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DIALYSIS OF SILICIC ACID GELS

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A thesis presented to the
Department o f Chemistry of Union
College, in partial fulfillment of
the requirements for the degree of
Bachelor of Science in Chemistry,

by Arthur C. Hamm Jr.

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INTRODUCTION

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The primary purpose of this investigation was to prove or disprove the existence of an equilibrium between polysilicic acid molecules and simple silicic acid molecules in a set silicic acid gel. The investigation involved the controlled dialysis of typical gels from their time of mixing, thru the time of set and into the aging period.

Since numerous silica determinations were to be made, it was thought advisable to disregard the time consuming gravimetric method. The secondary purpose of this investigation was therefore, to determine if the colorimetric method for the determination of silica, as devised by Winkler (1) in 1914 and used by Witzel (2), could be adapted to handle the larger amounts of silica that were to be dealt with in this investigation.

COLORIMETRIC DETERMINATION OF SILICA

A. HISTORICAL

Two methods are in use at the present time for the colorimetric determination of small amounts of dissolved silica. The " molybdenum blue reaction " involves the controlled reduction of the heteropoly compounds, such as molybdisilicic acid, $H_4Si(Mo_3O_{10})_4$, to give molybdenum blue (3). The procedure must be carefully controlled, since the excess molybdate reagent itself may be reduced to molybdenum blue.

The second method, and the one to be used in this investigation, depends upon the formation of the yellow heteropoly compound, molybdisilicic acid. This acid is formed by the reaction of ammonium molybdate and the silica, in the presence of a mineral acid. In the original procedure, Jolles and Neurath (4), in 1898, used potassium molybdate and nitric acid as reagents and known solutions of silica for comparison. Winkler (5) modified the method by substituting hydrochloric acid for nitric acid and using aqueous solutions of potassium chromate as standards. Potassium chromate solutions were used as standards since the solutions of silica

and their yellow color were found to be unstable. Dienert and Wandenbulcke (6) used ammonium molybdate and sulfuric acid as reagents, an aqueous solution of picric acid as a standard. Swank and Mellon (7) stated that a buffered solution was necessary if a potassium chromate solution was to be used as the standard. Winkler's potassium chromate standard was adopted, however, by the American Public Health Association in 1933 (8).

Winkler's method of analysis involves the addition of 5 ml of an ammonium molybdate solution to 50 ml of the unknown solution, containing the dissolved silica. This method is set up for a 55 ml total volume solution. The intensely yellow colored solution produced is then matched colorimetrically against a solution, totaling 55 ml and also containing a known number of milliliters of the standard colorimetric solution. The standard colorimetric solution contains 5.30 gm. of potassium chromate per liter. Each milliliter of this solution is equivalent to 20 mg. of silica per liter, therefore, the amount of silica present in the unknown solution can be calculated.

B. EXPERIMENTAL

1. The ammonium molybdate solution used thruout was prepared by adding 11 grams of the molybdate to a solution of 30 mls of concentrated HCl and 35 mls of distilled water. When all the solid had dissolved, the total volume was increased to 200 mls. It was necessary to first add the molybdate to the more

concentrated HCl, in order to keep the molybdate in solution. This reagent was kept in the dark when not in use, since it would decompose in sunlight, the blue oxide separating out. The resulting normality was 1.87 and the per cent molybdate by weight was approximately 5.2. It has been found (7) that an optimum amount of acid is required for the full development of the yellow color. The acidity given above is near this maximum.

Color transmittancy was measured by means of a Cenco electrophotometer. A blue filter is used since it gives the greatest sensitivity. By waiting twenty seconds after switching the photometer to the ON position, a reading $\pm$.25 could be obtained.

2. In order to determine the effect of buffering on the standard colorimetric solution, the following experiment was performe d. Two series of solutions were formed, each solution of each series having a total volume of 55 ml. and each series having a solution containing an equal amount of the standard colorimetric solution as the other. The only difference was that Series B had 25 mls. of distilled water replaced by 25 mls. of a 1% borax solution. The transmittancy of each solution was determined. The results are shown in Table # 1 and by Graph # 1.

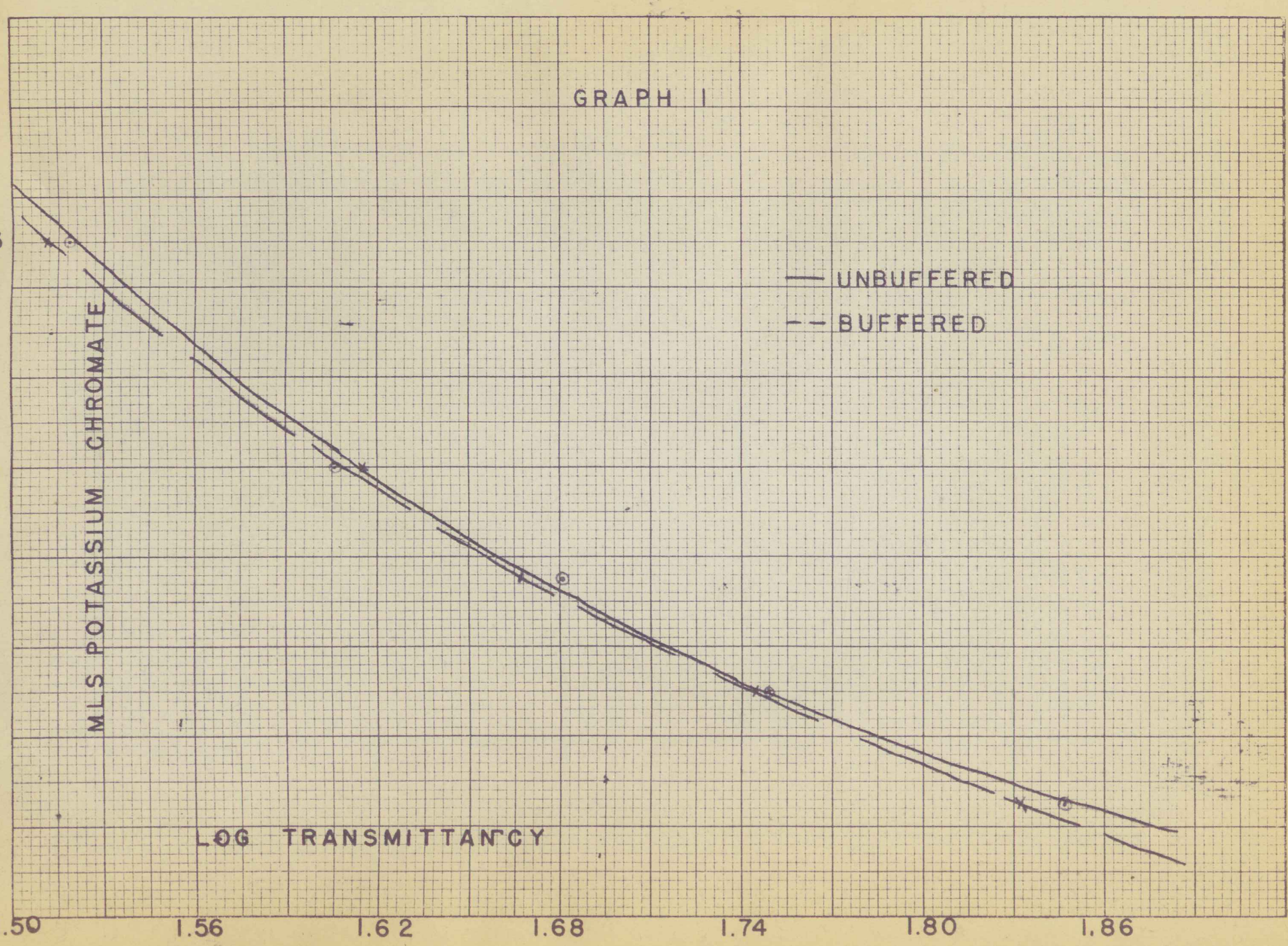
TABLE # 1

Calibration and Buffered Transmittancies

Series A (unbuffered)	ml. of K_2CrO_4	Series B (buffered)
84.4	.20	
74.8	.40	
70.25	.50	68.0
56.0	1.00	55.5
48.0	1.50	46.5
40.5	2.00	41.25
36.9	2.50	
33.0	3.00	32.5

The differences between the transmittancies of the buffered and the unbuffered solutions were shown in each case to be within the error caused by volume differences. Therefore, all colorimetric determinations were made against unbuffered K_2CrO_4 as the standard.

3. Next, the Cenco electrophotometer was calibrated, using the unbuffered K_2CrO_4 standard solution. The transmittancy was determined for each of several solutions, totaling 55 ml. in each case, and containing varying amounts of the unbuffered K_2CrO_4 standard. The first two columns of Table # 1 show the results. The log of the transmittancy was then plotted against the mls. of K_2CrO_4 in the solution, giving the calibration curve, Graph # 2. Knowing the transmittancy of the unknown silica solution, it was now possible to approach the calibration curve


GRAPH 1
UNBUFFERED
BUFFERED
MLS POTASSIUM CHROMATE
LOG TRANSMITTANCY
3
2
1
1.50
1.56
1.62
1.68
1.74
1.80
1.86

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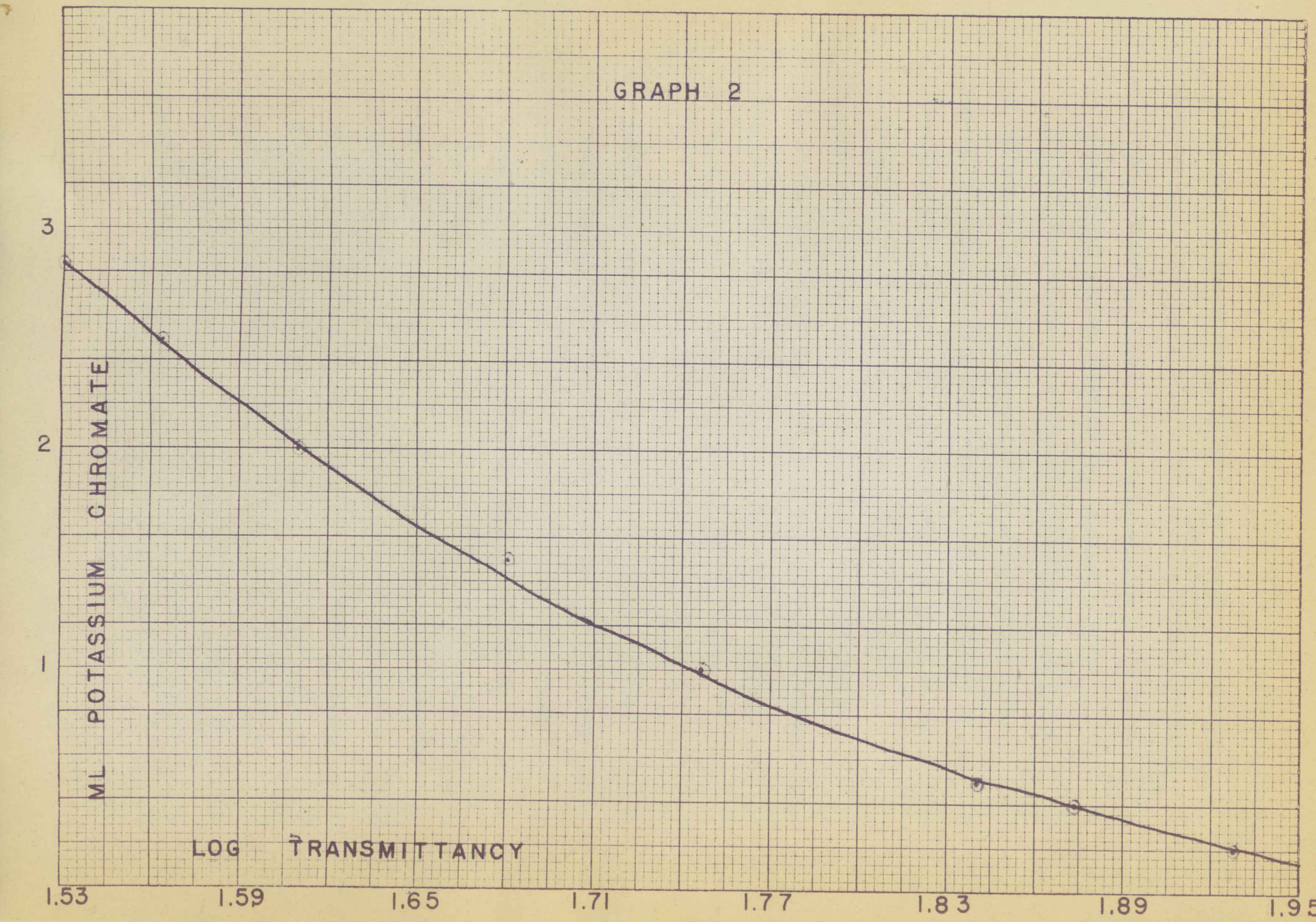

and determine the mls. of K_2CrO_4 needed to produce an identical transmittancy. Bringing into use the conversion factor (1 ml. of K_2CrO_4 = 20 mg. of silica per liter of unknown), the amount of silica in the unknown solution was apparent.

4. All that was now needed to complete a colorimetric silica determination was some consistent method for obtaining the silica transmittancy of the unknown. All colorimetric silica determinations have been devised with 100 ppm of silica as the maximum amount that could be analyzed. Above 100 ppm a deviation from the Beers-Lambert Law becomes evident. In graph # 2, it will be noticed that the calibration curve shows a deviation from the Beers-Lambert Law. Silica amounts from the dialysis work to be carried out was expected to be as high as 6000 ppm.

It was decided that no reading below 34.0, corresponding to 3000 ppm, would be used. If the reading did fall below this value, a dilution would be made. The following will explain the dilution method as well as show the procedure to be followed in obtaining the silica transmittancy of the unknown. The unknown silica solution is diluted to 50 mls or if all ready greater than this amount, a 50 ml. portion is taken for analysis. To this, 5 mls. of the ammonium molybdate reagent is added, making a total volume of 55 mls. A transmittancy reading is now taken. If the reading is above 34.0, the calibration curve is consulted and the silica in the unknown solution calculated as shown previously. If the reading is below 34.0, a 5 ml. portion of the 55 ml. solution is taken, diluted to 50 mls. with distilled

water and brought back to the 55 ml. total volume by the addition of 5 ml. more of the molybdate reagent. A transmittancy reading is again taken. If the reading is above 34.0, proceed as above, if below 34.0. dilute again. The first dilution brings in a multipling factor of 11, ie, from 5 mls. to 55 mls.. A second dilution of 5 mls. to 55 mls. would introduce the factor 121. The molybdate reagent is added at each dilution to insure a complete reaction to the heteropoly acid. All transmittancy readings are taken twenty minutes after the addition of the reagent. This is to obtain maximum intensity of the yellow color. The intensity was found to decrease after twenty minutes, the decrease being as much as 6 units per 100 by the twenty-fourth hour.

5. In order to test the accuracy of this adapted colorimetric method, a silica unknown was divided into four portions. The silica unknown was a diluted water glass solution in which essentially all the silica was in a dissolved state. Two portions of the unknown were analyzed gravimetrically and the other two portions were analyzed colorimetrically. In the gravimetric runs, the portion was evaporated to dryness twice with HCl and the silica determined by the loss ofweight when treated with hydrofluoric acid.

By the gravimetric method,

Sample # 1	.0290 gm silic a
Sample # 2	.0284 gm silica

By the colorimetric method,

Sample # 1	1st dilution	56.5	.0301 gm silica
Sample # 2	1st dilution	57.5	.0287 gm silica

The average per cent difference from the gravimetric(taken to be the more accurate) is 2%.

Possible sources of errors in the colorimetric method include 1) the deviation from the Beers-Lambert Law at the higher amounts of silica. 2) the error introduced by dilution, altho dilution should reduce the preceding error somewhat.

6. The correlation between the gravimetric and the colorimetric methods is high enough to justify the use, for general purposes, of the colorimetric method for silica amounts above 100 ppm. Also, the time saved by using the colorimetric method, especially when a large number of determinations are to be made, may be an influencing factor in favor of the colorimetric method.

For the above reasons, it was decided that the adapted colorimetric analysis of silica would be used thrucut the dialysis work.

DIALYSIS OF SILICIC ACID

A. HISTORICAL

Zsigmondy (9), prior to 1900, made the observation that in the dialysis of a silicic acid hydrosol, the amount of silicic acid dialyzing thru decreased, reaching a zero value at the time of set.

Merz (10), from his dialysis study of silicic acid in 1940, suggested that the condensation of the simple acid molecules does not take place completely to the polysilicic acid. He found that even after the gel had set, a small, nearly constant amount of silicic acid was capable of passing thru the membrane. The possibility of an equilibrium existing between polysilicic acid molecules and simple silicic acid molecules was put forth. Whenever this equilibrium is disturbed, for instance when simple acid molecules dialyze thru a membrane, a new equilibrium is believed to be established, at the expense of the polysilicic acid molecules.

The data collected by Witzel (2) also showed the possibility of the existence of this equilibrium.

B. EXPERIMENTAL

1. An approximately 1 N solution of NaOH was standardized against standard oxalic acid. A 2.± N solution of H_2SO_4 was standardized against this NaOH solution. The sodium silicate used was E Brand obtained from the Philadelphia Quartz Co. This was diluted to 1.± N and standardized against the H_2SO_4. The normality of the sodium silicate was .9458 in terms of NaOH equivalent. The normality of the NaOH was .9471 An acetic acid solution was prepared from glacial acetic acid, the resulting normality being 1.7358.

2. All of the membranes used were prepared by filling 6 inch test tubes with Merck U.S.P. collodion. The tubes were then drained, inverted and allowed to dry for a period of 15 minutes. At this time the tubes were filled with distilled water and allowed to stand for ten minutes. The membranes were then removed from the tubes and placed under distilled water until used.

3. To prevent Na^+ and Ac^- ions from diffusing thru the membrane and thus changing the composition of the gel mixture, the liquid outside the membrane contained the same concentration of Na^+ and Ac^- ions as the gel mixture. The pH values of the gel mixture and the outside liquid were also the same.

4. In order to determine if the pores of a collodion membrane would clog with continual dialysis, the following experiment was performed. All times mentioned here and thruout the rest of the dialysis work are taken with the time of mixing

of the hydrosol as zero time.

Ten mls of the silicate solution and 50 mls of the acid solution were mixed to form a hydrosol. Three 10 ml portions were pipetted from the gel mixture at the twenty first hour into three individual membranes. Each membrane sack was placed in an 8 inch test tube containing 50 mls of a buffered dialysate. The sacks were held in place by means of a wax coated cork. At the 50th hour, 5 mls were transferred from one of the original sacks to a new sack, leaving 5 mls in the old sack. Both sacks were then placed in a fresh dialyzing medium and dialyzed continually for 93 hours. At this time, the dialyzing medium of both were analyzed for silica.

The gel mixture set in 168 hours, while the gel in the sacks set soon thereafter. After 308 hours, the gel mixture in another original sack was subdivided, half going into a new sack. Both had dialyzed continually for 76 hours before the dialyzing mediums were analyzed. At 838 hours, the 3rd original was subdivided, dialyzed for 68 hours, before the dialyzing mediums were analyzed for silica. The results are tabulated below.

TABLE # 2

Clogging Experiment

Sample	Amount SiO_2 thru original sack	Amount SiO_2 thru newer sack
1	.0050	.0052
2	.0029	.0028
3	.0029	.0025

Less silica dialyzed thru the original sack in the first instance

than thru the newer sack. In case # 2 and # 3, the reverse is apparent. As to whether or not the pores of a membrane colg on aging, no conclusive answer can be given, due to insufficient data. The data shown indicates little effect.

5. A blank run was carried out to determine the amount of silica picked up from the glassware and other sources by the acid dialyzing medium. Fifty mls. of a buffered solution were introduced into each of four 8 inch test tubes. After 10 minutes, the buffered solution of one was analyzed for silica. The second was analyzed after one hour, the third after 70 hours and the fourth after 170 hours. Table # 3 shows the results.

TABLE # 3

Results of Blank Run

Length of time	Reading and dilution factor		Amount of SiO_2 (ppm)
10 mins	90.0	(1)	154
1 hr	90.0	(1)	154
70 hrs.	91.0	(1)	152
170 hrs.	88.0	(1)	187

The amount of silica picked up by the solution appears to be about constant, at an average of 155 ppm. Therefore this amount has been substracted from all silica readings that are to follow.

6. The gel mixture of Gel # 1 consisted of sodium silicate solution and HAc solution in the proportion of one to six respectively. The time of set of the gel was 288 hours. A long setting gel was chosen in order to reduce the error of the ten minute dialysis. The buffered dialyzing medium consisted of NaOH and HAc in the proportion of one to six respectively. The temperature

of the setting gel was kept at 20° ± .2° C, the temperature of thegel from the time of set on was 21° ± 1° C.

Run # 1 consisted of a 10 minute dialysis period at various intervals during the setting of the gel and following the setting of the gel. In each case, 10 mls of the setting gel was placed into the dialysis sack. The sack was placed into an 8 inch test tube containing 50 mls of the buffered dialyzing medium and then dialyzed for 10 minutes. At the end of this period, the sack was removed and the dialyzing medium analyzed for silica. Table # 4 and Graph # 3 show the results. In Table # 4, a new sack and a new 10 ml portion of the setting gel was used for the first 10 readings. For the rest of the readings, the sack(and contents) of reading # 10 was used at the following appropriate time s.

TABLE # 4

Gel # 1 Run # 1

Dialysis #	Time after mixing (hr)	Reading and dilution factor		Amount SiO_2 (ppm)
1	.12	54	11	13245
2	1.08	59.6	11	10145
3	21.85	43	1	1845
4	48	55		945
5	94	59		845
6	119	62		685
7	142	64		585
8	166	66		505
9	240	66		505
10	287	64.5		565
11	333	66		505
12	353	65.8		525
13	406	65.5		535
14	428	68		435
15	453	70		375
16	477	71.5		325
17	502	71		335
18	576	66		505
19	646	65		545
20	768	64.5	1	565

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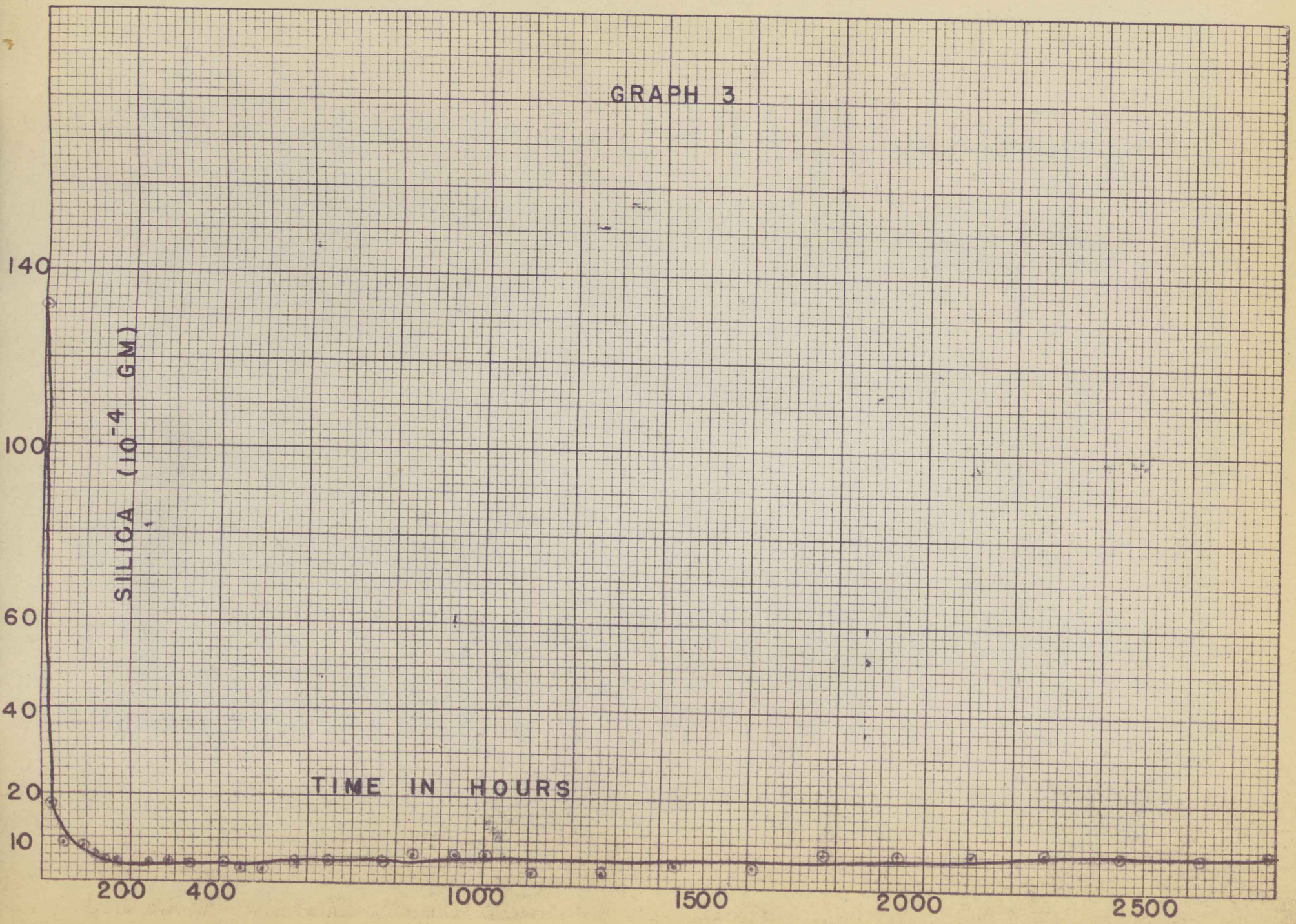


TABLE # 4 (con't)

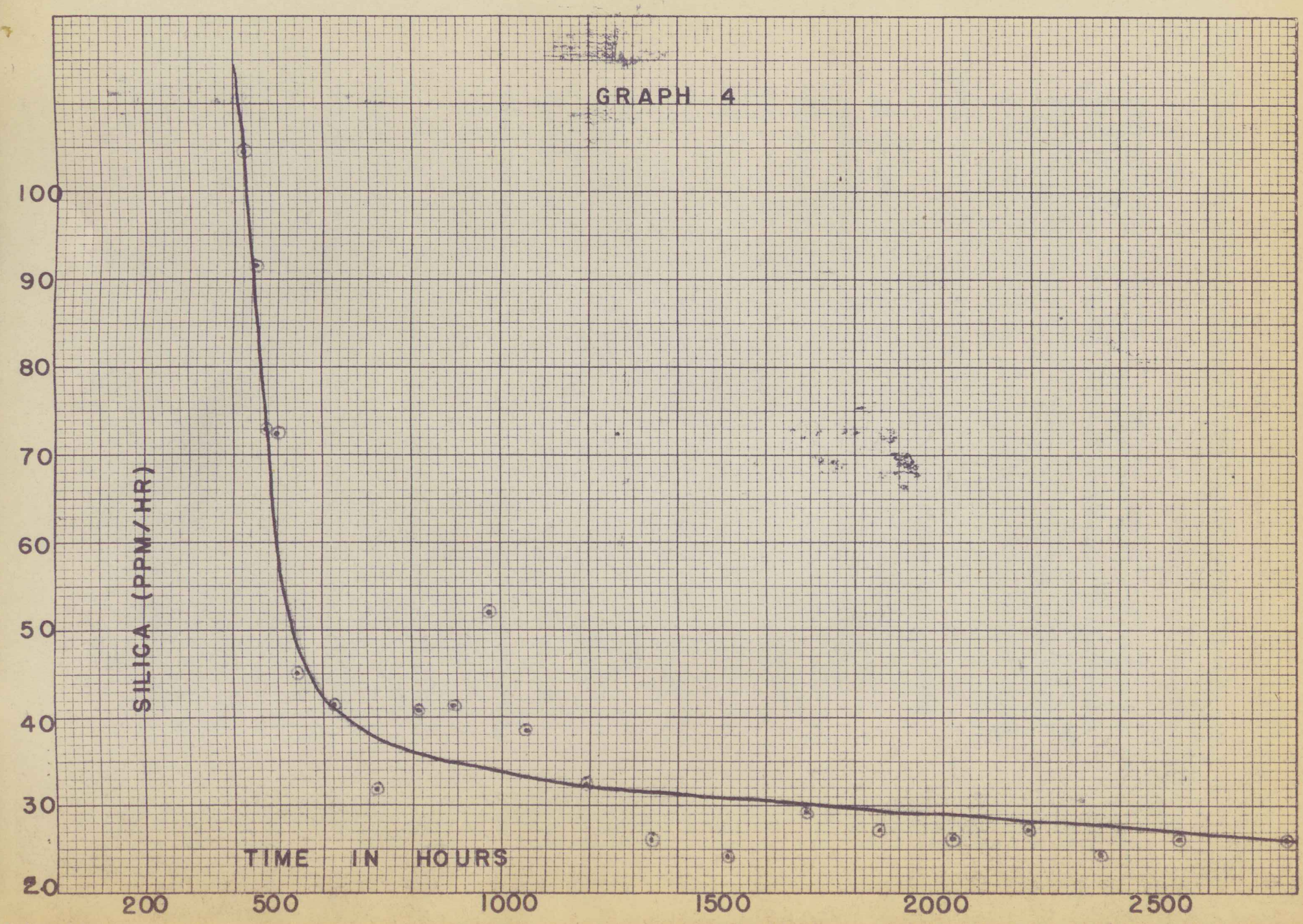
21	840	61	1	715
22	936	60.5		735
23	1007	61		715
24	1103	72		315
25	1269	70.5		355
26	1437	66		505
27	1608	64		585
28	1773	59		845
29	1943	58		875
30	2111	58.5		855
31	2277	56		925
32	2445	58		875
33	2613	58		875
34	2781	56	1	925

Beginning at the 428th hour, the dialyzing medium, in which the sack was kept between the 10 minute dialysis, was analyzed and the ppm per hour of silica passing thru the membrane found. This constituted Run # 2. The results are shown in Table # 5 and Graph # 4. In the graph, the mean time was plotted against the ppm/hour.

TABLE # 5

Gel # 1 Run # 2

Time(hr)		Reading-Dilution factor		Am't SiO_2(gm)	ppm/hr
406	to 428	86.2	11	.00214	95.0
428	453	40	1	.00212	91.4
453	477	46		.00159	66.1
477	502	45.5		.00164	65.6
502	576	32.5		.00317	42.8
576	646	35.5	1	.00272	38.8
646	768	79	11	.00359	29.4
768	840	35	1	.00279	38.7
840	936	78	11	.00380	39.6
936	1007	79.5		.00353	49.6
1007	1103	79.5		.00353	36.8
1103	1269	71		.00523	31.5
1269	1437	76		.00424	25.2
1437	1608	77		.00402	23.5
1608	1773	74		.00468	28.3
1773	1943	75		.00446	26.3
1943	2111	76		.00424	25.2
2111	2277	75		.00446	26.8
2277	2445	77.5		.00393	23.3
2445	2613	76	11	.00424	25.2


GRAPH 4
SILICA (PPM/HR)
100
90
80
70
60
50
40
30
20
TIME IN HOURS
200
500
1000
1500
2000
2500

7. From the experience gained with Gel # 1 and knowing the general behavior of the dialysis, Gel # 2 was prepared. The gel mixture proportion, of silicate to acetic acid was reduced to 1 to 5. This was also the proportion of NaOH to HAc in the buffered dialyzing medium. The gel set in 168 hours. The temperature during the setting of the gel was maintained at $20^{\circ} \pm .2^{\circ}$ C. The temperature from the time of set on was $21^{\circ} \pm 1^{\circ}$ C.

The amount of SiO_2 present in a 10 ml portion of the above gel mixture at zero time was determined colorimetrically. The results of the three samples taken are shown below.

TABLE # 6

Silica at Zero Time

Sample	Reading	Dilution Factor	gm silica
#1	49.5	121	.1813
#2	48.5	121	.1919
#3	48.5	121	.1919

The average is .1881 gm of silica per 10 ml of gel mixture. Knowing this, it is possible to calculate the percent of silica that passes thru the membranes in the dialysis that follow.

Run # 1 for Gel # 2 was conducted in the same manner as Run # 1 of Gel # 1, ie, ten minute dialysis at various intervals of time. Table # 7 and Graph # 5 show the results.

TABLE # 7

Gel # 2 Run # 1

Dialysis #	Time(hr)	Reading	Dilution Factor	Silica(mg)
1	1	48	11	17.75
2	21	36	1	2.66

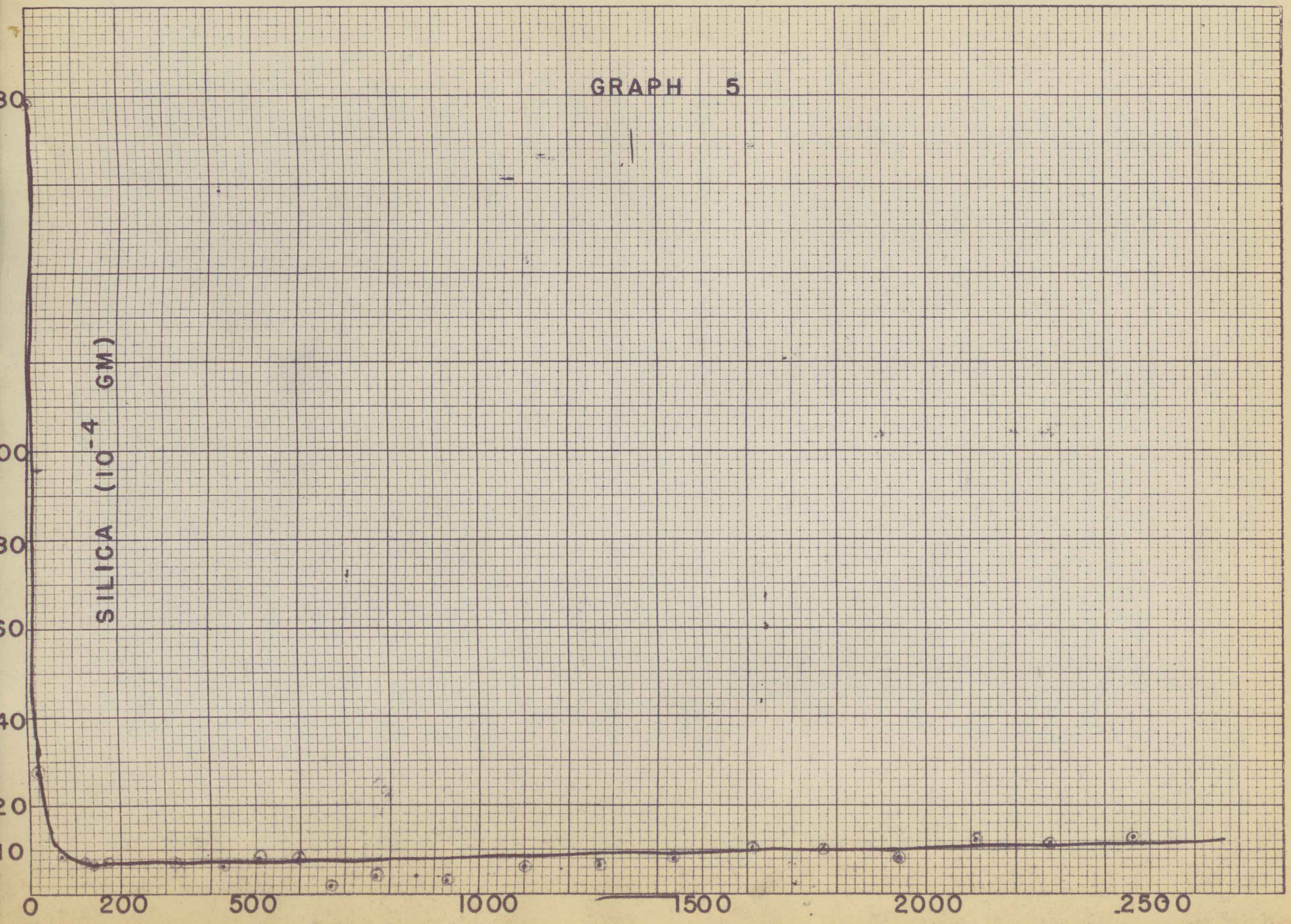

GRAPH 5
SILICA (10-4 GM)
0
200
500
1000
1500
2000
2500

TABLE # 7 (con't)

3	71	60.5	1	.73
4	93	61.5		.69
5	118	63		.63
6	142	65.5		.55
7	168	63.5		.60
8	311	63		.63
9	432	64		.58
10	505	60.5		.73
11	601	60		.75
12	672	80		.17
13	768	74		.28
14	934	76.5		.23
15	1102	66		.50
16	1275	64		.58
17	1438	60		.75
18	1608	56.5		.91
19	1776	56		.92
20	1942	62		.68
21	2110	53.5		1.12
22	2278	54		1.06
23	2446	52	1	1.30

In Run # 2, 10 mls of the gel mixture were placed in a dialysis sack for continuous dialysis at zero time. At intervals, the dialyzing medium was replaced by a fresh medium and the old medium analyzed for silica. In this run, no gel was formed, since the simpler silicic acid molecules dialyzed thru before the necessary polysilicic acid molecules could be built up. The results are shown in Table # 8 and Graph # 6. Here again, mean time was plotted against ppm/hour.

TABLE # 8

Gel # 2 Run # 2

Time		Reading-Dilution Factor		Silica(mg)	ppm/hour
0 to	1	68	121	71.72	71720
1	21	64	121	90.35	4518
21	71	64	11	8.07	161
71	93	50	1	1.33	60.5
93	118	64		.59	23.6
118	142	70		.36	15.0
142	168	70.5		.35	13.5
168	241	68		.43	5.9
241	311	66		.50	7.2
311	432	66	1	.50	2.4

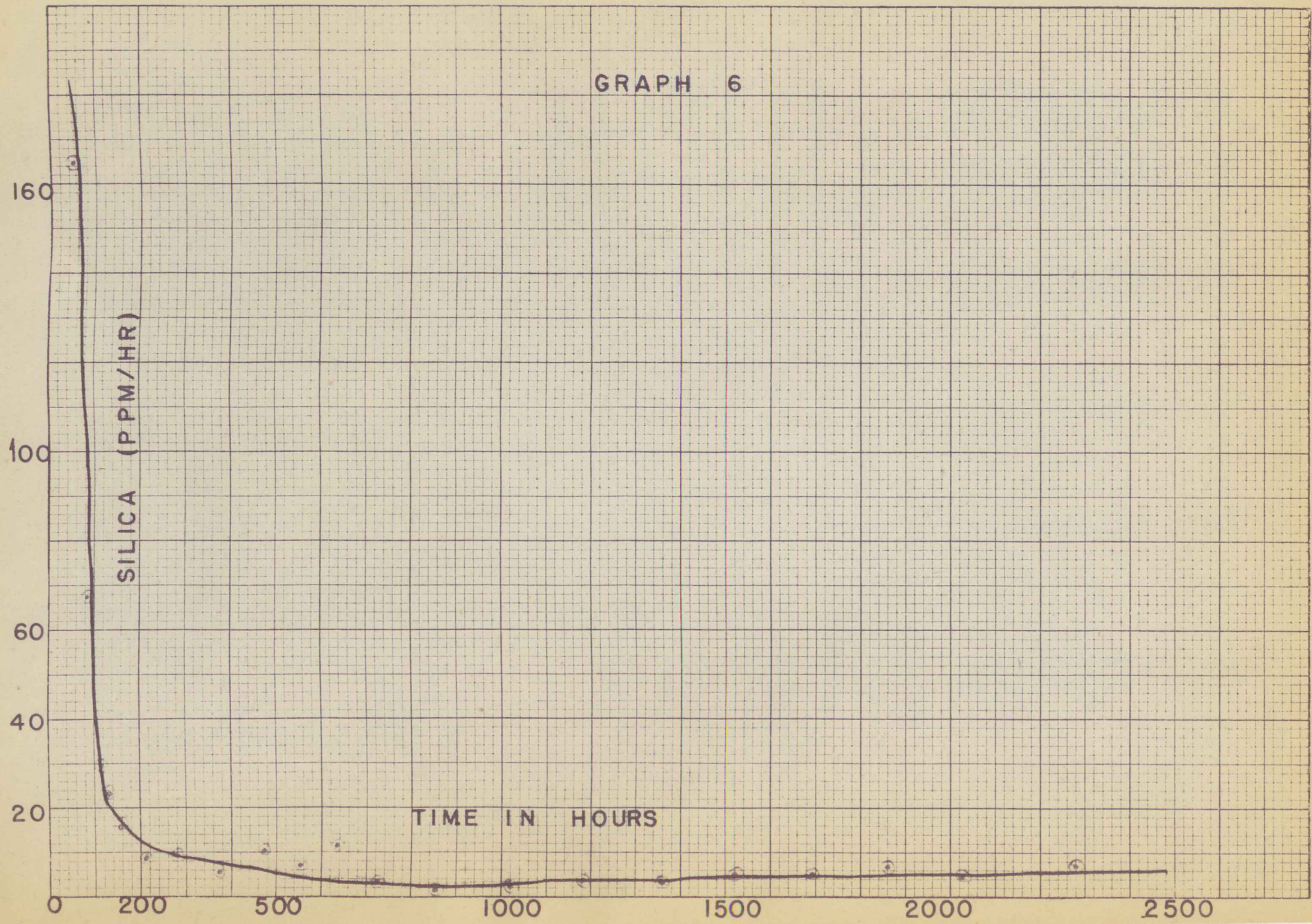

GRAPH 6
SILICA (PPM/HR)
160
100
60
40
20
TIME IN HOURS
0
200
500
1000
1500
2000
2500

TABLE # 8 (con't)

432	505	66.0	1	.58	8.0
505	601	66.0	1	.58	5.2
601	672	65.0	1	.65	3.7
672	768	80.0	1	.17	1.7
768	934	82.0	1	.14	2.1
934	1102	77.5	1	.21	1.2
1102	1275	72.5	1	.30	1.8
1275	1438	69.0	1	.39	2.4
1438	1608	60.5	1	.75	4.3
1608	1776	59.5	1	.79	4.6
1776	1942	58.0	1	.87	5.2
1942	2110	65.0	1	.56	3.3
2110	2278	54 .5	1	1.00	6.0
2278	2446	56.0	1	.92	5.5

In Run # 3, the continual dialysis was not started until one hour had passed. The dialysis sack(and contents) of the first reading in Run # 1 was used here. That is, 10 ml of the gel mixture were placed in a dialysis sack, given a 10 minute dialysis (first reading, Run # 1), then placed in a new dialysing medium for continual dialysis (readings of Run # 3). Here again, the dialysate was replaced at intervals, the old dialysate being analyzed for silica. The results are shown in Table # 9 and Graph # 7.

TABLE # 9

Gel # 2 Run # 3

Time		Reading-Dilution Factor		Silica(mg)	ppm/hr.
1 to	168	44.0	11	21.12	126.3
168	241	72.5	11	4.92	67.4
241	311	48	1	1.47	21.0
311	429	56.5	1	.91	7.5
429	505	60	1	.75	11.3
505	601	59.5	1	.79	8.2
601	672	72.5	1	.30	4.2
672	769	80	1	.17	1.8
769	934	68	1	.43	2.6
934	1102	68	1	.43	2.6
1102	1273	66	1	.50	2.9
1273	1438	66	1	.50	3.0
1438	1608	59.5	1	.79	4.6
1608	1776	59.5	1	.79	4.7
1776	1942	57	1	.89	5.4
1942	2110	64	1	.58	3.4
2110	2278	58.5	1	.85	5.0
2278	2446	55	1	.96	5.7

In Run # 4, the continual dialysis started at the 21st hour. Here, the dialysis sack of reading 2 of Run # 1 was used. The results are shown in Table # 10 and Graph # 7.

TABLE # 10

Gel # 2 Run # 4

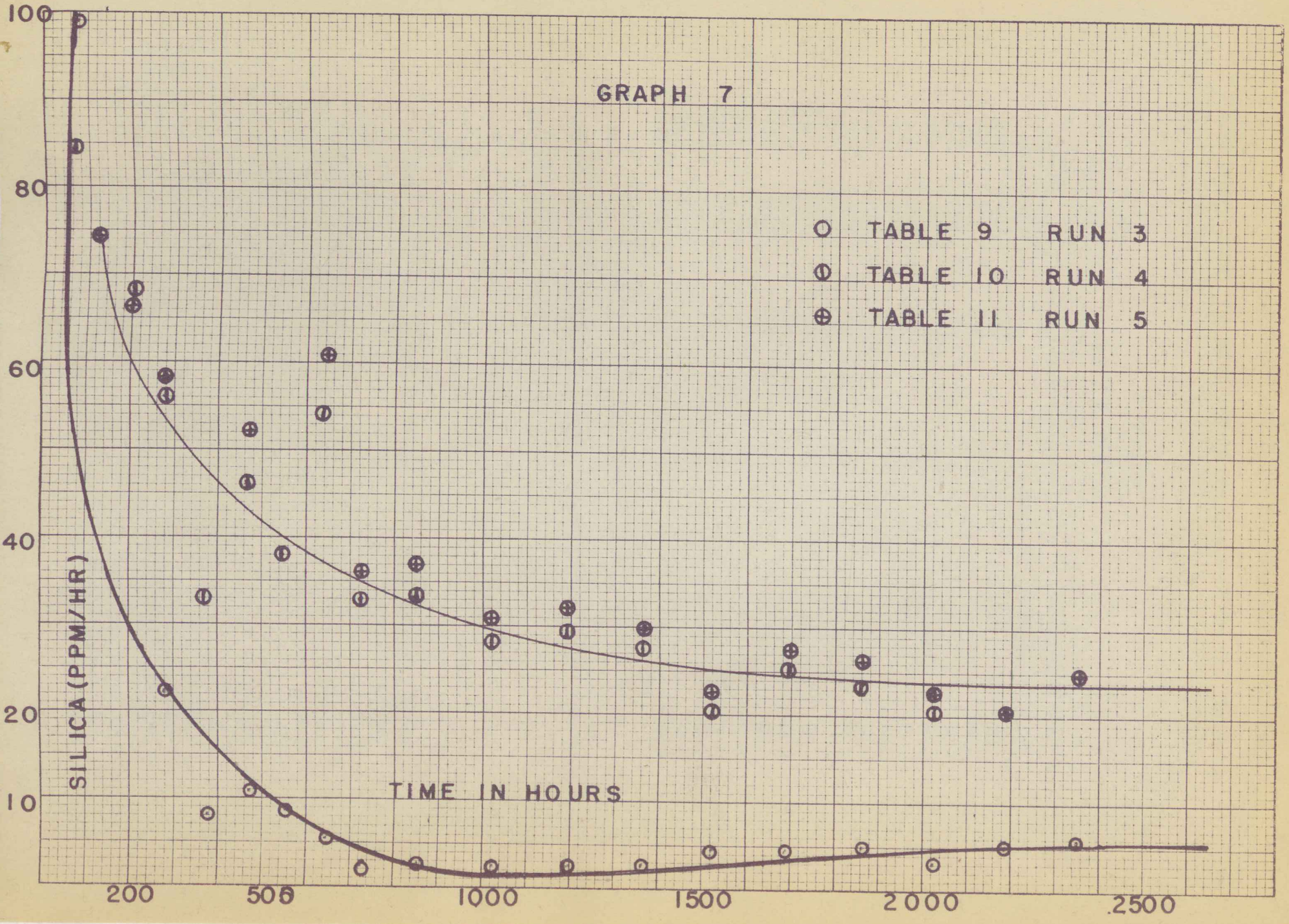
Time	Reading-Dilution Factor		Silica(mg)	ppm/hr.
21 to 168	55.0	11	12.42	84.5
168 241	72.5	11	4.92	67.5
241 311	78	11	3.80	54.1
311 429	78	11	3.80	32.1
429 505	80	11	3.47	45.7
505 601	79	11	3.59	37.4
601 672	78	11	3.80	53.5
672 769	82	11	3.14	32.7
769 934	70	11	5.56	33.8
934 1102	73.5	11	4.74	28.1
1102 1273	72	11	5.04	29.4
1273 1438	75	11	4.46	27.0
1438 1608	80	11	3.47	20.4
1608 1776	76	11	4.24	25.2
1776 1942	77.5	11	3.91	23.6
1942 2110	80.5	11	3.39	20.1
2110 2278	79.5	11	3.50	20.8
2278 to 2446	76	11	4.24	25.1

In Run # 5, the continual dialysis started at the 71st hour. Here, the dialysis sack of reading 3 of Run # 1 was used. The results are shown in Table # 11 and Graph # 7.

TABLE 11

Gel # 2 Run # 5

Time	Reading-Dilution Factor		Silica(mg)	ppm/hr.
71 to 168	66	11	7.17	74.0
168 241	73	11	4.80	65.6
241 311	77	11	4.02	57.6
311 429	76	11	4.24	36.2
429 505	77.5	11	3.91	51.5
505 601	77	11	4.02	41.9
601 672	76	11	4.24	59.8
672 769	80	11	3.47	36.2
769 934	68.5	11	6.11	37.0
934 1102	71	11	5.23	31.0
1102 1273	70	11	5.56	32.6
1273 1438	72.5	11	4.92	29.8
1438 1608	79	11	3.59	21.1
1608 1776	74	11	4.68	27.8
1776 1942	75	11	4.46	26.9
1942 2110	78	11	3.80	22.6
2110 to 2278	79	11	3.59	21.4
2278 2446	76	11	4.24	25.1


GRAPH 7
TABLE 9 RUN 3
TABLE 10 RUN 4
TABLE 11 RUN 5
SILICA (PPM/HR)
TIME IN HOURS
100
80
60
40
20
10
200
500
1000
1500
2000
2500

In Run # 6, the continual dialysis started at the 93rd hour. Here, dialysis sack of reading 4 of Run # 1 was used. The results are shown in Table # 12 and Graph # 8.

TABLE # 12

Gel # 2 Run # 6

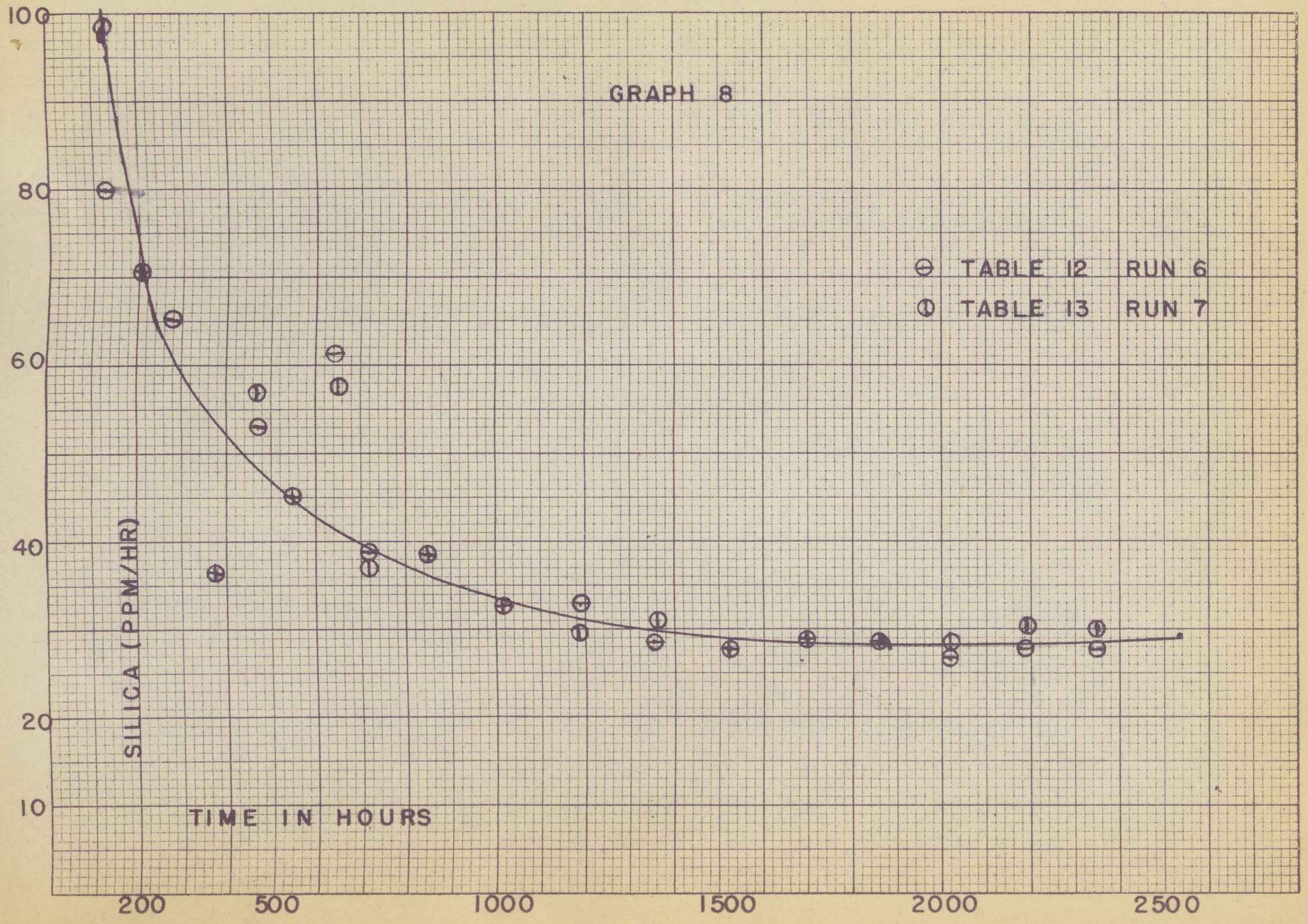
Time	Reading-Dilution Factor		Silica(mg)	ppm/hr.
93 to 168	69	11	5.89	78.5
168 241	72	11	5.04	69.0
241 311	75	11	4.46	63.8
311 429	76	11	4.24	55.9
429 505	77.5	11	3.96	52.0
505 601	76	11	4.24	42.4
601 672	76	11	4.24	59.6
672 769	78.5	11	3.69	38.4
769 934	68	11	6.33	38.5
934 1102	70.5	11	5.40	32.2
1102 1275	70	11	5.56	32.5
1275 1438	73.5	11	4.74	28.7
1438 1608	74	11	4.68	27.5
1608 1776	73.5	11	4.74	28.2
1776 1942	74	11	4.68	28.2
1942 2110	75	11	4.46	26.6
2110 2278	74	11	4.68	27.8
2278 to 2446	74	11	4.68	27.8

In Run # 7, the continual dialysis started at the 118th hour. Here, dialysis sack of reading 5 of Run # 1 was used. The results are shown in Table # 13 and Graph # 8.

TABLE # 13

Gel # 2 Run # 7

Time	Reading-Dilution Factor		Silica(mg)	ppm/hr.
118 to 168	73	11	4.80	96.0
168 241	72	11	5.04	69.0
241 311	75	11	4.46	64.0
311 429	76.5	11	4.13	35.0
429 505	76	11	4.24	55.9
505 601	76	11	4.24	44.1
601 672	77	11	4.02	56.5
672 769	79	11	3.59	37.4
769 934	68	11	6.36	38.6
934 1102	70.5	11	5.40	32.2
1102 1275	72	11	5.04	29.4
1275 1438	72	11	5.04	30.5
1438 1608	75	11	4.46	26.2
1608 1776	74	11	4.68	27.8
1776 1942	73	11	4.80	28.9
1942 2110	74.5	11	4.57	27.2
2110 2278	72	11	5.04	30.0
2278 to 2446	73	11	4.80	28.6


GRAPH 8
TABLE 12 RUN 6
TABLE 13 RUN 7
SILICA (PPM/HR)
TIME IN HOURS
100
80
60
40
20
10
200
500
1000
1500
2000
2500

In Run # 8, the continual dialysis started at the 142nd hour. Here, the dialysis sack of reading 6 of Run # 1 was used. The results are shown in Table # 14 and Graph # 9.

TABLE # 14

Gel # 2 Run # 8

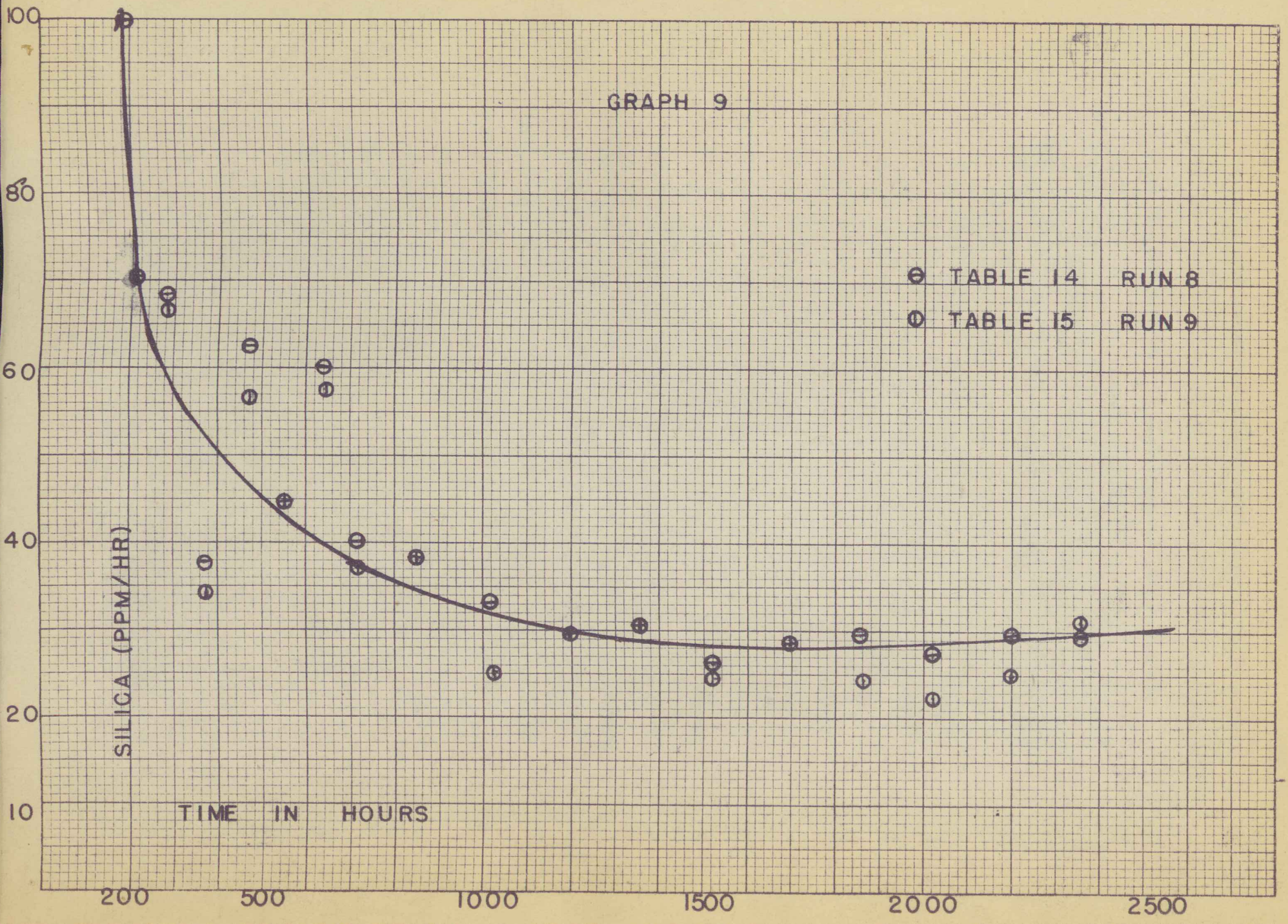
Time		Reading-Dilution Factor		Silica(mg)	ppm/hr.
142 to	168	79	11	5.59	138
168	241	72	11	5.04	69
241	311	74	11	4.68	66.9
311	429	75.5	11	4.35	36.8
429	505	74	11	4.68	61.5
505	601	76	11	4.24	44.1
601	675	76	11	4.24	59.5
675	769	78	11	3.80	39.6
769	934	68	11	6.55	58.4
934	1102	70	11	5.56	33.1
1102	1273	72	11	5.04	29.4
1273	1438	72	11	5.04	30.5
1438	1608	75	11	4.46	26.2
1608	1776	73.5	11	4.74	28.2
1776	1942	73	11	4.80	28.9
1942	2110	74	11	4.68	27.9
2110	2278	72	11	5.04	30.0
2278 to	2446	73	11	4.80	28.6

In Run # 9, the continual dialysis started at the 168th hour. Here, the dialysis sack of reading 7 of Run # 1 was used. The results are shown in Table # 15 and Graph # 9.

TABLE # 15

Gel # 2 Run # 9

Time		Reading-Dilution Factor		Silica(mg)	ppm/hr.
168 to	241	72	11	5.04	69.0
241	311	75	11	4.46	63.8
311	429	77	11	4.02	34.1
429	505	76	11	4.24	55.7
505	601	76	11	4.24	44.0
601	675	77	11	4.02	56.7
675	769	79.5	11	3.53	36.8
769	934	68	11	6.56	38.6
934	1102	76	11	4.24	25.2
1102	1273	70	11	5.56	32.6
1273	1438	71.5	11	5.13	31.0
1438	1608	76	11	4.24	24.9
1608	1776	73.5	11	4.74	28.2
1776	1942	77	11	4.02	24.2
1942	2110	78	11	3.80	22.6
2110	2278	76	11	4.24	25.2
2278	2446	72	11	5.04	30.0


GRAPH 9
TABLE 14 RUN 8
TABLE 15 RUN 9
SILICA (PPM/HR)
TIME IN HOURS
100
80
60
40
20
10
200
500
1000
1500
2000
2500

8. The percent of silica that passed thru the membrane in each Run of Gel # 2 is given in Table # 16. This percent is based on the total amount of silica present at zero time.

TABLE # 16

Percent of Silica Dialyzing Thru

Run #	Total Amount of Silica	% thru
2	.1821	96.9
3	.0549	29.2
4	.0743	39.4
5	.0827	43.9
6	.0863	45.9
7	.0852	45.1
8	.0856	45.5
9	.0896	47.6

All the graphs show a rapid initial decrease in the amount of silica that passed thru the membranes. However, the amount of silica that passed thru did not decrease to a zero value. In each case, the amount remained indefinitely at a nearly constant, finite value.

SUMMARY

1. Winkler's method for the colorimetric determination of silica has been adapted to handle amounts of silica up to .1 gram with an accuracy of ±2%.

2. After 2800 hours of being in a fairly strong acid medium, collodion membranes showed no visible signs of deterioration.

3. These experiments have shown that the amount of silica dialyzing thru a collodion membrane from a silicic acid gel mixture of sodium silicate and acetic acid is relatively large immediately after the hydrosol has been formed but as the age of the hydrosol increases, this amount falls off sharply.

4. A significant fact is that a certain minimum amount of silica continues to dialyze out of the mixture up to and even passed the time of set.

5. The presence of an equilibrium between polysilicic acid molecules and simple silicic acid molecules in a set gel has been proven to exist. Although the equilibrium is disturbed by the removal of the simple acid molecules, degradation of polysilicic acid molecules re-establishes this equilibrium.

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* *

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