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I hereby recommend that the thesis prepared under my
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entitled Quantitative Determinations with the
Centrifuge and Factors Affecting Them

be accepted as fulfilling this part of the requirements for the
degree of Doctor of Philosophy

Approved by:

Henry Max Goettch

QUANTITATIVE DETERMINATIONS
with the
CENTRIFUGE
and
FACTORS AFFECTING THEM

A Dissertation

presented to the Faculty of the Graduate
School of the University of Cincinnati
in partial fulfillment of the requirements
for the Degree of Doctor of Philosophy

by

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INTRODUCTION

Since the beginning of the 20th century the centrifuge has found numerous applications in chemical, industrial and biological laboratories, and the growth of its usefulness is by no means at a standstill. New industrial applications of the machine are being found almost daily.

Thus in the chemical and industrial laboratories it has been used as a method of rapid filtration, of breaking colloidal solutions, of increasing the efficiency of flotation methods; and even of making quantitative determinations by virtue of the difference in specific gravities of substances. In fact Colcar and Lobry de Bruyn have stated that they were able to separate sodium sulphate from its saturated solution by using a centrifugal force of 4×10^5 dynes. Friedenthal ⁽¹⁾, however, has shown that this is not possible with a centrifugal force of 8×10^8 dynes. For drying precipitates, crystals, etc., it is very useful, not to mention its use in modern laundries as a dryer. The centrifuge may in fact be used to advantage whenever an increase in force over that of gravity is desired. One of the earliest applications of the centrifuge in the chemical laboratory was to increase the rate of settling of precipitates in calibrated capillary tubes. From the volume of the precipitate thus settled and packed, its approximate weight could be obtained. This process, however, has received

very little development despite the fact that it can be made an enormous time saver. Perhaps this neglect is due to the mistaken belief that the process is by nature very inaccurate. As will be shown in this paper, the process can be made accurate under careful control of the conditions employed.

The uses of the centrifuge in the biological laboratory are exceedingly numerous. We might mention the sterilization of solutions from micro-organisms; the analysis of cell suspensions, such as blood, etc.; the separation of casein from milk. With a centrifugal force of 8×10^8 dynes, Friedenthal (loc. cit.) has been able to separate quantitatively the casein in milk. The milk plasma after the removal of this casein is still opalescent and contains the remaining albuminous substances of the milk. Thus we have for the first time a quantitative separation of two albuminous substances from a colloidal solution by means of centrifugal force. The centrifuge is almost indispensable in the dairy industry for the separation of cream from whole milk.

At the present time a well-built centrifuge is not beyond the means of any small but well-equipped laboratory. Most of the machines now being designed are for use with electric power, being made to operate on 110 and 220 volt A.C. or D.C. circuits, and most laboratories have electrical power available. However, there are some machines still designed for use with hand power, where electrical power is not available.

Since the centrifuge is a great time saver any investigation which would increase its usefulness in the laboratory is desirable and of great advantage. It was with this view in mind that the following investigation was carried out.

HISTORICAL

In the year 1875 Professor Eggertz, then of the University of Berlin, suggested a very crude method of estimating the phosphorus content of iron and steel. This method consisted in oxidizing the phosphorus to phosphate, precipitating with molybdic acid, allowing the phospho-molybdate thus formed to settle in a capillary tube, and measuring its volume. By comparing this volume with the volume produced from a standard sample and assuming direct proportionality between volumes and phosphorus content, an estimation of the phosphorus content could be readily made. As would be expected this method gave very poor and inconsistent results, and therefore could not be used for steel-control method, or for any other process which required a fair estimation of the phosphorus content. M. A. von Reis (2) has shown that even after remaining undisturbed for 60 hours the volume of the phospho-molybdate did not attain a constant volume.

However, in the year 1886 George W. Goetz, then director of the steel works of the Otis Steel Company of Cleveland, Ohio, began using in the laboratories of that company a modification of Professor Eggertz's method. He not only allowed the precipitate to settle out but packed it into the capillary by centrifugal force. This proved to be a more satisfactory method and could be used for control work since it was more accurate and a constant volume could be attained

in a relatively short time.

In the Fall of 1886 Goetz communicated with his former teacher, Dr. Wedding of Berlin, Germany, and mentioned the method he was using. Dr. Wedding, after making a few experiments in the Berlin Bergakademie Laboratory, described this method at a general meeting of the German United Iron Foundrymen in January 1887. His communication was published in *Stahl und Eisen* (3) and dealt almost entirely with the procedure of the process and gave no experimental data whatever. Mention was made of the fact that the duration of centrifuging had something to do with the resulting volume of the precipitate, but no quantitative relations were given. No mention was made of the effects of the other conditions of the procedure, such as rate of precipitation, rate of centrifuging, temperature of precipitation, etc., on the resulting volume of the precipitate. He claimed for the method a variation of not more than .01% for steels containing less than .1% carbon. For steels of higher carbon contents the results were not consistent, because all of the phosphorus was not precipitable with molybdic acid.

M. Ukena (4) was the first to publish some experimental results. He showed that for steels of low carbon content (less than .1%) the method gave values which varied not more than $\pm .01\%$ from the actual phosphorus content as determined by gravimetric methods. He attributed the inaccuracy for steels of higher carbon contents to the formation of

organic acids during oxidation. He attempted to remedy this situation by evaporation and ignition of the iron salts and also by oxidation with potassium permanganate. With this change in procedure he obtained no better results and came to the conclusion that the method was applicable only to steels of low carbon and silicon content.

In 1889 Karl Bormann (5) published some researches on high carbon steels in which he showed that the method was applicable to such steels, provided the carbon compounds were oxidized with potassium permanganate before precipitation of the phosphorus. He also gave results to show that the method was applicable to steels containing not more than .25% silicon. If the silicon content is greater than this value a gelatinous precipitate settles out and the method cannot be used unless the silicon is separated. At about the same time M. A. von Reis (6) also published some researches showing that the phosphorus content of high carbon steels could be determined if potassium permanganate was used to oxidize organic compounds that were formed. Data were given to substantiate these claims. The variation in phosphorus content in general was not more than $\pm .01\%$ from the actual content as determined gravimetrically. A study was made of the effect of the relative amounts of nitric acid, ammonium nitrate, and molybdic acid upon the volume of the precipitated ammonium phospho-molybdate. This study was made on four grades of ingot steel and led him to conclude that the volume of the

precipitated phospho-molybdate was to a great extent dependent upon the physical conditions of the precipitate and therefore on the relative amounts of reagents used. No mention was made of the effect of temperature of precipitation, rate of precipitation, rate of centrifuging, and length of centrifuging upon the volume of the precipitate produced.

In December 1890 Reis (7) in another publication showed that the results of his own former researches were inaccurate and that his procedure would not give consistent results. He remedied the procedure by making several changes, one of which was to raise the temperature of precipitation to 95°C. It was not indicated how this change affected the volume of the precipitate.

In the same year C. Reinhart (8) showed that in order to obtain consistent results, the temperature of precipitation, and the rate and duration of centrifuging must be kept constant; however, no quantitative relations between the volume and these conditions were given. He outlined a specific procedure for carrying out the determination of phosphorus and showed that the difference in the percentage of phosphorus as determined by gravimetric and centrifuge methods was rarely more than $\pm .02$.

From the year 1891 onward interest in the centrifuge methods of determination seemed to be lacking for it was not until the year 1907 that any further such publications were made. In that year H. G. Parker (9) gave a general review of

some of the uses of the centrifuge in quantitative analysis, dealing mostly with the use of the centrifuge as a method of rapid filtration. For instance, he gave a method for packing the precipitate directly into a platinum crucible. The precipitate was then washed by pouring off the mother liquor, adding water, and centrifuging again. Finally the platinum crucible was removed, dried and weighed, and the weight of precipitate obtained. This method was recommended for the determination of silver chloride. Precipitation was carried out in a separating flask 14 cms. long and about 3.5 cms. in diameter. The neck of the separating flask fits into a platinum crucible in a water-tight joint made by means of a short section of pure gum rubber tubing which is held between the outside of the neck of the flask and the inside of the crucible. The crucible is weighed and then connected to the flask. After precipitation has been carried out, the crucible and the flask are placed together in a metal casing and centrifuged. A simple type of centrifuge which gives a maximum of 1500 to 1800 r.p.m. was also described.

In 1911 Hans Friedenthal (10) discussed the use of the centrifuge in coagulating colloids, in separating casein from milks, etc. He also described a method of separating substances with different specific gravities. It is claimed that sodium and potassium chlorides are separable in this manner, although no data were given. For this separation it is necessary to obtain two liquids which are miscible and

yet will not dissolve the substance to be analyzed. The specific gravities of the liquids must be such that by mixing, a liquid with a specific gravity lying between those of the two solids to be separated can be obtained. Take the specific example of potassium and sodium chlorides. Friedenthal suggests the use of xylene and bromoform. Xylene has a specific gravity of .865 and bromoform that of 2.88. Since these two liquids are miscible in all proportions, a liquid with any specific gravity between .865 and 2.88 may be obtained by mixing them in the correct proportions. Now KCl has a specific gravity of 1.987 and NaCl that of 2.161. If we therefore prepare a liquid of specific gravity 2.000, add a mixture of NaCl and KCl to this and centrifuge, the NaCl will be driven to the bottom while KCl remains at the top. Friedenthal made use of a flask with a stopcock in the center so that the top portion of the liquid might be drawn off after centrifuging. This method of separation is merely a modification of the old flotation method.

Finally in 1922 Arrhenius (11) published some researches showing that the centrifuge method might be applicable to precipitates other than ammonium phospho-molybdate. He used the method to determine calcium, magnesium, sulphate and nitrate. However, no information was given as to the conditions of precipitation and as to how variations in conditions affected the results. These data given by Arrhenius are therefore of little value since, as will be shown in this

paper, the volume of the precipitate is to a great extent dependent on the conditions of precipitating and centrifuging.

THEORETICAL

As has been stated before, the centrifuge is advantageous in any process where an acceleration greater than that due to gravity is desirable. All the uses of the centrifuge at the present time are dependent upon this fact. Thus in the milk industry the rate of separation of the cream from the rest of the milk is dependent upon the greater acceleration given the milk particles. If this acceleration were due to gravity alone the separation of the milk and cream would require many hours, whereas when the centrifuge is used a separation is accomplished in a relatively short time. The cream particles, being less dense than the water or casein of the milk, seek the center of rotation and are allowed to flow off. With a much greater centrifugal force the casein may also be separated from the milk. Likewise when any liquid or solid is suspended in another liquid of different specific gravity, separation may be accomplished by means of the centrifuge, provided, of course, that there is a great enough difference between the two specific gravities. In many cases two solids may be separated from each other by making use of the same principle. In the following work the centrifuge was applicable because it increased the rate of settling of solid particles out of a less dense liquid and also increased the intensity of packing of these particles into a capillary tube.

According to Stokes' Law the limiting velocity of

a spherical particle is given by

$$v = \frac{2}{9} \frac{g r^2 (d - d_0)}{n} \quad (1)$$

where v is the velocity of settling of a particle of radius r and density d falling through a medium of viscosity n and density d_0 under the influence of gravity g . Thus we see that if a substance is suspended in a liquid of greater density than itself $d - d_0$ will be negative and since all the other members of the right hand side of the equation are essentially positive, v will be negative, i.e. directed upward. Thus the substance rises to the top. This is the case with cream and casein separating from milk.

Stokes' Law is strictly true only for spherical particles, but for particles of other shapes it may be applied as an approximation.

For a given substance in a given medium, d , d_0 and n are constant. If we assume r constant, an assumption which we shall justify later, we may write

$$\frac{dv}{dg} = \frac{2}{9} \frac{r^2 (d - d_0)}{n} \quad (2)$$

which gives us the rate of change of velocity per unit change of acceleration causing that velocity. If the particles are not settling under the acceleration of gravity but under any other acceleration a we may write

$$v = \frac{2}{9} \frac{a r^2 (d - d_0)}{n} \quad (3) \quad \text{or} \quad \frac{dv}{da} = \frac{2}{9} \frac{r^2 (d - d_0)}{n} \quad (4)$$

Now since we have assumed r , d , d_0 , and n constant

the right hand member of equation (4) is constant. Obviously the units of this constant are seconds. Integrating this equation we obtain

$$v = k a + c \quad (5)$$

where c is the constant of integration. But we have the condition that when $v = 0$, $a = 0$. Therefore $c = 0$ and we may write

$$v = k a \quad (6)$$

which is our original equation.

If r is not constant then we must write

$$v = k r^2 a \quad (7)$$

that is, the velocity of falling of a particle is directly proportional to the square of the radius times the acceleration.

For constant acceleration we write

$$v = k r^2 \quad (8)$$

or $\frac{dv}{dr} = 2 k r \quad (9)$

That is, for a constant medium and a constant acceleration the limiting velocity of a falling particle through this medium is directly proportional to the square of its radius. Therefore, the larger the particle the more rapid it will fall. This fact was brought out in this research, for every variation in procedure which tended to give larger particles (all other factors such as rate of centrifuging, etc. remaining constant) increased the rate of settling and packing of the particles.

Since the velocity of settling of particles is proportional to the first power of the acceleration causing that velocity, it would be well to find out how the acceleration of the centrifuge compares with that due to gravity. The efficiency of a centrifuge is dependent upon the acceleration which it is able to produce.

The ratio of the acceleration of the centrifuge to that of gravity we shall define as the Relative Centrifugal Acceleration and shall denote it by R.C.A.

Now centrifugal force is given by the equation

$$F_1 = M W^2 R \quad (10)$$

where F_1 is the centrifugal force, M the mass of the particle, R the radius of rotation, i.e. the radius of the circle described by the rotating particle, and W the angular velocity in radians per second.

Now the effective mass of the particle is given by

$$M = \frac{4}{3} \pi r^3 (d-d_0) \quad (11)$$

where d is the density and r the radius of the particle. Substituting this in equation (10) we obtain

$$F_1 = \frac{4}{3} \pi r^3 (d-d_0) W^2 R \quad (12)$$

But according to Stokes' Law the frictional force between a falling particle of radius r and velocity v_2 and a liquid of viscosity n is given (12) by

$$F_2 = 6 \pi n r v_2 \quad (13)$$

Now the velocity of a particle will reach a limiting value when this frictional force just equals the centrifugal force. Therefore we may equate F_1 and F_2 to obtain the limiting velocity.

$$6 \pi n r v_2 = \frac{4}{3} \pi r^3 (d-d_0) W^2 R$$

$$\text{or } v_2 = \frac{2}{9} \frac{r^2 (d-d_0) W^2 R}{n} \quad (14)$$

But we found above that the velocity v_1 of a particle falling under the influence of gravity is

$$v_1 = \frac{2}{9} \frac{r^2 (d-d_0) g}{n}$$

Thus g is the acceleration due to gravity and $W^2 R$ that due to the centrifuge. Thus it will be seen that the acceleration toward the center of a rotating system is given by

$$a_2 = W^2 R \quad (15)$$

also

$$\frac{v_2}{v_1} = \frac{W^2 R}{g} = \text{R.C.A.} \quad (16)$$

Now $W = \frac{2\pi}{T}$ where T is the time in seconds of one revolution.

Let N = the number of revolutions per minute = r.p.m. Then $N/60$ = r.p.s. = revolutions per second; and $60/N = T$.

Therefore

$$W = \frac{2\pi N}{60} \text{ radians per second.}$$

Substituting this in equation (15) we obtain for the acceleration a_2 due to centrifuging

$$a_2 = \frac{(2\pi N)^2 R}{60^2} = \frac{4\pi^2 N^2 R}{3600}$$

or $a_2 = .011018 r^2R$

Therefore we see that the acceleration due to the centrifuge is directly proportional to the square of the r.p.m. times the radius of rotation.

Therefore

$$R.C.A. = \frac{W^2R}{g} = \frac{.011018N^2R}{g} \quad (17)$$

The average radius of rotation used was 17 cms. With this value and an r.p.m. of 2000 we have

$$R.C.A. = \frac{.011018 (2000)^2 \times 17}{980.1} = 764.5$$

That is, the acceleration given a particle at 2000 r.p.m. is 764.5 times that of gravity.

Since these quantitative methods by means of the centrifuge depend upon the degree of packing of the precipitate, it would be expected that a change in the conditions of precipitation would cause a change in the volume of the centrifuged precipitate. It is well known that if the conditions of precipitation are varied, the physical properties of the precipitate will vary, and therefore we would expect a variation in the packing ability of the particles. Furthermore it would be expected that within certain limits any conditions which would tend to give larger precipitated particles would in consequence of this property give particles that would pack more closely, and therefore would occupy less volume. This would be expected for two reasons: (1) The amount of packing is

proportional to the centrifugal force acting on a particle and this, in turn, is proportional to the mass of the particle as given by equation (10) above, namely

$$F_1 = M W^2 R$$

That is, the larger the particle the greater will be the centrifugal force and therefore the extent of packing;

(2) The extent of packing is determined by the amount of space between the particles after packing. This space will depend upon the size and shape of the particles and, within certain limits of sizes, the larger the particles the less space there will be between them for a given mass of substance. Especially is this true for non-uniform particles, i.e. some small particles to fill in the spaces between the larger ones.

Since the volume of the centrifuged precipitate depends upon the physical properties of the particles, it is important that the conditions of precipitation be taken into account. Those conditions of precipitation which probably affect most the physical properties of the precipitated particles are: (1) Temperature of precipitation; (2) Concentration of reagents; (3) Rate of addition of precipitant; (4) Nature of reagents; (5) Time of settling of the precipitate before centrifuging.

Also the amount of packing will depend upon the length, cross-section, and shape of the capillary into which the particles are packed, since it is known that the

frictional resistance offered to particles flowing through or into a tube depends upon these properties of the tube. Therefore, in comparing the results obtained with two different tubes it is necessary to keep in mind that these will be the same only when the two tubes used have the same diameters, lengths, and shapes.

OBJECT OF THIS INVESTIGATION

The use of the centrifuge for quantitative determinations was suggested more than a half century ago. Nevertheless, no complete study of centrifuge methods, their limitations, accuracies, or applicability has been published. The object of this investigation is therefore four-fold, viz:

- (1) To determine the degree of accuracy one can expect from such centrifuge determinations.
- (2) To determine what factors enter into these determinations, i.e. to determine how and to what extent the conditions of precipitation, centrifuging, etc., affect the volume of the centrifuged precipitate.
- (3) To discover to what type or types of precipitates this method is applicable.
- (4) To apply, if possible, this method to rapid technical analysis.

EXPERIMENTAL

A. Apparatus and Manipulation

The centrifuge machine used in this investigation was the Type C, manufactured by the International Equipment Company of Boston, and operating on 110 volts A.C. The speed of this machine was controlled by a rheostat with nine contacts. Graphs were furnished with the machine on which the r.p.m. were plotted against the rheostat contacts for different loads. By knowing the load and noting the point of contact on the rheostat, the r.p.m. could be obtained. The brushes of the motor, however, were somewhat worn and it seemed advisable to make a recalibration of the speed. This calibration showed that the graphs furnished by the company were quite inaccurate for this machine. The following method of calibration was used: an accurate voltmeter was connected across the terminals of the rheostat and the machine was loaded with the usual number of tubes. By means of a tachometer with an extension, the r.p.m. could be obtained for the different rheostat contacts. At the same time the terminal voltages were also noted. These voltages were plotted against the r.p.m., giving a graph from which the r.p.m. for any load and any contact could be obtained provided the terminal voltage of the rheostat be known. This necessitated only that a voltmeter be kept permanently connected across the terminals of the rheostat. The accuracy of this method depends upon the validity of

the following assumptions: (1) That the voltage of the line was non-variable, which assumption is valid in that there were no other loads on the line; (2) That the terminal voltage read gave a measurement of the voltage applied to the motor of the centrifuge. With clean rheostat contacts this assumption is valid. The contacts were kept clean and smooth with fine sandpaper.

The tubes used were of the Goetz type, and also manufactured by the International Equipment Company. They were pear shape bulbs ending in capillaries. The total capacity of the tubes was approximately 125 cc. with calibrations for each 25 cc. Tubes with terminal capillaries of different bores and capacities are obtainable. In this investigation three sizes were used depending upon the type of precipitate employed. For dense crystalline precipitates, such as barium sulphate, a capillary of approximately 1.1 mm. inside diameter was used. These capillaries were divided into 20 equal calibrations extending over a total range of 25 mm. The total capacity of the capillary was approximately 20 cu.mm. or .02 cc. Each division, therefore, represents approximately 1 cu.mm. For less dense, but crystalline, precipitates such as calcium oxalate a tube with a capillary of approximately 200 cu.mm. was used. This capillary was approximately 2.6 mm. in diameter and was divided into 20 equal calibrations extending over a range of 35 mm. Each division represents, therefore, approximately 10 cu.mm.

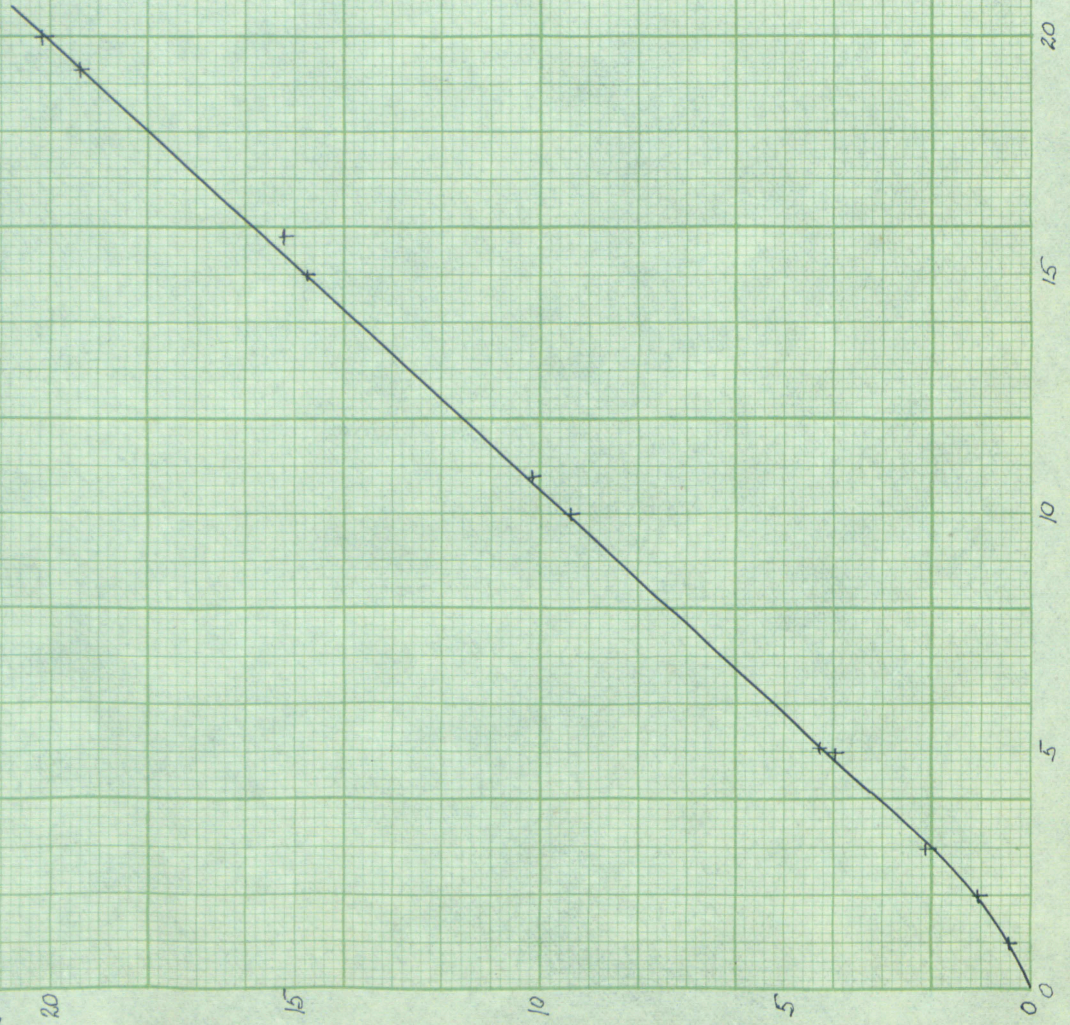
For gelatinous and voluminous precipitates such as hydrous aluminum oxide and nickel dimethylglyoxime, a flask with a larger terminal tube was used. The calibrated part of this tube had a capacity of 5 cc. and extended over a range of 5.8 cms., and with an inside diameter of approximately 1.04 cms., calibrations were made for each .1 cc.

The bore and therefore the capacity of the capillaries varied from tube to tube and also within the same tube-near the bottom of the capillary and it was therefore necessary to calibrate each tube. This was accomplished by filling the capillary to the desired mark with mercury, withdrawing the mercury with a smaller capillary tubing made by drawing out a piece of ordinary glass tubing, and weighing. From the weight of the mercury the volume could be ascertained. Near the bottom, this was done for each division; beyond the fifth, for every second division. The actual volumes were then plotted against the volumes as read from the tubes and a smooth curve drawn. These relations are given in graphs 1-6 and from these the actual volume can be obtained provided only the volume read be known. Graphs 1 and 2 are for tubes with the smaller capillaries, while 3 and 4 are for the capillaries of approximately 200 cu. mm. capacity. It will be seen that there is a considerable difference in the capacities of tubes 1 and 2. The total capacity of 2 is 14% greater than that of 1. Calibration of all tubes is therefore quite necessary.

mm³ Vol. correct.

mm³ Vol. read.

Graph I
Calibration of Flask I



mm.³ Vol. correct.

20

15

10

5

0

0

1

2

3

4

5

6

7

8

9

10

11

12

13

14

15

16

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36

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42

43

44

45

46

47

48

49

50

51

52

53

54

mm.³ Vol. read.

25

20

15

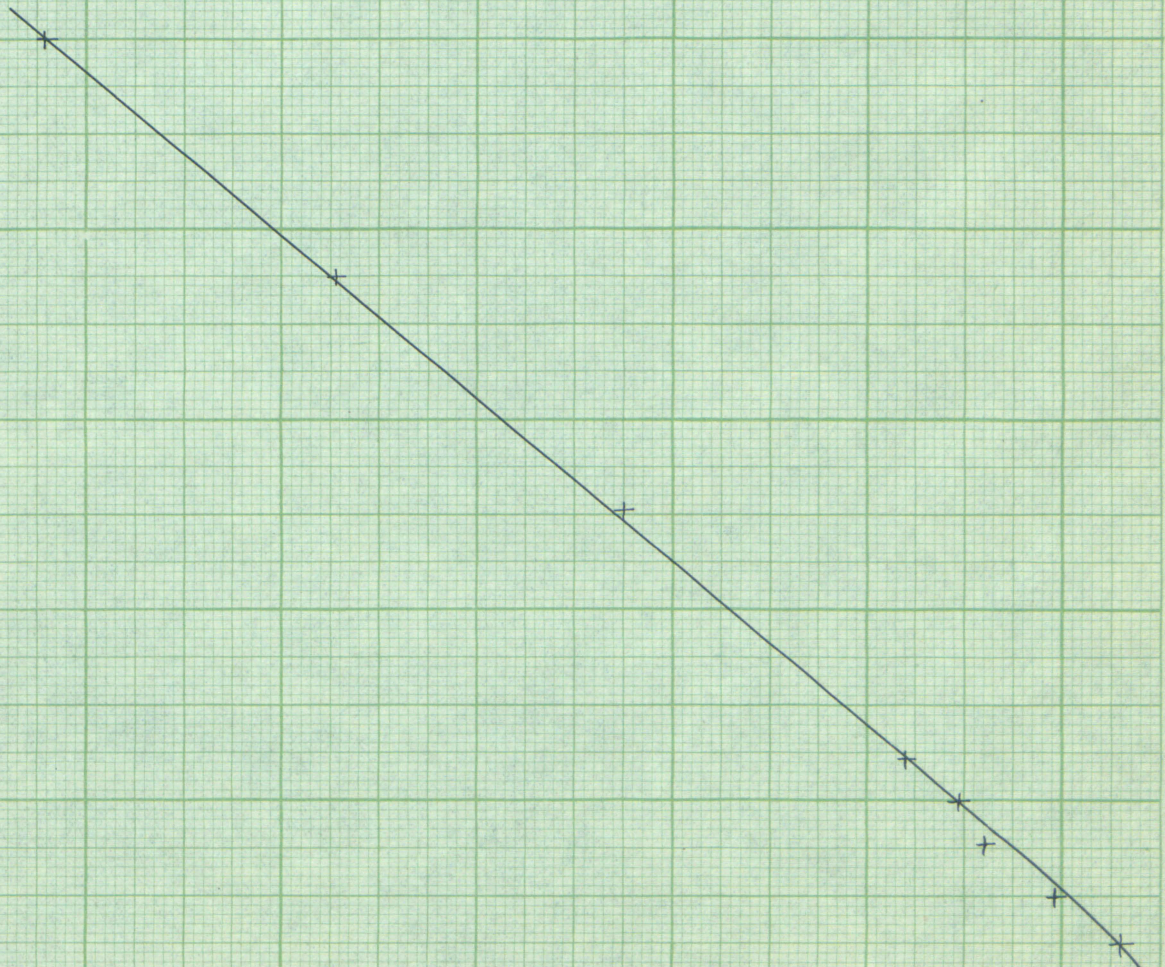
10

5

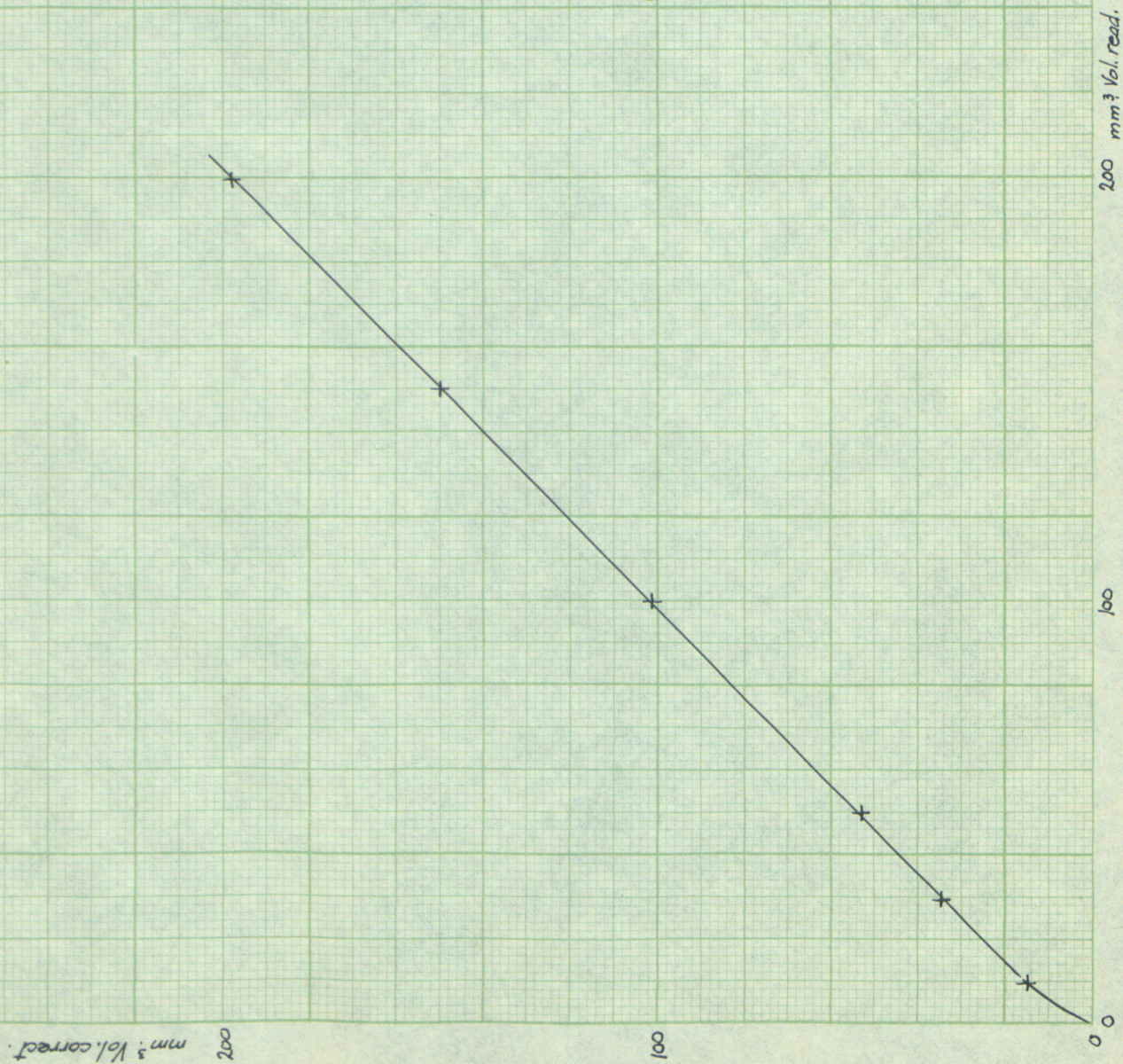
0

Graph 2

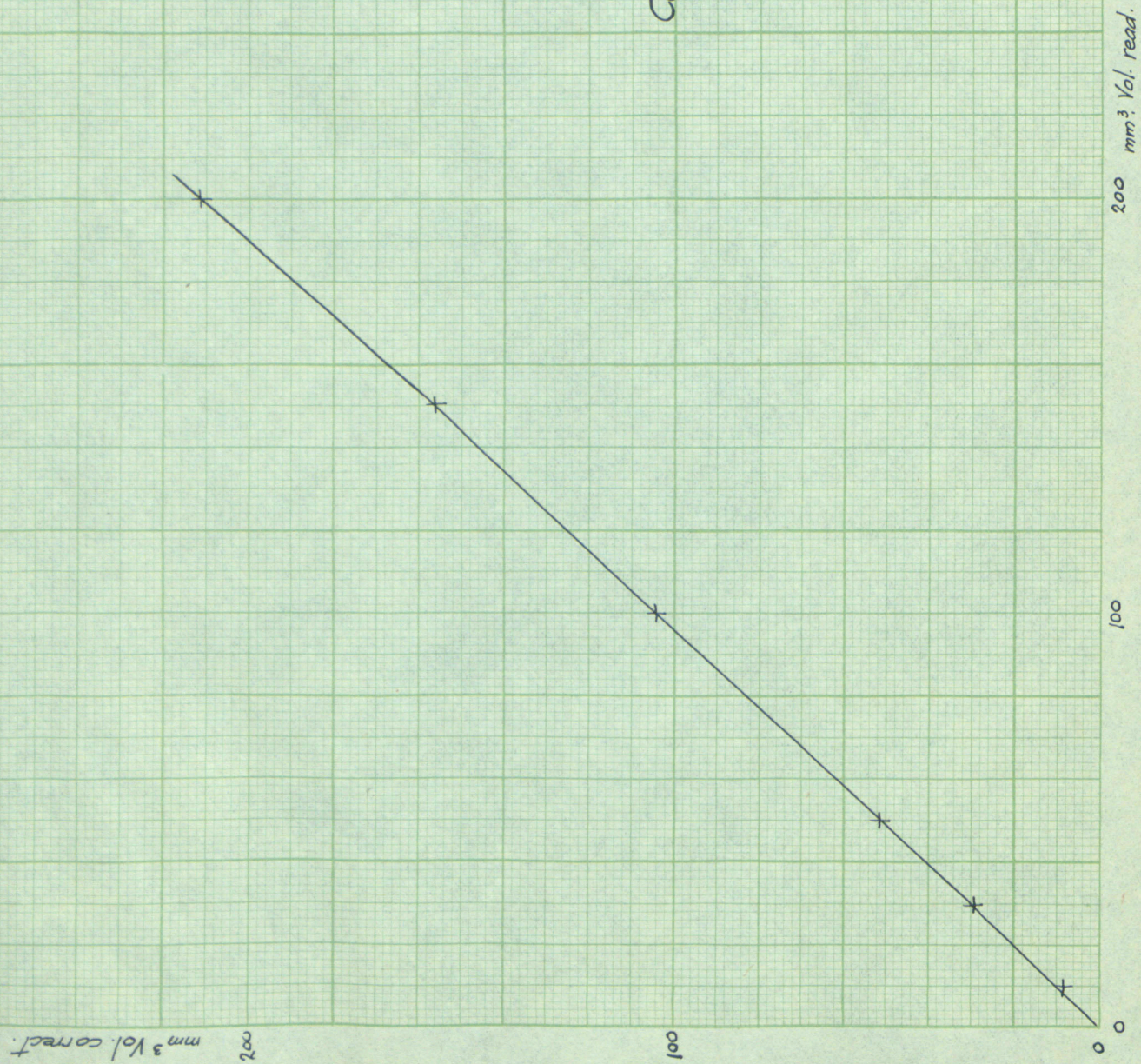
Calibration of Flask II



Graph III
Calibration of Flask III



Graph IV
Calibration of Flask IV



cm³ Vol. correct.

5

4

3

2

1

0

0

1

2

3

4

5

6

7

8

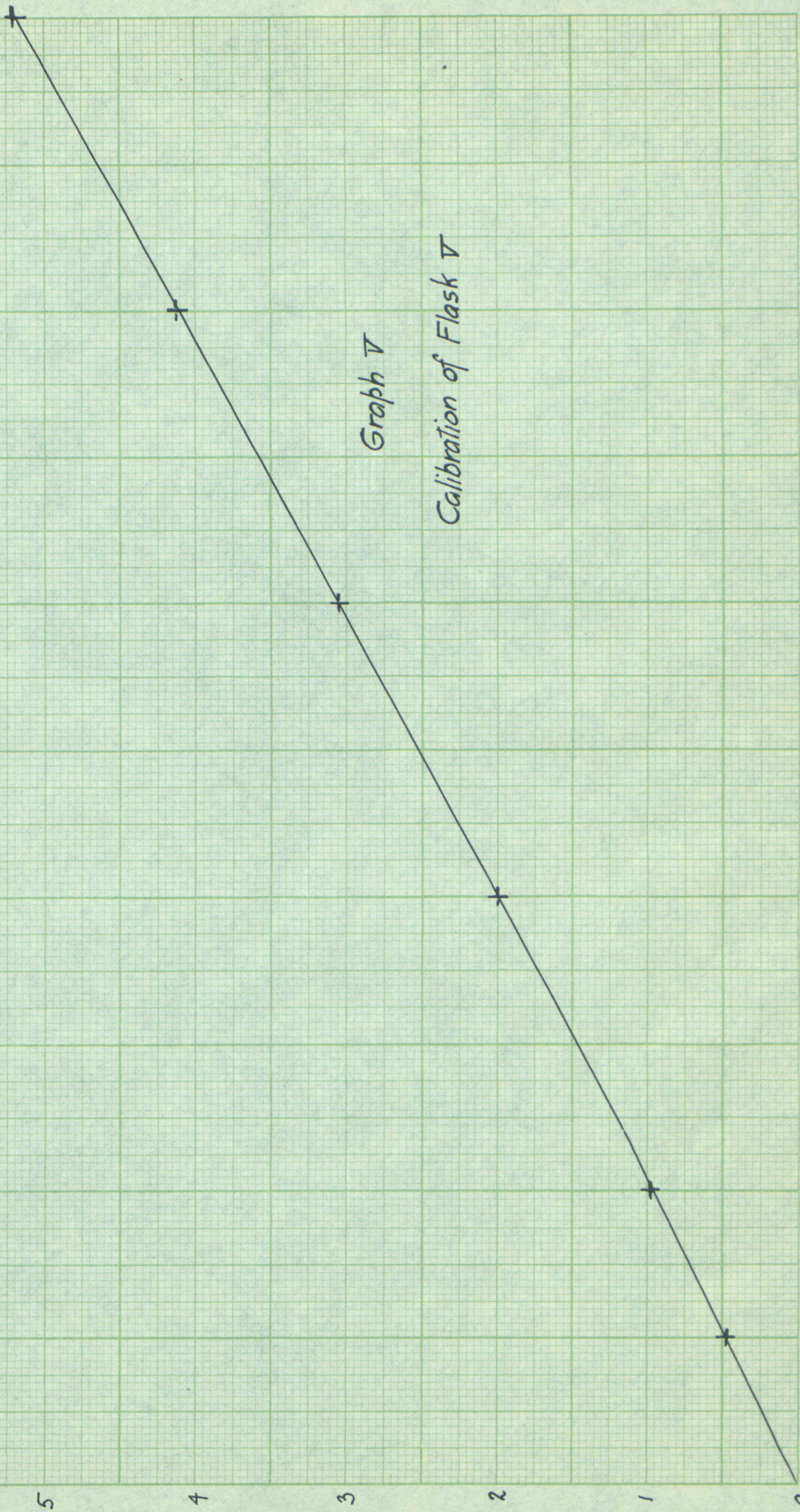
9

10

Div. read.

Graph V

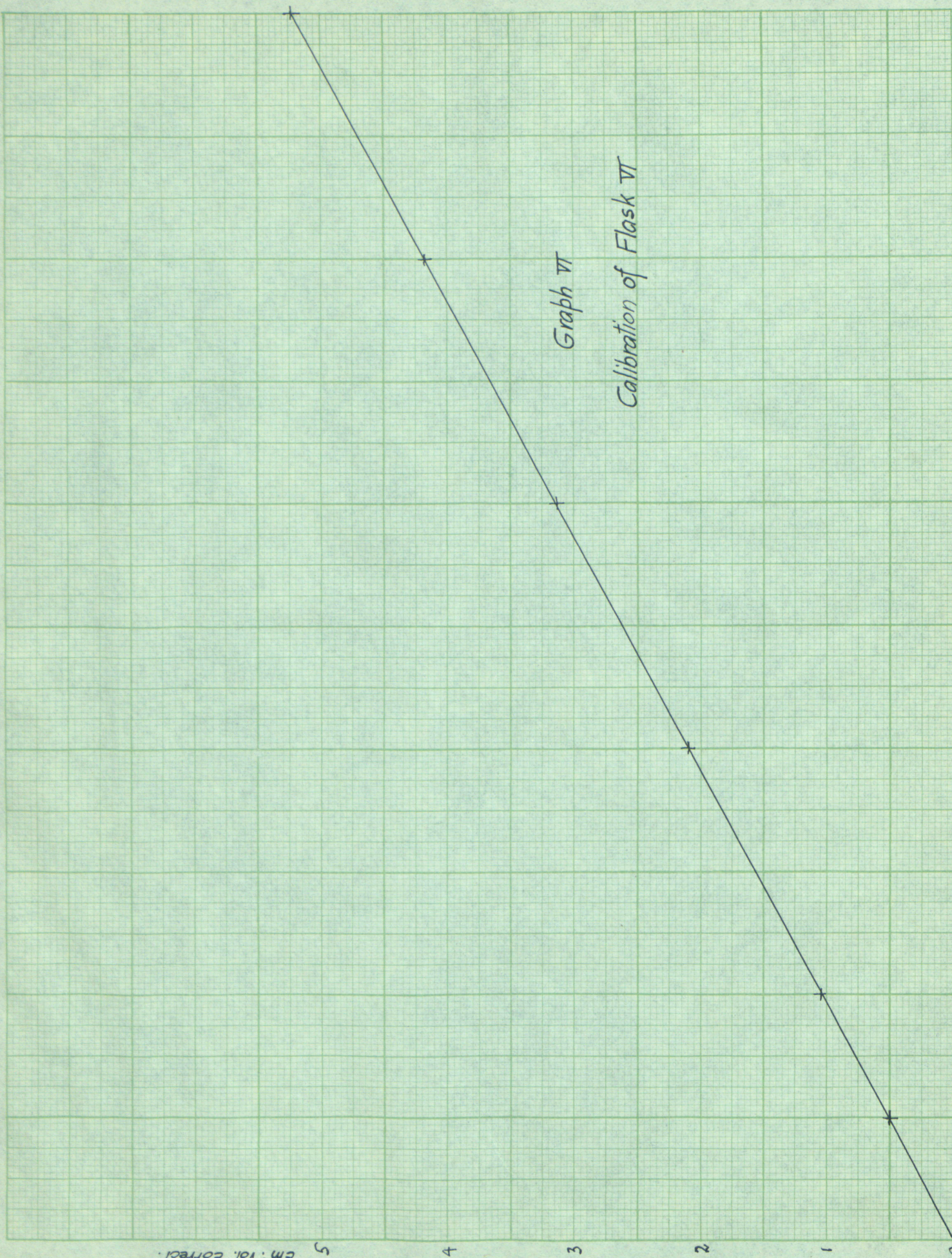
Calibration of Flask V



cm³ Vol. correct.

Graph VI
Calibration of Flask VI

0 0 1 2 3 4 5 6 7 8 9 10



The centrifuge head used carried only two tubes. These tubes were placed in tightly fitting rubber cushions which in turn fitted into metallic casings which rode in small slots on the centrifuge head. The distance from the slots to the center of rotation was 8-1/2 cms. The tubes were fitted with glass stoppers for use in closing them when shaking, etc. They were never centrifuged with the stoppers because the centrifugal force was great enough in many cases to cause the stoppers to break the head of the flasks.

The packed precipitates may be removed from the capillaries by the use of a smaller capillary tubing. This is filled with water by suction and the water then forced out into the capillary of the centrifuge vessel thus rinsing out the precipitate. To prevent particles of precipitate from clinging to the sides each vessel is rinsed with cleaning solution after each determination.

B. The Determination of Barium as BaSO₄

1. Calibration of flasks with respect to weight of BaSO₄

It was desirable in the beginning to know if results with the centrifuge are reproducible, and if so, with what accuracy. For this investigation barium sulphate was chosen as the precipitate to be used. It is dense and crystalline, and, as will be shown later, this is the type of precipitate that packs most consistently. One would immediately suspect that the volume of this precipitate would depend upon the physical properties of the crystals composing it. Therefore, in the present investigation, any conditions of precipitation, etc., which affected the physical properties of the crystals in any way were kept constant. The following procedure was used:

A solution of barium chloride was made up and standardized by the ordinary gravimetric method. One cubic centimeter of this solution was equivalent to .00612 g. of BaSO₄. Different amounts of this solution were used in precipitations in order to determine the volume of the precipitate throughout the volume range of the capillary. This served as a method of calibrating the capillary with respect to weight of BaSO₄. The volume of barium chloride taken was diluted until 60 cc. of solution contain approximately 18 mg. of barium. The precipitation may be carried out either in the centrifuge tubes or in beakers. Since barium sulphate is easily transferable from one container to

another, and since it is more convenient at higher temperatures, the latter method was chosen. Precipitations were carried out at 90°C in 250 cc. beakers by the addition of N/20 H₂SO₄ at the rate of 30 drops per minute and with constant stirring. Within one hour after precipitation, the precipitate with the liquid was transferred to the centrifuge tube, making sure that no precipitate was left adhering to the sides of the beaker. The tube was then placed in the metal casing carrying the rubber cushion, centrifuged at 2000 r.p.m. for four minutes, and the volume of precipitate noted. It is always necessary to exclude air bubbles from the capillaries or there will be uneven packing and gaps will show up in the packed precipitate. This exclusion of air bubbles may be accomplished by filling the capillaries with distilled water by the use of the above-mentioned drawn-out glass tubing before the transference of the precipitate is made.

It was found that BaSO₄ tended to form a scum on the top of the solution which was not broken by centrifuging and thus the volume of the packed precipitate did not represent all of the available BaSO₄. It was found, however, that the addition of 1 cc. of ethyl acetate before centrifuging aided in the prevention of this scum.

The results of determinations as made by this procedure for two different flasks are given in Table I. Column 1 shows the theoretical weight of BaSO₄ in milligrams

that is produced. This value is obtainable from the amount of standard barium chloride used, and was increased until the volume of BaSO₄ produced was enough to completely fill the capillary. The second and third columns give the average volume of BaSO₄ produced after it has been corrected for volume deviations of the flask used. Each of these values is an average of five determinations whose average variation from the average is not greater than that given. For instance, the volume of 6.12 mg. of BaSO₄ as determined by this procedure is 2.5 cu.mm. with a variation of not more than .08 cu.mm. From these values it will be seen that the deviation is not more than 5% for smaller volumes and less than 1% for larger volumes. The fourth and fifth columns give the average apparent densities for flasks I and II, obtained by dividing the theoretical weight of BaSO₄ produced by its observed volume.

TABLE I

Precipitation at 90°C. Centrifuged at 2000 r.p.m. for 4 minutes

Wt. BaSO ₄ mg.	Vol. BaSO ₄ cu. mm.		Apparent density	
	Flask I	Flask II	Flask I	Flask II
6.12	2.5 ± 0.08	2.4 ± 0.12	2.45	2.55
12.25	4.9 ± 0.10	4.8 ± 0.20	2.50	2.55
18.37	7.3 ± 0.10	7.3 ± 0.14	2.52	2.52
24.50	9.6 ± 0.12	9.6 ± 0.10	2.55	2.55
30.62	11.9 ± 0.10	11.7 ± 0.12	2.57	2.62
36.74	14.0 ± 0.16	13.7 ± 0.10	2.62	2.68
42.87	16.2 ± 0.10	15.7 ± 0.20	2.65	2.73
49.00	18.2 ± 0.13	17.6 ± 0.08	2.69	2.78
55.10	±	19.6 ± 0.13		2.81

It will be noted that the density gradually rises as the amount of BaSO_4 increases. Two factors are at work in the change, viz: (1) As the weight of barium sulphate increases the packing effect increases. That is, particles will pack more closely when there are other heavy particles above them than when there are none; and (2) As the volume of BaSO_4 increases, the center of gravity of the precipitate changes and the radius of rotation shortens. This decreases the force acting on the particles since this force is directly proportional to the radius of rotation.

Now, the two above-mentioned factors oppose each other. In the case of dense precipitates such as BaSO_4 , however, the former outweighs the latter and we thus have an increase in the apparent density of the precipitate with an increase in its volume.

Therefore, in order to determine an unknown sample, the relation between the volume of BaSO_4 , precipitated and centrifuged under definite conditions, and its weight must be known. To get this relationship, the volumes from Table I were plotted for flasks I and II against the corresponding weight of BaSO_4 , giving Graphs 7 and 8. Thus if the volume of BaSO_4 , precipitated and centrifuged under the above conditions, is known we can obtain its weight directly from the graph. It will be noted that this relationship must be obtained for each tube used for it varies from tube to tube according as the shape, cross-section, etc. of the capillary

varies. This variation, in general, is only slight for a slight variation in the capillary, but in some cases it is great enough to make a considerable difference. Note the difference in the densities of corresponding precipitates obtained with flasks I and II. For each flask it is therefore necessary only to calibrate the observed volume with respect to actual weight of precipitate by using standard samples.

Graph 7

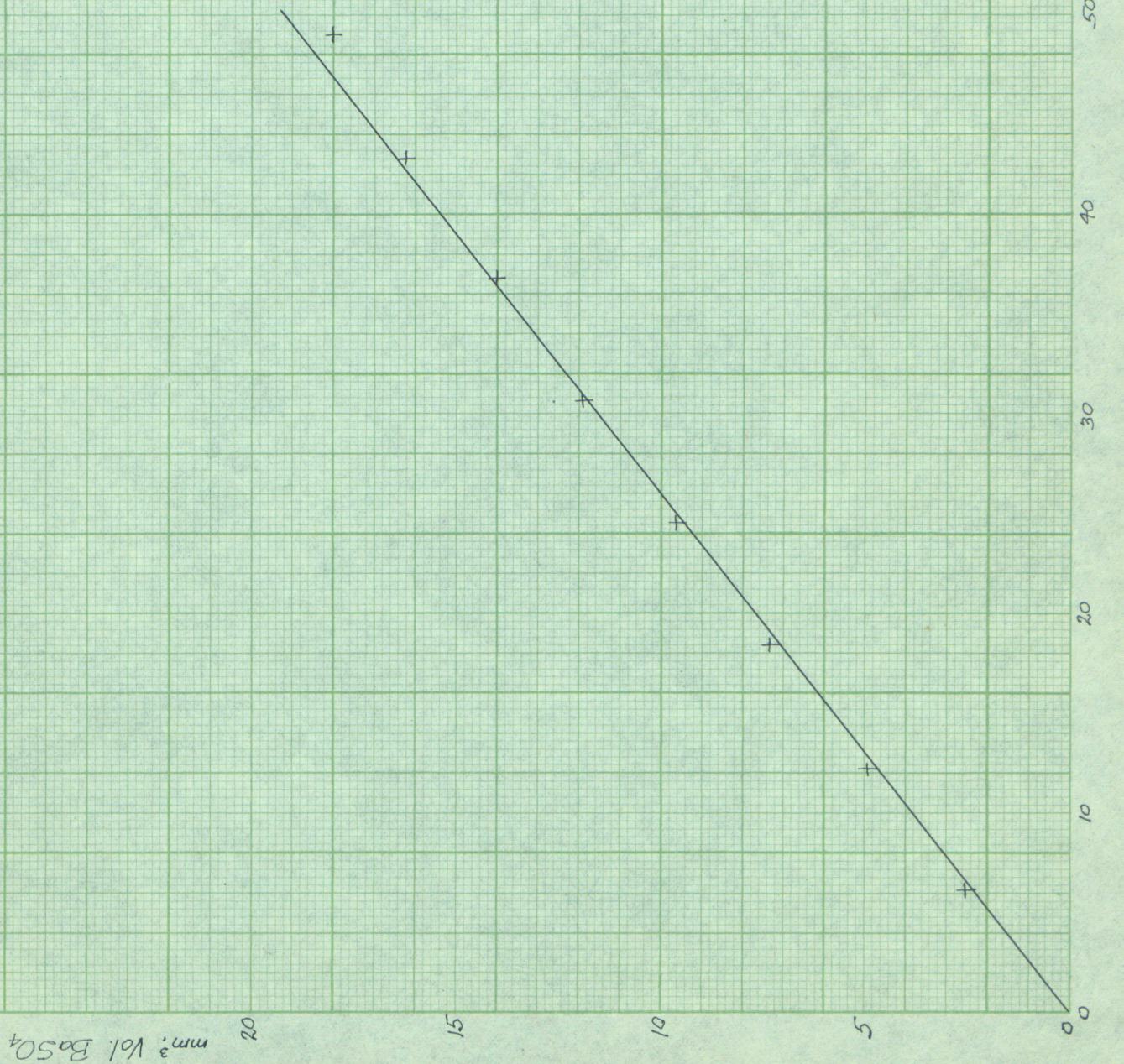
Vol. vs. Wt. BaSO_4 Flask I

18 mg. Ba per 60 cc.

Temp. 90°C . $\text{N}/20 \text{ H}_2\text{SO}_4$; 30 drops/min.

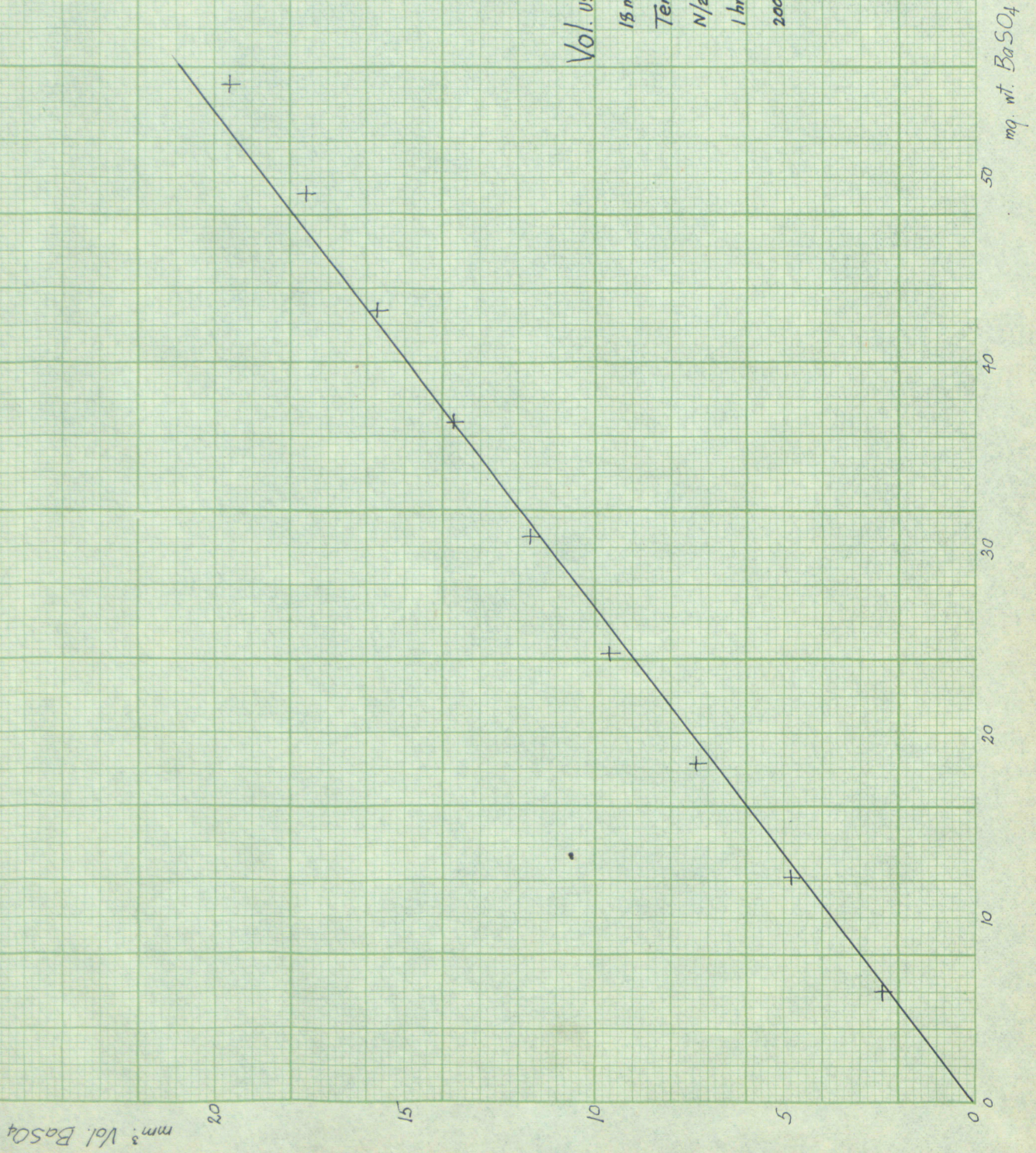
1 hr. standing

2000 r.p.m. for 4 min.



Graph 8
Vol. vs. Wt. BaSO_4 Flask II

15 mg. Ba per 60 cc.
Temp. 90°C .
 $\text{N}/20 \text{ H}_2\text{SO}_4$; 30 drops/min.
1 hr. standing
2000 r.p.m. for 4 min.



2. Effect of temperature of precipitation

It is well known that the physical properties of a precipitate are to a great extent dependent upon the temperature of its precipitation. Precipitations at high temperatures tend to give larger particles than at lower temperatures, all other conditions of course remaining constant. This phenomenon is explained by the difference in solubilities of solids at high and low temperatures. At high temperatures, solids in general are more soluble and the rate of growth of crystals is thus greater at the higher temperature. The purpose of this part of the investigation is to determine the quantitative relationship between the volume of a precipitate and its temperature of precipitation, while all other conditions of precipitation and centrifuging are kept constant.

Precipitations were carried out at various temperatures by the addition of .05 N H_2SO_4 at the rate of 30 drops per minute, and with constant stirring, to a solution of barium chloride which contained approximately 18 mg. of Ba in 60 cc. of solution. After standing for one-half hour, the solution and precipitate were centrifuged at 2000 r.p.m. for four minutes and the volume of precipitate read. From this observed volume by reference to Graphs 1 and 2, the actual volume could be obtained. Results of determinations at various temperatures are given in Table II. Column one gives the temperature of precipitation and columns two and three, the volumes of BaSO_4 produced with the use of flasks I and II

respectively. In each case enough standard barium chloride was used to produce 30.62 mg. of BaSO_4 . The average deviation of the volumes of five determinations from the average is given. The fourth and fifth columns give the apparent densities of the precipitates for flasks I and II respectively.

TABLE II

Theoretical weight of BaSO_4 = 30.62 mg.
Centrifuged at 2000 r.p.m. for 4 minutes

Precipitation temp.	Vol. BaSO_4 cu.mm.		Apparent density	
	Flask I	Flask II	Flask I	Flask II
26°	20.0 ± 0.10	19.8 ± 0.18	1.53	1.55
40°	17.2 ± 0.08	17.0 ± 0.13	1.78	1.80
60°	14.3 ± 0.08	14.0 ± 0.18	2.14	2.19
80°	13.0 ± 0.14	12.9 ± 0.13	2.36	2.37
90°	11.9 ± 0.12	11.8 ± 0.13	2.57	2.60
100°	11.8 ± 0.14	11.6 ± 0.10	2.60	2.64

From these results it will be noted: (1) That the accuracy of the determinations does not depend upon the temperature of precipitation so long as the flasks or tube used is calibrated at this temperature by the use of standard samples, and the other conditions of precipitation, centrifuging, etc., are kept constant; (2) That the apparent density of the packed precipitate increases with increase in temperature. Graph 9 was obtained by plotting the apparent density of BaSO_4 against the temperature of precipitation. Flasks I and II gave the same type of curve. Therefore, all

Apparent Density

2.5

2.0

1.5
2.5

50

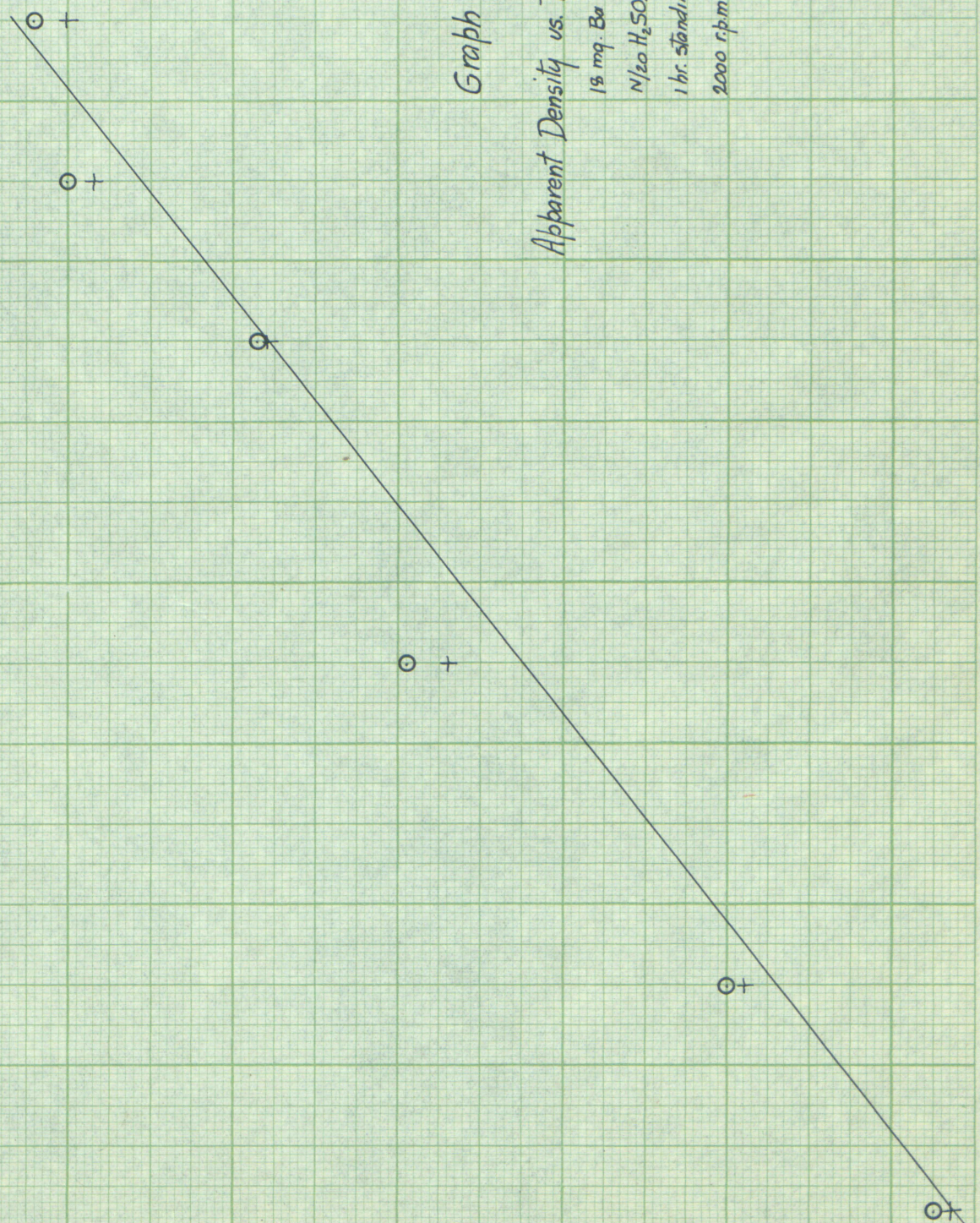
75

100

°C. Temp.

Graph 9

Apparent Density vs. Temp. of Pbth. of BaSO_4
18 mg. Ba in 60 cc. Flask I +
N/20 H_2SO_4 ; 30 drops/min. Flask II
1 hr. standing
2000 r.p.m. for 4 min.



the values for flasks I and II are plotted on the same graph and the best curve drawn.

These values show that there is a decrease in the apparent specific volume with an increase in temperature of precipitation. This would be expected from the laws of precipitation because an increase in the temperature of precipitation means an increase in the size of the precipitated particles, and this in turn means an increase in the centrifugal force acting on the particles. Again it is well known that within certain limits of sizes, larger particles pack more closely than smaller particles, i.e., the space between the particles decreases with an increase in the size of the particles. For flask I there is an increase of about 54% in the apparent density of the precipitate between precipitation temperatures of 26°C. and 100°C. Therefore, in order that two determinations may be comparable, it is quite necessary that they be carried out at the same temperature.

In order to test the validity of our assumption as regards particle size and temperature of precipitation, particles of BaSO_4 precipitated at 90°C. and at 100°C. were examined under the microscope. A microscope carrying a micrometer and an objective that magnified 120 times was used. With this arrangement the actual size of a particle could be measured. For both temperatures the particles were surprisingly uniform in size, there being mostly large particles and

approximately 1% of dust. The particles were hexagonal with rectangular faces. Thus the size of a particle could be determined by making two measurements, viz., a length and a breadth. These measurements were made on a large number of particles from each of several precipitations, the results of which are given in Table III. Precipitations were carried out under as nearly identical conditions as possible with the exception that the temperature was varied as indicated.

TABLE III

Precipitated by the addition of N/20 H_2SO_4 at the rate of 30 drops per minute. Examined after standing one half hour.

Temp. pptn.	Average length mm. x 10^{-3}	No. Readings	Average width mm. x 10^{-3}	No. Readings
90°	7.0 ± 0.2	5	5.1 ± 0.5	10
90°	6.3 ± 0.1	6	5.2 ± 0.5	7
90°	7.5 ± 0.4	6	4.8 ± 0.5	9
100°	13 ± 1	4	11 ± 1	4

From the above results it is evident that there is an increase in particle size when the temperature of precipitation is raised from 90° to 100°, all other conditions being constant. The average ratio of the mass of particles precipitated at 90° and at 100° is 7/29. These results, therefore, are in harmony with those of Table II above since the amount of packing is dependent upon the size of the particles.

3. Effect of Rate of Centrifuging

The centrifugal force acting on a particle is directly proportional to the square of its angular velocity and therefore to the square of the r.p.m. if the radius of rotation remains constant. It would thus be expected that the volume of the packed precipitate is more or less dependent upon the r.p.m. Table IV gives the results of determinations carried out to determine this relationship. The following procedure was used:

A solution containing a known amount of barium chloride was diluted until 60 cc. of solution were equivalent to 18 mg. of Ba. The solution is then heated to 95°C. and precipitated with constant agitation by the addition of N/20 H₂SO₄ at the rate of 30 drops per minute. Within one hour after precipitation the precipitate and solution were transferred to a Goetz tube and centrifuged for four minutes at the r.p.m. indicated in the table, the true r.p.m. being ascertained as described heretofore. The results given are the average of five determinations, the variation from the average being not more than that given.

It is noted that for four minutes centrifuging the apparent density increased with increase in r.p.m. This density, however, seems to approach a maximum and further increase in the r.p.m. beyond 2000 affects it very little. If the apparent density is plotted against the r.p.m., graph 9A is obtained. This is for flasks I and II.

That for flask II is very similar in form, thus indicating that the volume of packed precipitate is similarly affected for two or more flasks by the same change in r.p.m.

TABLE IV

Precipitated at 90°C with N/20 H₂SO₄. Centrifuged for four (4) minutes. Theoretical weight of BaSO₄ produced = 30.62 mg.

r.p.m.	Vol. BaSO ₄ cu.mm.		Apparent density	
	<u>Flask I</u>	<u>Flask II</u>	<u>Flask I</u>	<u>Flask II</u>
800	16.3 ± 0.08	16.1 ± 0.14	1.94	1.90
1250	14.1 ± 0.14	13.8 ± 0.14	2.17	2.22
1600	12.3 ± 0.18	12.2 ± 0.20	2.49	2.51
2000	12.0 ± 0.12	11.9 ± 0.14	2.55	2.57
2200		11.9 ± 0.10		2.57

Apparent Density

2.5

2.0

1.5

500

1000

1500

2000

r.p.m.

Graph 9A

Apparent Density vs. Rate of Centrifuging of BaSO_4

Flask I +

Flask II o

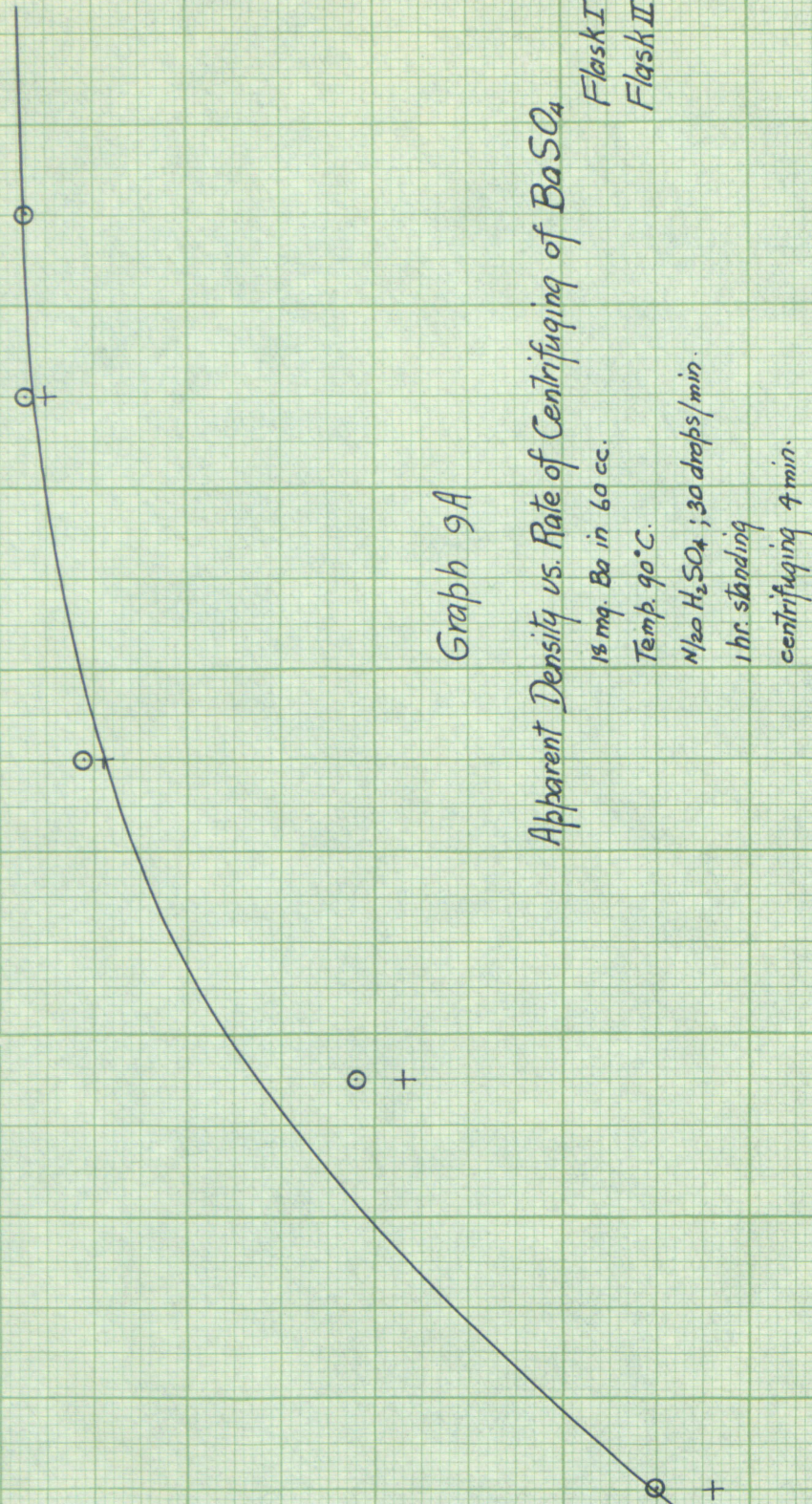
18 mg. Ba in 60 cc.

Temp. 90°C.

$\text{N}/20 \text{ H}_2\text{SO}_4$; 30 drops/min.

1 hr. standing

centrifuging 4 min.



4. Effect of Duration of Centrifuging

Table V gives results which show the relation between the time of centrifuging and the volume and density of the resulting packed precipitate. The data in this table were obtained by using the following procedure:

A known volume of standard BaCl_2 was diluted until 60 cc. of solution were equivalent to approximately 18 mg. of Ba. This solution was then heated to 90°C . and BaSO_4 precipitated by addition with constant stirring of $\text{N}/20 \text{ H}_2\text{SO}_4$ at the rate of 30 drops per minute. Within one hour after precipitation the solution and precipitate were transferred to Goetz tubes and centrifuged at 2000 r.p.m. for the time indicated in the table.

TABLE V

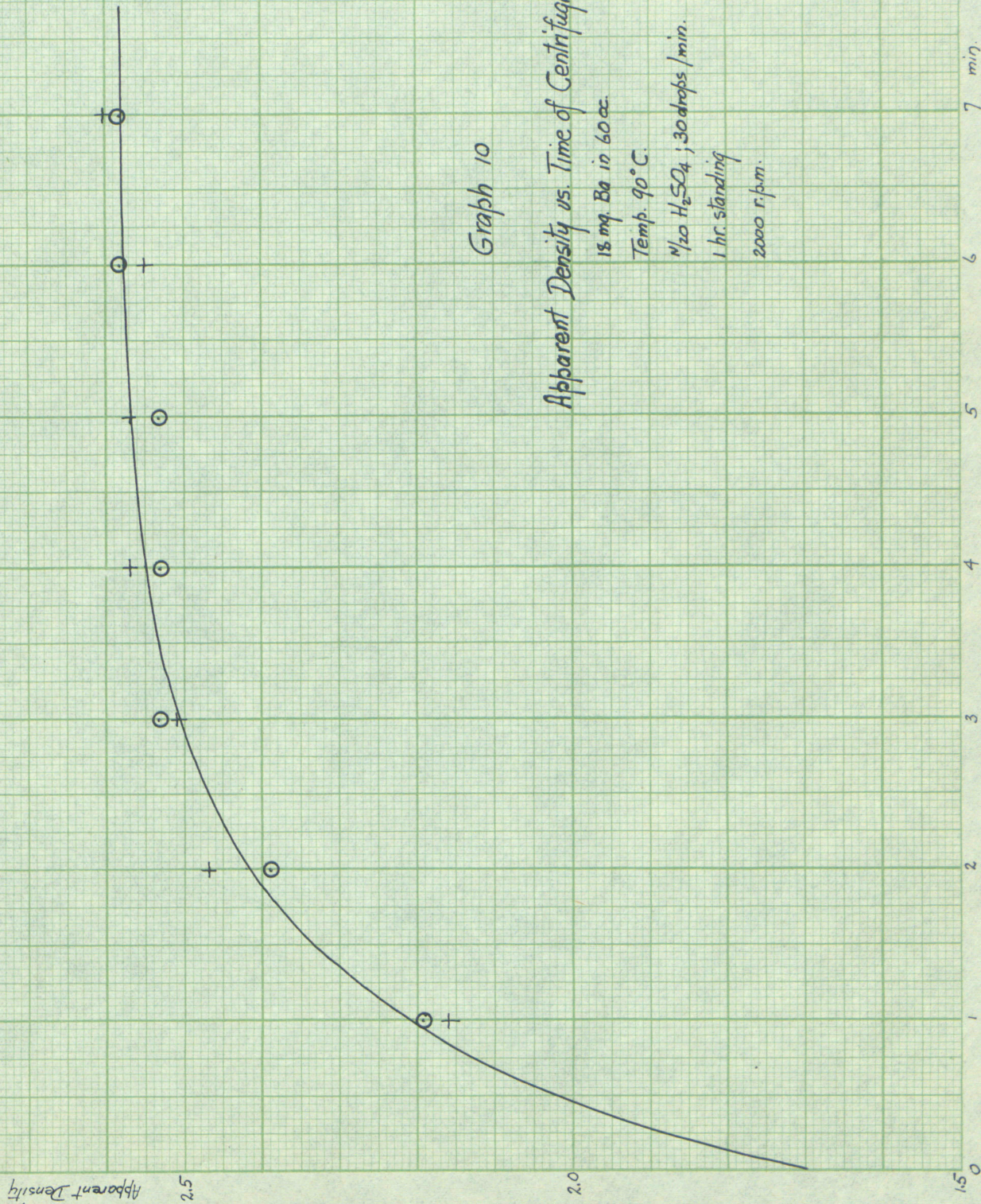
Precipitated at 90°C . Centrifuged at 2000 r.p.m.
Theoretical weight of BaSO_4 produced = 30.62 mg.

Duration of centr'g min.	Vol. BaSO_4 cu.mm.		Apparent density	
	Flask I	Flask II	Flask I	Flask II
1	14.2 ± 0.16	14.0 ± 0.12	2.16	2.19
2	12.4 ± 0.10	12.8 ± 0.12	2.47	2.39
3	12.2 ± 0.10	12.1 ± 0.12	2.51	2.53
4	11.9 ± 0.12	12.1 ± 0.10	2.57	2.53
5	11.9 ± 0.16	12.1 ± 0.13	2.57	2.53
6	12.0 ± 0.10	-	2.55	2.58
7	11.8 ± 0.24	-	2.60	2.58

Column one gives the duration of centrifuging in minutes. The second and third columns give the volumes of 30.62 mg. of BaSO_4 when packed into the capillaries of

flasks I and II respectively by centrifuging at 2000 r.p.m. for the number of minutes indicated. Each value given represents the average of five determinations whose variations from the average were not more than that given after the value. The fourth and fifth columns give the average apparent densities for flasks I and II.

From the above data it will be observed that for 2000 r.p.m. the apparent density of the packed precipitate increases with the time of centrifuging until approximately four (4) minutes are reached. At this point the density seems to reach a maximum as limit and further centrifuging has little or no effect. In Graph 10, the apparent density of the BaSO_4 is plotted against the duration of centrifuging in minutes. The curves for flasks I and II are very similar, and only the mean is shown.



5. Effect of Rate of Precipitation

In general the size of precipitated particles is dependent upon the rate of addition of precipitant. With a slow rate of addition and with constant stirring the tendency to supersaturation is minimized, the crystals have more time for growing and thus are larger at the end of the precipitation. Table VI gives the results of a study of the relationship between rate of addition of precipitant and the volume and density of the resulting precipitate after centrifuging. The following procedure was used:

A known volume of standard BaCl_2 solution was diluted until 60 cc. are equivalent to 18 mg. of Ba. The solution is then heated to 90°C . and the BaSO_4 precipitated by the addition of $\text{N}/20 \text{ H}_2\text{SO}_4$ at the rate shown in the table. Within one hour after precipitation the precipitate and solution were transferred to the Goetz tube and centrifuged for four minutes at 2000 r.p.m. and the volume of the precipitate noted. In each case an amount of BaCl_2 equivalent to 30.62 mg. of BaSO_4 was used.

TABLE VI

Precipitated at 90°C and centrifuged for 4 minutes at 2000 r.p.m.

Drops H_2SO_4 per minute	Vol. BaSO_4 cu.mm.		Apparent density	
	Flask I	Flask II	Flask I	Flask II
10	11.7 ± 0.08	11.6 ± 0.13	2.62	2.64
20	11.9 ± 0.08	11.7 ± 0.13	2.57	2.62
30	11.9 ± 0.13	11.8 ± 0.18	2.57	2.60
50	12.5 ± 0.23	12.5 ± 0.18	2.45	2.45
70	13.6 ± 0.23	13.3 ± 0.15	2.25	2.30
∞	14.3 ± 0.15	14.3 ± 0.15	2.09	2.09

The first column of this table gives the rate of addition of N/20 H_2SO_4 in drops per minute. The second and third columns show the average volumes of 30.62 mg. of BaSO_4 when packed into the capillaries of flasks I and II respectively. Each of these values represents the average of five determinations whose variations from the average are not more than that given after the value. This variation is never greater than 2%. The apparent densities of these precipitates are given in the fourth and fifth columns which are for flasks I and II respectively. It will be seen from these results that a denser precipitate is produced with the slower rate of precipitation. This would be expected since the slower rate of precipitation produces the larger particles. Graph 11 was obtained by plotting the density of BaSO_4 against the corresponding rate of addition of N/20 H_2SO_4 during its precipitation. The curve given is for flasks I and II combined, since the individual curves were quite similar. In other words all the values for flask I and II are plotted on the same graph and the best curve drawn through the points thus formed. The effect of the rate of addition of precipitant thus seems to be independent of the flasks used.

Apparent Density

2.5

2.0

1.5

Graph 11

Apparent Density vs. Rate of Addition of H_2SO_4

18 mg. Ba in 60 cc.

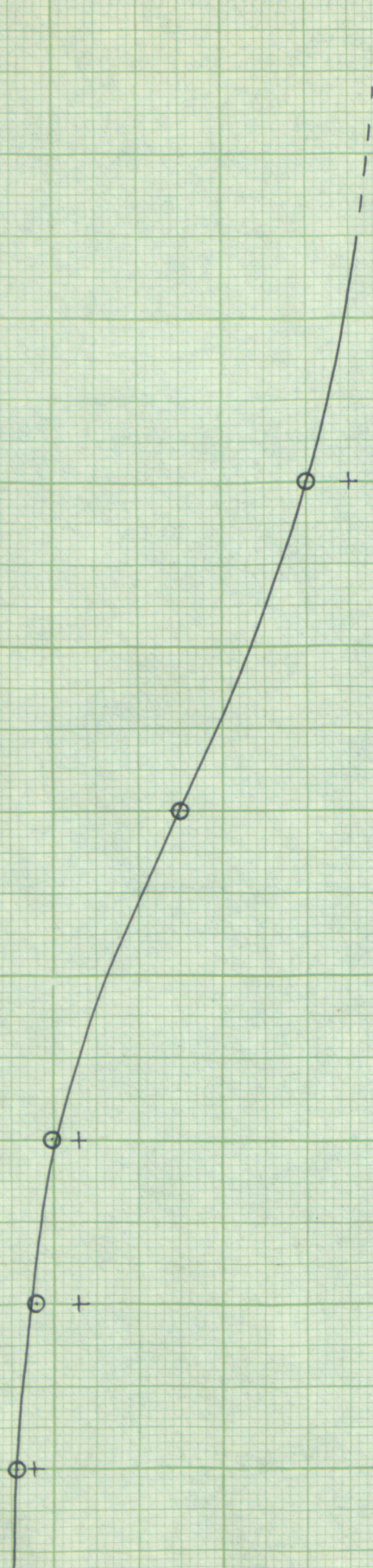
Temp. 90°C.

$N/20 H_2SO_4$

1 hr. standing

2000 r.p.m. for 4 min.

Flask I +
Flask II O



8

-50-

70 drops per min.

6. Effect of Concentration of Reagents

Heretofore in all precipitations we have used a constant concentration of BaCl_2 solution, viz., one which contains 15 mg. of Ba per 50 cc. of solution. The results given in Table VII, however, were obtained by varying the concentration of BaCl_2 as indicated. The following procedure was used in these determinations:

A volume of the standard BaCl_2 solution equivalent to 30.62 grams of BaSO_4 was measured out and diluted until the concentration indicated in the table was reached. The solution was then heated to 90°C . and the BaSO_4 precipitated by the addition with constant stirring of $\text{N}/20 \text{ H}_2\text{SO}_4$ at the rate of 30 drops per minute. After one hour the precipitate and solution are transferred to a Goetz tube, centrifuged for four minutes at 2000 r.p.m., and the volume noted.

TABLE VII

Theoretical weight of BaSO_4 = 30.62 mg. Precipitated at 90°C . with $\text{N}/20 \text{ H}_2\text{SO}_4$. Centrifuged at 2000 r.p.m. for four (4) minutes.

Normality BaCl_2	Vol. BaSO_4 cu.mm.		Apparent density	
	Flask I	Flask II	Flask I	Flask II
0.025	13.1 ± 0.25	13.0 ± 0.15	2.34	2.36
0.0125	12.7 ± 0.18	12.5 ± 0.15	2.41	2.45
0.01	12.5 ± 0.18	12.3 ± 0.18	2.45	2.49
0.005	12.0 ± 0.18	12.0 ± 0.20	2.55	2.55
0.002	11.8 ± 0.15	11.9 ± 0.13	2.60	2.62

The first column of this table gives the normality of the solution with respect to BaCl_2 when precipitation is begun. The second and third columns show the observed volume of BaSO_4 for flasks I and II respectively. Each of these values is the average of five determinations carried out under as nearly identical conditions as possible. The average deviation of these determinations from the average is given with each value. The fourth and fifth columns give the average apparent densities of the precipitates.

The above results show that the density of the packed precipitate increases with dilution of the BaCl_2 used and seems to reach a maximum when the concentration of BaCl_2 is approximately $N/200$. Graph 12 was obtained by plotting the normality of barium chloride against the apparent density of the corresponding BaSO_4 precipitate using flasks I and II. The best curve is then drawn through the points thus obtained.

Apparent Density

2.5

2.0

1.5

Graph 12

Apparent Density vs. Conc. of $BaCl_2$

Flask I +
Flask II O

18 mg. Ba

Temp $90^{\circ}C.$

$M/20 H_2SO_4$; 30 drops/min.

1 hr. standing

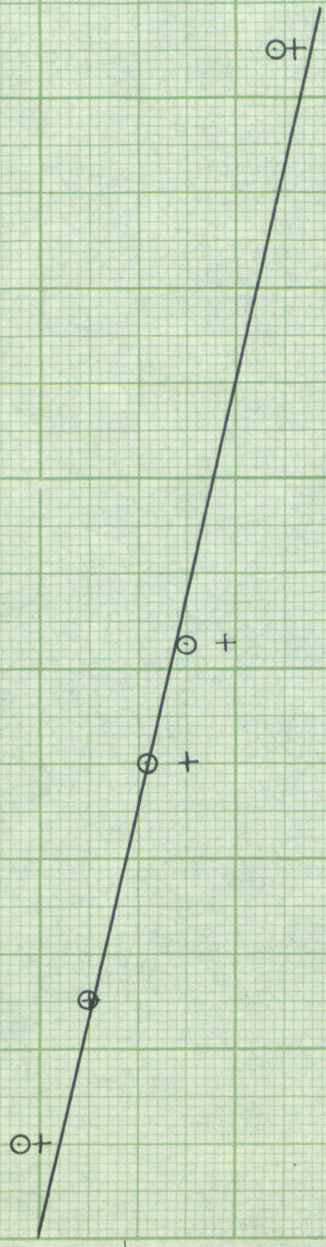
2000 r.p.m. for 4 min.

0.01

0.02

0.03

Normality of $BaCl_2$



7. Effect of Nature of Precipitant

It is a well known fact in quantitative analysis that barium sulphate has the power of adsorbing other substances and carrying them down with it and thus increasing the weight of precipitate formed beyond the theoretical weight of BaSO_4 . This sometimes causes serious errors in sulphate determinations by this method. The relative adsorbing power of BaSO_4 is different for different substances. In previous determinations only dilute H_2SO_4 has been used as a precipitant and it is well known that H_2SO_4 is only very slightly adsorbed by BaSO_4 . This, however, is not the case with salts. Determinations carried out by using an excess of a metallic sulphate as the precipitant always gave a slightly larger volume for the same amount of BaCl_2 than did H_2SO_4 . Table VIII gives the results of the determinations carried out under as nearly identical conditions as possible with the exception that the precipitant was varied as indicated. The procedure was as follows:

An amount of standard BaCl_2 solution equivalent to 30.62 mg. of BaSO_4 is measured out and diluted until 60 cc. of solution contain approximately 18 mg. of Ba. This solution is then heated to 90°C and the BaSO_4 precipitated by the addition of the precipitant at the rate of 30 drops per minute. Within half hour the precipitate and solution are transferred to a Goetz tube, centrifuged at 2000 r.p.m. for four minutes and the volume of precipitate noted.

TABLE VIII

Precipitation at 90°C; centrifuged at 2000 r.p.m.
for four (4) minutes.

Pptnt.N/20	Vol. BaSO ₄ cu.mm.		Apparent density	
	Flask I	Flask II	Flask I	Flask II
H ₂ SO ₄	11.9 ± 0.12	11.7 ± 0.13	2.57	2.62
Na ₂ SO ₄	13.0 ± 0.16	12.7 ± 0.15	2.36	2.41
K ₂ SO ₄	13.4 ± 0.18	13.2 ± 0.18	2.29	2.32
MgSO ₄	13.7 ± 0.18	13.5 ± 0.20	2.24	2.27

The increase in volume of precipitate when metallic sulphates are used as precipitants is attributed to two causes, viz., (1) the adsorption of the metallic salts by the BaSO₄; and (2) the decrease in the size of the BaSO₄ particles. The latter effect is probably due to the hindrance which the metallic salt molecules offer to the formation of BaSO₄ particles. Through this hindrance smaller particles are formed and thus the volume is increased, as it has been shown heretofore that this is the case when the size of the particles decreases. It will be noted that of the three sulphates used Na₂SO₄ was the least adsorbed. K₂SO₄ was next while MgSO₄ was adsorbed most. However, for a definite substance under definite conditions, the amount of adsorption and the hindrance effect are constant as evidenced by the consistent results given in the table, the variations of individual determinations from the average value being not more than 1.5%.

8. Effect of Duration of Standing before Centrifuging

In working with BaSO_4 it was soon found that the duration of standing in contact with the solution from which it was precipitated had some effect on the resulting volume of the packed precipitate. Table IX gives the results of determinations carried out under the same conditions with the exception that the duration of standing after precipitation was varied as indicated. The following procedure was used:

A volume of standard BaCl_2 solution equivalent to 30.62 mg. of BaSO_4 was measured out and diluted until 60 cc. of solution contained approximately 18 mg. of Ba. The solution was then heated to 90°C and precipitated by the addition of $\text{N}/20 \text{ H}_2\text{SO}_4$ at the rate of 30 drops per minute. The solution and precipitate were allowed to stand in contact with each other for the time indicated, then transferred to a Goetz tube and centrifuged at 2000 r.p.m. for four minutes.

The first column of Table IX gives the duration of standing before centrifuging. The second and third columns give the average volume of the BaSO_4 for flasks I and II. Each of these values is the average of five determinations whose average deviation from the average is given after each value. The fourth and fifth columns show the densities of the different precipitates for flasks I and II, respectively.

TABLE IX

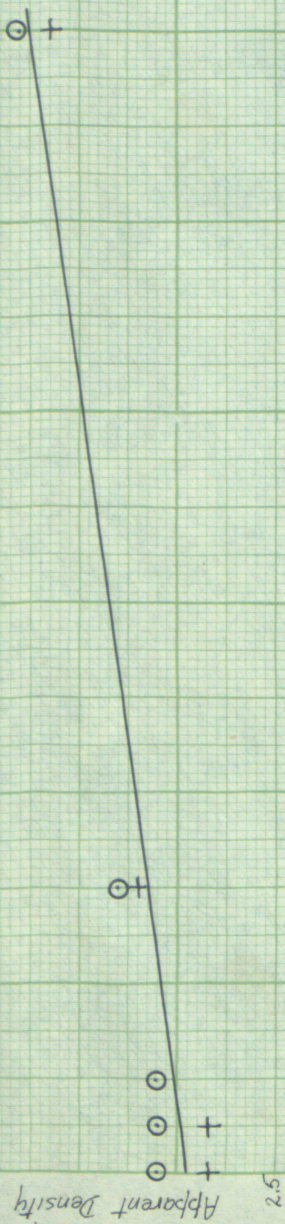
Precipitated at 90° with N/20 H₂SO₄. Centrifuged
for four (4) minutes at 2000 r.p.m.

<u>Duration before centrif'g hrs.</u>	<u>Vol. BaSO₄ cu. mm.</u>		<u>Apparent density</u>	
	<u>Flask I</u>	<u>Flask II</u>	<u>Flask I</u>	<u>Flask II</u>
0	11.9 ± 0.10	11.7 ± 0.15	2.57	2.62
1	11.9 ± 0.13	11.7 ± 0.20	2.57	2.62
2	11.8 ± 0.20	11.7 ± 0.18	2.60	2.62
6	11.6 ± 0.28	11.5 ± 0.15	2.64	2.66
24	11.2 ± 0.18	11.1 ± 0.13	2.73	2.76

The above results show that the longer the precipitate remains in contact with its solution after precipitation the more efficiently it can be packed into the capillary. This is attributed to the increase in particle size on standing. Whenever a precipitate is allowed to remain in contact with the solution from which it was precipitated, according to the dynamical theory the smaller particles dissolve up and precipitate out on the larger crystals thus causing crystals in general to grow larger. And as has been shown before, the larger the crystals of BaSO₄ the more compactly they can be packed into the capillary. Therefore in order to obtain consistent results, the duration of standing after precipitation must be standardized.

Graph 13 was obtained by plotting the duration of standing in hours against the apparent density of the packed precipitate corresponding to this duration. Points are given for the values obtained with both flask I and II. These values bear a very close relationship and therefore only one curve is drawn, that is, the best curve between all the points.

From these results it appears that the effect of duration of standing is practically independent of the flasks used.



Graph 13

Apparent Density vs. Duration of Standing

Flask I +

Flask II ○

18 mg. Ba in 60cc.

Temp. 90°C .

$N/20 \text{ H}_2\text{SO}_4$; 30 drops/min.

2000 r.p.m. for 4 min.

C. The Determination of Sulphur in Steel

In literature there is no record of the centrifuge method having been used for the determination of sulphur in steel. Consequently, numerous analyses have been carried out in order to determine the applicability of this method in the technical analysis of steel. For this purpose standard samples of steel obtained from the United States Bureau of Standards were used and determinations were carried out by the following procedure:

A definite weight of the sample is weighed out and dissolved in concentrated nitric acid, using 10 cc. of the acid for each gram of steel. Solution is carried out in 250 cc. beakers and with the aid of heat when necessary. The solution is then evaporated to dryness and the residue taken up with 10 cc. of concentrated HCl. One gram of sodium carbonate is then added, the solution again evaporated to dryness, and the residue gently ignited for the purpose of dehydrating the silica. The residue is again taken up with HCl and then diluted to 100 cc. It is filtered to remove any silica and the filter paper and residue well washed. The solution is now heated to 90°C. and the sulphur precipitated by the addition of N/20 BaCl₂ at the rate of 30 drops per minute. After standing for one half hour the precipitate and solution are transferred to a Goetz tube, centrifuged at 2000 r.p.m., and the volume of precipitate noted. Results obtained by this procedure are given in Table X.

TABLE X

Precipitated at 90°C and centrifuged for 4 minutes at 2000 r.p.m.

Wt. Steel g.	Vol. BaSO ₄ mm ³	Wt. BaSO ₄ mg. obs.	Wt. BaSO ₄ mg. cor.	Wt. BaSO ₄ mg. theor.	% dev. from obs.	% dev. from cor.
3	9.8 ± 0.4	25.1	20.2	19.9	26	1.5
4	12.6 ± 0.4	32.5	27.0	26.5	23	1.9
5	14.8 ± 0.4	39.0	32.0	33.2	21	3.7
5	5.5 ± 0.3	13.8	11.4	11.3	22	0.9

The first column of this table gives the weight of steel in grams, the first three values being from the same sample of steel while the last is from a different sample. The observed volume of BaSO₄ is given in column 2. Each of these values is the average of five different determinations whose average deviation from the average is given after each value. The third column gives the observed weight of BaSO₄ as read from Graph 7 by the use of the observed volume given in Column 2. In other words, the third column gives the weight of BaSO₄ that would have been present in the volume given in column 2 if the precipitation had been carried out in water solution with no iron salts present. The fifth column gives the theoretical weight of BaSO₄ present. This value is obtained by knowing the weight of sample taken and the percentage of sulphur present. It was found that if the observed volume of BaSO₄ was increased by 20% and then this value used with Graph 7 to obtain the weight of BaSO₄, that a weight was obtained which approximated closely to the theoretical weight. These values are given in the fourth column and are called the "corrected weights of BaSO₄." The sixth and

seventh columns give the percentage deviations of the observed and corrected weights respectively from the theoretical weight of BaSO_4 .

It will be observed from these results that the deviation of the corrected weight from the theoretical weight, in general, is very small. Therefore, we conclude that, in general, the increase in volume of the BaSO_4 when precipitated in the presence of iron salts over that when precipitation is made in water solution with no foreign substance present, is approximately 20%. This 20% increase in volume is attributed to two factors, viz., (1) the adsorption of iron salts by the BaSO_4 thus increasing its volume, and (2) a decrease in the size of the BaSO_4 particles due to the hindrance of the salt molecules present, which also increases the volume occupied by the BaSO_4 .

Graph 14 was obtained by plotting the observed volume of BaSO_4 as found in Column 2 against the theoretical weight of BaSO_4 . The points for the curve thus plotted are shown by a small circle with a dot in its center. On this same graph is also duplicated the curve found in Graph 7. The values for this curve are given by crosses. Also we have increased the volumes found in Graph 7 by 20% and plotted the volumes thus obtained against the weights of BaSO_4 corresponding to the volumes before they are increased. This curve is also included on Graph 14 and its values are marked with a dot surrounded by a small triangle. This curve gives

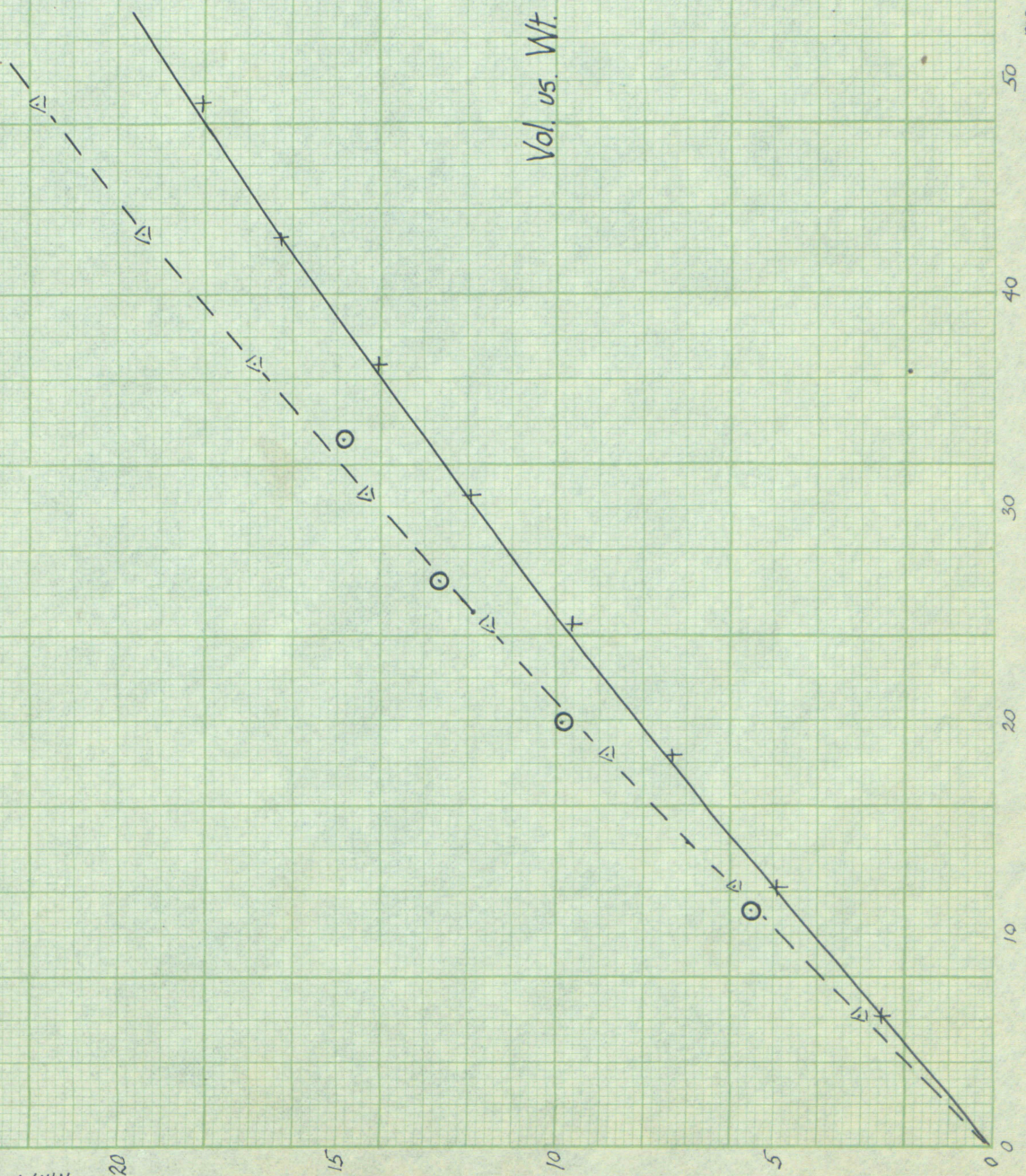
mm³ Vol. BaSO₄

mg. wt. BaSO₄

Graph 14

Vol. vs. Wt. BaSO₄ from Steel Flasks I and II

- Observed value
- + Computed value from Graphs 7 and 8
- △ Corrected computed value



the approximate relations between the weight of BaSO_4 derived from steels and its volume, provided the determinations are carried out under the conditions specified. Therefore, since the increase in volume due to adsorption and decrease in particle size is consistently uniform, we may conclude that this method is applicable to the determination of sulphur in steel provided the flask used is calibrated against standard sample of steel and that subsequent determinations are carried out under the same conditions as the standard.

The above method requires a very short time in comparison with the gravimetric method and its accuracy is quite comparable. It will be noticed from the table that the average deviation of individual determinations from the average is not greater than 6%. The deviation of any individual determination from any other is never more than 14%. This accuracy is indeed comparable with that given by the Bureau of Standards. As a specific example let us consider one of the standard samples used in this investigation, viz., Standard Sample No. 50 of the Bureau of Standards. The average value given for the sulphur content of this steel is .031%. Analyst No. 5 obtained .033% which is a variation of 6.4% from the average. Other analysts obtained percentages which varied more than this from the average but their determinations were not carried out by the recommended method.

D. The Determination of Calcium as Calcium Oxalate

Theoretically the centrifuge method of determination which has been described can be extended to any precipitate which is of such a nature that it will pack into a capillary. It would be advisable and profitable to find out if this method actually works in practice for precipitates other than barium sulphate. The investigation of other precipitates thus leads us to the consideration of calcium oxalate.

Calcium oxalate is quite an insoluble substance, having a solubility of the order of magnitude of BaSO_4 . It is less dense than BaSO_4 , crystalline, and quite easy to produce. It therefore fulfills the requirements for centrifuge determinations.

A solution of calcium nitrate was made up and standardized by the ordinary gravimetric method. One cc. of this solution was equivalent to .00391 gram of calcium oxalate. Flasks of two different sizes were used for this precipitate, i.e. flasks, the total capacities of whose capillaries were 20 cu.mm. and 200 cu.mm. respectively. For the flasks of 20 cu.mm. capacity, the following procedure was used:

A definite amount of the standard calcium nitrate was measured out and diluted until 50 cc. are equivalent to approximately 4 mg. of calcium. This solution was then heated to 90°C . and the calcium precipitated by the addition of N/40 ammonium oxalate at the rate of 30 drops per minute and with constant stirring. The temperature was kept

within $\pm 1^{\circ}\text{C}$. of that specified. After standing for one hour, the precipitate and solution were transferred to the centrifuge flasks, centrifuged for four minutes at 2000 r.p.m., and the volume noted. The corrected volume is obtained by the use of Graphs 1 and 2. Results obtained by this method are given in Table XI, from which Graph 15 was obtained. This graph gives the relation between the weight of calcium oxalate and its corresponding volume when packed into a standard capillary by centrifugal force. This relation seems to be direct proportionality. Results are reproducible with an accuracy of 3%. Column 2 of the table gives the average volume corresponding to the weight of CaC_2O_4 in the first column. Each of these values represents the average of five determinations whose average deviation from the average value is that given. The third column gives the corresponding apparent density of the CaC_2O_4 . The disadvantage of this process is that only small amounts can be determined due to the very small capacity of the capillary. For a sample which has an appreciable calcium content only a very small weight can be taken for analysis. However, in such a case one may use the alternative method of weighing out a 2 or 3 gram sample, dissolving in the desired amount of water, and using aliquot portions for analysis. This is the method recommended.

Graph 15

Vol. vs. Wt. CaC_2O_4 Flasks I and II

4 mg. Ca. per 50 cc.

Temp. 90°C .

$\frac{1}{40} (\text{NH}_4)_2\text{C}_2\text{O}_4$; 30 drops/min.

2000 r.p.m. for 4 min.

mm³ Vol.

5

10

5

7.5

10

mg. wt. CaC_2O_4

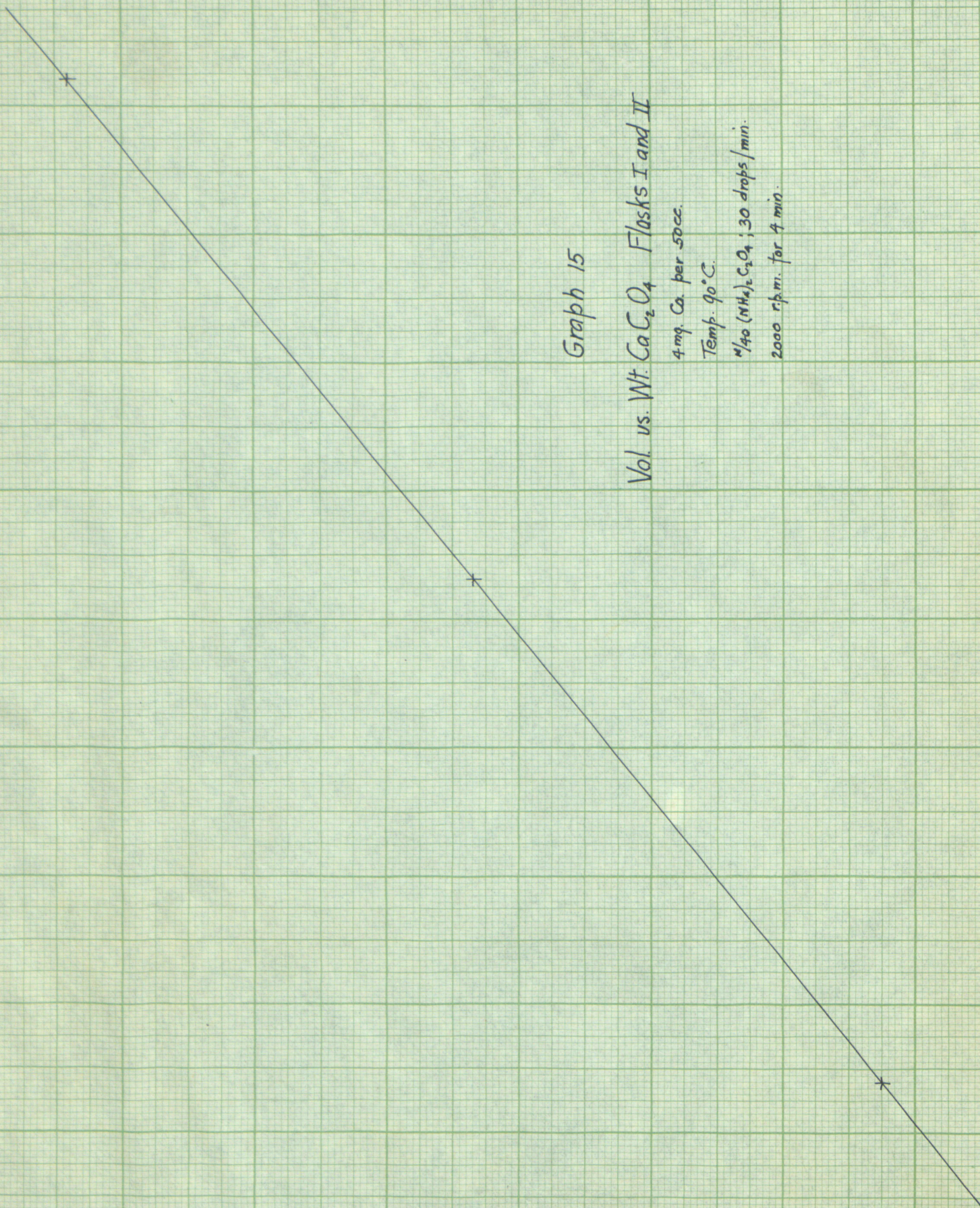


TABLE XI

Precipitated at 90°C. and centrifuged for 4 minutes at 2000 rp.m.

<u>Wt. CaC₂O₄ mg.</u>	<u>Vol. CaC₂O₄ cu.mm.</u>	<u>Apparent density</u>
3.91	6.5 ± 0.25	0.602
7.82	12.7 ± 0.25	0.616
11.73	18.8 ± 0.20	0.624

With the use of capillaries of 200 cu.mm. capacity, larger samples may be used and the analysis may be extended over a larger range of percentages. In using flasks with this size capillary the procedure is the same as for those with the smaller capacity with the exception that the solution is diluted until 50 cc. of solution is equivalent to approximately 25 mg. of Ca. Results with this size flask are given in Table XII. The first column gives the weight of calcium oxalate produced, which value is obtained by knowing the amount of standard calcium nitrate used. The second column gives the corresponding average volume of calcium oxalate and the average deviation of the individual determinations from this average value. As will be seen, these values check within 5% for smaller volumes and within 1% for larger volumes. The third column gives the average apparent density of the CaC₂O₄ when packed into the capillary.

TABLE XII

Precipitated at 90°C. and centrifuged for 4 minutes at 2000 r.p.m.

<u>Wt. CaC₂O₄ mg.</u>	<u>Vol. CaC₂O₄ cu.mm.</u>	<u>Apparent density</u>
15.64	36 ± 1.7	0.434
23.46	53 ± 0.7	0.443
31.28	65 ± 1.0	0.489
39.10	77 ± 1.0	0.508
46.92	85 ± 1.0	0.553
57.74	105 ± 0.3	0.550
62.56	121 ± 1.3	0.517
70.38	135 ± 1.0	0.521
78.20	151 ± 1.0	0.518
86.02	176 ± 1.0	0.489
93.84	201	0.467

Graph 16 shows the weight of calcium oxalate in mg. plotted against its corresponding volume when packed into a capillary of the size used. With this size capillary, the accuracy is not so great as with the smaller size, but nevertheless readings may be checked quite consistently as shown in the table and the use of these flasks has the advantage that larger samples may be used and determinations may be carried out over a larger range of percentages without changing the weight of the sample taken. Therefore, if we know the volume of calcium oxalate, precipitated and centrifuged as specified above, we may obtain its weight from the graph. For speed, this method has a great advantage over the ordinary gravimetric method in that a complete determination may be made in 10 to 15 minutes. Also the accuracy is comparable to that of the gravimetric method and is sufficient for many purposes.

Graph 16

Vol. vs. Wt. of CaC_2O_4 Flasks III and IV

25 mg. Ca per 50 cc.

Temp. 90°C .

$\frac{1}{40}$ (NH₄)₂C₂O₄; 30 drops/min.

1 hr. standing

2000 rpm. for 4 min.

mm³ Vol.

75 mg. wt. CaC_2O_4

50

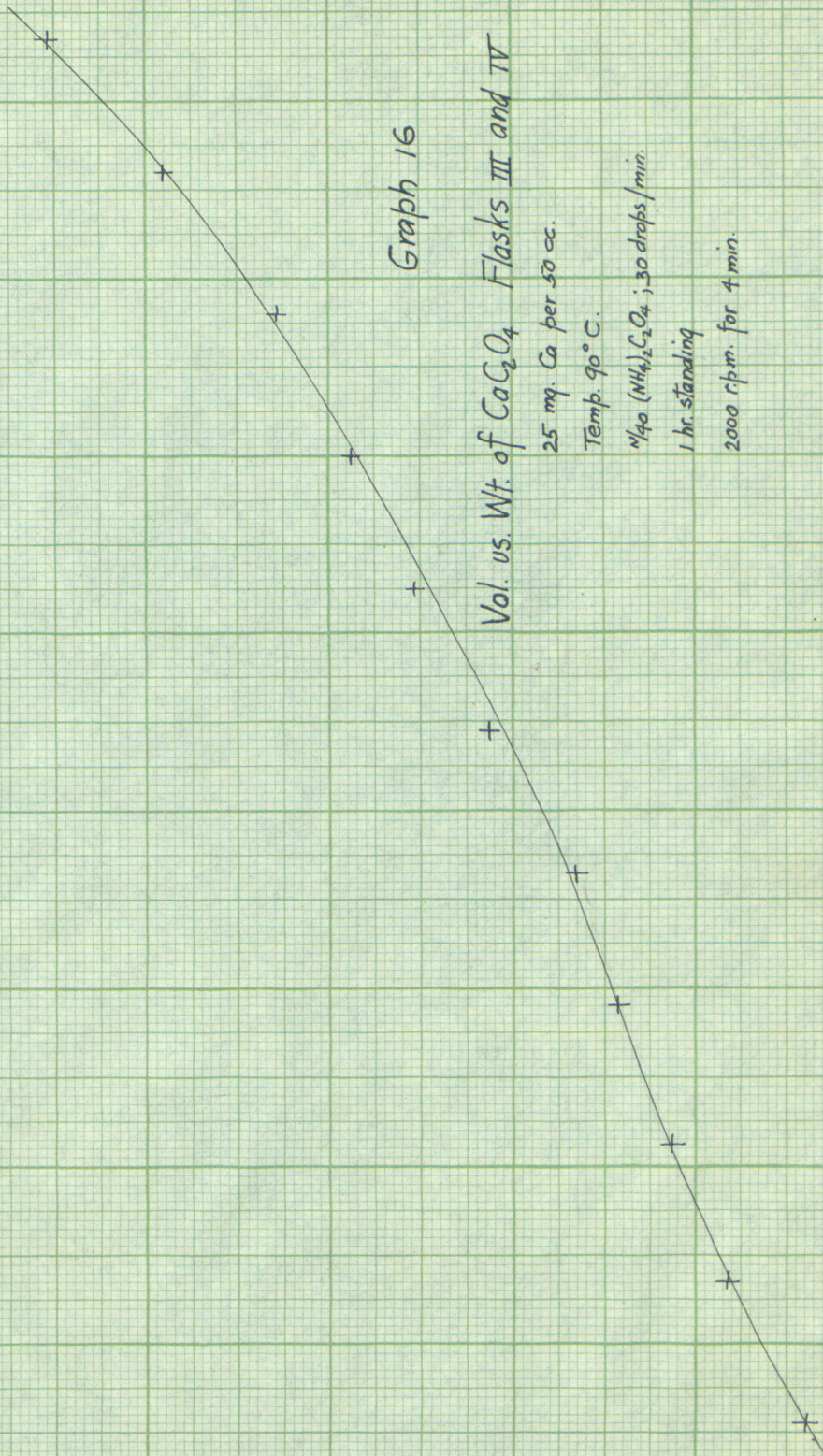
25

00

150

100

50



E. The Determination of Silver as Silver Chloride.

Silver chloride tends to precipitate as a curdy solid which does not pack into capillaries on centrifuging with the ease of crystalline precipitates. Sometimes a precipitated silver chloride would pack into the 200 cu.mm. capillary most excellently while at other times the packing was non-uniform and small gaps or spaces were left between the different portions of the precipitate. Some of the best values in this work are tabulated in Table XIII. Column 1 gives the precipitant used while columns 2 and 3 give the volume and apparent density of the precipitate. When HCl is used as the precipitant, results are not readily reproducible. When NaCl is used, however, the curdiness of the precipitate is somewhat reduced and results are reproducible with an accuracy of 7%. But even with NaCl as the precipitant, gaps would occur in the precipitate due to non-uniform packing. With a still larger capillary, in all probability this precipitate would pack more uniformly, although the accuracy of the method would be reduced. This method for AgCl is therefore not recommended.

TABLE XIII

Precipitated at 90°C and centrifuged at 2000 r.p.m. for 4 minutes

<u>Precipitant</u>	<u>Vol. AgCl- cu.mm.</u>	<u>Apparent density</u>
HCl 0.1 N	87	1.26
	92	
	75	
	98	
	73	
	<u>85 ± 8.8</u>	

TABLE XIII (Cont.)

<u>Precipitant</u>	<u>Vol. AgCl - cu.mm.</u>	<u>Apparent density</u>
NaCl .05 N	105	1.00
	102	
	113	
	105	
	108	
	110	
	106	
	<u>107 ± 3</u>	

F. The Determination of Aluminum as Hydrous Aluminum Oxide

Aluminum hydroxide precipitated by ammonium hydroxide or ammonium carbonate is a bulky, gelatinous precipitate of almost the same refractive index as water. It does not correspond to the formula $\text{Al}(\text{OH})_3$ but seems to be a hydrated oxide of formula $\text{Al}_2\text{O}_3 \cdot \text{N}\text{H}_2\text{O}$, where N depends upon the conditions of precipitation, etc. The compound freshly precipitated with ammonium hydroxide corresponds roughly to the formula $\text{Al}_2\text{O}_3 \cdot 8\text{H}_2\text{O}$ and if this is exposed to dry air it loses water by insensible gradations passing over imperceptibly into the anhydrous condition. Aluminum hydroxide is therefore a misnomer. Hydrous aluminum oxide is a better name for this compound.

The hydrous aluminum oxide described above does not pack well into small capillaries due to its gelatinous and bulky nature. Even with capillaries of 2.6 mm. inside diameter, the precipitate tended to collect around the opening without any appreciable amount packing into the capillary. Substitution of flasks with larger calibrated tubes gave very interesting results. The tube finally adopted for this precipitate was the Hart Casein Type, or No. 535 of the Catalogue of the International Equipment Company. The calibrated portion of this tube has a uniform cross-section of approximately 1.04 cm., is calibrated over a range of approximately 5.8 cm., and has a total capacity of 5 cc. Each calibration represents .1cc. and reading may therefore be made accurately to this value.

The procedure used in all determinations is as follows:

A known amount of standard solution is diluted until 25 cc. contain approximately 10 mg. of aluminum. This solution is then heated to 90°C., a few drops of a 1% solution of sodium alizarine sulphonate added, and the aluminum precipitated by the addition of N/40 ammonium carbonate solution at the rate of 30 drops per minute until the solution smells distinctly of ammonia. After cooling, the precipitate and solutions are transferred to the centrifuge tube and centrifuged for 5 minutes at 2000 r.p.m. The resultant precipitate is red, due to the adsorption of the sodium alizarine sulphonate, which is a distinct aid in reading its volume. If the dye is not added, difficulty is experienced in reading the volume due to the fact that the precipitate has a refractive index not far removed from that of the solution. Table XIV gives the results of determinations carried out with different amounts of the standard solution. The first column gives the weight of aluminum present in mg., the second column, the volume of precipitate in cc. with the average deviation, and the third column, the amount of aluminum present per cc. of precipitate.

It will be noticed that results always check within 1 cc., which is an accuracy of 98% for a volume of 5 cc. Graph 17 was obtained by plotting the weight of aluminum in milligrams against the volume of the packed precipitate in

cubic centimeters. This is not quite a straight line but a curve whose slope increases with an increase in the amount of aluminum present. That is, the apparent density of the precipitate increases with an increase in its volume.

TABLE XIV

Precipitated at 90°C and centrifuged at 2000 r.p.m. for 5 minutes

<u>Wt. Al</u> <u>mg.</u>	<u>Vol. ppt. cc.</u>	<u>g. Al per cc.</u>
4.5	1.01 ± 0.04	0.00446
9.0	1.81 ± 0.05	0.00497
13.4	2.64 ± 0.02	0.00508
18.0	3.40 ± 0.05	0.00529
22.5	4.14 ± 0.02	0.00544
27.0	4.83	0.00559

From all observations it appears that this method would be ideal for the rapid estimation of aluminum in steels and alloys. With a tube of somewhat smaller diameter, the method would be still more accurate due to a greater accuracy in reading. It may be well to mention here the fact that the volume of this precipitate depends to a great extent upon the rate and duration of centrifuging.

Graph 17.

Vol. vs. Wt. Al. Flasks V and VI

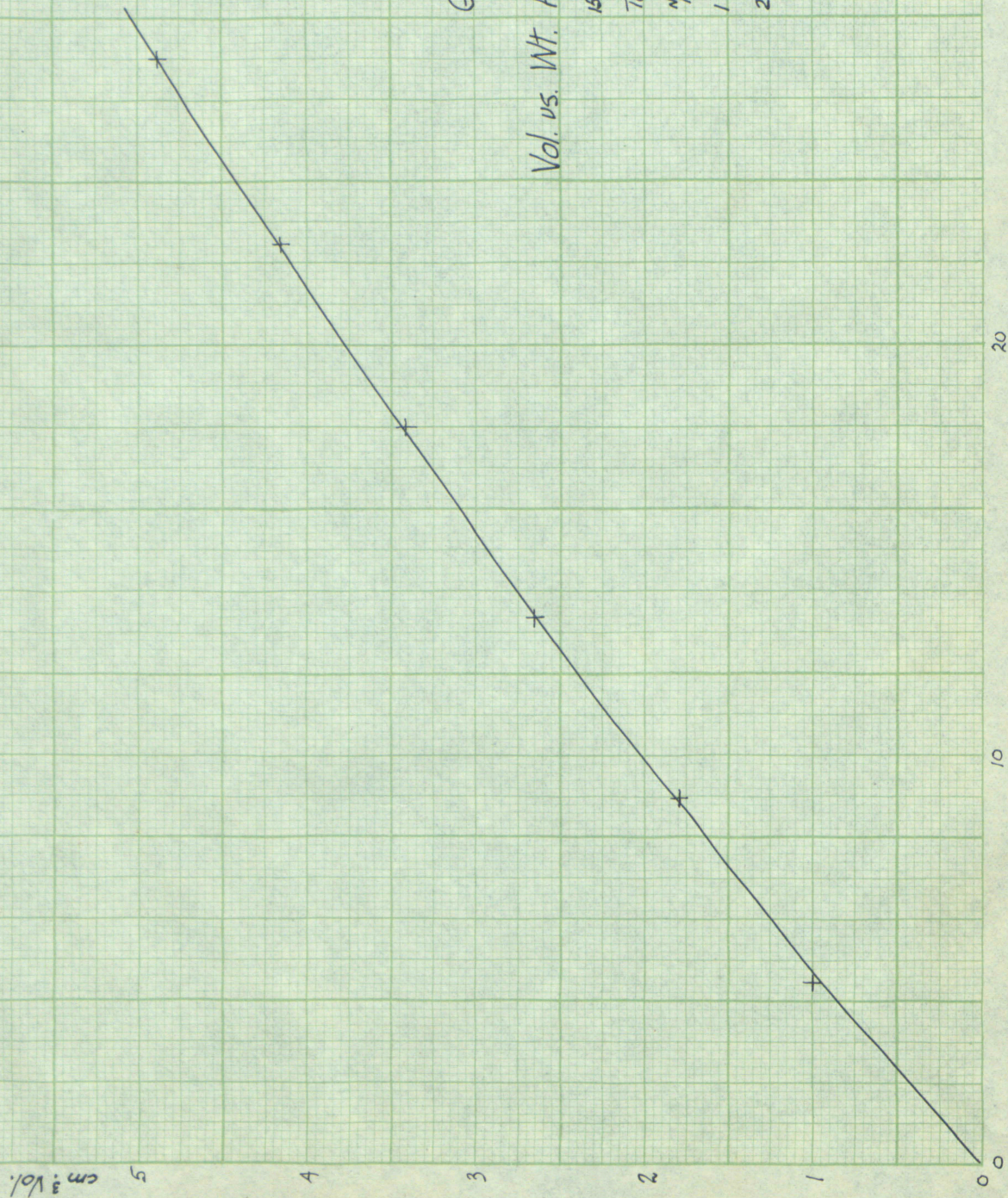
15 mg. Al. per 25 cc.

Temp. 90°C.

$N/40$ $(NH_4)_2CO_3$; 30 drops/min.

1 hr. standing

2000 r.p.m. for 5 min.



G. The Determination of Nickel as Nickel Dimethylglyoxime

In neutral or slightly basic solutions, nickel forms a fairly insoluble compound with dimethylglyoxime. This compound, although crystalline, is quite voluminous and does not pack well into small capillaries. With the Hart Casein tubes used for aluminum, however, consistent packing can be obtained. Table XV shows the results of several determinations carried out with these tubes. The following procedure was used:

A known volume of a standard solution containing .001467 g. of nickel per cc. was diluted until 50 cc. of the solution contained approximately 35 mg. of Ni. This solution is then heated to 90°C., and the nickel precipitated by the addition of five times the theoretical amount of a 1% alcoholic solution of dimethylglyoxime necessary to precipitate the nickel. This solution is added all at once and with vigorous stirring. The solutions at first turn orange and after a few seconds the nickel dimethylglyoxime settles out as a red precipitate. After cooling, the precipitate and solution are transferred to a Hart Casein tube, centrifuged for 5 minutes at 2000 r.p.m., and the volume of precipitate noted. The first column of Table XV gives the weight of Ni present in mg., the second column, the corresponding volume, and the third, the weight of nickel per cc. of precipitate.

TABLE XV

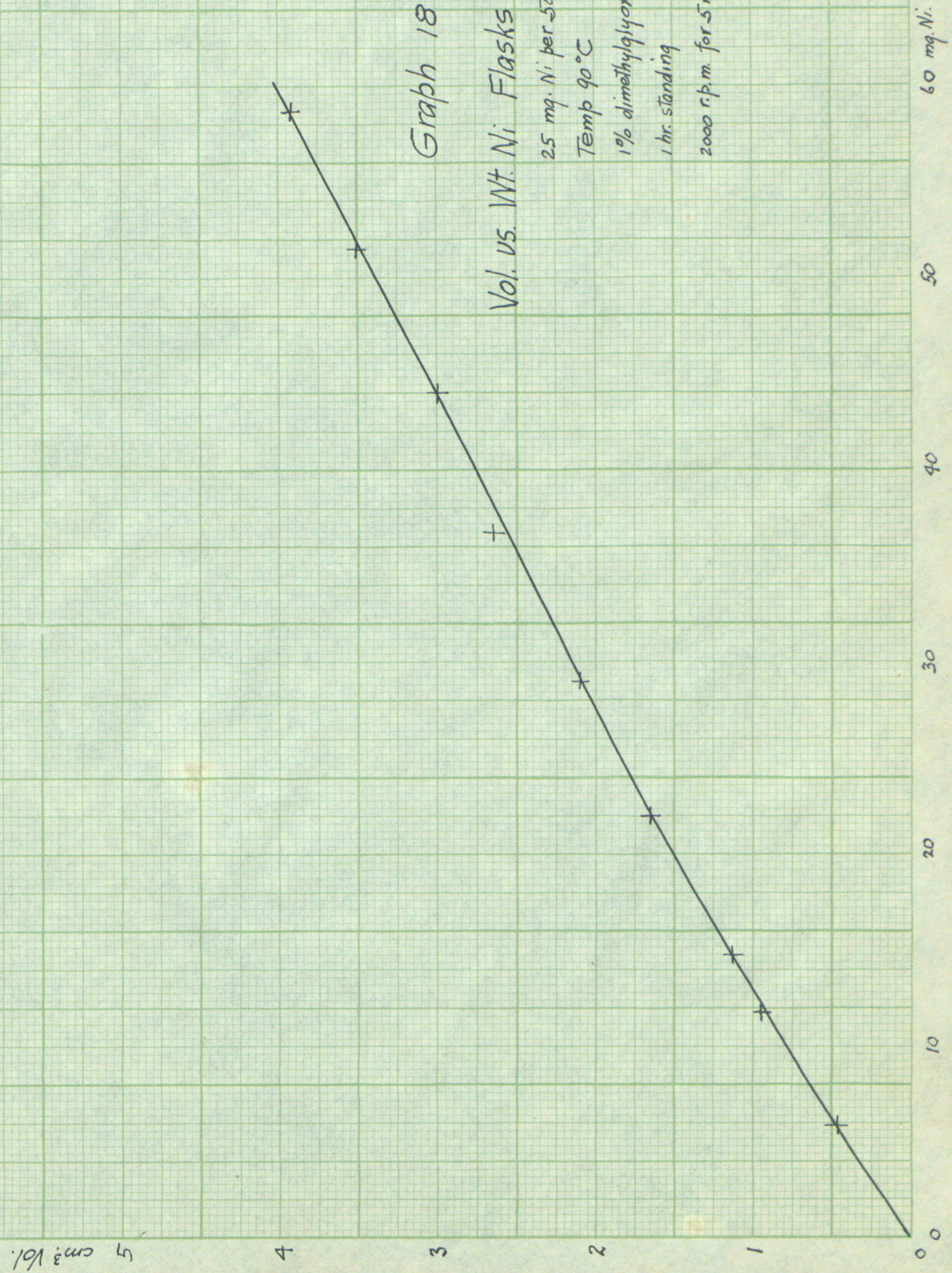
Precipitated at 90°C and centrifuged at 2000 r.p.m. for 5 minutes

<u>Wt. Ni mg.</u>	<u>Vol. ppt. cc.</u>	<u>g. Ni per cc.</u>
5.87	0.49	0.0120
11.74	0.94	0.0125
14.67	1.14	0.0129
22.00	1.67	0.0132
29.34	2.11	0.0139
36.67	2.64	0.0139
44.00	2.90	0.0152
51.34	3.51	0.0146
58.68	3.92	0.0150

Graph 18 was obtained by plotting the weight of nickel in mg. against the corresponding volume of precipitate in cc. As will be seen, the apparent density of the precipitate increases with increase in volume of precipitate present. Results with identical samples are reproducible within .2 cc. This, however, does not represent as great an accuracy as does the same degree of reproducibility with hydrous aluminum oxide since the amount of aluminum per unit volume of precipitate is less than the amount of nickel per unit volume. However, for a volume of 5 cc., this represents an accuracy of 96% for the total nickel present. This method appears quite commendable for a quick estimation of nickel present since precipitations may be carried out at room temperature and in the centrifuge flasks, thus avoiding any transference of precipitate. The volume of the precipitate, however, is sometimes hard to read due to the formation of an uneven meniscus.

Graph 18
Vol. vs. Wt. Ni Flasks V and VI

25 mg. Ni per 50 cc.
Temp 90°C
1% dimethylglyoxime; added all at once
1 hr. standing
2000 r.p.m. for 5 min.



H. The Determination of NO_3 as Nitron Nitrate

If a solution of nitron, or diphenylendoanilohydro-triazole, in 5% acetic acid is added to a solution containing the NO_3 radical, quite an insoluble precipitate is formed. This precipitate is crystalline and like nickel dimethylglyoxime it is quite voluminous and does not pack well into capillaries. However, with Hart Casein Tubes, consistent packing is obtained.

Table XVI gives the results of determinations carried out by the use of the following procedure:

A known volume of standard potassium nitrate is measured out and diluted until 25 cc. of solution is equivalent to approximately 25 mg. of NO_3 . Then add 1 cc. of glacial acetic acid for every 100 cc. of solution. This solution is heated to boiling and 10 cc. of nitron solution added for each 100 cc. of solution. This solution and precipitate are then cooled, allowed to stand in the dark for several hours, transferred to a Hart tube, centrifuged at 2000 r.p.m. for five minutes and the volume of precipitate noted. The nitron solution is prepared by dissolving 10 grams of nitron in 100 cc. of 5% acetic acid and then kept in a dark bottle to prevent decomposition. The first column of the table gives the weight of NO_3 in mg.; the second and third, the volume of the precipitate and the weight of NO_3 per unit volume, respectively. Again results are reproducible within .2cc., which for 5 cc. represents an accuracy of 96% for

the total NO_3 present.

TABLE XVI

Precipitated at 90°C . and centrifuged at 2000 r.p.m. for 5 min.

<u>Wt. NO_3</u> <u>mg.</u>	<u>Vol. ppt. cc.</u>	<u>g.NO_3 per cc.</u>
3.18	0.28 ± 0.02	0.0114
9.54	0.80 ± 0.03	0.0119
15.9	1.31 ± 0.03	0.0121
22.3	1.79 ± 0.05	0.0125
31.8	2.58 ± 0.05	0.0123
47.7	3.65 ± 0.01	0.0131
63.6	4.83 ± 0.10	0.0132

Graph 19 shows the weight of NO_3 in mg. plotted against the volume of precipitate in cc. It will be noted that the apparent density of the precipitate increases with increase in volume of the precipitate.

This method is recommended for the rapid determination of NO_3 . As with nickel dimethylglyoxime, the only difficulty is in reading the volume of the precipitate. The top of the packed precipitate is uneven in many cases, thus making it difficult to obtain an accurate reading.

Graph 19

Vol. vs. Wt. NO_3 Flasks V and VI

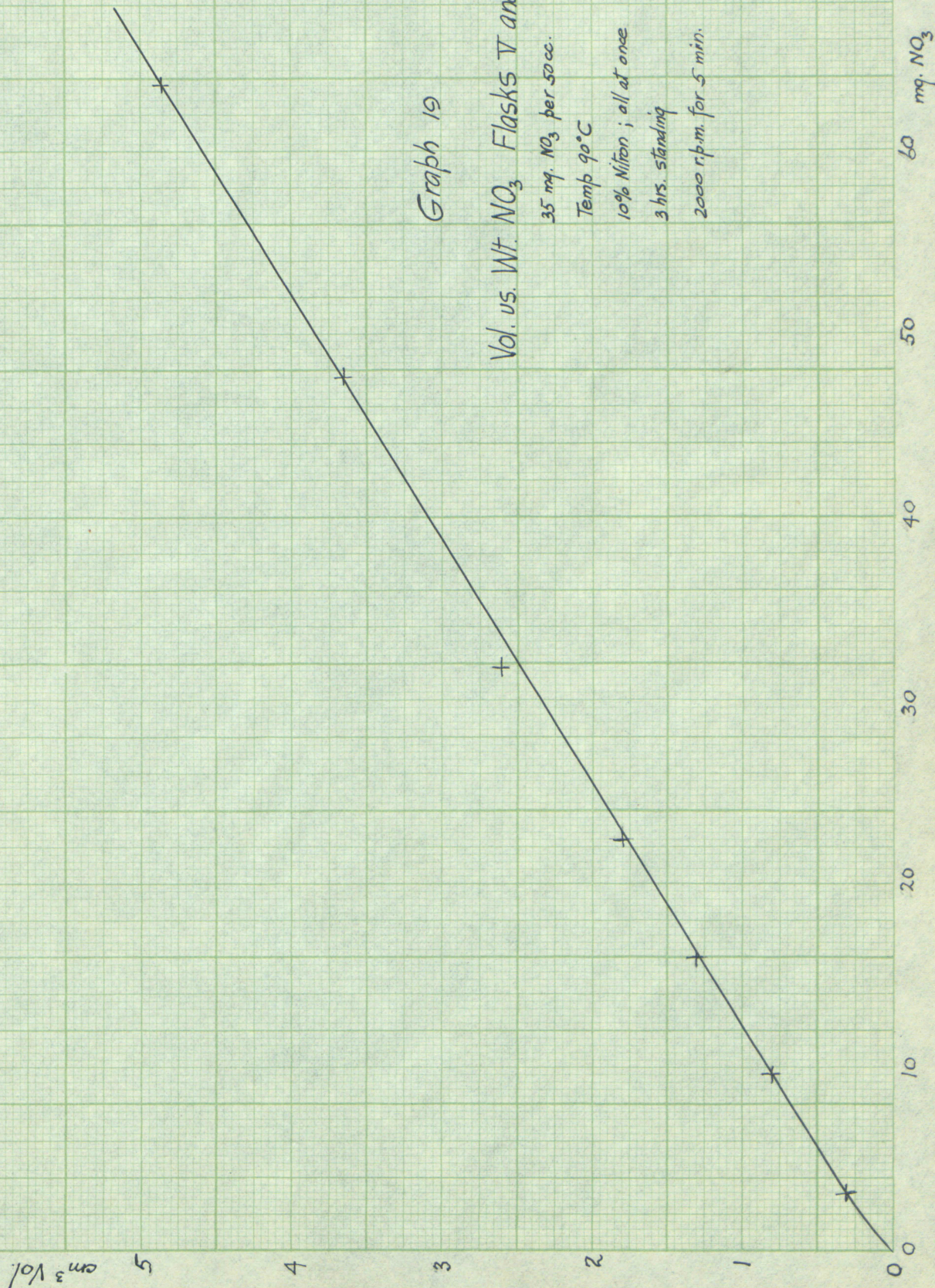
35 mg. NO_3 per 50 cc.

Temp 90°C

10% Nitron ; all at once

3 hrs. standing

2000 r.p.m. for 5 min.



SUMMARY AND CONCLUSIONS

The quantitative relationship between the weight of BaSO_4 and its volume when precipitated and packed into capillaries by centrifugal force under specified conditions has been worked out and its accuracy determined. It has been shown that results are reproducible with an error of not more than 5% for small volumes and of not more than 1% for larger volumes.

A comprehensive study has been made of the quantitative relationships between the conditions of precipitation and centrifuging and the volume of BaSO_4 when packed into standard capillaries. The following factors were found to affect the volume of the precipitate: (1) Rate of Centrifuging; (2) Duration of Centrifuging; (3) Temperature of Precipitation; (4) Rate of Precipitation; (5) Concentration of solutions; (6) Time of standing of precipitate before centrifuging; and (7) The nature of the precipitant. Quantitative relationships were given for all these factors.

The centrifuge method has been applied to the determination of sulphur in steel, and has been shown to have a considerable degree of accuracy if conditions of precipitation and centrifuging are controlled.

The centrifuge method has been extended to the following: (1) The determination of calcium as calcium oxalate; (2) The determination of aluminum as the hydrous oxide; (3) The determination of nickel as nickel

dimethylglyoxime; (4) The determination of silver as silver chloride; and (5) The determination of nitrate as nitron nitrate. For all the above determinations the volume-weight relationships are given when the determinations are carried out under the specified conditions.

It is concluded that the centrifuge method may be extended to the determination of any insoluble substance. The size of the capillary used is dependent upon the nature of the precipitate. For dense crystalline precipitates such as BaSO_4 , it is most advantageous to use capillaries of approximately 1.1 mm. bore. For less dense precipitates, but still crystalline, a capillary of 2.6 mm. inside diameter is advisable. For gelatinous and very voluminous precipitates, capillaries with still larger bores are necessary.

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