THESIS

BY

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A STUDY OF THE NATURE OF THE ADSORPTIVE PROPERTY OF FULLER'S EARTH.

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Class 1921.

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Introduction.

There is a large industrial demand for an inexpensive adsorptive material for clarifying various liquids such as lubricating oils and numerous aqueous solutions. This demand has been met chiefly by charcoal and two classes of earths, namely, fuller's earth and diatomaceous earth. Fuller's earth is a clay or kaolin of an indefinite composition. It consists largely of a hydrated aluminum silicate ($Al_2O_3 \cdot 2SiO_2 \cdot 2H_2O$) with small amounts of calcium oxide, magnesium oxide, titanium oxide, etc. Diatomaceous earth, also known as kieselguhr, is on the other hand an almost pure silica with traces of aluminum oxide and others of the above impurities. Its formation results from the deposition of the remains of minute microorganisms. It consequently has a very large internal surface. Large deposits of both of these materials are found in various parts of the globe.

Very little is known as to the nature of the adsorptive power of these materials, and consequently no definite procedure as to use, treatment, or revivification is available that has as a basis real scientific facts. The adsorptive power, however, has been shown to be practically independent of the composition of the adsorbent. It has been thought by some[1.] to be connected with the "acidity" of the adsorbent.

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1. C. L. Parsons, "Fuller's Earth." Bull. 71, Bureau of Mines.

W. D. Bancroft, however, attributes the apparent acidity to selective adsorption of bases, and asserts that actual acidity is not an essential to adsorption.

The following simple empirical relation between the amount of substance adsorbed (x) from solution, the equilibrium concentration (c) of the solution, and the weight of the adsorbent (w) has been found to hold for relatively large concentration changes for many types of adsorption.

$$x/w = \alpha\, c^{\frac{1}{n}}$$

α and 1/n are constants which depend upon the nature of the solvent, adsorbent, and adsorbed material. Adherence to this equation has been tested in a few instances for adsorption by fuller's earths etc., but no extensive data are available on the subject. The results of Pelet and Grande, and of Atherton Sidell, who made a few experiments with these earths, will be considered later.

Object.

This investigation was undertaken in order to determine whether the adsorption of dyes from aqueous solution by means of fuller's earth is in accordance with the above adsorption equation, and if so to determine the constants α and 1/n. By obtaining these constants for various fuller's earths, diatomaceous earths, silicas, etc., under the same conditions and with the same solute and solvent, a basis of comparison of the earths is afforded, and some light shed upon the nature of the active adsorbing constituent.

Adsorbents Employed.

Various adsorbents were employed in this investigation, namely, fuller's earths, diatomaceous earths, artificial sodium aluminum silicate, silicic acid, charcoal, sand, and alumina.

The fuller's earths were from three different sources. One of these was obtained from Midway Florida in three different meshes, 30-60 mesh, 60-100, and 100 up. Another of 100 mesh was obtained from the C. W. Hill Chemical Co. Its source is unknown. Two samples of fuller's earth were obtained from the Standard Oil Co. One sample was a natural earth, and the other the earth after it had been subjected to an acid treatment. This treatment increases to a very great degree the power of this earth to clarify lubricating oils for which purpose it is used very extensively. These two samples are referred to as the untreated and treated Standard Oil Earths. The treated sample does not cause water to become acid to litmus, but a one gram sample of it is equivalent to about 5.6 cc. of .1 N acid when the titration is performed in the presence of the earth and phenolphthalein used as indicator.

The following table gives the analysis of a typical batch of the treated Standard Oil Co. earth which they furnished with the sample.

Celite, a diatomaceous earth, was also used. It is mined at Lompoc, California, and is used extensively in filtering. It is extremely light and porous. Its analysis is given below.

		Celite.		Standard Oil Earth	
		As rec'd.	Dry basis	(treated)	
Silica	SiO_2	80.05%	89.24%	66.3%	73.9%
Alumina	Al_2O_3	1.34	1.49	21.4	20.4
Iron Oxide	FeO	1.54	1.77	1.9	0.7
Titanium Oxide	TiO_2	0.80	0.88	——	trace
Lime	CaO	0.03	0.03	0.5	0.7
Magnesia	MgO	0.00	0.00	3.6	3.1
Loss on ignition		4.78	5.33	6.3	8.0
Moisture	H_2O	10.28	——	——	——
Undetermined		1.13	1.26	——	——
	Total	1100.00	100.00	100.00	105.80

The silicic acids employed were from two different sources. One was Merck's pure silicic acid, and the other was prepared in this laboratory by adding a slight excess of HCl to a sodium silicate solution. The gel was washed free from acid, and dried at 100–105 degrees C. All of these were ground to 100 mesh.

An earth was artificially prepared by adding a concentrated solution of sodium silicate to a concentrated solution of sodium aluminate. The precipitate was filtered and washed until it gave only a faint pink color with phenolphthalein. This slight alkalinity, which could not be removed, was likely due to the hydrolysis of the sodium aluminum silicate. This earth was not analyzed, but according to A. S. Cushman[1] the composition

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[1] "The Colloid Theory of Plasticity," Trans. Am. Ceramic Soc. vol. 6.

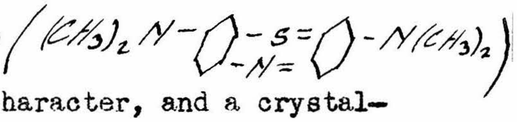
of the earth prepared in this way is

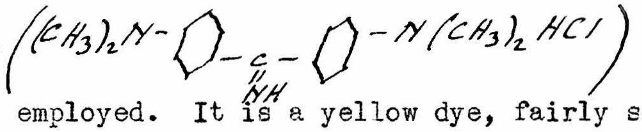
Silica	46.1%
Alumina	26.1
Soda	15.8
Water	12.0

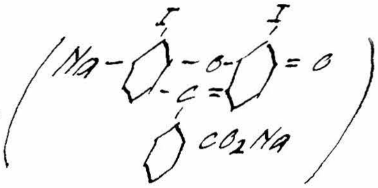
This corresponds to the formula $Na_2O\cdot Al_2O_3\cdot 3SiO_2\cdot 3H_2O$.

The sand employed was pure sea sand. It was ground to pass 100 mesh. Part became so fine on grinding that it remained suspended when placed in water, and would not settle out completely even on centrifuging. The material was hence separated by sedimentation and only the heavier part used for experiments.

Dyes Employed.

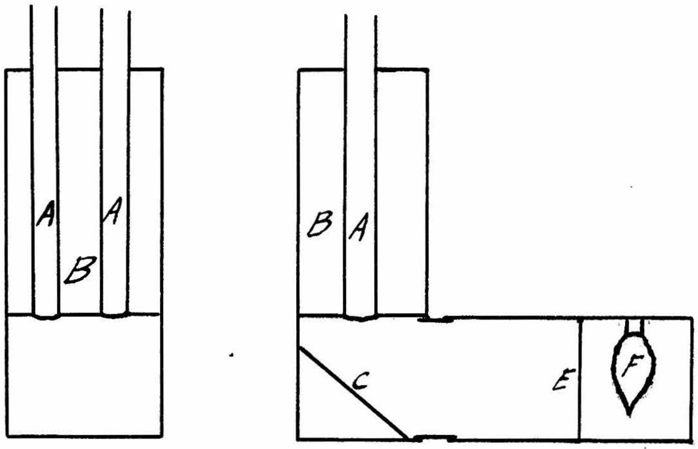
For most of the experiments methylene blue  was employed. It is a deep blue dye of basic character, and a crystalloid which forms true solutions. There are a number of reasons for this choice, first the fact that it is appreciably soluble in water, second that it is unaffected by acids and is precipitated only with concentrated alkalies, third that basic dyes are strongly adsorbed, fourth that it is a crystalloid and thus avoids all complications of colloidal action, and fifth that the concentration of methylene blue solutions can be determined very simply by colorimetric means.

Auramine  another basic dye, was also employed. It is a yellow dye, fairly soluble in water. The concentration of its solutions can be readily determined colorimetrically and in general it possesses the same advantages as methylene blue.

Erythrosine  is an acid dye that was employed. It was used to obtain any relations between the adsorption of the two distinctive types of dye. It has a bright red color, and also lends itself readily to colorimetric analysis. It has, however, the disadvantage that it is precipitated by a slight excess of acid.

Colorimetric Analysis.

The simplest and most convenient method of determining the concentration of the dye solutions was found to be by colorimetric comparisons. A simple colorimeter which served the purpose satisfactorily is shown diagrammatically in the following figure.



It consists of a wooden case B. with two openings above to admit 100 cc. Nestler tubes A, and slightly smaller openings below over which the bottom of the tubes rest. This is supported on a box open on one side to the source of light. An inclined white porcelain plate C served as a reflector. A mirror was tried but it proved to give too bright an illumination for the concentration of solutions matched. E is a frosted glass plate; F a tungsten lamp (40 watts). The entire inside of the apparatus was painted black to eliminate counter reflections. The apparatus was at first used without the artificial light, and set so as to face a large window, just outside of the range of the direct rays of the sun. Due to variations in the intensity and nature of the light, and the fact that analysis could not be made at night or on dark cloudy days, it was deemed advisable to employ artificial light. The device used does not give a pure white light but a yellowish light which imparts a greenish color to the methylene blue solutions. It was found by experiment that this did not interfere with the colorimetric comparisons. On the contrary, it was slightly advantageous as an increase of depth not only varied the intensity of the color, but also produced a slight color change from green to blue. A black hood was used over the apparatus when employing artificial light to cut out the light from the room. With erythrosine and auramine solutions, on the other hand, it was found that natural light gave more reproducible and reliable results than artificial light.

The best concentration for matching the three dyes employed ranges from .0002 to .0006 grams per liter for a height of column of solution of eight inches (8 in. column = 100 cc.). The standard used for the investigations with methylene blue contained .0004145 grams per liter. This was just one-tenthousandth of the concentration of the stock solution (4.145 g. per l.) used for making up solutions for adsorption. The standards of auramine and erythrosine contained .0004467 and .0006295 grams per liter respectively, and were just one-fivethousandth of the concentration of the stock solution. Solutions to be matched were diluted to approximately the concentration of the standards, and then the height of the solution in the Nestler tubes varied until the depth of color was identical. The heights were measured with a scale 32 divisions equal to 8 inches or 100 cc., on which tenths of a division could be read (about .3 of a cc.). The error from readings did not exceed on half division or fifteen hundredths percent.

The following results on a series of solutions of unknown concentration show the degree of accuracy of the colorimetric analysis of methylene blue. The concentrations are given in terms of one of the solutions as unity.

Natural Light.

Obs. conc.	Cal. conc.	% error.
.620	.574	+ 7.4
.500	.424	+15.2
.495	.473	+ 4.4
.322	.326	– 1.2
.308	.279	+ 9.4
.502	.506	– 0.8
.638	.604	+ 5.3
	Av.	6.24%

Artificial Light.

Obs. conc.	Cal. conc.	% error
.830	.735	+ 12.9
.530	.506	+ 4.7
.770	.683	+ 11.1
1.020	1.00	+ 2.0
.630	.580	+ 8.6
.980	.856	+ 14.5
	Av.	8.90%

In the case of the comparisons using artificial light all errors are in the same direction, and an error in the standard was suspected. The same series of solutions was therefore referred to a new standard with the results given in the following table.

Artificial Light.

Obs. conc.	Cal. conc.	% error.
.780	.735	+ 6.1
.496	.506	– 2.0
.745	.683	+ 9.1
.947	1.013	– 6.5
.574	.580	– 1.0
.878	.856	+ 2.6
	Av.	4.55%

From these data it may be assumed that the analyses are reliable to at least seven percent.

Experiments showed that glassware in which the solutions to be matched were placed should not be wiped out with towels as the slightest amount of lint adsorbs sufficient of the dye from solution to appreciably affect the concentration. It was found that an error of from ten to twenty percent could readily be caused by a scarcely visible amount of lint in the Nestler comparison tubes.

The following data give the results of the colorimetric analysis of a series of erythrosine solutions of unknown concentration. The same set of solutions are shown in both columns, but were matched against standards of different concentrations.

Obs. conc.	Cal. conc.	% error	Obs. conc.	Cal. conc.	% error.
1.765	1.71	+ 3.2%	.570	.585	– 2.6%
1.290	1.28	+ 0.8	.711	.746	– 4.7
1.420	1.39	+ 2.1	.784	.812	– 3.4
1.995	1.96	+ 1.8	1.110	1.14	– 2.6
1.145	1.115	+ 2.7	.613	.650	– 5.7
1.600	1.75	+ 8.6	.892	1.02	–10.8
		Av. 3.2%			Av. 4.9%

Procedure.

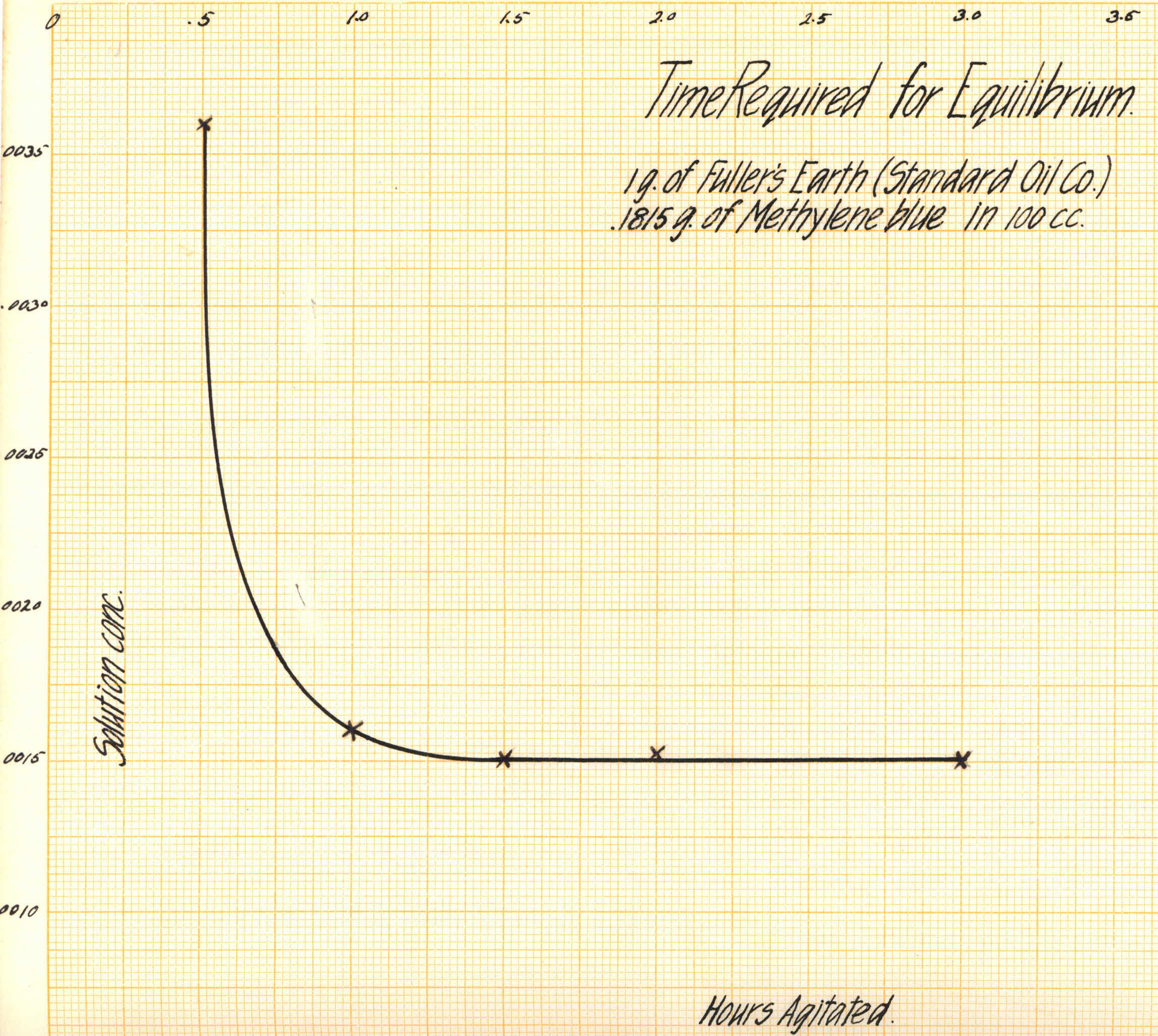
The adsorption mixtures were made up in 150 cc. glass stoppered bottles by weighing a definite amount of earth into the bottle, and then pipetting in the amount of water and of stock dye solution necessary to make 100 cc. of solution of the desired concentration. The bottles containing these mixtures were placed on a rotary agitating device in such a way that they were turned end over end thirty to forty times per minute. The time of agitation varied for different samples, and will be considered under the heading of "Equilibrium."

In order to determine the concentration of the solutions they were decanted into 100 cc. oil sample bottles, and centrifuged in a milk tester centrifugal for 15–30 minutes. This time was adequate in most cases for separating the earth from the dye solution. Experiments showed that when a solution was once clear, further centrifuging did not affect the concentration. Samples were then pipetted off and diluted for analysis. In a few cases solutions had to be recentrifuged after dilution.

Equilibrium.

The graph on the following page shows the effect of time of agitation on the amount of dye adsorbed. For this case, and cases of lower initial concentration, two hours was found to be adequate. The time for equilibrium to be established, however, increases with an increase of initial concentration, and also varies with the adsorbent. To be assured that equilibrium had been reached in every case all the samples were agitated for 10-20 hours, and those of higher concentration were analyzed, reagitated for at least eight hours, and again analyzed until the change in concentration was negligible. The time of agitation is given in the tables of data for each sample.

The reversibility of adsorption was tested in a number of instances, giving further indications that equilibrium had been established. This is shown in Table I, Series 4., Table VII, Series 1., and Table VIII, Series 1. Points No. $3^{rev.}$ and $4^{rev.}$, Table I, Series 4 show less adsorption than No. 3 and 4, thus indicating that on diluting the solution part of the adsorbed dye returned to the solution. If equilibrium conditions had not been reached the dye would not have reverted to the solution. A similar indication, but less apparent, is given in Table II, Series 1., in which the amount of adsorbent was increased in samples No. 3 and 4. The amount of dye adsorbed per unit of adsorbent decreased. This shows that part of the dye was given up by the original earth, and taken up by that added.



Time Required for Equilibrium.

1 g. of Fuller's Earth (Standard Oil Co.)
.1815 g. of Methylene blue in 100 cc.

Temperature Effect.

As convenient facilities were not available for agitating the mixtures in a thermostat, they were rotated at room temperature, and hence were subjected to a certain temperature variation. It was found, however, that this temperature change had a negligible effect on the equilibrium. The agitating apparatus was placed on an exposed porch on a cool night. The air temperature at 8 a. m. when the run was completed was 8.5° C and 15° C respectively on two different occasions. The average temperature throughout the night may be assumed not to have exceeded this final temperature. The agitating apparatus was also placed under a hood in which a temperature of 36° was maintained by means of an electric hot plate. Following is the experimental data. Each of the two samples was subjected to the three different temperatures.

No. of Sample.	Time of Agitation.	Temperature.	Equilibrium Conc.
1	14 hr.	8.5° C max.	.657
2	14 "	8.5° C max.	1.018
1	16 "	15° C mas.	.650
2	16 "	15° C max.	1.015
1	24 "	36° C av.	.664
2	24	36° C av.	1.030

The deviation in equilibrium concentration is obviously within the experimental error and the variations in temperature in these experiments were much greater than would be met under the usual experimental conditions, and hence no temperature regulation is necessary.

Accuracy of Results.

It was shown under the heading "Colorimetric Analysis" that the error for the determination of the concentration of methylene blue was less than seven percent, and still less for erythrosine. The error arising from the dilution of the samples to the desired concentration for analysis is entirely negligible in comparison with the analytical error. It may hence be assumed that the equilibrium concentrations were determined with an accuracy of at least seven percent.

The amount adsorbed per unit of weight of adsorbent (x/m) is given by the following relation:

$$x/m = \frac{(C_o - C)V}{m}.$$

All of these quantities can be determined very accurately with the exception of the equilibrium concentration (C) which is reliable to about seven percent. In order to make the error in the amount adsorbed quite small, (C) must be small in comparison with (C_o) the initial concentration. Preliminary experiments were run with the different earths in order to determine the amounts of earth and the initial concentrations necessary for obtaining the greatest degree of accuracy. With the exception of the data for sand and alumina (with methyline blue), the maximum error in the amount adsorbed is seven tenths percent. This was calculated from point No. 1, Table No. II, Series No. 3 (Artificial Earth). An average error in the amount adsorbed for a seven percent error in the equilibrium concentration is four hundredths percent. It may hence be assumed that the error in the amount adsorbed is negligible in most cases in comparison with the error in the equilibrium concentration. This means that the points in the logarithmic curves can be shifted only seven percent in a vertical direction, and not at all horizontally; and the resulting error in 1/n should not be greater than ten percent.

In the case of sea sand the degree of accuracy of the data is less than in the other cases, due to the relatively small concentration changes. For an error of seven percent in the equilibrium concentration an error of one and one-half percent might result in the amount adsorbed, and an error of ten to twenty-five percent in the value of 1/n.

Data.

The empirical adsorption equation

$$x/m = \alpha c^{1/n}$$

is a logarithmic relation which may be written

$$\log x/m = \log \alpha + 1/n \log c.$$

If the logarithms of the amount adsorbed per unit weight of adsorbent are plotted against the logarithms of the equilibrium concentration, a straight line will result if the relation holds. The constant 1/n is represented by the slope of the line, and $\log \alpha$ by the value of log x/m at the intercept with the logarithm of unit concentration. The value of 1/n given in the following tables was calculated from the slope of the most representative line through the logarithmically plotted points, and α calculated for the concentration of one gram per liter.

TABLE I. METHYLENE BLUE AND NATURAL EARTHS.

Series 1. Fuller's Earth (Midway, Florida) 100 mesh.

$1/n = .0667$ $\alpha = .0980$

No.	Hr. rotated.	Wt. earth (g)	Equilibrium conc. (g. per l.)	Adsorbed (g.perg.of earth)	Orig. g. dye pres.	Vol. (cc.)
1.	17	1.900	.00195	.0654	.1243	100
1'	23	1.900	.00778	.0706	.1347	80 (a)
2	17	2.003	.00925	.0720	.1450	100
2'	23	2.003	.0256	.0764	.1554	95 (a)
3	17	2.004	.0451	.0807	.1658	100
3'	23	2.004	.0940	.0833	.1760	95 (a)
4	17	2.203	.135	.0868	.2073	120
4'	23	2.203	.136	.0866	.2060	115 (b)

Series 2. Fuller's Earth (Midway, Florida) 60–100 mesh

$1/n = .0678$ $\alpha = .113$

No.	Hr. rotated.	Wt. earth (g)	Equilibrium conc. (g. per l.)	Adsorbed (g.perg.of earth)	Orig. g. dye pres.	Vol. (cc.)
5	4	2.018	.00156	.0724	.1450	100
4	23	2.528	.00690	.0816	.2070	100
3	8	2.002	.00870	.0825	.1658	100
3'	13	2.002	.0167	.0871	.1760	95 (a)
2	8	2.000	.0408	.0911	.1867	110
2'	13	2.000	.0688	.0947	.1968	105 (a)

Series 3. Fuller's Earth (Midway, Florida) 30–60 mesh

$1/n = .0663$ $\alpha = .0994$

No.	Hr. rotated.	Wt. earth (g)	Equilibrium conc. (g. per l.)	Adsorbed (g.perg.of earth)	Orig. g. dye pres.	Vol. (cc.)
1	16	1.706	.000617	.0608	.1036	100
2	16	1.631	.00106	.0634	.1036	100
3	16	1.514	.00324	.0682	.1036	100
4	16	1.455	.00693	.0708	.1036	100

(a) The prime numbered solutions were made by adding 5 cc. more dye solution to the same numbered solutions after removing that required for analysis.

(b) Removed 10 cc. for analysis from No. 4 and added 5 cc. of water.

Series 4. Fuller's Earth (Midway, Florida) 100 mesh from 60

$1/n = .0635 \quad \alpha = .115$

No.	Hr. rotated	Wt. earth (g)	Equilibrium Conc. (g. per l.)	Adsorbed (g. per g. of earth)	Orig. g. dye pres.	Vol. (cc.)
1	4	2.001	.00516	.0827	.1658	100
2	4	2.001	.0257	.0919	.1865	100
$3^{rev.}$	4 more	2.000	.0688	.0978	.2027	105 (d)
3	10	2.000	.0917	.0988	.2070	100
$4^{rev.}$	4 more	2.100	.0976	.1002	.2211	105 (d)
4	10	2.100	.155	.1013	.2280	100

Series 5. Fuller's Earth (C. W. Hill Chem. Co.)

$1/n = .0675 \quad \alpha = .174$

6	5	1.378	.00062	.1050	.1450	100
8	5	1.322	.00098	.1095	.1450	100
4	5	1.263	.00213	.1150	.1450	100
3	5	1.020	.00447	.1213	.1243	100
7	29	1.151	.00895	.1253	.1450	100

Series 6. Fuller's Earth (Standard Oil Co.) Treated. 21.7% water and volatile.

$1/n = .0706 \quad \alpha = .344$

3	6	1.001	.000704	.2069	.2070	100
2	7	1.001	.00123	.2176	.2177	100
5	10	..932	.00166	.2220	.2070	100
4	6	1.002	.00314	.2277	.2280	100
6	15	.860	.00720	.2430	.2070	100
1	16	1.007	.00850	.2480	.2488	100

Maximum Adsorption

1s	94	1.004	.650	.2712	.3362	100
1	51 days(e)	1.301	.576	.2740	.4145	100
1	71 days	1.301	.578	.2740	.4145	90
2	51 days	1.360	.448	.2720	.4145	100
2	71	1.360	.405	.2745	.4145	90
2s	94 hr.	1.000	.294	.2648	.2942	100
4s	116 hr.	1.002	.1215	.2611	.2733	100
4s	152 hr.	1.002	.0928	.2640	.2733	90
3s	94 hr.	1.000	.0810	.2614	.2695	100
3s	130	1.000	.0387	.2656	.2695	90

(d) Removed 45 cc. and replaced with 50 cc. water.

(e) Where the time is given in days the samples were shaken by hand several times a day, and agitated on the agitator when it was not in use.

Series 7. Fuller's Earth (Standard Oil Co.) Untreated. 100 mesh.

$1/n = .0595$ $\alpha = .477$

No.	Hr. rotated.	Wt. earth (g)	Equilibrium conc. (g. per l.)	Adsorbed (g. per g. of earth)	Orig. g. dye pres.	Vol. (cc.)
3	32	.3400	.000530	.3042	.1036	100
1	32	.3300	.000865	.3140	.1036	100
2	32	.3205	.00160	.3233	.1036	100
4	32	.3095	.00294	.3342	.1036	100

Series 8. Diatomaceous Earth (Celite) 10.4% water and volatile.

$1/n = .0654$ $\alpha = .0279$

3	15	11.903	.000847	.0174	.2070	100
6	20	5.493	.00265	.0188	.1036	100
1	15	8.652	.00288	.0191	.1650	100
8	20	6.394	.00364	.0194	.1243	100
4	15	5.132	.00635	.0201	.1036	100
5	15	6.696	.0173	.0214	.1450	100
2	40	7.006	.0576	.0229	.1650	100

Series 9. Silica (Sea Sand) 100 mesh

$1/n = .0695$ $\alpha = .000838$

1	60+	62.482	.0151	.000625	.04055	100
2	60+	48.772	.0740	.000698	.04145	100

TABLE II. METHYLENE BLUE AND ARTIFICIAL ADSORBENTS.

Series 1. Silicic Acid. (Merck) 100 mesh. 11.8% water.

$1/n = .143$ $\alpha = .0657$

4'	6 more	3.324	.00448	.0305	.1020	90 (f)
4	28	3.284	.00523	.0310	.1020	100
3'	6 more	3.203	.00600	.0317	.1025	90 (f)
6	40+	3.149	.00693	.0327	.1036	100
1	28	3.102	.00870	.0329	.1032	100
5	60+	3.082	.00987	.0333	.1036	100
3	28	2.978	.0106	.0341	.1025	100

(f) Added more earth to Nos. 3 and 4.

Series 2. Silicic Acid (Dr. S. J. Bates) 100 mesh

$1/n = .151 \qquad \alpha = .225$

No.	Hr. rotated	Wt. earth (g)	Equilibrium conc. (g. per l.)	Adsorbed. (g. per g. of earth)	Orig. g. dye pres.	Vol. (cc.)
1x	12+	2.000	.0002	.0622	.1243	100
1y	12+	2.222	.000370	.0652	.1450	100
2x	12+	2.000	.000368	.0725	.1450	105 (g)
2y	12+	2.222	.000560	.0746	.1658	105 (g)
3x	12+	2.000	.00133	.0828	.1658	85
3y	12+	2.222	.00143	.0838	.1865	85
4x	20	2.000	.00246	.0930	.1865	80
4y	20	2.222	.00274	.0931	.2070	80
5x	26	2.000	.00683	.1031	.2070	75
5y	26	2.222	.00752	.1023	.2280	75

Series 3. Artificial Earth 20.5% water.

$1/n = .159 \qquad \alpha = .0502$

3	20	2.502	.00995	.0244	.0621	100
3'	10 more	2.502	.0266	.0279	.0725	95 (h)
1	20	2.501	.0439	.0312	.0828	110
2	27	2.755	.0752	.0342	.1036	125
1'	10 more	2.501	.0872	.0337	.0933	105 (h)

Series 4. Animal Charcoal (Kahlbaum)

$1/n = .134 \quad \alpha = .351$

6	6	1.328	.00239	.1560	.2070	100
4	6	1.256	.00353	.1650	.2070	100
5	6	1.204	.00527	.1715	.2070	100
3	22	1.102	.00829	.1870	.2070	100
2	22	1.005	.0164	.2040	.2070	100

Series 5. Alumina

1/n approaches α is indeterminate

3'	40	166.49	.0820	.000163	.0414	175 (i)
3	20	112.80	.0706	.000253	.0414	185
4	20	91.74	.0772	.000296	.0414	185
4'	40	91.74	.0740	.000310	.0414	175

(g) Added 5 cc. more dye sol. to each successive number of x and y.

(h) Added 5 cc. more dye sol. to Nos. 1 and 3.

(i) Added more alumina to No. 3.

TABLE III. METHYLENE BLUE AND CALCINED ADSORBENTS.

Series 1. Fuller's Earth (Standard Oil Co.) Treated. Calcined at 320° C for 7 hr.

$1/n = .0615$ $\alpha = .270$

No.	Hr. rotated	Wt. earth (g)	Equilibrium conc. (g. per l.)	Adsorbed (g. per g. of earth)	Orig. g. dye pres.	Vol. (cc.)
1	60	.552	.00241	.1875	.1036	100
2	60	.530	.00487	.1945	.1036	100
3	60	.500	.0112	.2050	.1036	100
4	60	.482	.0252	.2110	.1036	100

Series 2. Diatomaceous Earth (Celite) Calcined at 320° for 8 hr.

$1/n = .0621$ $\alpha = .0258$

No.	Hr. rotated	Wt. earth (g)	Equilibrium conc. (g. per l.)	Adsorbed (g. per g. of earth)	Orig. g. dye pres.	Vol. (cc.)
1	32	5.987	.00190	.0173	.1036	100
2	32	4.563	.00224	.0179	.0828	100
3	32	5.234	.0100	.0196	.1036	100
4	32	4.911	.0300	.0205	.1036	100

Series 3. Silicic Acid (Merck) 100 mesh. Calcined at 320° C for 16 hr.

$1/n = .270$ $\alpha = .150$

No.	Hr. rotated	Wt. earth (g)	Equilibrium conc. (g. per l.)	Adsorbed (g. per g. of earth)	Orig. g. dye pres.	Vol. (cc.)
1	20	2.678	.00283	.0308	.0828	100
4	20	2.638	.00311	.0313	.0828	100
3	20	2.601	.00317	.0317	.0828	100
2	20	2.517	.00358	.0328	.0828	100

Calcined at 330° C for 14 hr.

$1/n = .262$ $\alpha = .127$

No.	Hr. rotated	Wt. earth (g)	Equilibrium conc. (g. per l.)	Adsorbed (g. per g. of earth)	Orig. g. dye pres.	Vol. (cc.)
1	20	2.770	.00360	.0298	.0828	100
3	20	2.600	.00450	.0316	.0828	100
4	20	2.515	.00490	.0327	.0828	100
2	20	2.419	.00617	.0341	.0828	100

TABLE IV. MIXTURE WITH METHYLENE BLUE.

3 parts Silicic Acid (Merck) 100 mesh.
1 part Fuller's Earth (Midway, Florida) 100 mesh from 60

$1/n = .105$ $\alpha = .0733$

No.	Hr. rotated	Wt. earth (g)	Equilibrium conc. (g. per l.)	Adsorbed (g. per g. of earth)	Orig. g. dye pres.	Vol. (cc.)
4	56	2.728	.00281	.0379	.1036	100
6	60	2.500	.00442	.0412	.1036	100
3	56	2.347	.00706	.0438	.1036	100
2	56	2.200	.0133	.0465	.1036	100
1	44	2.100	.0192	.0483	.1036	100

Theoretical Calculation of Mixture.

$1/n = .102$ $\alpha = .0743$

log c	log x/m(F)	log x/m(s)	x/m(F)	x/m(s)	x/m(mixture)	log x/m (mixture)
4.8	2.858	2.361	.0722	.0229	.0352	2.547
3.5	.903	.463	.0800	.0290	.0418	.621
3.6	.910	.476	.0813	.0299	.0427	.630
3.725	.918	.491	.0828	.0311	.0440	.644
3.85	.926	.510	.0843	.0324	.0454	.657
3.95	.932	.523	.0855	.0334	.0464	.667
2.05	.938	.536	.0867	.0344	.0475	.677
2.15	.945	.549	.0881	.0354	.0486	.687
2.25	.951	.562	.0893	.0365	.0497	.696
2.35	.957	.575	.0906	.0376	.0508	.706
1.30	1.020	.721	.1045	.0526	.0658	.819

TABLE V. EFFECT OF HCl AND KCl ON ADSORPTION OF METHYLENE BLUE.

Series 1. Fuller's Earth (C. W. Hill Chem. Co.) Acidity .093 N. with HCl.

$1/n = .0627$ $\alpha = .160$

No.	Hr. rotated	Wt. earth (g)	Equilibrium conc. (g. per l.)	Adsorbed (g. per g. of earth)	Orig. g. dye pres.	HCl conc. (normality)	Vol. (cc.)
2	22	1.008	.000850	.1027	.1036	.093	100
3	22	.970	.00156	.1066	.1036	.093	100
4	34	.937	.00282	.1105	.1036	.093	100
1	34	.885	.00768	.1162	.1036	.093	100

Series 2. Fuller's Earth (Midway, Florida) 30-60 mesh.

KCl added as indicated

No.	Hr. rotated	Wt. earth (g)	Equilibrium conc. (g. per l.)	Adsorbed (g. per g. of earth)	Orig. g. dye pres.	KCl conc. (percent)	Vol. (cc.)
2'	22	1.631	.0005	.0635	.1036	2.5	100 (j
3'	22	1.514	.00123	.0685	.1036	2.5	115 (j
4'	22	1.455	.00218	.0711	.1036	2.5	115 (j
5	40	1.450	.00545	.0711	.1036	2.5	100
6	40	1.452	.00327	.0712	.1036	—	100
7	42	1.508	.00465	.0683	.1036	5.0	100
8	42	1.513	.00177	.0684	.1036	—	100

TABLE VI. ERYTHROSINE

Fuller's Earth (Standard Oil Co.) Treated.

$1/n$ approaches α is indeterminate.

No.	Hr. rotated	Wt. earth (g)	Equilibrium conc. (g. per l.)	Adsorbed (g. per g. of earth)	Orig. g. dye pres.	Vol. (cc.)
6	40	2.729	.00820	.0284	.0783	100
7	40	2.475	.00800	.0313	.0783	100
8	40	2.355	.00865	.0330	.0783	100
5	40	2.252	.00800	.0344	.0783	100

(j) Points No. 2', 3', and 4' were previously run to equilibrium (Table I Series3) and then the KCl added.

TABLE VII. AURAMINE AND NATURAL EARTHS.

Series 1 Fuller's Earth (Standard Oil Co.) Treated.

$1/n = .408 \qquad \alpha = 2.44$

No.	Hr. rotated	Wt. earth (g)	Equilibrium conc. (g. per l.)	Adsorbed (g. per g. of earth)	Orig. g. dye Pres.	Vol. (cc.)
3	28	.499	.000522	.1116	.0558	100
1	28	.543	.000688	.1233	.0670	105
2	28	.605	.000740	.1290	.0781	110
5	12	.410	.000875	.1360	.0558	100
6	12	.393	.000923	.1420	.0558	100
$9^{\text{rev.}}$	16	.380	.00101	.1465	.0558	100
9 (K)	16	.380	.00102	.1467	.0558	100
4	28	.724	.00176	.1540	.1117	125
8	40+	.343	.00124	.1605	.0558	100
7	40+	.297	.00201	.1875	.0558	100

Series 2 Fuller's Earth (C. W. Hill Chem. Co.)

$1/n = .389 \qquad \alpha = .796$

No.	Hr. rotated	Wt. earth (g)	Equilibrium conc. (g. per l.)	Adsorbed (g. per g. of earth)	Orig. g. dye Pres.	Vol. (cc.)
1	16	1.468	.000948	.0533	.0781	110
3	16	.994	.00110	.0562	.0558	100
2	16	1.831	.00136	.0610	.1117	125
6	40+	.862	.00154	.0647	.0558	100

Series 3. Fuller's Earth (Midway, Florida) 100 mesh

$1/n = .381 \qquad \alpha = .377$

No.	Hr. rotated	Wt. earth (g)	Equilibrium conc. (g. per l.)	Adsorbed (g. per g. of earth)	Orig. g. dye Pres.	Vol. (cc.)
1	16	2.202	.000842	.0254	.0558	100
4	16	2.043	.00101	.0273	.0558	100
5	16	1.862	.00125	.0299	.0558	100
2	32	1.756	.00153	.0317	.0558	100
3	32	1.684	.00178	.0330	.0558	100

(K) Removed 50 cc. of solution, and added 50 cc. water.

Series 4. Diatomaceous Earth (Celite)

$1/n = .385 \qquad \alpha = .136$

No.	Hr. rotated	Wt. earth (g)	Equilibrium conc. (g. per 1.)	Adsorbed (g. per g. of earth)	Orig. g. dye pres.	Vol. (cc.)
3	16	4.793	.00168	.01163	.0558	100
5	16	4.386	.00202	.01270	.0558	100
4	16	4.195	.00246	.01330	.0558	100
6	16	4.000	.00271	.01395	.0558	100

TABLE VIII. AURAMINE AND ARTIFICIAL ADSORBENTS

Series 1. Animal Charcoal (Kahlbaum)

$1/n = .161 \qquad \alpha = .366$

2	16	.620	.00132	.1257	.0781	110
4	16	.422	.00178	.1320	.0558	100
3	16	.390	.00281	.1425	.0558	100
$1^{\text{rev.}}$	16 more	.512	.00366	.1510	.0788	90
1 (1)	46	.512	.00416	.1517	.0781	110
$5^{\text{rev.}}$	16 more	.349	.00502	.1575	.0554	80
5 (1)	46	.349	.00577	.1585	.0558	100
6	72	.330	.00860	.1670	.0558	100

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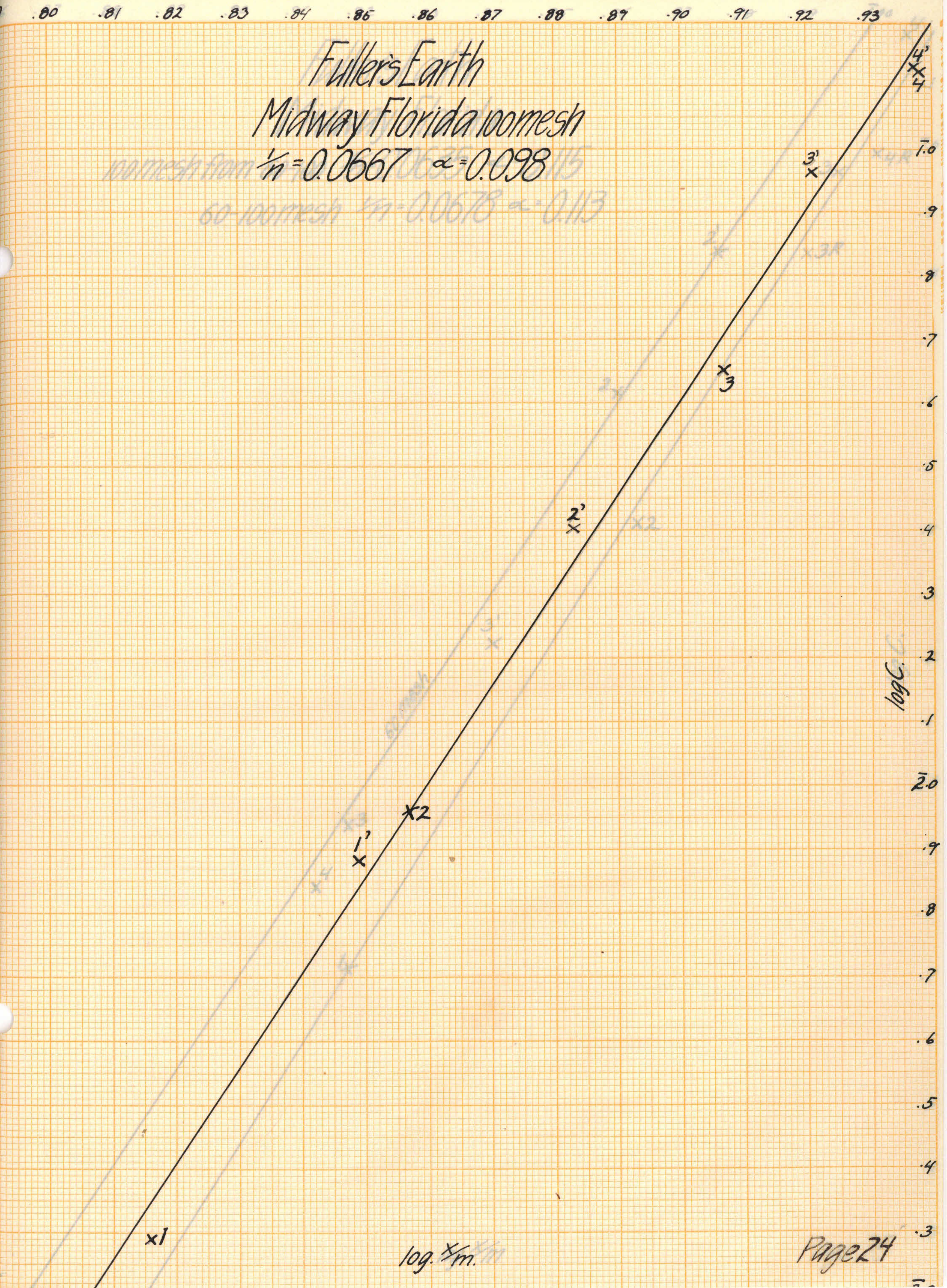
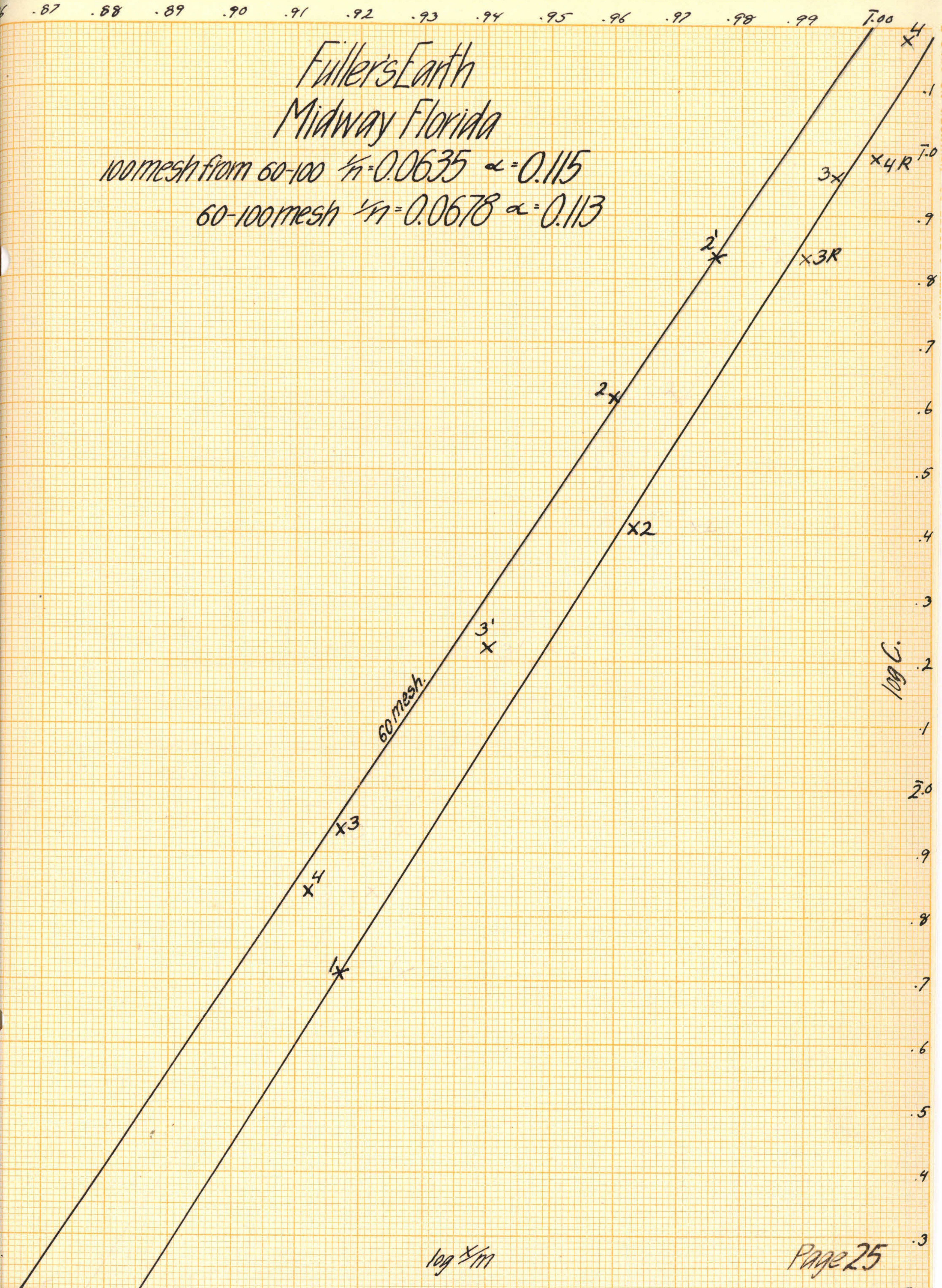
(1) Removed 70 cc. of solution, added 50 cc. water.

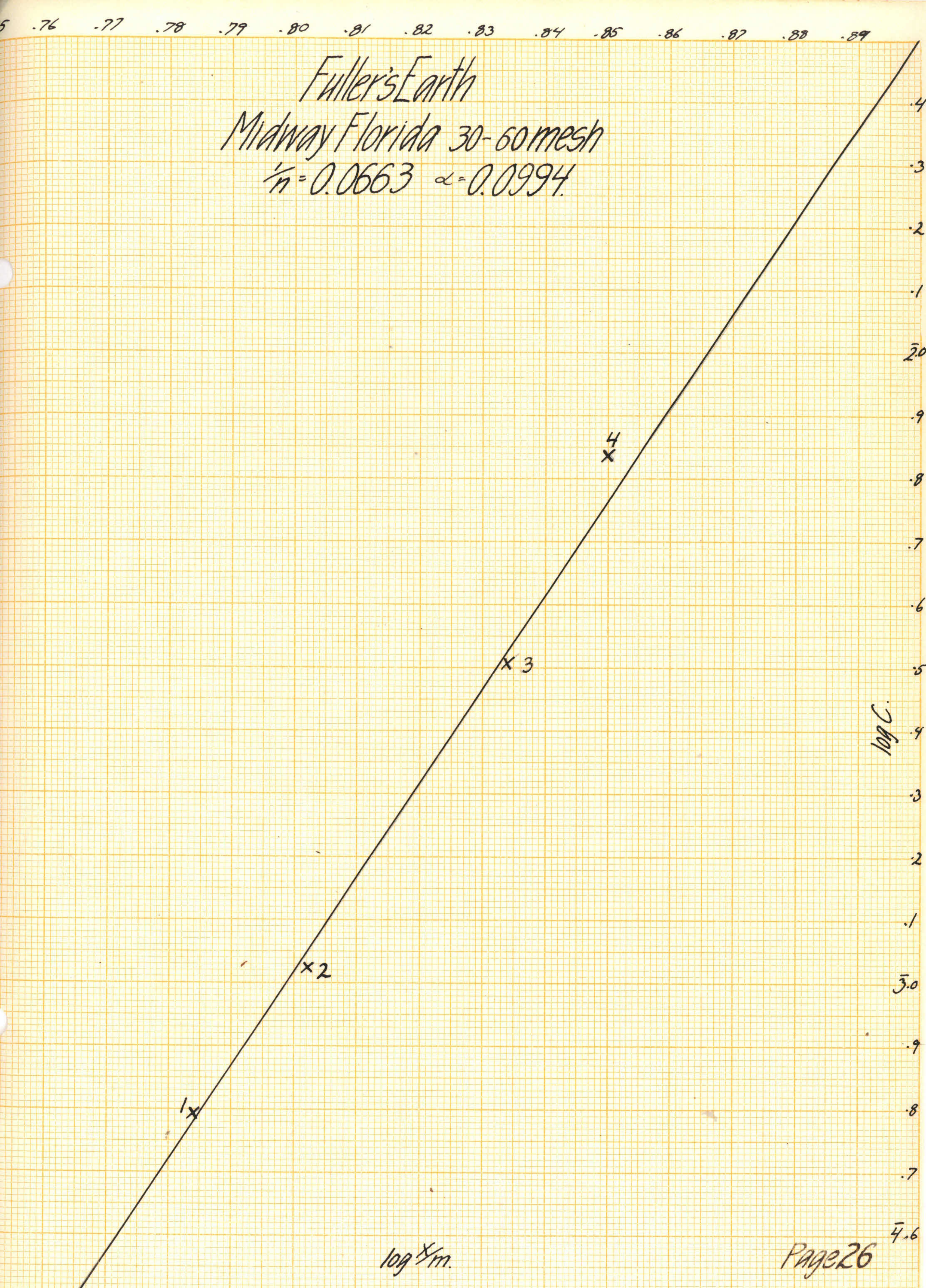

Fuller's Earth
Midway Florida 100mesh
$1/n = 0.0667$ $\alpha = 0.098$



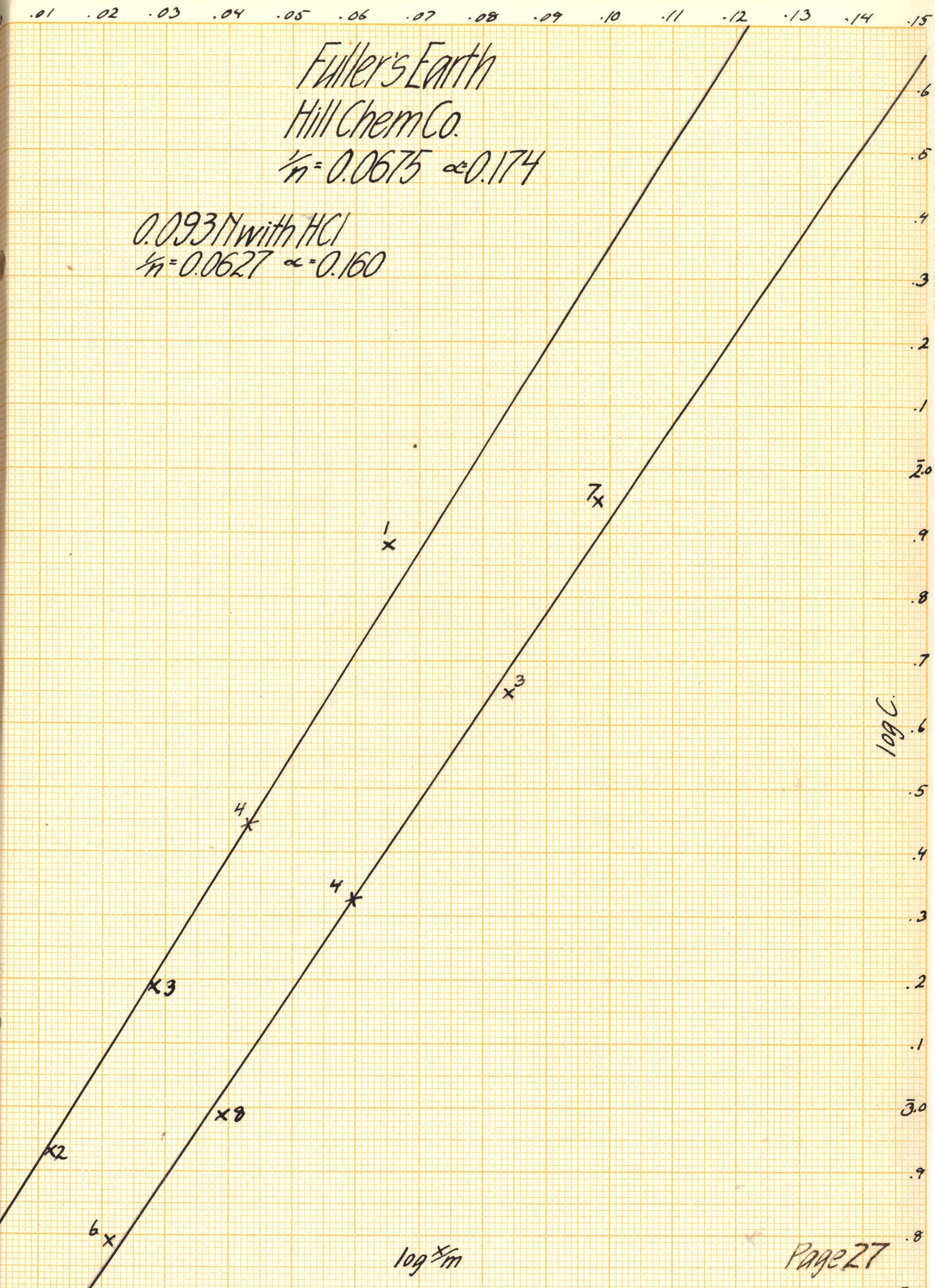
Fuller's Earth Midway Florida

100 mesh from 60-100 $1/n = 0.0635$ $\alpha = 0.115$

60-100 mesh $1/n = 0.0678$ $\alpha = 0.113$



Fuller's Earth
Midway Florida 30-60 mesh
$1/n = 0.0663$ $\alpha = 0.0994$

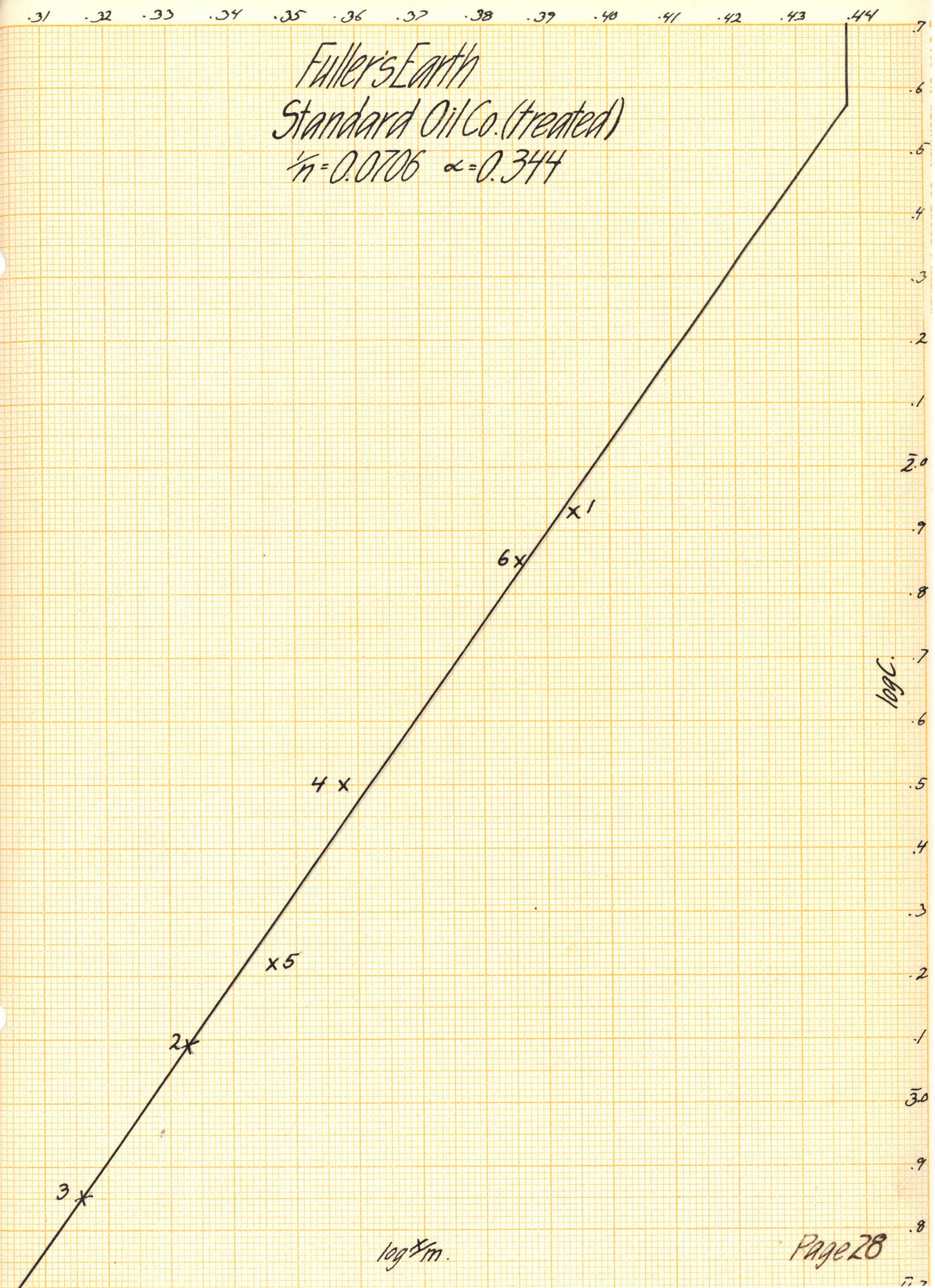


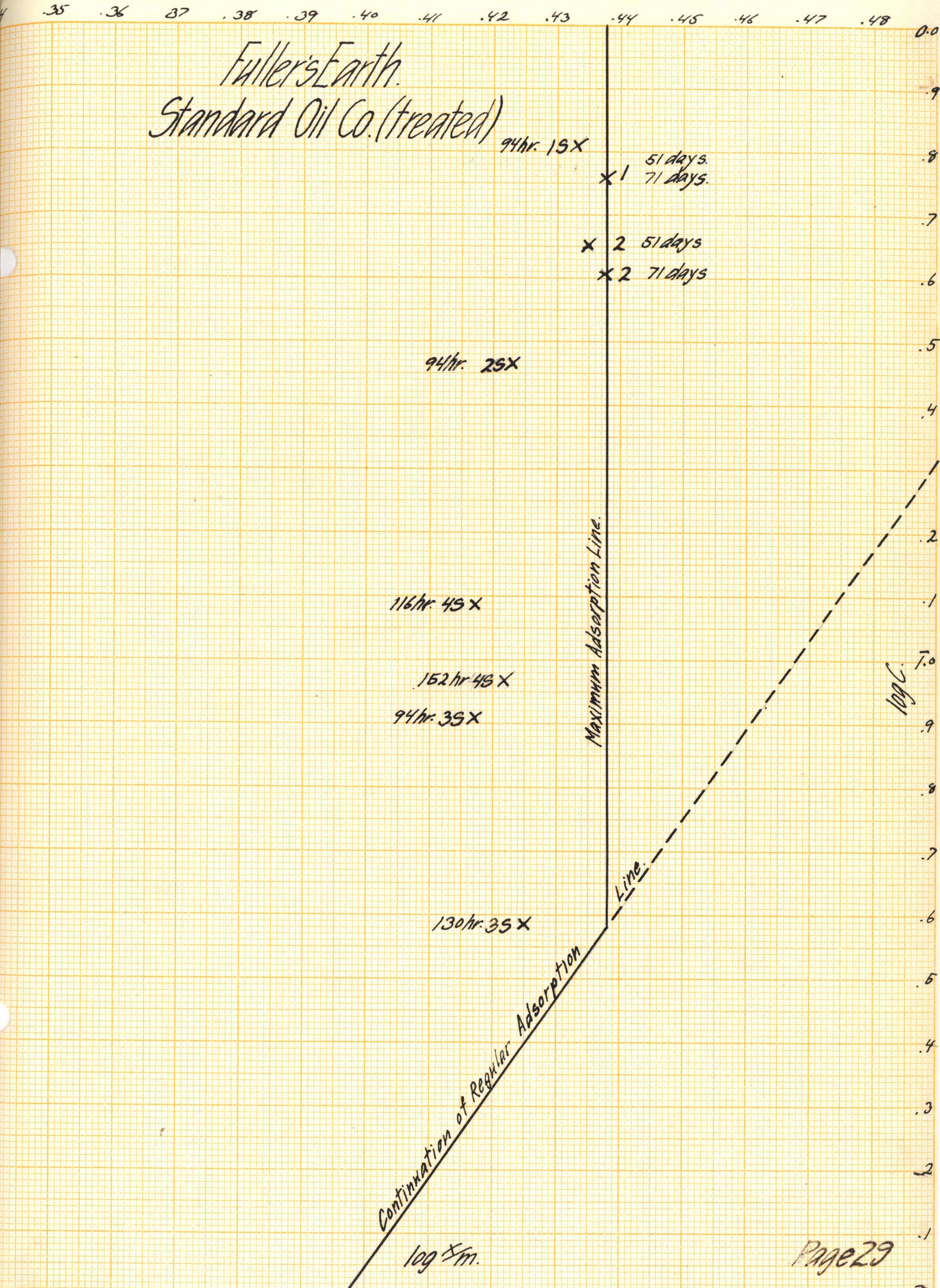
Fuller's Earth
Hill Chem Co.
$1/n = 0.0675$ α 0.174

0.093 N with HCl
$1/n = 0.0627$ $\alpha = 0.160$

Fuller's Earth
Standard Oil Co. (treated)

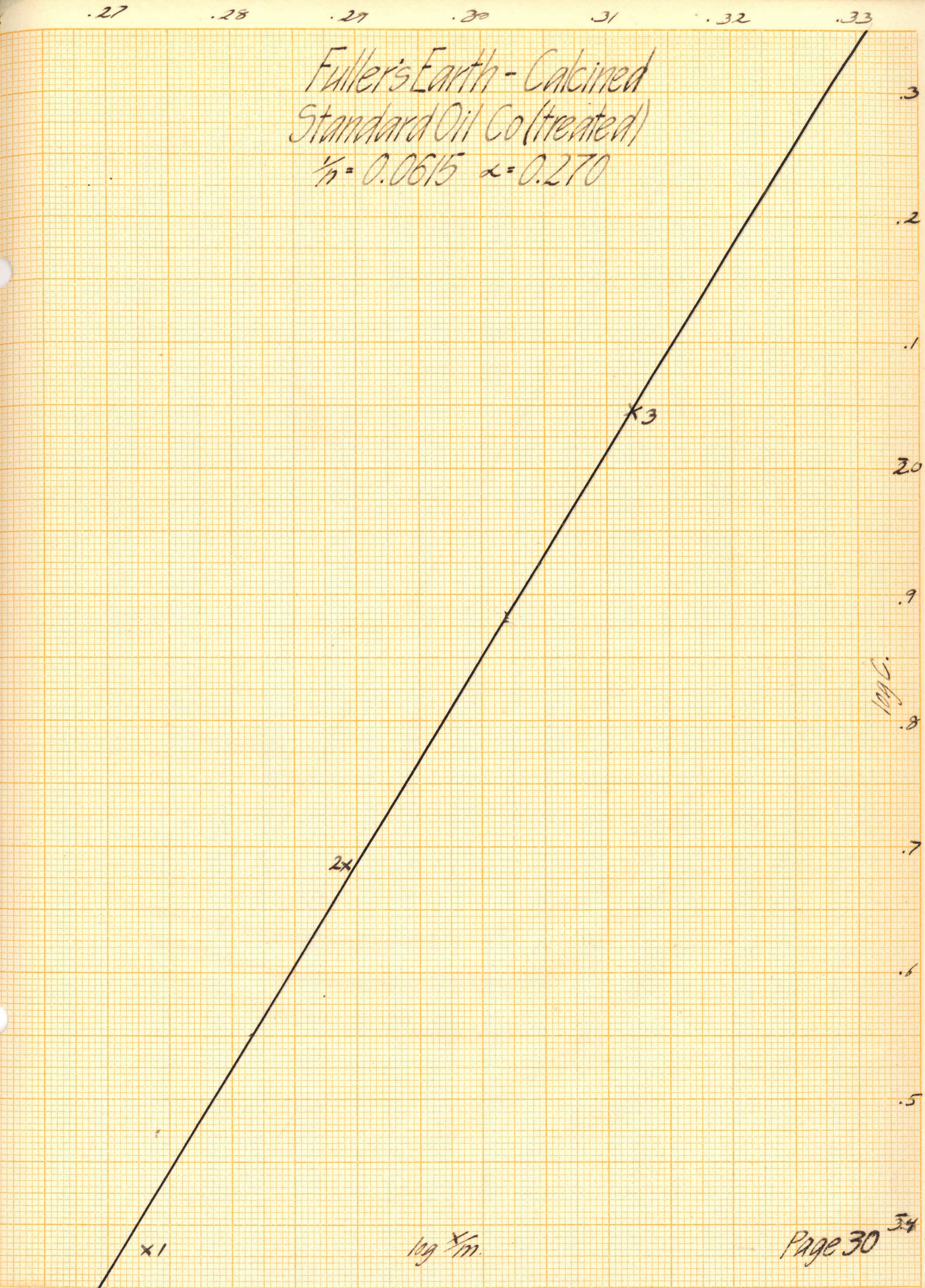
$1/n = 0.0706$ $\alpha = 0.344$



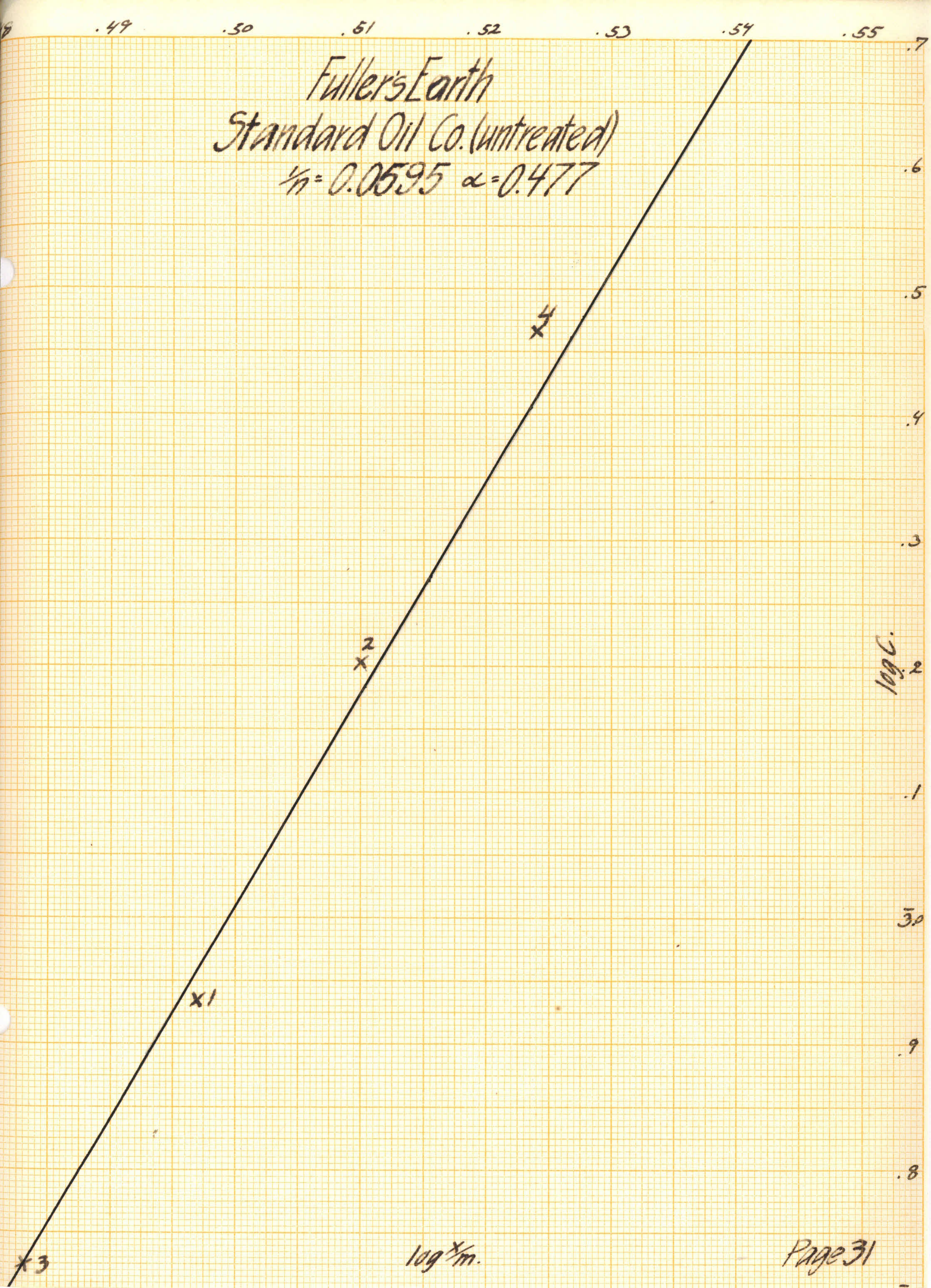


Fuller's Earth.

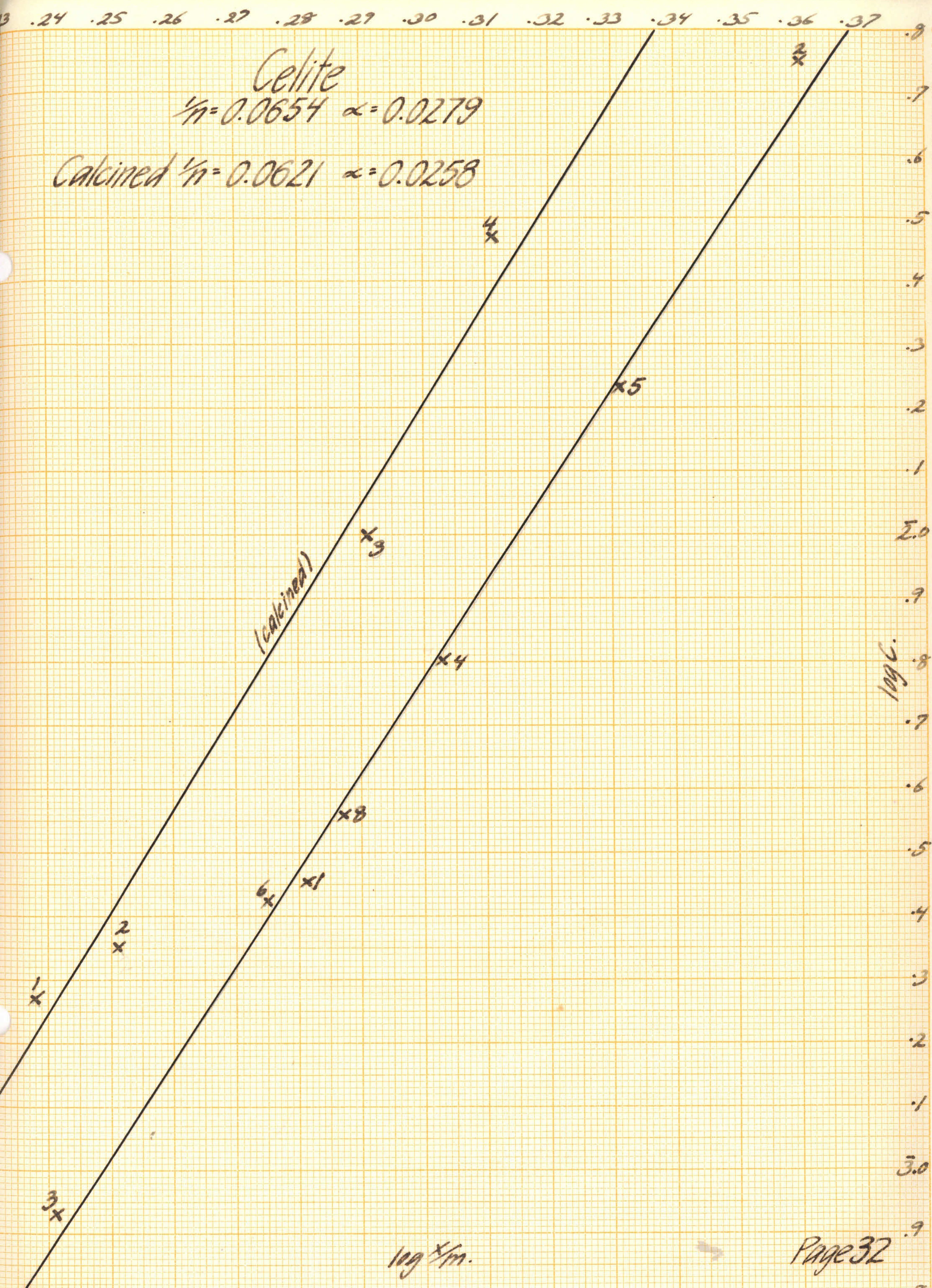
Standard Oil Co. (treated)

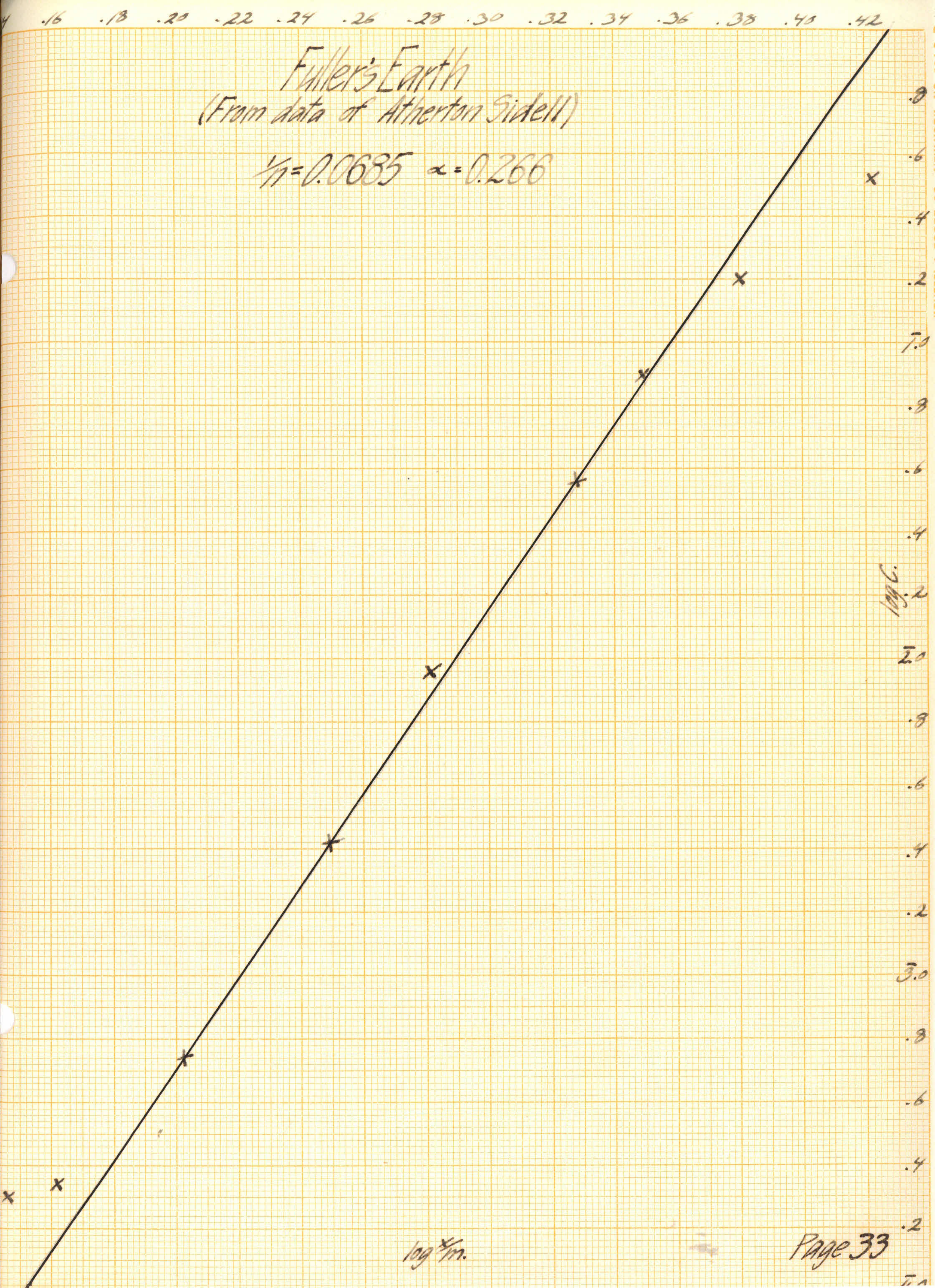


Fuller's Earth - Calcined
Standard Oil Co (treated)
$1/n = 0.0615$ $\alpha = 0.270$



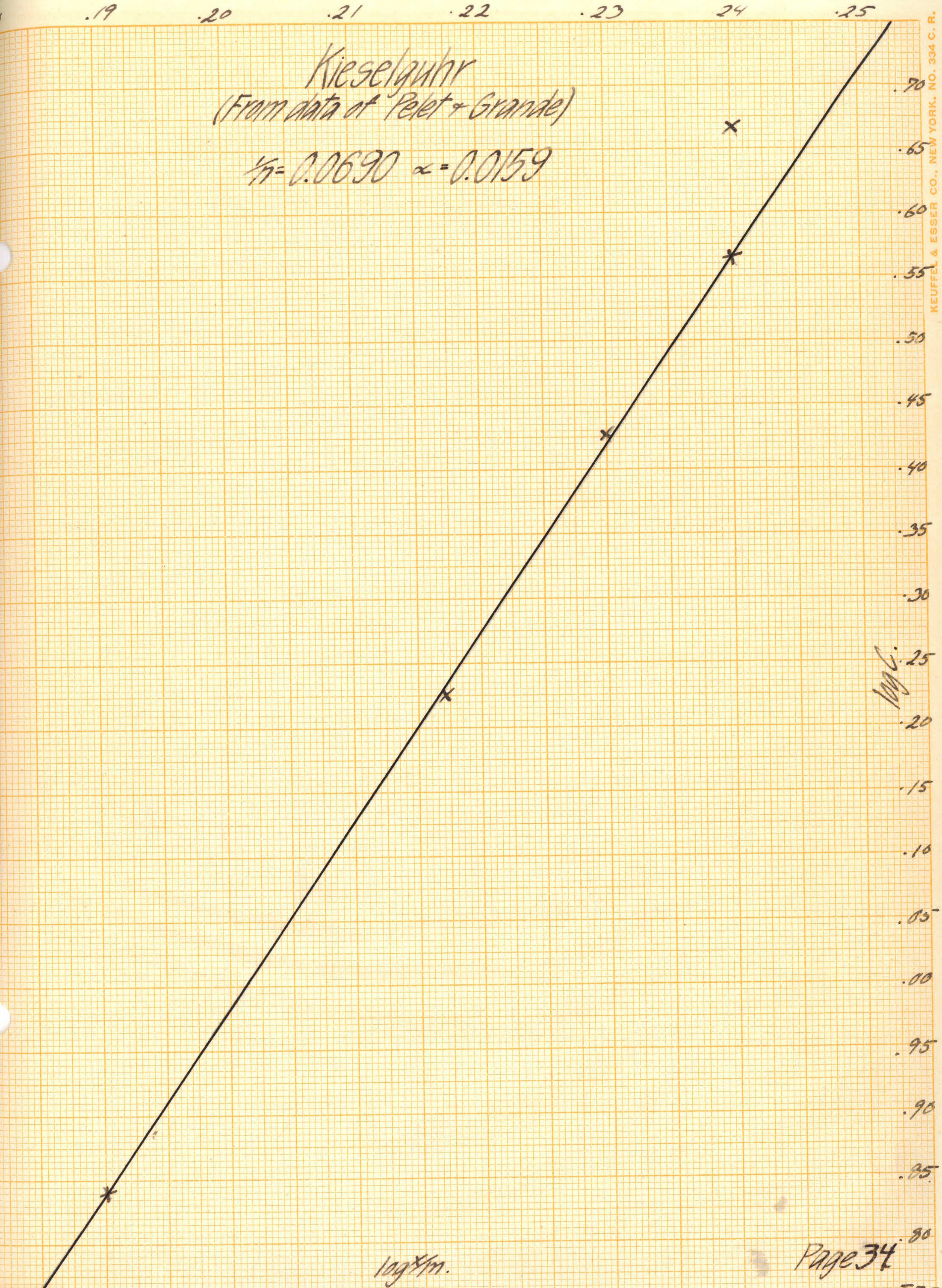
Fuller's Earth
Standard Oil Co. (untreated)
$1/n = 0.0595$ $\alpha = 0.477$


Celite
1/n = 0.0654 α = 0.0279
Calcined 1/n = 0.0621 α = 0.0258
.24
.25
.26
.27
.28
.29
.30
.31
.32
.33
.34
.35
.36
.37
.8
.7
.6
.5
.4
.3
.2
.1
2̄.0
.9
.8
.7
.6
.5
.4
.3
.2
.1
3̄.0
.9
log c
log x/m
(calcined)
1
2
3
4
5
6
8
1
2
3
4



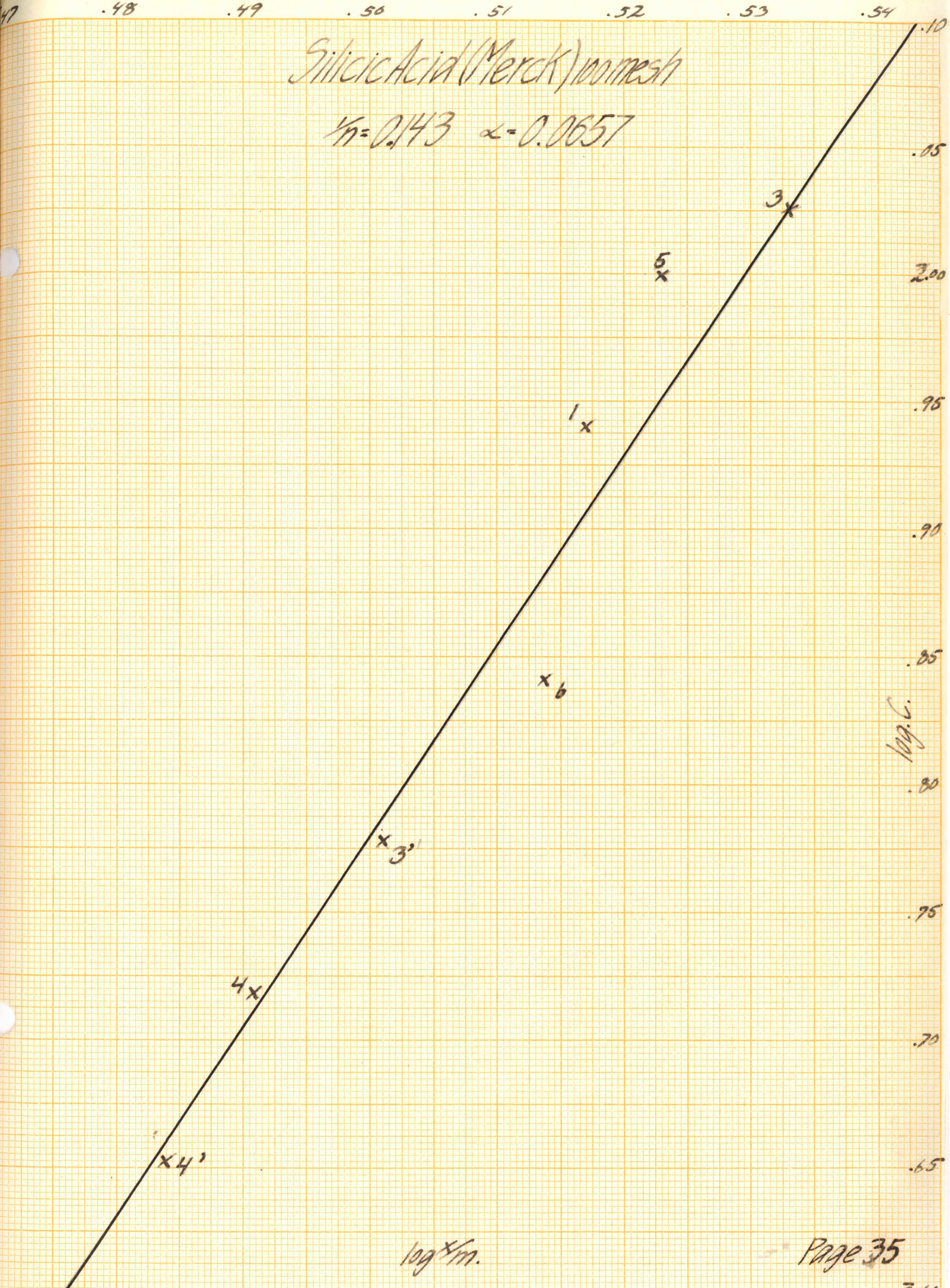
Fuller's Earth
(From data of Atherton Sidell)

$1/n = 0.0685 \quad \alpha = 0.266$



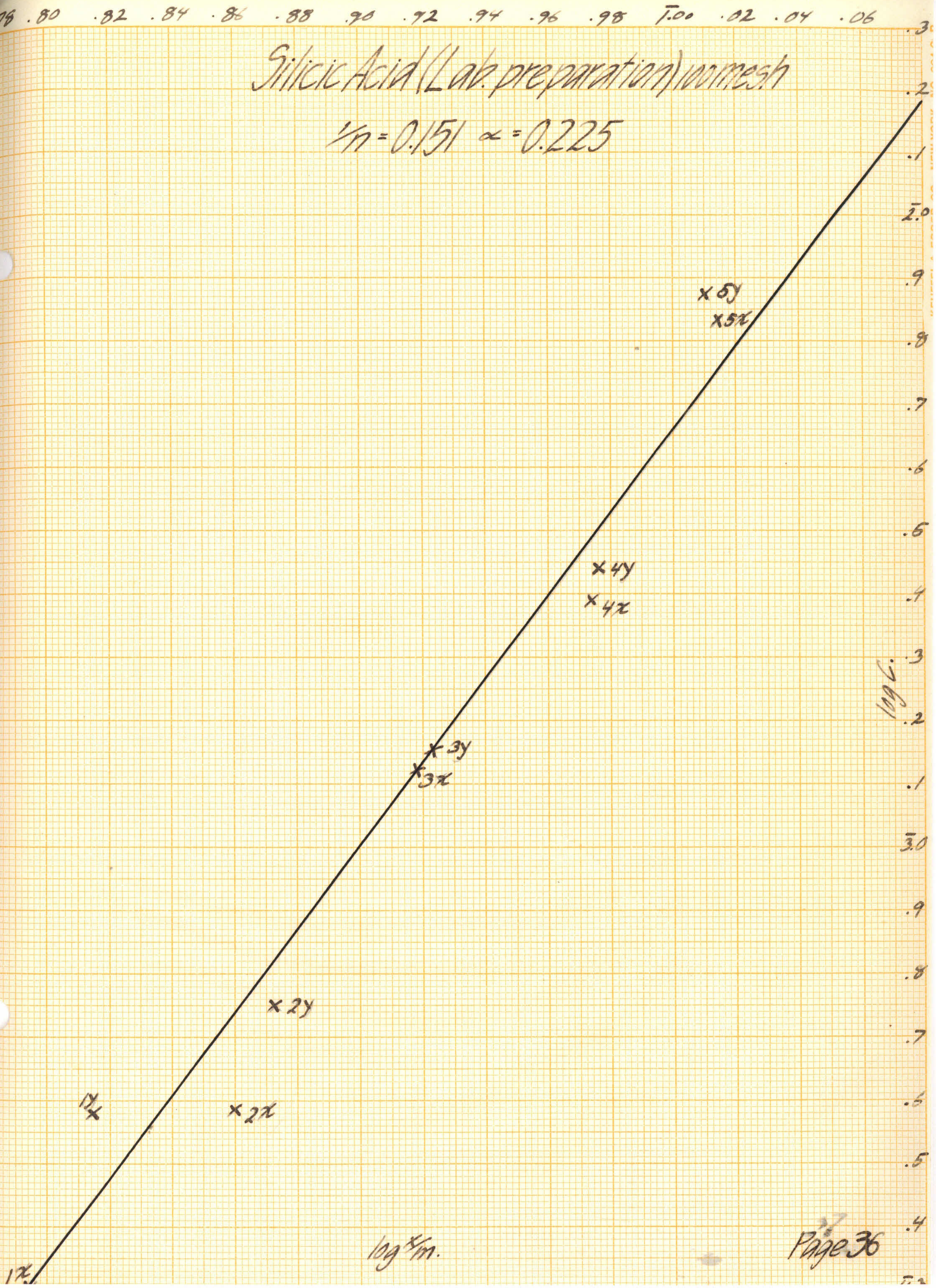
Kieselguhr
(From data of Pelet + Grande)

$1/n = 0.0690 \quad \alpha = 0.0159$



Silicic Acid (Merck) 100 mesh

1/n = 0.143 α = 0.0657

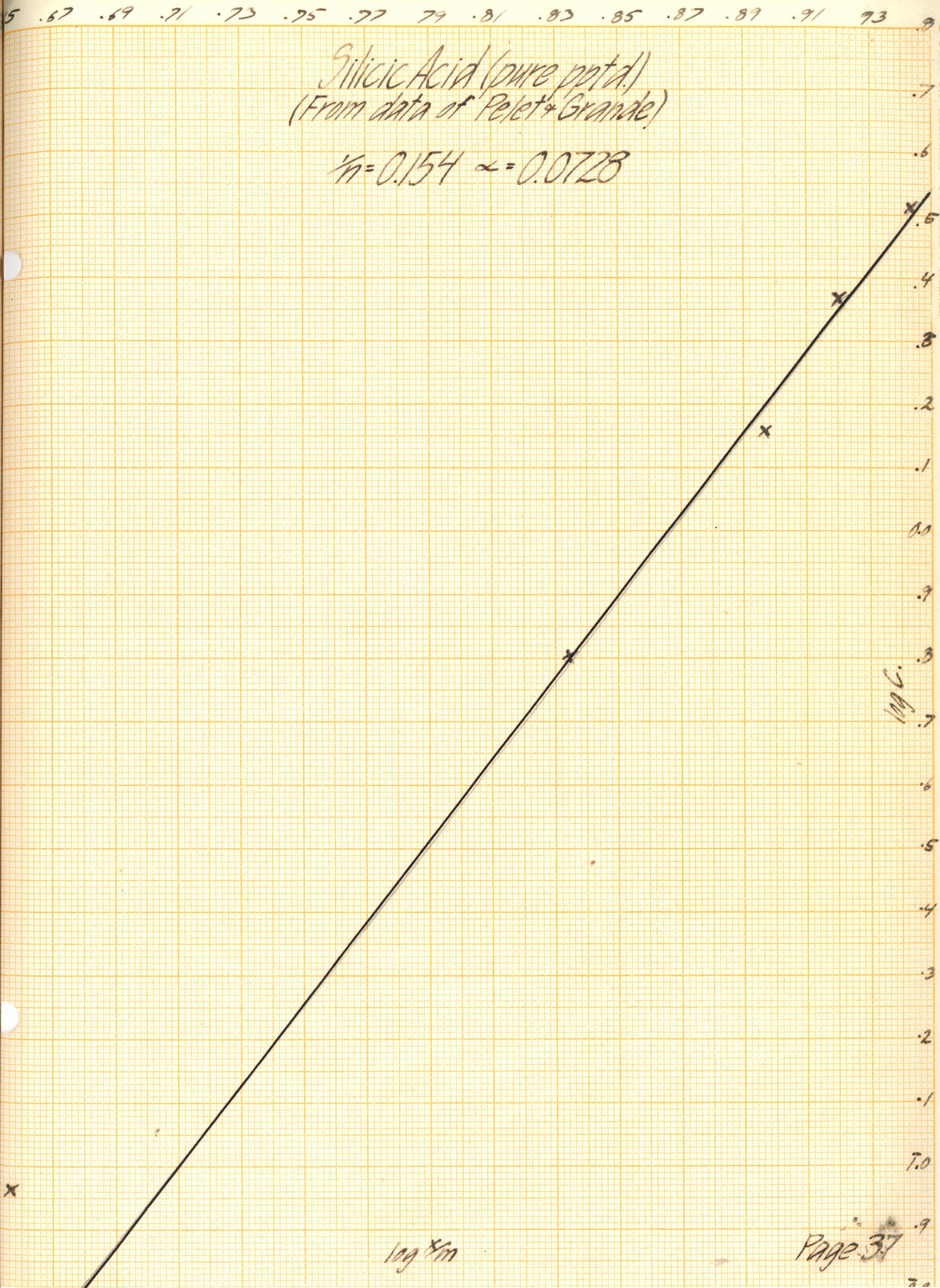


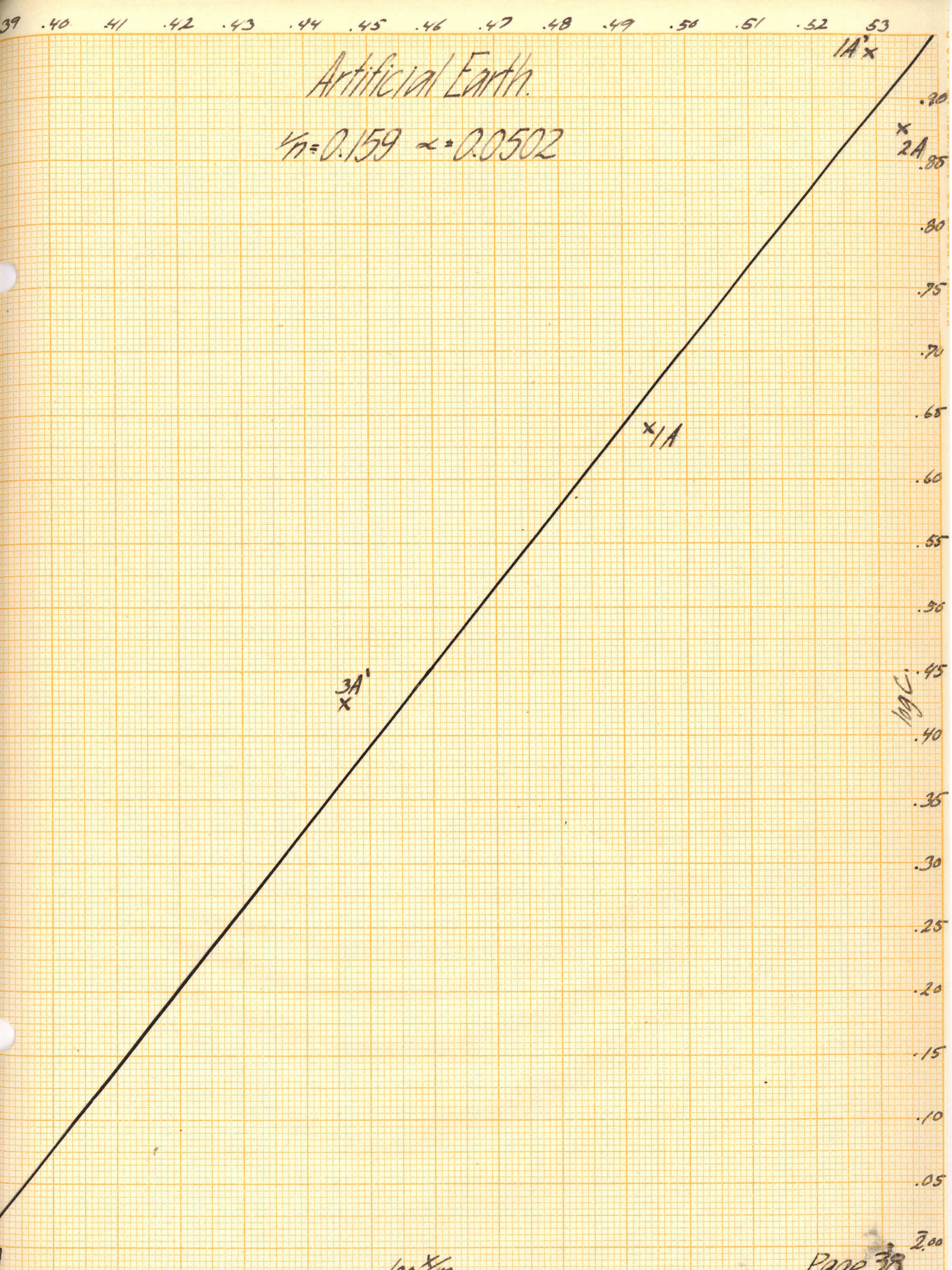
Silicic Acid (Lab. preparation) 100mesh

1/n = 0.151 α = 0.225

Silicic Acid (pure pptd.)
(From data of Pelet + Grande)

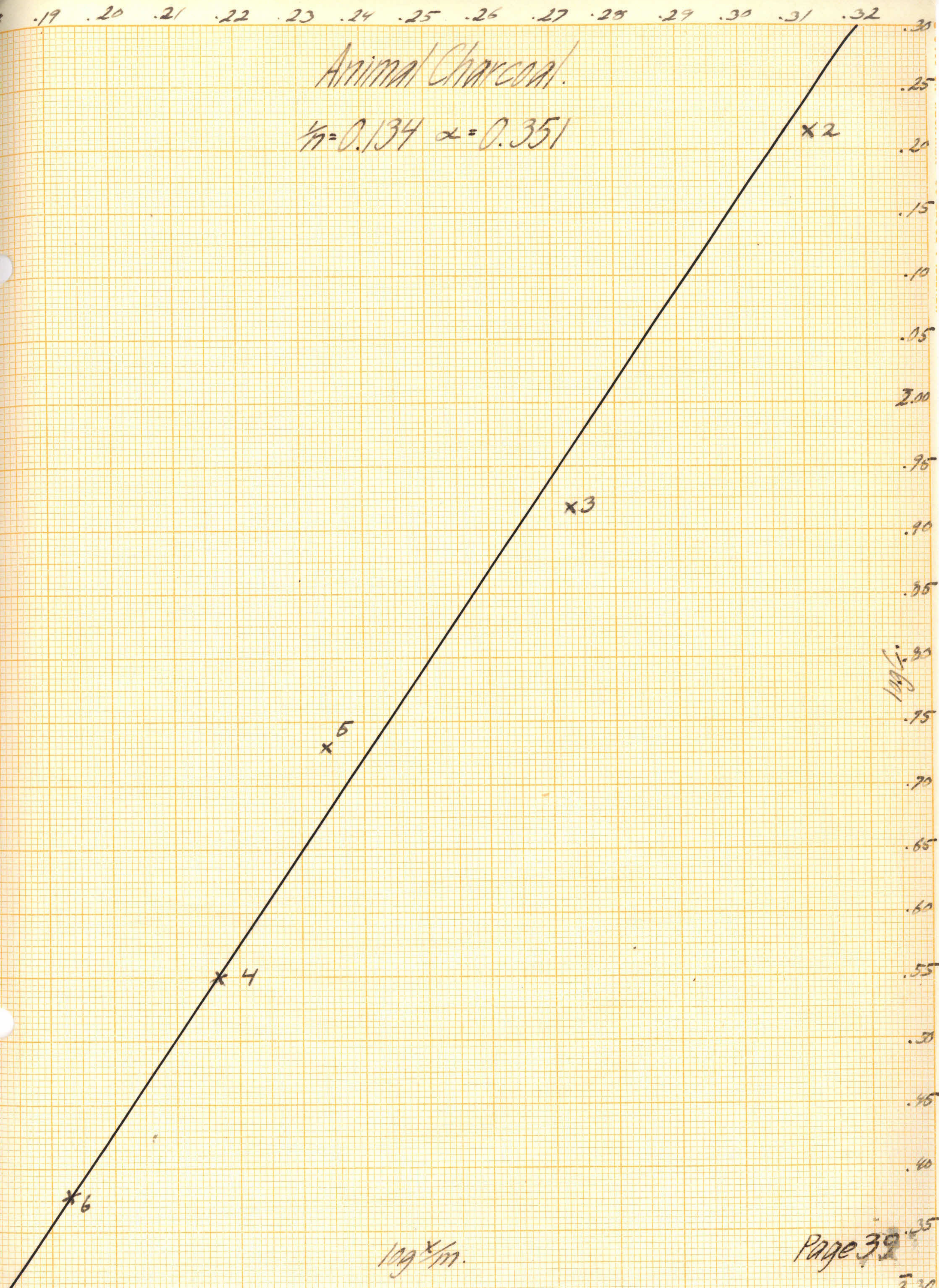
$1/n = 0.154 \quad \alpha = 0.0728$

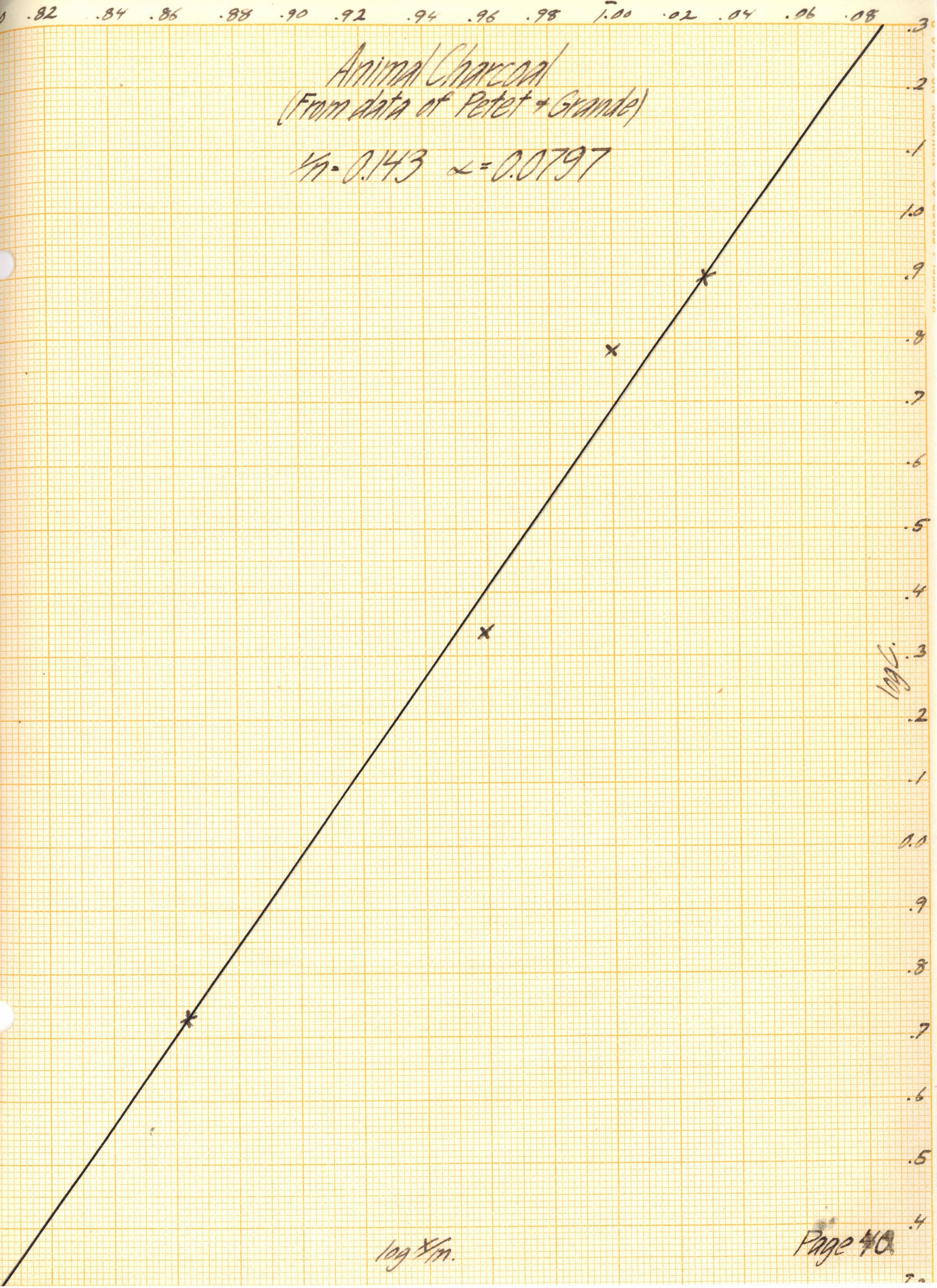




Artificial Earth.

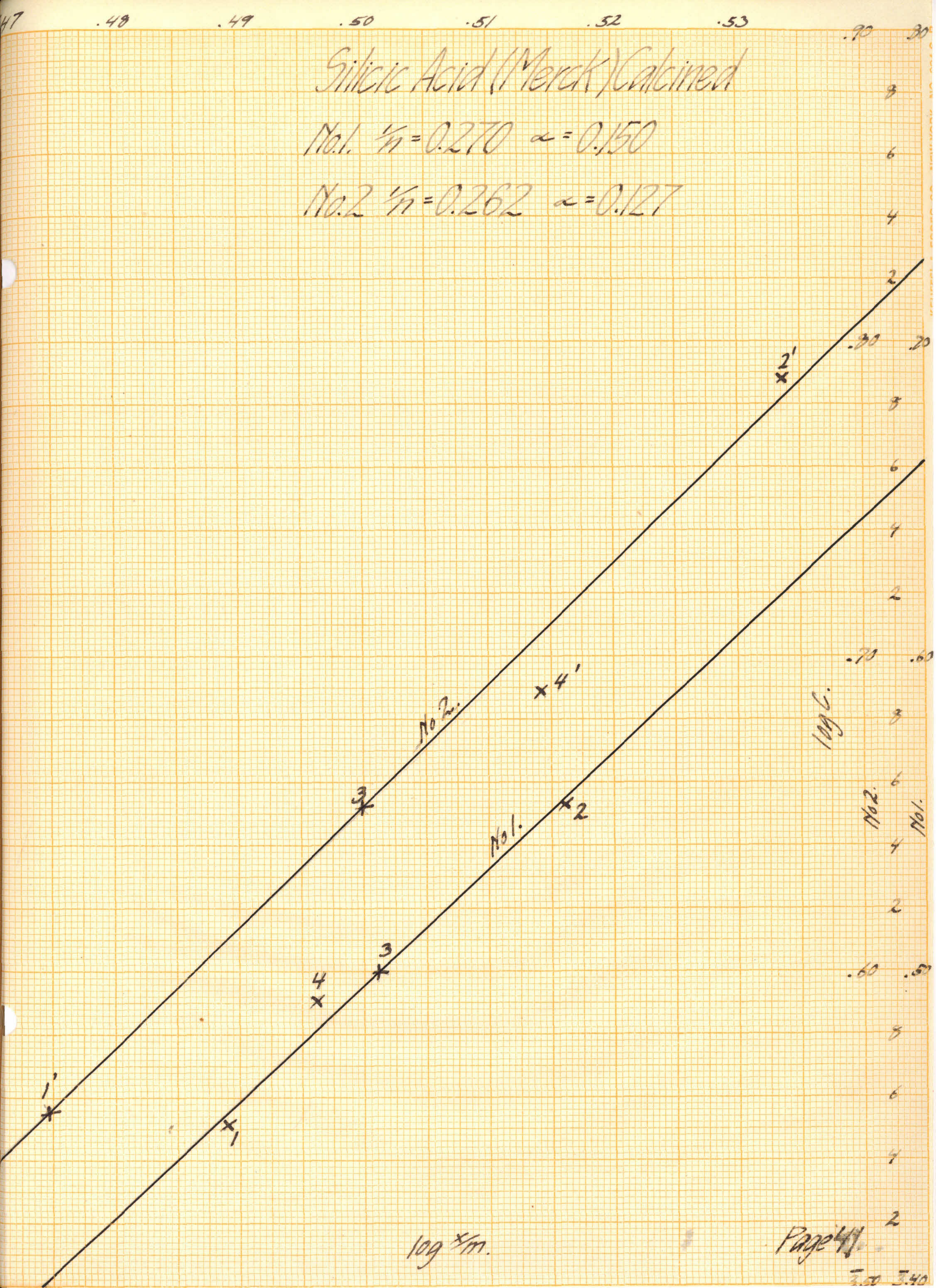
$1/n = 0.159$ $\alpha = 0.0502$

Animal Charcoal.
$1/n = 0.134$ $\alpha = 0.351$
.19
.20
.21
.22
.23
.24
.25
.26
.27
.28
.29
.30
.31
.32
.30
.25
.20
.15
.10
.05
$\bar{2}$.00
.95
.90
.85
.80
.75
.70
.65
.60
.55
.50
.45
.40
.35
.30
log c.
×2
×3
×5
×4
×6
log x/m.



Animal Charcoal
(From data of Petet + Grande)

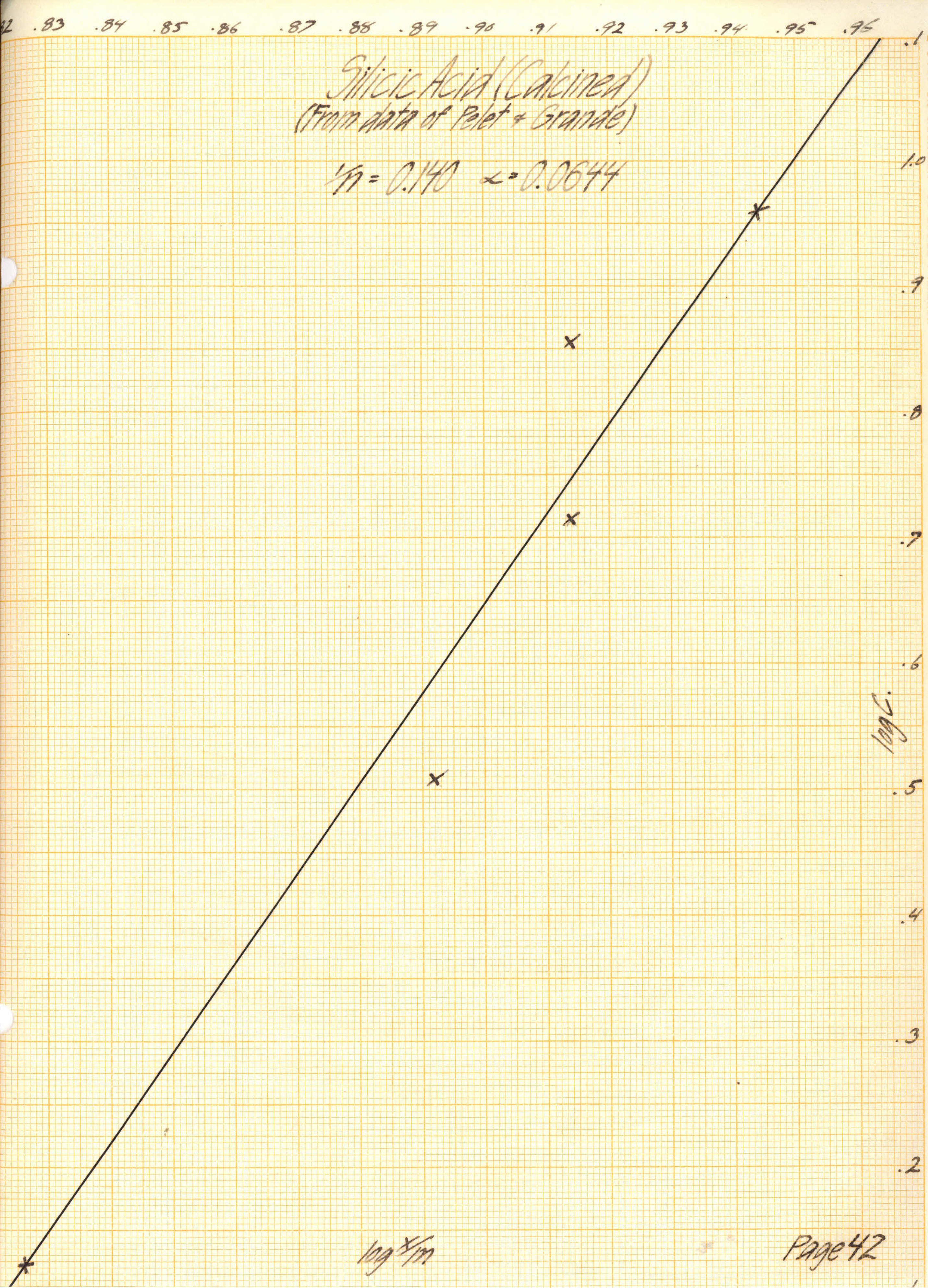
$1/n = 0.143$ $\alpha = 0.0797$



Silicic Acid (Merck) Calcined

No.1. $1/n = 0.270$ $\alpha = 0.150$

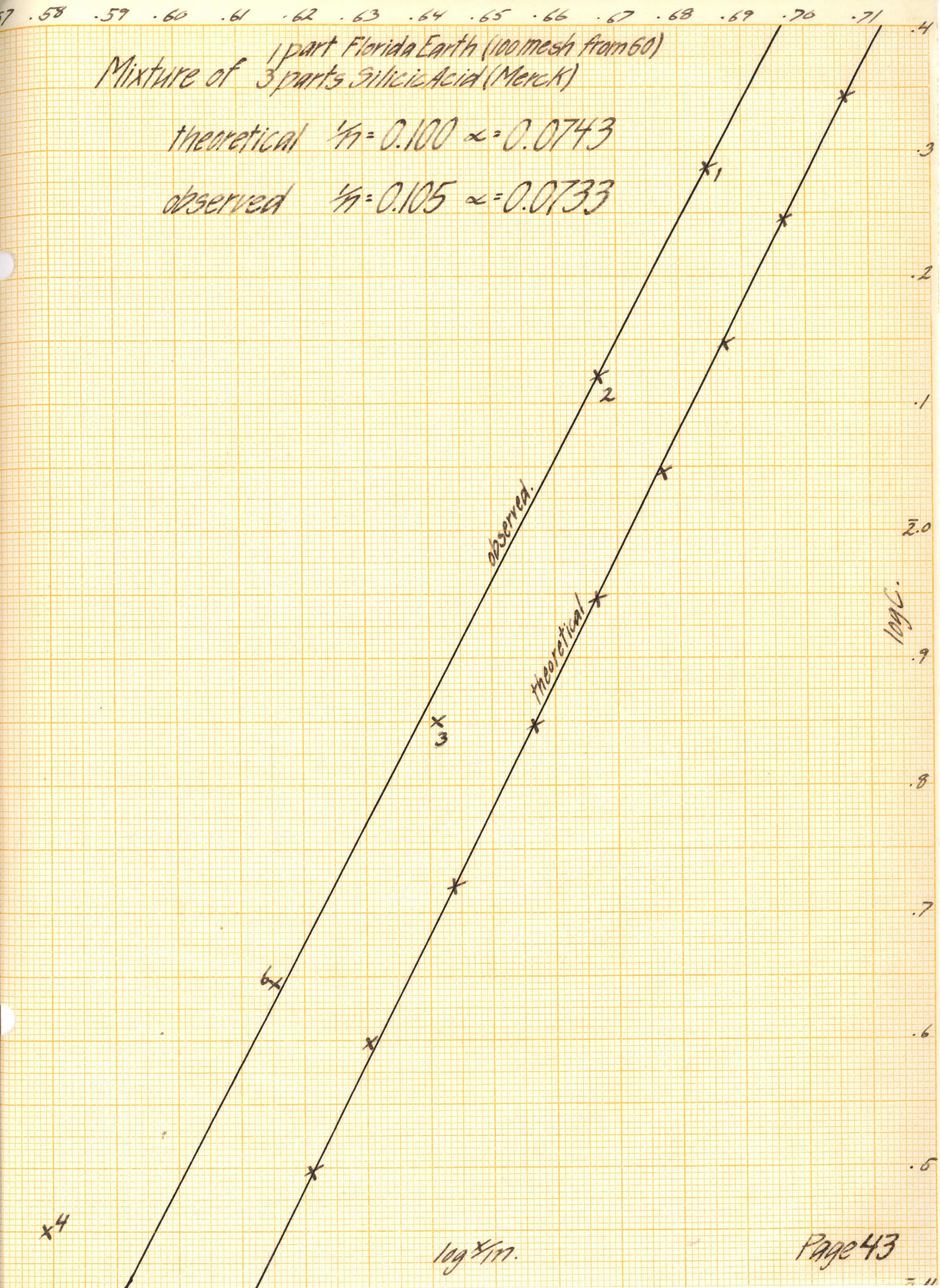
No.2 $1/n = 0.262$ $\alpha = 0.127$



Silicic Acid (Calcined)

(From data of Pelet + Grande)

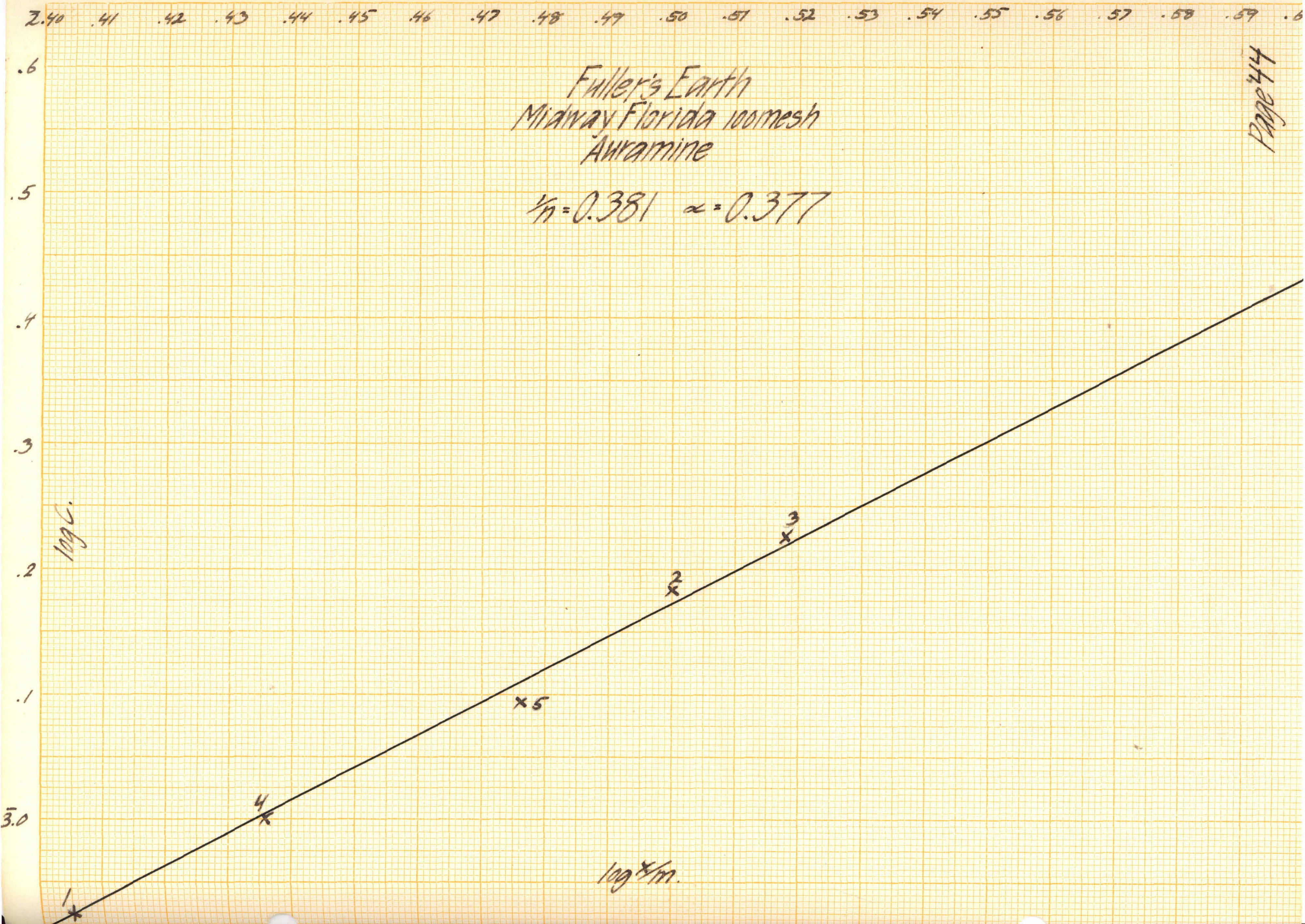
$1/n = 0.140 \quad \alpha = 0.0644$



Mixture of 1 part Florida Earth (100 mesh from 60) 3 parts Silicic Acid (Merck)

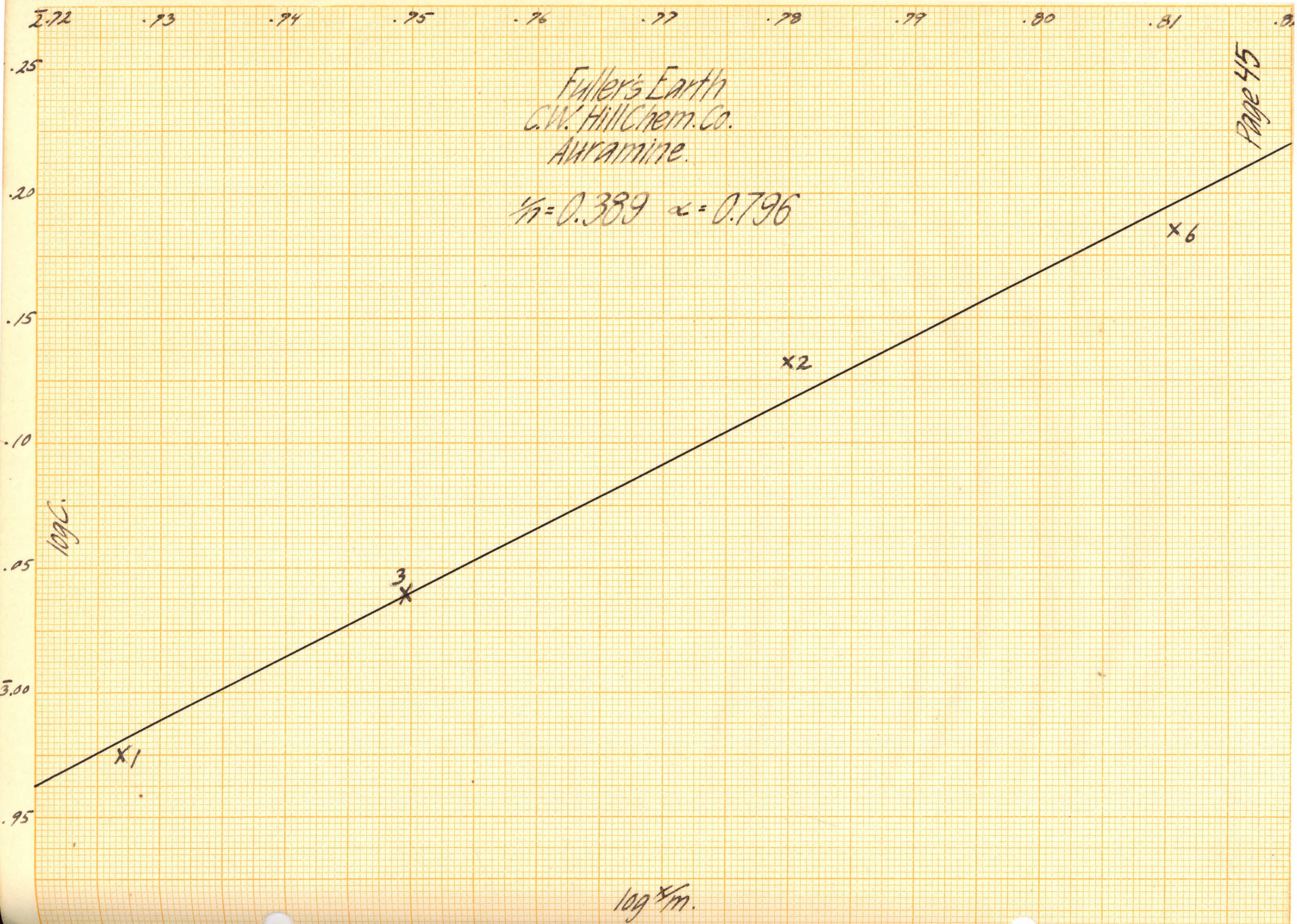
theoretical $1/n = 0.100$ $\alpha = 0.0743$

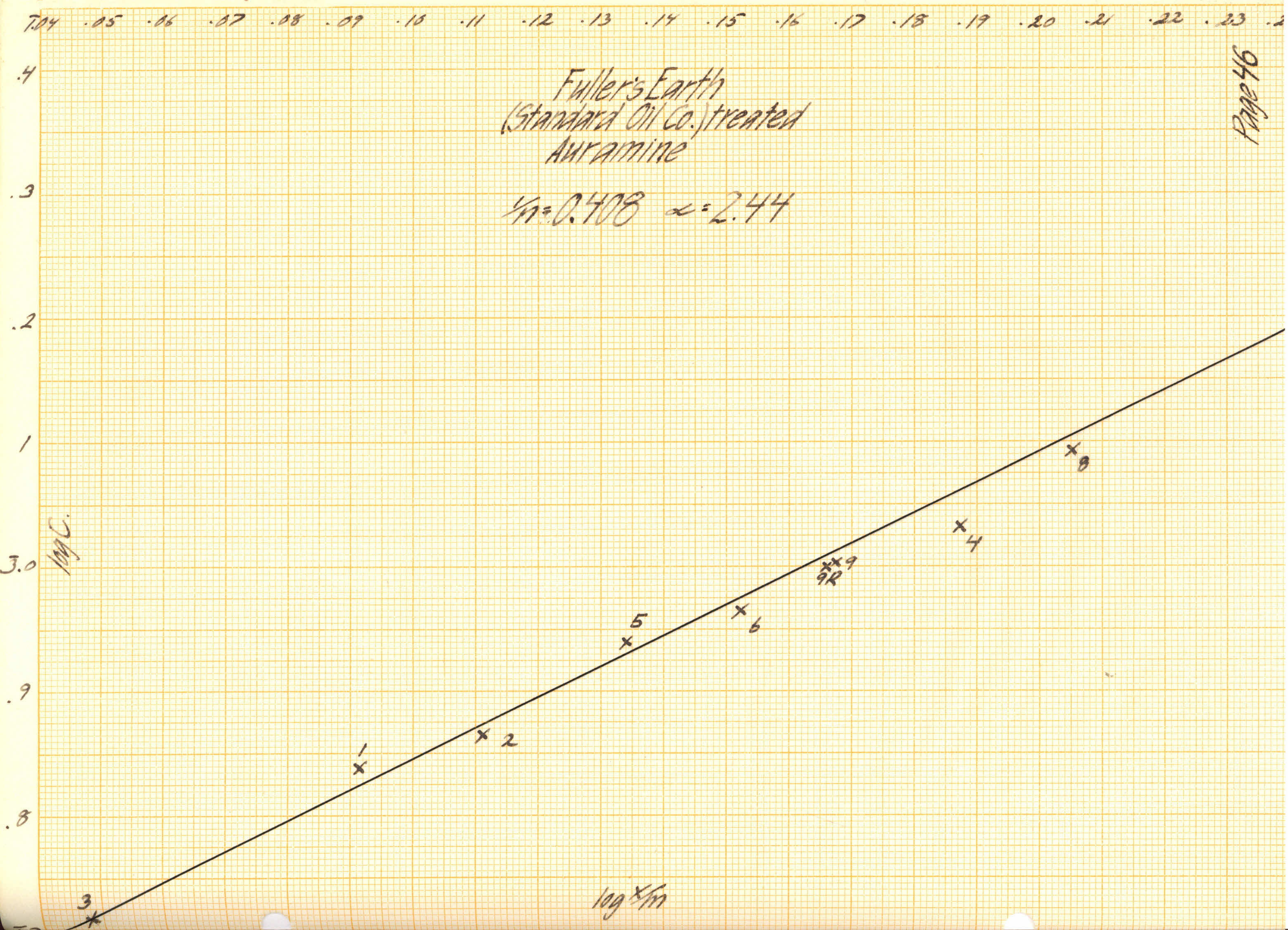
observed $1/n = 0.105$ $\alpha = 0.0733$



Fuller's Earth
Midway Florida 100mesh
Auramine

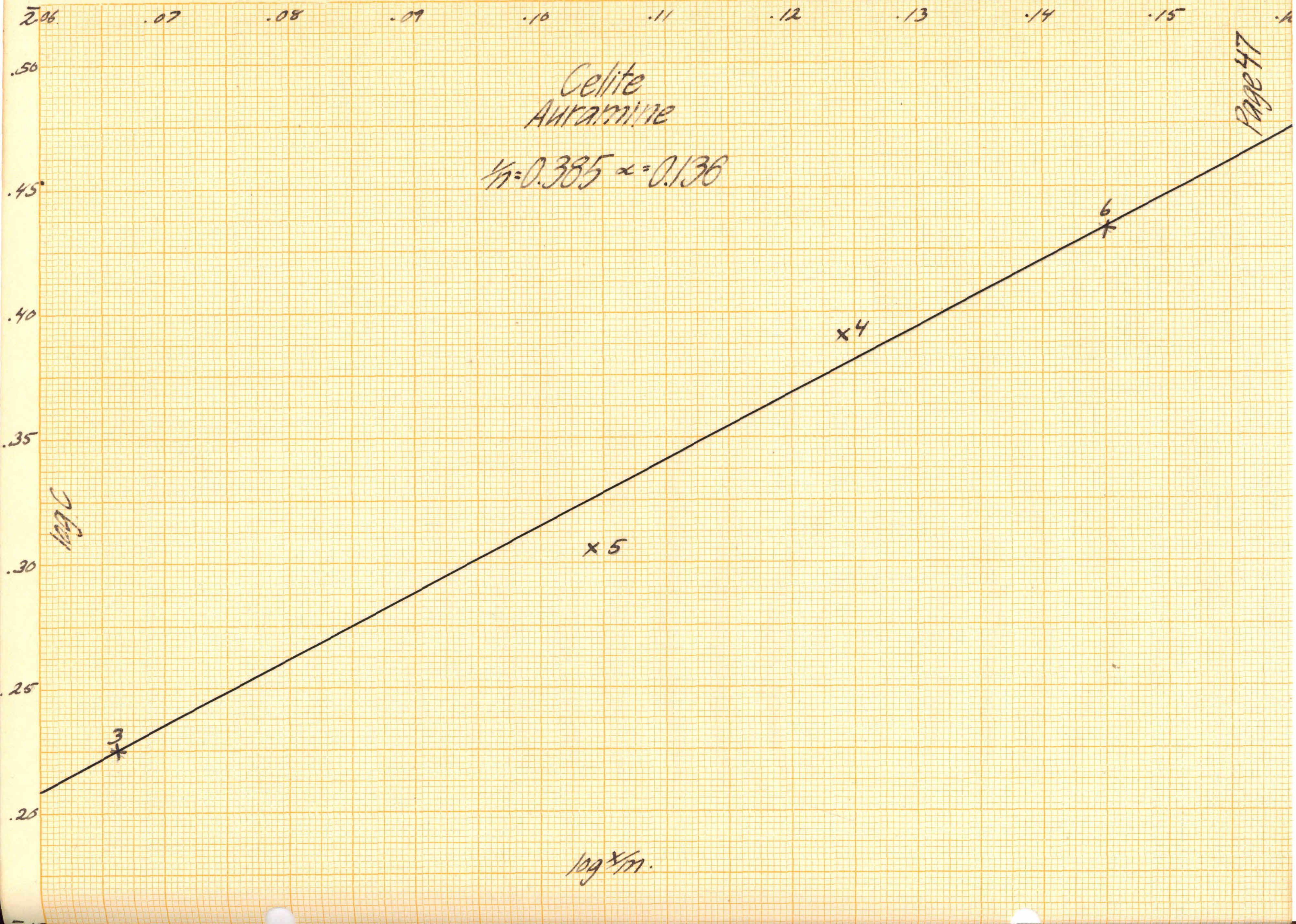
$1/n = 0.381$ $\alpha = 0.377$

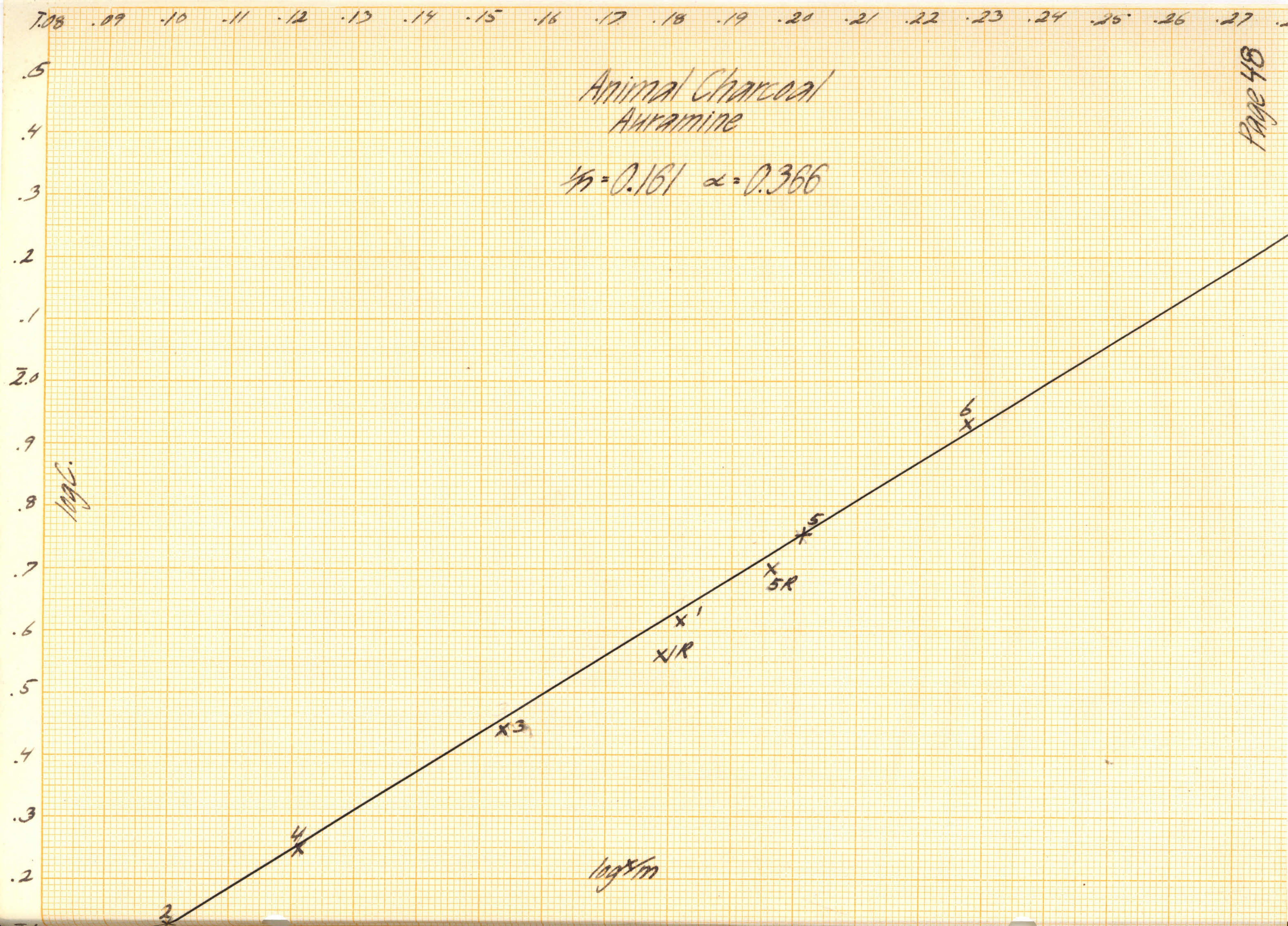

Fuller's Earth
C.W. Hill Chem. Co.
Auramine.
$1/n = 0.389$ $\alpha = 0.796$
$\bar{2}$.72
.73
.74
.75
.76
.77
.78
.79
.80
.81
.25
.20
.15
.10
.05
$\bar{3}$.00
.95
log C.
log x/m.
1
3
2
6



Fuller's Earth
(Standard Oil Co.) treated
Auramine

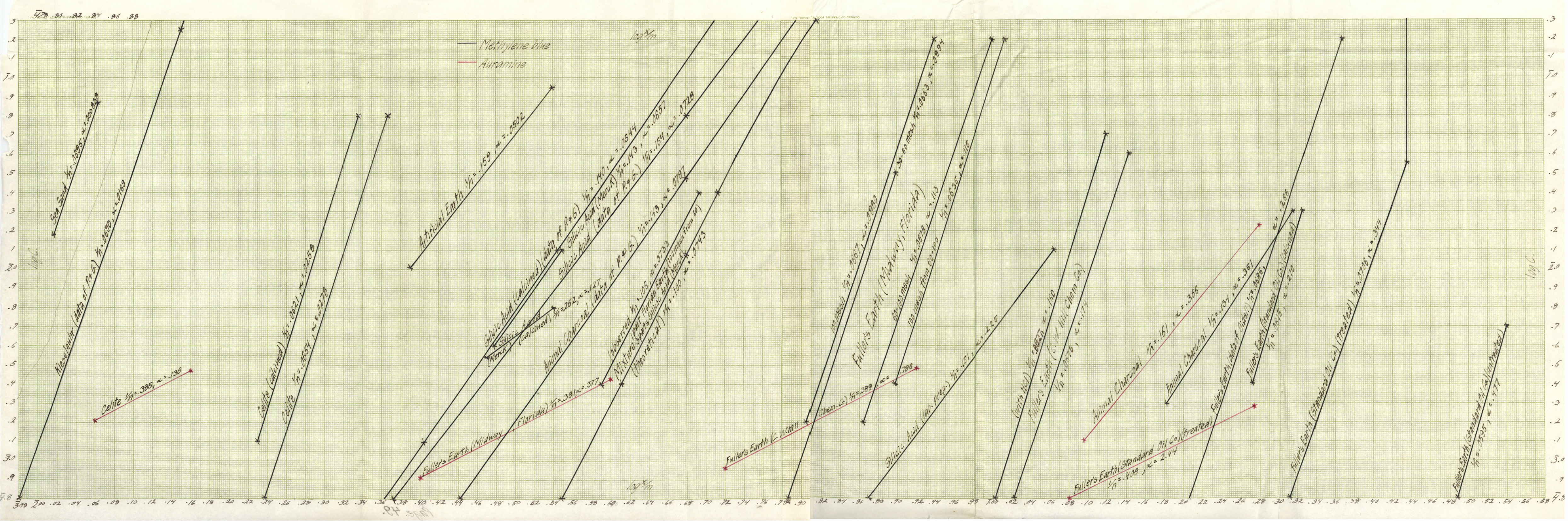
$1/n = 0.408$ $\alpha = 2.44$


Celite
Auramine
1/n = 0.385 α = 0.136
log C
log x/m.
$\bar{2}$.06
.07
.08
.09
.10
.11
.12
.13
.14
.15
.20
.25
.30
.35
.40
.45
.50
3
4
5
6



Animal Charcoal
Auramine

$1/n = 0.161$ $\alpha = 0.366$


Methylene blue
Auramine
log x/m
log C
Sea Sand 1/n = .0895, α = .000839
Kieselguhr (data of P. & G.) 1/n = .0690, α = .0169
Celite 1/n = .385, α = .138
Celite (calcined) 1/n = .0621, α = .0258
Celite 1/n = .0854, α = .0278
Artificial Earth 1/n = .159, α = .0502
Silicic Acid (calcined) (data of P. & G.) 1/n = .140, α = .0544
Silicic Acid (Merck) 1/n = .143, α = .0657
Silicic Acid (data of P. & G.) 1/n = .154, α = .0728
Silicic Acid (Merck) (calcined) 1/n = .262, α = .127
Animal Charcoal (data of P. & G.) 1/n = .143, α = .0797
Fuller's Earth (Midway, Florida) 1/n = .381, α = .377
(observed) 1/n = .105, α = .0733
Mixture 1 part Florida Earth (100 mesh from 60) 5 parts Silicic Acid (Merck)
(theoretical) 1/n = .100, α = .0743
Fuller's Earth (C. W. Hill Chem. Co.) 1/n = .389, α = .796
100 mesh 1/n = .0667, α = .0980
30-60 mesh 1/n = .0683, α = .0994
Fuller's Earth (Midway, Florida)
60-100 mesh 1/n = .0678, α = .113
100 mesh from 60-100 1/n = .0635, α = .115
Silicic Acid (lab. prep.) 1/n = .151, α = .225
(with HCl) 1/n = .0827, α = .150
Fuller's Earth (C. W. Hill Chem Co.) 1/n = .0676, α = .174
Animal Charcoal 1/n = .161, α = .366
Fuller's Earth (Standard Oil Co.) (treated) 1/n = .408, α = 2.44
Animal Charcoal 1/n = .134, α = .351
Fuller's Earth (data of Gidell) 1/n = .0686, α = .266
Fuller's Earth (Standard Oil Co.) (calcined) 1/n = .0615, α = .270
Fuller's Earth (Standard Oil Co.) (treated) 1/n = .0706, α = .344
Fuller's Earth (Standard Oil Co.) (untreated) 1/n = .0595, α = .477
4̄.78 .80 .82 .84 .86 .88
3̄.98 2̄.00 .02 .04 .06 .08 .10 .12 .14 .16 .18 .20 .22 .24 .26 .28 .30 .32 .34 .36 .38 .40 .42 .44 .46 .48 .50 .52 .54 .56 .58 .60 .62 .64 .66 .68 .70 .72 .74 .76 .78 .80 .82 .84 .86 .88 .90 .92 .94 .96 .98 1.00 .02 .04 .06 .08 .10 .12 .14 .16 .18 .20 .22 .24 .26 .28 .30 .32 .34 .36 .38 .40 .42 .44 .46 .48 .50 .52 .54 .56 .58
.3 .2 .1 1̄.0 .9 .8 .7 .6 .5 .4 .3 .2 .1 2̄.0 .9 .8 .7 .6 .5 .4 .3 .2 .1 3̄.0 .9 4̄.8

Discussion.

From the data and graphs several interesting relations may be noted, and conclusions drawn. The result of prime significance is that the adsorption of dyes by fuller's earth, diatomaceous earths, silicic acids and charcoal is quite closely in accordance with the adsorption equation. That equilibrium conditions were actually attained is shown by the results of certain reversal experiments in which the adsorbent was caused to give up part of the dye which it had previously adsorbed. (Table I Series 4, Table VII Series 1, Table VIII Series 1, and Table II Series 1.) In the first of these, part of the solution which had come to equilibrium was withdrawn and replaced by water, and in the latter the amount of adsorbent was increased by the addition of a second portion of earth. A slight tendency of incomplete reversion was noted in a few cases, indicating that a true equilibrium had not been reached in the original or reverse solutions. These deviations, however, are almost within the experimental error.

Only one variation from the adsorption relation $x/m = \alpha c^{1/n}$ was noted. In the case of the treated Standard Oil earth a point of maximum adsorption or a rather abrupt change in equilibrium was reached. Not all of these solutions of high concentration were carried to equilibrium, but the data shows that they tend to approach with increasing time of agitation a possible saturation value. Sample No. 1, however, – the one indicating the highest adsorption, – did not change in concentration in twenty days. The amount adsorbed at this point is more than one-quarter the weight of the earth, and may represent the state of complete covering of the elementary adsorption spaces.[1]

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[1] Langmuir, J. Am. Chem. Soc. 38, 2221 (1916).

A very striking relation to be noted is the constancy of the exponent 1/n for all the earths of natural origin, namely fuller's earth, diatomaceous earth, and sand with each of the dyes, methylene blue and auramine. This constancy of 1/n is further confirmed by the data of Atherton Sidell[1] for a fuller's earth, and of Pelet and Grande[2] for a diatomaceous earth.

Adsorbents.	Methylene blue.		Auramine.	
	α	1/n	α	1/n
Fuller's Earth.				
Midway, Florida, 100 mesh	0.0980	0.0667	0.0377	0.381
" " 60-100 "	0.113	0.0678		
" " 30-60 "	0.0994	0.0663		
" " 100 from 60-100	0.115	0.0635		
Hill Chem. Co.	0.174	0.0675	0.796	0.389
" " " (.093 N with HCl)	0.160	0.0627		
Standard Oil Co. (treated)	0.344	0.0706	2.44	0.408
(treated, calcined 320° C 7 hr.)	0.270	0.0615		
(untreated)	0.477	0.0595		
(data of Atherton Sidell, 1.)	0.266	0.0685		
Diatomaceous Earth				
Celite	0.0279	0.0654	0.136	0.385
" (calcined 320° C, 8 hr.)	0.0258	0.0621		
Kieselguhr (data of Pelet and Grande, 2.)	0.0159	0.0690		
Sea Sand (100 mesh)	0.000838	0.0695		
Silicic Acid				
Merck's 100 mesh	0.0657	0.143		
" (calcined 320° C, 16 hr)	0.150	0.270		

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1. J. Am. Chem. Soc. 40, 312 (1918). This author did not apply the adsorption equation to his results, but the calculations of α and 1/n were made from his data.
2. Zeit. Chem. u. Ind. Koll. 2, 41, 1907. These authors gave 0.11 as their value of 1/n for kieselguhr, but recalculation from their original data gave 1/n = 0.0690. Their other values of 1/n proved to be substantially correct.

Adsorbents.	Methylene blue.		Auramine.	
	α	1/n	α	1/n
Silicic Acid				
Merck's (calcined 330° C, 14 hr)	0.127	0.262		
(prepared in this laboratory)	0.225	0.151		
(data of Pelet and Grande, 2.)	0.0728	0.154		
(" " " " " (calcined))	0.0644	0.140		
Artificial Earth				
($Na_2O.Al_2O_3.3SiO_2.3H_2O$)	0.0502	0.159		
Animal Charcoal				
(Kahlbaum)	0.351	0.134	0.366	0.161
(data of Pelet and Grande)	0.0797	0.143		

It is of interest to note here that the values of 1/n obtained for the natural adsorbents with methylene blue are smaller than any other values listed in the literature.

The fact that the value of 1/n is the same for these various substances indicates that the nature of the active adsorbing constituent or surface is similar for all these adsorbents even though they differ greatly in chemical composition and physical structure.

The artificial adsorbents with methylene blue fall into another group with practically a constant value of 1/n which is approximately twice that for the natural earths. Further confirmation of these values is given by the results of Pelet and Grande (recalculated) for a silicic acid, and animal charcoal (see above table).

The value of 1/n for animal charcoal and auramine, however, does not have this ratio of two to one with the natural earths as in the case of methylene blue. Time was not available for securing the corresponding data for silicic acid and artificial earth with auramine, which would be necessary before any relation could be deduced. It is nevertheless of interest to note that artificially prepared sodium aluminum silicate, and precipitated silica with methylene blue should have the same value of $1/n$, which is just twice that for fuller's earth and for the natural silicas.

Another important point shown by the data is the large variation of α. This variation can hardly be accounted for by merely considering the extent of surface of the particles. It is true that the extent of surface is a rather indeterminable quantity, and does not necessarily depend on the mesh because of the great variations in porosity or internal surface; but a rough comparison can be made by means of microscopic examination of the particles. The Celite and Hill Chemical Co. fuller's earth were thus examined. The Celite has a very fine shell structure of varying but definite shape. The fuller's earth particles have an indefinite shape and are considerably more opaque than the Celite. The opaqueness of the particles which is a rough measure of the thickness or porosity, indicates that the Celite has the greater surface. This same conclusion can be drawn from the fact that the density of the Celite is much smaller than that of the fuller's earth. If then the Celite has the greater surface, it is evident that α is not alone dependent on the surface, as α for the Hill Chemical Co. earth is over ten times that for the Celite. The value of α may, however, vary with the number of elementary adsorption spaces (Langmuir's theory), or extent of active surface which is different for the various adsorbents irrespective of the surface.

An attempt was made to determine the value of α for the same earth of different meshes to see if it varied with the extent of surface, or roughly with the mesh. Fuller's earth (Midway, Florida) of different meshes was used for this purpose. The coarse samples, however, were found to disintegrate on agitation, and hence such comparisons could not be made. The 100 mesh earth gave a smaller value of α than the 60–100, and 30–60 mesh just the reverse of what would be expected. A lack of homogeneity of the samples as received was suspected, and so the 60–100 mesh sample was ground to 100 mesh and the constants redetermined. As was expected, this gave a greater value of α than that for the 60–100 mesh.

The order of the values of α for the various earths is not changed by using different dyes of the same character. This can be shown by comparing the ratios of the values of α for two earths with methylene blue and with auramine. In order to make this comparison of the adsorption power of the various earths, which should be free from uncertainties in the values of 1/n, the actual amount of dye adsorbed at some one equilibrium concentration within the experimental range (0.00159 g. per l.) was determined for the various earths. These values and their ratios are given in the following table.

	Methylene blue.	Auramine.	% deviation.
Celite	0.0183	0.0115	
Fuller's Earth (Midway, Florida)	0.0639	0.0324	
Fuller's Earth (Hill Chem. Co.)	0.113	0.0649	
Fuller's Earth (Standard Oil Co.)	0.219	0.174	
$\frac{\text{Florida Earth}}{\text{Celite}} =$	3.49	2.82	+ 23.8
$\frac{\text{Standard Oil Earth}}{\text{Celite}} =$	11.95	15.10	– 20.8

	Methylene blue (Cont.)	Auramine (Cont.)	% deviation (Cont.)
$\frac{\text{Hill Chem. Co. Earth}}{\text{Celite}}$ =	6.18	5.65	+ 9.4
$\frac{\text{Standard Oil Earth}}{\text{Hill Chem. Co. Earth}}$ =	1.94	2.68	- 27.6
$\frac{\text{Hill Chem. Co. Earth}}{\text{Florida Earth}}$ =	1.77	2.00	- 11.5
$\frac{\text{Standard Oil Earth}}{\text{Florida Earth}}$ =	3.43	5.37	- 36.2

Though these deviations of the ratio are large, they are not all in the same direction and hence cannot be attributed to the nature of either of the adsorbed substances. Only in the case of the treated Standard Oil earth was erythrosine sufficiently adsorbed to obtain quantitative data. From a qualitative standpoint, however, the order of adsorption was the same as that given by methylene blue and auramine. It hence appears that even such totally different adsorbed substances as acid dyes and basic dyes place the earths in the same order of adsorptive power.

The fact that with methylene blue the natural and artificial adsorbents have two distinct values of 1/n suggests that this difference may be due to some physical difference between the adsorbents. Thus Celite and silicic acid have practically the same chemical composition, while the value of 1/n for the former is 0.0654 and the latter 0.143. An important distinction between the natural and the artificial substances may result from the differences in the pressure or temperature to which they may have been subjected.

Several of the adsorbents were hence heated at about 320° C for 7–16 hours to determine whether the value of 1/n would be affected. In the case of the Celite and Standard Oil earth (treated) 1/n was unchanged by calcining. The value of α , however, decreased. If the effect of calcining were merely to remove the free water, an increase in the value of would be expected as more earth would have been used per unit of weight.

	Decrease of , %.	Loss of Water, %	Total % decrease of .
Celite	7.5	10.4	17.9
Standard Oil earth	21.5	21.7	43.2

The calcining in this case may hence be said to reduce the extent of active surface but not to affect its nature.

In the case of the silicic acid, however, the values of both α and 1/n were changed. Instead of being decreased as might be expected, 1/n increased in value, being practically doubled. Further data of Pelet and Grande is not in accordance with these results, but rather with those of the Celite and Standard Oil earth in which 1/n was not affected by heating the substance. Pelet and Grande, however, did not give the temperature and time of calcining which would likely affect the results, and perhaps account for the deviation (see table of values of α and 1/n). Sufficient data is not available to make any generalization concerning this phenomenon, which would undoubtedly repay further investigation.

It was at first thought that an adsorbent which followed the experimental adsorption equation was necessarily a simple adsorbent as a mixture of two adsorbing constituents with different values of 1/n would give a curved line when plotted logarithmically. This line is, however, only slightly curved over a considerable range for mixtures of adsorbents whose values of 1/n differ by one hundred percent or less. The determination for a mixture of three parts of silicic acid and one part of Florida earth (100 mesh from 60) gave a straight line with the same value of 1/n as the theoretical, but a slightly smaller value of α. It is evident from this that a practically straight logarithmic curve does not prove the presence of a single type of adsorbing constituent in the earth.

The addition of acids and salts to the solution does not alter the value of 1/n, but does affect that of α (see table of values of α and 1/n). Both the addition of acid to the adsorption mixture, and the treatment of the earth with acids, as in the case of the Standard Oil earth, lower the value of α for the basic dyes. This may be explained by the theory of selective adsorption. The earths have a special affinity for bases, even when neutral, and will adsorb the bases from a basic dye, leaving the solution acid. When more acid is added it has the effect of reversing the reaction or in other words diminishing the adsorption.

It is of interest to note here that the effect on the adsorptive power, or value of α of treating an earth with acid is quite different in clarifying lubricating oils from the adsorption of basic dyes. In oil purification the acid treatment has the effect of increasing the adsorptive power several fold. This difference may be due either to the nature of the solvent, the nature of the adsorbed substance, or both. It appears as though the earths which are negatively charged towards water are positively charged towards oils.

It was not possible to obtain results from the addition of a base to the adsorption mixture in the case of methylene blue, as this dye is precipitated by alkalies, and hence complications would arise. Potassium chloride was used to determine the effect of a neutral salt. Like hydrochloric acid, it decreased the value of α . Complications entered into the effect, however, because of further disintegration of the earth. Identical adsorption mixtures, differing only in that potassium chloride was added to some, were run under parallel conditions. The presence of the salt caused a decrease in the adsorptive power (Table V Series 2.).

Peculiar results were obtained with alumina and methylene blue, and the Standard Oil earth (treated) and erythrosine. In both cases a definite amount of dye was adsorbed irrespective of the amount of adsorbent employed. It is questionable in both of these cases if the phenomena represent a true adsorption as methylene blue is precipitated with alkalies, and erythrosine with acids. The adsorbents do not contain free soluble base and acid, however, as shown by experiment.

If some of the alumina is agitated with water and then phenolphthalein add, the water turns pink; but if it is filtered before adding the phenolphthalein there is no color change. Similarly, if the treated Standard Oil earth is shaken with water and a piece of blue litmus paper touched to the earth, it will turn red,; but if the mixture is filtered and the litmus paper dipped into the filtrate there is no color change. This may be explained by the theory of selective adsorption. The alumina which evidently has a greater affinity for acids than bases adsorbs the acid from the phenolphthalein, leaving the solution alkaline. When phenolphthalein is added after filtering off the alumina, there is no chance for adsorption, and as the alumina is insoluble in water, the water remains neutral. In the case of the Standard Oil earth the base is adsorbed, leaving the solution acid.

From this standpoint the alumina may adsorb the acid from the methylene blue, leaving the solution alkaline, and then the base of the methylene blue is precipitated. Conversely the treated earth adsorbs the base from the erythrosine, leaving the solution acid, and then the acid of the erythrosine is precipitated. This, however, does not account for the peculiar fact that the adsorption, or at least the amount of dye removed from saturation, is independent of the amount of adsorbent. The constant equilibrium concentrations may represent the solubility of the dyes in basic and acid solutions respectively, under conditions such that a slight change in alkalinity or acidity does not affect the solubility.

Summary.

In conclusion this investigation has shown several important points.

(1) The adsorption of dyes from aqueous solutions by fuller's earth, diatomaceous earth, silicic acid, and animal charcoal is, over the range tested, in close accordance with the adsorption equation, $x/m = \alpha c^{1/n}$.

(2) The value of $1/n$ is the same for all natural earths, namely fuller's earth, diatomaceous earth, and sand, both with methylene blue and auramine.

(3) The value of $1/n$ is constant for the artificial adsorbents with methylene blue, and is approximately twice that for natural adsorbents with methylene blue.

(4) The value of α varies greatly for the different adsorbents, and is probably not dependent on the extent of surface alone.

(5) The order of the values of α for the various adsorbents is independent of the dye used.

(6) Adherence to the adsorption equation does not indicate a single type of adsorbing constituent in the adsorbent.

(7) Calcining the natural earths does not affect the value of $1/n$, and reduces that of α. Calcining silicic acid, however, does affect the value of $1/n$ as well as that of α.

(8) The addition of acids and potassium chloride to the earths decreases the value of α for basic dyes, while that of $1/n$ is not affected. This is in accordance with the selective adsorption theory.