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Special Projects (1955)

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Androscoggin River and Pool Studies

Special Projects

1955

A. Bay Sixteen

B. The Tyrosine Test for Lignin.

Reports by Walter A. Lawrance

Laboratory Work B. Project D. H. Robertson

Lewiston, Maine
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SUMMARY

BAY SIXTEEN

1. No additions of alkali were made in 1955.

2. The Benthal in the west end of Bay 16 is less alkaline than in 1954.

Bay Sixteen

The publication (Tappi. vol. 37, #12, 705-708.) of Nicholas J. Lardieri's work on Benthal oxidation December 1954, led to a re-examination of the entire alkalization project. Lardieri's investigation of oxidation rates under anaerobic and aerobic conditions at the "natural" pH and a pH adjusted to 7.00 lead to the conclusion that neutralizing the sludge acidity increases the oxygen demand about 100%.

This Benthal study was a project of the National Council for Stream Improvement and arrangements were made for a conference between the Council's representatives and the Androscoggin River Committee. A meeting was held on January 19, 1955 at the Eastland Hotel, Portland, Maine. After an extended discussion it was agreed

(1) To repeat the work in Lewiston during the summer of 1955, and that
(2) the National Council would finance the project.

At Rumford on February first a decision was made to suspend work on alkalizing the deposits in Bay 16 until the results of repetition of Lardieri's work were available.

The Alkali program for Bay 16 during 1955 was suspended. A few pH determinations were made on the water and the sludge. The results may be summarized as,

1. pH of the water in the Bay was substantially the same as that outside in the Pool adjacent to the Bay. The values ranged from 6.3 to 6.4
2. The Benthal deposits were slightly more acid than in 1954.
   (a) area treated 1953 but not 1954
   pH range 5.93-6.20
   (b) area treated 1954 but not 1953
   pH range 6.26-6.60

These results appear to indicate a small but consistent loss of alkalinity.

BAY 16

JUNE 1955

Date		Temp C	D.O. ppm	O.C.P. ppm	MeB Days
15	(1)	17.0	6.15	39.5	6.75
	(2)	17.2	5.95	52.0	8.75
21	(1)	22.6	3.20	32.5	6.0
	(2)	22.2	3.95	35.5	7.0
24	(1)	22.0	1.81	61.0	3.75
	(2)	22.0	2.28	66.0	5.0
25	(1)	21.5	2.54	79.0	---
	(2)	21.4	2.23	75.0	---
27	(1)	22.0	1.30	72.0	---
	(2)	21.9	2.60	83.5	---
29	(1)	22.9	2.36	69.0	4.5
	(2)	23.2	2.15	67.0	4.75

JULY 1955

1	24.2	1.06	66.0	3.75
5	25.1	0.01	62.0	2.25
20	24.7	0.10	67.0	1.25
26	25.8	0.11	69.0	0.75
27	25.9	0.10	68.5	0.50

AUGUST 1955

8	24.0	0.31	53.5	2.75
13	22.0	1.80	43.5	-
20	24.0	1.30	33.0	5.00
24	23.8	0.40	45.0	-

SEPTEMBER 1955

2	22.3	1.14	43.5	-
6	21.7	0.11	45.0	-
13	17.3	1.37	48.0	-
18	18.9	1.38	55.0	3.5

(1) Sampled at edge of bay.
(2) Sampled in middle of bay.

SUMMARY

Tyrosine Test for Lignin

1. The Tyrosine method has been used for estimating the lignosulphonate present in the waste sulphite liquors of Brown Company, Oxford Paper Company and International Paper Company.

2. Comparisons have been made between the tyrosine lignin and oxygen consumed permanganate tests. A sample of "pure calcium lignosulphonate" was investigated.

3. A series of determinations on Androscoggin River water from eighteen sampling stations made on June 30, 1955 indicated low concentrations of lignin while a similar series of samples on September 1, 1955 contained a higher percentage of lignin. Oxygen consumed permanganates and pollution factors reveal that the reverse should have been indicated.

4. The Tyrosine Lignin test could be used for estimating sulphite waste liquor pollution loads at any given point in the river if and when supporting data become available.

5. The contours of the Lignin and Oxygen Consumed Permanganate curves obtained from Androscoggin River water data are very similar.

The Tyrosine for Lignin Sulphonates in Waste Sulphite Liquor and Androscoggin River Water

Introduction. In 1912 Folin and Dennis* at Harvard University discovered that a phosphotungstic molybdic reagent yielded a bluish color with the amino acid tyrosine. The intensity of this color was found to be quantitatively proportional to the tyrosine present when the concentration was very small.

Other work has demonstrated that this color test is essentially a phenolic reaction and has wide application but does not always yield quantitative results. Lignin possesses a phenolic hydroxyl and reacts with this reagent to produce a bluish color.

Several investigations have been made to determine the value of this color test for the estimation of the lignin content in pulp and mill wastes. Opinion is divided as to its value and reliability. Some work done in the Oxford Paper Company's laboratory aroused an interest in this test as an additional rapid means of determining the extent of lignin wastes in the Androscoggin River water.

The work described in this paper should be considered as a preliminary study and further work is being planned.

Procedure. Sulphite waste liquors direct from the digestor were obtained from all three companies. These were analyzed for volatile solids, total solids and oxygen consumed permanganate. Data were also obtained for the pH and density. A

*J. Biol. Chem. 12 245-51 (1912). C.A. 6, 3433 (1912)

mixture of these liquors was studied; Brown Company (hardwood) and Oxford Paper Company (softwood) in the ratio 53.7% and the 46.3% respectively. These are the ratios recorded in the Decree and Stipulation of 1948. For purposes of comparison a sample of dry "pure calcium lignosulphonate" was dissolved in distilled water and tested by the same procedures.

Two series of tests were made from water taken at every sampling station from Berlin to Lisbon Falls, the first on June 30, 1955, the second on September 1, 1955.

Methods. Tappi methods were used for total and volatile solids.

Oxygen consumed permanganates were obtained by the river testing procedure. Lignin was determined colorimetrically using the Tyrosine method with a Bausch and Lomb "Spectronic 20". This instrument was found to give just as reliable results as the Beckmann equipment.

"Pure" Calcium Lignosulphonate.

In 1948 a sample of calcium lignosulphonate was obtained from the University of Washington. The material was prepared from softwood calcium base sulphite waste liquor by lime precipitation, then washing, redissolving and reprecipitating several times then dialyzed. The sample is believed to be reasonably free from carbohydrates and mineral salts.

The Tyrosine test and oxygen consumed permanganates were made on solutions containing 5 to 100 ppm of this "lignin". The results are recorded in Table #A.1 and plotted in the accompanying figure.

Tyrosine-Lignin Test.

Percent Transmission and O.C.P. ppm.

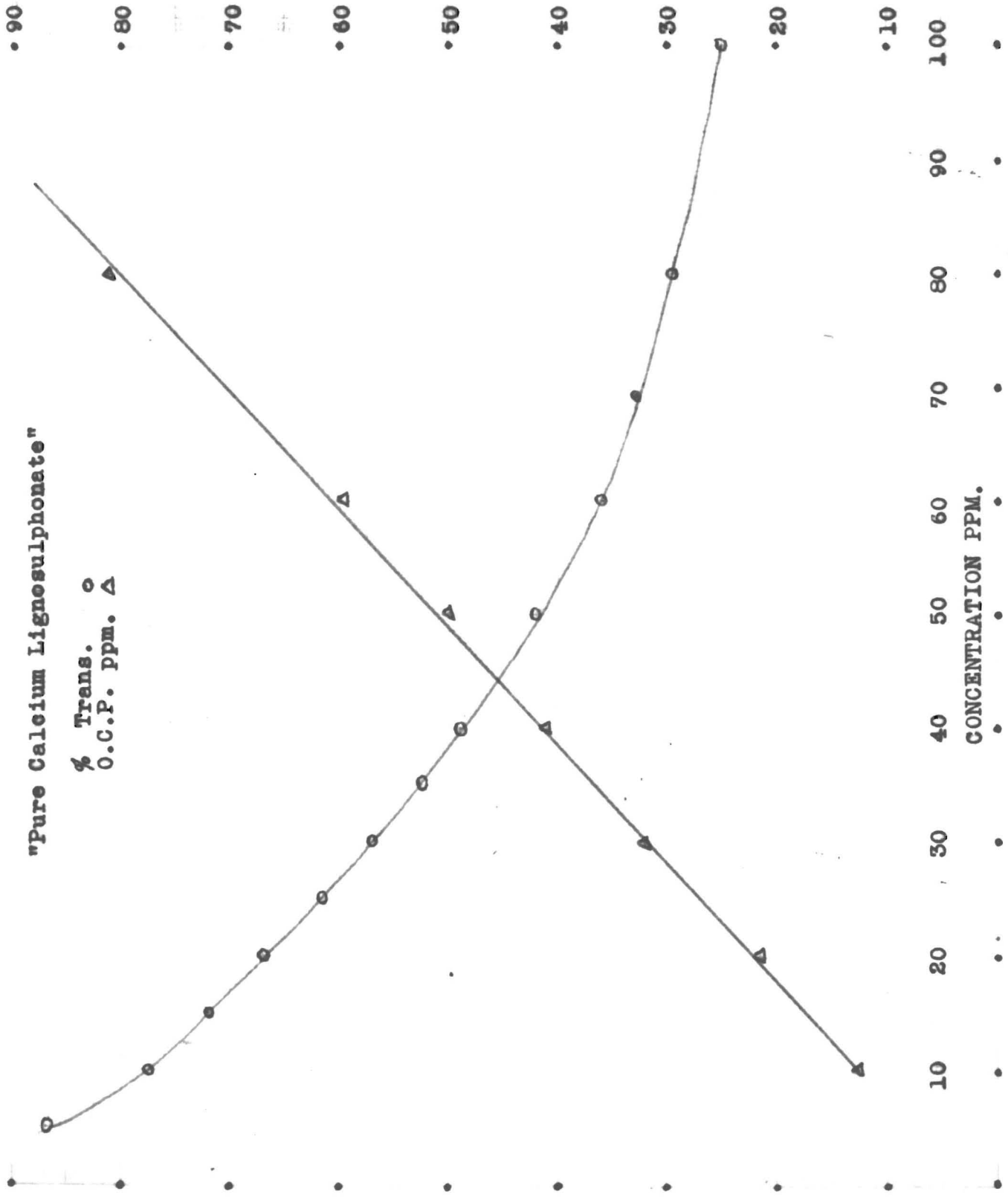


TABLE #A1

"Pure Calcium Lignosulphonate"

C.L.S. ppm	Transmission 700µm.%	O.C.P. ppm
5	87	-
10	77	12.5
15	72	-
20	66	21.5
25	62	-
30	57	32.0
35	53	-
40	49	41.0
50	43	50.0
60	36	59.5
80	29	83.0
100	25	110.0

Assuming that this sample is a lignin approximating the empirical formula $C_{43}H_{42}O_{14}$ then the complete oxidation of this material will take place according to the following equation,

$$2\ C_{43}H_{42}O_{14} + 93\ O_2 \rightarrow 86\ CO_2 + 42\ H_2O$$

Hence one (1) part lignin requires one and nine tenths (1.9) parts of oxygen (O_2) to completely convert it into carbon dioxide and water.

Acid potassium permanganate solutions when employed as in the river testing program, appear to oxidize about 50% of this lignin in concentrations up to 80 ppm.

For purposes of comparison the results of the tyrosine tests obtained from the various sulphite waste liquors are interpreted as to lignin content with the "pure" lignin as a standard. Such a comparison leads to the conclusions that assuming the dry solids of softwood liquor should contain from 50 to 58% of alkali lignosulphonate then

(a) Brown Company's sample of softwood waste sulphite liquor contained considerably less lignin than should be expected.

(b) Softwood waste sulphite liquors from Oxford and International Paper Company contained somewhat more lignin than the quoted range.

(c) The International Paper Company's waste liquor was from a ten hour cook which gave a pulp chlorine number of less than three. This would account, in part at least, for the high lignin content of the liquor.

(d) Hardwood lignin is known to be different from that present in softwood both chemically and physically. For these reasons the results of the tyrosine test on hardwood lignins should not be based on tyrosine softwood tests. Such comparisons when made in this report are considered to be worth recording because of the high values obtained.

Table #A2 records the percentages of lignin indicated as present in various waste liquors when the results of the tyrosine tests are compared with those of "pure calcium lignosulphonate"

TABLE #A2
Percentage Lignin Indicated
Sulphite Waste Liquors

Conc. T.S. ppm	Brown Co. Soft	Brown Co. Hard	Oxford Soft	Brown + Oxford Hard + Soft	International Soft
5	40	60	60	90	60
10	35	60	50	85	60
15	30	73	53	90	66
20	30	70	55	95	67
25	28	96	64	104	79
30	28	100	66	100	80
35	29	107	68	106	85
40	30	110	75	107	85
45	30	113	78	111	83
50	32	108	78	111	83
55	32	105	80	105	84
60	32	102	83	106	84
65	33	103	82	108	83
70	34	104	82	108	82
75	35	107	80	114	82
80	34	111	80	115	84

Sulphite Waste Liquor. Samples of liquor taken from the digestors were provided by Brown Company (hardwood, June 29, and softwood, July 19), Oxford Paper Company (softwood, June 29), and International Paper Company (softwood, June 28).

General Data. Each sample was tested for pH, density and total solids. Table #1 records the data obtained for each waste sulphite liquor and for one mixture of liquor from Brown Company and Oxford Paper Company in the ratio of 53.7% and 46.3% respectively.

TABLE #1
Sulphite Waste Liquor General Data

	Brown Co. Hard	Brown Co. Soft	Oxford Soft	Brown + Oxford Hard + Soft	International Soft
pH	2.60	2.40	1.79	1.90	3.45
Density at	1.057 22°C	1.033 23°C	1.064 22°C	1.062 22°C	1.048 23°C
% Total Solids	12.20	6.95	12.19	12.20*	11.5
Date Sampled	June 29	July 19	June 29		June 29

* Total solids figured 53.7% Brown liquor plus 46.3% Oxford liquor

Lignin and O.C.P. Each sample of liquor and the mixture was filtered and then diluted with distilled water to obtain a series of concentrations ranging from 5 to 80 ppm of total solids. Portions of the diluted samples were immediately mixed with tungstate reagents and tested for transmission of light at 700 millimicrons and for the Oxygen Consumed from Permanganate.

The tables contain the following data

1. the concentration of total solids present in each sample of liquor.
2. percent transmission of 700 millimicron light.
3. "lignin content" ppm. (these values were obtained by comparing the transmission with that obtained with a known concentration of "pure calcium lignosulphonate".)
4. O.C.P. of the sample.
5. ratio of total solids to O.C.P.
6. ratio of "lignin" to O.C.P.

The percentage transmission, O.C.P. and total solids data for each of the series are plotted in the accompanying figures. In most cases the slope of the curve, concentration vs transmission, is such that the most useful range

lies between concentrations of 10 and 40 ppm.

Brown Company Sulphite Waste Liquors.

Brown Company produce sulphite pulp by the soda base sulphite method from both hardwoods and softwoods. The waste liquor from these two classes of woods differ from each other in the type of lignin, ratio of sugars to lignin and to total solids. A sample of each type of liquor was investigated.

Hardwood Sulphite Waste Liquor. This sample of waste liquor had the highest phenolic content of any of the liquors investigated. When compared with a sample of "pure lignin" from softwood the lignin content appears to exceed the total solids present in the liquor. Such data indicates

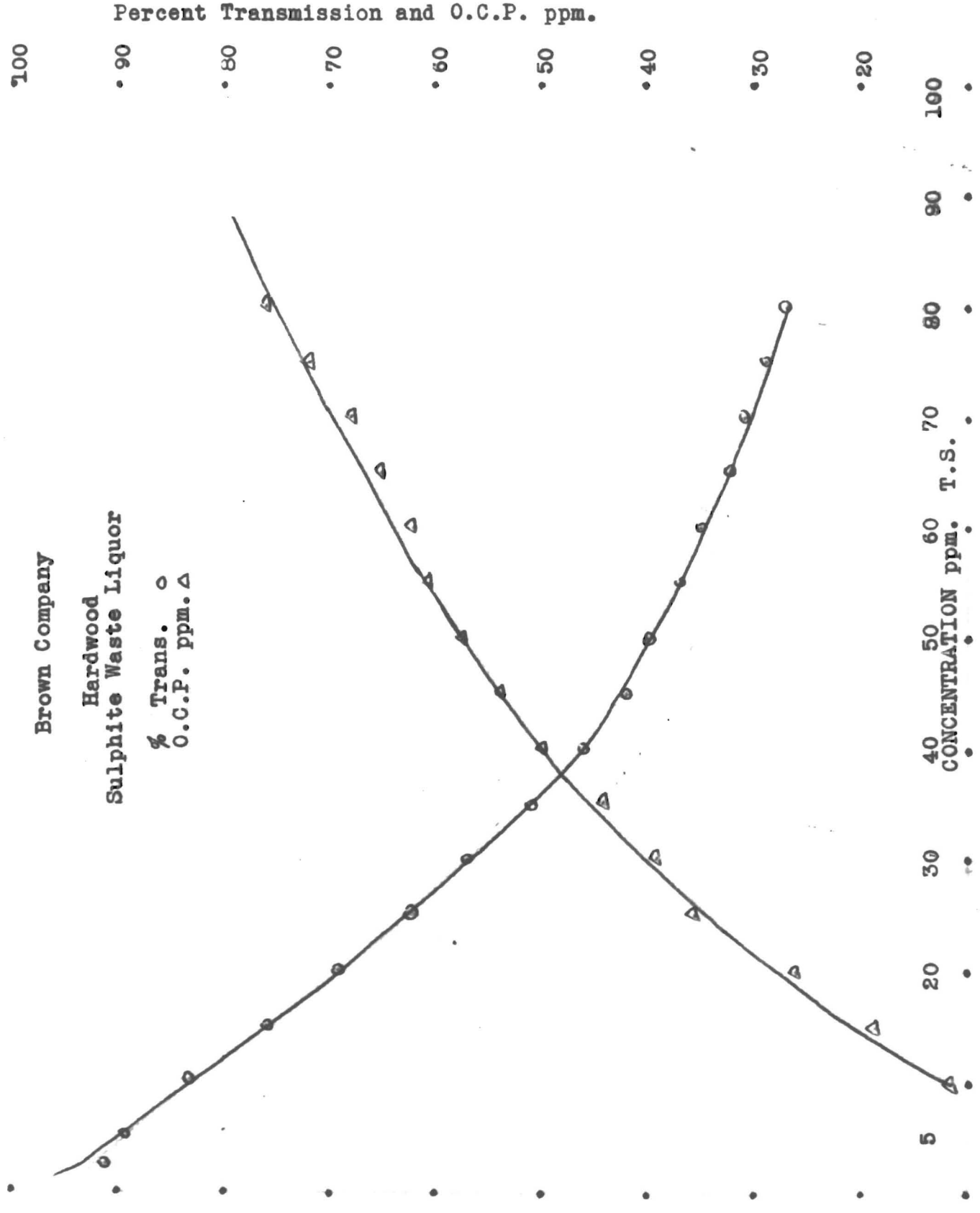
(a) that hardwood lignin is much more phenolic than that from softwood and
(b) softwood lignin should not be used as a standard for estimation of lignin in hardwood liquor.

The O.C.P. data appear to indicate that hardwood waste liquor has a somewhat more erratic oxidizability than that from softwood. The ratio of O.C.P. to total solids is higher for hardwood than for softwood liquor.

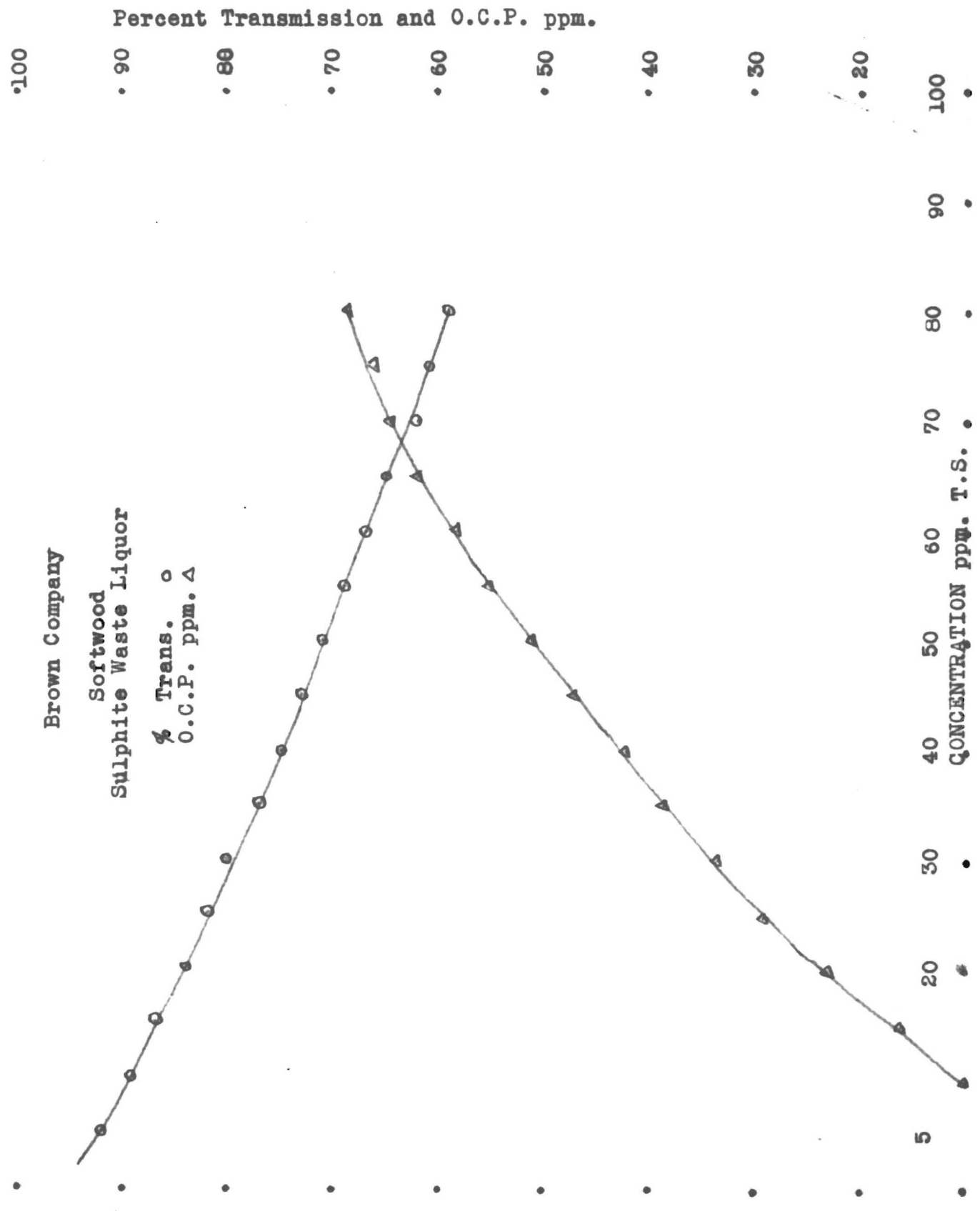
Softwood Sulphite Waste Liquor. This sample of liquor had a relatively low total solids content. Some doubt exists as to the location of the place of sampling. The employee was requested to take the sample from the digestor but he may have withdrawn it from the washer.

The lignin present in this liquor does not appear to approximate that of the "pure lignin" used for comparison purposes. The percentages of lignosulphonate found by

Tyrosine-Lignin Test.



Tyrosine-Lignin Test.



calculation from the transmission data are much lower than those recorded in the literature for softwoods. Oxford Paper and International Paper softwood liquors gave much higher lignin values.

TABLE #2
Brown Company Hardwood
Sulphite Waste Liquor

Conc. T.S. ppm	Transmission per cent	"Lignin" ppm	"Lignin" %	O.C.P. ppm	O.C.P. / T.S.	O.C.P. / Lignin
5	91	3.0	60	7.0	1.4	2.33
10	84	6.0	60	11.5	1.15	1.92
15	76	11.0	73	18.5	1.23	1.68
20	69	17.5	70	26.0	1.30	1.48
25	62	24.0	96	36.5	1.41	1.52
30	57	30.0	100	39.0	1.30	1.30
35	51	37.5	107	44.0	1.25	1.17
40	46	44.0	110	46.0	1.15	1.045
45	42	51.0	113	54.0	1.20	1.062
50	40	54.0	108	57.5	1.15	1.065
55	37	58.0	105	60.5	1.10	1.041
60	35	61.0	102	62.0	1.03	1.015
65	32	70.0	103	65.0	1.00	0.93
70	31	73.0	104	68.0	0.97	0.93
75	29	80.0	107	72.0	0.96	0.90
80	27	89.0	111	76.0	0.95	0.85

TABLE #3
Brown Company Softwood
Sulphite Waste Liquor

5	92	2.0	40	7.5	1.50	3.75
10	89	3.5	35	10.0	1.00	2.86
15	87	5.0	30	16.0	1.065	3.20
20	84	6.0	30	23.0	1.15	3.84
25	82	7.0	28	29.0	1.16	4.14
30	80	8.5	28	33.0	1.10	3.88
35	77	10.0	29	36.0	1.03	3.60
40	75	12.0	30	42.0	1.05	3.50
45	73	13.5	30	47.0	1.04	3.48
50	71	16.0	32	51.0	1.02	3.18
55	69	17.5	32	55.0	1.00	3.14
60	67	19.0	32	58.0	0.985	3.05
65	65	21.5	33	62.0	0.955	2.88
70	62	24.0	34	64.5	0.920	2.68
75	61	26.0	35	66.0	0.880	2.54
80	59	27.0	34	68.5	0.860	2.54

Tyrosine-Lignin Test.

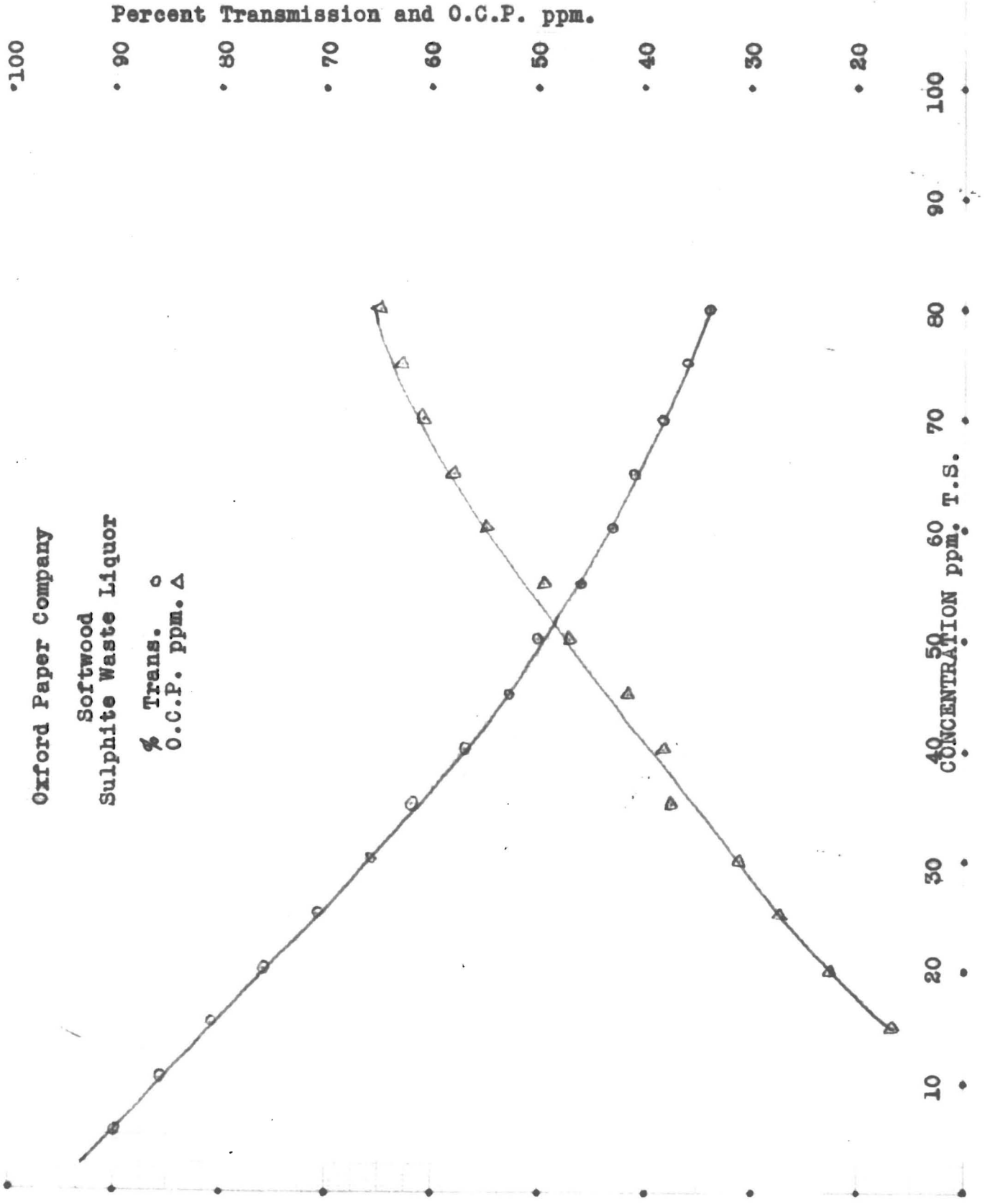


TABLE #4
Oxford Paper Company Softwood
Sulphite Waste Liquor

Conc. T.S. ppm	Transmission per cent	"Lignin" ppm	"Lignin" %	O.C.P. ppm	O.C.P. / T.S.	O.C.P. / Lignin
5	90	3.0	60	6.5	1.30	2.18
10	86	5.0	50	9.5	0.95	1.90
15	81	8.0	53	16.5	1.10	2.08
20	76	11.0	55	22.5	1.12	2.04
25	71	16.0	64	27.0	1.08	1.685
30	66	20.0	66	31.0	1.03	1.55
35	62	24.0	68	37.5	1.07	1.56
40	57	30.0	75	38.0	0.95	1.265
45	53	35.0	78	41.5	0.92	1.18
50	50	39.0	78	47.0	0.94	1.20
55	46	44.0	80	49.5	0.90	1.125
60	43	50.0	83	55.0	0.915	1.10
65	41	53.0	82	58.0	0.895	1.09
70	38	57.0	82	61.0	0.87	1.07
75	36	60.0	80	63.0	0.84	1.05
80	34	64.0	80	65.0	0.815	1.015

Considering the differences in lignin content the O.C.P. data for the hard and soft wood liquor dilutions are amazingly similar. Hard wood liquor yielded only slightly higher oxidation numbers although the indicated lignin content was very high. As stated elsewhere in this report permanganate appears to oxidize about one-half the lignin hence the higher lignin content in the hardwood liquor would not increase the O.C.P. proportionately but this alone does not account for the data that were obtained.

Oxford Paper Company

Softwood Sulphite Waste Liquor.

The indicated lignin content of the Oxford softwood liquor was much more varied than that from Brown Company. Over the range of dilutions studied the lignin varied from 50 to 83%, however, in the lower concentrations the differences range from 50% to 68%. The O.C.P.'s are slightly but uniformly lower than Brown Company's softwood liquor.

Brown Company Hardwood
Oxford Paper Company Softwood

Hardwood 53.7%
Softwood 64.3%
Sulphite Waste Liquors.

A mixture of these two liquors was made in the ratio similar to the discharge ratio stated in the Decree-Stipulation of 1948.

The usual dilutions were made and tested for lignin and O.C.P. values. The results are recorded in Table #5 and illustrated in the accompanying figure.

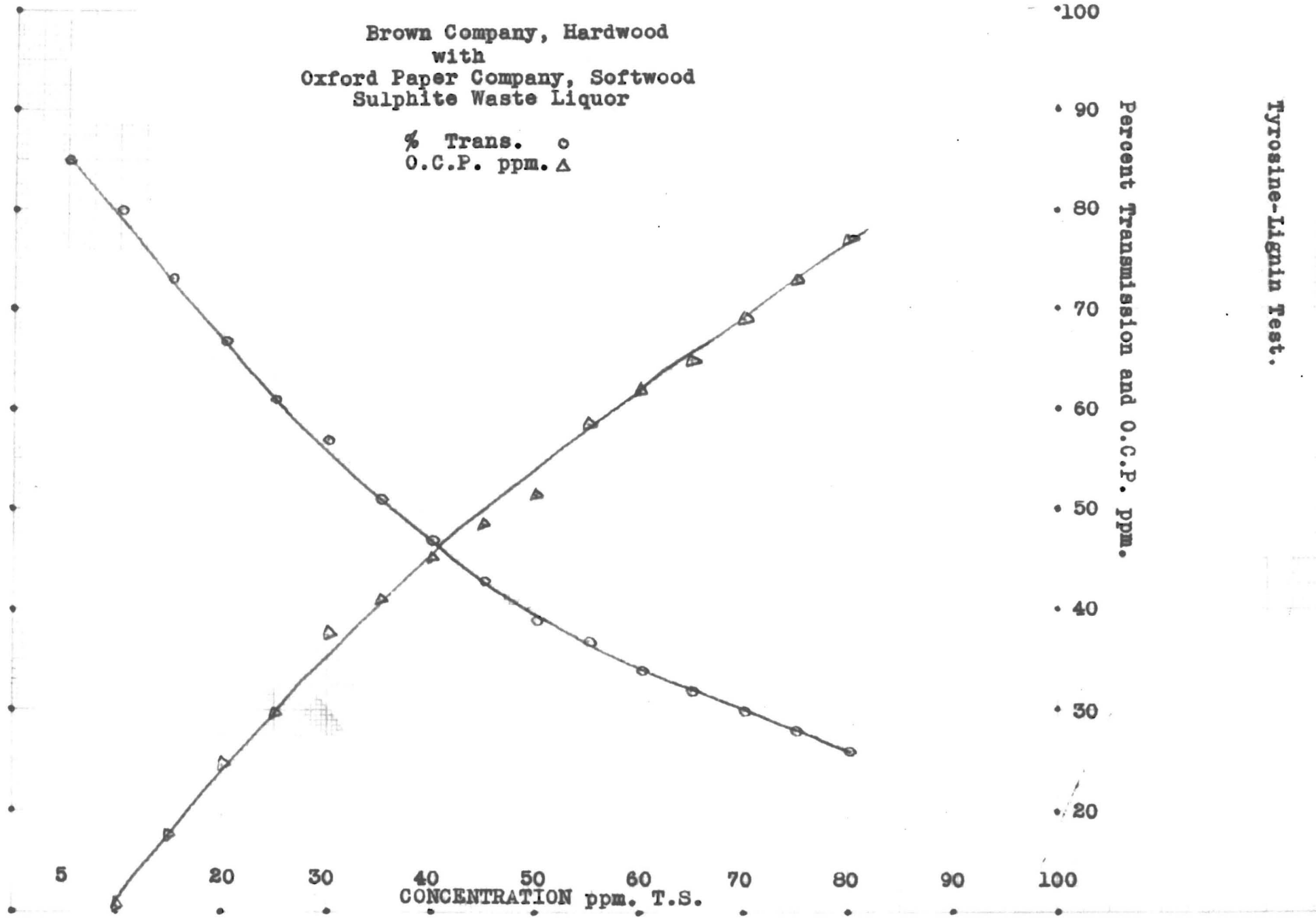
The O.C.P. data are reasonable and about what should be expected but the lignin results are very high; much higher than those which were anticipated. In the lower concen-

tration Brown Company hardwood liquor appears to yield proportionally higher results with the tyrosine test when diluted with Oxford liquor than when mixed with distilled water to the same total solids content. Such results are not reasonable and similar mixtures should receive further study if considered necessary.

TABLE #5
Brown Company Hardwood
Oxford Paper Company Softwood
Sulphite Waste Liquors*

Conc. T.S. ppm	Transmission per cent	"Lignin" ppm	"Lignin" %	O.C.P. ppm	O.C.P. / T.S.	O.C.P. / Lignin
5	85	5.0	90	7.0	1.40	1.40
10	80	8.5	85	10.5	1.05	1.23
15	73	13.5	90	17.5	1.16	1.29
20	67	19.0	95	24.5	1.22	1.29
25	61	26.0	104	29.5	1.18	1.13
30	57	30.0	100	37.5	1.25	1.25
35	51	37.5	106	41.0	1.17	1.09
40	47	43.0	107	45.0	1.12	1.045
45	43	50.0	111	48.5	1.07	0.970
50	39	55.0	111	51.5	1.03	0.935
55	37	58.0	105	58.5	1.17	1.005
60	34	64.0	106	62.0	1.03	0.97
65	32	70.0	108	65.0	1.00	0.93
70	30	76.0	108	69.0	0.99	0.91
75	28	86.0	114	73.0	0.975	0.85
80	26	92	115	77.0	0.905	0.835

* Composite 53.7% Brown liquor
46.3% Oxford liquor
based on total solids


Brown Company, Hardwood
with
Oxford Paper Company, Softwood
Sulphite Waste Liquor
% Trans. o
O.C.P. ppm. Δ
Tyrosine-Lignin Test.
Percent Transmission and O.C.P. ppm.
100
90
80
70
60
50
40
30
20
5
20
30
40
50
60
70
80
90
100
CONCENTRATION ppm. T.S.

International Paper Company

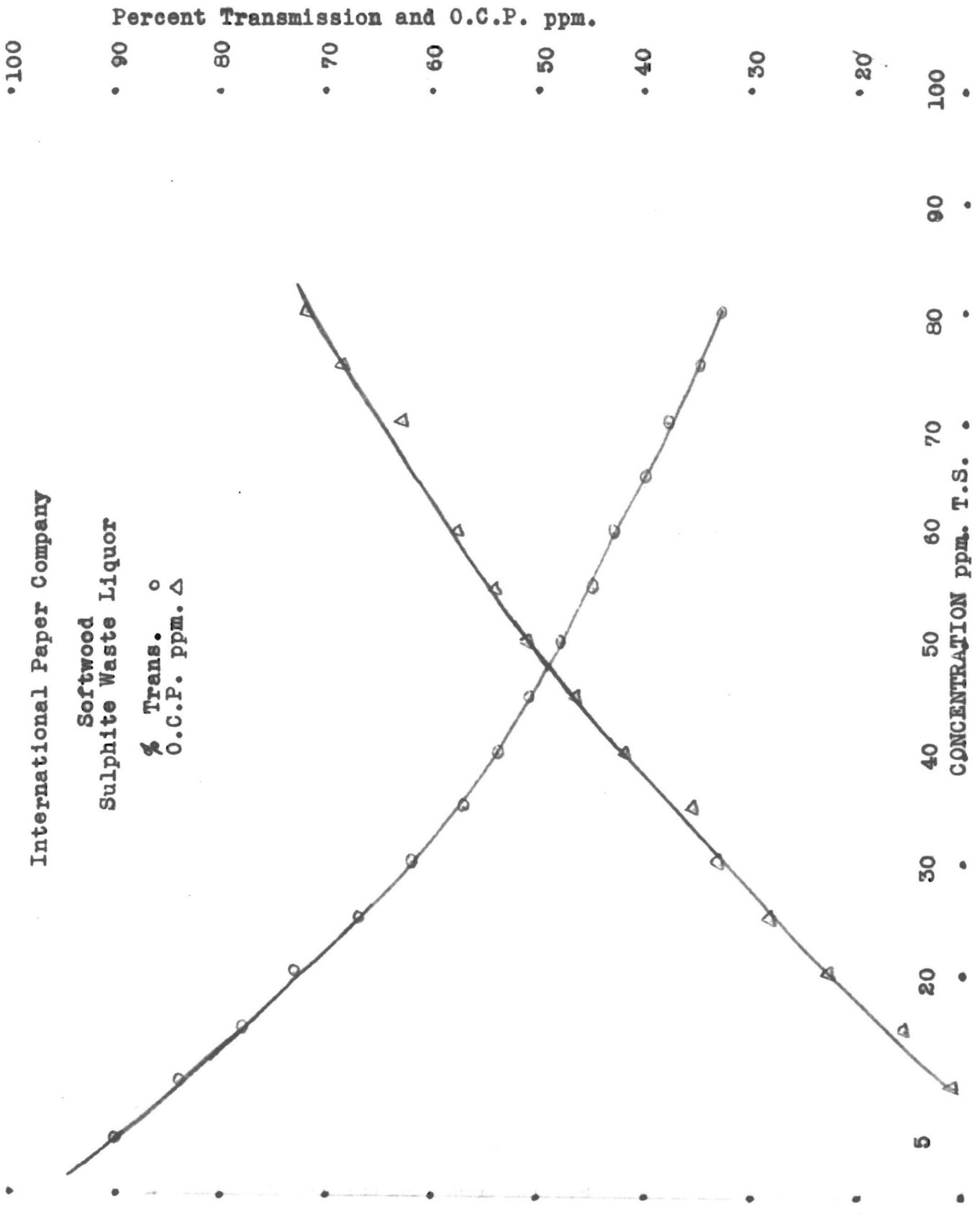
Softwood Sulphite Waste Liquor. This liquor yielded oxygen consumed from permanganate and tyrosine data somewhat higher than those of the other two companies. The acidity of this waste liquor was less than that of any of the samples investigated.

Later information revealed that this waste liquor was removed from a ten hour cook which produced a pulp with a chlorine demand of less than three, This indicates that the liquor should possess a somewhat higher lignin content than that from more rapid cooks.

TABLE #6
International Paper Company
Sulphite Waste Liquor

Conc. T.S. ppm	Transmission per cent	"Lignin" ppm	"Lignin" %	O.C.P. ppm	O.C.P. / T.S.	O.C.P. / Lignin
5	90	3.0	60	5.0	1.00	1.62
10	84	6.0	60	11.0	1.10	1.83
15	78	10.0	66	15.5	1.03	1.55
20	73	13.5	67	22.5	1.12	1.62
25	67	19.0	79	28.0	1.12	1.47
30	62	24.0	80	33.0	1.10	1.375
35	57	30.0	85	35.5	1.015	1.185
40	54	34.0	85	42.0	1.05	1.235
45	51	37.5	83	46.5	1.03	1.24
50	48	41.5	83	51.0	1.02	1.23
55	45	46.0	84	54.0	0.98	1.17
60	43	50.0	84	57.5	0.96	1.15
65	40	54.0	83	61.5	0.945	1.14
70	38	57.0	82	65.5	0.975	1.15
75	35	61.0	82	68.5	0.915	1.12
80	33	67.0	84	72.0	0.90	1.07

Tyrosine-Lignin Test.



Tyrosine Test on Androscoggin River Water

Two series of tests were made on river water taken at all the regular sampling stations and at mile intervals through the Pool between Turner Center Bridge and Gulf Island Dam. The first series was conducted on June 30, 1955 when the pollution factors were high and the second on September 1, 1955 when the pollution loads were much lower.

The data obtained from these two series are recorded in Tables R.L.T. one and two, and illustrated in the accompanying figures.

The pollution load and water temperatures from Berlin to Virginia Bridge were very similar on both test days but there was a considerable difference in the apparent lignin values; the September first series had a much higher lignin content than the June 30 series. South of Rumford the June 30 tests gave high O.C.P. and low lignin whereas the September first series gave low O.C.P. and high lignin value. The O.C.P.'s in both series are in agreement with the pollution factors but the tyrosine lignin values are just the reverse to what one would logically expect.

Lower Lignin concentrations when the O.C.P.'s and Pollution Factors are high may be due to

a. precipitation of lignin in the river in June
b. presence of substances which would interfere with the "tyrosine" color, or
c. the time of passage was less in June than during late August.

Consideration of the possibility of precipitation of lignin in June suggests that the September high lignin may be

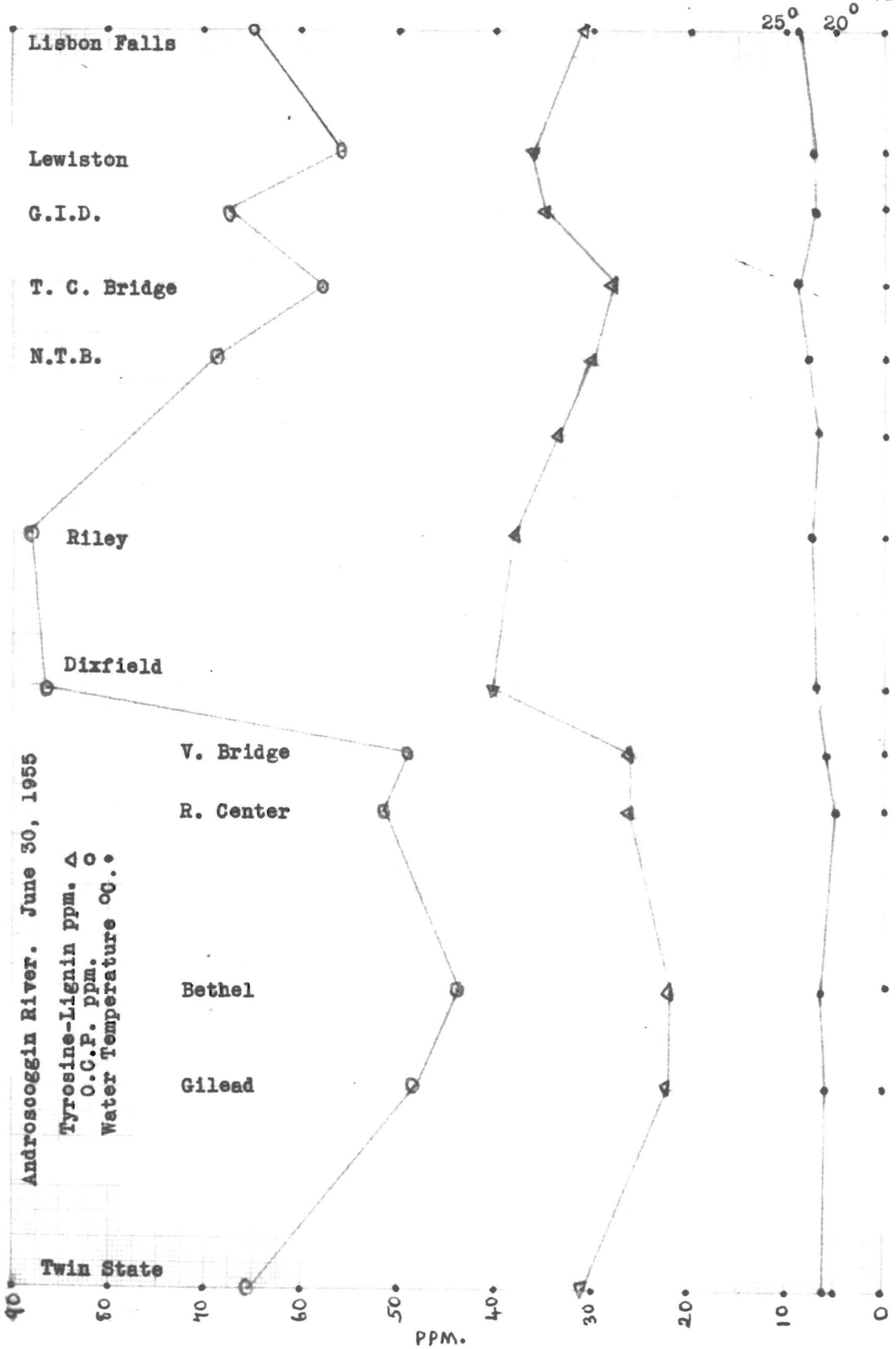
TABLE #R.L.T.1
Androscoggin River Lignin Tests
June 30 1955

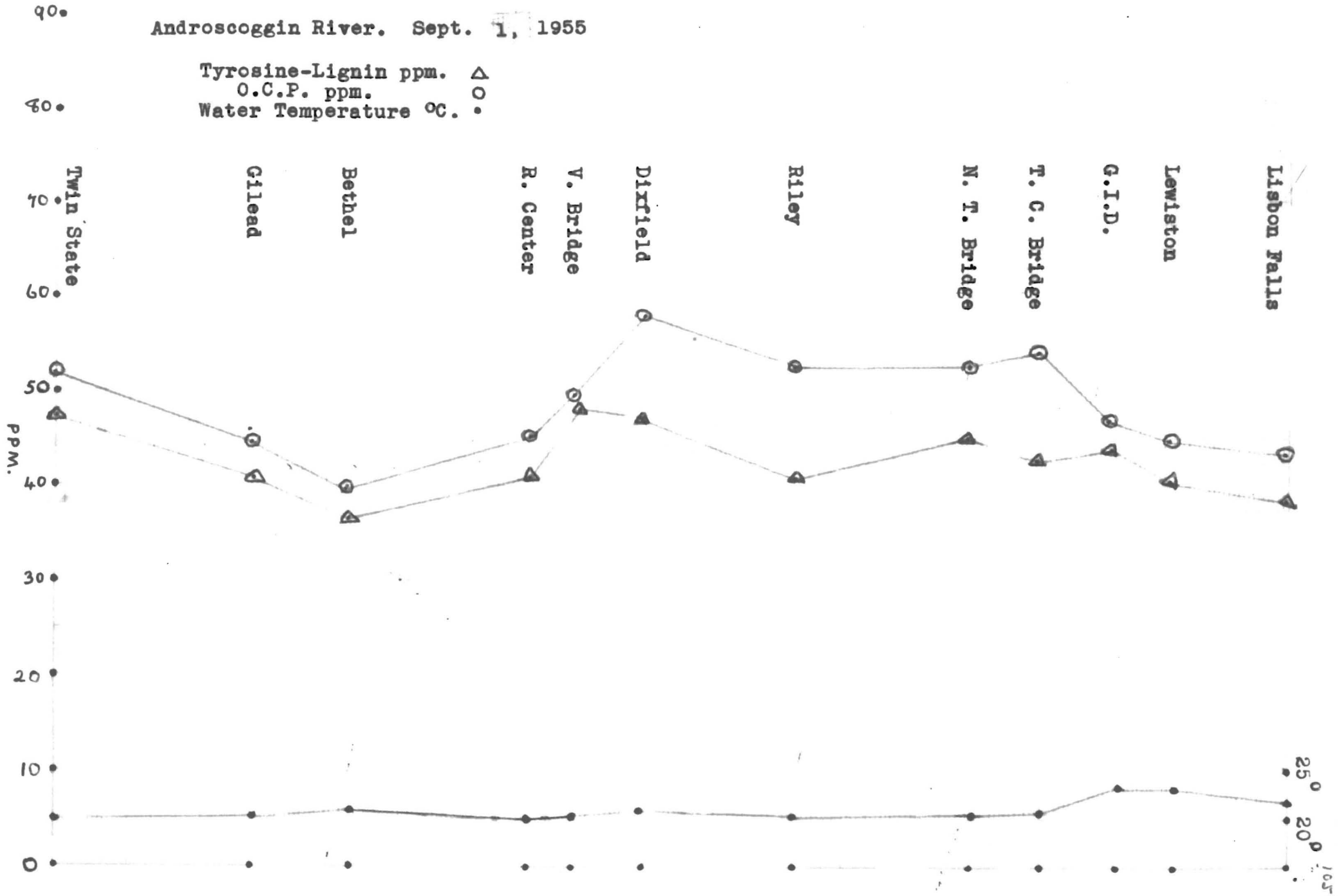
Station	Trans. per cent	"Lignin" (x) ppm	"lignin" (xx) ppm	O.C.P.* / Lignin (xx)	O.C.P. Total ppm	Temp C	Approx. P.F.
Twin State	51	37	31	2.11	65.5	21.3	0.98
Gilead	62	24	22	2.20	48.5	21.0	
Bethel	62	24	22	2.00	44.0	21.5	0.78
R. Center	58	29	26	1.98	51.5	20.0	
V. Bridge	58	29	26	1.88	49.0	21.0	0.93
Dixfield	42	51	40	2.16	86.5	22.0	1.50
Riley	44	48	38	2.31	88.0	22.5	1.68
N.T.Bridge	53	35	30	2.30	69.0	22.0	1.58
T.C.Bridge	55	32	28	2.07	58.0	23.0	1.40
Mile 6	56	31	27.5	2.16	59.5	22.8	
Mile 5	57	29.8	27	2.35	63.5	22.8	
Mile 4	55	32	28	2.43	68.0	23.0	
Mile 3	55	32	28	2.57	72.0	23.1	
Mile 2	46	44	36	2.03	73.0	23.9	
Mile 1	54	33.8	29	2.29	66.5	23.6	
G.I.D.	47	44	35	1.93	67.5	22.48	1.57
Lewiston(CSB)	46	43	36	1.55	56.0	22.5	
Lisbon Falls	53	35	30	2.17	65.0	24.0	

TABLE #R.L.T.2
Androscoggin River Lignin Tests
September 1 1955

Bell's	87	5			6.5	20.2	
Twin State	40	54	48	1.081	52.0	20.1	1.03
Gilead	45	46	41	1.085	44.5	20.2	0.95
Bethel	49	40	37	1.04	39.5	20.8	0.75
R. Center	45	45	41	1.095	45.0	20.0	0.91
V. Bridge	40	55	48	1.03	49.5	20.0	
Dixfield	36	60	47	1.235	58.0	21.0	0.94
Riley	41	52	41	1.28	52.5	20.0	1.19
N.T.Bridge	38	57	45	1.175	53.0	20.5	1.32
T.C.Bridge	37	58	43	1.265	54.5	21.0	1.36
Mile 6	40	55	42	1.165	49.0	21.6	
Mile 5	38	57	45	1.085	49.0	21.7	
Mile 4	40	55	42	1.13	47.5	22.2	
Mile 3	41	52	41	1.085	44.5	22.8	
Mile 2	41	52	41	1.12	46.0	22.9	
Mile 1	40	55	42	1.06	44.5	22.9	
G.I.D.	39	55	44	1.08	47.5	23.61	1.10
Deer Rips D.	41	52	41	1.12	46.0	22.0	1.10
Lewiston(CSB)	41	52	41	1.10	45.0	23.0	
Lisbon Falls	44	48	38	1.145	43.5	22.0	

(x) Based on the "pure Calcium Lignosulphonate" data
(xx) Twin State to Virginia Bridge based on Brown Company hardwood waste sulphite liquor data, Dixfield to Lisbon Falls(L.F.) Brown Company plus Oxford Paper softwood waste sulphite liquor data.
* Ratio between O.C.P. and Lignin(xx)


Androscoggin River. June 30, 1955
Tyrosine-Lignin ppm. △ ○
O.C.P. ppm.
Water Temperature °C. •
Lisbon Falls
Lewiston
G.I.D.
T. C. Bridge
N.T.B.
Riley
Dixfield
V. Bridge
R. Center
Bethel
Gilead
Twin State
25°
20°
40
50
60
70
60
50
40
30
20
10
0
PPM.


Androscoggin River. Sept. 1, 1955
Tyrosine-Lignin ppm. Δ
O.C.P. ppm. O
Water Temperature °C. •
PPM.
90
80
70
60
50
40
30
20
10
0
25°
20°
Twin State
Gilead
Bethel
R. Center
V. Bridge
Dixfield
Riley
N. T. Bridge
T. C. Bridge
G.I.D.
Lewiston
Lisbon Falls

due to redispersion when the pollution load was lower.

Interfering substances may be a possible but not probable explanation since the differences extended from Berlin to Lisbon Falls.

The most probable explanation appears to be, that the water which was passing more rapidly between the sampling stations in June than in September would have higher O.C.P. to lignin ratios because the time for microbial oxidation of carbohydrate was much shorter. In June flushing of winter accumulated solids may have contributed some soluble non-lignin oxidizable material.

Of course, more "runs" should have been made and if conducted at planned intervals sufficient data would have been available to judge whether these differences are related solely to the time of passage.

The Tyrosine test reveals the presence of lignin (and phenolics) and of course do not record the ever changing carbohydrate concentration in the river water due to fresh additions from diffusion of cellulose degradation products at certain locations and the continuous loss of sugars due to microbial action. The lignin values changed very slightly across the Pool in both series; the oxygen consumed from permanganates were more varied.

Laboratory Procedures and Reagents.

Tyrosine Test for "Lignin".

The reagent solutions required for the Tyrosine test were prepared as follows:

(a) Sodium Tungstate -Phosphomolybdic acid solution.

50 g sodium tungstate
10 g phosphomolybdic acid
25 ml phosphoric acid (85%)
375 ml water (distilled)

This mixture was refluxed for two hours, cooled and diluted to 500 ml with distilled water.

(b) Sodium Carbonate, saturated solution.

108 g sodium carbonate
500 ml water (distilled)

After heating and cooling excess sodium carbonate crystallized out.

The tungstate solution usually is stable for about three months but it was discarded when the blue color was very slow in appearing. When a white precipitate forms fifteen to twenty minutes after the addition of the sodium carbonate the tungstate solution should be replaced by a freshly prepared mixture.

Standardized Procedure

(a) The sample to be tested was adjusted with distilled water so as to contain from ten to forty ppm of equivalent waste sulphite liquor solids.

(b) To twenty-five millimeters of the adjusted sample, 1.0 ml. of tungstate solution was added, stirred thoroughly and allowed to stand for five minutes. Then 5.0 ml. of the carbonate solution was intro-

duced and the mixture stirred until uniform. The time measurements were begun at this point. Maximum stability was reached after a five minute interval.

(c) The Spectronic 20 with red tube and filter was employed to measure the relative transmission of 700 millimicrons of light through matched cells, one containing distilled water and the other the sample to be tested.

(d) The data from known samples yield curves which indicate that Beer's law is applicable over the usable portion of the plot.

Oxygen Consumed from Permanganate

The procedure employed was the regular method used for river water testing. Ten millimeters of Potassium permanganate standard solution were used when the total O.C.P. demand was less than 60 ppm and fifteen millimeters when the demand exceeded this amount.