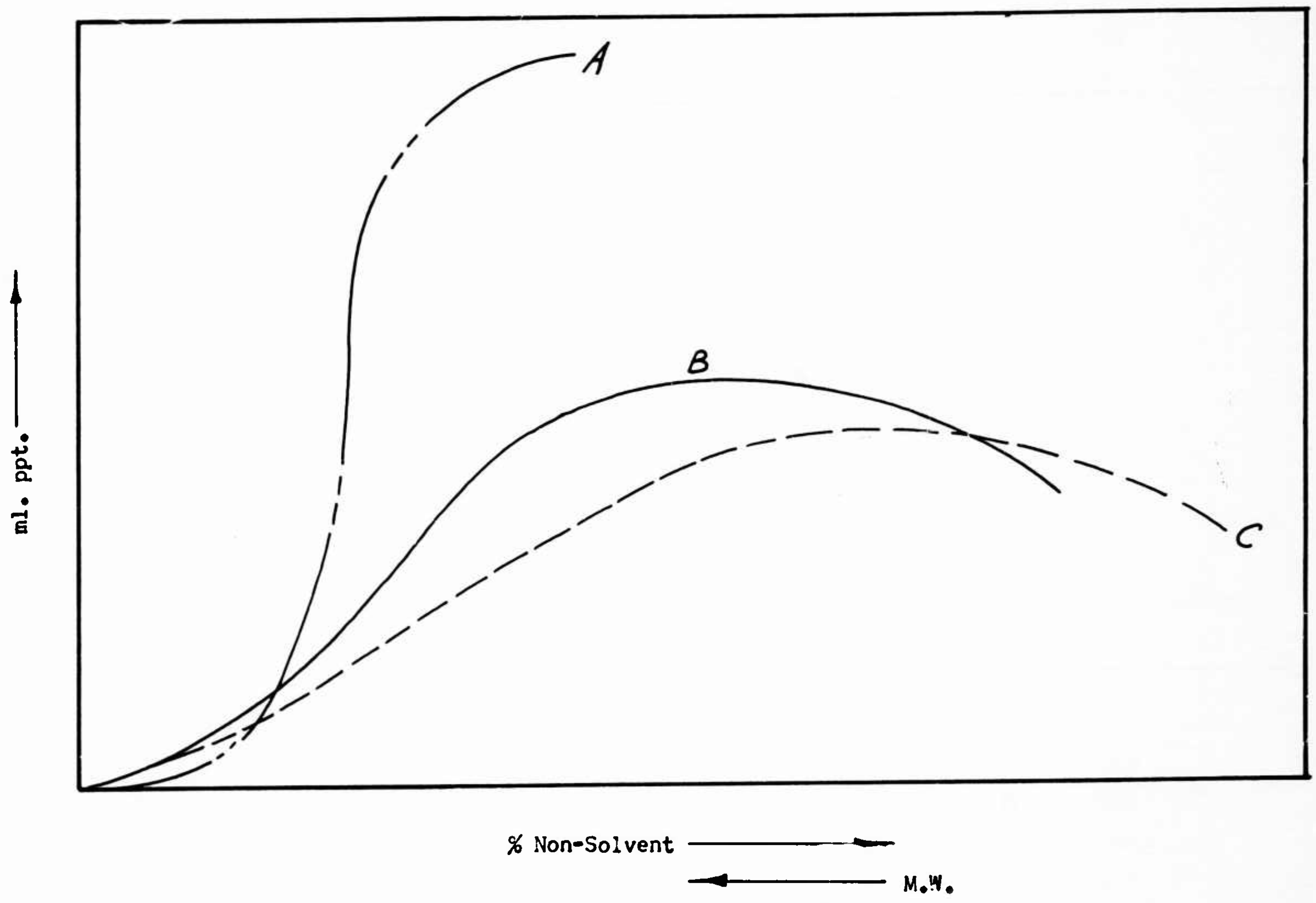


Figure 8. Schematic

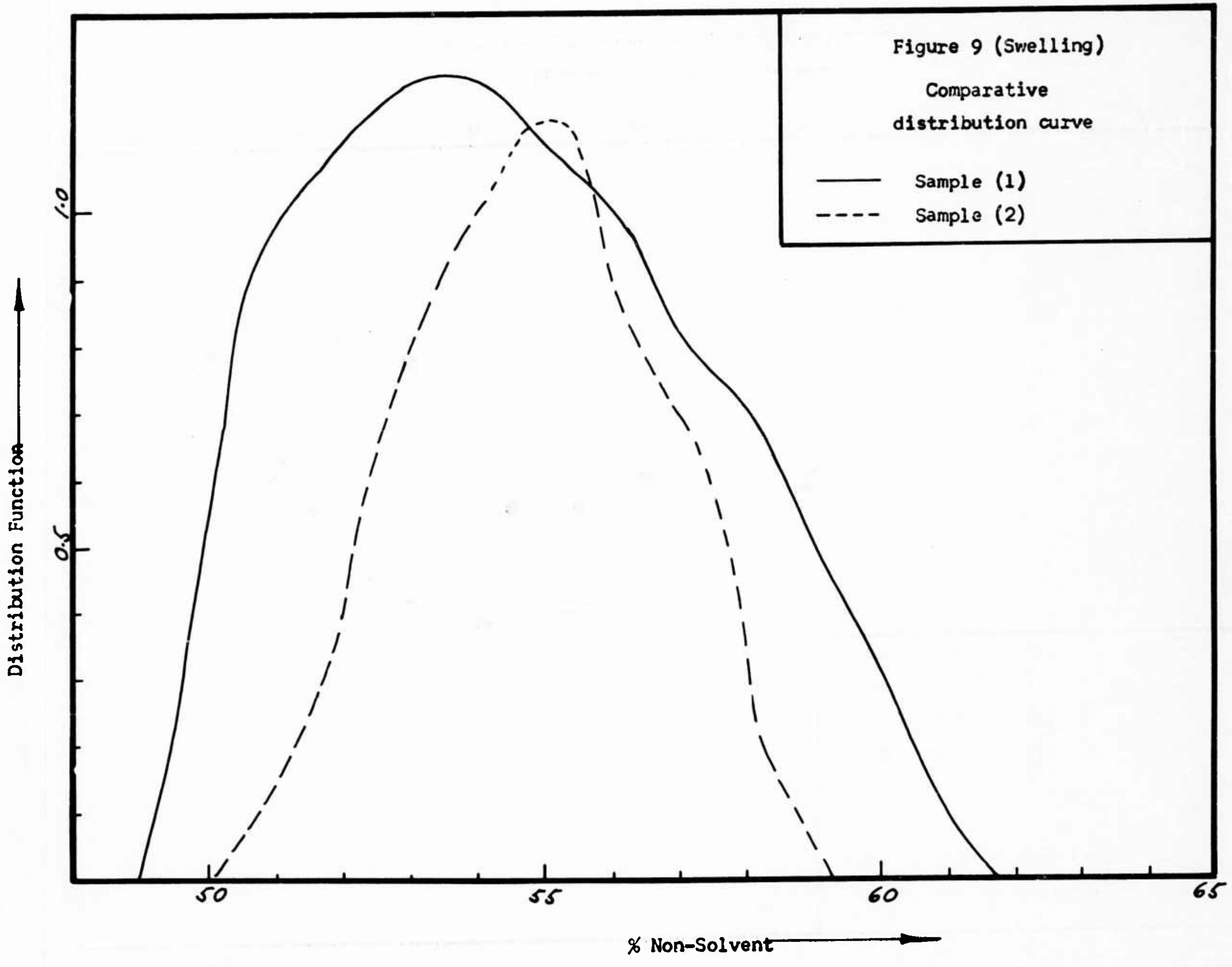


Figure 9 (Swelling)

Comparative distribution curve

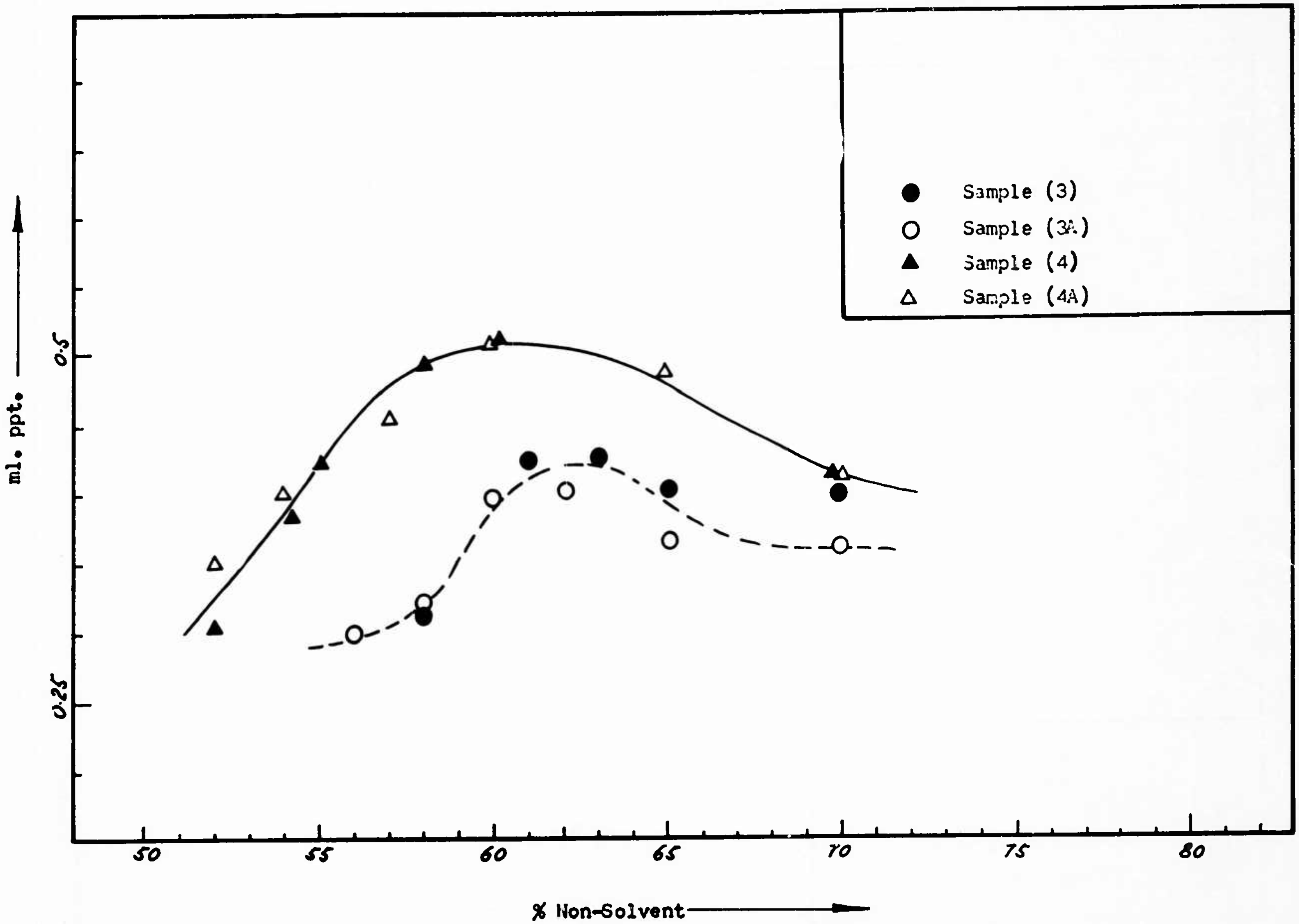


Figure 10. Swelling - 0.25 $\frac{\text{g. Solute}}{\text{100 ml. Solvent}}$

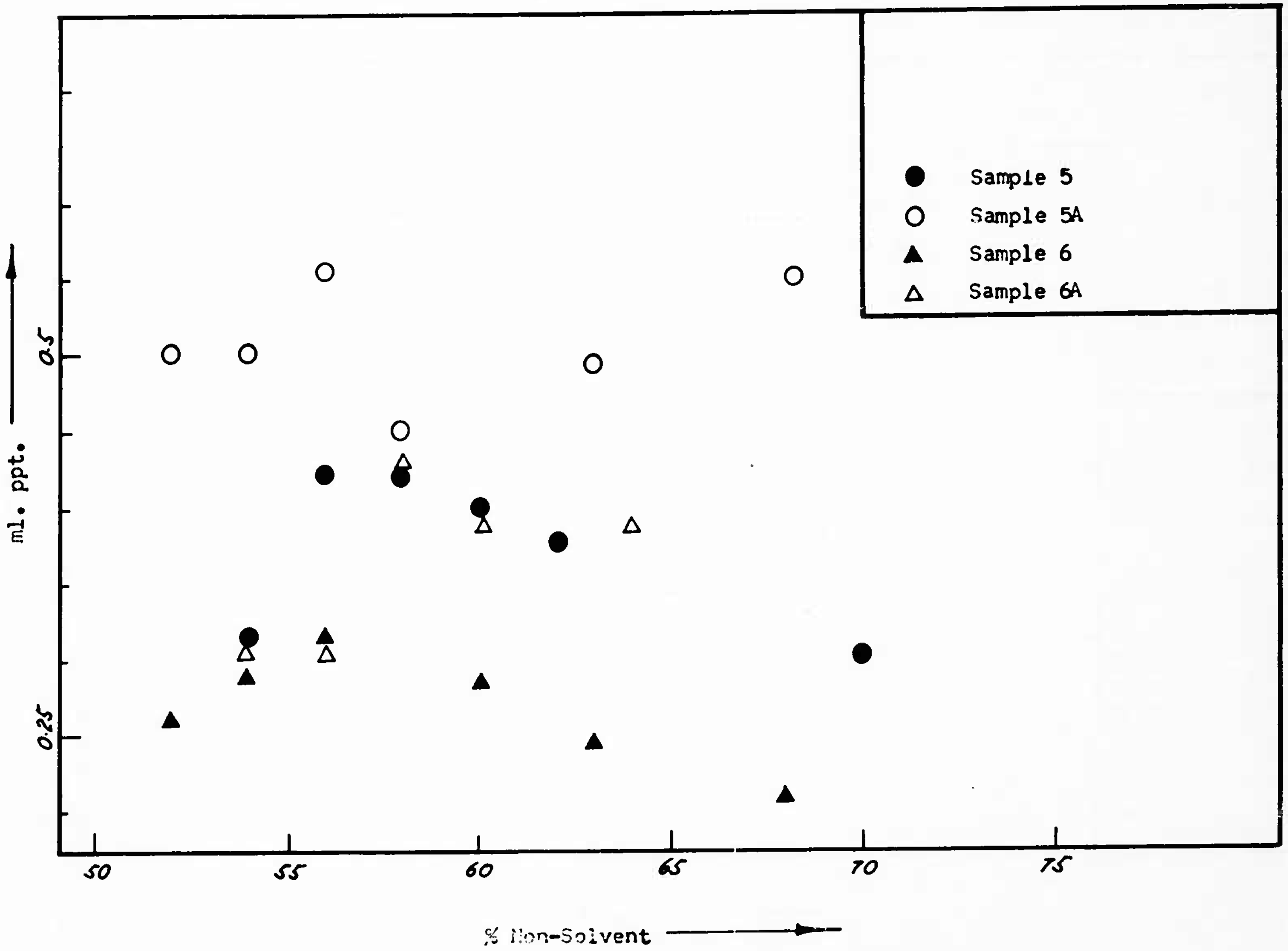


Figure 11. Swelling - 0.25 $\frac{\text{g. solute}}{\text{100 ml. Solvent}}$

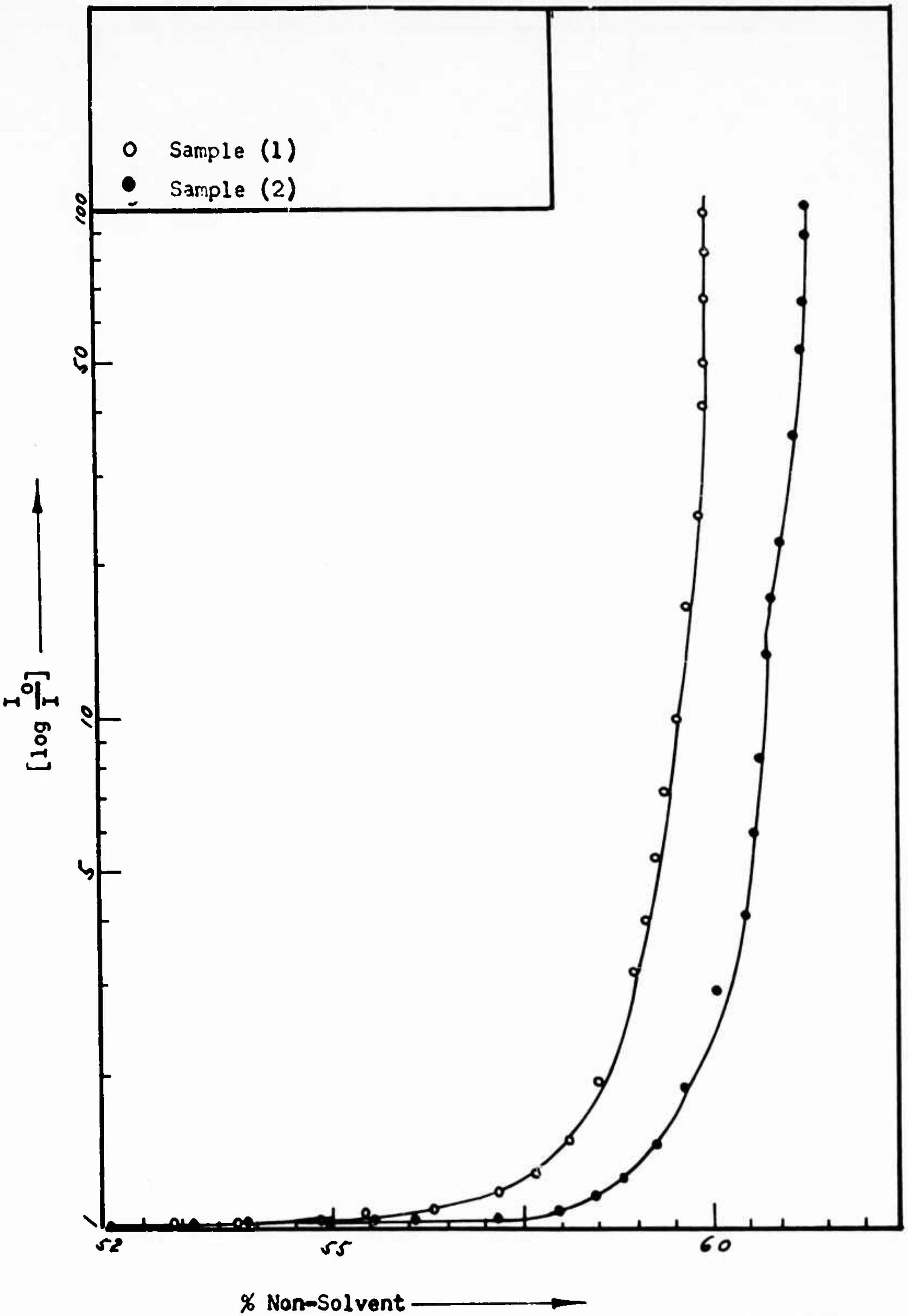


Figure 12. Turbidimetric Titration - 0.25 $\frac{\text{g. solute}}{\text{100 ml. Solvent}}$

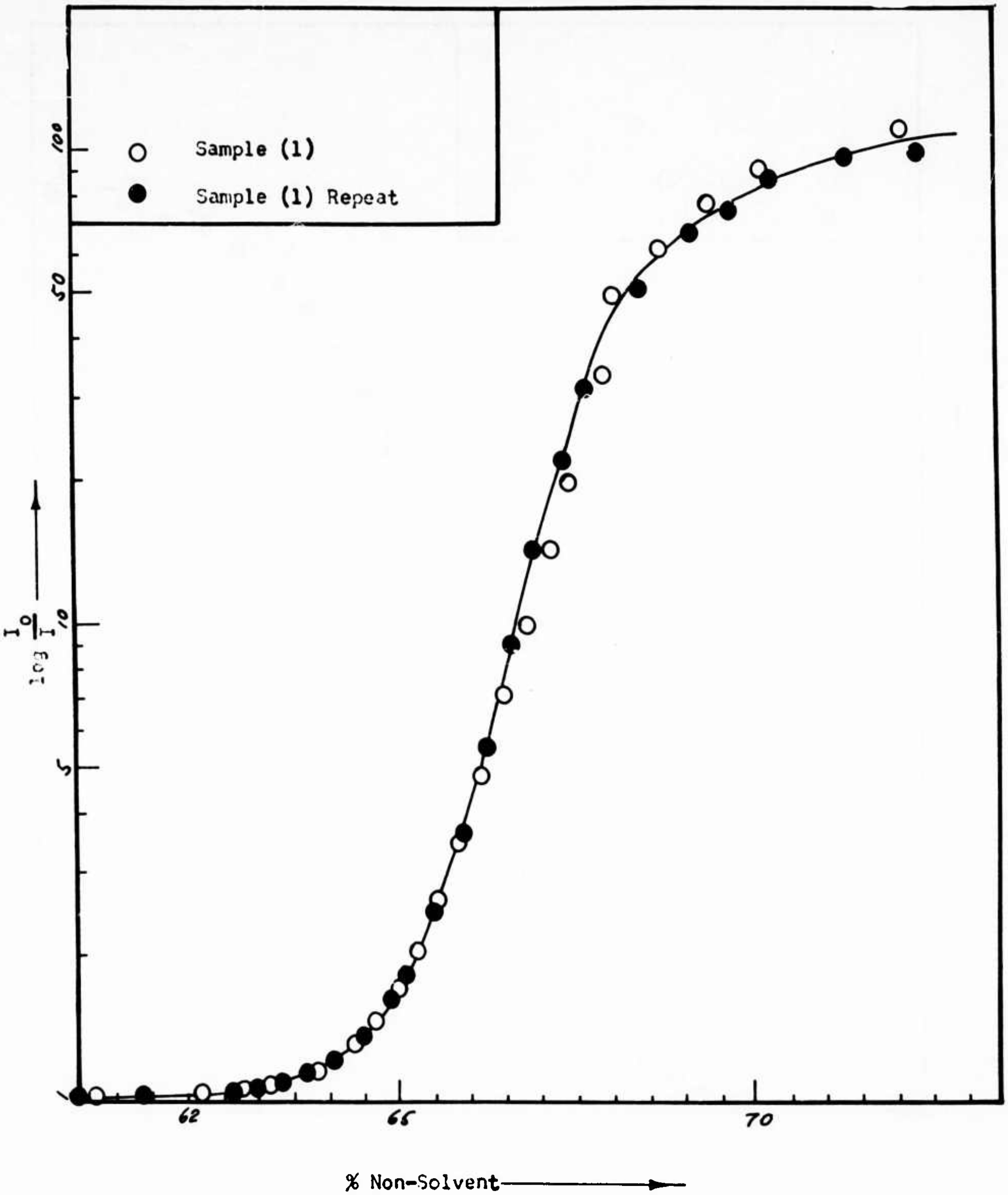


Figure 13. Turbidimetric Titration - 0.0625 $\frac{\text{g. solute}}{\text{100 ml. Solvent}}$

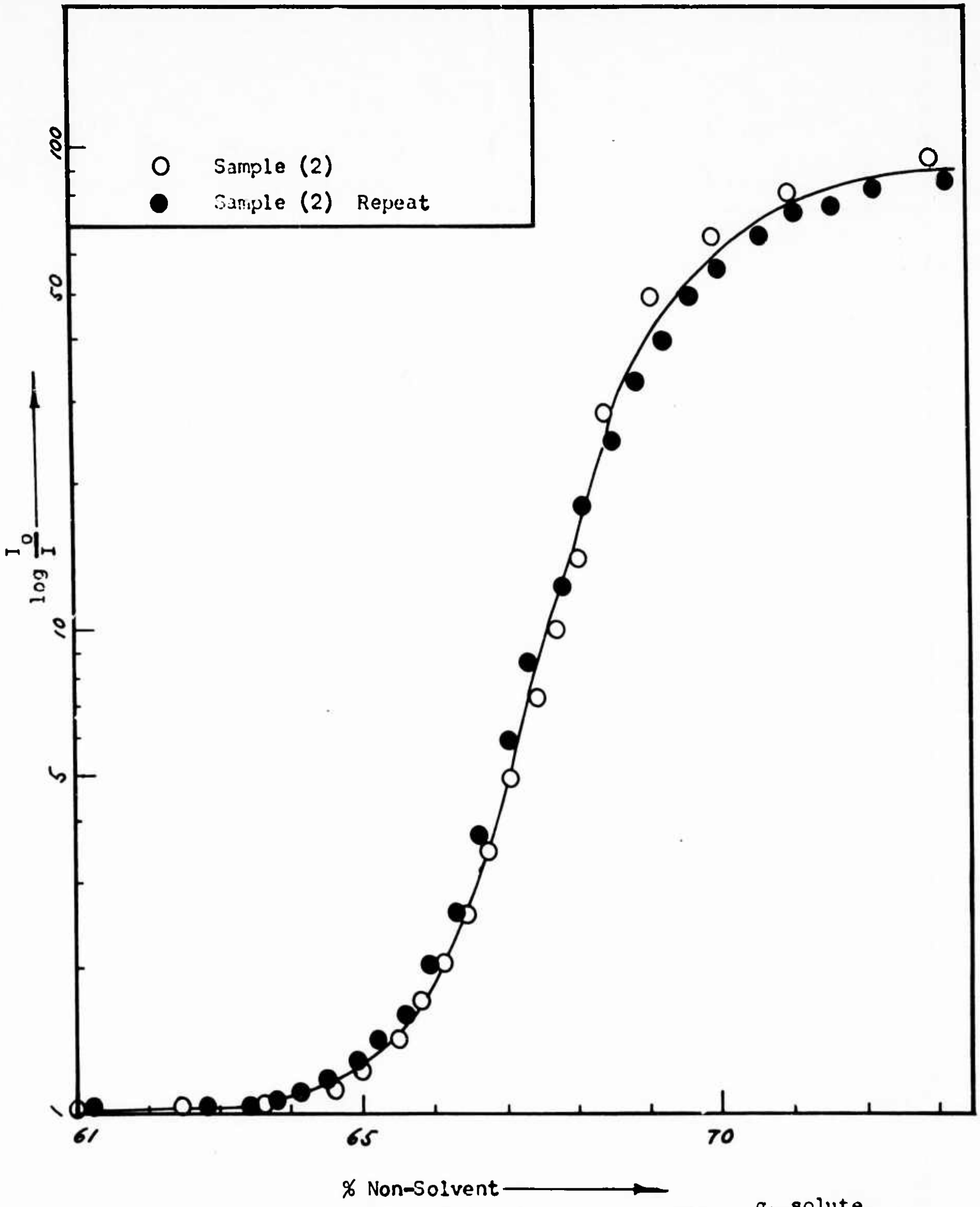


Figure 14. Turbidimetric Titration - 0.0625 $\frac{\text{g. solute}}{\text{100 ml. Solvent}}$

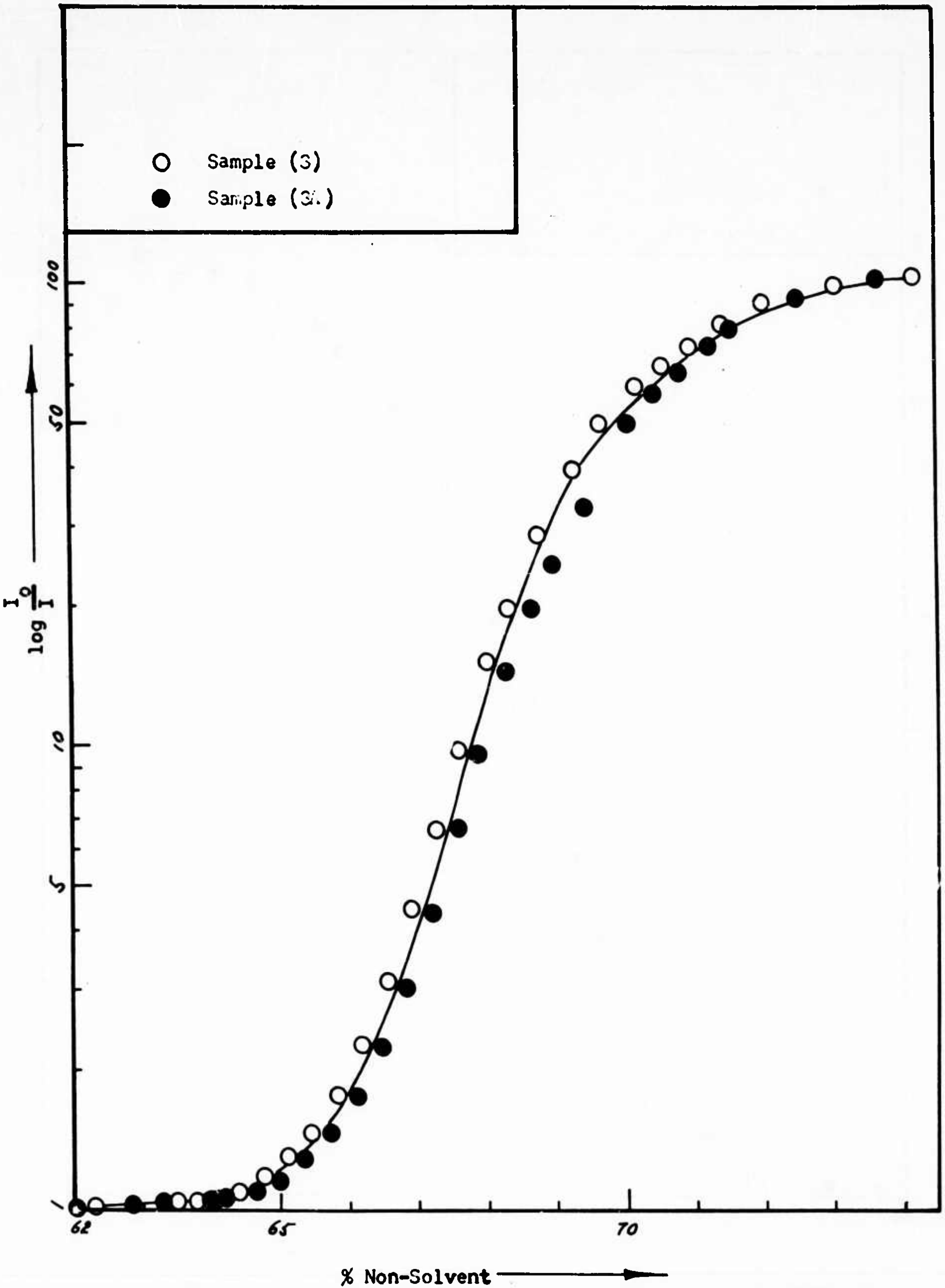


Figure 15. Turbidimetric Titration - 0.0625 $\frac{\text{g. solute}}{\text{100 ml. Solvent}}$

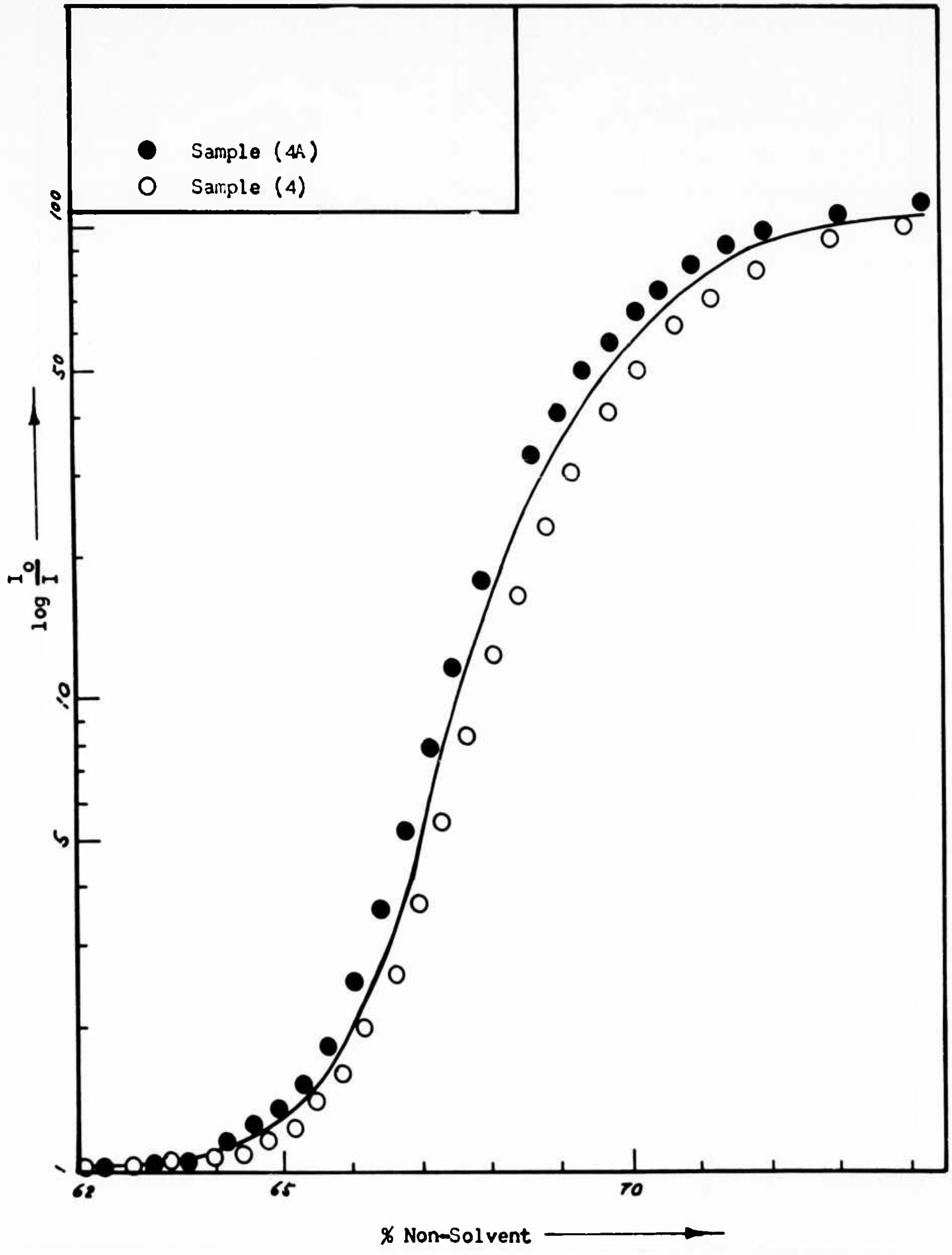


Figure 16. Turbidimetric Titration - 0.0625 $\frac{\text{g. solute}}{\text{100 ml. Solvent}}$

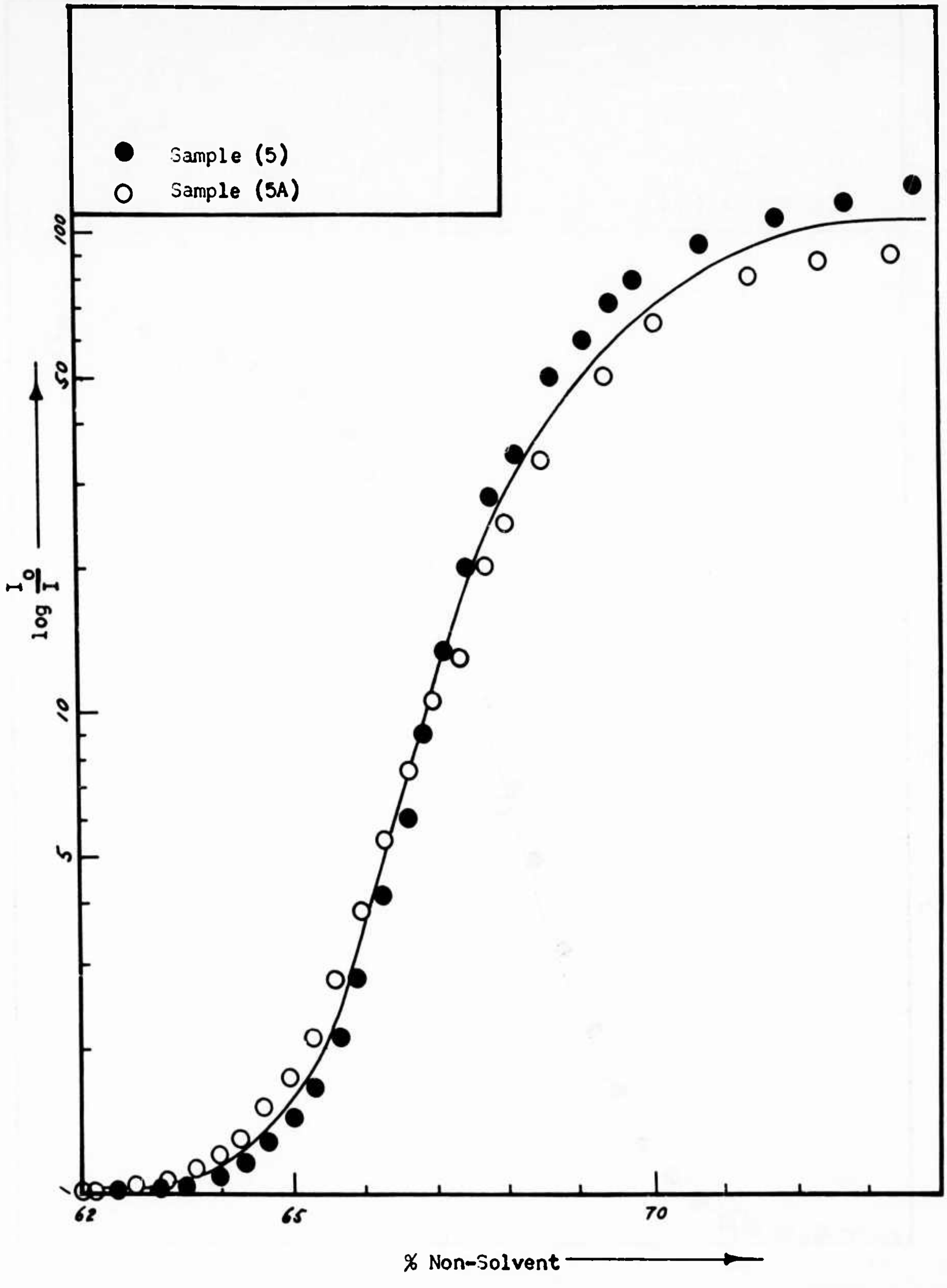


Figure 17. Turbidimetric Titration - 0.0625 $\frac{\text{g. solute}}{\text{100 ml. Solvent}}$

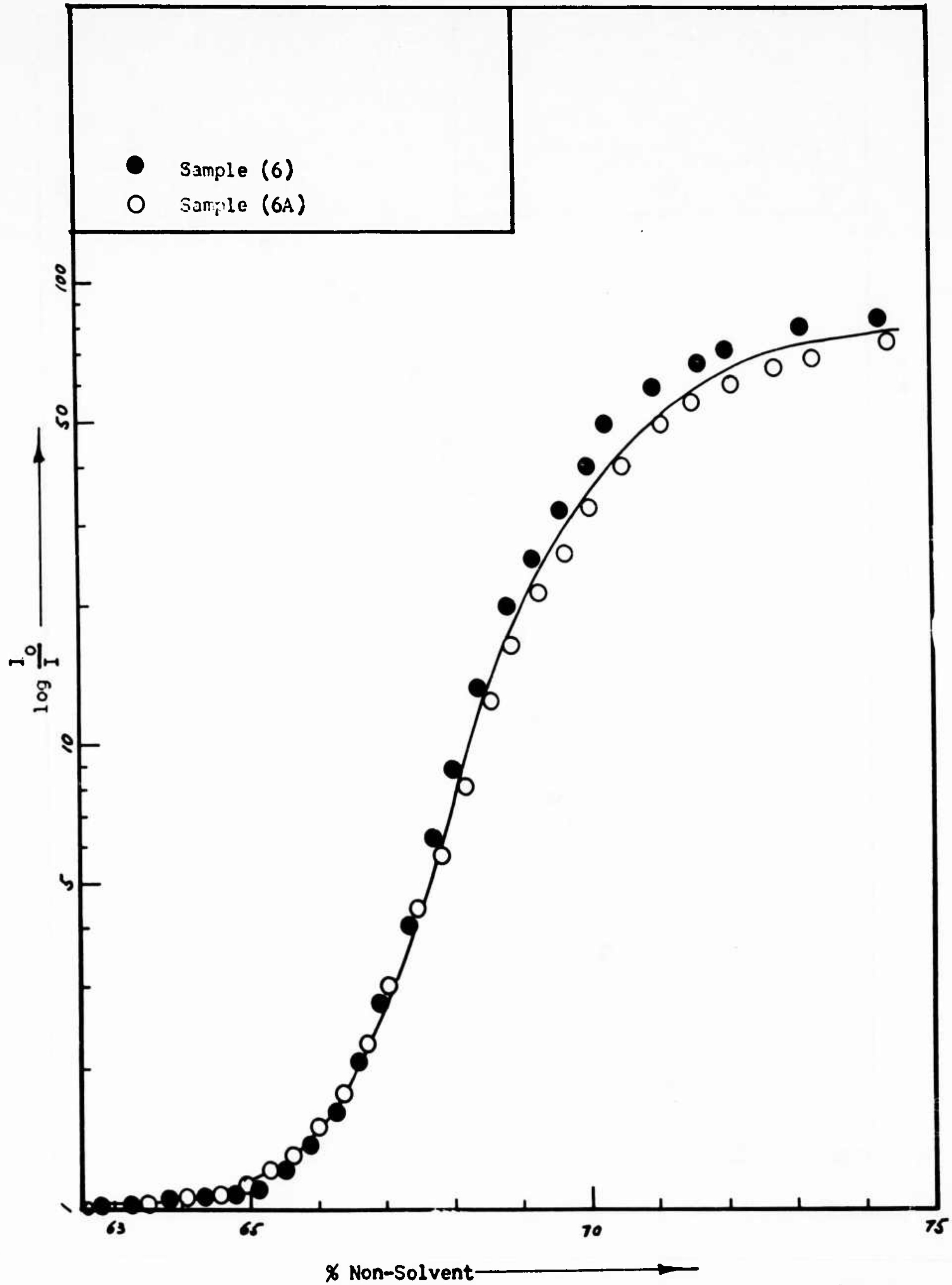


Figure 18. Turbidimetric Titration - 0.0625 $\frac{\text{g. solute}}{\text{100 ml. Solvent}}$

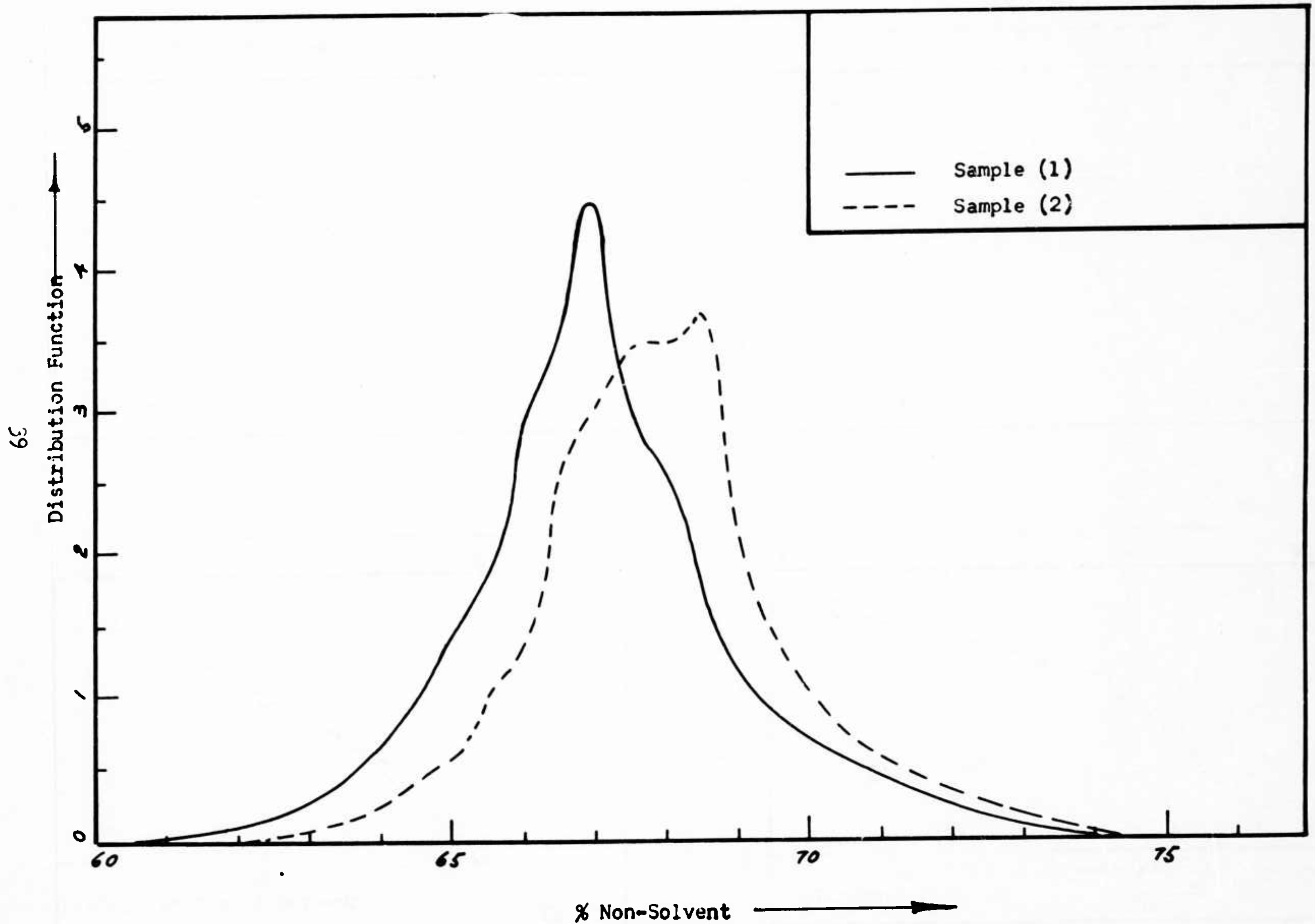


Figure 19. Comparative Distribution Curve (Turbidimetric Titration)

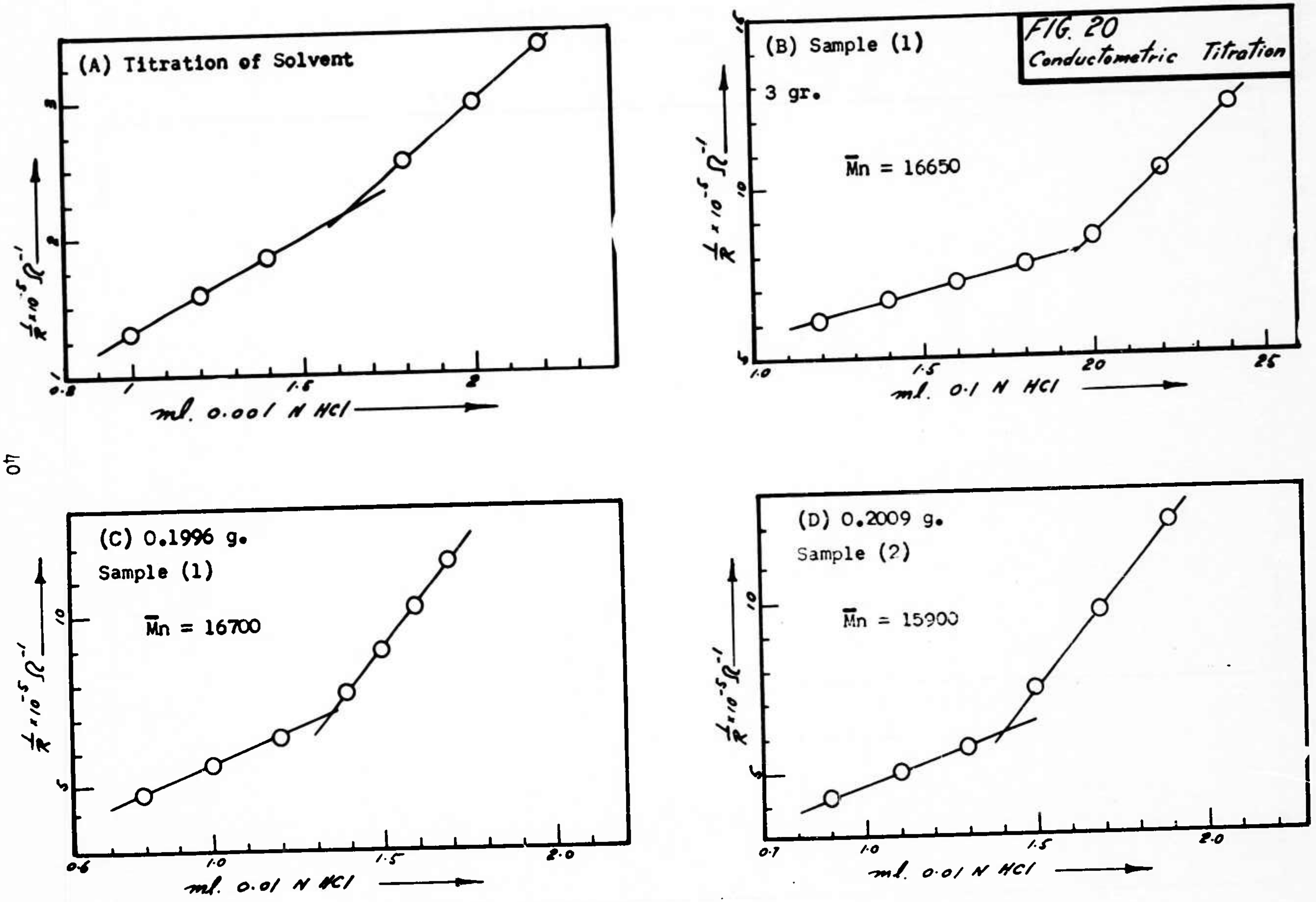


FIG. 20
Conductometric Titration

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Rpt Nr ASD-TDR-62-879. RAPID METHODS TO ESTIMATE THE MOLECULAR WEIGHT DISTRIBUTIONS OF POLYMERS. Final report, Dec 62, 42p inc illus., tables, 33 refs.

Unclassified Report

A comparative study of three rapid, inexpensive methods for determination of polymer molecular weight distribution was carried out on 66 nylon samples. The methods were cumulative precipitation fractionation, swelling and turbidimetric titration.

(over)

The most rapid and precise of these was found to be turbidimetric titration.

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2. Molecular weight
3. Fractionation
4. Titration
I. AFSC Project 7360 Task 736005
II. Contract AF 33 (616)-7450
III. Univ. of Cincinnati Cincinnati, Ohio
IV. Siu-Yuen Fok Richard G. Griskey
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