8-1968

The Dispersion of Titanium Dioxide in Paper

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THE DISPERSION OF TITANIUM DIOXIDE IN PAPER

by

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A Thesis submitted to the
Faculty of the Department of Paper Technology
in partial fulfillment
of the
Degree of Bachelor of Science

Western Michigan University
Kalamazoo, Michigan

August 1968

ABSTRACT

It has been recognized in the past that certain means of dispersing titanium dioxide in paper yielded better results. An optimum dispersion is one that results in the best optical efficiency of the pigment in the sheet.

In an attempt to pinpoint the optimum conditions the following facts were revealed. Increased mechanical action on the stock slightly increases the brightness and opacity. Pigment addition to higher consistency stock increases brightness and opacity considerably. The alum agglomerated impurities of soft water slightly increase opacity and decrease brightness in unpigmented papers; do not appreciably change the optical properties of pigmented sheets. Untreated water probably would magnify the effects. Excessive use of pigment dispersant, or alum is detrimental to brightness and opacity. Neither the order of addition of alum and pigment, nor extending the time of mixing measurably change the optical properties.

Certain factors affecting the dispersion of titanium dioxide in paper were revealed, but certain other mysteries about the pigment-fiber relationship still remain. Other means must be found to resolve them since small deviations and variations in handsheet formation and analysis are unavoidable, and tend to obscure results.

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LITERATURE SURVEY

Brightness and opacity are the principle optical properties of paper and indicate quality. Today, the market for papers with high brightness and opacity is exceedingly large. Writing, envelope, publication, photographic, reproduction and waxed grades of all sorts have been improved in this direction to meet the growing needs of the consumer.

Many pigments are marketed today which enhance the optical properties of paper. Some, like clay, have been in use for more than a century while others, such as TiO_2, are comparatively recent. The rate of increase of titanium pigment consumption has been greater than the growth of the paper industry itself. An estimated 185 thousand tons of TiO_2 will be used by the industry this year, as compared with less than about 10 thousand tons in 1941.(1) The tremendous increase in the use of an expensive material such as TiO_2 by an industry as cost conscious as the paper industry can be explained by the fact that it does something no other pigment can do. The average refractive index of TiO_2 is the highest known of any colorless substance. For this reason titanium dioxide has more "opacifying," or light scattering power per unit weight or volume than any other pigment.

Although optical properties are often of paramount importance, other properties including physical properties such as weight, strength, thickness, and finish, and chemical properties including water, ink or oil resistance, wet strength, and so on are also desired. Some papers have additional specific use properties such as printability which must be incorporated into the design of the sheet. Sheet specifications are generally interdependent. For example, a ten percent filler loading used to

(1) W.R. Willets, "Titanium Dioxide in Paper," Pulp & Paper, V.39, (3/29/65), 23.

obtain the desired opacity may result in a more than tolerable reduction in strength properties of the sheet.(2) Thus, TiO_2 may be necessary to achieve both optical and physical properties when little filler for fiber substitution is possible.

Opacity is a function of the scattering coefficient and brightness according to the theory of Kubelka and Munk.(3) In order to raise opacity at high brightness, the scattering power must be increased. The scattering power of each material in the sheet is, in turn, dependent upon the refractive index of the material, its shape, and its dispersion in the system.

Due to the unavoidable expense of manufacturing titanium dioxide, the most that the paper industry can do to minimize the cost of the pigment is to maximize the results of its use. Much time and effort has already been spent investigating TiO_2 and its use in papermaking systems. The scope of this report is to conduct a fundamental investigation of a system composed only of pigment, fiber, alum, and water, with emphasis on dispersion of the pigment rather than retention, since it is essentially the maximization of dispersion which effects a maximization of scattering power. Retention of the pigment is important, especially in an open system or one in which furnish changes are frequent, but high retention does not necessarily result in an optimum dispersion or maximum efficiency.

As is well known, light is scattered when it passes through adjacent materials of different refractive indices. For example, bleached cellulose (R.I.- 1.53) surrounded by air (R.I.- 1.00) appears bright and opaque because of the difference in refractive indices. When fibers are crushed

(2) D.A. Hughes, "Methods of Obtaining the Optical Properties of Papers Containing TiO_2 and Mixtures of TiO_2 and Other Fillers," Tappi 45,2, 159A-161A.

(3) H.B. Clark, "TiO_2 in Papermaking," Paper Ind., V46, Aug.64, 394.

close together by calendering, or the air spaces between the fibers are filled by oil or wax, R.I. about 1.45, there is a loss of opacity and brightness because the difference in refractive indices is diminished.

Titanium dioxide is produced in two forms, anatase with a refractive index of 2.55, and rutile with refractive index of 2.70. Rutile has a more compact molecular structure. This fact is considered to account for its higher refractive index.(4) Theoretically then, rutile particles have twenty or thirty percent more opacifying power than anatase particles.

In addition to the refractive index, the shape or geometry of the particle plays an important role in the development of scattering power and consequently, opacity. Light scattering increases as the size of the particle decreases to about half the wavelength of light. Retention of the pigment alone is not the final answer in the maximization of the use of TiO_2 for this reason. "Large clumps" of particles are not as effective opacifiers as small particles although they are more easily retained in the fiber mat. Particle sizes below a half a wavelength are too small to interfere with passing light rays, and so they are of little pigmentary value. The maximum scattering efficiency is obtained when the particles are about 0.3 microns in diameter.(5)

The particles of titanium dioxide should be spaced about one wavelength from each other in order to obtain maximum scattering and uniformity. (6) This would require each pigment particle in the sheet to be approximately a half micron from the neighboring pigment particles.

However, a fiber mat is not such an orderly arrangement. Looking at

(4) Titanium Pigment Corporation, Handbook, Copyright 1955, 13.

(5) Ibid., 18.

(6) H.B. Clark, "TiO_2 in Papermaking," Paper Ind., V.46, 394.

one closely with a microscope, one might compare it with the arrangement in an amorphorous substance with short range order, but certainly not with the orderly arrangement of atoms or molecules of a crystalline substance. The question of how pigment particles of any size are arranged and held in the sheet is an important one. Two principle theories have been proposed.(7) Mechanical filtration is one popular theory in which the TiO_2 agglomerate particles are caught in the pores between bonded fibers and fibrils. Mechanical filtration does not involve the formation of a chemical bond between the pigment and fiber. Factors affecting the pore sizes in the mat or the particle agglomerate size will affect the retention. An increase in the agglomerate size, reducing the pore size by beating, the use of gelatinuous materials such as aluminum hydrate will improve the retention. Reducing the drainage rate, and increasing the basis weight and consequently, mat thickness should also increase the retention of pigment particles.

The other theory of TiO_2 retention does involve electrostatic attraction between pigment and fiber, and is frequently refered to as coflocculation. Both cellulose fibers and TiO_2 particles have a negative charge in water. Alum can neutralize the charge of the pigment particles, and an induced attractive force can develop as the pigment contacts the surface of a fiber. It has been observed that the coflocculation type forces between pigment and fiber is sufficiently great to withstand the flow of water past it as the web is formed. Coflocculation allows smaller particles to be trapped in the mat than would be possible if mechanical filtration were the only mechanism. The drainage rate is the principle factor

(7) M.P. Boland and B.J. DeWitt, "Evaluation of Optical Properties," Paper Trade J., V.145, 2/13/61, 36-39.

affecting coflocculation of the pigment and fiber.

It is hoped that the factors affecting the light scattering power of the pigment particles in the mat and the resultant sheet opacity as well as the mechanisms of dispersion and retention of titanium dioxide in paper will become more apparent as the experimental procedure is carried out.

OBJECTIVE & EXPERIMENTAL DESIGN

The object of this study is to measure the optical properties of handsheets, and relate those properties to the various conditions of pigment dispersion and stock preparation.

The following list of materials, equipment, and methods of analysis pertain to all of the trials. Each trial involves the preparation of a beater of stock equivalent to 360 grams of OD fiber, and the formation of four to seven sets of handsheets. About ten or twelve handsheets are in each set, and represent a single set of experimental conditions.

MATERIALS

Stock: The furnish for all trials was a mixture of 75% Thorso Hardwood Bleached Kraft and 25% Celgar Softwood Bleached Kraft.

TiO_2: NJZ - A410; characteristics:

Type	Anatase
Refractive Index	2.55
Specific Gravity	3.9
Minimum Percent TiO_2	98
Lbs Water/100Lbs Pigment	30
Particle Size (microns)	0.30

Water: All water used in making furnishes and handsheets was soft water, unless specified otherwise.

Alum: The stated weight in grams of granulated aluminum sulfate was disolved in water prior to addition to the stock or water system.

EQUIPMENT

Beater: The method described in TAPPI STANDARDS, T-200 was followed.

Sheetmold: A Noble and Wood mold with proportioner, white water storage and recirculation system was used.

Pressing: The handsheets were wet pressed and then removed from the wires. A single stage pressing for 30 seconds at 50 psi in a British sheetmold press with plates facing the felt sides of the handsheets

followed.

Drying: The handsheets were air dried at standard conditions in in drying rings. They were tested at those conditions.

TESTING

Sheet Weight: In trials A, B, and C, rectangular areas of 6.52 in.^{2} were cut from the handsheets and weighed on an analytical balance. A punch press was used in trials D and E to cut circular sheets of 28.27 in.^{2} area. They were weighed on the same balance as had been used in the previous trials. In the final tabulation, all weights are proportional to 28.27 in.^{2}

Opacity: Each handsheet was tested twice on the wire side and twice on the felt side. Those readings were averaged. A Bausch and Lomb opacimeter with a digital read-out attachment was used.

Brightness: An average of one felt side reading and one wire side reading was recorded. A G. E. Brightness tester was used.

Percent Ash: At the conclusion of the optical testing the handsheets were ashed by subjecting them to 800 degrees Centigrade for three hours.

The following is a list of the specific objectives of each trial:

Trial A-

1. Samples taken at time intervals show how much contact time between the pigment and fibers is necessary to obtain an optimum dispersion.
2. Dry addition of pigment in this trial will be compared with subsequent slurry additions.
3. Low freeness will be compared with high freeness in terms of optical efficiency and time required to attain it.

4. The order of addition of pigment and alum will be reversed in another trial.

Trial B-

1. To note the time for development of optical properties.
2. To determine the effect of the order of addition of alum and pigment by comparison with trial A.

Trial C-

1. To note the time required for development of optical properties.
2. To measure the effect of beating on optical properties.

Trial D-

1. To determine the effect of alum.
2. To evaluate slurry addition versus dry addition of pigment.
3. To note the effect of stock consistency as the pigment is added, on the optical properties of the handsheets.
4. To note the effect of Calgon-T pigment dispersant.

Trial E-

1. To determine if the substitution of distilled water for tap water affects the optical properties of the handsheets.
2. To measure the effect of alum on optical properties.
3. To note the effect of using half as much pigment.

TRIAL A

Beater Conditions:

Furnish------ 360 grams OD fiber

Alum--------- 30 grams added at start

Consistency-- 1.65%

CSF---------- 280

TiO_2--------- 35 grams added dry after beating to 280 CSF.

Sheet Making: Samples of 2.25 liters of stock were taken at intervals; before adding the pigment and 10, 20, 35, and 70 minutes after adding it. Each sample was diluted to 13.8 liters and sets of handsheets were made using approximately 900 cc. of diluted stock per handsheet. Twelve liters of fresh water were in the white water reservoir at the begining of each set. No alum or water was added to the mold or system while making a set of handsheets. The sets were separately pressed and air dried at standard conditions in drying rings.

The test results for each handsheet in trial A, labeled handsheet number 1, 2, ..., are plotted graphically in tables I through IV. The handsheet numbers also correspond to the order of their formation. This is also true of trials B through E.

TABLE I

TRIAL A: HANDSHEET WEIGHT

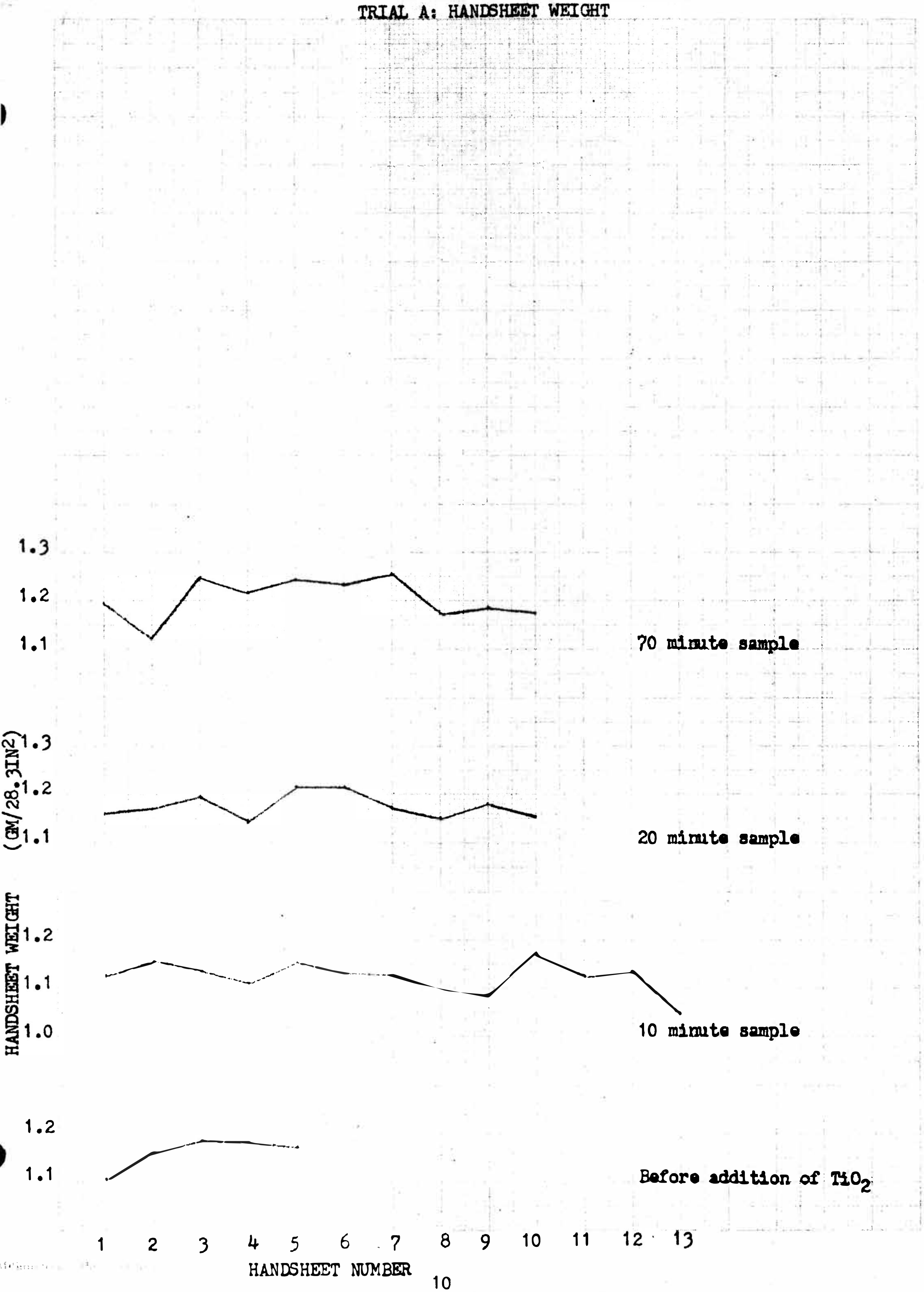


TABLE II

TRIAL A: OPACITY

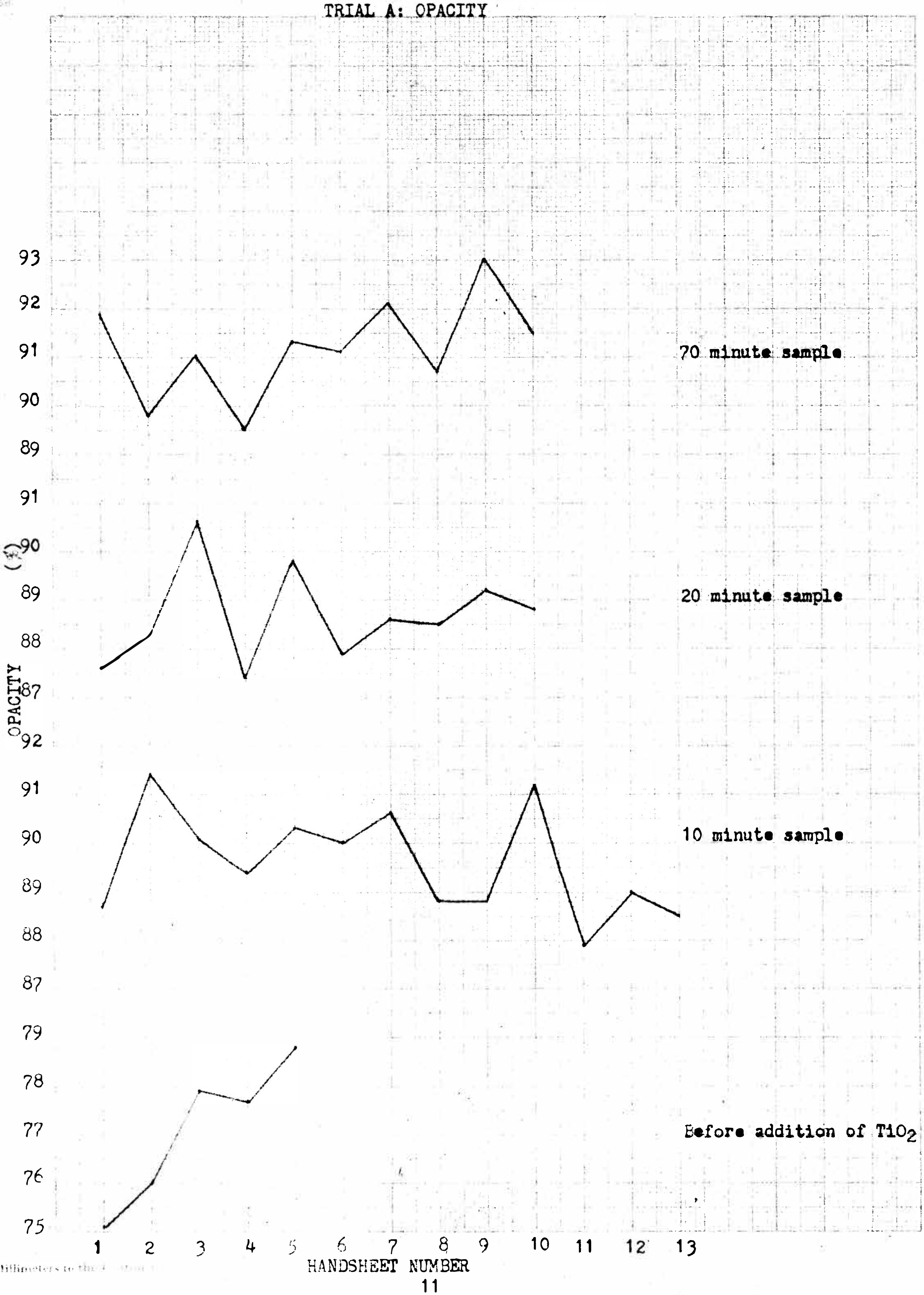


TABLE III

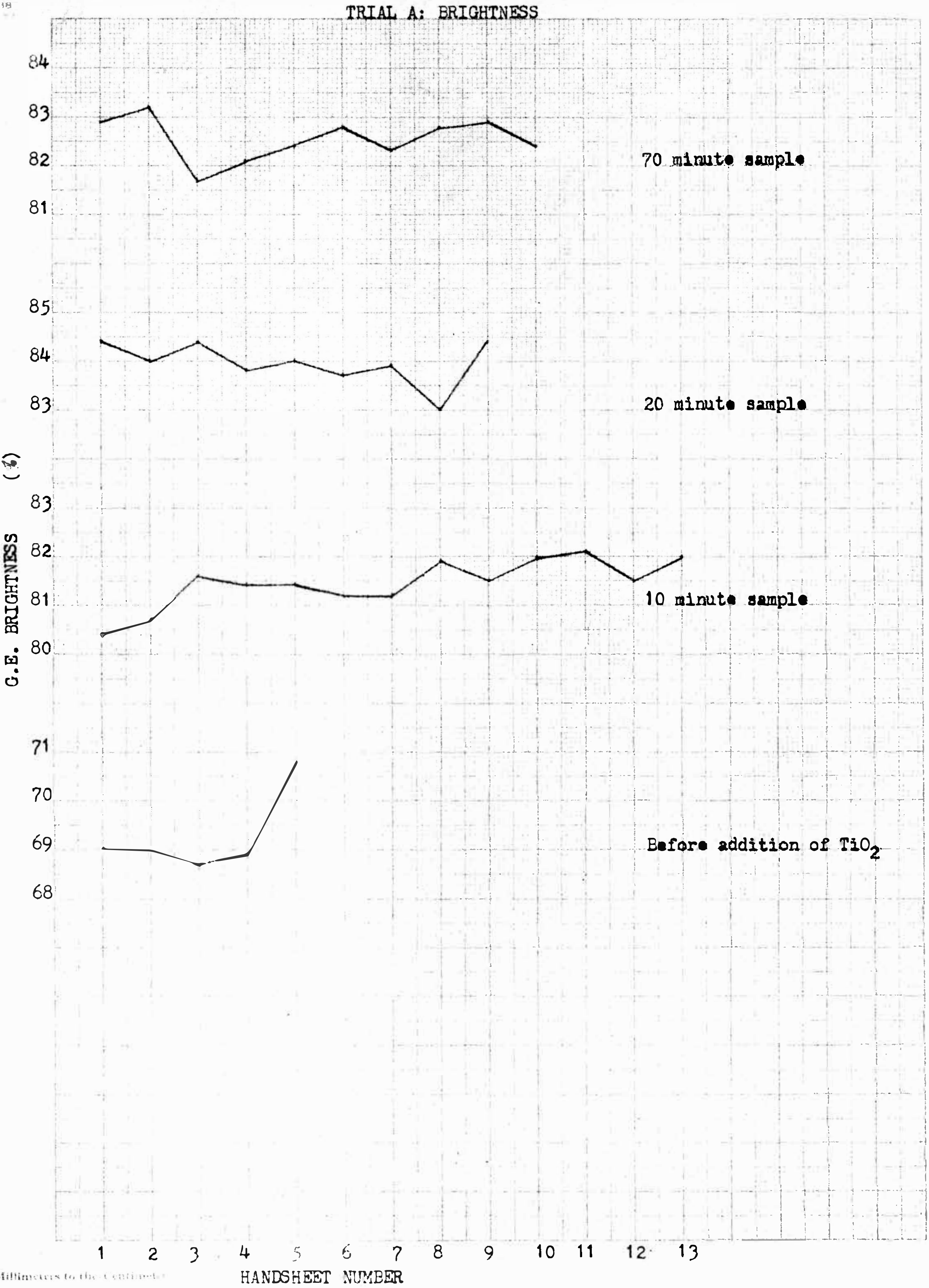
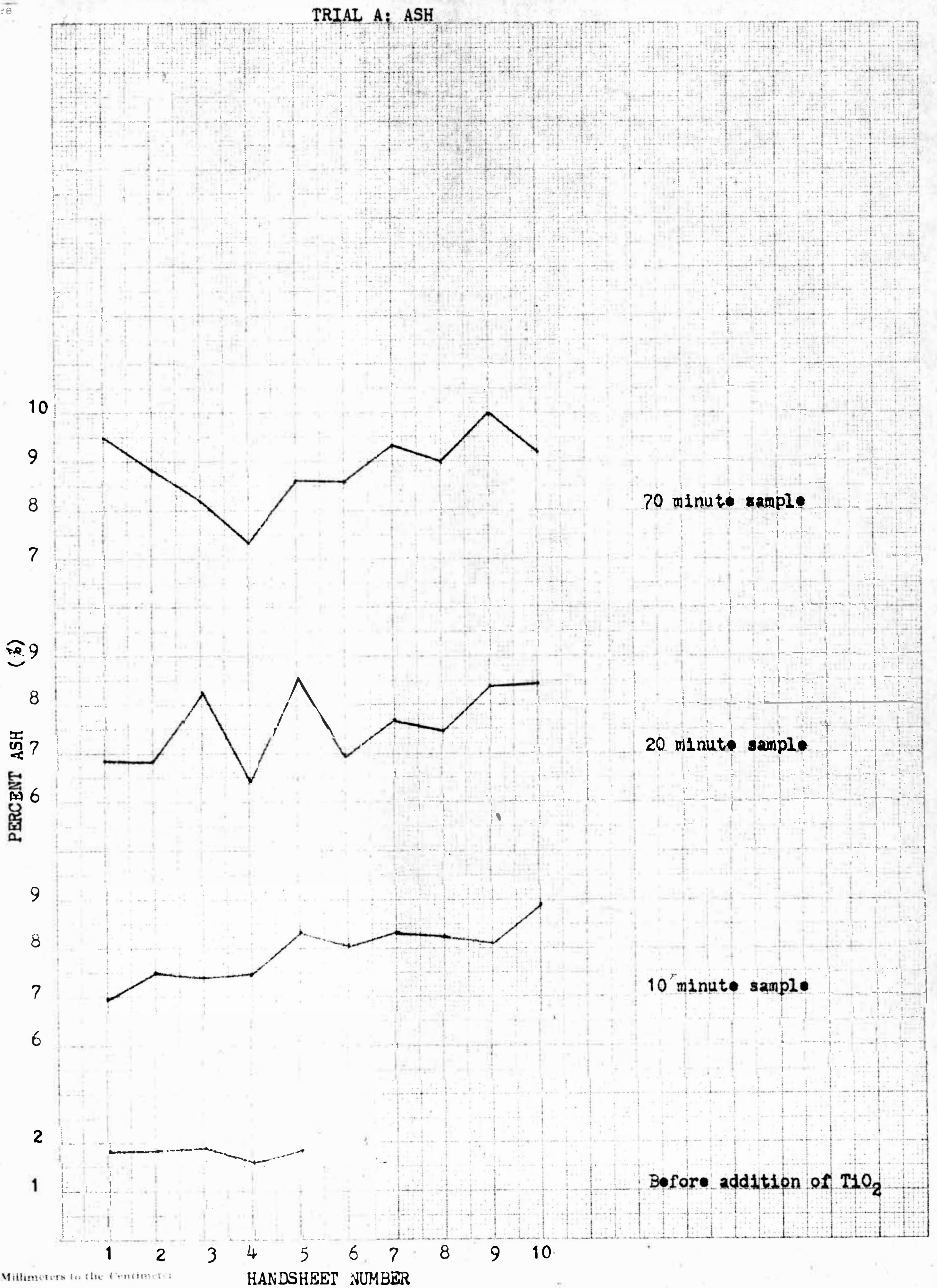

TRIAL A: BRIGHTNESS
84
83
82
81
70 minute sample
85
84
83
20 minute sample
G.E. BRIGHTNESS (%)
83
82
81
80
10 minute sample
71
70
69
68
Before addition of TiO_2
1 2 3 4 5 6 7 8 9 10 11 12 13
HANDSHEET NUMBER

TABLE IV


TRIAL A: ASH
PERCENT ASH (%)
10
9
8
7
9
8
7
6
9
8
7
6
2
1
70 minute sample
20 minute sample
10 minute sample
Before addition of TiO_2
1
2
3
4
5
6
7
8
9
10
HANDSHEET NUMBER
Millimeters to the Centimeter

TRIAL B

Beater Conditions:

Furnish------ 360 grams OD fiber

Alum--------- 30 grams added 5 minutes after pigment

Consistency-- 1.65%

CSF---------- 260

TiO_2--------- 35 grams added dry after beating to 260 CSF.

Sheet Making: Samples of 2.25 liters were taken before the addition of pigment and 10, 20, and 75 minutes after the addition. Each of these samples were diluted to 14 liters and a set of about ten handsheets were made from each sample of stock. The water system was again closed, twelve liters of fresh water was in the reservoir at the start of each set, and the pH of the white water was not controlled. This trial is the same as trial A, except for the time of addition of alum to the beater.

The test results of the handsheets of trial B are plotted graphically in tables V through VIII.

TABLE V

TRIAL B: HANDSHEET WEIGHT

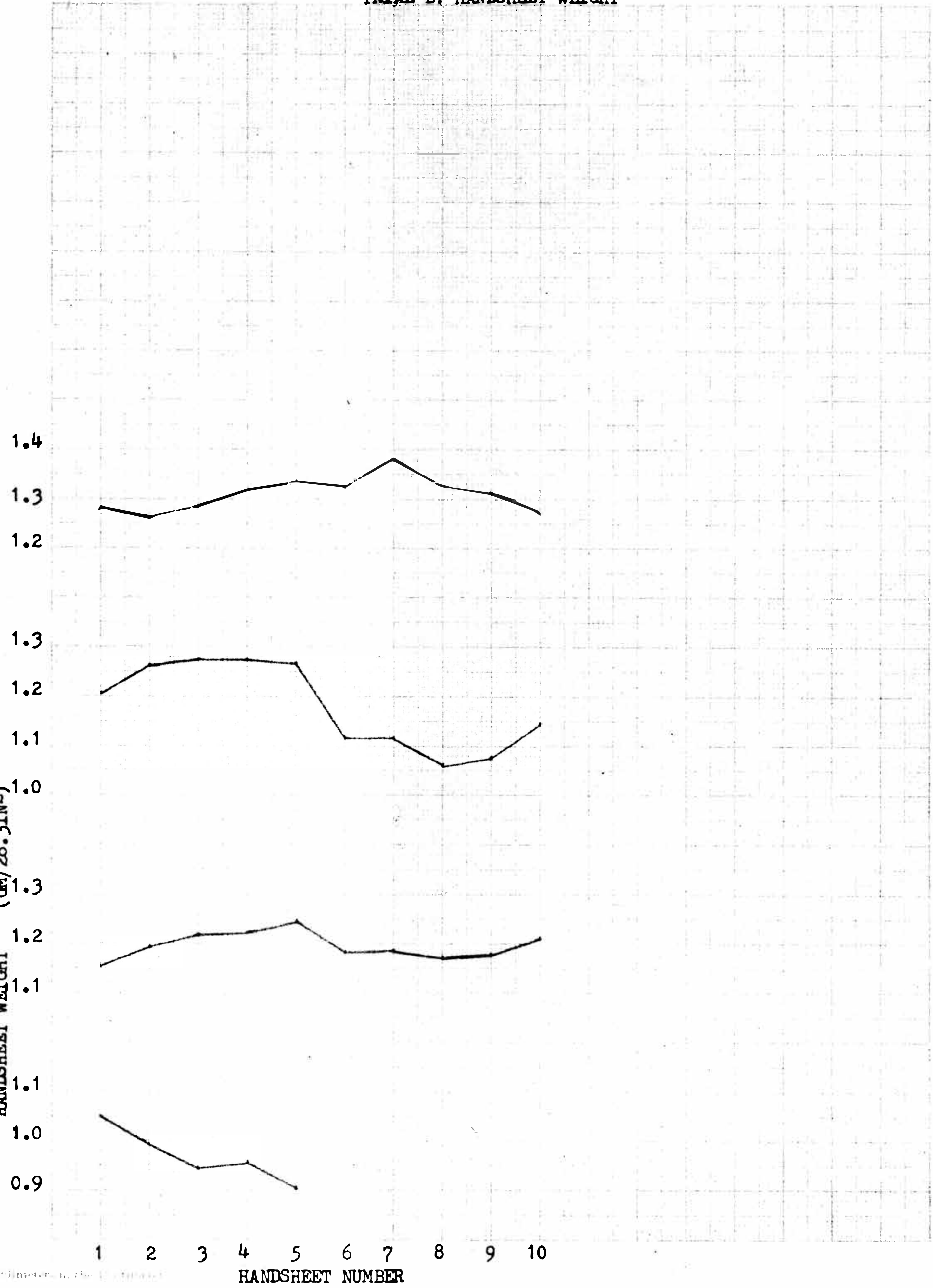


TABLE VI

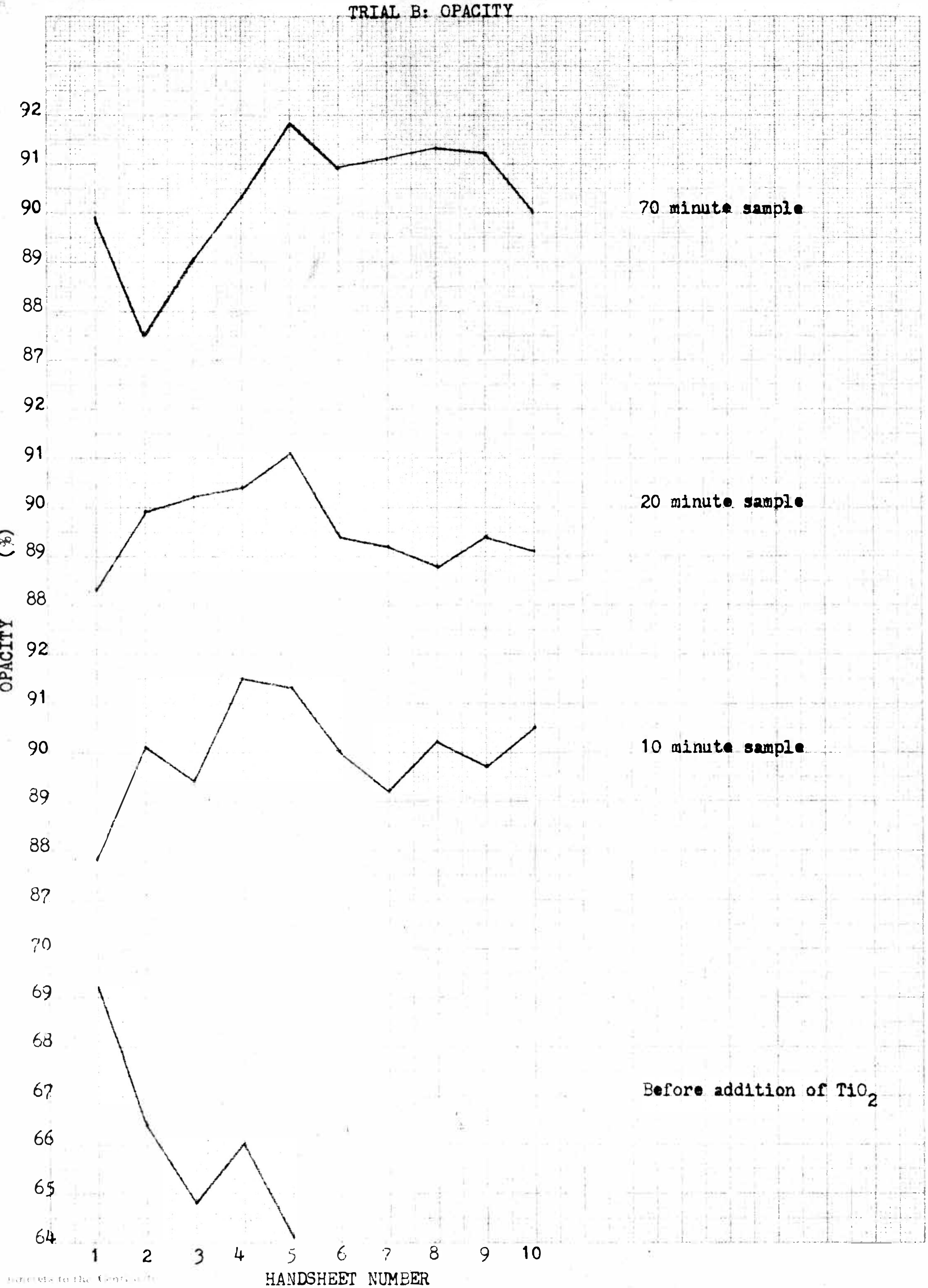

TRIAL B: OPACITY
92
91
90
89
88
87
70 minute sample
92
91
90
89
88
20 minute sample
OPACITY (%)
92
91
90
89
88
87
10 minute sample
70
69
68
67
66
65
64
Before addition of TiO_2
1 2 3 4 5 6 7 8 9 10
HANDSHEET NUMBER

TABLE VII

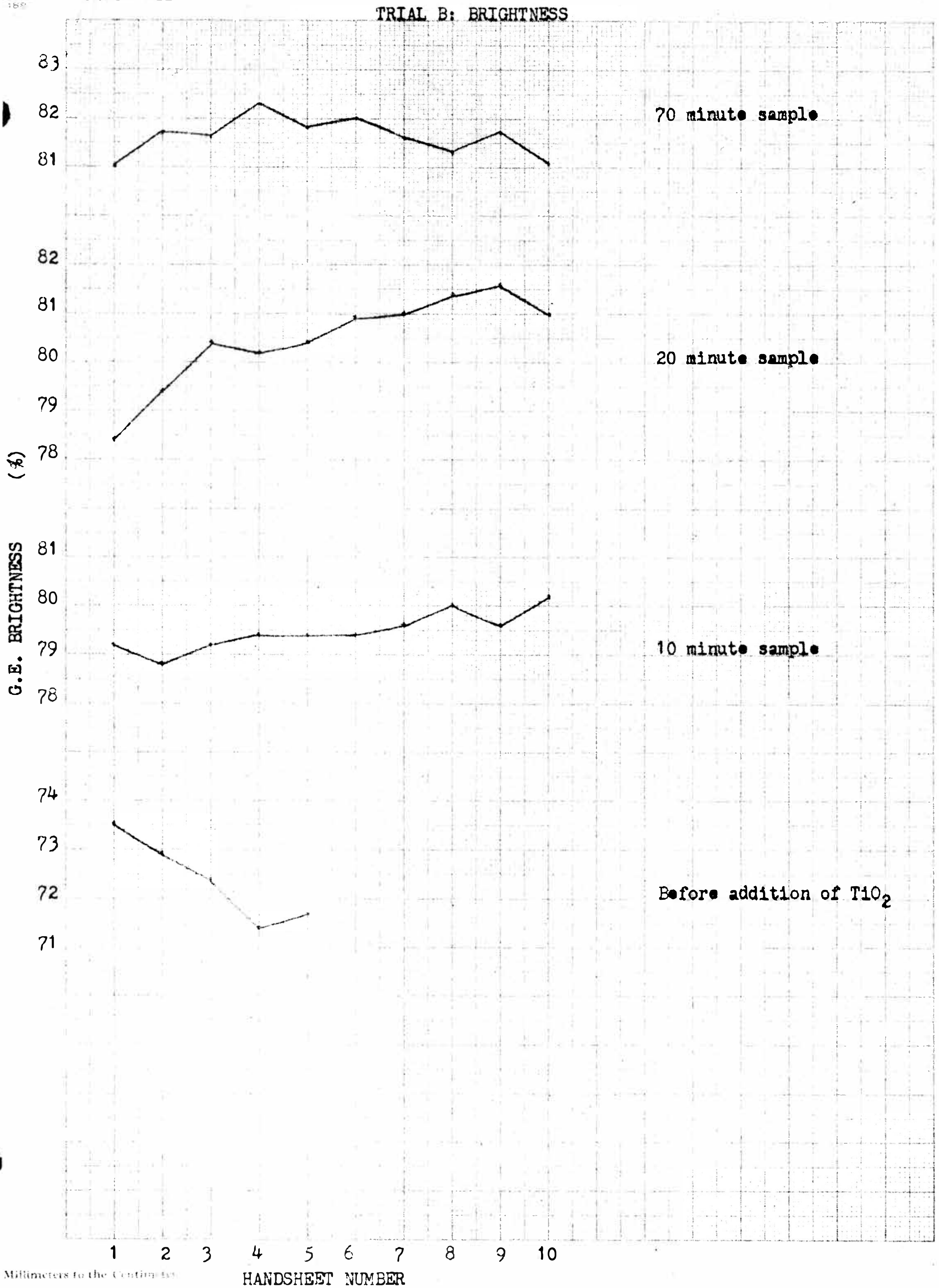
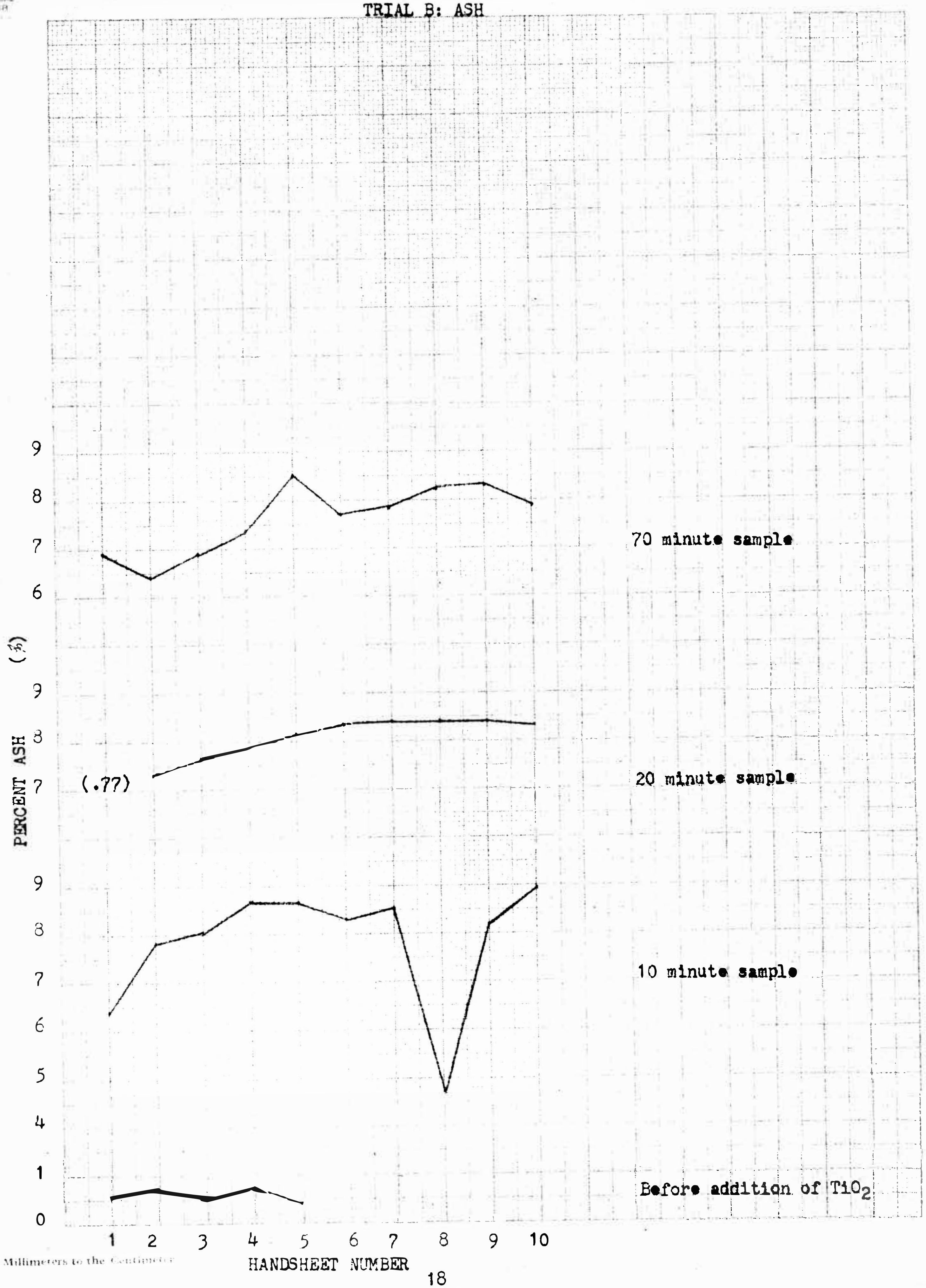

TRIAL B: BRIGHTNESS
83
82
81
70 minute sample
82
81
80
79
78
20 minute sample
G.E. BRIGHTNESS (%)
81
80
79
78
10 minute sample
74
73
72
71
Before addition of TiO_2
1 2 3 4 5 6 7 8 9 10
HANDSHEET NUMBER

TABLE VIII


TRIAL B: ASH
9
8
7
6
70 minute sample
(%)
PERCENT ASH
9
8
7
(.77)
20 minute sample
9
8
7
6
5
4
10 minute sample
1
0
Before addition of TiO2
1 2 3 4 5 6 7 8 9 10
HANDSHEET NUMBER

TRIAL C

Beater Conditions:

Furnish------ 360 grams OD fiber

Alum---------- 30 grams added at start

Consistency-- 1.65%

CSF----------- 550

TiO_2---------- 35 grams added dry after beating to 550 CSF.

Sheet Making: Samples of 1.4 liters were taken before the addition of pigment and 10, 20, and 70 minutes after the addition. Each of the samples was diluted to 8.56 liters and 2.5 gram handsheets were made in the same way as in preceding trials. Trial C is the same as trial A, except for freeness.

Tables IX through XII show the test results of trial C.

TABLE IX

TRIAL C: HANDSHEET WEIGHT

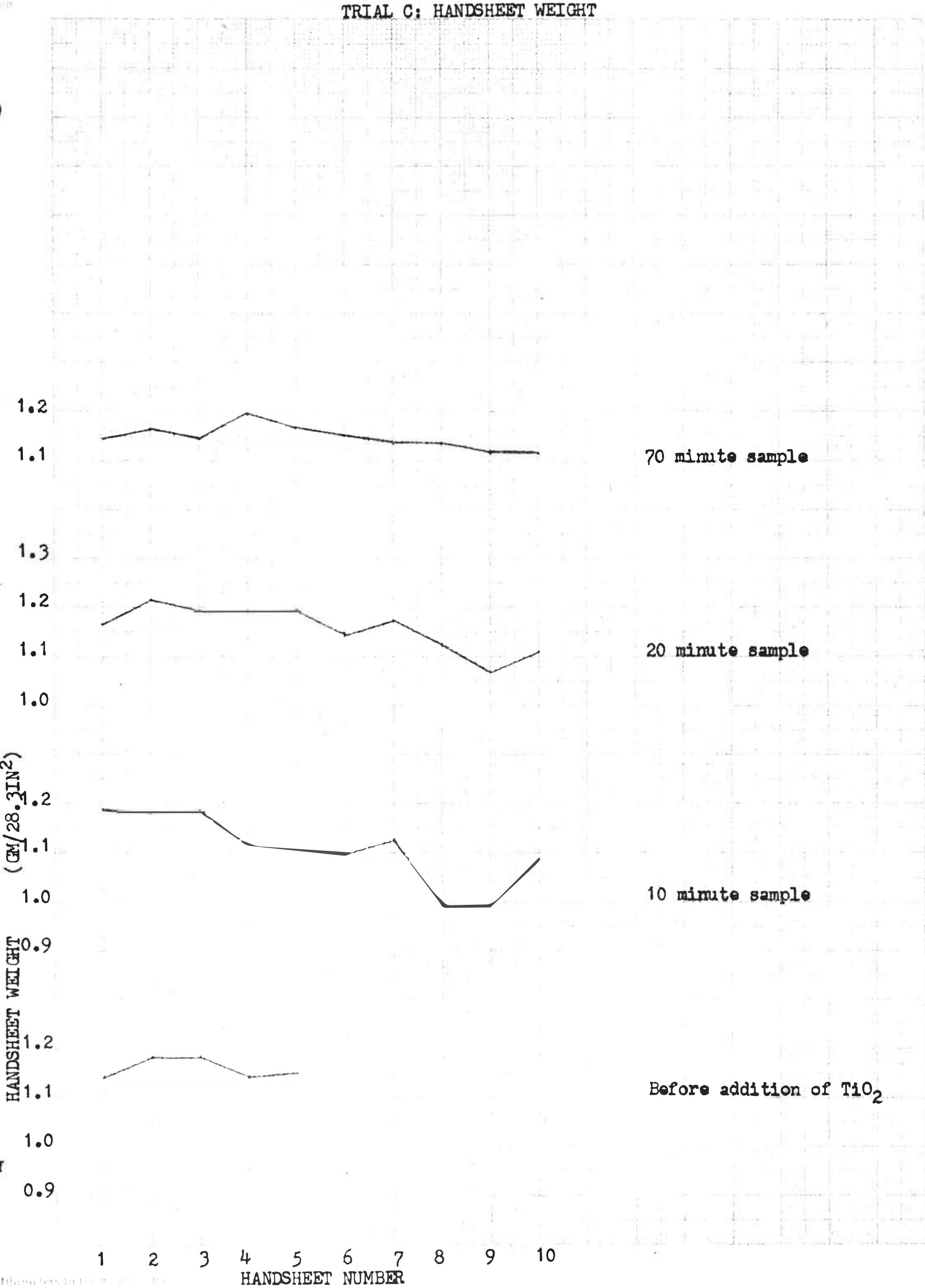
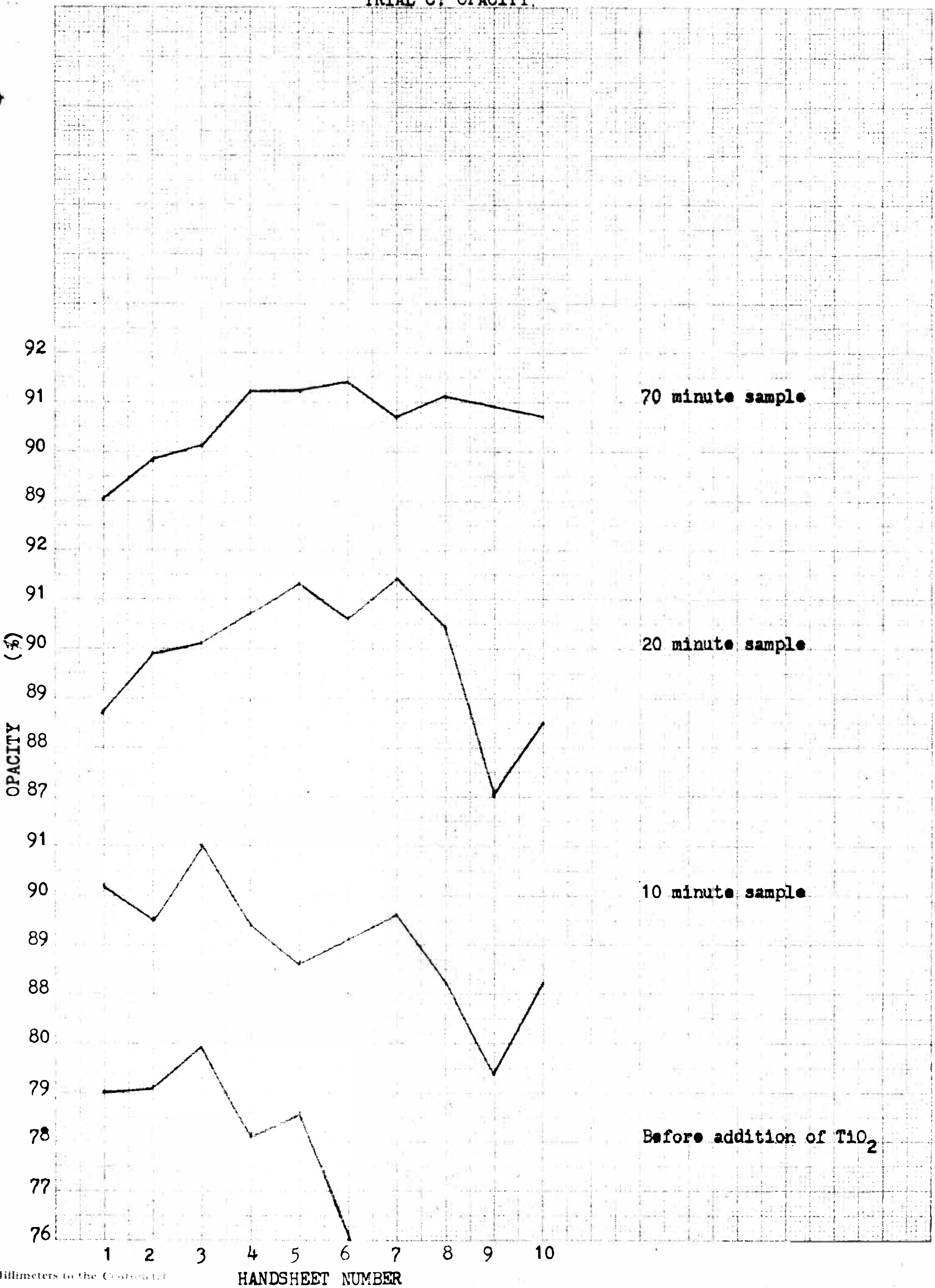


TABLE X

TRIAL C: OPACITY



Millimeters to the Centimeter

TABLE XI

TRIAL C: BRIGHTNESS

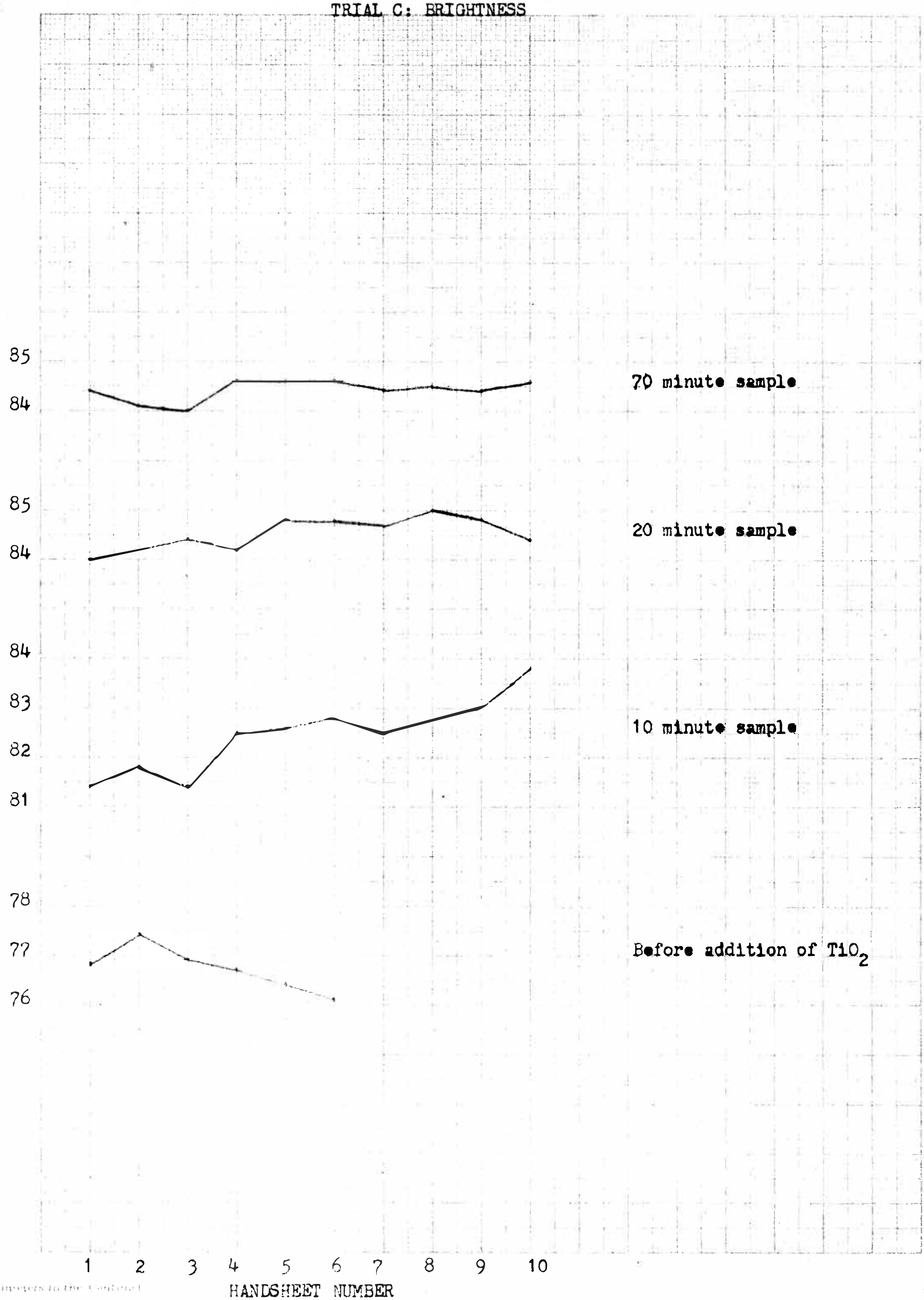
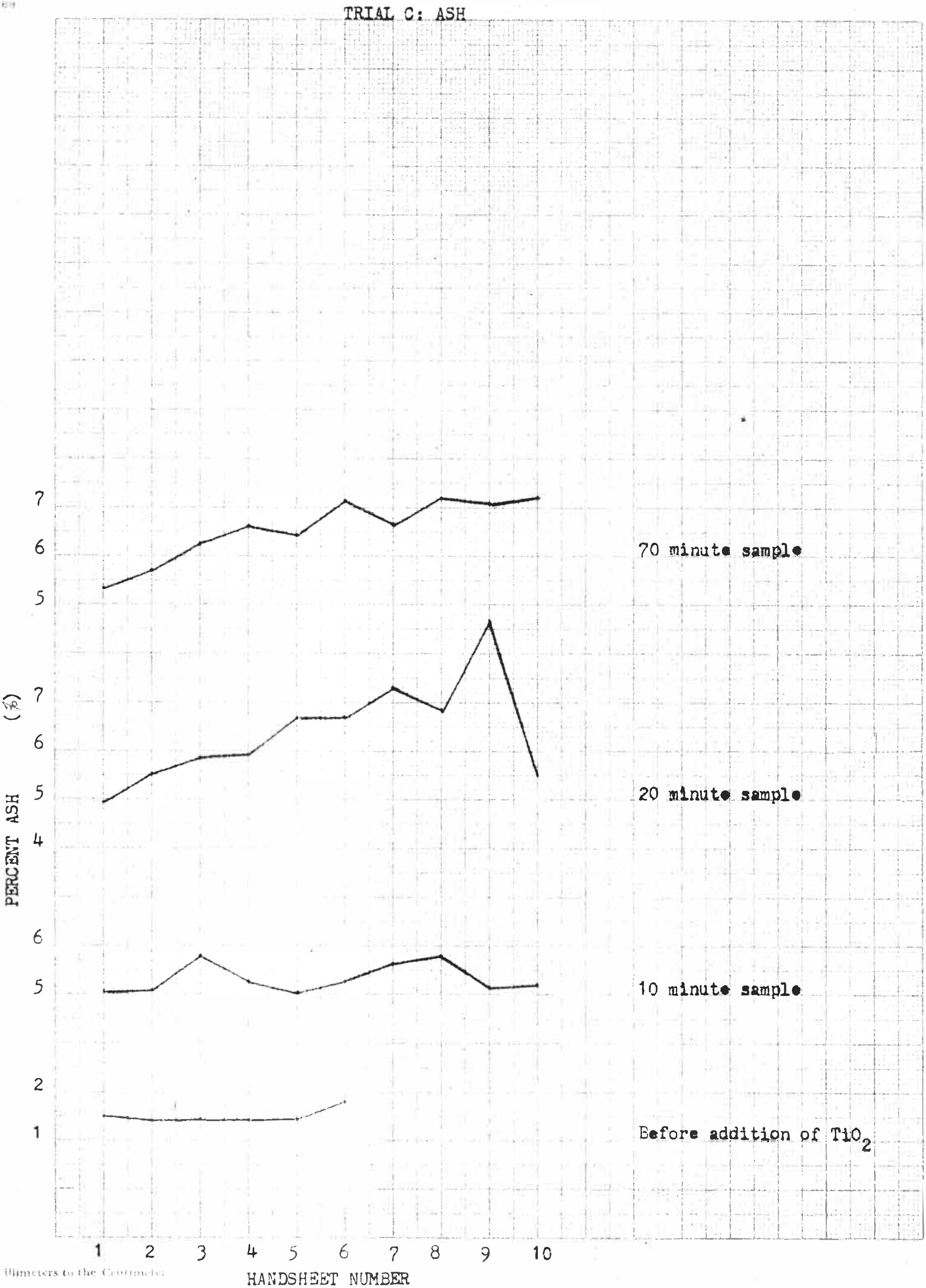


TABLE XII


TRIAL C: ASH
7
6
5
70 minute sample
7
6
5
4
20 minute sample
PERCENT ASH (%)
6
5
10 minute sample
2
1
Before addition of TiO_2
1 2 3 4 5 6 7 8 9 10
HANDSHEET NUMBER

TRIAL D

Beater Conditions:

Furnish------ 360 grams CD fiber

Alum--------- 30 grams added at start

Consistency-- 1.60%

CSF----------- 290

TiO_2----------- None added to beater

Sheet Making: Sample Set 1

Beater Sample---- 2.5 liters

Final Volume----- 14.3 liters in the proportioner

Additional Alum-- None (pH- 6.9)

TiO_2------------- None

pH--------------- 6.7 (final white water)

Sample Set 2

Beater Sample---- 2.5 liters

Final Volume----- 14.2 liters in the proportioner

Additional Alum-- None (pH- 6.9)

TiO_2------------- 100 cc of a 2% dispersion without dispersant, added at proportioner

pH--------------- 6.9 (final white water)

Sample Set 3

Beater Sample---- 2.5 liters

Final Volume----- 14.3 liters in the proportioner

Additional Alum-- 15.5 grams to proportioner (pH- 5.5)
15.6 grams to reservoir (pH- 5.5)

TiO_2------------- 93.7 cc of the 2% dispersion used in set 2 added to proportioner after alum and two handsheets were made.

pH--------------- 5.5 (final white water)

Sample Set 4

Beater Sample---- 2.5 liters

Final Volume----- 14.3 liters in the proportioner

Additional Alum-- 80 grams to proportioner(pH- 5.0)
80 grams to reservoir (pH- 5.1)

TiO_2------------- 86.5 cc of the 2% dispersion used in set 2, added to proportioner after alum, and two handsheets were made.

pH--------------- 5.2 (final white water)

Sample Set 5

Beater Sample---- 2.5 liters

Final Volume----- 14.3 liters in the proportioner

Additional Alum-- 15.6 grams to proportioner (pH- 4.4)
15.6 grams to reservoir (pH- 4.3)

TiO_2------------- 92 cc of a 2% dispersion with dispersant, added to proportioner after alum, and two handsheets were made.

pH--------------- 3.95 (final white water)

Sample Set 6

Beater Sample---- 2.5 liters

Final Volume----- 14.3 liters in the proportioner

Additional Alum-- 30 grams to proportioner (pH- 4.0)
30 grams to reservoir (pH- 3.95)

Approximately twelve handsheets were made from each beater sample in the same way as in previous trials. Twelve liters of fresh water was again in the reservoir at the begining of each set.

The amount of TiO_2 slurry used for each set is based on the weight of fiber in the proportioner, and should be equivalent to 35 grams of pigment per 360 grams of CD fiber, as was used in previous trials. The ratio of pigment to fiber is actually close to ten percent since several three gram samples of stock were removed during the beating cycle for freeness tests.

The pigment was added after the final freeness was reached in all trials. Before making handsheets, the stock was mixed thoroughly for ten minutes after adding the pigment slurry.

The beater samples were taken simultaneously. The bedplate of the beater was released while the samples were taken.

The following tabulation pertains to the pigment slurries used in this trial:

Wt. TiO_2 (gm)	Wt. Water (gm)	Wt. Calgon-T (gm)	Percent Solids		
			Test 1	Test 2	Test 3
10	490	None	2.16	2.09	1.93
10	490	0.035	2.04	2.07	1.68

Handsheet test results are presented in tables XIII through XVI.

TABLE XIII

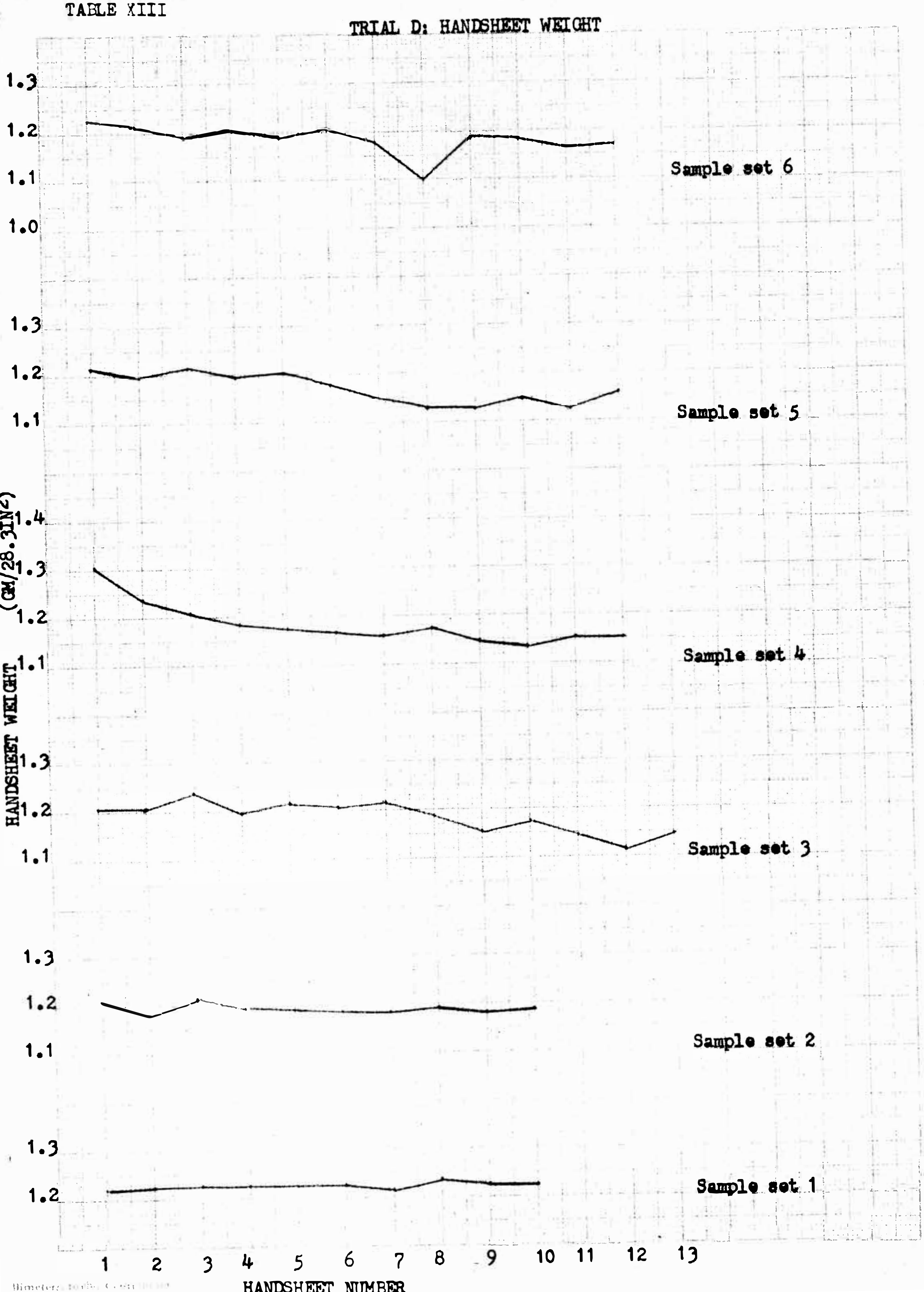

TRIAL D: HANDSHEET WEIGHT
1.3
1.2
1.1
1.0
Sample set 6
1.3
1.2
1.1
Sample set 5
1.4
1.3
1.2
1.1
Sample set 4
1.3
1.2
1.1
Sample set 3
1.3
1.2
1.1
Sample set 2
1.3
1.2
Sample set 1
HANDSHEET WEIGHT (GM/28.3IN2)
1 2 3 4 5 6 7 8 9 10 11 12 13
HANDSHEET NUMBER

TABLE XIV

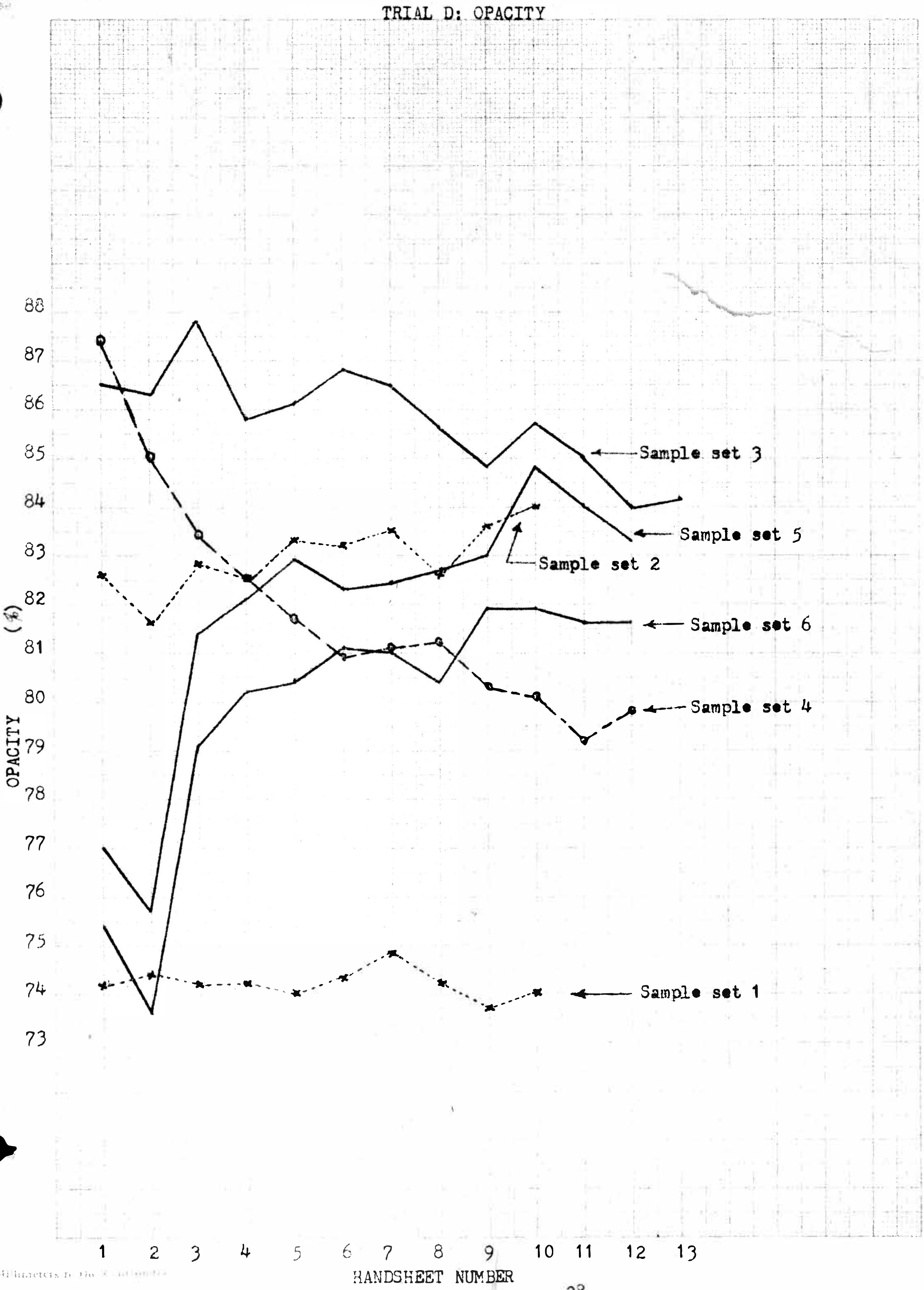

TRIAL D: OPACITY
OPACITY (%)
88
87
86
85
84
83
82
81
80
79
78
77
76
75
74
73
Sample set 3
Sample set 5
Sample set 2
Sample set 6
Sample set 4
Sample set 1
1
2
3
4
5
6
7
8
9
10
11
12
13
HANDSHEET NUMBER

TABLE XV

TRIAL D: BRIGHTNESS

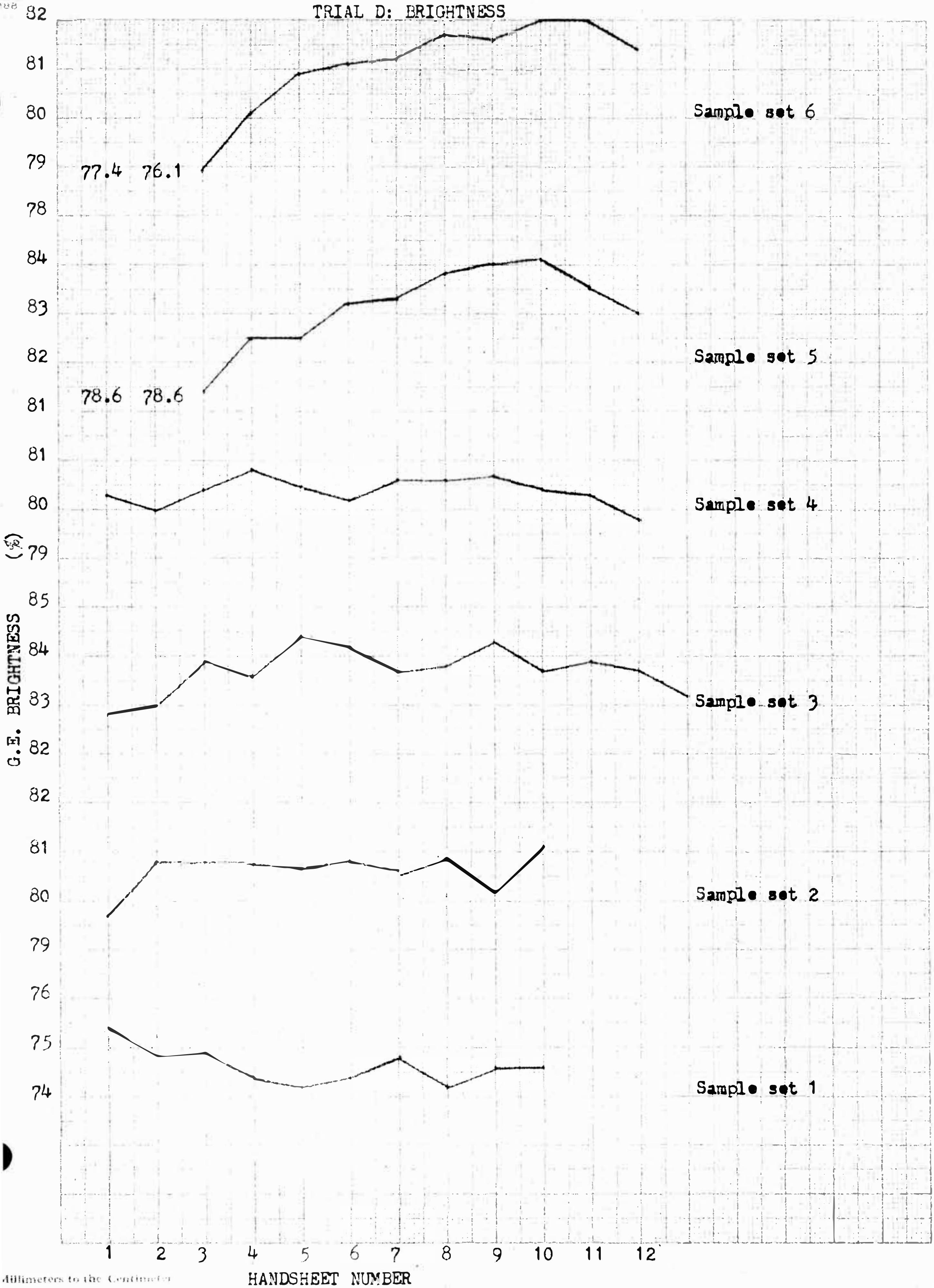
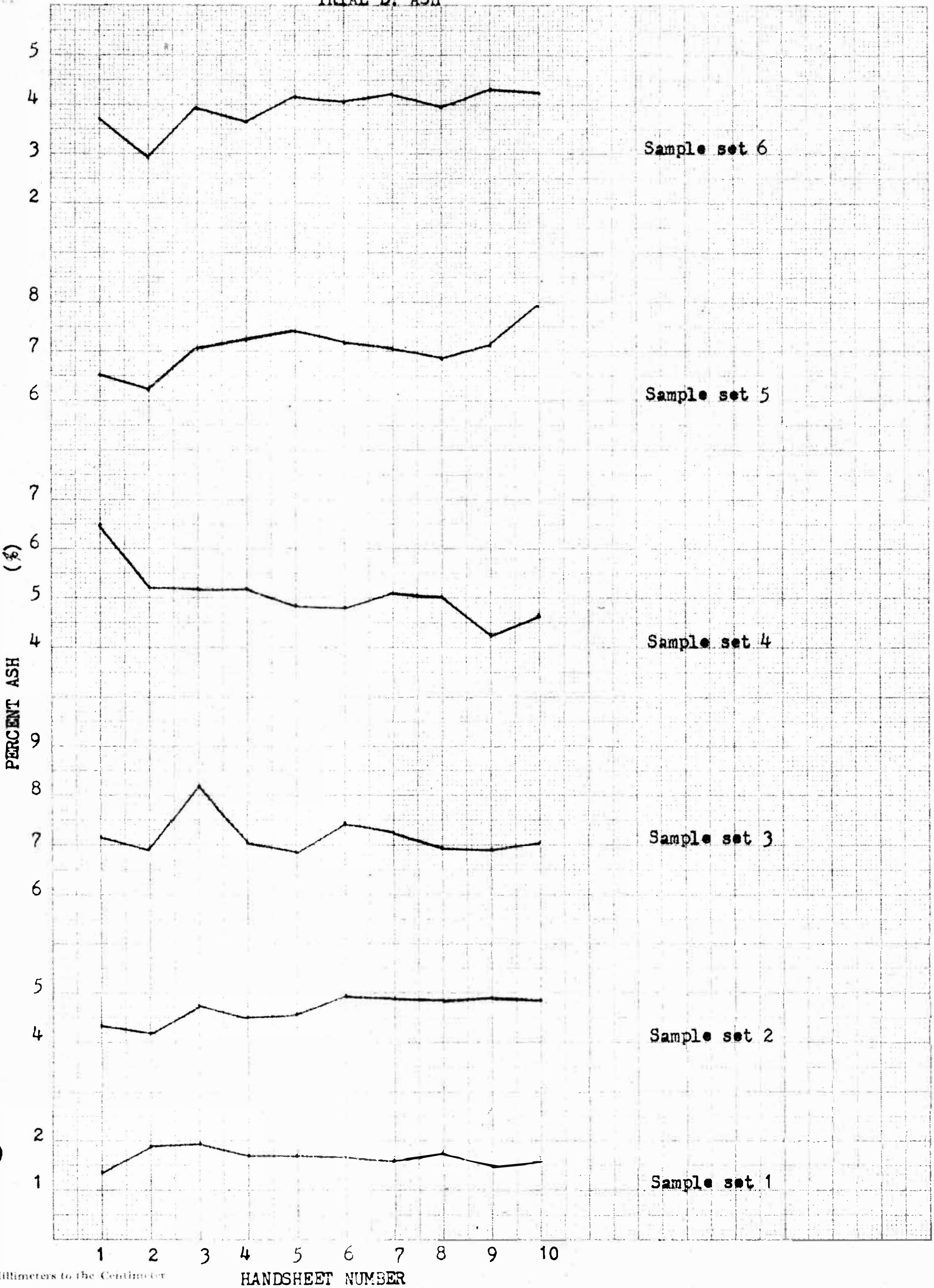


TABLE XVI

TRIAL D: ASH



TRIAL E

Beater Conditions:

Furnish------ 360 grams OD fiber

Alum--------- None added to beater

Consistency-- 1.65%

CSF---------- 250

TiO_2--------- None added to beater

Water-------- Distilled

Sheet Making: Sample Set 1

Beater Sample---- 2.5 liters

Final Volume----- 14.3 liters in the proportioner

Alum------------- None

Water------------ Distilled

pH--------------- 6.5

Sample Set 2

Beater Sample---- 2.5 liters

Final Volume----- 14.3 liters in the proportioner

Alum------------- 30 grams to proportioner (pH- 4.0)
30 grams to reservoir (pH- 4.1)

TiO_2------------- None

Water------------ Distilled

Sample Set 3

Beater Sample---- 2.5 liters

Final Volume----- 14.3 liters in the proportioner

Alum------------- 30 grams to proportioner (pH- 4.2)
30 grams to reservoir (pH- 4.3)

TiO_2------------- None

Water------------ Soft water

Sample Set 4

Beater Sample----	2.5 liters
Final Volume-----	14.3 liters in the proportioner
Alum-------------	30 grams to proportioner (pH- 3.8) 30 grams to reservoir (pH- 3.8)
TiO_2-------------	100 cc of a 1% slurry added after the alum, and two handsheets had been made.
Water------------	Distilled

Sample Set 5

Beater Sample----	2.5 liters
Final Volume-----	14.3 liters in the proportioner
Alum-------------	30 grams to proportioner (pH- 3.9) 30 grams to reservoir (pH- 4.0)
TiO_2-------------	100 cc of the 1% slurry used in set 4 was added after the alum, and two handsheets had been made.
Water------------	Soft water

The 2.5 liter sample of stock for each set of handsheets was taken from the beater immediately after the final freeness was attained, as was done in trial D. Handsheets were made in the same way as in all other trials. The pigment slurry was again added to the diluted stock in the proportioner. It was mixed ten minutes before the handsheets were made.

The following is a tabulation of the slurry data for this trial:

Wt. TiO_2 (gm)	Wt. Water (gm)	Wt. Calgon-T (gm)	Percent Solids Test 1	Test 2	Test 3
10	990	0.085	1.02	1.01	1.00

Trial E testing results are presented in tables XVII through XXI.

TABLE XVII

TRIAL E: HANDSHEET WEIGHT

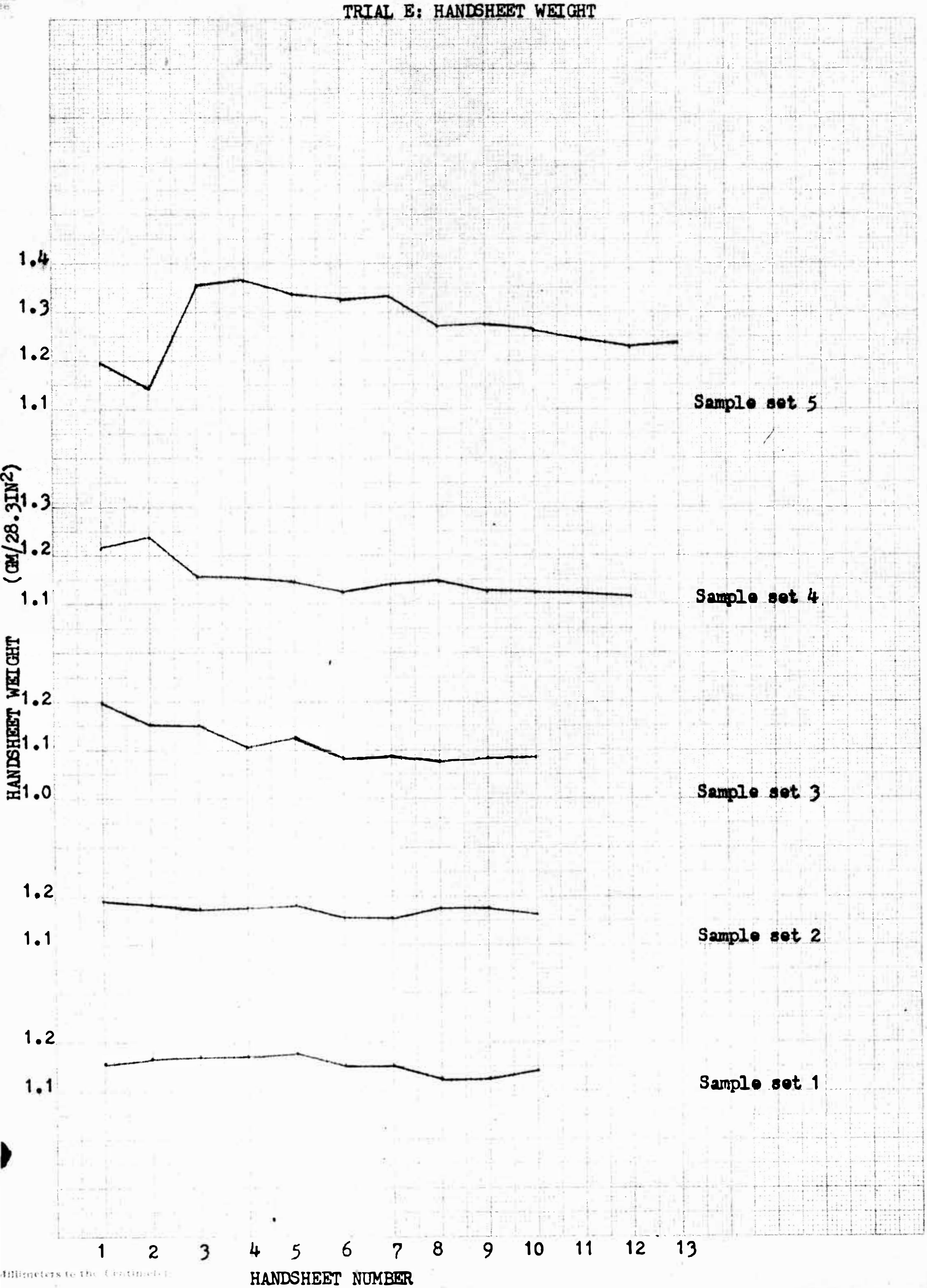


TABLE XVIII

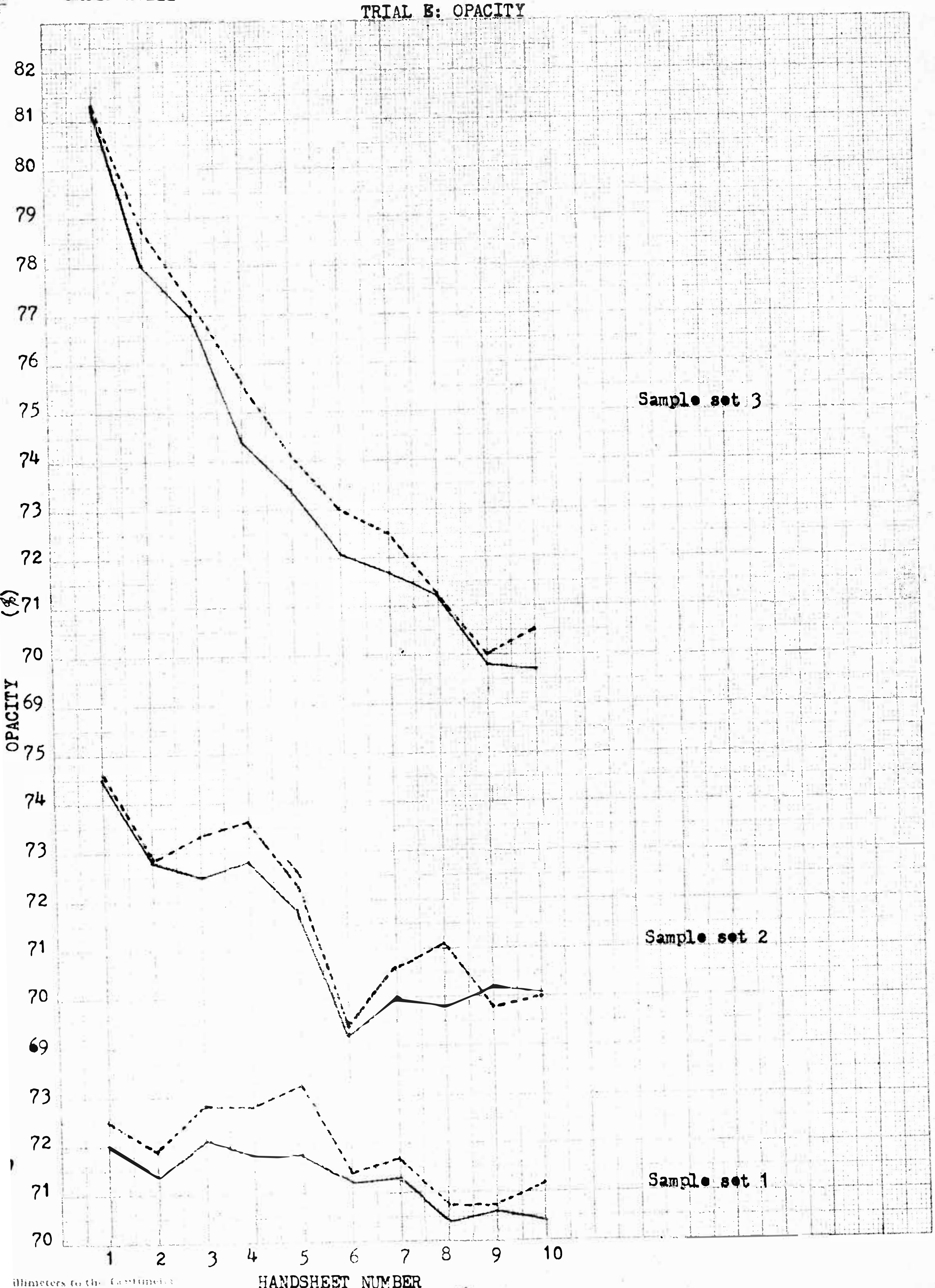

TRIAL E: OPACITY
82
81
80
79
78
77
76
75
74
73
72
71
70
69
75
74
73
72
71
70
69
73
72
71
70
OPACITY (%)
Sample set 3
Sample set 2
Sample set 1
1
2
3
4
5
6
7
8
9
10
HANDSHEET NUMBER

TABLE XIX

TRIAL E: OPACITY

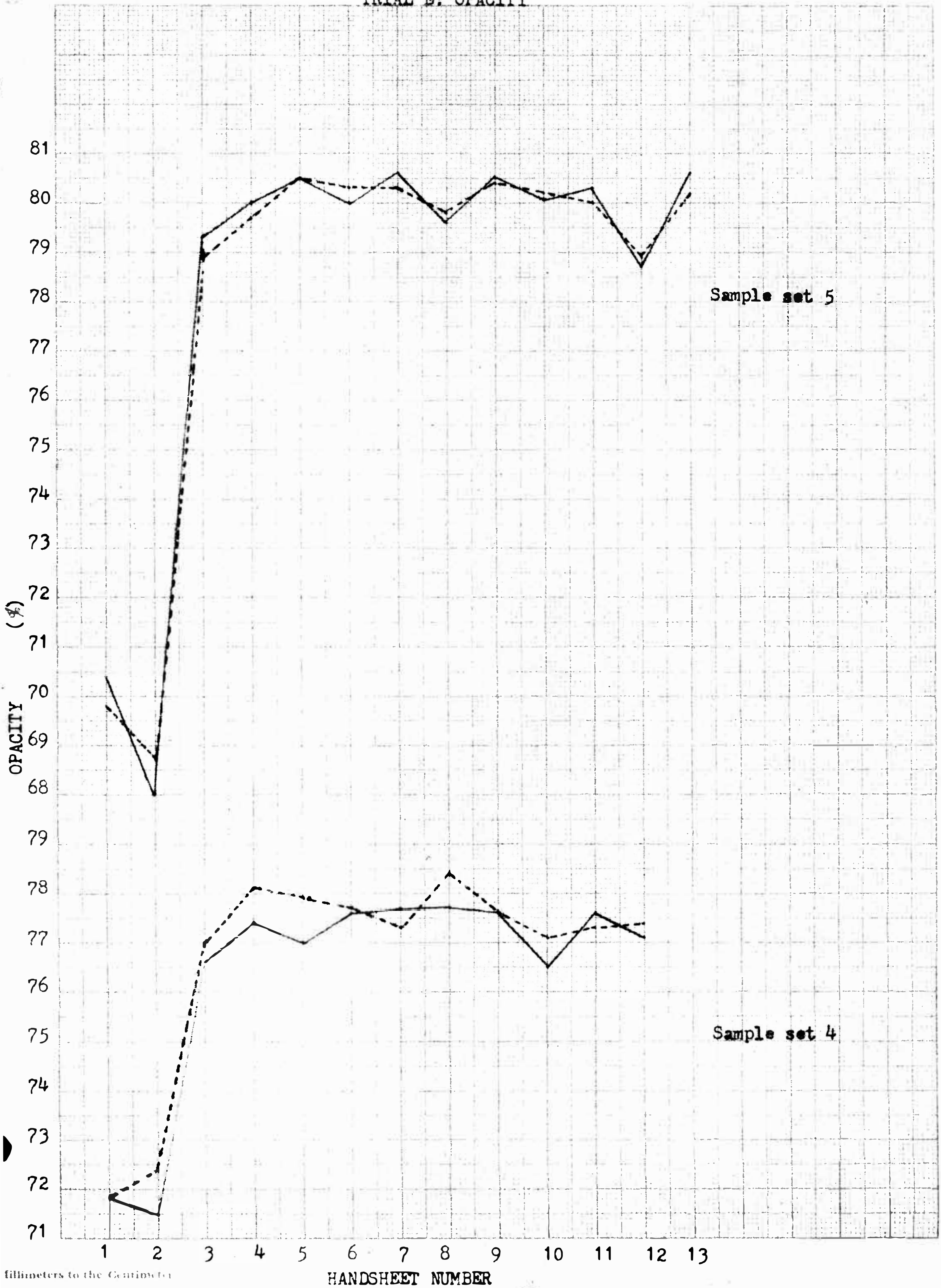
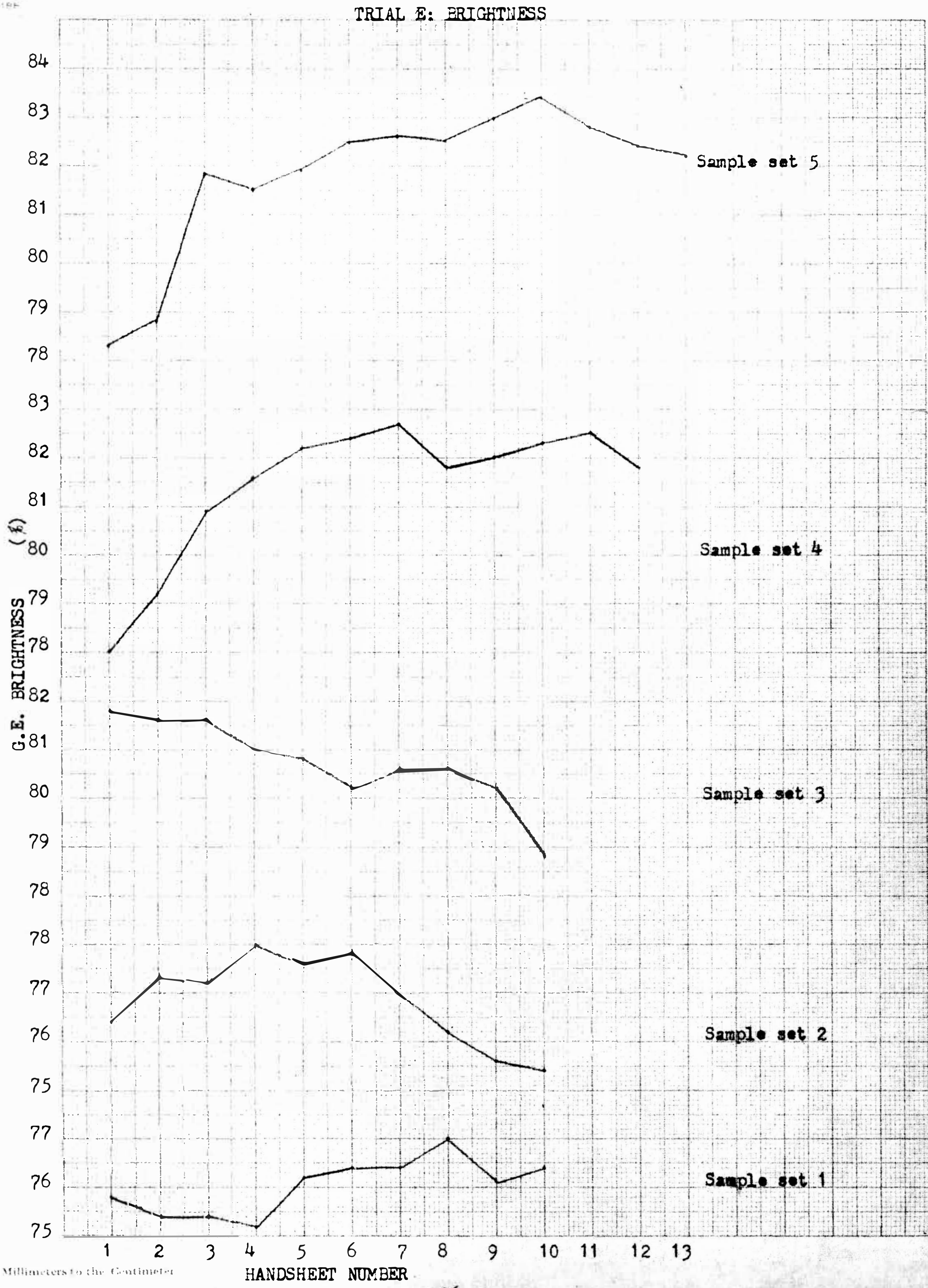


TABLE XX



0 Millimeters to the Centimeter

TABLE XXI

TRIAL E; ASH

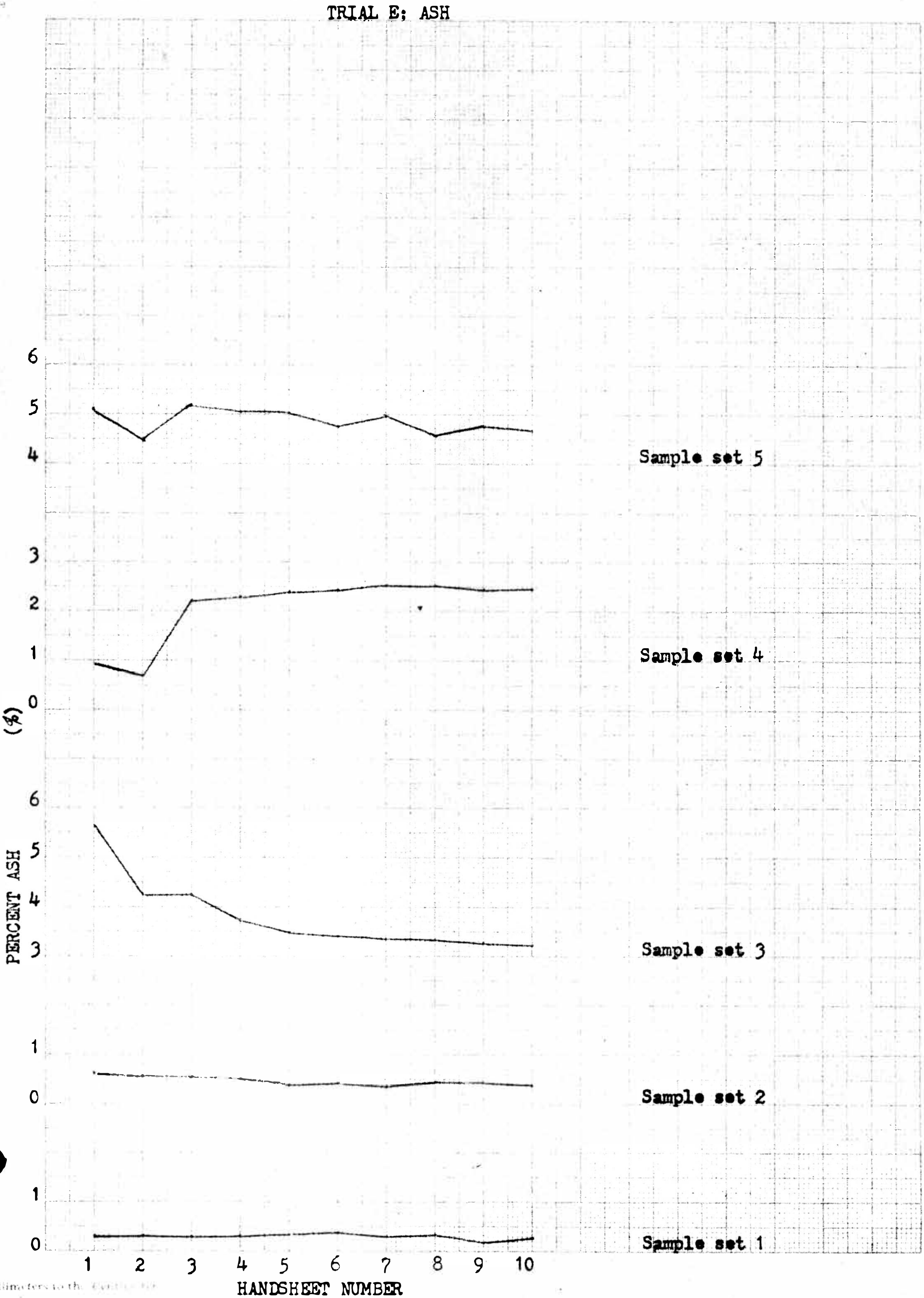


TABLE XXII SUMMARY OF DATA

TRIAL NO.	SHEET WEIGHT ($Gm/28.2744 in^2$)		AVERAGE OPACITY (%)		AVERAGE BRIGHTNESS (%)		AVERAGE PERCENT ASH (%)		REFERENCE NOTES
A:									
No TiO_2	1.1628	1.9%	77.1	1.6%	69.3	0.9%	1.82	4.2%	1
10 min.	1.1303	1.8%	89.6	1.0%	81.4	0.6%	7.92	6.1%	1
20 min.	1.1771	1.7%	88.7	0.8%	83.9	0.4%	7.58	9.0%	1
70 min.	1.2048	2.9%	91.2	0.9%	82.6	0.4%	8.79	6.1%	1
B:									
No TiO_2	0.9698	4.2%	66.1	2.1%	72.4	0.9%	0.58	17%	1
10 min.	1.1962	1.8%	90.0	0.9%	79.5	0.4%	8.23	5.2%	1, 4
20 min.	1.1810	6.6%	89.6	0.7%	80.5	0.9%	8.10	3.8%	1, 5
70 min.	1.3093	2.2%	90.3	1.1%	81.6	0.4%	7.60	7.6%	1
C:									
No TiO_2	1.1610	1.6%	78.9	0.6%	76.8	0.3%	1.44	2.1%	1, 2
10 min.	1.1077	4.8%	89.0	1.0%	82.5	0.6%	5.33	4.7%	1
20 min.	1.1597	3.1%	89.9	1.2%	84.5	0.3%	6.40	13%	1
70 min.	1.1472	1.6%	90.6	0.8%	84.4	0.2%	6.55	7.6%	1
D:									
Set 1	1.2236	0.3%	74.2	0.3%	74.6	0.4%	1.68	7.1%	
Set 2	1.1916	0.7%	83.0	0.7%	80.6	0.4%	4.69	4.7%	
Set 3	1.1850	2.4%	85.8	0.9%	83.7	0.4%	7.18	3.8%	
Set 4	1.1827	2.8%	81.9	2.2%	80.4	0.3%	5.08	6.9%	
Set 5	1.1740	2.1%	82.9	0.8%	83.1	0.8%	7.22	3.2%	3
Set 6	1.1845	1.8%	80.9	0.9%	81.1	0.8%	4.06	4.2%	3
E:									
Set 1	1.1546	0.1%	71.9	1.1%	76.0	0.6%	0.30	10%	
Set 2	1.1725	0.7%	71.8	2.2%	76.8	1.0%	0.46	15%	
Set 3	1.1158	2.9%	74.4	4.0%	80.7	0.8%	3.79	14%	
Set 4	1.1493	2.4%	77.6	0.5%	82.0	0.5%	2.41	3.7%	3
Set 5	1.2734	4.2%	79.9	0.5%	82.4	0.5%	4.86	3.7%	3

Reference notes:
1. Average sheet weight converted from 6.5213 $in.^2$ basis to 28.2744 $in.^2$ basis.
2. Sheet number 6 ommitted.
3. Sheets #1 and #2 ommitted.
4. Ash sample from sheet #8 ommitted.
5. Ash sample from sheet #1 ommitted.

The deviations are the average deviation of the sheets in each set from the mean value of that set.

Outline of Experimental Conditions:

The furnishes for all of the trials was a mixture of 75% hardwood and 25% softwood bleached kraft pulps. Tap water was used throughout, except where specified. The alum was dissolved before addition to the system in every case.

Trial A- 30 gm. alum to beater, beat to 260 CSF, 10% TiO_2 added dry.

Trial B- Beat to 260 CSF, 10% TiO_2 added dry, then 30 gm. alum added.

Trial C- 30 gm. alum to beater, beat to 550 CSF, 10% TiO_2 added dry.

Trial D- 30 gm. alum to beater, beat to 290 CSF, samples for six sets of handsheets taken. TiO_2 and additional alum to be added in white water system.

Set 1. No TiO_2, no additional alum, pH- 6.8.

Set 2. No additional alum, 10% TiO_2 added to proportioner in a 2% slurry. pH- 6.9.

Set 3. 31 gm. additional alum, 10% TiO_2 added to proportioner in a 2% slurry. pH- 5.5.

Set 4. 160 gm. additional alum, 10% TiO_2 added to proportioner in a 2% slurry. pH- 5.1.

Set 5. 30 gm. additional alum, 10% TiO_2 added to proportioner in a 2% slurry with Calgon-T dispersant. pH- 4.35.

Set 6. 160 gm. additional alum, 10% TiO_2 added to proportioner in a 2% slurry with Calgon-T dispersant. pH- 4.0.

Trial E- No alum, no TiO_2, beat to 260 CSF, samples for five sets of handsheets taken.

Set 1. Distilled water, no alum, no TiO_2.

Set 2. Distilled water, 60 gm. alum, no TiO_2, pH- 4.0.

Set 3. Soft water, 60 gm. alum, no TiO_2, pH- 4.25.

Set 4. Distilled water, 60 gm. alum, 5% TiO_2 in a 1% slurry, pH- 3.8.

Set 5. Soft water, 60 gm. alum, 5% TiO_2 in a 1% slurry, pH- 3.95.

TABLE XXIII. TABULATION OF THE SCATTERING COEFFICIENT OF TiO_2 IN THE HANDSHEETS

TRIAL NO.	EXPERIMENTAL PERCENT ASH	CALCULATED % CONTRIBUTIONS TO ASH FIBER	TiO_2	OTHER	SX	S_{sheet}	S_{TiO_2}
A:							
No TiO_2	1.82	.5	0	1.32	1.76	1.51	0
10 min.	7.92	.5	6.1	1.32	3.72	3.29	33.2
20 min.	7.58	.5	5.8	1.32	3.82	3.24	33.9
70 min.	8.79	.5	7.0	1.32	3.95	3.28	29.0
B:							
No TiO_2	0.58	.5	0	0	1.28	1.32	0
10 min.	8.23	.5	6.6	1.15	3.68	3.08	27.6
20 min.	8.10	.5	6.5	1.15	3.72	3.18	29.1
70 min.	7.60	.5	6.0	1.15	3.90	2.98	28.5
C:							
No TiO_2	1.44	.5	0	.94	2.13	1.83	0
10 min.	5.33	.5	3.9	.94	3.72	3.36	52.3
20 min.	6.40	.5	5.0	.94	4.05	3.49	44.2
70 min.	6.55	.5	5.1	.94	4.10	3.57	44.9
D:							
Set 1	1.68	.5	0	1.2	1.75	1.43	0
Set 2	4.69	.5	3.0	1.2	2.72	2.28	32.3
Set 3	7.18	.5	3.0	3.7	3.15	2.66	45.0
Set 4	5.08	.5	3.0	1.6	2.50	2.11	26.7
Set 5	5.22	.5	3.0	3.7	2.80	2.38	35.7
Set 6	7.06	.5	2.0	1.6	2.40	2.03	35.5
E:							
Set 1	0.30	.5	0	0	1.59	1.38	0
Set 2	0.46	.5	0	0	1.60	1.36	0
Set 3	3.79	.5	0	3.3	1.87	1.68	0
Set 4	2.41	.5	2.0	0	2.19	1.90	29.0
Set 5	4.86	.5	1.1	3.3	2.38	1.87	48.6

DISCUSSION

The actual data collected in each trial is presented graphically for easy comparison. Trends in the data resulting from the recirculation of the white water do not appear in them. The average value for each set and the average deviation are listed in table XXII on page 38 . An outline of the conditions in each trial is on page 39. The general conclusions were drawn from tables XXII and XXIII. The average deviation of the handsheet weights was generally less than two percent, corresponding to about a pound variation in a basis weight of 45 pounds per 25X40-500 ream size (1.17gm/ 28.27 in.^{2} equals 45lbs/25X40-500). The variation of the opacity and brightness were both less than one percent in most cases. The greatest deviations occurred in the percent ash tests, but it was expected because of the inherent uncertainties in the calculation of the percent ash, and because small changes in small numerical figures reflect larger percentage fluctuations than when dealing with larger figures. The average deviation in the ash percentage was in the order of five percent in most of the sets.

The opacity of paper is dependent upon the thickness of the sheet, and consequently, on the basis weight. It was concluded however that the range of sheet weights in the trials were sufficiently small that a correction factor for opacity was unnecessary. Attempts to correct the opacity for sheet weight were unsuccessful; they appeared to increase the uncertainty of the results.

The contribution of the impurities in the water to the percent ash of the handsheets was much greater than originally assumed. Softened water was used because of its availability and ample supply. Its purity was checked visually by comparing a ten centimeter collumn of the softened

water with a ten centimeter collumn of distilled water, both were backed by a white sheet. The water was not used if a difference in color was seen. All water was checked before use. Nevertheless, a significant quantity of alum agglomerated materials were present in the sheets, and undoubtedly affected the optical properties. Distilled water should have been used in all of the trials.

The beater, sheetmold, white water system, and all related equipment were scroupously cleaned with hot detergent solution, and thoroughly rinsed before each trial. The system was rinsed between each set of handsheets. New wires and a wet press felt were maintained and used solely for these trials. Utmost care was taken to avoid introducing foreign materials, and some meaningful conclusions can be drawn from the data.

Trial E, set 2 and set 3 show a three point opacity increase and a four point brightness increase as a result of using distilled water rather than softened water in the white water system. No TiO_2 was present. With about two percent TiO_2 in the handsheets there was practically no difference in the brightness and opacity by using distilled water. The small difference in opacity is more likely due to sheet weight. These results are shown by trial E, set 4 and set 5.

Trial E, set 1 and set 2 show that alum has no effect on the optical properties of paper by itself when using distilled water and no TiO_2 in the system. The effect of alum when TiO_2 was present can be seen in trial D, sets 2, 3, and 4. No Calgon-T dispersant was used. There was a three point increase in brightness and opacity with 31 grams of alum in the system, and a slight decrease in both properties when 160 grams of alum were used. Excessive use of alum is detrimental to the optical properties.

Calgon-T dispersant was added to the pigment slurry in trial D, set 5 and set 6. The optical properties were again higher (two points) when 30 grams of alum were used, than when 160 grams of alum were initially in the water system. The retention of the pigment was also higher in both cases.

The order of addition of the pigment and alum to the system seems to have had negligible effect on the brightness or opacity, as can be seen by comparing trial A with trial B. The scattering power of the pigment and the retention were also about equal in the two trials.

Looking at trials A, B, and C, it is apparent that the optical properties change very little with mixing. The results after 70 minutes of circulation in the beater were the same as those obtained 10 minutes after adding the pigment to the beater.

Trials A and C were the same except that the freeness of the stock in C was 300 points higher than in A. However, again there was not a substantial difference in the optical properties. The scattering power of the pigment in the less refined stock was considerably greater, possibly indicating a better distribution throughout the fibers. Almost the same amount of pigment was trapped in the handsheets of the two trials. The less refined stock caught slightly less pigment as expected. This result tends to rule out mechanical filtration as the primary means of incorporating pigment in the mat. The fact that the properties did not change with mixing also supports electrostatic attraction of coflocculation theory, since mixing in the beater for 70 minutes would inevitably do sufficient work on the fibers that an increase in the pigment concentration in the sheets with mixing would result if mechanical filtration were the primary mechanism.

The effect of Calgon-T pigment dispersant can be seen by comparing

trial D, sets 3 versus 5, and sets 4 versus 6. The optical efficiency of the pigment was decreased by the dispersant. There was three points less opacity in set 5, but the brightness and ash were about the same as set 3. The optical efficiency was about the same in the second case, sets 4 versus 6, with 160 grams of alum in the system.

The consistency of the stock at the time of addition of pigment made a considerable difference in the optical properties of subsequent handsheets. The average opacity of all handsheets corresponding to pigment addition in the beater, 1.67 percent consistency, was 89.9 percent, and those corresponding to addition of pigment in the proportioner, 0.003 percent consistency, averaged 82.9 percent opacity. Thus, mixing TiO_2 in higher consistency stocks resulted in greater optical efficiency and retention. The particles were in more intimate contact with fibers at higher consistency. These results indicate that most of the retention of TiO_2 in the handsheets was due to coflocculation before sheet formation, rather than mechanically trapping the particles as the mat formed. The brightness results of both types of addition were about identical.

Judging the overall experimental results, it is felt that the basic mechanisms of retention and dispersion of titanium dioxide particles in paper were not adequately uncovered. The natural uncertainties in making similar furnishes and handsheets may mask the effects of the changing variables. In regards to subsequent testing, the reliability of the opacity readings should be noted in trial E, which was rechecked. Both values (each value is the average of four readings per handsheet.) are plotted, and are very similar. But, the significance of the macroscopic measurements of opacity and brightness are of more practical value than tools for basic

theoretical enlightenment. It is felt that a means other than handsheet analysis should be used to gain further insight into the TiO_2 particle-fiber relationship in the sheet.

APPENDIX

Calculation of the Scattering Power of TiO_2 (8)

Formulas:

$$S_{TiO_2} = \frac{S_{paper} - (1 - a)\, S_{pulp}}{a}$$

$$a = \frac{b - c}{100}$$

where, a = percent pigment in the paper,
b = percent ash in the paper,
c = percent ash in the pulp,
S = specific scattering coefficient of the sheet tested,
SX = scattering power of the sheet of paper,
, and X = sheet weight

It was assumed that the contribution of the pulp to the percent ash was 0.5 percent in all of the trials. It was also assumed that the amount of pigment and agglomerates resulting from the impurities in the water being flocculated by alum was the same for each set of a given trial as that calculated from a single set of the trial, provided the concentration of pigment or alum was not changed. For example, in trial A, set 1, with no pigment, it was concluded that 1.32 percent of the total ash was alum- water impurity complexes since no pigment was present. It was concluded that the 1.32 percent was constant for the other three parts of trial A, so the contributions of pigment in those parts could then be estimated. The 1.15 percent in trial E is the average of the calculated values of trials A, C, and D.

Admittedly, the uncertainty of the percentages is large. It is an attempt to show trends only. The average brightness, R_0, and average opacity, $C_{0.89}$, were used to find SX. The sheet weight, X, was in grams per 28.27 $in.^2$ so the scattering coefficients are relative rather than specific.

(8) M.P. Boland & B.J. DeWitt, "Evaluation of Optical Properties," Paper Trade J. 145, p.37, Feb. 13, 1961.

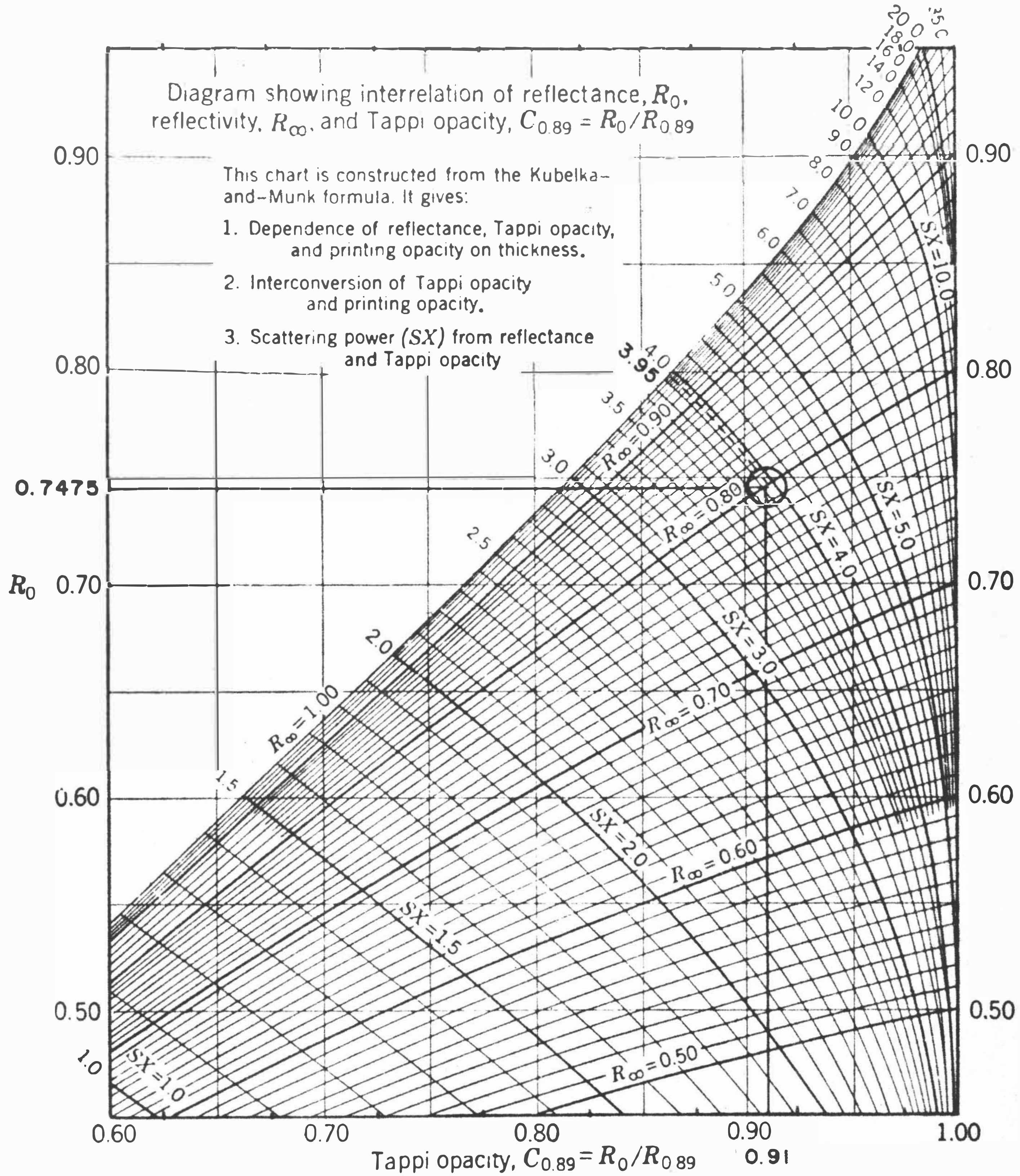


Diagram showing interrelation of reflectance, R_0, reflectivity, R_∞, and Tappi opacity, $C_{0.89} = R_0/R_{0.89}$
This chart is constructed from the Kubelka-and-Munk formula. It gives:
1. Dependence of reflectance, Tappi opacity, and printing opacity on thickness.
2. Interconversion of Tappi opacity and printing opacity.
3. Scattering power (SX) from reflectance and Tappi opacity
0.7475
3.95
R_0
R_∞ - REFLECTIVITY
Tappi opacity, $C_{0.89} = R_0/R_{0.89}$
0.91
$R_\infty = 1.00$
$R_\infty = 0.90$
$R_\infty = 0.80$
$R_\infty = 0.70$
$R_\infty = 0.60$
$R_\infty = 0.50$
SX = 1.0
SX = 1.5
SX = 2.0
SX = 3.0
SX = 4.0
SX = 5.0
SX = 10.0

Figure 1

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