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An Investigation of the Coloring Matter of Sulfite Liquor

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AN INVESTIGATION OF THE COLORING MATTER OF SULFITE LIQUOR

A thesis submitted by

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TABLE OF CONTENTS

TABLE OF CONTENTS - Continued

LIST OF ILLUSTRATIONS

LIST OF ILLUSTRATIONS - Continued

LIST OF ILLUSTRATIONS - Continued

I

INTRODUCTION

The change in the color of sulfite cooking liquor during the course of the digestion is of fundamental and practical importance. The entire progress of a sulfite cook is shown by the constituents and the color of the liquor, as well as by the composition of the remaining solid fraction, the pulp. It is possible to follow the heterogeneous reaction, i.e., the sulfonation of wood, by optical differentiation of the various stages of reaction of cooking acid on the several components of wood. This involves determination of the nature of the coloring matter or materials at all stages of the cook.

The exact nature of the mechanism of the reaction of sulfite acid with lignin, to mention only one wood component, is still uncertain. The changes in the spectral absorption of the cooking liquor should be of assistance in determining the course of the heterogeneous reaction. The small amount of data published on sulfite liquor color is concerned with the ultraviolet portion of the spectrum because of the possibility of compound identification by characteristic absorption groups.

The color of sulfite liquor has been important in control since the time when Tilghman burned his first cook. Almost all mills use liquor color to show the end point; they measure color more or less scientifically and use it along with a perfectly maintained schedule and determinations of permanganate number, bleachability, cooking stain, total sulfur dioxide titration, the Mitscherlich test, smell, stickiness, and taste. Color is measured by comparison with old liquor samples, coffee solutions, oil, glass standards and, in a few mills, by photoelectric means.

This research had three objectives: (1) To determine the nature of coloring matter in sulfite liquor throughout the cook; (2) To furnish information on the rate and mechanism of reaction of cooking acid on wood; and (3) To develop the fundamental basis for scientific cook control by photoelectric instruments.

II

HISTORICAL SURVEY

The color developed in the liquor in the course of a sulfite cook is due to organic material extracted from the wood by the action of the hot acid. The constituents of wood then are of fundamental importance in any study of liquor color.

A. WOOD CONSTITUENTS

All woods are composed chiefly of cellulose, hemicellulose, lignin, and resin. Spruce has been selected as an example as it is the most widely used wood for sulfite pulping. The published analyses of sprucewood vary widely, particularly in the carbohydrate fraction. These variations are due in part to the source of raw material, but chiefly to differences in arbitrary analytical procedures. Hägglund (1, p. 252) analysed European spruce with the following results:

A. Cellulose		41.0%	Sulfite cellulose	47.1%
B. Hemicellulose				
1. Difficultly hydrolysable				
Mannan	2.8%			
Xylan	2.1			
Levulan	1.2	6.1		
2. Easily hydrolysable				
Mannan	8.6%			
Xylan	4.1			
Glucan	6.9			
Galactan	1.0			
Levulan	Trace			
				20.6
C. Lignin				28.6
D. Acetyl				1.4
E. Resin, ash, protein				2.3
				100.0

Johnson and Hovey (2, p. 12) obtained the following values for Canadian spruce:

Cellulose	55%
Pentosan	11
Lignin	26
Resin	1

Von Euler (3), Schwalbe and Becker (4), and Klason (5) have published data which agree substantially with those given above.

The yield of unbleached pulp from the sulfite process is 47 to 55 per cent, depending upon the cooking conditions. A normal quick cook will give a pulp containing 2 to 3 per cent of lignin, 6 to 8 per cent of pentosans, and about 85 per cent of alpha-cellulose. The cellulose content of spruce is at most 41 per cent (Hägglund 1, p. 121); this cellulose fraction is most resistant to acid attack and is, therefore, least important in sulfite liquor color.

The hemicellulose material, on the other hand, is readily hydrolyzed and degraded by cooking acid.

Norman and Hawley (6) classified hemicelluloses as follows:

A. Skeletal substance (no uronic acids). Cellulosans--xylan, mannan, and glucosan.

B. Hexosans, pentosans and hexosan-pentosans.

C. Incrusting material, containing uronic acids. Polyuronides--pentosans + uronic acids, hexosan-pentosans + uronic acids.

On hydrolysis, the hexosans yield mannose, levulose, glucose, and galactose, totalling about 15 to 18 per cent of spruce. The pentosans yield xylose and arabinose to the extent of 8 to 10 per cent of the original wood. Hexosan-pentosans, such as galacto-araban, etc., are also present.

Ritter and Kurth (7) have given the following analyses of the easily hydrolyzable portion of spruce hemicellulose:

Constituent	Material %	Wood %
Mannan	17.7	1.8
Glucosan	8.0	0.8
Galactan	7.8	0.8
Araban	12.5	1.3
Xylan	20.9	2.2
Methoxyl	3.2	0.3
Glucuronic acid	14.6	1.5
Volatile acids (acetic and formic)	8.0	0.8
Undetermined	7.3	0.8
	100.0	10.3

Lee, in "The Manufacture of Pulp and Paper," Volume III (8, section 1, 3d edition, p. 56) reported the average pentosan content of sprucewood as 8 to 11 per cent. Hawley and Wise (9, p. 36) criticised Schwalbe and Becker's high figure of 14.3 per cent for pentosans and methyl pentosans. Sherrard and Blanco (10) hydrolysed spruce with dilute sulfuric acid, by which 20 to 27 per cent of the weight of the wood were removed; analysis gave the following percentages of sugar constituents in this solution:

Mannose	37.7%
Glucose	29.3
Galactose	6.4
Xylose	13.3
Arabinose	5.4
Other reducing substances	7.9
	100.0

Hägglund (1, p. 110) gave the mannan content of spruce as 10.5 per cent by his method, whereas Schorger's method yielded 8.0 per cent. On hydrolysis of sprucewood by sulfuric acid, Hägglund (1, p. 112) obtained 20.6 per cent of a sugar solution, analysis of which revealed the following composition:

Mannose	41.0%
Xylose	19.7
Galactose	5.1
Fructose	0.0
Glucose	34.2

The total water-soluble material which can be removed from sprucewood depends upon the temperature and the time of extraction. When carried to the extreme of pressure cooks, a large amount of the hemicellulose can be hydrolysed. Klason (11) stated that 12 per cent of sprucewood is soluble in water; Schorger (12), on the other hand, found only 3.36 per cent total hot and cold water-soluble material. Kurth (13) has published a scheme for separation of the various substances present in the water-soluble fraction, which he has divided into six groups:

A. Tannins—mostly phlobotannins, alcohol-soluble
B. Natural dyestuffs
C. Sugars
D. Salts of organic acids (acetic, formic, oxalic)
E. Non-sugar polysaccharides, gums, musilages, starch, galactans, pectin-like materials
F. Humic acid-like substances.

There are no published data on the amounts of these substances in sprucewood.

The lignin content of sprucewood, as reported by many investigators, varies between 27 and 30 per cent. This lignin, the removal of which is one of the objects of the pulping operation, is a major constituent of sulfite waste liquor, in which it is present as a highly chromophoric substance, calcium lignosulfonate.

Schorger (14, p. 106) has reported the total methoxyl content of sprucewood as varying from 4.43 to 5.33 per cent. All of this methoxyl is not present in the lignin; thus, Hägglund (1, p. 198) has shown that of a total percentage of 4.60, 4.04 per cent were in the lignin. The remainder of the methoxyl is associated with carbohydrate material. Schorger (p. 113) has further stated that the methoxyl groups are hydrolysed only to a very limited extent in sulfite pulping.

The resin and pitch of sprucewood, extractable by organic solvents, are dark red-brown in color. The material extracted by organic solvents is a mixture of fat and resin in about equal proportions, but both quantity and proportion are much affected by the origin and the age of the wood. The ether-soluble fat (0.2 to 0.8 per cent) is the cause of later pitch troubles. The subsequent alcohol-benzene soluble material (0.4 to 1.0 per cent) may include such substances as phlobaphenes. The total organic soluble pitch (0.5 to 2.5 per cent) is dissolved only to a limited extent in the cooking process (8, Vol. III, Section 4, p. 55). However, Browning (15) has reported the following analyses for sprucewood and for the sulfite pulp prepared from it:

Sprucewood	2.13% alcohol-benzene soluble
Normal sulfite cook	47.7 % yield
Unbleached pulp	0.94% alcohol-benzene soluble

These values account for only 21.0 per cent of the original alcohol-benzene soluble substance; the remainder must be dispersed in the waste liquor.

The normal ash content of spruce is low (0.2 to 0.8 per cent) and, from the cooking standpoint, is not important. The common metals are calcium, potassium, and magnesium, combined as carbonate, phosphate, and silicate. There are no chromophoric ions, and the color of the liquor and of the pulp is not affected by ash.

The nitrogen content is low (0.1 to 0.5 per cent) and is usually under 0.3 per cent (Hägglund 1, p. 237). Most of the nitrogenous material is present as dried protoplasm and is probably negligible from the color standpoint.

B. THE SULFITE PROCESS

The two constituents charged into a digester are chips and fresh sulfite acid. The coloring matter developed in the cooking liquor during the course of the digestion has its origin entirely in the wood. Normal cooking acid is a solution of calcium bisulfite with excess sulfur dioxide. The strength of acid is expressed as percentage of sulfur dioxide and usually runs 5 to 6 per cent free and 1.0 to 1.3 per cent combined sulfur dioxide. The base may be calcium, magnesium, or sodium, or a mixture of these. Beazley, Campbell, and Maass (16) have presented the best treatise on the physical properties of sulfite cooking liquor. The inorganic fresh cooking acid is absolutely colorless. However, some color is generally introduced with the fresh liquor at the start of the cook by the commercial practice of using side relief liquor in making up fresh liquor. This side relief liquor is drawn off as late as the eighth hour of a ten-hour cook and is used in a volume as great as 30 per cent of the total fresh liquor volume.

The course of the quick 10-hour cook sulfite process is divided into three stages by the temperature schedule, which in turn is determined by the physical and chemical processes involved. A normal cook schedule might be:

1st period	-	25 - 110° C.	-	3 hours
2d period	-	110 - 140° C.	-	4 hours
3d period	-	140 - 140° C.	-	3 hours

The first stage is primarily penetration of the chips by acid, the second stage is sulfonation of the lignin, and the third is the hydrolysis and solution of the lignin, the "Qualitatskochung" period. Hägglund (1, p. 279) has reduced the above three stages to two, sulfonation and hydrolysis. Steinschneider (17) disagreed with the Hägglund two-stage theory, claiming that the action is one of continuous sulfonation, with lignin dissolving as fast as it is sulfonated. It must be emphasized that the cooking process cannot be sharply divided into two or three stages. The penetration of chips by acid and the two topochemical reactions of sulfonation of lignin and solution of that lignin are consecutive processes and take place in that order primarily in the indicated periods. However, within a single chip and the entire mass of chips all three reactions are going on simultaneously during most of the cooking period.

In the first stage the cooking liquor diffuses into the chips, displacing water or air, at a rate depending upon the wood used, the free and combined sulfur dioxide in the cooking liquor, and the pressure. At the same time sulfurous acid adds to lignin, forming a solid reaction product which is deposited on the fibers. According to Heuser (18), this reaction should be complete before a temperature of 110° C. is reached. It is agreed that this is the critical temperature for most woods. Otherwise, lignin will be polymerized and chip capillaries will be blocked, preventing further penetration. Cooking acid, particularly one containing a high percentage of combined sulfur dioxide, is liable to precipitate calcium monosulfite and hydroxide at about 120° C., according to Birchard (19), and time must be allowed for penetration.

At 110° C. the temperature schedule starts the slow rise to maximum (the so-called second stage); this allows time for complete sulfonation and simultaneous solution of the sulfonated lignin. Hägglund (20) believes that the lignin is chemically combined with a certain part of the carbohydrate and that this combination is maintained during the sulfonation of the lignin. This carbohydrate-lignin-sulfur dioxide compound is stable and insoluble in water. The dissolution to soluble products is a hydrolysis catalysed by the hydrogen-ion concentration of the liquid phase and is independent of the hydrogen-ion concentration of the solid lignosulfonic acid. The rate of removal is proportional to the amount of solid lignosulfonic acid present and to the pH of the liquor (21). Hägglund further claimed that the pH inside the chips is high (3 to 4) as compared with a pH of 2 for the liquor; this condition protects the fibers against degradation. The hydrogen-ion concentration in the liquor results from the dissociation of sulfurous acid and its salts, and sulfuric acid, organic acids, and their salts formed from the wood. Up to 110° C. the hydrogen-ion concentration decreases, because sulfurous acid is being taken up by the lignin; it increases as soon as the strong lignosulfonic acid begins to go into solution.

In the so-called third stage, in which the cook is held at constant temperature, the hydrolysis of lignin is carried to the desired point with simultaneous carbohydrate removal. Hägglund (22) in 1926 reported that the increase in sugar content in the liquor paralleled that of the lignosulfonic acid, but in 1934 (23) he stated that the rates of solution of sugars and lignin are independent of each other.

Hägglund (24), on the basis of constant yield, strength, and bromine number of the resulting pulp, concluded that the cooking reaction is independent of temperature in the range of 120° to 135° C. and that time is the only variable. The sugar content, the pH, and the sulfuric acid in the liquor are also constant. However, above 135° C., for the same degree of delignification, the yield is 3 per cent lower with a lower grade of pulp and a higher sugar content in the liquor. These all indicate increased carbohydrate hydrolysis.

According to Klein (25), the cooking reaction is monomolecular, depending upon the speed of solution of the sulfonated lignin. Corey and Maass (26) agreed that between 100° and 140° C.

the delignification is approximately monomolecular. The rate change with temperature obeys Arrhenius' law, and the conclusion is reached that the reaction speed of the cook is doubled for each 10° C. increase in temperature. Miller and Swanson (27, p. 57) agreed with the temperature increase rule.

Brauns and Brown (28) stated that the chemical reactions actually taking place between the lignin in wood and the cooking acid are still unknown. Undoubtedly, however, one or the other of the hydroxyl groups of native lignin participates in sulfonation. After methylation, lignin is still capable of taking up sulfurous acid but less (about half as much) sulfur enters the molecule. They agreed with the two-stage sulfonation theory; solid lignosulfonic acid is first formed; then there is a rearrangement of the sulfonic group in the complex, with the participation of a hydroxyl group, forming soluble lignosulfonic acid. With methylated wood, only the first stage takes place. The second stage is hindered by methoxyl covering the specific hydroxyl group necessary for sulfonation.

Hägglund (29) found that lignosulfonic acid, both solid and dissolved, has varying sulfur and methoxyl content depending upon cooking conditions. High combined acid gave a high sulfur content in solid lignosulfonic acid, whereas low combined acid gave a low sulfur content.

Klason (30) believed that lignosulfonic acid is a dibasic acid, and that at low temperatures the monobasic calcium lignosulfonic acid is first formed. He (31) further believed that the acid exists in two forms; the alpha-acid is that which is precipitated by beta-naphthylamine hydrochloride; the remainder, precipitated only by lead acetate, he termed the beta-acid. These two acids, which differ widely in color, were thought to be chemically combined in a ratio of about 2 parts alpha- to 1 part beta-acid. Klason (32) explained the beta-naphthylamine precipitation of the alpha-acid as a true aldehyde addition, pointing out that aldehydes react, while ketones do not. He (33) stated that pentoses, particularly xylose, are the parent lignin substances. In waste liquor, 70 per cent of the lignin (the alpha-acid) is present as condensed coniferylaldehyde. The beta-lignosulfonic acid contains no aldehyde groups. Hägglund (34) thought that beta-lignosulfonic acid is a degradation product of native lignin, of lower molecular weight. The beta-form does not exist as such in sprucewood but is formed in pulping; the relative amounts of alpha- and beta-lignosulfonic acid depend on the pulping conditions. The bisulfite sugars present form an oxidation-reduction system with the original lignosulfonic acid, yielding gluconic acids and beta-lignosulfonic acid. He (29) further stated that the precipitation of lignosulfonic acids with salts, aromatic amines, alkaloids, etc., is essentially a salting out process. The cooking liquor and the pulping conditions affect the particle size of the dissolved acids and their precipitation. Beta-lignosulfonic acid has a high degree of sulfonation and a low methoxyl content. Half of this methoxyl content is split off in cooking by sulfonation, oxidation, and hydrolysis. The loosely bound sulfur dioxide present in the liquor is mostly held by the sugars, but part of the sulfur dioxide is also held by the beta-lignosulfonic acid. A high yield of alpha-lignosulfonic acid results from low combined sulfur dioxide, 90 per cent being obtained in a cook with free sulfur dioxide alone. Kullgren (35) stated that there is no definite evidence that there are two different lignosulfonic acids in sulfite pulp.

Hägglund (36) concluded from the values of the reaction constants that lignosulfonic acids are of uniform molecular size and that they are not polyvalent compounds but monobasic sulfonic acids of low molecular weight. In the solid phase and in solution they have a strong tendency to condense with the formation of larger complexes.

The pentosans and hexosans present in wood are the chief sources of sugars in sulfite waste liquor. The carbohydrates in wood range from simple sugars to cellulose, i.e., from water-soluble polysaccharides to those containing 150 glucose unit chains; all are attacked to some extent by hot sulfite acid in the digester. Complex sugars are split by acid hydrolysis to simple units; these simple units form -onic and -uronic acids, form addition compounds with bisulfites, and break down with the formation of caramel.

The Ritter-Kellner or 10-hour cook, with higher cooking temperature, produces more sugars and furfural than the longer and milder Mitscherlich cook. The yield of pulp is usually 2 to 3 per cent lower because of the increased attack on the cellulose. The sugar yield is decreased by the use of high combined acid, due to its strong oxidizing of sugar. The sugar content of waste liquor reaches a maximum and then decreases, due to degradation by the acid present and to oxidation.

Hägglund and Johnson (37) found that 12 per cent of wood hydrolyses to glucose equivalent in the liquor. Zherebov (38) concluded that the pentosans hydrolyse more readily than the hexosans, and that their decomposition is more complete; carbon is the final product. Norman (39) stated that the removal of hemicelluloses with sulfite acid is effected to almost the same degree as that of lignin. Hemicelluloses and lignin are believed to exist in some sort of combination, and solution of the hemicelluloses depends upon the rupture of this linkage. Miller and Swanson (40) followed the rates of removal of lignin and cellulose, and found that the carbohydrate is removed much faster than the lignin. Lignin removal, therefore, is the controlling factor in pulping. Schwalbe (41) claimed that the pentosans in wood are very resistant and remain constant in the pulp up to five hours of the cook, with hexosans breaking down first. On the other hand, Hägglund (29) found that, after six hours, the dissolved pentosans in the cooking liquor represent 66 per cent of the total sugar, whereas at the end of the cook they form only 20 per cent. This would indicate that the pentosans hydrolyse faster than the hexosans. In a study of "synthetic lignin" Hawley and Harris (42) heated Cross and Bevan cellulose and noted that the hexosans are destroyed completely at 125° C., whereas the pentosans are only partially changed. Miller, Swanson, and Soderquist (27, p. 80-91) stated that sugar in the liquor is due simply to acid hydrolysis—the more acid, the faster the sugar is formed—and that addition of strong acid to a cook hastens carbohydrate removal but retards the removal of lignin. Hägglund and Johnson (43) stated that solid lignosulfonic acid behaves like a strong inorganic acid (sulfuric acid), in spite of its insolubility, and exerts considerable catalytic effect on the hydrolysis of sucrose. Hägglund (34) has done most of the work on the relation of sugars to bisulfites and the effect of sugars in the cooking process. Aldoses (glucose), mannose, and xylose accelerate the decomposition of bisulfite into sulfur and sulfuric acid to about the same degree. This simultaneous reduction and oxidation is caused by the sugar-bisulfite compound which acts as a reducing agent on bisulfite ions or lignosulfonic acid. Fructose is not nearly as active in this role as are the aldoses. His conclusions were given graphically as follows:

Simple sugars plus hot bisulfite acids:

Aldoses (glucose)	⟶	gluconic acid.
Ketoses	⟶	relatively stable bisulfite acids.
Bisulfite sugars + bisulfite	⟶	free sulfur, sulfuric acid, thiosulfate, polythionic acids, and aldonic acids.

Hägglund's theory is that the portion of the lignin which is reduced represents the beta-lignin fraction, i.e., that not precipitated by beta-naphthylamine. The theoretical amount of free sulfur and sulfuric acid produced in the above reaction cannot be determined. Sugar added to hydrolysing lignosulfonic acid produces a higher yield of beta-lignin.

Reutala (44) concluded that the carbon dioxide produced in sulfite cooking came only from the hemicellulosic material, and not from the cellulose or the lignin. This conclusion is supported by the fact that high combined acid gave 50 per cent more carbon dioxide than low combined acid. Birchard (45) studied relative rates of degradation of cellulose by sulfite and concluded that the purer the pulp, the easier it is degraded. Cotton was degraded faster than wood pulp, which in turn was degraded faster than wood itself. Berl and Schmidt (46) have studied extensively the degradation of cellulose in water with heat. Cellulose hydrolyses to glucose which is degraded to humic acid. Fuchs (47) agreed that the probable course was: Cellulose ⟶ glucose ⟶ "humic acids." Hilpert and Littmann (48) stated that the decomposition of sugars is a controllable reaction, depending upon the time, the temperature, and the kind of sugar. Glucose and mannose are degraded at about the same rate and fructose very much faster. The elementary composition of the residue is the same as that of lignin. Runkel (49), writing on the subject of hemicelluloses, stated that the pentosans change on aging to ligneous material. Hilpert and Hellwage (50) concluded that the total beechwood lignin (beechwood is rich in xylan and low in lignin) as isolated by acid treatment is a product of the isolation procedure-- condensation of carbohydrate material to "lignin" by the acid.

One of the most important variables in sulfite pulping is the composition of the cooking acid. The normal cooking acid ranges from 4 to 7 per cent of free sulfur dioxide. High free sulfur dioxide speeds up the cook, but the upper limit is set by the temperatures of the water in the acid system (refrigeration is needed in summer) and by the mechanical strength of the digester and the type of acid storage system used (Chemipulp).

Samuelson and Haug (51), working with the glass electrode, checked Campbell's conclusion that sulfurous acid does not exist above 100° C. The pH approached neutrality above this temperature, due to complete dissociation into sulfur dioxide and water. The glass electrode can only be used at normal temperatures, over a limited range. The best paper on the subject of the effect of liquor composition on the rate of sprucewood delignification is that of Calhoun, Yorston, and Maass (52). They concluded that the cooking rate is a quantitative function of (a) the partial pressure of the sulfur dioxide and (b) the pH. This disagrees with Hägglund's theory (1, p. 279). They also found that increased free sulfur dioxide concentration does not alter the relative rates of sulfonation and hydrolysis. The yield, to the same lignin content, is independent of total sulfur dioxide concentration, but the pH of the cooking liquor is lowered and the time is decreased. Increased combined sulfur dioxide greatly improves the yield, at the same degree of delignification, but the time is increased. There is a systematic deviation from the first order relation that is the same for any composition of liquor.

The combined sulfur dioxide is very important in the cooking process. Free acid penetrates faster than base; therefore, time is required for total acid penetration, and without sufficient penetration the cook will burn. A portion of the free lignosulfonic acid is neutralized as formed by the base and goes into solution; however, an appreciable amount remains in the solid form, as may be seen by the increase in the ash content of the pulp with cooking. Sugars and calcium base liquor form slightly soluble addition compounds which consume a portion of the base. For the same degree of delignification, a higher combined acid will give higher yield, better defibering and lighter liquor with lower sugar content; and a whiter pulp, which is more stable to light, softer, and more absorbent; the pulp also has increased burst and tear. Longer cooking time is required with high combined acid, with higher lime and sulfur consumption. The other disadvantage is that excess lime precipitates on fibers, heaters, and blowpits, mainly in the form of the monosulfite. The minimum combined sulfur dioxide for safe use is about 0.8 per cent, and the commercial range which has been used is from 0.9 to 2.0 per cent, with 1.1 to 1.2 per cent the usual practice. The formation of sulfuric acid in a normal cook is usually slight, and the precipitation of calcium sulfate is negligible. Soda base has every advantage over calcium except in cost. The advantages are increased yield, strength, bleachability, and less trouble from pitch and dirt. Kullgren (35) stated that sulfur dioxide has a stronger solvent action on lignin than bisulfite and sulfur dioxide have. Free lignosulfonic acid is less stable but more soluble than its metallic salts; the sodium salt is more soluble than the calcium salt. Kullgren thought that calcium base is better for cooking than the soda base, because the calcium of calcium lignosulfonate cannot as easily be replaced by hydrogen ions.

C. COOK CONTROL

The color of sulfite liquor is almost universally used in cook control, but only as a corroborative test. The most commonly used variable in sulfite cooking control is time. Time is used to compensate for differences in wood and wood condition, acid strength, design of digesters (size, direct and indirect heating, chip packing, etc.), and for changes in schedule, whether due to inadequate pressure and temperature control equipment or mechanical failures. On the other hand, Swanson, Lang, and Smith (53) are the outstanding exponents of what they believe to be a more rational system, in which the time of cooking is constant, and the maximum temperature of the cook is the variable; this is used to compensate for all the other factors involved.

The determination of the cooking end point with time as the variable is possible by any one of a half dozen methods, but several are commonly used. Undoubtedly, those methods which measure the degree of lignification are fundamentally most sound. The pulp, rather than the liquor, is the best place to measure the degree of cooking.

The tests which are usually run on the pulp all measure, directly or indirectly, the lignin content. The permanganate test is probably the best and most widely used, since it correlates well with the actual bleaching requirement and requires only 15 to 20 minutes' time. The cooking stain is claimed to be as good as the permanganate test and requires at least as long. Actual bleaching tests require too long a time, as do actual lignin content determinations. Nippe (54) in 1937 proposed a control test which determines the amount of lignin present by addition of benzidine hydrochloride to the pulp. He claimed that the amount of benzidine absorbed, the "amine" number, correlates perfectly with the Sieber chlorine number. An important point in connection with the testing of pulp in digester control is the procedure for sampling the digester. A few pounds of pulp sampled from a single point may or may not be representative of the entire 15-ton digester.

The other component in a cooking digester is the liquor. Liquor samples, like pulp samples, may not be representative, but they may be very good, particularly when taken from digesters with circulating systems. Pulp samples are not uniform because of uneven heating and nonuniform liquor; the liquor is not uniform because of uneven heating and dilution by direct steaming. The common tests which are carried out on the liquor measure a variety of physical and chemical properties.

The total sulfur dioxide content is not critical, although it is always determined to check other evidence. The combined sulfur dioxide content, usually found by the Sander method, is not critical and is used to show the presence of uncombined base. The Mitscherlich test, another test for uncombined base, is still being used though discredited by Öman (55), Petterssen (56), and Zherebov (57). Birchard (58) found that the loosely combined sulfur dioxide increased to a constant value of 0.384 per cent, for each of 12 cooks. He concluded that the cook was finished as soon as the loosely combined sulfur dioxide had reached this maximum, and that cook control was possible by this test.

Several authorities have referred to the use of the odor, taste, and stickiness as a test of the liquor. These properties are a good indication of the progress of the cook, but standardization of the tests has been difficult. Escourrou and Carpentier (59) thought that measurement of the hydrogen-ion concentration of the liquor is the best way to control the sulfite cook. Kommál (60) agreed that pH is important but stated that it is impossible to blow cooks on this test alone. The consensus of opinion today is that it is impossible to measure the pH inside a sulfite digester.

The lignin content of the liquor has been measured in several ways. Escourrou and Carpentier (59) mentioned a procedure for determining the permanganate number of the liquor. Rassow and Kraft (61) checked the course of the cook by the addition of an excess of benzidine hydrochloride to the liquor, with titration of the excess not precipitated by the lignosulfonic acid. Haider (62) in 1935 proposed a new control method in which he followed the course of the sulfite cook by precipitation of the lignosulfonic acid. Hennig (63) determined lignin content by the volume of the precipitate formed with Fuchsine.

By far the most commonly examined property of the liquor is the color. Practically every mill checks the color and depends upon it more or less. Lunak (64, p. 12-13), in 1915, discarded sulfur dioxide tests, the Mitscherlich test, bleaching and cooking stain tests on the pulp, and stated that color, checking against coffee standards, is the most practical and satisfactory. Paulsen (65), Larrabee (66), and Klein (67) all recommended color as a critical test. Okada (68) found a relationship between the initial point of viscosity drop of the pulp and the darkening of the liquor. At each temperature a relationship also existed between pH and viscosity. Fleury (69) treated the liquor sample with ammonia and methanol, filtered off the precipitate, and then tested the color. Zherebov (57) recommended the use of the Hess-Ives tint photometer, as used at that time (1925) in a Canadian mill, for a numerical, reproducible value for color. Chidester (70) used the Hess-Ives tint photometer to determine the color of liquor in order to calculate the allowable amount to reuse in the cook. Photoelectric color testing is gradually coming into use. French patent 729,513 (71), in 1931, covered design and installation of a photoelectric cell so arranged that on completion of a cook a light is flashed, a horn is blown, or the cook blown by action of a solenoid valve. Hauff (72) has published the only paper on the use of the photoelectric cell in testing liquor.

Failure in sulfite cooking results in either a raw or burned cook, and it is the function of control testing to prevent these possibilities. A black or burned cook may mean one in which the chip is not thoroughly penetrated and defibered, resulting in blackened exterior and raw center, or one which is satisfactorily defibered but overcooked by too high a temperature or too long a time. The first type usually occurs when too little time is allowed for penetration of the chips, especially with woods having particularly dense heartwood. The second type is liable to occur with low combined acid, where the base may become exhausted and the organic acids present in the liquor may burn the remaining cellulose and hemicellulose in the pulp and the sugars which are in solution. Free lignosulfonic acid is as strong as sulfuric acid. Öman (73) stated that burning occurs when there is no longer an excess of sulfur dioxide above that necessary to form bisulfite and that burning is independent of lime content. The darkening of liquor is a function of pH. Goodwin and Birchard (74) thought that a dark cook is due to decomposition of lignosulfonic acid, caused by low lime content. Hägglund and Arnold (75) claimed that a burnt cook may occur where solid lignosulfonic acid is hydrolyzed to a soluble form before it is completely sulfonated. Partially sulfonated lignin resinifies more readily than that which is completely sulfonated. Earlier, he (76) had stated that bisulfite combines with an active carbonyl group of lignin and prevents darkening (chromophoric group developed from the carbonyl group on burning) only as long as an excess of bisulfite is present. If lignin is not completely sulfonated before the base is exhausted, a burnt cook is unavoidable. During a cook, acidity remains constant as long as base is present and no gases are released. Kullgren (35) stated that a burnt cook is caused when free solid lignosulfonic acid is not neutralized by base. The degree of displacement of hydrogen ion by calcium ion depends on the pH of the liquor and the ratio of calcium to hydrogen in the liquor. Birchard (77) said that burning can take place in a very few minutes, resulting in a total loss or in a weak stock with a high bleach consumption. Discoloration and burning are due to the effects of acid on hexosans, pentosans, and cellulose, and to the effect of alkali and temperature on aldehydes present in cooking liquor, forming insoluble resins. He had previously (19) claimed that the liquor contains free alkali during the latter part of the cook. If the total sulfur dioxide drops below 0.1 per cent, free calcium hydroxide is actually present in the liquor. The aldehyde comes mainly from the lignin. Lignosulfonic acid has two (HSO_3) groups and is strongly acid, but when only one (HSO_3) group is added it acts as an aldehyde and is condensed by calcium hydroxide to form black resins.

With insufficient base, burning has been attributed to polymerization of free lignosulfonic acid. Birchard (77) denied this, claiming that sulfonic acids do not polymerize but that aldehydes do. He cooked 2.6 per cent of butylaldehyde-beta-sulfonic acid with bleached sulfite and obtained a degraded stock but no discoloration. Two and two-tenths per cent crotonaldehyde produced discoloration and a strong resin odor, but the stock was easier to bleach than burnt sugar-stained stock. Pentosans charred more easily with 2 per cent of sulfuric acid than did hexosans. Both had strong dye action on the fiber.

The use of side relief liquor has been mentioned previously in connection with the introduction of color into fresh acid. Practically all mills use side relief liquor, as well as relief sulfur dioxide gas. Side relief starts at about four to five hours and continues to eight to nine hours and may amount to as much as 30 per cent of the cooking acid. This relief liquor contains considerable lignin and sugar. The consensus of opinion is that the use of normal relief liquor is not harmful and that it actually speeds up the cook. However, sugars present are supposed to accelerate sulfuric acid formation, and abnormal amounts of cymene and turpentine affect the pulp adversely. Chidester (10) used the color as an indication of how much to use and how late liquor can be used.

D. WASTE SULFITE LIQUOR CONSTITUENTS

Johnsen and Hovey (2) covered the field of sulfite waste liquor very thoroughly up to about 1919. They stated that Ritter-Kellner liquor normally contains about 12 per cent of organic and 1 to 1.5 per cent of inorganic matter. The dry residue then contains 10 to 15 per cent of ash. Of the 6 to 10 per cent of sulfur originally present, only 2 per cent remains in the ash, mainly as calcium sulfate and calcium sulfide. Klason (2, p. 16) gives the following summary of the waste products obtained per short ton of pulp produced:

Lignin	1200 lb.
Carbohydrates	650
Proteins	30
Resin and fat	60
Sulfurous acid combined with lignin	400
Lime	280
	2520 lb.

Krause (2, p. 14) analyzed sugars from sulfite liquor as follows:

Total sugars	1.47%
Pentoses	0.41
Mannose	0.48
Galactose	0.01
Fructose	0.25
Dextrose	Trace

Klason (2, p. 15) found these sugars:

Mannose	0.526%
Galactose	0.279
Glucose	1.65
Arabinose	0.90

Benson and Partansky (76) have said that the sugars in waste sulfite liquor are all reducing sugars and not polysaccharides. About 10 to 30 per cent are pentoses, the rest hexoses, including dextrose, levulose, and mannose.

The principal constituents, then, are calcium lignosulfonic acid, carbohydrates, and inorganic lime salts. All the rest are present in small quantities, if at all. The complete list of all substances reported in sulfite waste liquors is presented in the following table:

Waste Sulfite Liquor Constituents

1. Inorganic

SO_2—H_2SO_3	CO_2
$Ca(HSO_3)_2$ or Mg, Na	Free S
$CaSO_3$	H_2SO_4
$CaSO_4$	Si, Fe, Al
CaS	
Thiosulfuric acid	
Dithionic and polythionic acids	

2. Organic

   a. Lignosulfonic acid, from free acid to mono- and dicalcium salts; with 1 to 4 SO_2 groups per lignin molecule, in all stages of polymerization and resinification.

Waste Sulfite Liquor Constituents - Continued

b. Sugars

(1) Hexosans--mannan, glucan, fructan, galactan, and the simple hexoses, mannose, etc.

(2) Pentosans--xylan and araban and pentoses.

(3) Acids from above sugars, -onic and -uronic.

(4) Ca salts of simple and higher sugars and acids from sugars.

c. Sugar degradation products--humic acids and caramel.

d. Small amounts of:

Formic, acetic, oxalic, succinic and citric acids.
Formaldehyde and acetaldehyde.
Furfural, methylfurfural and hydroxymethylfurfural.
Methyl and ethyl alcohols.
Acetone, cymene, turpentine, solid terpene alcohol,
di-, sesqui-, and polyterpenes.
Protocatechuic and diprotocatechuic acids.
Protein
Phenols
Rosin and fat
Vanillin
Sulfite liquor lactone
Borneol.

B. THE COLORING MATTER OF SULFITE WASTE LIQUOR

There exist a great deal of experimental data pointing out that wood contains potentially strong chromophoric groups. Organic chromophoric groups are directly due to unsaturation, and the greater the degree of unsaturation, the greater will be the compound's absorption of some part of the visible spectrum. All organic compounds absorb in the ultraviolet, but only the highly unsaturated compounds absorb visible light. Since the nitrogen content of wood is negligible, the color must be attributed to cyclic unsaturation, and to the double bonds, carbon to carbon, and carbon to oxygen. The auxochrome groups of hydroxyl, methoxyl, and carboxyl are all present. In sulfite liquor there is, in addition, the auxochromic sulfonic acid group. The presence of sulfur dyes at any time in the course of the sulfite cook must be ruled out, since sulfur dyes, though of unknown structure, are defined in the commercial sense as being made from sulfur or sulfides and organic nitrogen compounds such as aromatic amines or nitrophenols.

The potential coloring materials present in sulfite liquor, then, are lignosulfonic acid, caramel, furfural, methylfurfural and hydroxymethylfurfural, and the minor wood constituents such as water and alcohol-benzene soluble materials. All isolated lignin and lignin compounds are colored. Brauns (79) has prepared native lignin which is a very light cream color. Other isolated lignins are colored in proportion to the changes and degradation caused by the severity of the isolating procedure. Soluble sodium lignin compounds such as are present in soda and kraft black liquors are colored dark brown. Lignosulfonic acid and its salts are dark brown, the depth depending greatly upon the cooking conditions. Fairly light colored calcium lignosulfonic acid may be isolated before the temperature has exceeded 125° C. Lignosulfonic acid undergoes a change in color from yellow in acid solution to deeper orange or red-brown with alkali. King, Brauns, and Hibbert (80), among others, have noted this change and made use of the indicator action. Hirano (81) determined the acidity in sulfite liquor by photometric titration. This color shift with pH is a true indicator action, and is the result of replacement of acidic hydrogen by metallic ion, with resulting molecular rearrangement of the aromatic nucleus, comparable perhaps to that taking place in Methyl Orange.

There has been much research on the ultraviolet absorption spectra of various lignin preparations, all in attempts to determine the structure of lignin. Herzog and Hillmer (82) found identical absorption curves for sulfite waste liquor, technical lignosulfonic acid, alpha-lignosulfonic acid according to Klason, isoeugenol, coniferyl alcohol, and coniferyl aldehyde. Hägglund and Klingstedt (83) published the curves for amyl and methyl lignins and calcium lignosulfonate from several woods, isoeugenol, and coniferin, and checked Herzog and Hillmer's conclusions. Rassow and Wagner (84) noted a resemblance between the absorption spectra of pure lignin in several solvents, and coniferin. Stamm, Semb, and Harris (85) found a definite difference between hard and softwood lignins. Calcium lignosulfonate gave the sharpest maxima. Hachihama and coworkers (86) discovered a similar definite difference between bagasse and softwood lignin. The absorption spectrum of bagasse lignin resembles that of hardwood lignin.

Certain staining reagents have been used for many years in testing for lignin. Practically all amines and phenols give a color reaction with lignin. The question whether or not the color is due to some characteristic group of the lignin complex or to some minor constituent has been a controversial subject for years. Phillips (87) has reviewed the literature and concluded (p. 108) that the color reactions are probably due to coniferyl alcohol.

Wichelhaus and Lange (88) extracted wood with superheat steam and obtained products which gave color reactions similar to those of lignified wood. One fraction, which gave a cherry-red precipitate with phloroglucinol-hydrochloric acid, was thought to be a condensation product of ketofurfuraldehyde, derived from hexose material. Singer (89) considered that the coloration was possibly due to vanillin and coniferin. Czapek (90) isolated "hadromal" by digesting wood with stannous chloride and extracting the residue with benzene. "Hadromal" was isolated as a brown crystalline substance melting at 70° to 80° C., with phenolic and aldehydic properties, and readily gave the various lignin color reactions. Hoffmeister (91) and others have checked Czapek and reached the conclusion that "hadromal" is identical with coniferyl aldehyde. Grafe (92) considered "hadromal" a mixture of vanillin, methylfurfural, and catechol. However, Grafe prepared his "hadromal" by extraction of wood with 10 per cent hydrochloric acid or by heating with water under pressure at 180° C. for one hour.

Among those disagreeing with Czapek is Podbresnik (93), who stated that the color reactions of lignin were due mainly to "native" lignin and not to methyl pentosans, vanillin, coniferyl alcohol or Czapek's "hadromal." Extracted lignin and oxidized lignin gave the same reactions as lignified tissue. Campbell, Bryant, and

Swann (94) found that the chlorine-sodium sulfite color reaction given by woody tissues is also given by hot and cold water extracts of wood and even by cold water extracts of isolated lignin. They concluded that the reaction is probably specific for phenolic bodies containing the 1, 2, 3-trihydroxybenzene nucleus, such as exists in tannin or pyrogallol.

Evidence has been presented to prove that there may be relatively simple unsaturated compounds present in wood and lignin which are responsible for the staining reactions with amines, phenols, and inorganic reagents. Those suggested include condensed keto-furfuraldehyde, methylfurfural, vanillin, catechol, coniferyl aldehyde, and phenolic bodies containing the 1, 2, 3-trihydroxybenzene nucleus. The dissenting investigators insist that the whole lignin molecule takes part in the stain reaction. The elements of the wood, and lignin molecule, which enter the stain reaction are probably the same unsaturated groups or compounds which are responsible for all lignin color, from that of isolated lignin to that of lignosulfonic acid.

The furfural family of compounds are frequently mentioned in connection with both lignin and caramel color. Pentoses on acid degradation yield furfural quantitatively, while hexoses when heated with strong acids undergo complicated reactions which follow no single definite course. Furan and furan derivatives are produced by acid degradation of hexoses, through the dicarboxylic acids. Methyl-furfural and hydroxymethylfurfural are also end products in the degradation of hexoses by acids. Caramelization is a term usually applied to the process of dehydration of dry sugar by heating to about 100° C. Among the other products of decomposition are carbon dioxide, formaldehyde and acetaldehyde, formic and acetic acids, and acrolein. The brown residue, known as caramel, has a slight acid reaction, and is a strong dye. Browne (95, p. 467) stated that one part of caramelan in 10,000 parts of water colors it a deep brown, which is intensified by alkali. Yen and Leung (96) thought that caramel was an indicator, with a color change in the pH range of 5.6 to 6.6. The reducing power of caramel from various sugars is proportional to the amount of sugar left undegraded. All of the commercial tests for caramel from hexoses (in beer, vanilla, etc.) are based on the color reactions obtained with amines or phenol reagents on the hydroxymethylfurfural which is present in the caramel, according to Joszt and Molinski (97). Garino and Tosonotti (98) found that the amount of coloring matter produced from sucrose was much greater than that from glucose. Kwieciński and Marchlewski (99) agreed and from their work in the ultraviolet decided that levulose and dextrose could not be the only products of inversion of sucrose by 0.5 N hydrochloric acid. Later (100) they found that methylglyoxal, a degradation product of glucose and a likely impurity in sugars, showed pronounced selective absorption in the ultraviolet. Cohn (101) has published the spectral absorption curves of a series of glucose glasses, ranging from white to dark brown. The glasses show flat transmission maxima from 580 to 640 millimicrons, with a shift in transmission maxima to the red end with increasing caramelization.

Tanaka (102) has studied the constitution of anhydrosugars and the action of superheat steam in degrading them. Anhydrosugars hydrolyze with water starting at 100° C., forming hydroxymethylfurfural which polymerizes to humus material, while the pH of the solution decreases. For each sugar an intermediate product resembling chitose (2, 5-anhydroglucose) is formed. Thermal data and the similarity between the absorption spectra of chitose and hydroxymethylfurfural are advanced as proof.

Pentosans and pentoses when heated with acids yield furfural quantitatively by splitting off water. Furfural is a colorless liquid, which, however, polymerizes readily to dark red compounds, particularly with heat and light. Furfural undergoes the benzoin type condensation, which may be at least one step in the above polymerization. Furfural forms deeply colored compounds with amines and phenols. The color formed with aniline, etc., is the basis for qualitative and quantitative tests for furfural, while the precipitation with phloroglucinol is the standard quantitative test. The presence of furfural, furan, furan derivatives, methylfurfural and hydroxymethylfurfural, all forming deeply colored polymerization products, in the products of acid degradation of sugars is the most significant clue to the identity of the coloring material in caramel. Bandow (103) has shown the significance of the aldehyde group in the ultraviolet absorption spectra of glucose, mannose, and arabinose by comparison with the absorption spectra of furfural. All these compounds, while colorless in the visible, have sharp maximum absorption bands at about 320 millimicrons. Marcusson (104) synthesized humin and humic acid by heating furfural with hydrochloric acid. Dark red-brown substances were obtained, which could be separated into acid- and alkali-soluble fractions. Hurd and Isenhour (105) checked Marcusson, finding that furfural is destroyed when refluxed with acid, with the formation of polymeric, highly complex humins, cherry-red in color. Xylose yields furfural much faster than arabinose. They also stated that the formations of hydroxymethylfurfural from hexoses and methylfurfural from methylpentoses are exactly analagous to the dehydration mechanism of the formation of furfural from pentoses.

III

EXPERIMENTAL WORK, DATA, AND DISCUSSION

A. CHEMICAL AND OPTICAL ANALYSES OF SAMPLES OF LIQUOR TAKEN AT INTERVALS IN A NORMAL SPRUCE COOK

1. Wood and the Cooking Procedure

Canadian black spruce was used throughout the first phases of this study. This spruce was summer cut three months previous to barking and chipping for use. The physical properties (an average of six sticks) are summarized in Table I.

TABLE I

AVERAGE WOOD DATA

Age in years	86
Diameter in inches	6.0
Density in pounds per cubic foot	25.6
Percentage of moisture	39.9

Six 8-foot sticks were barked, chipped to 3/4-inch chips, screened, mixed thoroughly, and stored in bags in a moistureproof box to minimize moisture loss.

The following procedure was used in making the cooks. A weighed charge of chips of known moisture content was packed in the stainless steel digester, which was equipped for liquor circulation and indirect steam heating. Cooking acid, previously prepared and adjusted to 6.20 per cent free and 1.20 per cent calcium base combined sulfur dioxide, was admitted until the liquid level in the digester was one inch below the top flange. The quantity of acid required was measured. The wood-liquor ratio is very important in a study of liquor color, particularly when the color is used in cook control. In this first phase of the work, however, the four cooks made were not check cooks and no attempt was made to hold the wood-liquor ratio constant.

After charging the digester, which holds about 6000 grams of oven-dry wood and 25 liters of acid, the cover was bolted on, the circulating pulp started, and the steam turned on. The temperature and pressure schedule shown in Table II was used for all cooks, except Cook 2. Cook 2 was carried to twelve hours and was deliberately burned. All other cooks were made at the normal 10-hour schedule.

TABLE II

COOKING TEMPERATURE AND PRESSURE SCHEDULE

Time, hr.	Temperature, °C.	Pressure, lb./sq. in.
0	25	0
3	110	—
7	140	—
9	—	75
10	140	50

Temperature rises are linear.

The 75-pound maximum pressure was reached in 4-3/4 hours on all cooks and held by top relief to the ninth hour, when the linear blow down to 50 pounds was started.

Liquor samples were taken from a valve in the circulating line, through a coil of 1/4-inch copper tubing cooled by ice water. Two hundred cubic centimeters of liquor at less than room temperature could be drawn off per minute with no appreciable loss of free sulfur dioxide. The terms "liquor" and "sulfite liquor" used in this investigation will refer to samples of sulfite cooking liquor which were withdrawn from the digester in the interval from a few hours after the start of the digestion to the end of the cook. The strong fresh liquor which was added to the chips at the start of the cook will be referred to as "fresh sulfite liquor."

After blowing the digester, the liquor was drained off and the pulp was covered with fresh hot water, agitated vigorously for fifteen minutes, drained, and again covered with fresh water. The stock was agitated for two additional 5-minute periods, finally drained, screened, and pressed for storage until the desired tests could be run.

2. Analytical Procedures

a. Optical analysis. The liquor samples taken at intervals in the cook were tested immediately for spectral transmission in the range of 400 to 700 millimicrons on the General Electric recording spectrophotometer. The samples as drawn from the digester were free from fiber and dirt, but to insure uniform results all samples were filtered through a Gooch crucible with an asbestos mat. This method was chosen on the grounds of accuracy and simplicity over the alternatives of filtering through filter paper or of centrifuging. The change in spectral transmission from that of the original cooking liquor was approximately one per cent higher transmission over the entire range, for all three methods. This indicates that a small amount of neutral colored suspended material was being removed.

The absorption cell used was Eimer and Amend No. 31180, 30 x 20 x 5 mm. inside dimensions, U-shaped, with a liquid thickness of 5 mm. Two matched cells were used with two matched magnesium carbonate blocks, the entire system giving 100 per cent transmission for distilled water over the 400 to 700 millimicron range. In practice the instrument operated at a reproducibility of ± 0.2 per cent transmission.

__Theory__: In homogeneous translucent substances the light absorption depends upon the nature of the chromophoric solute, the concentration of solute, and the thickness of the liquid-absorbing layer. If a layer of 1-cm. thickness transmits a fraction t of the incident light, a thickness x of the material will transmit the fraction t^x, and the intensity of light transmitted will be $I = I_0 t^x$, where I_0 is the incident intensity. This may be written $I = I_0 e^{-kx}$, where k, the absorption coefficient, equals $(\log_e (I_0/I))/x$. In many cases the absorption coefficient of a solution is proportional to the concentration of the solute. Then the absorption coefficient may be written $k = k_o c$, where c is the concentration and k_o is the absorption coefficient for unit concentration. The transmittance is then given by the equation $T = I/I_o = e^{-k_o c x}$, in which form it is known as Beer's law. Using values of the transmittance obtained as described above, the absorption coefficient k was calculated from the equation: $k = (\log_e(1/T))/x$, with T expressed as a fraction (25 per cent $\cong$ 0.25), and where x is the thickness of the liquid layer of the cell in centimeters. The actual measured thickness of the cell was 0.524 centimeter.

Color is measured as the spectral transmittance, i.e., the percentage of transmittance of monochromatic light over the wavelength range from 400 to 700 millimicrons. Practically, however, the transmittance values are converted to absorption coefficients, and the absorption spectrum is used because of the direct proportionality of absorption coefficients to concentration of chromophoric substance in solution. The absorption spectrum is obtained by plotting k against wavelength in millimicrons.

With a solution conforming to Beer's law, concentration changes may be calculated from the absorption coefficients. When two or more substances are in solution, the monochromatic absorption coefficient is the sum of the several individual absorption coefficients. In complex solutions, such as sulfite liquor, the relation of absorption coefficients to concentration of chromophoric material is an analytical tool.

Another useful treatment of absorption spectra is the plotting of log $\underline{k}$ against wavelength in millimicrons. A series of dilutions of a solution obeying Beer's law will give on such a graph a family of curves of exactly similar shape which may be made to fit each other by translational shifts. This "parallelism" makes possible the identification or differentiation of colored substances at various concentrations.

b. Chemical analyses. The total and combined sulfur dioxide content of fresh sulfite liquors was determined by the method of Palmrose (106). The total sulfur dioxide in the liquor during the course of the cook was also obtained by the Palmrose method, but no attempt was made to determine the combined sulfur dioxide after the start of the digestion. All pH measurements were made with the Cameron glass electrode pH meter. The procedures of Partansky and Benson (75) were used for the determination of total solids, ash, lime, oxygen consumed (from alkaline permanganate), and furfural.

The lignosulfonic acid content was determined by precipitation with a solution of benzidine hydrochloride, rather than the beta-naphthylamine hydrochloride used by Partansky and Benson. The benzidine solution was prepared according to Rassow and Kraft (61). The ideal agent for use in this connection would effect quantitative separation of lignin and carbohydrates in the liquor by forming an easily removable precipitate with the lignin compounds present in the liquor. There is no ideal agent, and benzidine hydrochloride was chosen as the most suitable. Metallic salts, such as lead acetate, precipitate carbohydrate and caramel material as well as lignin, and the precipitates are difficult to handle. Organic compounds, such as Fuchsine, quinoline, alpha- and beta-naphthylamine, and benzidine, do not effect quantitative removal of lignin, but the precipitation products can be filtered, and sugars are left in solution, except for a small fraction which may be entrained mechanically or adsorbed on the bulky precipitate. Benzidine hydrochloride has a further disadvantage in that inorganic sulfites and sulfates are precipitated completely with the lignin compounds. However, the sulfates were assumed to be present only in negligible quantity, and the sulfites were removed as completely as possible by addition of hydrochloric acid and vacuum evaporation before precipitation.

The exact mechanism of the precipitation of calcium lignosulfonate by amine hydrochlorides is still unknown. Reference is again made to the pioneering work of Klason (31, 32) in which the formation of a yellow cyclic salt of alpha-lignosulfonate with beta-naphthylamine was taken as proof of the existence of an aldehyde group in the lignin compound, because aldehydes condense with the amine but ketones do not. A white precipitate was first obtained which changed to yellow on heating gently. After two days of heating glucose with beta-naphthylamine hydrochloride, he (32) obtained a slight precipitate resembling peat. The compound could not be acetylated or methylated, and it decomposed on heating. There is no evidence to show that the presence of the amine was necessary to obtain this product. Arabinose and xylose gave similar products, which are probably analogous to those obtained by several investigators (49, 50, 102, 104, 105), by heating sugars with acid alone. Hintikka (107) disagreed with Klason's theory and suggested that the lignosulfonic acid, which "may contain an aldehyde group (?)," forms a kind of Schiff's base, $HO_3S.R.CH:N.C_{10}H_7$, with beta-naphthylamine in acid solution. Later (108) he stated that the precipitation product was a simple salt. Dorée and Hall (109) agreed with the simple salt theory because of the decomposition of the precipitate by alkalies and by pyridine to liberate beta-naphthylamine. Hägglund (29) thought that the precipitation of calcium lignosulfonic acid by salts, aromatic amines, and alkaloids is essentially a salting out, with the amount salted out depending mainly on cooking conditions; 90 per cent was precipitated by beta-naphthylamine from a cook with sulfurous acid containing no base. Dorée and Hall precipitated 96 per cent of the total lignin from the same type of liquor.

The latest and best work on the amine precipitations is that of Nippe (110). He prepared three homogeneous products from sulfite liquors by consecutive precipitation with sodium chloride, alpha-naphthylamine in sulfurous acid, and benzidine hydrochloride. The homogeneity of the three products was determined by (a) carbon, hydrogen, methoxyl, hydroxyl, sulfur, and sodium content, (b) the stoichiometrical relationships of their toluenesulfonates and phenolates, and (c) the constancy of acid composition, from different liquors. This did not hold true for dark, highly heated liquors in which decomposition and cleavage of methoxyl had started. The precipitates with the amines were purely salt-like with no evidence of cyclic union or condensation. The alpha-naphthylamine saturated only one of the three firmly held sulfonic acid groups on the lignin acid, but benzidine saturated all three. The benzidine salts are yellow green in alkali and red in acid solution; this color change pointed to enolate formation. Hippe (54) based his control method for sulfite cooking on the empirical finding that one "mole" of lignosulfonic acid (molecular weight 485) containing firmly bound sulfonic acid groups is capable of taking up approximately four moles of benzidine.

The conclusions of Hippe concerning the homogeneity of the precipitation products of amines with lignosulfonic acids agreed with the previous work of Klason (111) and Dorée and Hall (109), demonstrating constancy of composition by elemental analysis of the precipitates.

The precipitation procedure adopted for this investigation was as follows:

Twenty-five cubic centimeters of liquor were pipetted into a 125-cc. suction flask, and suction was applied carefully to avoid loss by foaming. The flask was warmed gently until all free sulfur dioxide had been removed; 5 cc. of dilute hydrochloric acid (1:5) were then added; and suction was applied again, warming to about 35° C. on the water bath. This procedure removed all sulfites. The solution was transferred quantitatively to a 100-cc. beaker, using as little wash water as possible. The final volume should not exceed 25 cc., provided the vacuum evaporation period is long enough.

Twenty-five cubic centimeters of benzidine hydrochloride (40 grams per liter) were added, and the mixture was placed on a water bath just long enough (about fifteen minutes) to coagulate the precipitate into a red, sticky mass resembling chewing gum. The precipitate became very brittle on cooling, and after pulverizing with a stirring rod it was filtered on a weighed 1 G 3 Jena fritted glass crucible. Occasionally the filtrate had to be refiltered through the cake formed, in order to clarify it. The precipitate was washed with 50 cc. of distilled water, in small portions, air-dried for twenty-four hours, dried at 105° C. for three hours, and weighed. The fresh precipitate was slightly soluble in water, and only enough water was used to wash it free from acid.

The filtrate contains the unprecipitated lignin, the carbohydrates, some of the coloring matter of the original liquor, and the excess benzidine. The benzidine was precipitated by addition of 5 cc. of 4 per cent sulfuric acid and removed by filtering. Acid precipitation was used in preference to the alkaline procedure of Partansky and Benson, which gives a very difficultly filterable, flocculent precipitate.

The filtrate containing the sugars was diluted to 250 cc. in a volumetric flask (1:10 on the original liquor), and 25-cc samples were taken for the reducing sugars procedure of Partansky and Benson (78). The cuprous oxide was determined by reduction of the ferric sulfate solution and titration of the latter with potassium permanganate.

The methoxyl content of dried total solids and of the benzidine precipitate was determined by Institute Method 18, a modification of the Zeisel procedure.

Sugars do not form a precipitate with benzidine hydrochloride. Glucose, mannose, galactose, levulose, arabinose, xylose, cellobiose, and sucrose were subjected to the above procedure, and the heating was prolonged until the sugars burned, but no precipitate formed. Sulfurous acid, the bisulfite cooking liquors, inorganic sulfites, and colloidal sulfur do not reduce Fehling's solution in the procedure used here. Glucose solutions in fresh sulfite liquor were subjected to the benzidine precipitation procedure, and the glucose was recovered quantitatively. The sugar adsorbed on the two precipitates formed was negligible.

3. The Course of the Sulfite Cook

Four cooks were made on spruce, using the standard conditions as outlined. The first was purely exploratory in nature, and the succeeding cooks were made in order to extend the preliminary data obtained. The four cooks were not identical; there were slight variations in weight of wood charged and in volume of liquor added and withdrawn, which affected the absolute values obtained in the liquor analyses but which in no way affect the validity of the results.

a. Cook 1. Cook 1 was made on 5800 grams of chips (oven-dry equivalent) containing 39.9 per cent moisture, with 26 liters of acid. The transmittance curves are shown in Figure 1, and the curves of log k against wavelength are given in Figure 2. The values of the absorption coefficients (k), at 20 mm intervals are given in Table XXIX in the appendix. Table III gives the results of the chemical analyses, which are graphically presented in Figure 3.

The course of the cook as shown by the above optical and chemical analyses is as follows:

The spectral transmittance decreased steadily with time, showing a steady increase in concentration of coloring material in solution which, however, increased very rapidly near the end of the cook. This steady increase was not true for all wavelengths. It may be seen from Figure 2 that there was a slight reversion from three to six and one-half hours, in the region from 480 to 700 millimicrons. Color formed at three hours (110° C.) was evidently destroyed during the next two or three, but with increasing temperature the color again increased.

The character of the color (hue) showed a gradual change, as may be seen in Figure 2. The log k curves have a marked curvature for early liquor samples and gradually become practically straight lines as the cook progresses.

The results of the chemical analyses show that the concentration of coloring material is not being measured by determination of such constituents as total solids, ash, lignin, sugar and furfural. The rate of increase of concentration of these constituents in the

Figure 1

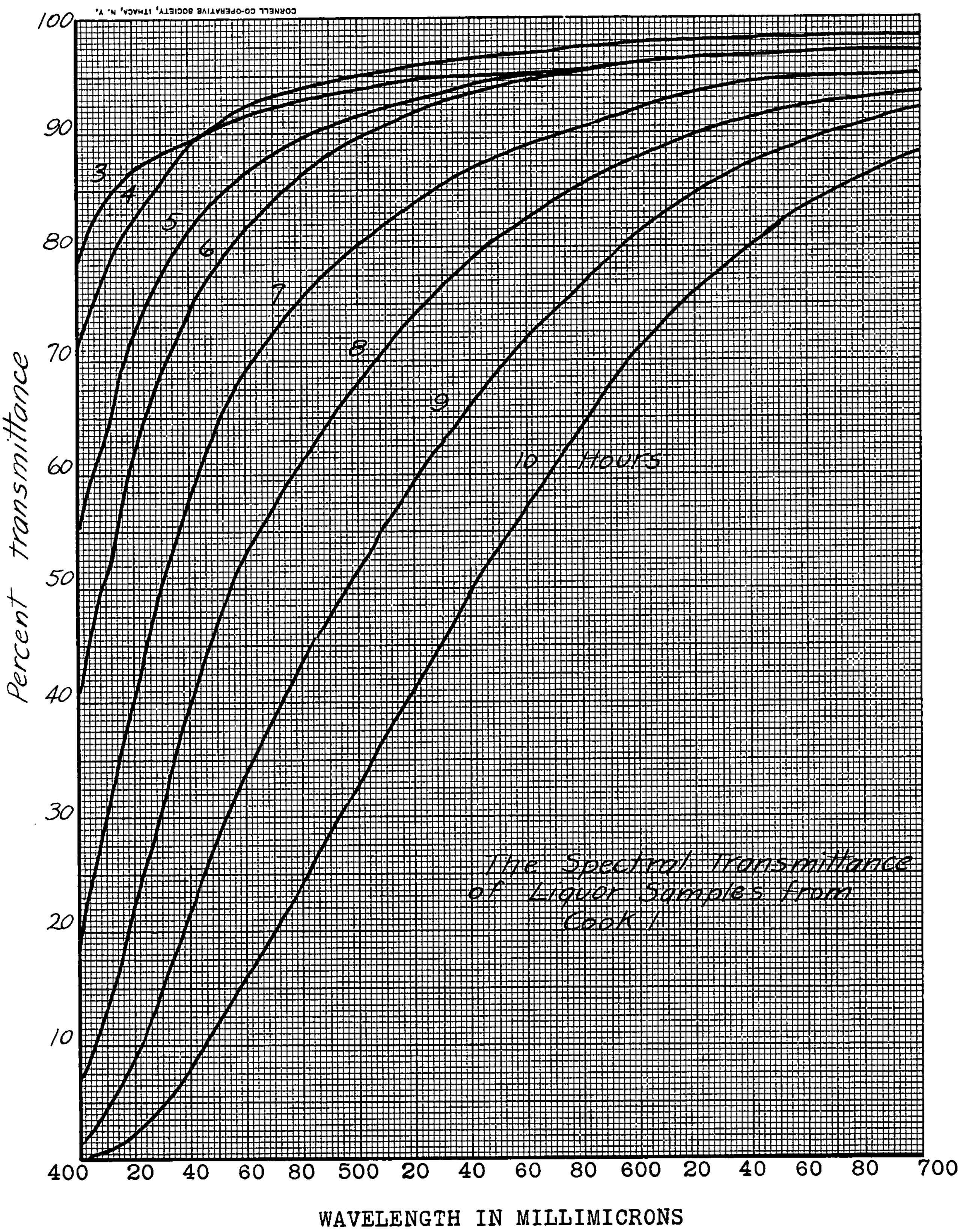

CORNELL CO-OPERATIVE SOCIETY, ITHACA, N. Y.
100
90
80
70
60
50
40
30
20
10
Percent transmittance
3
4
5
6
7
8
9
10 Hours
The Spectral Transmittance
of Liquor Samples from
Cook I
400
20
40
60
80
500
20
40
60
80
600
20
40
60
80
700
WAVELENGTH IN MILLIMICRONS

Figure 2

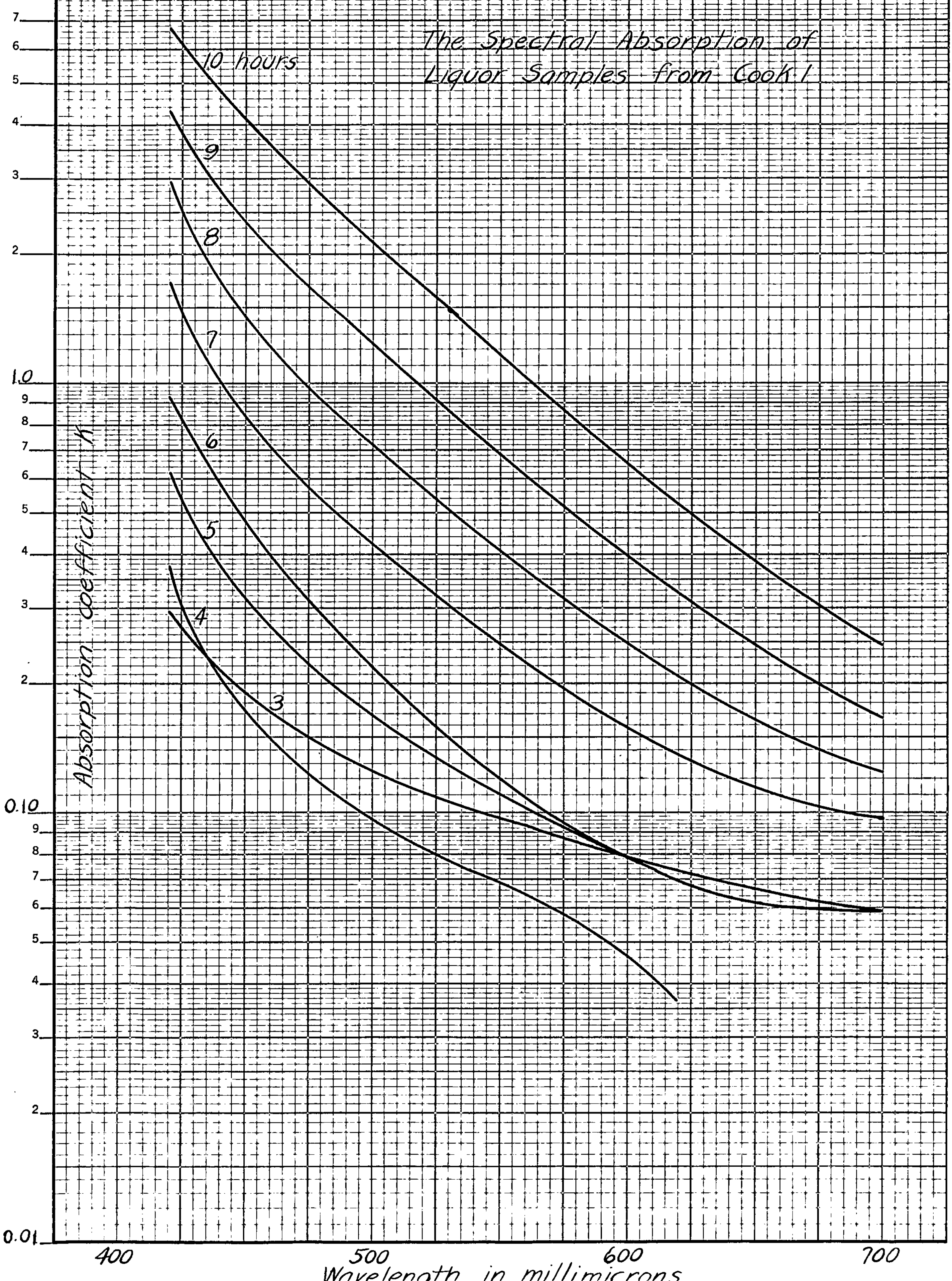

The Spectral Absorption of
Liquor Samples from Cook I
10 hours
9
8
7
6
5
4
3
Absorption coefficient K
10.0
9
8
7
6
5
4
3
2
1.0
9
8
7
6
5
4
3
2
0.10
9
8
7
6
5
4
3
2
0.01
400
500
600
700
Wavelength in millimicrons

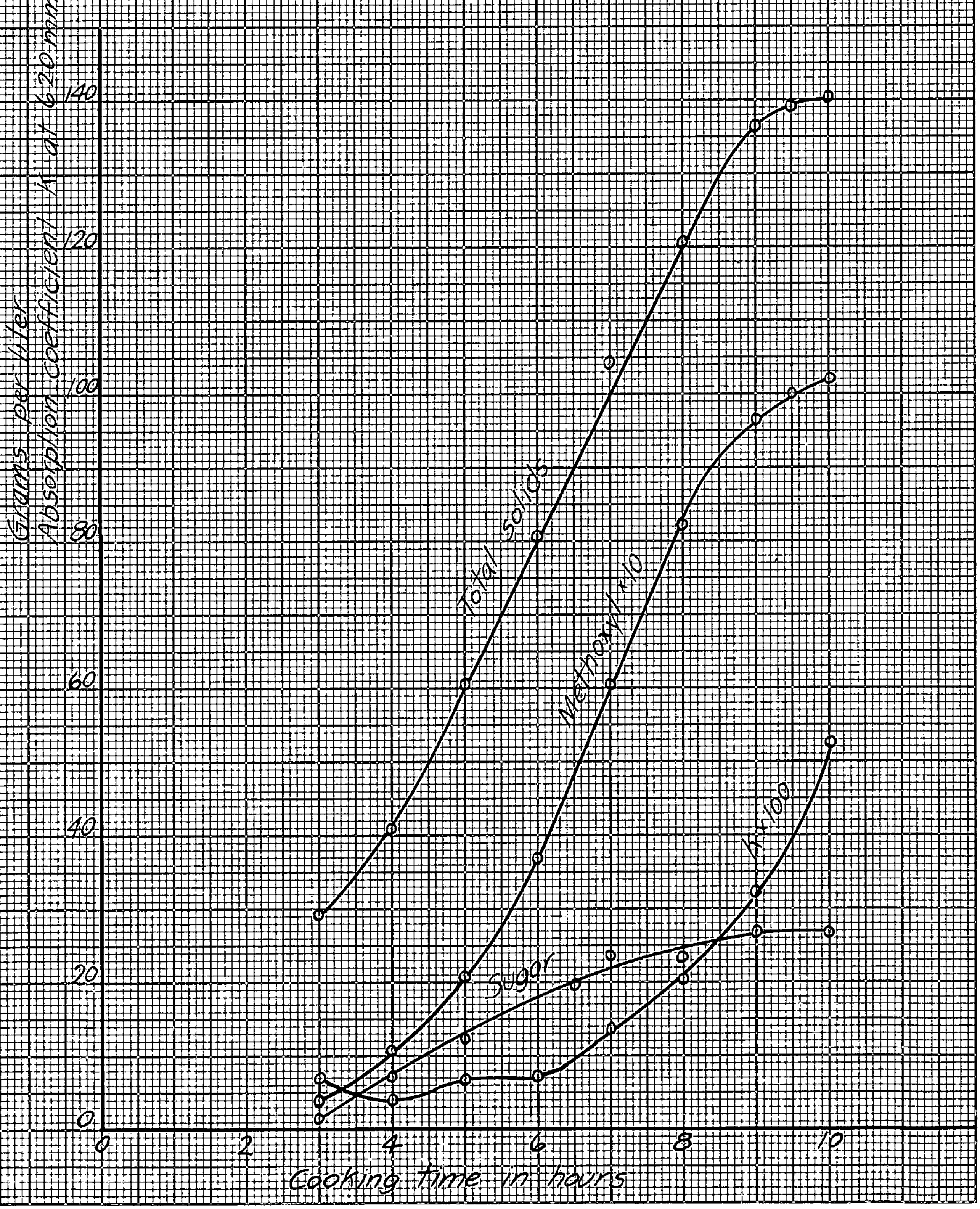
TABLE III

ANALYSES OF LIQUOR SAMPLES FROM COOK 1

Cooking Time hr.	Total Solids	Ash	Organic by Ignition	CaO	Oxygen Consumed	Methoxyl on Total Solids	Benzidine Precipitate	Reducing Sugar as Glucose	Furfural	k at 620 mμ
				All concentrations in grams per liter						
3	29.1	20.4	8.7	—	10.5	0.40	0.3	1.4	—	0.070
3.5	32.9	19.9	13.0	—	11.8	0.68	0.6	4.6	—	.056
4	40.8	19.6	21.2	—	18.4	1.07	1.6	7.0	—	.036
4.5	48.4	18.1	30.3	—	23.0	1.73	3.5	14.4	—	.036
5	60.3	18.8	41.5	7.3	35.6	2.08	7.3	12.2	—	.068
5.5	73.3	18.9	54.4	7.6	45.4	2.59	10.3	26.4	—	.059
6	80.8	18.8	62.0	7.3	64.5	3.69	15.6	—	—	.070
6.5	91.9	19.1	72.8	—	65.3	4.85	30.7	19.4	—	.086
7	104.3	19.7	84.6	7.6	74.7	6.05	45.7	23.6	—	.135
7.5	113.3	19.8	93.5	7.2	81.0	7.15	—	—	—	.147
8	120.8	19.4	101.4	8.5	93.5	8.22	66.2	23.1	—	.201
8.5	130.3	17.5	112.8	8.4	95.7	9.20	72.3	26.6	0.34	.267
9	136.6	17.9	118.7	8.6	97.4	9.67	78.0	26.6	0.38	.320
9.5	139.2	19.7	119.5	8.6	120.0	10.0	78.7	27.9	0.49	.422
10	140.6	17.0	123.6	8.2	117.9	10.2	80.9	26.6	0.49	.524

Figure 3

The Concentration of Chemical Components and Coloring Matter in the Liquor Samples from Cook 1



liquor is entirely different from that of the concentration of the coloring matter, as measured by the absorption coefficient k and as illustrated by Figure 3. The concentration of the major constituents approaches a maximum at nine to ten hours, whereas the rate of increase of coloring material concentration is very fast at this stage. Inasmuch as the color must result from some of these major constituents, the assumption may be made that lignin or sugar or both, in a small quantity, are degrading to form highly colored material.

Several changes in procedure and deletions of analyses were made on the basis of the above discussion. The determinations of ash and calcium oxide content were discarded as irrelevant to the color problem. The determination of oxygen consumed from alkaline permanganate was eliminated because it is a comparatively unsatisfactory procedure, and the results parallel the total solids data. The furfural determination was discarded from a consideration of the liquor constituents and the analytical procedure. The correct determination of furfural in waste sulfite liquor is difficult because the pentoses and acid in the boiling mixture produce additional furfural during the distillation.

b. Cook 2. Cook 2 was made on 6600 grams of chips (oven-dry equivalent) containing 39.9 per cent moisture, with 26 liters of liquor. This cook was carried to twelve hours, thus deliberately burning the charge. The blow down was started at the eleventh hour instead of the ninth. The spectral transmittance curves and the log *k* curves are presented in Figures 4 and 5, respectively. The course of the cook is represented by the curves given in Figure 6, which are based on the analytical data found in Table IV. The absorption coefficients are given in Table XXX in the appendix.

Several of the trends observed for Cook 1 were confirmed by this cook. The change in character of the color taking place from six to nine hours is particularly well illustrated in Figure 5. The slight reversion of color in the red end of the spectrum is again observed. The concentration of coloring matter increased very rapidly but smoothly from nine to twelve hours, with no sudden darkening in a few minutes, as has been reported. The concentrations of sugar and lignin remained constant for a period during which the concentration of the coloring material increased eightfold.

Further analyses indicated that the hydrogen-ion concentration in the liquor increased steadily and smoothly to a maximum, whereas the total sulfur dioxide concentration decreased steadily to almost zero. A study of the benzidine precipitate showed that, in the range of liquor samples from eight and one-half to twelve hours, the composition of the precipitate was constant as indicated by the methoxyl content and that 75 per cent of the total methoxyl content was being precipitated by the benzidine procedure.

c. Cook 3. Cook 3 was made on 6600 grams of chips (oven-dry equivalent) containing 39.9 per cent moisture, with 24 liters of

Figure 4

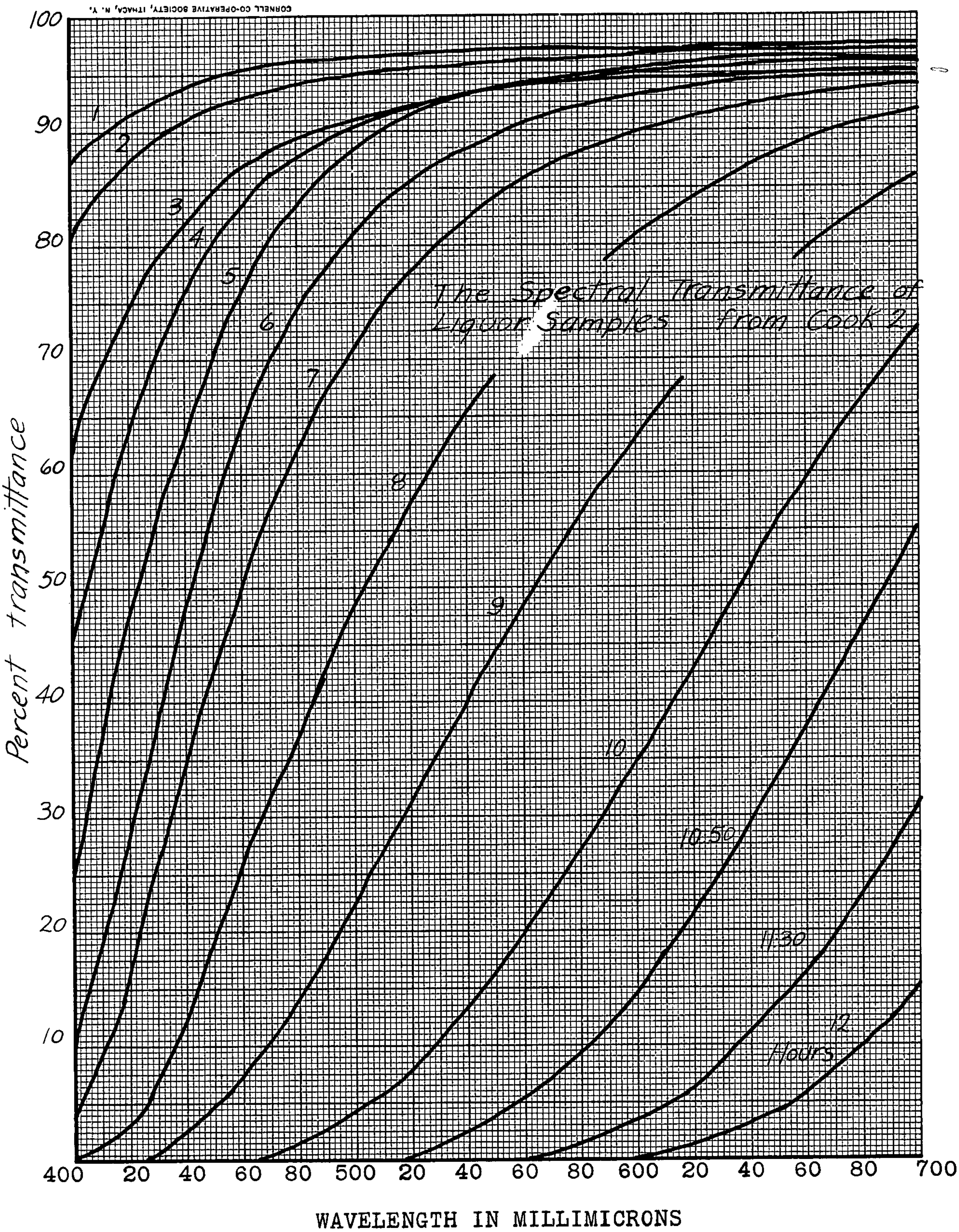

CORNELL CO-OPERATIVE SOCIETY, ITHACA, N. Y.
The Spectral Transmittance of Liquor Samples from Cook 2
Percent transmittance
100
90
80
70
60
50
40
30
20
10
1
2
3
4
5
6
7
8
9
10
10:50
11:30
12 Hours
400
20
40
60
80
500
20
40
60
80
600
20
40
60
80
700
WAVELENGTH IN MILLIMICRONS

Figure 5

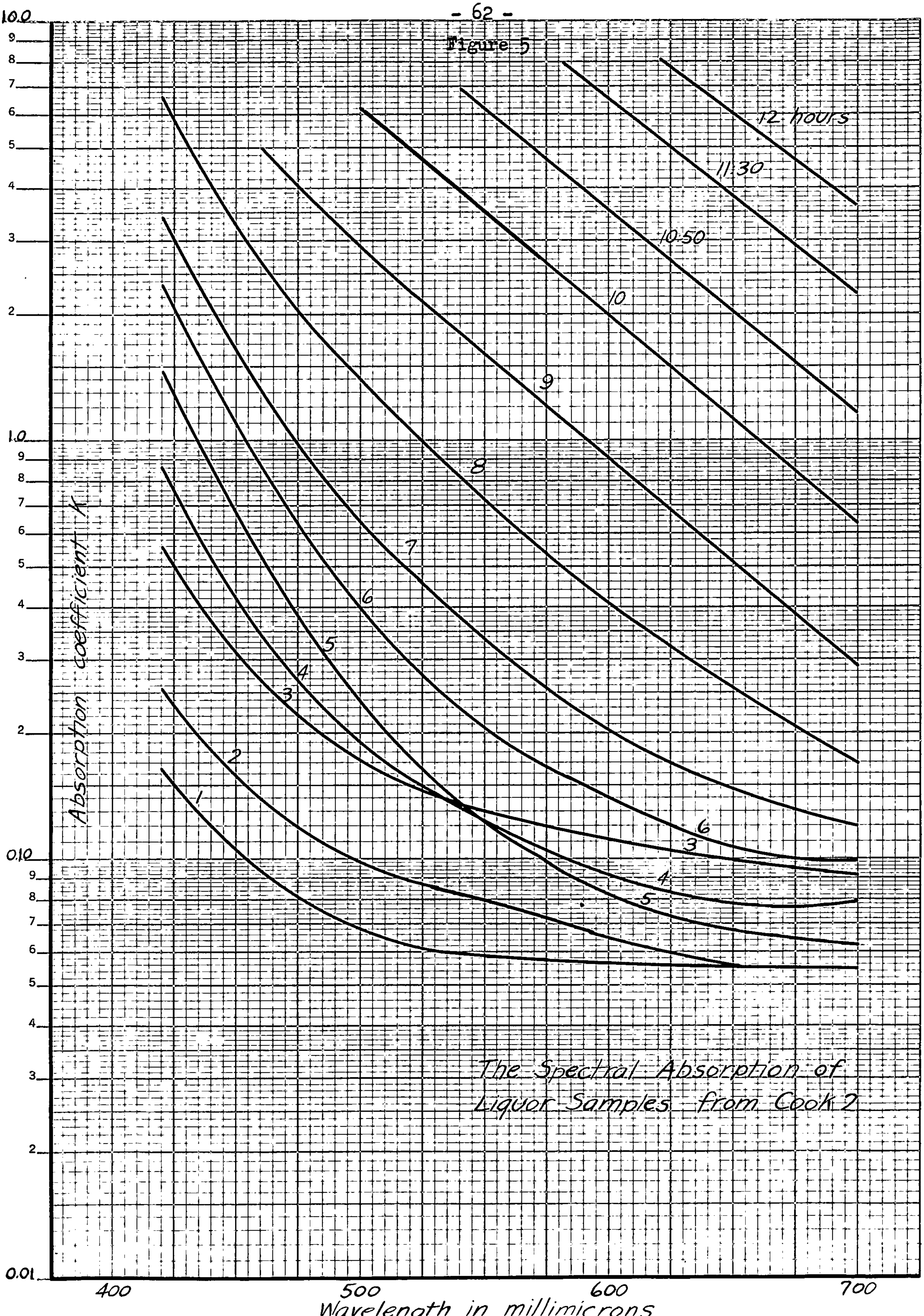
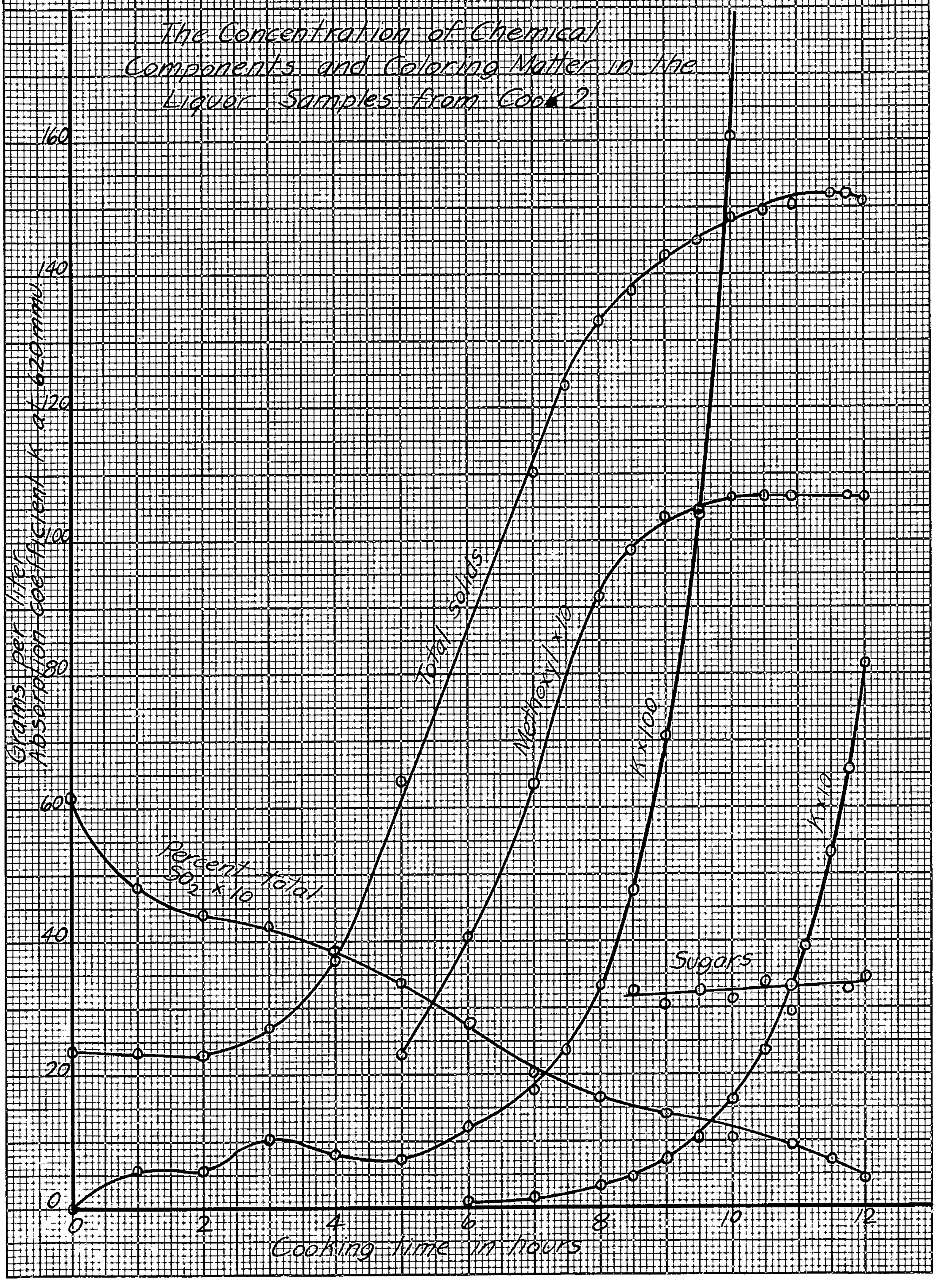

10.0
9
8
7
6
5
4
3
2
1.0
0.10
0.01
Absorption coefficient K
400
500
600
700
Wavelength in millimicrons
12 hours
11:30
10:50
10
9
8
7
6
5
4
3
2
1
The Spectral Absorption of Liquor Samples from Cook 2

TABLE IV

ANALYSES OF LIQUOR SAMPLES FROM COOK 2

Cooking Time hr.	pH	Total SO_2 %	Total Solids	Methoxyl from Solids	Benzidine Precipitate	Reducing Sugar as Glucose	Methoxyl on Benzidine Precipitate %	Methoxyl from Benzidine Precipitate	Methoxyl Precipitated by Benzidine %	k at 620 mμ
All concentrations in grams per liter										
0	1.61	6.22	23.6	——	——	——	——	——	——	0.0
1	1.62	4.84	23.5	——	——	——	——	——	——	.059
2	1.60	4.45	23.1	——	——	——	——	——	——	.059
3	1.61	4.27	27.2	——	——	——	——	——	——	.106
4	1.52	3.89	37.7	——	——	——	——	——	——	.084
5	1.55	3.39	64.3	2.34	——	——	——	——	——	.073
6	1.36	2.78	86.3	4.06	——	——	——	——	——	.122
7	1.30	2.05	110.7	6.38	——	——	——	——	——	.175
7.5	1.20	1.94	123.6	8.04	——	——	——	——	——	.228
8	1.20	1.67	133.5	9.20	——	——	——	——	——	.332
8.5	1.15	1.58	137.9	9.88	68.5	32.6	10.8	7.41	75.0	.478
9	1.10	1.43	143.3	10.4	75.3	30.6	10.4	7.83	75.0	.710
9.5	1.03	1.22	145.4	10.5	76.4	32.5	10.5	8.03	76.3	1.05
10	1.01	1.06	148.8	10.7	77.3	31.2	10.5	8.14	76.1	1.61
10.5	1.00	1.03	149.8	10.7	75.1	33.9	10.6	7.93	74.0	2.36
10.83	1.00	0.98	150.4	10.7	77.5	33.1	10.3	7.68	72.1	2.94
11.17	1.00	0.88	150.4	10.6	74.6	——	10.6	7.88	74.5	3.91
11.5	1.00	0.77	152.4	10.6	80.3	39.2	10.1	8.12	76.5	5.35
11.75	1.00	0.68	152.6	10.7	77.0	32.7	10.5	8.08	75.6	6.58
12	1.00	0.42	151.4	10.6	77.7	34.5	10.2	7.90	74.3	8.16

Figure 6

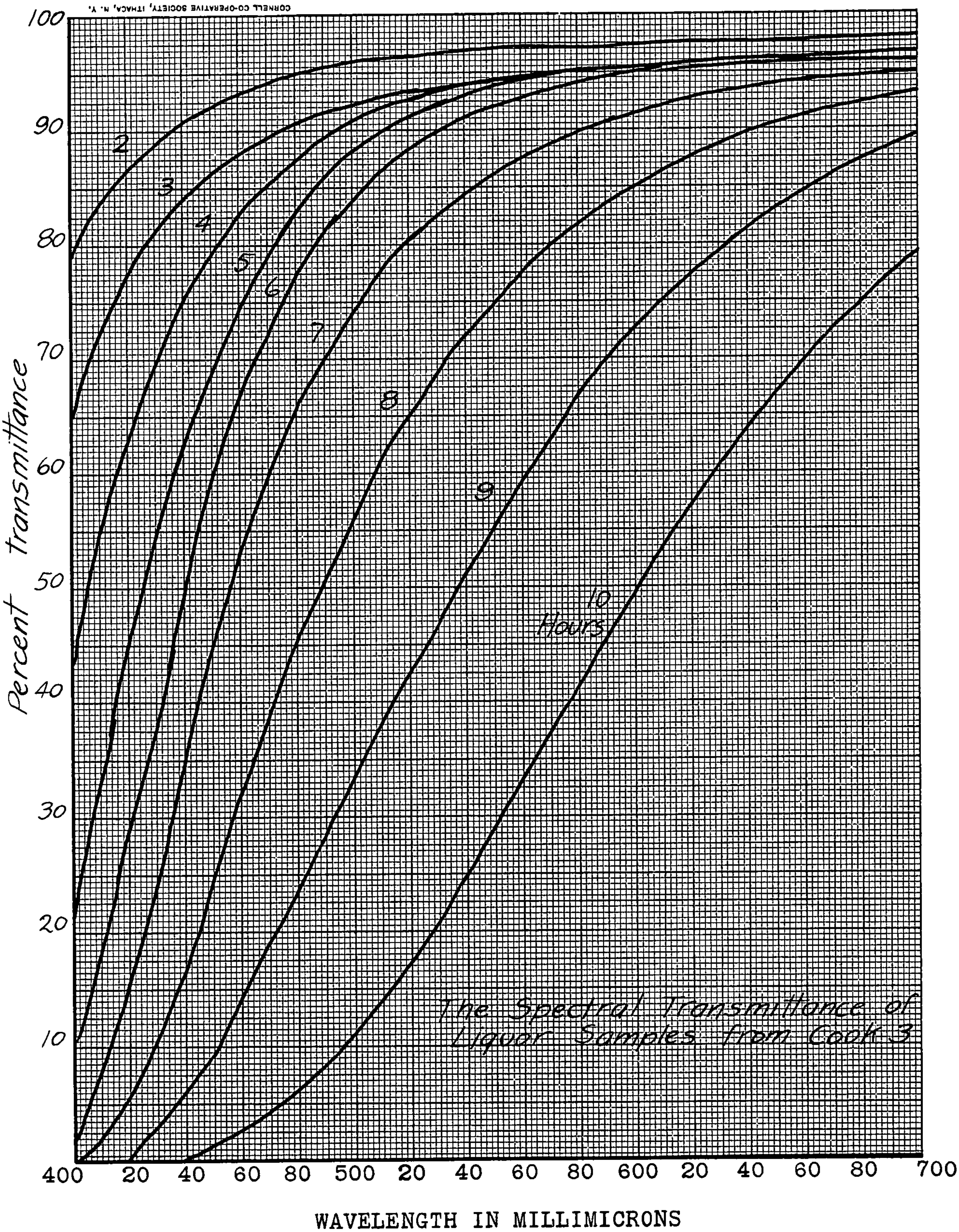

The Concentration of Chemical Components and Coloring Matter in the Liquor Samples from Cook 2
160
140
120
100
80
60
40
20
0
Grams per liter
Absorption coefficient k at 620mmu
Total solids
Methoxyl x10
K x 100
K x 10
Percent total SO_2 x 10
Sugars
0
2
4
6
8
10
12
Cooking Time in hours

acid. The spectral transmittance curves are given in Figure 7 and the curves of log k in Figure 8. The values of the absorption coefficients are in Table XXXI (Appendix). The results of the chemical analyses are given in Table V and Figure 9.

The results confirm and amplify these obtained with the previous cooks. The steady increase of color, the slight reversion, and the change of hue are all shown in Figure 8. The chemical analyses were extended to the early samples, and Figure 9 illustrates again the gradual, almost linear rise of the concentration of the major constituents of the liquor to a maximum value, in contrast to the high rate of increase of concentration of coloring material.

The mechanism of the benzidine precipitation was further investigated. The liquors were prepared for precipitation by heating in the water bath, without addition of hydrochloric acid as had been the standard procedure. The earlier benzidine precipitates were very light in color, indicating a high inorganic sulfite content. These early precipitates also had very low methoxyl contents, with the expected constant composition being reached at seven hours. The omission of the acid treatment, however, increased the percentage of total methoxyl content which can be precipitated by benzidine to a maximum of about 79 per cent after eight and one-half hours. The precipitations on earlier liquor samples were relatively ineffective in removing lignin as measured by the methoxyl content, the percentage precipitated increasing as the cook progressed.

Figure 7


CORNELL CO-OPERATIVE SOCIETY, ITHACA, N. Y.
Percent transmittance
100
90
80
70
60
50
40
30
20
10
2
3
4
5
6
7
8
9
10
Hours
The Spectral Transmittance of
Liquor Samples from Cook 3
400
20
40
60
80
500
20
40
60
80
600
20
40
60
80
700
WAVELENGTH IN MILLIMICRONS

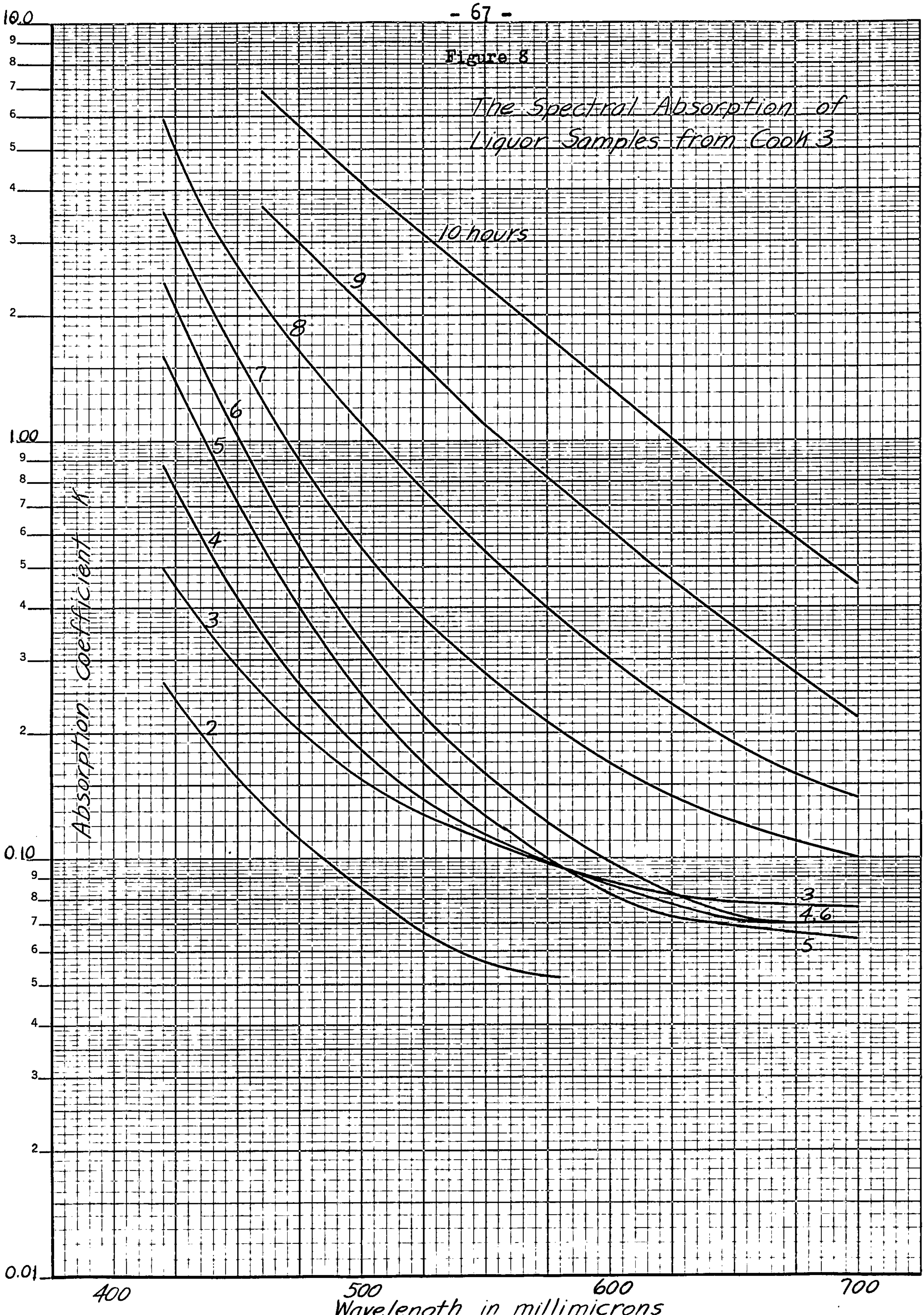


Figure 8
The Spectral Absorption of
Liquor Samples from Cook 3
10 hours
9
8
7
6
5
4
3
2
3
4.6
5
Absorption Coefficient K
10.0
1.00
0.10
0.01
400
500
600
700
Wavelength in millimicrons

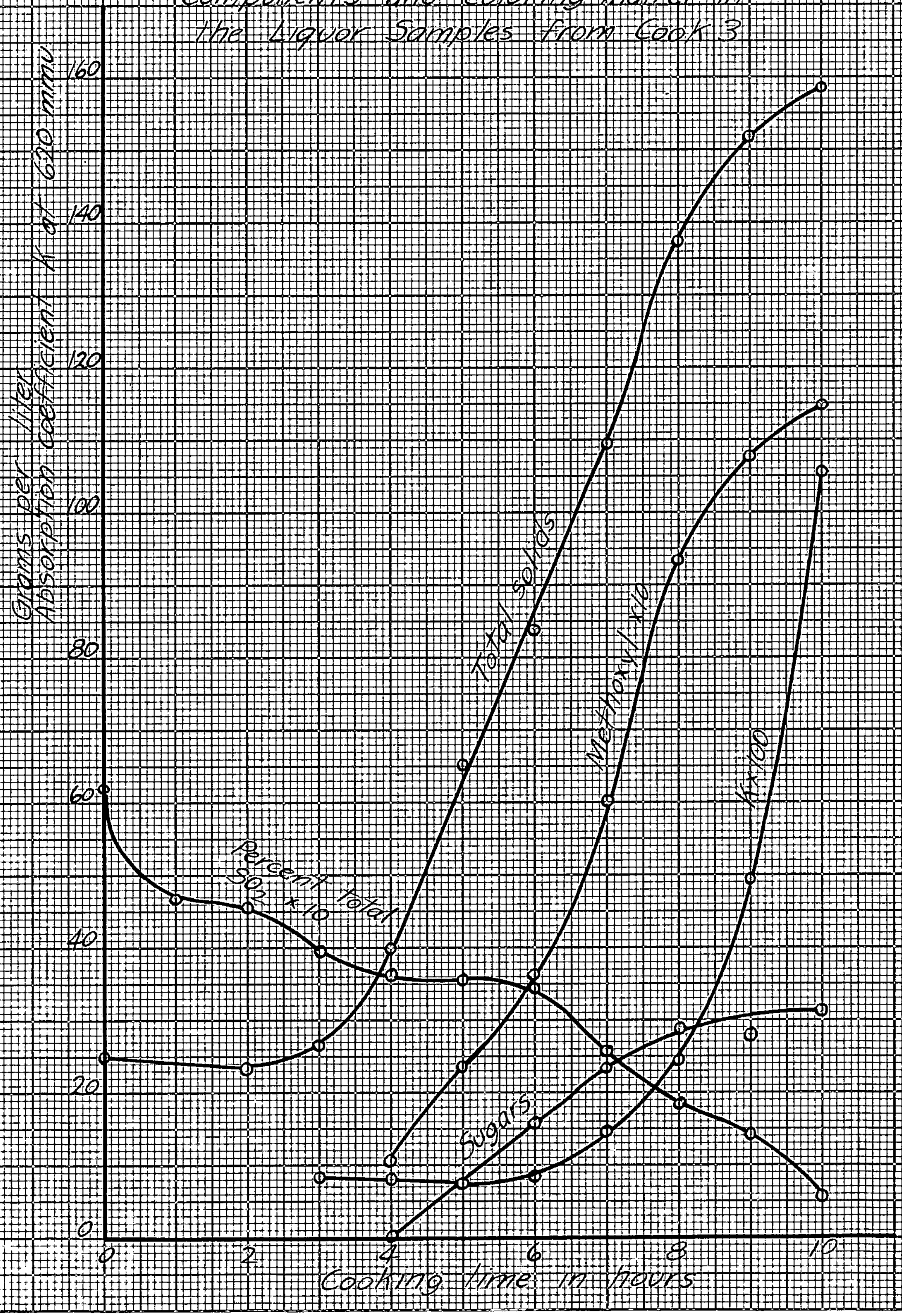
TABLE V

ANALYSES OF LIQUOR SAMPLES FROM COOK 3

Cooking Time hr.	pH	Total SO_2 %	Total Solids	Methoxyl from Solids	Benzidine Precipitate	Reducing Sugar as Glucose	Methoxyl on Benzidine Precipitate %	Methoxyl from Benzidine Precipitate	Methoxyl Precipitated by Benzidine %	k at 620 mμ
			All concentrations in grams per liter							
0	1.60	6.20	25.0	——	——	——	——	——	——	——
1	1.61	4.67	——	——	——	——	——	——	——	——
2	1.56	4.58	23.6	——	——	——	——	——	——	——
3	1.60	3.98	26.2	——	——	——	——	——	——	0.084
4	1.51	3.65	40.0	1.08	12.7	0.2	2.89	0.37	34.2	.086
5	1.45	3.56	65.2	2.38	12.4	——	6.14	0.76	31.9	.074
6	1.41	3.43	84.0	3.62	18.5	15.7	[illegible]	1.57	43.3	.086
7	1.40	2.55	109.7	6.03	36.6	23.5	10.2	3.75	62.2	.147
7.5	1.25	1.96	119.7	7.61	52.4	25.8	10.4	5.43	71.3	.199
8	1.11	1.84	137.7	9.35	67.7	28.7	10.5	7.11	76.1	.245
8.5	1.15	1.50	141.4	10.3	76.5	30.8	10.6	8.07	78.8	.356
9	1.10	1.41	152.2	10.8	82.0	27.8	10.5	8.57	79.2	.493
9.5	1.10	1.13	151.8	11.1	83.2	30.0	10.6	8.85	79.8	.708
10	1.16	0.56	159.0	11.5	87.1	31.4	10.5	9.15	79.3	1.07

Figure 9

The Concentration of Chemical Components and Coloring Matter in the Liquor Samples from Cook 3



4. Correlation of Optical and Chemical Analyses

It had become increasingly obvious that the analyses for the likely chromophoric materials in sulfite liquor were not measuring the coloring matter, and the question arose as to whether or not it was possible to determine the concentration of coloring material by other than optical means.

In order to determine the relation between concentration of coloring matter and concentration of lignin, Figures 10 and 11 were prepared, correlating methoxyl content of total solids, which is the best measure of lignin content used here, with the absorption coefficient k for several wavelengths, for Cooks 2 and 3.

There is an apparent linear relationship between absorption coefficient over the entire wavelength range (above 580 not shown) and the lignin content of the liquor, as measured by the methoxyl content, from about 1 to 6 grams of methoxyl per liter. This range corresponds to a calcium lignosulfonate content of 7.3 to 44 grams per liter (assuming 13.6 per cent methoxyl in calcium lignosulfonate), over the period of four to seven hours, during which the temperature is increasing from 118° to 140° C.

The assumption may be made, in spite of a few minor objections, that in this range the color is due primarily to lignin, and that above this range, at 140° C., the great increase in concentration of coloring matter is due to the acid degradation of pentoses and hexoses at higher temperatures.

Figure 10

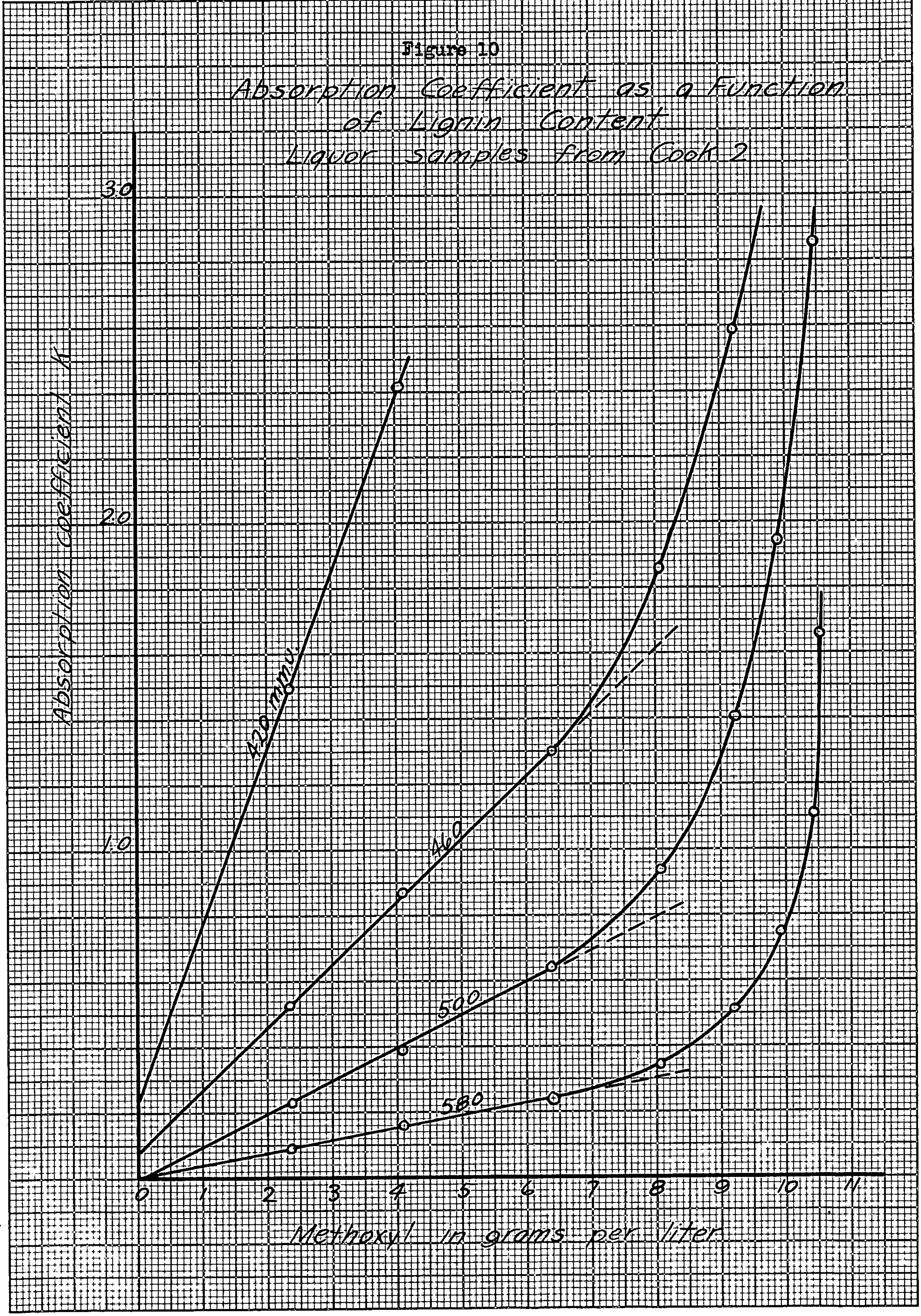

Absorption Coefficient as a Function
of Lignin Content
Liquor samples from Cook 2
Absorption coefficient K
3.0
2.0
1.0
420 mmu.
460
500
580
0
1
2
3
4
5
6
7
8
9
10
11
Methoxyl in grams per liter

Figure 11

MADE IN U. S. A.

One objection to the above assumption is that raised by the nonlinearity of the absorption coefficient-lignin relationship introduced by the reversion of color already noted, from three to seven hours, but which is confined to the red end of the spectrum. The cause of this reversion is not known, but it is probably caused by either sulfonation or reduction of certain of the water-soluble extractives in the wood, or it may be concerned with the mechanism of lignin sulfonation.

The other objection is that, since the rate of increase in concentration of lignin is paralleled by that of reducing sugars, it might be assumed that the sugar-absorption coefficient relationship will also be linear. When tested, this theory was found to be in error, although the sugar analyses did not cover the critical range very well. The major defect was the fact that with zero sugar in solution the liquor already possessed considerable coloring matter; the graphs on Figures 10 and 11 extrapolate back to zero lignin and absorption coefficient, but the sugar vs. k curves did not. The presence of sugar in solution does not necessarily mean that the conditions causing hydrolysis to simple pentose and hexose are causing degradation of the simple sugars to coloring matter. With the temperature, hydrogen-ion concentration, and time all comparatively low, it is believed that, up to seven hours in a normal spruce cook, no appreciable sugar degradation takes place. There is approximately two to four times as much known chromophoric calcium lignosulfonate in solution, over this range, as there is reducing sugar. The color of this calcium lignosulfonate is assumed to be that giving the typical curved characteristic noted on Figures 2, 5, and 8, up to seven hours. Degraded sugar is assumed to give the straight line absorption characteristic which masks the lignin curve in the last hours of the cook. However, evidence will be given later to show that some sugars when degraded with acid give a color which is very similar to that of the lignin compound.

Making the assumption that the absorption coefficient during the early stages of the cook is due to calcium lignosulfonate, (Figures 10 and 11), it was possible to calculate the absolute absorption coefficients of calcium lignosulfonate. These are given for Cooks 2 and 3 in Table VI.

TABLE VI

ABSORPTION COEFFICIENT k FOR CALCIUM LIGNOSULFONATE

	Wavelength - mmu							
Cook	420	460	500	540	580	620	660	700
2	5.84	1.98	0.99	0.57	0.37	0.34	0.26	0.20
3	6.50	1.98	0.88	0.55	0.32	0.30	0.24	0.20

The values correspond to a lignin concentration equivalent to 10 grams of methoxyl per liter.

These values give a characteristic curve when plotted on the log scale. Assuming that the total color is made up of lignin and degraded sugars, the absorption coefficients of the caramel alone are obtained by subtracting the lignin k from the total k. These values give the straight line degraded sugar characteristic.

5. Heating of Isolated Liquor

A correlation of liquor color with lignin content has been proposed for the 3- to 7-hour (110 to 140° C.) period of the cook. Up to the third hour the color is very slight and is negligible from the operating standpoint, although it may be connected with the first stages of lignin sulfonation. From seven hours to the end of the cook, the lignin color becomes increasingly unimportant as compared to the color of the products of sugar degradation, and no chemical analysis has been successful in determining this degraded component. The next experiment was an attempt to discover which of the components of the liquor were producing the color in this last part of the cook; this involved the heating of isolated liquor with no fiber present to act as a buffer. A supply of the 10-hour liquor from Cook 1 (which was 45 days old) was the only available material. Three hundred cubic centimeter portions were heated in a small stainless steel autoclave for two and six hours at 140° C., with one-half hour required to come up to temperature, and then analysed. The results are given in Table VII. The visual effect of aging is a slight darkening, with precipitation of white calcium sulfite. The disappearance of the sugar has not been satisfactorily explained. It is not fermented, since no microörganism was found by attempting culture on nutrient agar and in beef broth, and since the consensus of microbiological opinion is that no organism can grow at the low pH (1.0), in the presence of sulfurous acid, alcohols, furfural, and other toxic agents. The precipitate contained no sugar, and if compounds are formed, sugar with sugar, with calcium sulfite or with lignin, the linkage must be

TABLE VII

AUTOCLAVE HEATING OF 10-HOUR LIQUOR FROM COOK 1

Liquor Sample	Total Solids	Methoxyl from Solids	Benzidine Precipitate	Sugars as Glucose	Methoxyl on Benzidine Precipitate %	Methoxyl from Benzidine Precipitate (g.p.l.)	Methoxyl Precipitated by Benzidine %	k at 620 mm
All concentrations in grams per liter								
1. Original 10-hr. liquor	136.7	10.24	80.9	26.6	——	——	——	0.524
2. Same liquor 45 days old	118.5	8.51	60.6	7.14	10.5	6.36	74.8	.600
3. 2 hr. at 140° C.	116.2	8.40	58.9	1.0	10.5	6.14	73.1	1.70
4. 6 hr. at 140° C.	114.0	8.38	61.4	1.0	10.4	6.36	75.8	5.73

Percentage of Change with Treatment

Treatment	Total Solids Loss	Methoxyl Loss	Benzidine Precipitate Loss	Sugars Loss	k Increase
1. 45 days age	13.3	16.9	25.1	73.5	14.5
2. 2 hr. at 140° C.	1.9	1.3	2.8	86.0	184
3. 6 hr. at 140° C.	3.8	1.5	+1.3	86.0	855

very stable to withstand hydrolysis on further heating.

A study of Table VII demonstrates the great increase in coloring matter at the expense of small amounts of sugar or very small amounts of lignin. The lignin is more stable to both aging and heat than the sugar is. The test, however, was unsatisfactory, and Cook 4 was made to provide fresh liquor. Five thousand nine hundred and forty grams (oven-dry equivalent) of spruce chips containing 39.7 per cent moisture were cooked by standard schedule, using 25 liters of liquor. Liquor samples were drawn off at seven and ten hours, and reheated in the small 300-cc. autoclave. The results are given in Table VIII. The 7-hour liquor was heated at 140° C. for periods of one and one-half and three hours, the 10-hour liquor for three and six hours. The results are graphically presented in Figures 12 and 13.

The reheated liquors lost at least a part of their solids content by precipitation of inorganic calcium sulfite, and the heating produced the strong characteristic burned odor. The results of the reheating of 7-hour liquor indicated that some soluble polysaccharides were present. These hydrolysed to simple sugars, giving the maximum reducing sugar content after one and one-half hours of heating; then the sugars were degraded to form color with continued heating. The heating caused other liquor constituents, including some sugar, to precipitate with the lignin, resulting in a heavier benzidine precipitate with a lower methoxyl content. However, the total lignosulfonic acid precipitated remained constant. The total lignin in solution,

TABLE VIII

AUTOCLAVE HEATING OF LIQUORS FROM COOK 4

Sample	pH	Total Solids	Methoxyl from Solids	Benzidine Precipitate	Sugars as Glucose (benzidine)	Sugars from raw Liquor	Sugar not Precipitated %	Methoxyl of Benzidine Precipitate %	Methoxyl from Benzidine Precipitate (g.p.l.)	Methoxyl Precipitated by Benzidine %	k at 620 mμ
		All concentrations in grams per liter									
7-0	1.48	91.3	5.06	29.3	23.6	24.7	95.5	10.48	3.14	62.1	0.120
7-1.5	1.05	82.4	4.84	32.6	26.4	28.2	93.6	9.80	3.14	65.0	1.27
7-3	0.95	74.7	4.62	36.9	22.2	25.0	88.8	8.45	3.14	68.0	10.7
10-0	1.40	124.3	8.66	65.6	25.9	29.9	86.6	10.49	6.77	78.2	1.07
10-3	1.30	120.1	8.58	65.4	21.3	26.1	81.6	9.92	6.57	76.6	12.4
10-6	1.25	113.4	8.25	65.8	14.5	20.2	71.8	9.72	6.45	78.2	50.1

Absorption coefficients obtained by dilution of liquors when necessary.

Figure 12

The Effect of Heating of 7-hour Liquor Samples

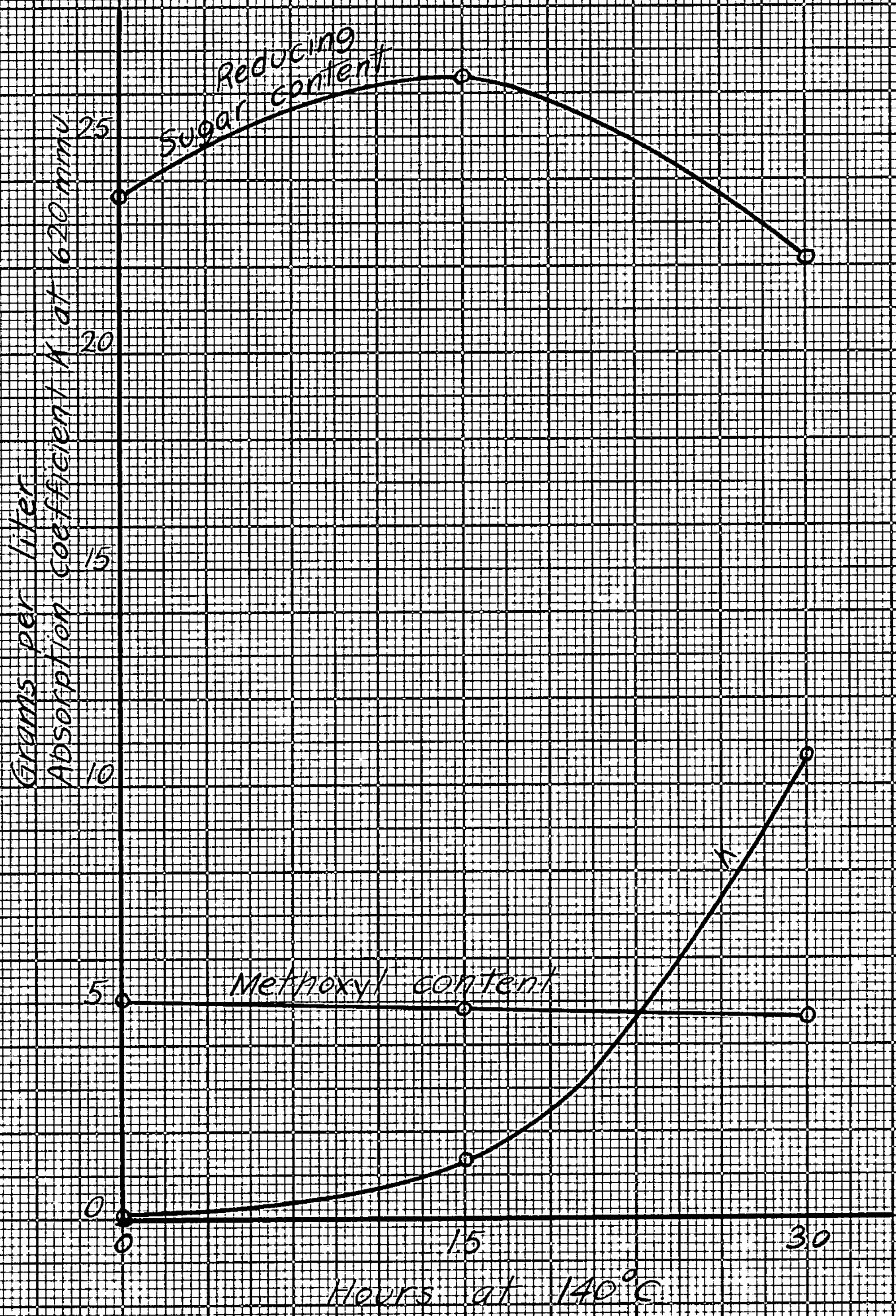
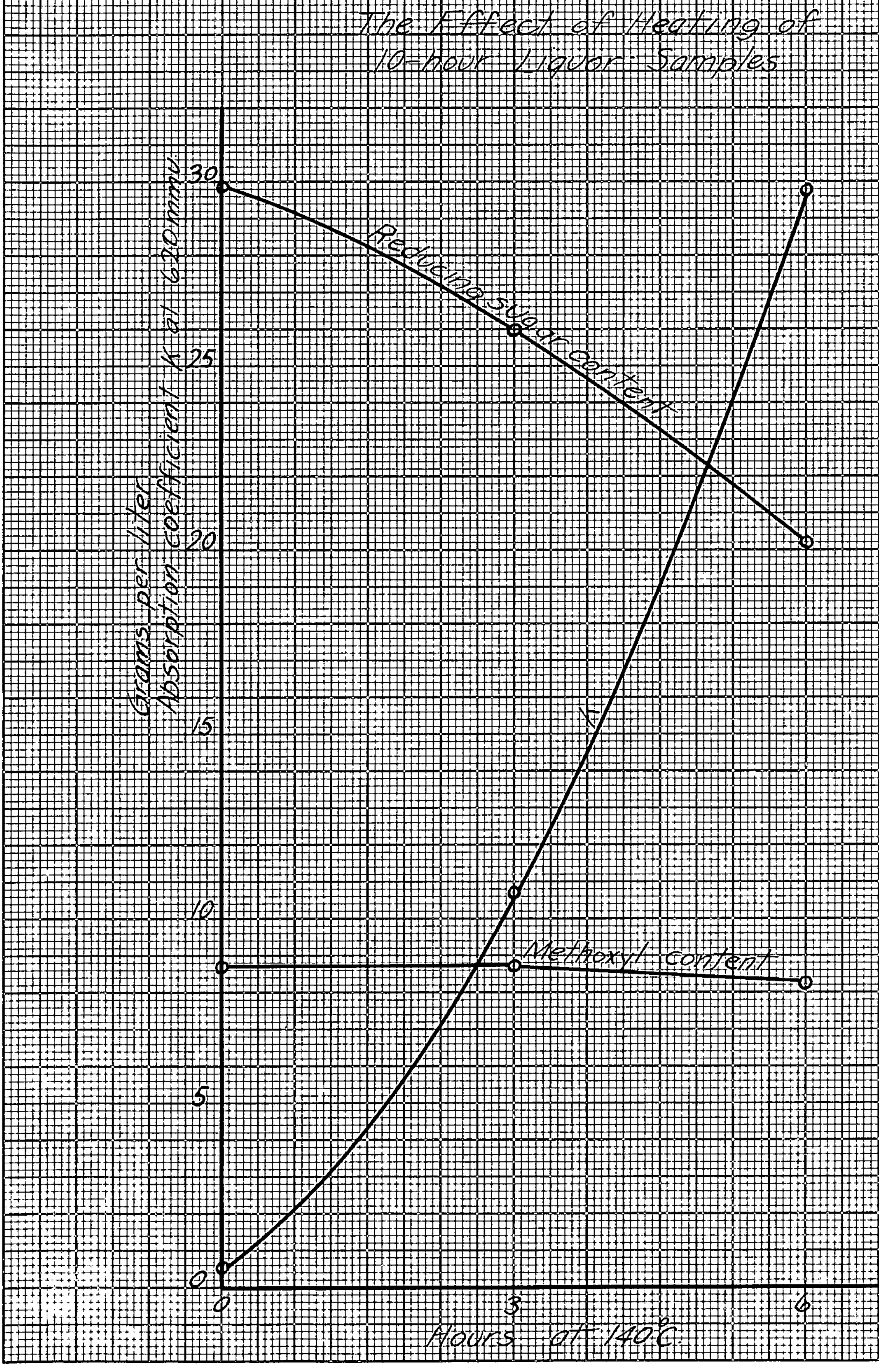


Figure 13


The Effect of Heating of
10-hour Liquor Samples
Grams per liter
Absorption coefficient K at 620mmu
Reducing sugar content
K
Methoxyl content
Hours at 140°C.
0
5
10
15
20
25
30
0
3
6

as measured by methoxyl on total solids, decreased 4.5 per cent in the last one and one-half hours, as compared with the 15.9 per cent loss in sugar. The absorption coefficient increased during this period by 840 per cent.

The 10-hour liquor analyses confirmed the conclusion that the sugar content was responsible for most of the color. In six hours, the lignin decreased 4.7 per cent, the sugar decreased 44 per cent, and the absorption coefficient increased 4600 per cent. Some of the methoxyl is split off and a small part of the lignin is degraded, but this contribution to the color, if there is any, is obscured by the degradation of the sugar. It will be noted that the isolated 7-hour liquor was degraded much faster than the same liquor in the digester. The 7-hour liquor after three hours at 140° C. has ten times as much color, as measured by absorption coefficient, as the regular 10-hour liquor. The 7-hour sample had the characteristic lignin color, as shown by the curve when plotted as log _k_ against wavelength. This changed to the straight line color characteristic on heating.

6. Effect of Age on Sulfite Waste Liquor Color

It has already been noted that liquor samples, when aged, precipitate calcium sulfite and increase in color slightly. The early samples, up to seven hours, precipitate the calcium salt within a week, whereas the normal 10-hour liquor is usually stable up to about two weeks. This precipitation is associated with the loss of free sulfur dioxide. Heavily burned liquors, when burned in the presence of pulp, are absolutely stable, with no precipitation after months of standing (e.g., Cook 2). Practically all the lime is combined with lignin, and the organic material, lignosulfonic acid and sugar, acts as a protective colloid. The higher degree of sulfonation resulting from the longer cook produces a calcium lignosulfonate which is more nearly a true solution, and this also helps prevent precipitation.

The first aging tests were run on a series of samples of liquor from Cook 3; spectral transmittance curves were determined at time intervals up to twenty-five days, with particular emphasis on the first hours after sampling, in which period it was thought that darkening and reddening might take place as they do in pulp in the blowpit. The data are given for only a few liquor samples and for the single wavelength, 620 mμ, but the trend is the same for all stages of the cook and for the entire spectrum. The data are given in Table IX.

TABLE IX

EFFECT OF AGING ON TRANSMITTANCE OF SULFITE LIQUOR, COOK 3

Sample hr.	Time after Sampling			
	15 min.	12 hr.	60 hr.	25 days
5	96.2	96.4	95.8	——
7	92.6	93.1	93.6	——
8-1/2	83.0	82.8	82.3	81.4
10	57.0	56.2	55.4	50.0

The drop in transmittance from 57 to 50 per cent in twenty-five days corresponds to an increase of k from 1.07 to 1.32, or 23.3 per cent. Up to sixty hours, however, the increase is only 5.6 per cent for the 10-hour liquor, and almost within the limit of accuracy of the instrument for the earlier samples. There is absolutely no change immediately or within a few hours after sampling. This has been checked on over a dozen cooks, over all stages of the cook and for six wood species. The samples were stored in tightly stoppered, plain glass bottles.

A further check on the amount of increase of color on aging was carried out on the 10-hour liquors from Cooks 15A and 15B, which were duplicate cooks on sprucewood, made by the Institute pulping class. The samples were filtered through filter paper immediately after sampling, and the clear liquor was decanted from the precipitate in the aged samples. The results of transmittance measurements at 620 mmu are given in Table X.

TABLE X

EFFECT OF AGING ON TRANSMITTANCE OF SULFITE LIQUORS, COOKS 15A AND 15B

Time	Transmittance at 620 mmu, %	
	15A	15B
15 min.	76.8	77.3
10 hr.	77.2	77.5
3 days	76.0	77.2
7	75.7	76.8
9	76.4	77.2
12	77.5	78.0
15	77.4	78.2
32	76.5	76.4
70	76.0	76.3

The change in transmittance is very slight and for practical purposes is negligible. This is in contrast to the change found in the liquor from Cook 3. The final conclusion must be that there is absolutely no change within a few days, and that the colors of the samples may remain constant for months.

7. Conformity to Beer's Law on Dilution

Very dark solutions present a problem when quantitative spectral transmittances are required. The thickness of the liquid layer may be reduced, but the practical limit is soon reached. The alternative is quantitative dilution of the colored material with some medium; under this condition the absorption coefficients may be calculated back to the original strength by multiplication by the dilution factor, provided the system obeys Beer's law.

Dilution with water was first tried, using a sample of 12-hour liquor from Cook 2 obtained from the blowpit. The absorption coefficients, for several wavelengths, as calculated back to the original liquor strength, are given in Table XI.

The effect of dilution is to increase the absorption coefficient, and, inasmuch as this increase is not uniform over the wavelength range, the color (hue) is changed slightly on dilution. At 600 mμ, there is an effective increase in k of 8.6 per cent on a dilution of 1:100, with even greater change at lower wavelengths. At 700 mμ, on dilution to 1:50 the increase is 17.8 per cent, but there

TABLE XI

VALIDITY OF BEER'S LAW WITH SULFITE LIQUOR
ON DILUTION WITH WATER, COOK 2,
12-HOUR LIQUOR

Liquor %	pH	Absorption Coefficient, k Wavelength--mμ 400	500	600	620	640	700
1	3.31	62.5	16.8	6.07	4.71	----	----
2	2.95	59.1	16.6	5.94	4.70	3.85	2.38
4	2.65	58.7	16.5	5.64	4.63	3.78	2.33
8	2.35	58.3	16.2	5.68	4.63	3.74	2.11
10	2.28	57.4	16.1	5.76	4.63	3.74	2.11
20	2.01	----	16.0	5.72	4.63	3.74	2.07
25	1.90	----	15.8	5.67	4.63	3.72	2.02
50	1.66	----	----	5.67	4.63	3.72	2.02
100	1.41	----	----	5.59	4.63	3.74	2.02

is a minimum of the dilution effect at 620 mμ, allowing a dilution of 1:25 with no change and a dilution of 1:100 with 1.7 per cent increase.

The pH increase on dilution was appreciable, and as there is a known k increase for decrease of hydrogen-ion concentration, the next experiment was dilution of the liquor with acidified water. Liquor from Cook 4 was diluted with approximately 0.02 N hydrochloric acid, to give a pH of 1.80. The absorption coefficients are given in Table XII.

TABLE XII

VALIDITY OF BEER'S LAW WITH SULFITE WASTE LIQUOR
ON DILUTION WITH 0.02 N HYDROCHLORIC ACID
COOK 4, 10-HOUR LIQUOR

Liquor %	pH	Absorption Coefficient, k Wavelength—mμ 400	500	600	620	640	700
1	1.80	9.50	----	----	----	----	----
2	1.80	11.4	2.64	----	----	----	----
4	1.80	11.8	2.29	0.95	----	----	----
8	1.79	14.7	3.13	1.04	0.90	0.73	0.59
20	1.76	17.2	3.96	1.17	0.95	0.76	0.55
25	1.76	18.9	4.37	1.25	0.97	0.77	0.51
50	1.76	----	4.98	1.32	0.99	0.78	0.47
100	1.75	----	5.10	1.34	0.99	0.76	0.45

The effect of the acid ions is apparent. With hydrochloric acid, a decrease in k of about 50 per cent is observed from 400 to 500 mμ, while at 700 an increase in k was found. At 640 mμ the absorption coefficient was almost constant, but the change of color produced in the liquor rules out 0.02 N hydrochloric acid as a diluent.

The next step in this investigation was the use as a diluent of fresh calcium base sulfite liquor, 6.80 per cent total and 1.20 per cent combined sulfur dioxide. The waste liquor used was from the balsam fir Cook 8. Table XIII presents the data.

TABLE XIII

VALIDITY OF BEER'S LAW WITH SULFITE WASTE LIQUOR ON DILUTION WITH FRESH SULFITE LIQUOR

Liquor %	pH	Absorption Coefficient, k Wavelength--mμ 400	500	520	580	640
1	1.60	31.8	----	----	----	----
2	1.60	28.6	2.07	1.41	----	----
4	1.61	25.6	2.07	1.41	0.53	----
8	1.58	23.9	2.02	1.40	0.56	0.24
10	1.54	22.7	1.99	1.40	0.57	0.24
25	1.50	19.3	1.89	1.41	0.57	0.28
50	1.45	----	1.81	1.41	0.60	0.28
100	1.37	----	1.82	1.41	0.66	0.31

In this case we have a system in which the absorption coefficient k increases on dilution in the range from 400 to 500 mμ, remains constant at 520 mμ, and decreases markedly above that. The sulfite cooking liquor used as diluent was water white, and the changes on dilution were due only to internal rearrangement of the chromophoric groups of the 10-hour liquor. This strength of sulfite acid is not satisfactory for dilution, since the color is changed radically.

Of the three diluents tried, water is the best, with the absorption coefficient increasing at both ends of the spectrum but remaining constant at 620 mμ. Hydrochloric acid causes a decrease of k at wavelengths lower than 640 mmu, does not affect k at 640 mmu, and increases it above that point. Fresh sulfite acid increases k below 520 mmu, is satisfactory at 520 mmu, and decreases k above 520 mmu. These tests were run on three different samples of waste liquor and the investigation was not thorough; however, no simple diluent is apparent, and all absorption spectra obtained where dilution of the original liquor is necessary are liable to be in error both in color and in depth of color.

5. The Effect of pH on Sulfite Liquor

Several investigators have reported that sulfite waste liquor changes from light yellow brown to deeper red brown when alkali is added. This phenomenon is thought to be associated with the chromophoric lignin groups present and is important both fundamentally and practically, for the hydrogen-ion concentration changes during the course of the cook and, after sampling, with aging and dilution.

The effect of hydrogen-ion concentration was determined on the 10-hour liquor from Cook 1 by addition of dilute sodium hydroxide and hydrochloric acid solutions to 50-cc. samples of the liquor and dilution with water to a final volume of 100 cc. The transmittances of the resulting solutions are given in Figure 14. The experimental data and absorption coefficients are in Table XIV, with the usual log k curves in Figure 15.

The change from the original light yellow brown to a deep red brown is very striking. There is no effect below pH 3.2 with

Figure 14

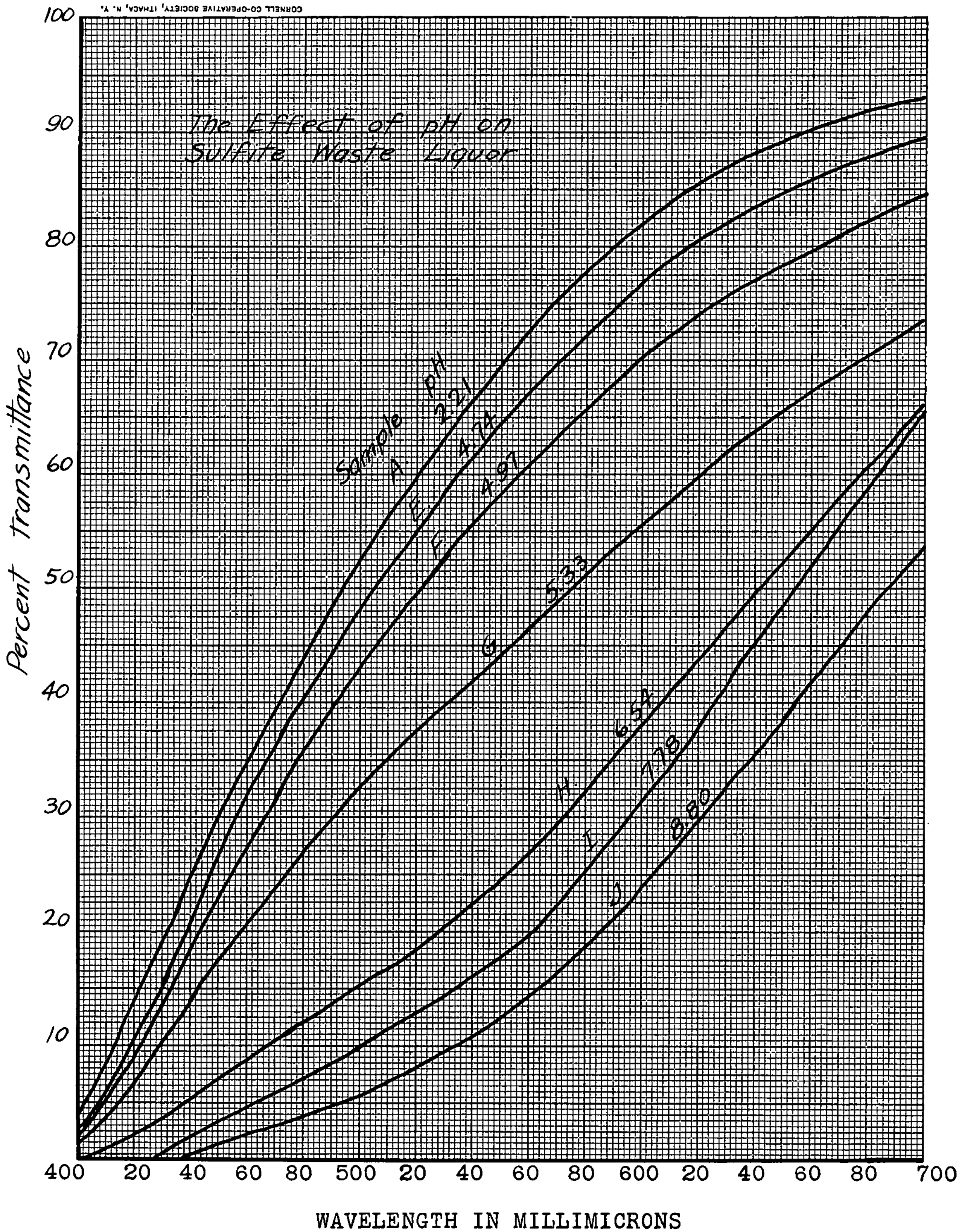

CORNELL CO-OPERATIVE SOCIETY, ITHACA, N. Y.
The Effect of pH on
Sulfite Waste Liquor
Sample pH
A 2.21
E 4.14
F 4.97
G 5.33
H 6.54
I 7.78
J 8.80
Percent transmittance
100
90
80
70
60
50
40
30
20
10
400
20
40
60
80
500
20
40
60
80
600
20
40
60
80
700
WAVELENGTH IN MILLIMICRONS

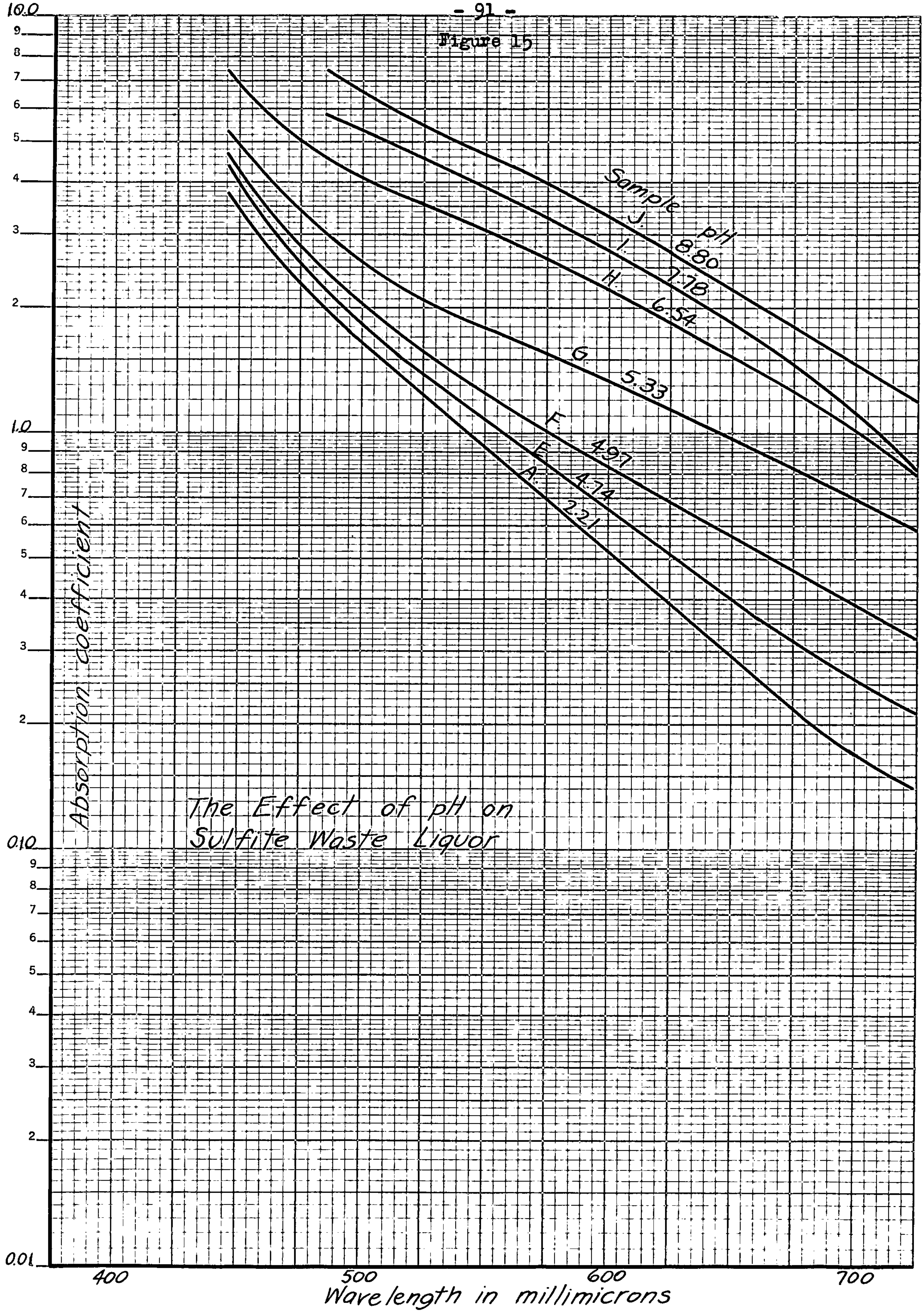
TABLE XIV

ABSORPTION COEFFICIENTS FOR TRANSMITTANCES OF FIGURE 14; EFFECT OF pH

Sample	HCl 0.97 N cc.	NaOH 0.47 N cc.	pH	Wavelength—mμ 420	460	500	540	580	620	660	700
1	2.5		1.60	3.76	2.01	1.23	0.780	0.473	0.305	0.197	0.141
2	5		1.30	3.76	2.01	1.23	0.780	0.473	0.305	0.197	0.141
3	10		1.04	3.76	2.01	1.23	0.780	0.473	0.305	0.197	0.141
A		0	2.21	3.76	2.01	1.23	0.780	0.473	0.305	0.197	0.141
B		3	3.20	3.76	2.01	1.23	0.780	0.473	0.305	0.197	0.141
C		6	4.21	3.97	2.05	1.25	0.824	0.515	0.330	0.220	0.159
D		7	4.51	4.12	2.11	1.30	0.855	0.550	0.356	0.240	0.170
E		8	4.74	4.28	2.21	1.38	0.930	0.630	0.417	0.292	0.213
F		9	4.97	4.60	2.45	1.59	1.12	0.805	0.585	0.430	0.323
G		10	5.33	5.37	3.03	2.13	1.66	1.28	0.990	0.766	0.590
H		12	6.54	7.48	4.58	3.56	2.67	2.17	1.58	1.13	0.792
I		16	7.78	——	5.84	4.42	3.53	2.65	1.84	1.24	0.810
J		20	8.80	——	7.48	5.47	4.28	3.23	2.33	1.65	1.19
K		24	9.52	——	——	5.55	4.06	2.91	1.99	1.35	0.93

All samples 50 cc. of liquor, with final dilution volume 100 cc.

Figure 15



10.0
9
8
7
6
5
4
3
2
1.0
0.10
0.01
400
500
600
700
Wavelength in millimicrons
Absorption coefficient
Sample
pH
J. 8.80
I. 7.78
H. 6.54
G. 5.33
F. 4.97
E. 4.74
A. 2.21
The Effect of pH on
Sulfite Waste Liquor

either hydrochloric acid or sodium hydroxide. The change is gradual up to pH 4.5 and is almost complete at pH 8. Above pH 9 precipitation started in this system, and the absorption coefficients of sample "K" show this upper limit. The greatest change of absorption coefficient is in the red end of the spectrum. At 700 mμ the k value increases 740 per cent with the pH change from 3.2 to 8.8, whereas at 500 mμ this increase is only 340 per cent. The course of the change in hue is not simple, as can be observed in Figure 15. The actual mechanism of the change, in an already complex liquid, is probably highly complicated.

B. COOKING OF ISOLATED COMPONENTS OF WOOD

The first section of the experimental work was an attempt to determine the sources of the liquor color by optical and chemical analysis of liquor samples taken during the course of the cook. This second section, in contrast to the above procedure of analyzing for chromophoric substances from cooked whole wood, is a proposal to cook the components of wood separately, and an attempt to show the nature and amount of color produced by sulfonation, acid hydrolysis, and acid and heat degradation of each constituent.

1. Isolation of Wood Components

A bolt of black spruce from the same lot as that used in the small scale cooks was barked and reduced to sawdust by a circular saw. This sawdust was further ground in an attrition mill and several pounds of two-screened fractions, 40- to 65-mesh and that finer than 65-mesh, were finally obtained.

A portion of the 40- to 65-mesh flour was used to prepare holocellulose according to the method of Van Beckum and Ritter (112), which used alternate chlorinations and extractions with hot 3 per cent monoethanolamine in alcohol. After ten such treatments the lignin was completely removed, according to the color test, and the product was washed with distilled water and with alcohol, and then air-dried. The data on the preparation are given in Table XV.

TABLE XV

PREPARATION OF SPRUCE HOLOCELLULOSE

Weight of raw sprucewood flour, g.	227.1
Percentage of moisture	6.6
Weight of oven-dry wood flour, g.	212
Number of chlorinations and extractions	10
Air-dry holocellulose yield, g.	139.4
Percentage of moisture	6.9
Weight of oven-dry holocellulose, g.	129.8
Yield on raw wood, per cent	61.2
Lignin content by 72 per cent sulfuric acid	0

The yield is low when compared with the 71.3 per cent obtained by Kurth and Ritter (7), because of the loss of water and alcohol extractives, and because of mechanical losses, since no attempt was made to obtain a quantitative yield.

Spruce hemicellulose and alkali resistant cellulose were prepared from a portion of the holocellulose by cold 8 per cent sodium hydroxide extraction. Eighty-one grams of holocellulose with 6.9 per cent moisture content were dispersed in 1775 cc. of 8 per cent sodium hydroxide at 25° C. for one hour. The mixture was then filtered, the cake pressed as dry as possible, and an additional 1000 cc. of 8 per cent sodium hydroxide were added to the fiber for one hour at 25° C. The mixture was then filtered, pressing out all the filtrate possible, and the two filtrates were combined.

Glacial acetic acid was added to just neutralize the combined filtrates, and no precipitate was observed. The total volume was 2800 cc., and to this an equal volume of 95 per cent ethyl alcohol was added to precipitate the hemicellulose fraction. The precipitate was removed by centrifuging and was washed successively with two portions each of 50 per cent alcohol, 95 per cent alcohol, absolute alcohol, ethyl ether, and petroleum ether, after which it was vacuum-dried.

The cellulose material, resistant to the alkali treatment, was washed with water, hot water, dilute acetic acid, water, and finally with alcohol, after which it was air-dried. The analyses of the two products are given in Table XVI.

TABLE XVI

HEMICELLULOSE AND ALKALI RESISTANT CELLULOSE
PRODUCTION AND ANALYSIS

Weight of holocellulose, oven-dry, g.	85.4
Weight of hemicellulose produced, g.	30.7
Ash in hemicellulose, per cent	2.21
Loss on drying (105° C.), per cent	8.0
Weight of hemicellulose, oven-dry, g.	27.6
Hemicellulose yield, per cent	32.3
Weight of resistant cellulose produced, g.	59.4
Ash in resistant cellulose, per cent	0.24
Loss on drying (105° C.), per cent	6.7
Weight of resistant cellulose, g.	55.8
Resistant cellulose yield, per cent	65.4

A portion of the wood flour which was finer than 65 mesh was extracted to obtain the ether-soluble, alcohol benzene-soluble, and water-soluble fractions. The results are given in Table XVII.

TABLE XVII

EXTRACTIVES FROM SPRUCEWOOD

Weight of wood, oven-dry, g.	247.5
Weight of ethyl ether-soluble material, 8 hours' extraction, g.	3.073
Weight of alcohol-benzene soluble, 12 hours' extraction, g.	0.724
Weight of water-soluble, 22 hours' time (copper Soxhlet), g.	5.403
Ether-soluble, per cent	1.24
Alcohol-benzene soluble, per cent	0.29
Water-soluble, per cent	2.18
Total extractives, per cent	3.71
Lignin on extracted wood, per cent	27.2
Methoxyl on extracted wood, per cent	4.96

The water-soluble fraction obtained was dark colored; the long boiling period may have degraded some of the constituents. The dry product was obtained by vacuum evaporation, which caused the precipitation of some solid material and final vacuum drying.

The water-soluble material was also obtained by another procedure. Three hundred and sixty-one grams of oven-dry equivalent raw wood flour, finer than 65 mesh, were covered with 4 liters of boiling water and heated for three hours at about 85° C. in the water bath. The mixture was filtered, the flour again covered with boiling water, and heated in the water bath for two hours. The combined filtrates were filtered several times until they were clear, evaporated in a vacuum to a syrup, and an equal volume of 95 per cent ethyl alcohol was added. The precipitate was centrifuged and washed successively with alcohol, ether, and petroleum ether. The filtrate containing the alcohol-soluble portion was again evaporated in a vacuum, and the solids were recovered by slow vacuum evaporation. The results are given in Table XVIII.

TABLE XVIII

HOT WATER EXTRACTIVES OF SPRUCEWOOD

Weight of raw sprucewood, oven-dry, g.	361
Weight of water soluble-alcohol insoluble, g.	4.5
Weight of water soluble-alcohol soluble, g.	3.22
Total water extractives, per cent	2.14

The water-soluble fraction of the wood obtained by the above water bath extraction was also highly colored.

Calcium lignosulfonate was isolated from the 10-hour liquor of Cook 3. Four liters of the liquor were evaporated in a vacuum to a heavy syrup and dialyzed in a cellophane bag for one week with running tap water, then for five weeks with distilled water, during which time the water was changed four times each day. The liquor was kept saturated with sulfur dioxide during the dialysis and was evaporated in a vacuum back to syrup about twice per week, as it became diluted by osmosis. The dialysate was highly colored for the first two weeks. The procedure was designed to free the liquor of all inorganic calcium salts, carbohydrate material, all volatile constituents, and acids, and to produce pure calcium lignosulfonate. At the end of the arbitrary dialysing period the equilibrium mixture of free lignosulfonic acid and calcium lignosulfonate was neutralized by the addition of thirty grams of calcium carbonate, the excess calcium carbonate filtered off (24 grams), the solution evaporated in a vacuum to about 200 cc. of very thick syrup, and the salt precipitated by slowly dropping the syrup into 4 liters of absolute methyl alcohol. The precipitate was centrifuged and washed successively with absolute methyl alcohol, ethyl ether, and petroleum ether and finally dried. The analysis is given in Table XIX.

TABLE XIX

ANALYSIS OF CALCIUM LIGNOSULFONATE

Volume of sulfite waste liquor, 10-hour, Cook 3	4 liters
Weight of solid calcium lignosulfonate produced, oven-dry, g.	81.9
Yield on liquor, per cent	2.04
Yield on calcium lignosulfonate, assuming 80 g. per liter, per cent	25.6
Methoxyl content of product, per cent	12.39
Sulfur, per cent	6.18
Ash, per cent	9.14
CaO, per cent	5.35
Reducing sugars as glucose, per cent	1.0

Analyses not calculated to ash-free basis.

Inasmuch as 6 grams of calcium carbonate were used to neutralize the free lignosulfonic acid, the composition of the equilibrium mixture may be calculated at about 76 per cent of free acid and 24 per cent of calcium salt.

2. Cooking Procedure

The oven-dry equivalent of 1.000 gram of the isolated wood constituents or other products was accurately weighed and introduced into dry, 25 by 250 mm. Pyrex test tubes. Fifty cubic centimeters of cooking acid were pipetted into each of the tubes, which were immediately sealed, leaving an approximately constant gas volume above the liquid. These sealed tubes, as many as twelve at one time, were placed in a small autoclave, which was about 9 inches deep. The autoclave was filled with water to a point just above the liquor level of the tubes, and was sealed and heated in a wax bath.

The temperature was taken by means of a thermometer inserted in a deep well in the autoclave. The temperature schedule used in all cases was one and one-half hours to 140° C., at this temperature as long as desired, and overnight air-cooling before opening the autoclave. The sealed tips were knocked off the tubes, and the desired tests were made, after filtering the liquor when necessary.

The fresh cooking liquor used was soda base with 1.20 per cent combined sulfur dioxide and 6.20 per cent total sulfur dioxide. The calcium base liquor used for the semicommercial chip cooking was found to be unsatisfactory because of the excessive precipitation occurring on heating, particularly with the sugars. The soda base liquor maintains a relatively homogeneous system inside the tube.

3. Cooks on Major Wood Components, with Time Variable

Completely extracted wood, calcium lignosulfonate, holocellulose, hemicellulose, resistant cellulose, glucose, and sucrose were heated with soda base acid under the conditions described above for periods of five, eight, and ten and one-half hours at the maximum temperature of 140° C. The percentage of total sulfur dioxide, the reducing sugar content, and the spectral transmittance were determined on each sample. Carbon dioxide was evolved and some sulfur dioxide was lost when the fresh cold acid was added to the neutral calcium lignosulfonate. The sugars were completely soluble in the acid, but the wood fractions were apparently unaffected, except that the hemicellulose was slightly gelatinized. The results of the analyses are in Table XX and are presented graphically for wood, calcium lignosulfonate, hemicellulose, and glucose in Figure 16.

The cooking of 1 gram of extracted wood flour in 50 cc. of soda base sulfite liquor followed exactly the same course as did the digestion of chips. The penetration period was eliminated in the schedule used because the wood was finely divided, and five hours in this cook corresponded roughly to seven hours in the chip-cooking schedule. At five hours, the color of the liquor was that of sulfonated lignin, with the typical curve on a plot of log k against wavelength. The sugar content had almost reached the usual maximum, 19 per cent of the weight of the wood. The 8-hour cook corresponded approximately to the 10-hour normal end of the cook, with greatly increased color at the expense of a small amount of sugar. The last

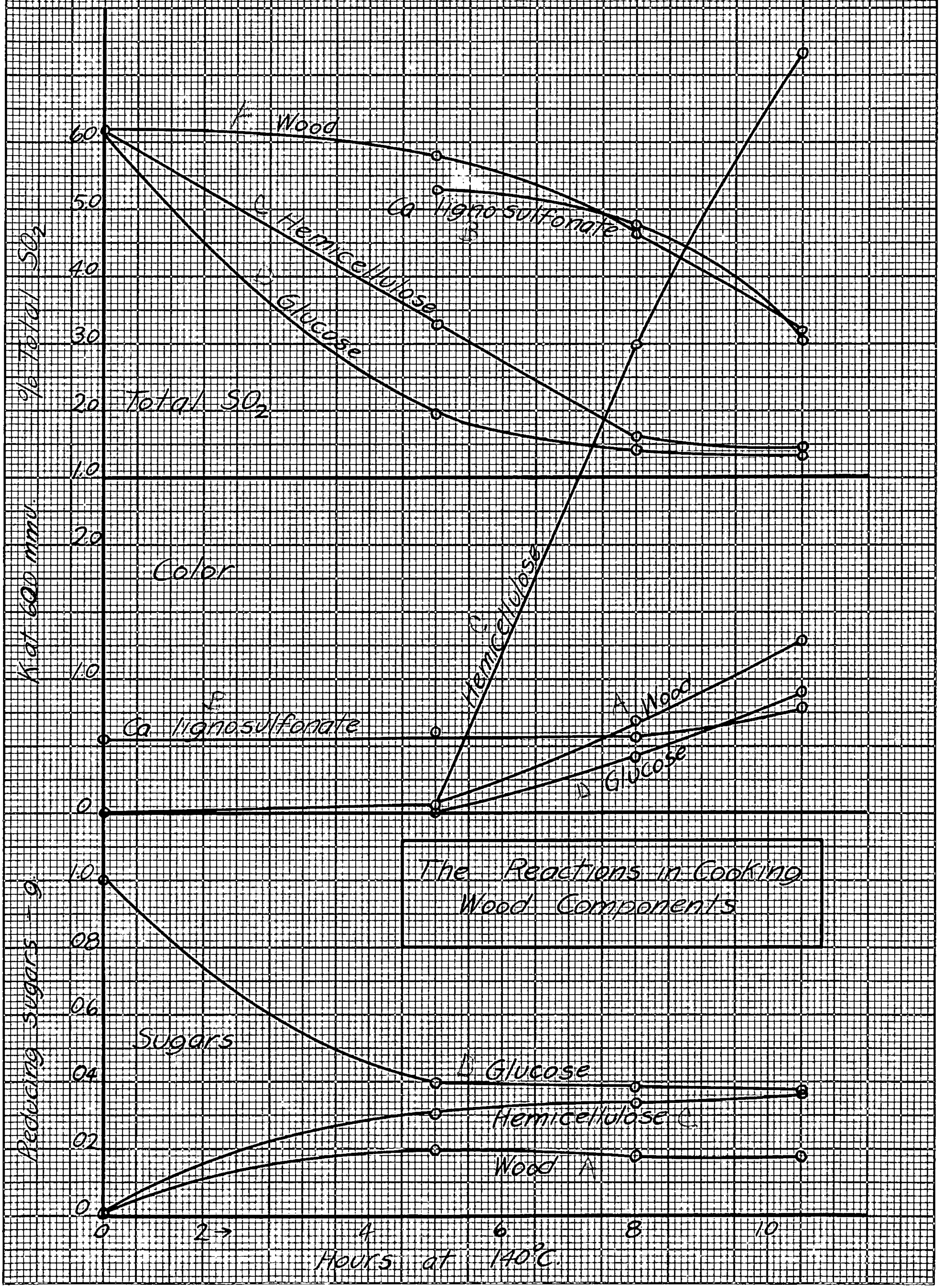
TABLE XX

EFFECT OF TIME IN SULFITE COOKING ON MAJOR WOOD COMPONENTS

Cook Time at 140° C.	Total SO_2 %	Sugar as Glucose g./50 cc.	Absorption Coefficient Wavelength--mμ 400	500	600	700
		A. Completely Extracted Wood				
0	6.20	0	0	0	0	----
5	5.82	0.19	2.09	0.151	0.049	0
8	4.67	0.17	6.70	1.76	0.678	0.269
10.5	3.17	0.17	----	2.99	1.29	0.60
		B. Calcium Lignosulfonate				
0	----	0.009	----	1.77	0.55	0.18
5	5.30	0.009	----	1.91	0.60	0.30
8	4.74	0.009	----	1.73	0.56	0.14
10.5	3.02	0.013	----	2.10	0.76	0.23
		C. Holocellulose				
0	6.20	0	0	0	0	0
5	5.81	0.12	0.85	0	0	0
8	4.84	0.13	1.85	0.038	0	0
10.5	3.58	0.15	1.85	0.115	0	0
		D. Hemicellulose				
0	6.20	0	0	0	0	0
5	3.28	0.30	0	0	0	0
8	1.62	0.33	----	----	3.50	1.98
10.5	1.45	0.37	----	----	5.93	3.83
		E. High Alpha-Cellulose				
0	6.20	0	0	0	0	0
5	5.51	0.04	0	0	0	0
8	5.35	0.05	0.91	0	0	0
10.5	5.32	0.05	1.12	0	0	0
		F. Glucose				
0	6.20	1.00	0	0	0	0
5	1.98	0.39	1.71	0.084	0	0
8	1.46	0.38	----	1.51	0.43	0.17
10.5	1.36	0.36	----	2.54	0.90	0.44
		G. Sucrose				
0	6.20	0	0	0	0	0
5	2.49	0.35	3.22	0.16	0	0
8	1.32	0.30	63.6	21.9	10.1	5.60
10.5	1.21	0.25	----	33.1	16.6	9.55

Blanks in absorption coefficient data are from solutions on which an accurate determination was impossible because the solutions were either too high or too low in concentration of color.

Figure 16


% Total SO2
K at 600 mmu.
Reducing Sugars - g.
Hours at 140°C.
E Wood
Ca lignosulfonate B
C Hemicellulose
D Glucose
Total SO2
Color
E Ca lignosulfonate
C Hemicellulose
A Wood
D Glucose
Sugars
D Glucose
Hemicellulose C
Wood A
The Reactions in Cooking Wood Components

sample, ten and one-half hours' time at 140° C., was definitely burned. The sulfur dioxide content decreased steadily, being consumed by the wood. Soda base liquor alone, when subjected to the same treatment of heat and pressure for these times, was unaffected and tested above 6 per cent total sulfur dioxide. At constant temperature, with a 50:1 liquor-wood ratio, the increase of absorption coefficient was linear with time from five to ten and one-half hours.

The calcium lignosulfonate color is very stable to the action of sulfite acid under cooking conditions. Some chemical action takes place, as the drop of total sulfur dioxide indicates; this is shown by the slight increase in absorption coefficient. This color increase might be due to the 1.0 per cent residual reducing sugar or to the increased sulfonation of the lignin compound.

Of the three cellulose fractions, the hemicellulose was, as was expected, the most sensitive to the cooking action. The resistant cellulose portion showed little change, although the hydrolysis and degradation had progressed slightly. The holocellulose fraction, containing the easily hydrolyzable hexosans and particularly the pentosans which burned very readily as the hemicellulose portion, was colored in proportion to the hemicellulose content. The hydrolysis to reducing sugars continued throughout the cook, and again the linear increase of color is noted from five to ten and one-half hours.

The study of sucrose was included in this work because it is an available, easily hydrolyzed disaccharide. It produces much more color than glucose, and the color increase, as in glucose, is approximately linear. The lignin-free cellulose fractions, the glucose, and the sucrose all produced degradation products with the characteristic burned sugar color. The 10-1/2-hour period at 140° C. did not approach the exhaustion of the sugar or the exhaustion of the potential color. The amount of color which might be produced from 1 gram of sugar was far from being realized in these experiments.

This series of cooks has demonstrated the first cases of reasonably slow color development by the sulfite cooking of wood and wood constituents. The earlier small-scale commercial cooks were made on chips with a liquor to wood ratio of about 4:1; with constant temperature the color was found to increase very rapidly over the 7- to 12-hour periods observed. It was assumed that, because the fiber present was hydrolyzing to simpler components which in turn were being changed to highly colored material, the presence of fiber prevented the existence of any simple color-time relationship.

The fiber definitely serves as a source of color, and in experiments on heating isolated liquor at constant temperature the increase of color was found to be slower (Figure 13). However, no simple relationship appeared to exist. The concentration of solids was very high in these isolated liquors, with 2-1/2 per cent sugar, 8 per cent calcium lignosulfonate, and 12 per cent total solids. In the course of the heating the sugar content decreased appreciably, and the hydrogen-ion concentration increased.

The next step in the attempt to determine the nature of the color increase-time relationship led to the artificial conditions of test tube cooks, where the liquor to solids ratio is 50:1 and where there is an attempt at homogeneous systems. In these systems, with wood, holocellulose, glucose, and sucrose, the color as measured by the absorption coefficient k develops as a linear function of time, in the 5- to 10-1/2-hour period at 140° C. The maintenance of the sugar concentration, within close limits, is probably most important in maintaining the color development relationship with time.

In the cooking of these four substances, the reducing sugar content increased slightly for the wood and hemicellulose, in which cases some hydrolysis was still going on, and decreased slightly in the glucose and sucrose solutions, in which all the sugar was present as the monosaccharide. The changes in all cases were slight, and because the coloring matter produced per sugar unit is relatively high, the systems were sufficiently constant in sugar to make possible the linear color development with time.

4. Comparison of All Wood Constituents, Pure Sugars, Lignin Preparations, and Related Compounds by Sulfite Cooking at 140° C. for 5 Hours

The first group studied here includes the strictly wood constituents. The ether- and alcohol-benzene-soluble constituents were prepared for cooking by drying from organic solvent solution on 1-gram masses of asbestos fiber which had been placed in the cooking tube. This procedure presented a large area of the pitch or resin to the attack of sulfite acid and simulated to some degree the physical occurrence of these products in the spruce chips.

TABLE XXI

THE ACTION OF SULFITE LIQUOR ON WOOD, WOOD CONSTITUENTS, AND RELATED COMPOUNDS

Cooking Conditions: 1 gram per 50 cc. of soda base sulfite acid, 6.20 per cent total and 1.20 per cent combined sulfur dioxide; 1-1/2 hours to 140° C. and at 140° C. for 5 hours.

Substance		Total SO_2 %	pH	Sugar g./50 cc.
Wood, 65-mesh		5.86	1.68	0.182
Wood, extracted		5.82	1.55	.187
Ether soluble		5.81	1.70	----
Alcohol-benzene soluble		4.65	1.65	.08
Water-soluble		3.10	1.00	.315
Water soluble-alcohol insoluble		2.05	----	.327
Water soluble-alcohol soluble		5.39	1.55	.207
Holocellulose		5.81	1.65	.122
Hemicellulose		3.28	----	.299
Resistant cellulose		5.51	----	.035
d-glucose		1.98	----	.394
d-levulose		5.07	1.40	.330
d-mannose		2.25	1.10	.560
d-galactose		1.87	1.00	.890
d-arabinose		1.77	1.20	.377
d-xylose		1.80	0.79	.483
Cellobiose		2.86	1.15	.550
Sucrose		2.49	----	.347
Ca lignosulfonate		5.30	----	.009
Ca lignosulfonate	Commercial	5.72	1.62	.072
Na lignosulfonate	Commercial	5.73	1.60	.072
Ca lignosulfonate	Dr. Brauns	5.68	1.60	.046
Na lignosulfonate	Dr. Brauns	5.64	1.55	.049
Cotton cellulose		6.06	1.60	.020
Corn starch		4.68	1.25	.789
Tannic acid		5.76	1.75	.343
Lemon pectin		5.02	1.30	.253

Figure 17

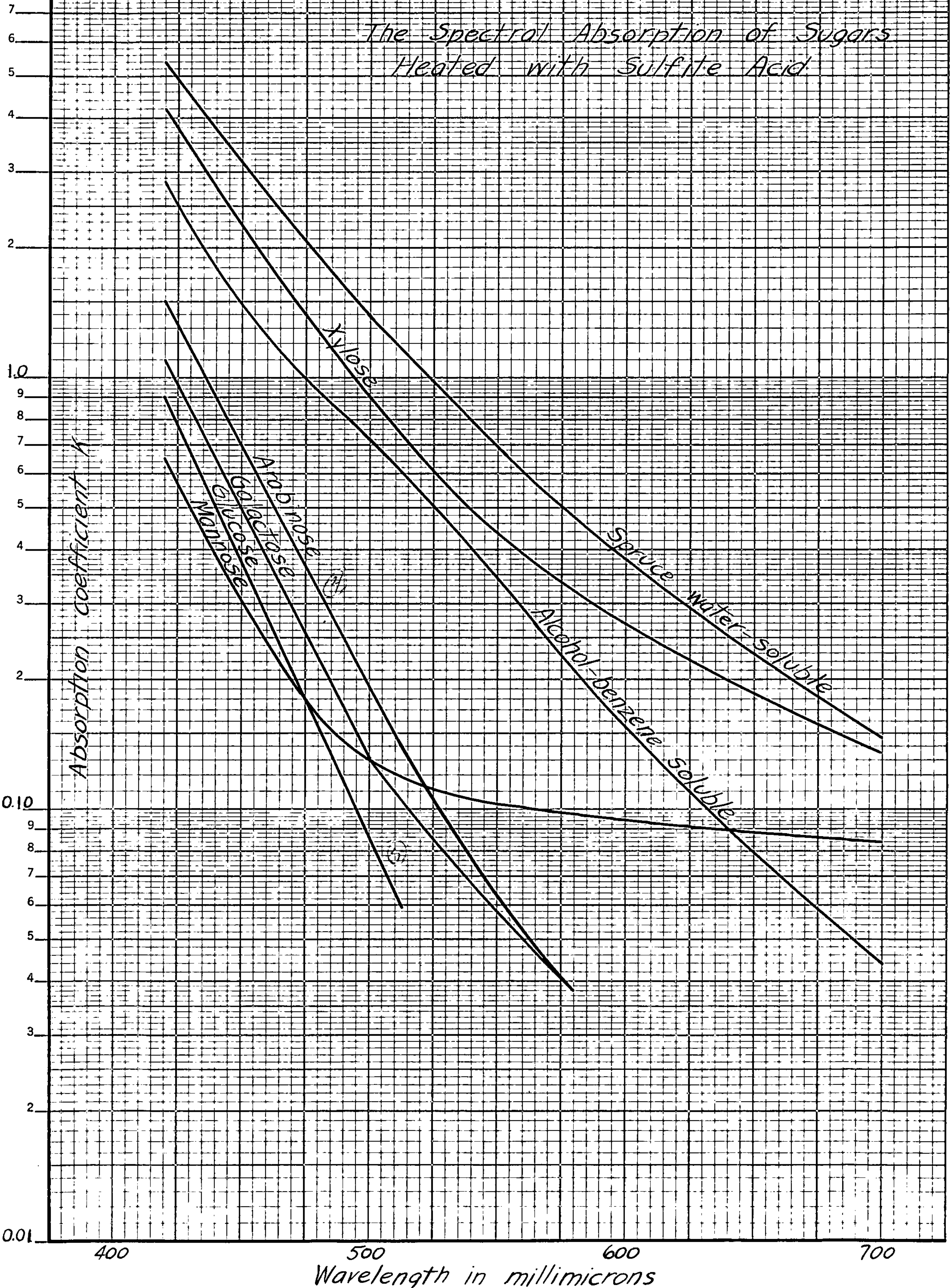
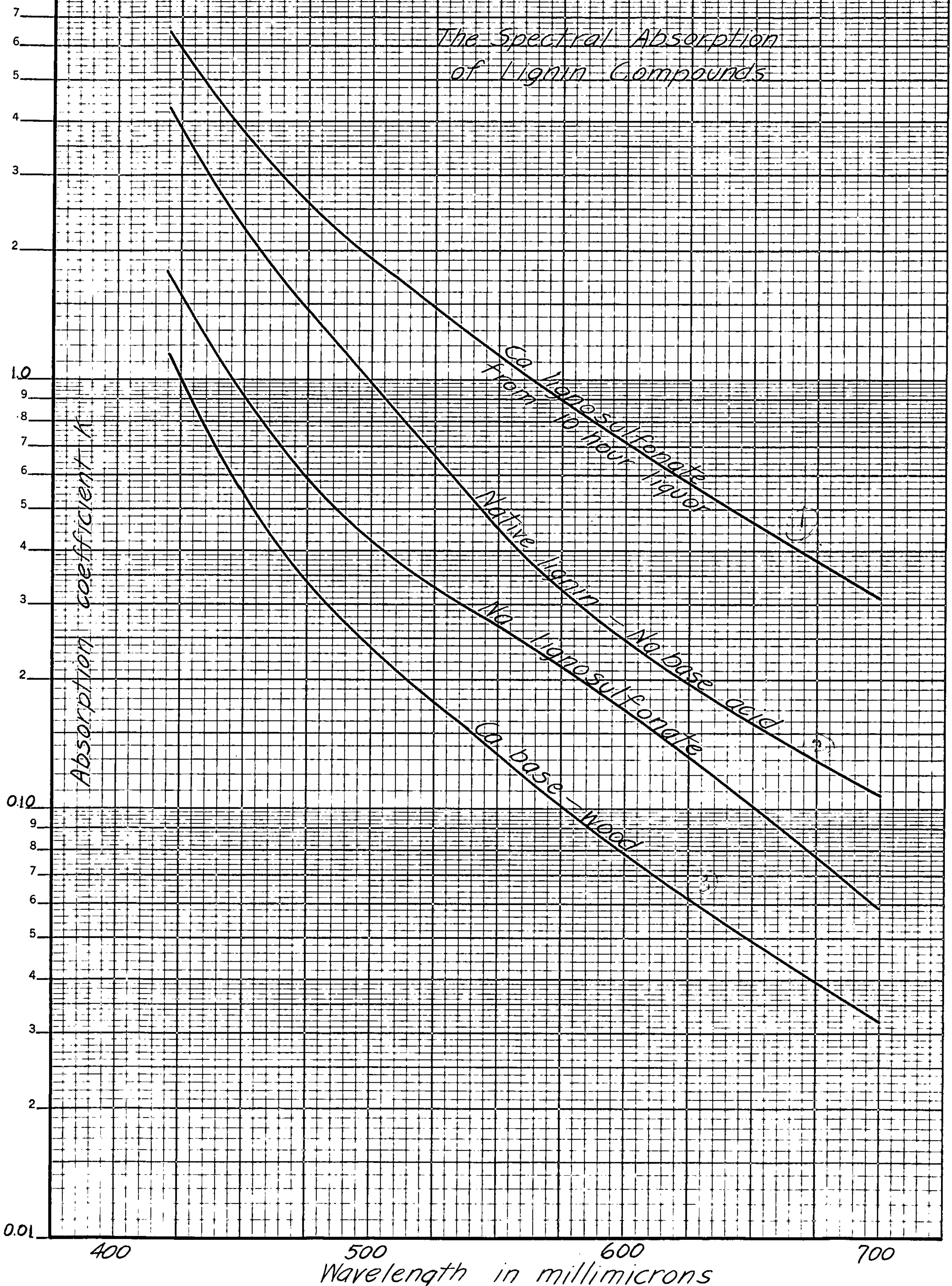

The Spectral Absorption of Sugars Heated with Sulfite Acid
Absorption coefficient K
Wavelength in millimicrons
10.0
1.0
0.10
0.01
400
500
600
700
Xylose
Arabinose
Galactose
Glucose
Mannose
Spruce water-soluble
Alcohol-benzene soluble

Figure 18


The Spectral Absorption of lignin Compounds
Ca lignosulfonate from 10 hour liquor
Native lignin - Na base acid
Na lignosulfonate
Ca base - wood
Absorption coefficient K
Wavelength in millimicrons
10.0
1.0
0.10
0.01
400
500
600
700

All values for reducing sugar content are expressed as grams of glucose per 50 cc., except for the pure sugars, which are calculated to their own weight. These samples of sugars, under the conditions of procedure used (Partansky and Benson (16)), have a reducing power which is expressed as a percentage of the reducing power of glucose in the following table.

TABLE XXII

REDUCING POWER OF SUGARS

	%
d-glucose	100.0
d-levulose	89.4
d-mannose	97.2
d-galactose	63.5
d-arabinose	99.6
d-xylose	95.5
Cellobiose	70.4

The ether-soluble fraction of sprucewood was only slightly attacked in the sulfite cook. Most of the pitch was found floating on the surface of the liquor. It was light yellow in color before cooking and apparently was not changed by the digestion. The alcohol-benzene soluble material, however, was deep red brown before cooking, and practically all of it went into solution to give a very dark-colored liquor. The extent of the action of acid on all these constituents is indicated by the percentage of total sulfur dioxide remaining in the liquor; in this case the sulfur dioxide content is comparatively low, indicating chemical action and change in the organic soluble material.

The water-soluble material associated with the two previous fractions was very dark both before and after cooking, with a high sugar content remaining, low pH, and low total sulfur dioxide after digestion. The two water-soluble fractions obtained from raw wood were also very deeply colored, with high sugar content remaining after digestion. This sugar would degrade to form more color with increased time.

The eight sugars tested vary widely in their resistance to darkening in the sulfite cooking process. Glucose, mannose, and galactose are aldohexoses, levulose is a ketohexose, arabinose and xylose are aldopentoses, cellobiose yields two glucose units on hydrolysis, and sucrose breaks down to give one glucose and one levulose molecule.

These sugars, in the order of intensity of color produced by sulfite acid, temperature, pressure, and time, are xylose, arabinose, sucrose (all very dark), galactose, glucose, mannose (medium color produced), cellobiose, and levulose (fairly resistant). As a confirmatory test, 1-gram samples of the sugar in 50 cc. of 4 per cent hydrochloric acid were heated on the water bath until sufficient color developed, which usually required from one-half hour to three hours. The sugars in order of appearance and intensity of coloration were sucrose, arabinose, xylose, galactose, glucose, levulose, mannose, and cellobiose. Some black condensation product appeared in all cases. The absorption coefficients of this purely qualitative test (some solutions were diluted) are found in Table XXXIII in the Appendix, while the color characteristics are shown in Figure 19.

The two series agree roughly in that the pentoses, arabinose and xylose, are by far the most sensitive to degradation by acid. This is a result of the characteristic decomposition of pentoses to furfural and the subsequent furfural condensation to highly colored material. Sucrose is very sensitive also, because, although the principal products of acid hydrolysis are glucose and levulose, an appreciable quantity of methylfurfural is also formed.

The three aldohexoses, glucose, galactose, and mannose, are all about equally sensitive to sulfite acid. Cellobiose must hydrolyze to glucose before color is produced and is evidently fairly stable to both sulfite acid and hydrochloric acid. The ketohexose, levulose, is very stable to sulfite acid. The absorption spectra of these sugars (Figure 17) also vary widely. Xylose and mannose have a decided curved color characteristic at this low heating period. The other sugars are characterized by straight lines on the plot of log k against wavelength, but the slope is very different from that found in the last stages of the sulfite cook. This, however, is a function of the cooking time and severity of treatment. This is illustrated by comparing the colors produced by heating sucrose for the 5- and 10-1/2-hour periods. The 10-1/2-hour period color resembles very closely the sulfite liquor color.

The hydrochloric acid-treated sugars offer proof that the color produced is probably a function of the specific acid ions present and of the time, temperature, and concentrations of the digestion.

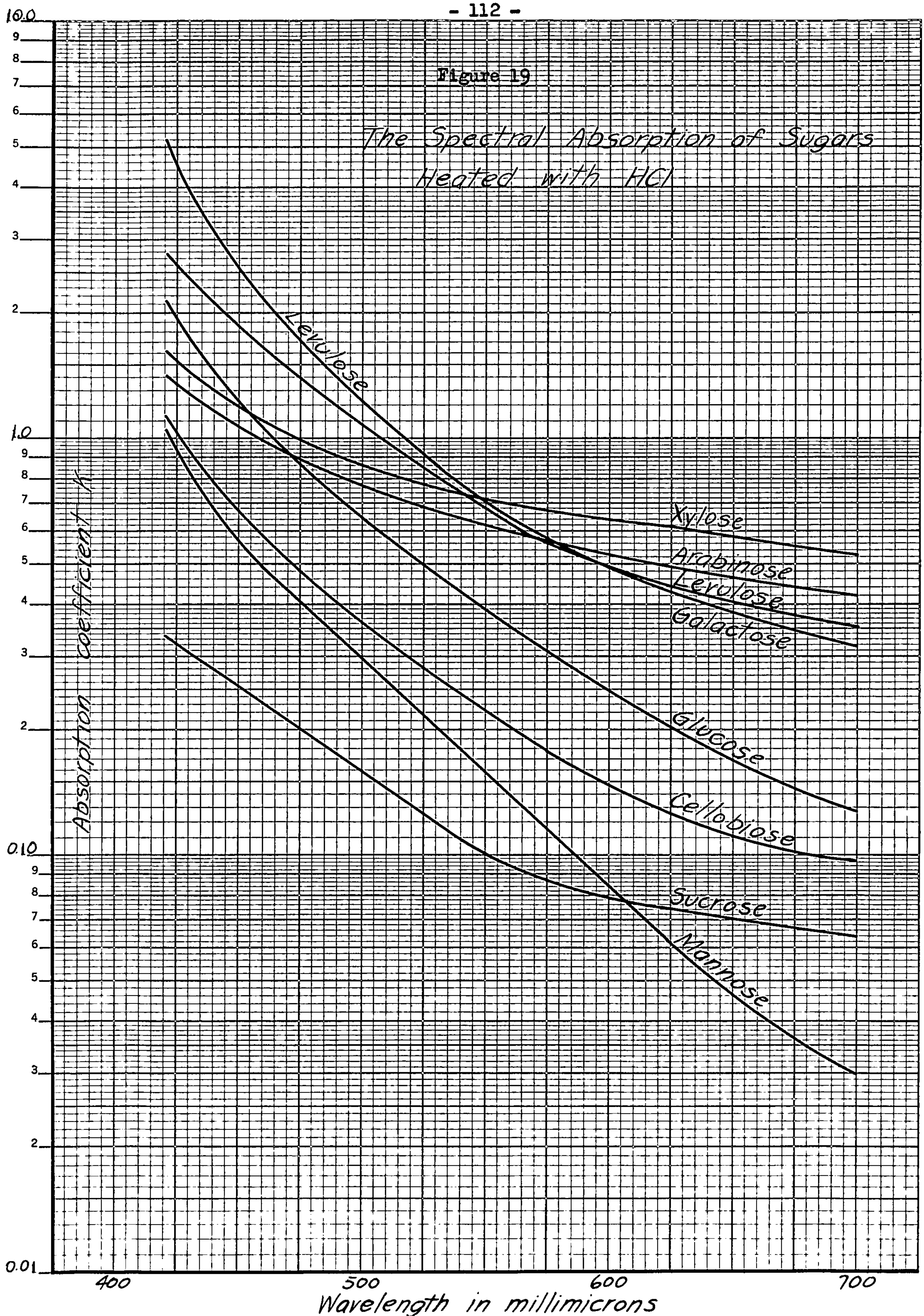


Figure 19
The Spectral Absorption of Sugars
Heated with HCl
Levulose
Xylose
Arabinose
Levulose
Galactose
Glucose
Cellobiose
Sucrose
Mannose
Absorption coefficient k
10.0
1.0
0.10
0.01
400
500
600
700
Wavelength in millimicrons
MADE IN U.S.A.

An added variable in the sulfite cook is the presence of calcium or sodium salts, which are known to form complex addition products with sugars. Some of the sugars on being heated with hydrochloric acid produced colors with the curved characteristic, but xylose and mannose did not, in contrast to their behavior with the sulfite acid 5-hour cook.

The lignin solutions listed in Table XXI and Figure 18 are similar in that they all exhibit the same color and are apparently unaffected by the sulfite acid treatment. The sodium lignosulfonate produced by cooking native lignin is particularly interesting, for it is the product of a low temperature cooking of carbohydrate-free material, and the color produced is that of a sulfite acid solution of the pure sodium lignosulfonate. The color curve agrees with those of the 7-hour samples on wood cooks and offers proof for the hypothesis that up to seven hours all the color of the liquor is due to lignin.

The pure cotton cellulose was practically unaffected by cooking, even less than the resistant spruce cellulose. Corn starch at five hours was almost completely hydrolyzed, but the potential degradation had only started. Tannic acid and lemon pectin are also easily hydrolyzed to produce high percentages of reducing substances which in turn degrade and produce the characteristic color.

5. Furfural and Related Compounds

The generally accepted hypothesis is that furfural, methylfurfural, and hydroxymethylfurfural, produced from acid degradation of pentoses and hexoses, in turn condense, polymerize, or by some other mechanism form highly colored water-soluble and water-insoluble materials. These furfurals are all very unstable and become colored very deeply with age alone, a reaction which is accelerated by acid and heat.

The furfural and furfuryl alcohol were from stock supply, and the furfural was redistilled when necessary to produce the water-white product. 5-Methylfurfural was prepared by the method of Rinkes (113). Hydroxymethylfurfural or ω-oxymethyl furfural was prepared from 5-chloromethylfurfural, made according to Rinkes, by reaction with silver acetate by the procedure of Erdmann (114). These products are highly colored on aging. The colors of these aged products were determined by spectral transmittances. The absorption coefficients of suitable concentrations of these naturally aged products are given in Table XXXIV in the Appendix, with the colors graphically presented in Figure 20.

The furfural, furfuryl alcohol, methylfurfural and hydroxymethylfurfural were dark colored after aging, and the color was the straight line characteristic as expected. The slope of the straight line color characteristic is again seen to be a function of the treatment to which the furfural is subjected. The colored compound formed

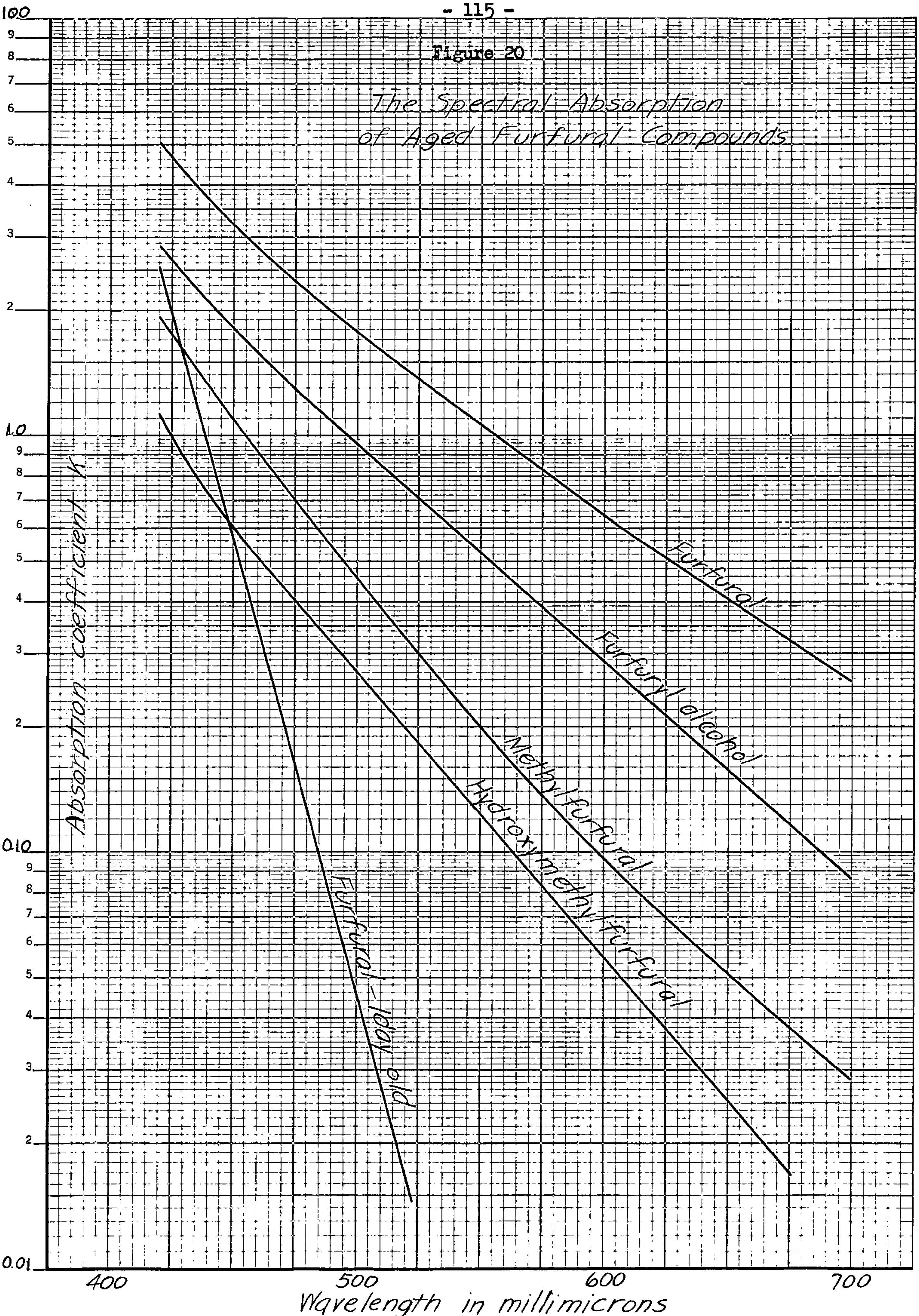


Figure 20
The Spectral Absorption
of Aged Furfural Compounds
Furfural
Furfuryl alcohol
Methylfurfural
Hydroxymethylfurfural
Furfural - 1day old
Absorption coefficient K
Wavelength in millimicrons
10.0
1.0
0.10
0.01
400
500
600
700

is bright yellow at first but becomes dark red brown with age, increasing concentration, and condensation. The marked similarity, if not identity, in the general progress of furfural condensation, sugar degradation, and the last stages of the sulfite cook should be noted. The sugars on treatment produce very yellow colors at first with steep slope log k curves; as the acid treatment progresses, the color changes from yellow to deep red brown, and the slope of the color characteristic decreases. The color change, however, ends with the stable, typical caramel color, and the only effect of continued treatment is the production of increased quantity, as is shown by the series of parallel curves on the log k figures (Figure 5). The colors of the final products in cooking liquor, simple sugar degradation, and condensation of furfural compounds are identical or very similar, visually and from the slope of the k curves.

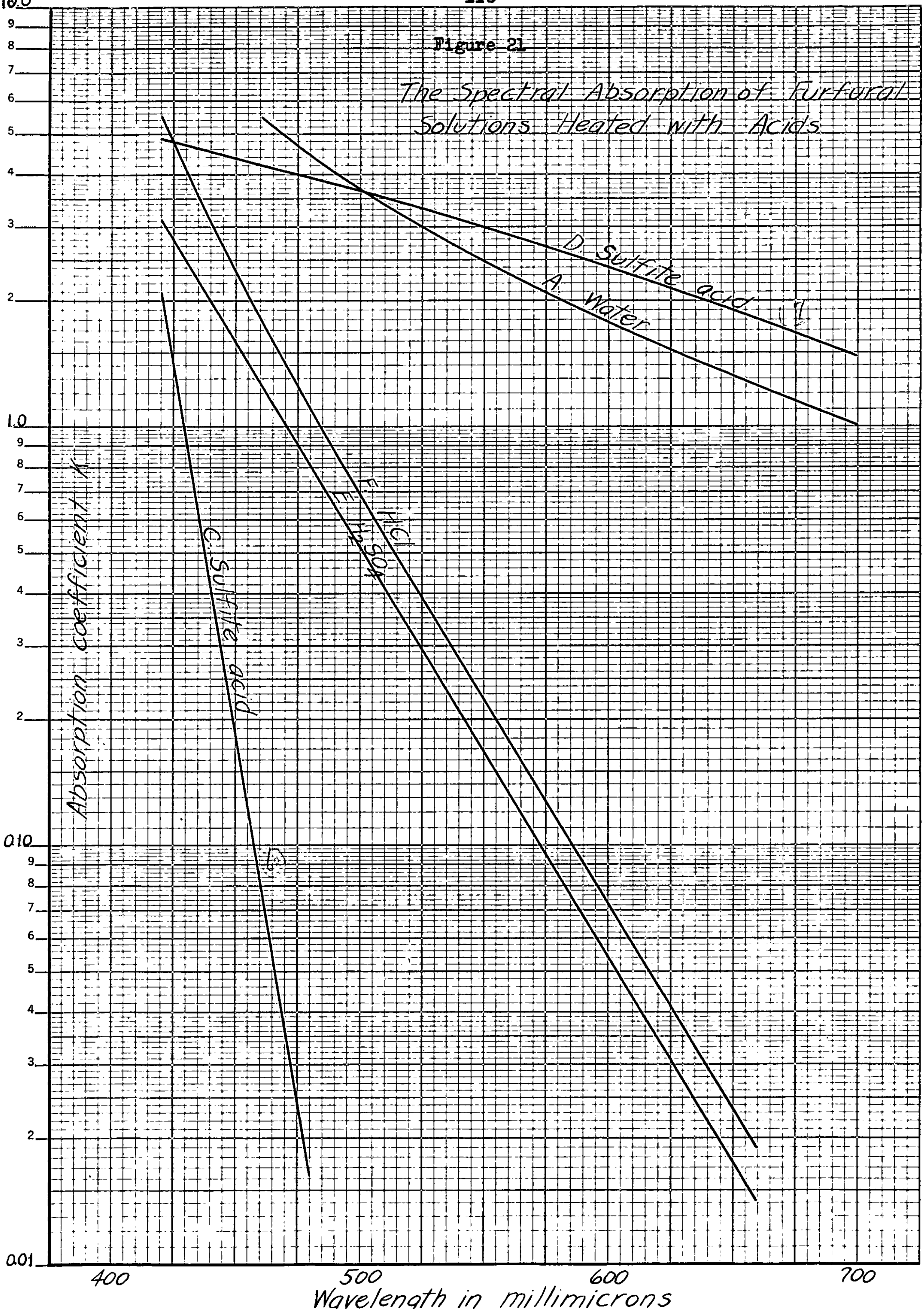
The preceding tests were all run on the pure liquids and not on water solutions. Furfural is soluble only to the extent of 9 per cent in water. A series of test-tube cooks were made with furfural and acids in order to determine the course of the condensation, with aqueous solutions of acids, and the color of the reaction products, particularly with sulfite acid. The cooks were made with the same procedure as in the preceding work on pure sugars; the schedule was five hours of heating at 140° C. The other experimental data are in Table XXIII. The absorption coefficients for the resulting liquors are in Table XXXV in the Appendix, and the colors are graphically presented in Figure 21.

TABLE XXIII

FURFURAL CONDENSATION WITH ACID

Tube	Furfural cc.	Acid 50 cc.	Color	Precipitate	Total SO_2 %	pH
A	1.0	Water	Deep red brown	Black	——	2.0
B	0.1	Sulfite	Water white	None	6.05	1.60
C	0.5	Sulfite	Light yellow	None	5.12	1.48
D	1.0	Sulfite	Deep red brown	Black	4.50	1.44
E	1.0	4 N H_2SO_4	Yellow	Black	——	——
F	1.0	1 N HCl	Yellow	Black	——	——

Figure 21



The Spectral Absorption of Furfural Solutions Heated with Acids
D. Sulfite acid
A. Water
F. HCl
E. H2SO4
C. Sulfite acid
Absorption coefficient K
Wavelength in millimicrons
10.0
1.0
0.10
0.01
400
500
600
700

Furfural condensation with acid and heat is dependent to a great extentupon its concentration in the acid solution. In B, C, and D there was a range of furfural concentration which gave a color range from water white to black. The log *k* plots of liquors C and D again illustrate the dependence of the slope of the color characteristic upon the cooking conditions. The extent of the action of heat alone on a water solution of furfural is shown by the results of the analysis of Tube A. The *p*H dropped from neutral to 2.0, a black precipitate formed, and the solution resembled sulfite waste liquor very closely, visually and by absorption spectra. The action of sulfuric and hydrochloric acids produced voluminous black precipitates and strong yellow solutions, of which the coloring material was some water-soluble stage in the furfural condensation. In all cases the straight line characteristic is evident; the slope of this line has been shown to be dependent on cooking conditions.

6. The Effect of *p*H on Calcium Lignosulfonate and on Sucrose Caramel

The effect of *p*H on sulfite liquor has already been demonstrated. Since sulfite liquor is a mixture of many chromophoric materials, the effect of *p*H on two of the main constituents was determined.

Eighteen grams of oven-dry calcium lignosulfonate, isolated from Cook 3 by dialysis, were dissolved in 500 cc. of water, and 25-cc. portions were pipetted for each *p*H step. To the liquor 0.0974 *N* hydrochloric acid or 0.129 *N* sodium hydroxide was added to the desired pH and then water was added to total 50 cc., making a final concentration of 0.9 gram of the salt per 50 cc. The experimental data are in Table XXIV. The spectral transmission curves are shown in Figure 22, and the corresponding k values are in Table XXXVI (Appendix), with the k values graphically presented in Figure 23.

TABLE XXIV

THE EFFECT OF ADDITION OF ACID AND ALKALI TO CALCIUM LIGNOSULFONATE

Sample	pH	0.0974 N HCl cc.	0.129 N NaOH cc.
A	10.25	----	4.0
B	9.20	----	1.0
C	7.60	----	0.30
D	6.40	Water solution	
E	5.75	0.10	----
F	5.24	0.30	----
G	4.05	0.50	----
H	2.45	2.50	----
I	1.50	20.0	----

There was no precipitation at any pH.

This sample of calcium lignosulfonate was isolated from dark 10-hour liquor. From such a liquor the calcium lignosulfonate is necessarily dark colored, and the k-color characteristic, in acid solution, is linear. This color is probably due to the adsorption

Figure 22

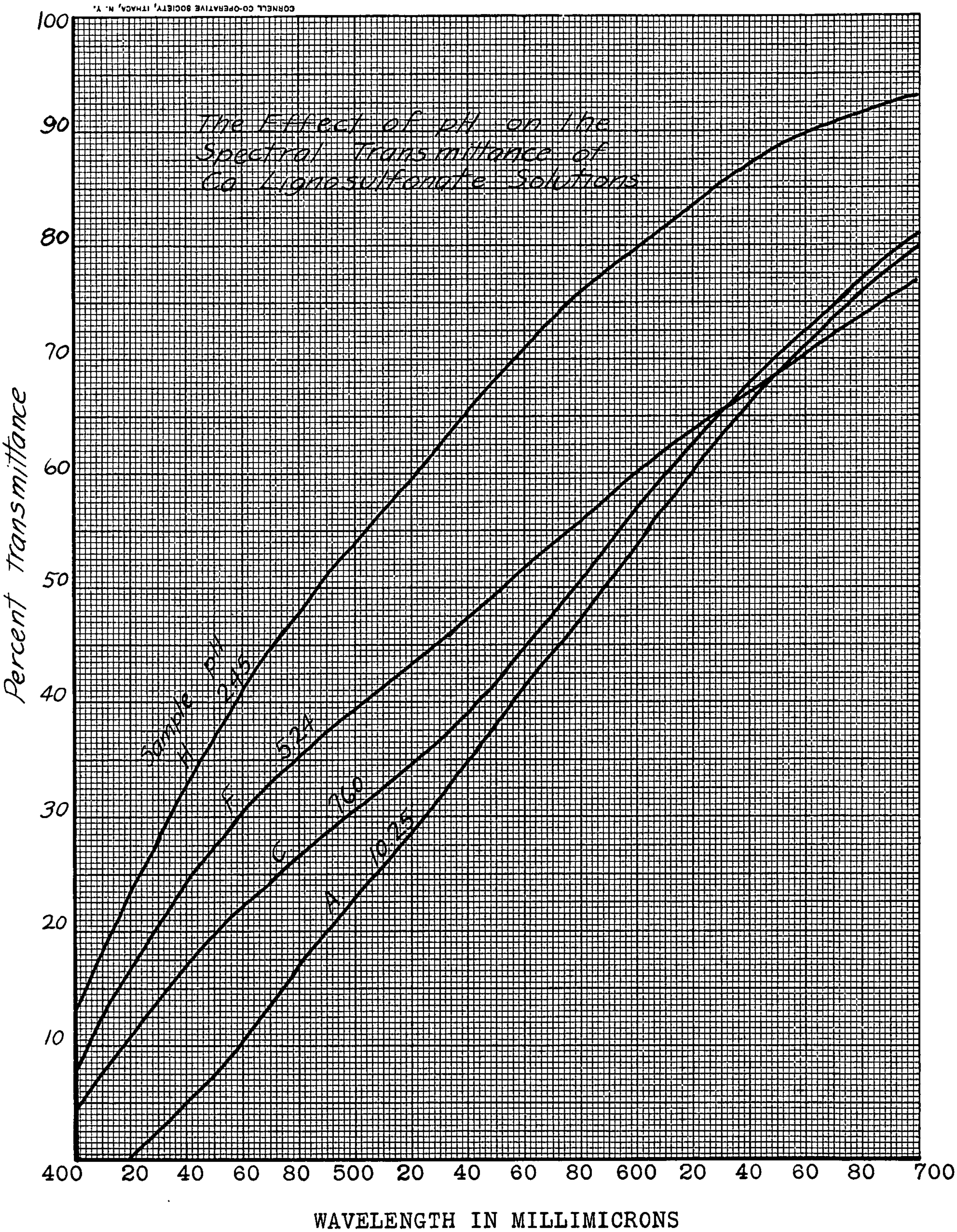
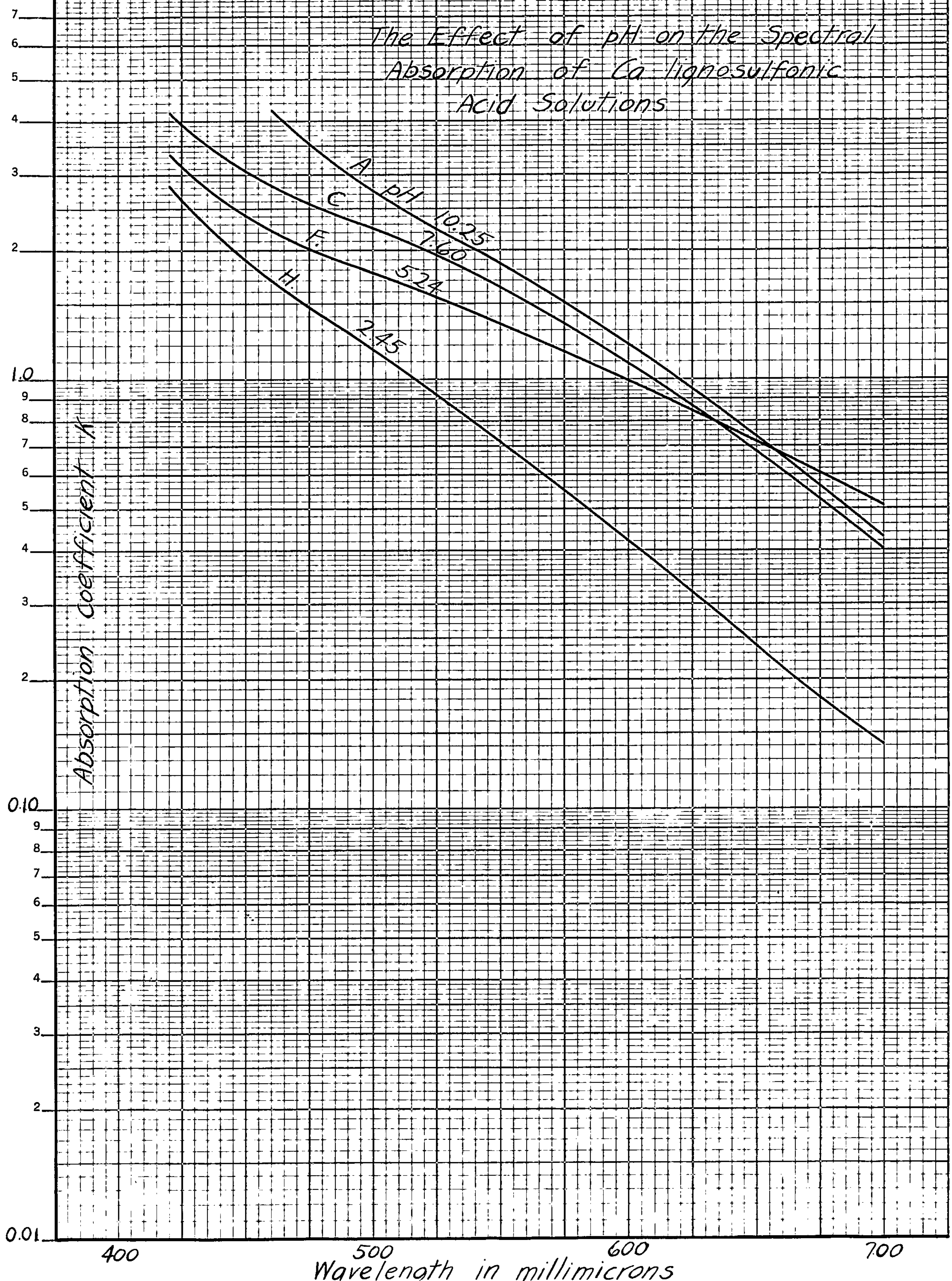

CORNELL CO-OPERATIVE SOCIETY, ITHACA, N. Y.
The Effect of pH on the Spectral Transmittance of Ca Lignosulfonate Solutions
Percent Transmittance
100
90
80
70
60
50
40
30
20
10
Sample pH
H 2.45
F 5.24
C 7.60
A 10.25
400
20
40
60
80
500
20
40
60
80
600
20
40
60
80
700
WAVELENGTH IN MILLIMICRONS

Figure 23


The Effect of pH on the Spectral
Absorption of Ca lignosulfonic
Acid Solutions
A pH 10.25
C 7.60
F. 5.24
H. 2.45
10.0
1.0
0.10
0.01
400
500
600
700
Absorption Coefficient K
Wavelength in millimicrons

of carbohydrate coloring material, rather than being typical of the actual lignin compound color. The kind of acid again seems to be important, because the sulfite liquor solution of Figure 18 is definitely of curved characteristic. As the pH of the solution increases, the depth of color increases, and the hue changes from yellow brown to deep red brown. The intensity of color increases 158 per cent at 460 mµ, 230 per cent at 700 mµ, in the pH range of 1.50 to 10.25.

To complete the picture, the effect of pH on sucrose caramel was studied. One hundred grams of dry sucrose were gently heated to a yield of 60 grams. This caramel was dissolved and diluted with water to suitable strength, and 50-cc. portions were pipetted for each pH step, for addition of hydrochloric acid and sodium hydroxide to suitable pH, with final dilution to 100 cc. Table XXV contains the experimental details. No precipitation occurred at any pH. The spectral transmittance curves of the resulting caramel solutions are in Figure 24, with the k values in Table XXXVII in the Appendix and the log k values plotted in Figure 25.

TABLE XXV

THE EFFECT OF ADDITION OF ACID AND ALKALI TO SUCROSE CARAMEL SOLUTIONS

Sample	pH	0.0974 N HCl cc.	0.116 N NaOH cc.
A	11.10	——	15.0
B	10.80	——	5.0
C	9.10	——	2.0
D	7.15	——	1.0
E	6.50	——	0.5
F	4.45	Water solution	
G	3.06	1.0	——
H	2.75	2.5	——
I	2.40	5.0	——

Figure 24

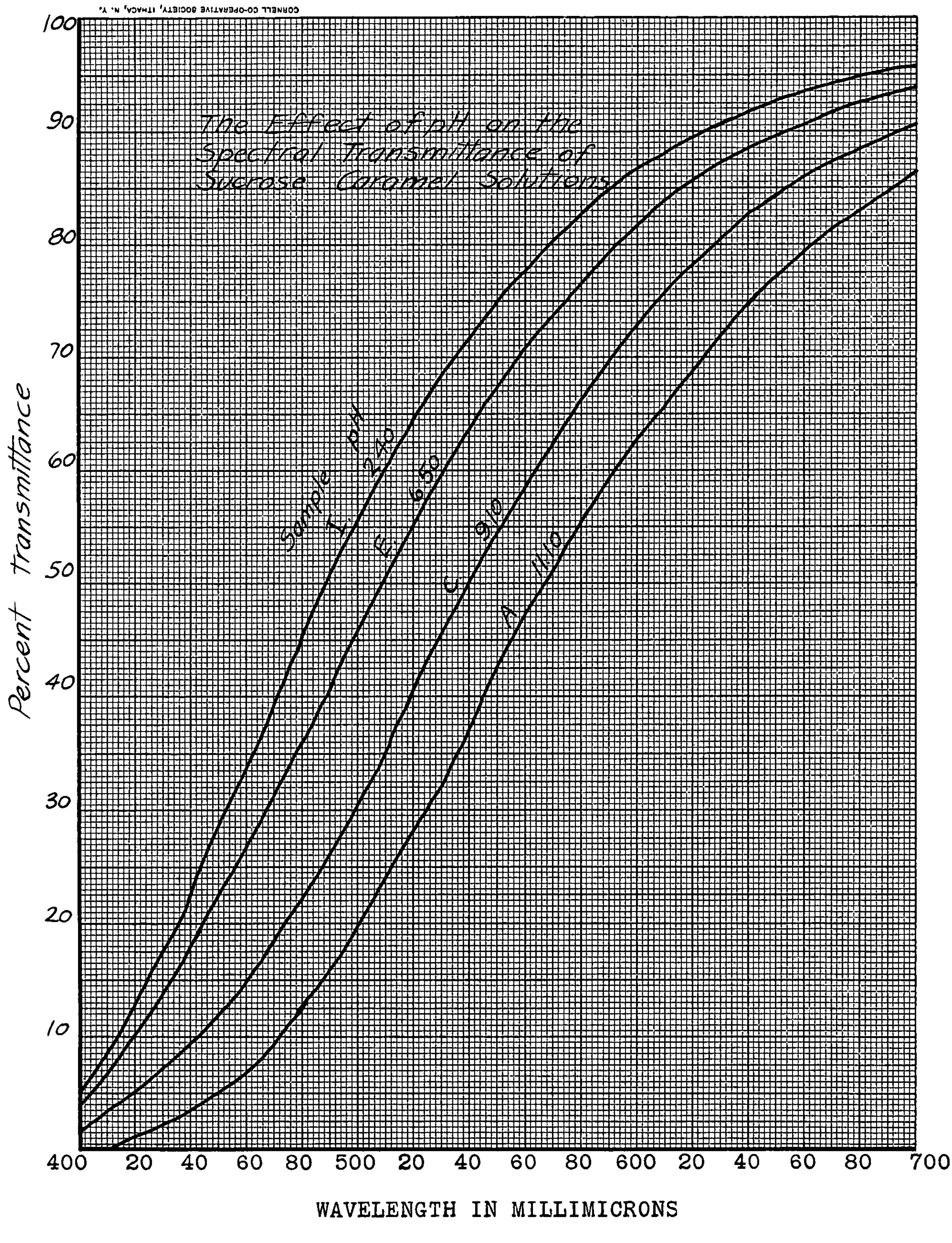
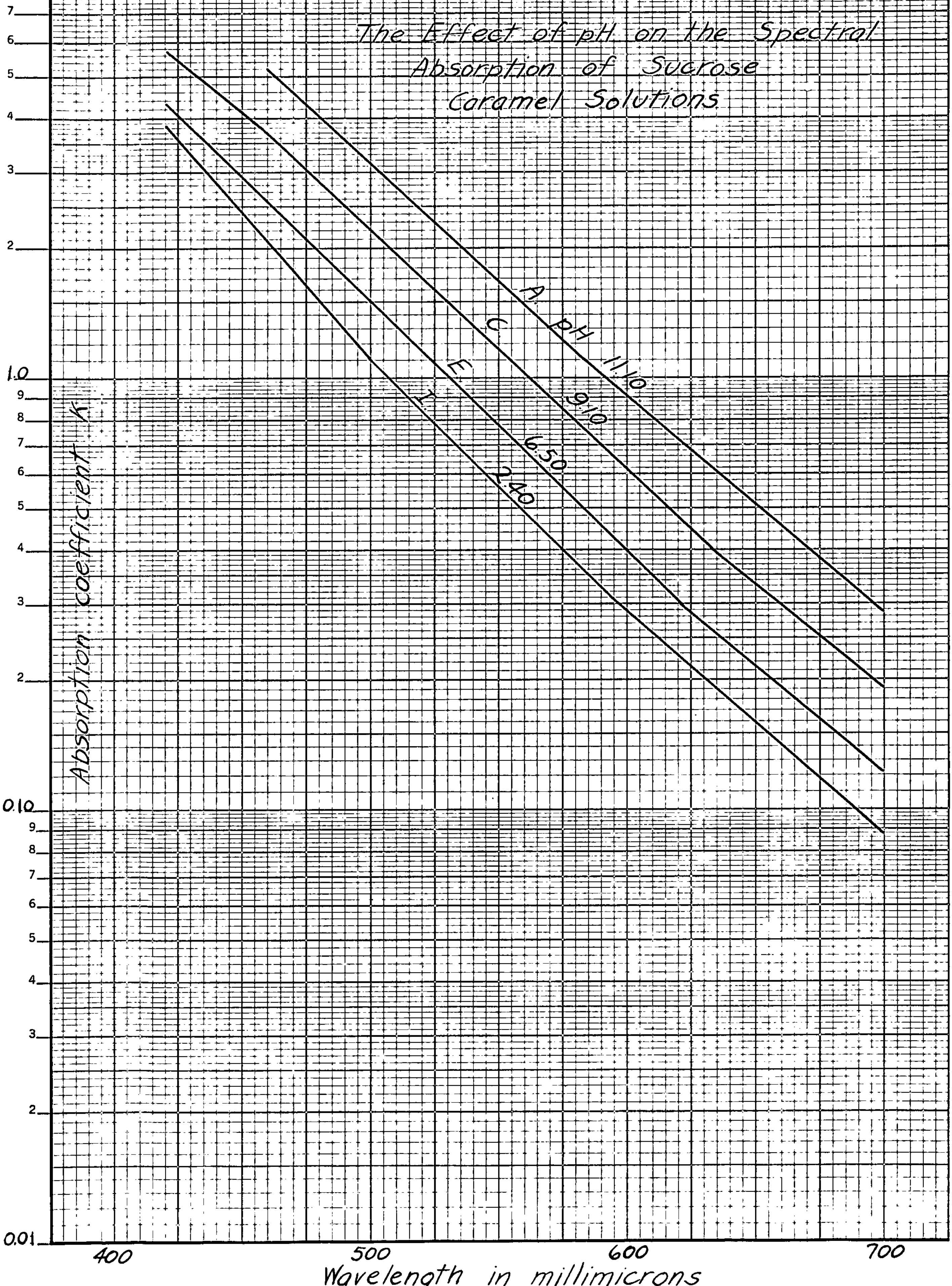

CORNELL CO-OPERATIVE SOCIETY, ITHACA, N. Y.
The Effect of pH on the Spectral Transmittance of Sucrose Caramel Solutions
Sample
pH
I. 2.40
E. 6.50
C. 9.10
A. 11.10
Percent Transmittance
100
90
80
70
60
50
40
30
20
10
400
20
40
60
80
500
20
40
60
80
600
20
40
60
80
700
WAVELENGTH IN MILLIMICRONS

Figure 25


The Effect of pH on the Spectral Absorption of Sucrose Caramel Solutions
A pH 11.10
C 9.10
E 6.50
I 2.40
Absorption coefficient K
Wavelength in millimicrons
10.0
1.0
0.10
0.01
400
500
600
700

The character of the color of sucrose caramel is almost entirely unchanged by the addition of acid or alkali. The straight line characteristic is observed over the entire pH range. The increase of absorption coefficient is 156 per cent at 460 mμ and 226 per cent at 700 mμ, with a pH increase of from 2.40 to 11.10. The increase of absorption coefficient with pH change was very much greater for waste sulfite liquor (Table XIV) than for either the isolated calcium lignosulfonate or caramel, 340 to 740 per cent as against 150 to 225 per cent.

C. THE VARIABLES OF COOKING SCHEDULE AND WOOD SPECIES

In the commercial production of sulfite pulp the most important factors affecting the color of the liquor are the cooking schedule employed and the raw material, wood, with variations in the wood from one species to another and within a species.

1. Schedule

The effect of schedule, pressure, and temperature was studied on a series of cooks made in the small digester used for the first part of this work, the cooks being made by the pulping class of The Institute of Paper Chemistry. Duplicate cooks were made at a range of 131° to 143° C. maximum temperature, with no relief (pressure dependent) but with the standard 10-hour temperature schedule already described, with 5940 grams (oven-dry equivalent) of spruce chips (standard lot), and with 26 liters of calcium base acid, 6.20 per cent total and 1.20 per cent combined sulfur dioxide.

The results of the analyses of this series of cooks are given in Table XXVI, and the transmission spectra are shown in Figure 26.

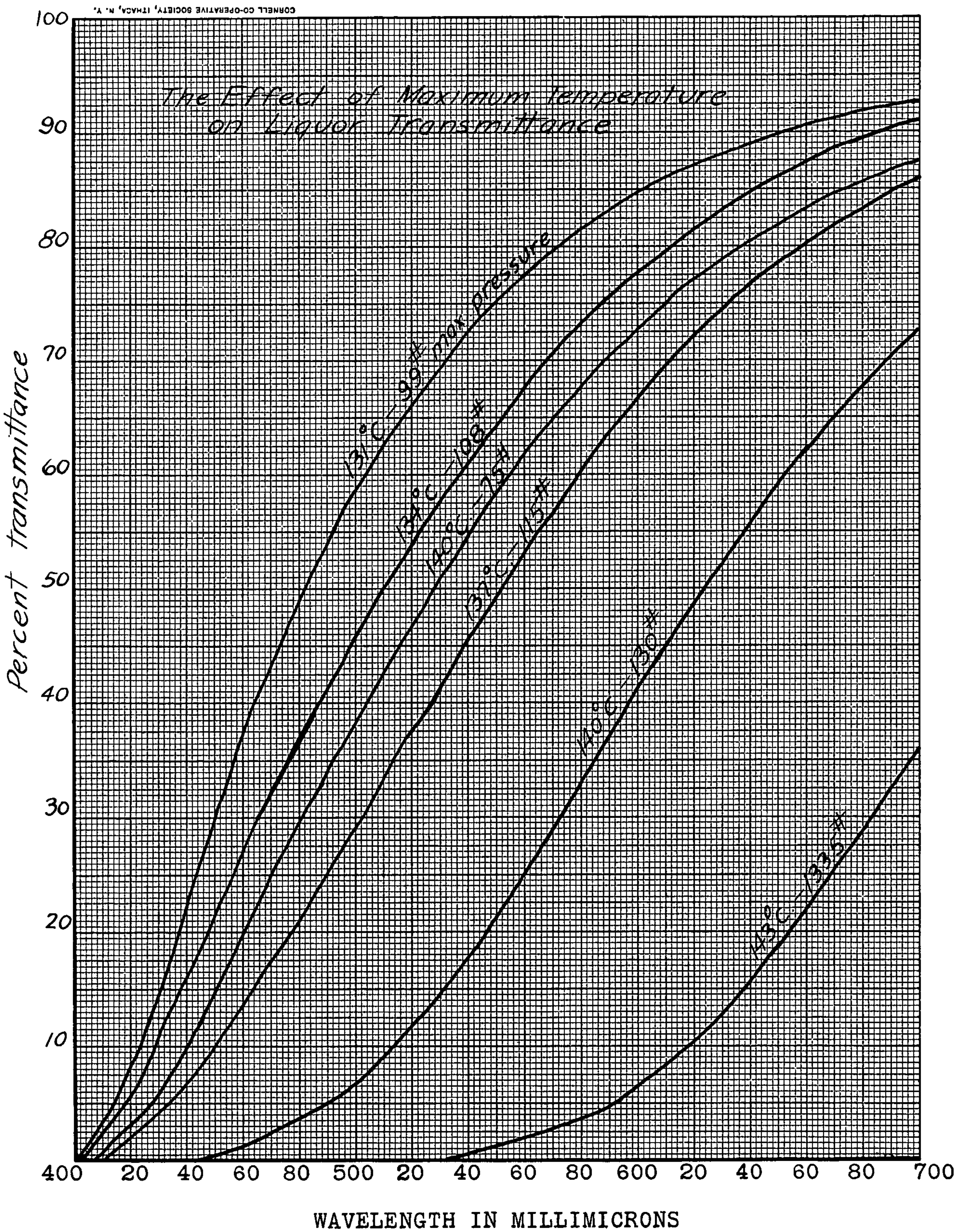
TABLE XXVI

EFFECT OF TEMPERATURE AND PRESSURE IN SULFITE COOKING

Cook Number	Maximum Temperature ° C.	Maximum Pressure lb./sq. in.	Total Yield %	$KMnO_4$ Number	Transmission 600 mμ %	Absorption Coefficient 600 mμ
15A	140	75	46.6	12.2	72.8	0.61
15B	140	75	46.7	12.6	73.5	0.59
21A	131	75	51.4	19.5	85.1	0.31
21B	131	75	50.7	18.3	84.8	0.31
16A	143	133.5	41.1	7.1	0.0	——
16B	143	133.5	41.4	7.2	6.5	5.25
17A	140	130	43.1	6.5	40.8	1.72
17B	140	123.5	43.8	7.3	34.4	2.04
18A	137	115	46.3	11.7	71.1	0.66
18B	137	115	46.6	10.4	66.7	0.77
19A	134	107	48.0	12.1	81.1	0.40
19B	134	108	47.5	12.4	76.0	0.52
20A	131	99	50.8	18.6	85.0	0.31
20B	131	99.5	49.7	17.7	57.2	——

Cooks 15 and 21 are included to give a comparison with commercial practice. These cooks were relieved, holding 75-pound maximum pressure, while in the others the excess pressure increased the effect of higher temperature. The effect of increasing maximum temperature was to decrease the yield, the permanganate number, and the lignin content of the pulp and to increase the absorption coefficient of the

Figure 26


CORNELL CO-OPERATIVE SOCIETY, ITHACA, N. Y.
The Effect of Maximum Temperature on Liquor Transmittance
131°C — 99# max pressure
134°C — 108#
140°C — 75#
137°C — 115#
140°C — 130#
143°C — 133.5#
Percent transmittance
100
90
80
70
60
50
40
30
20
10
400
20
40
60
80
500
20
40
60
80
600
20
40
60
80
700
WAVELENGTH IN MILLIMICRONS

liquor. The yield and permanganate number correlated well with the maximum temperature, and the absorption coefficient of the liquor is related to all three. This is illustrated by Figure 27.

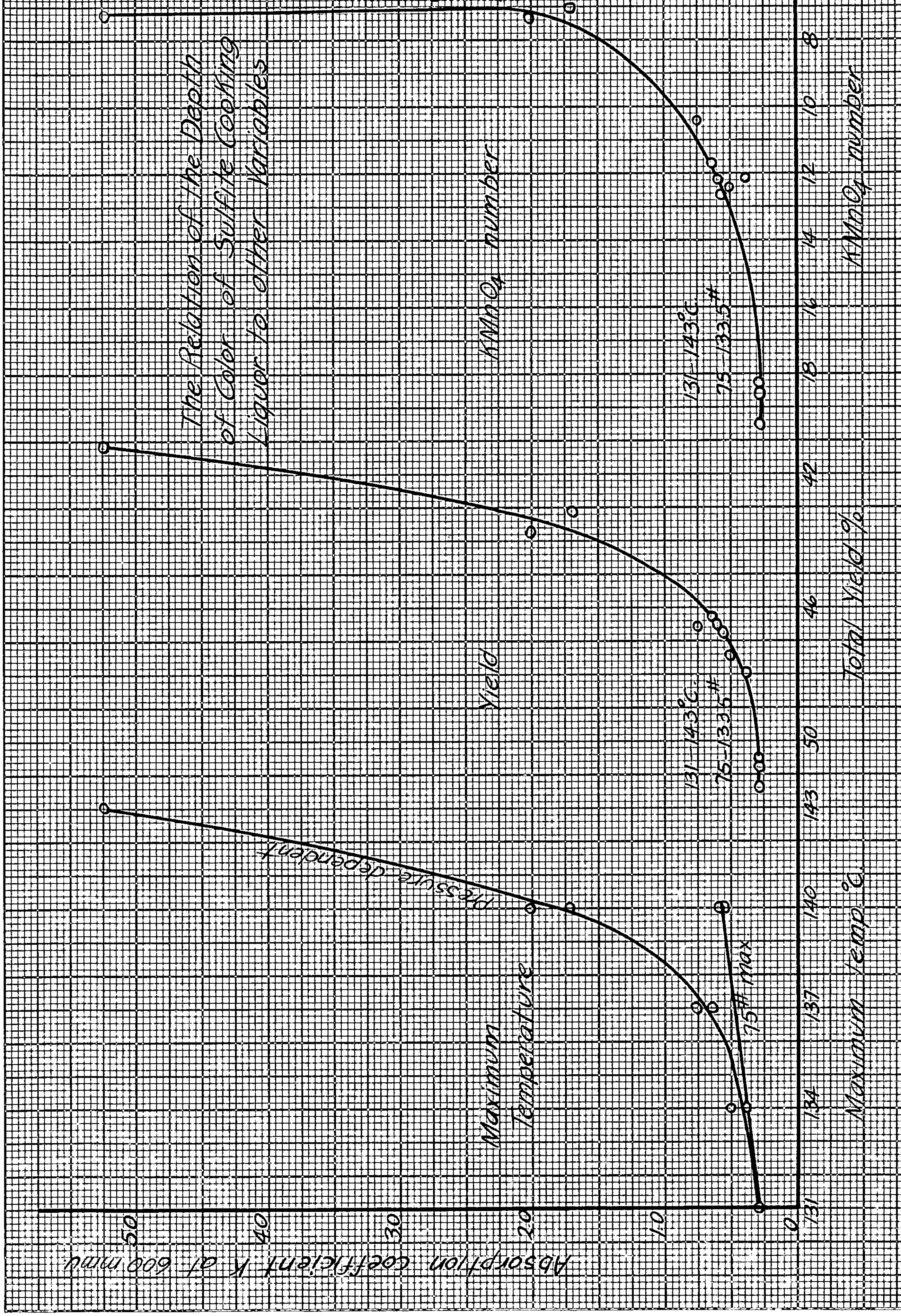
The most significant finding here was that the yield and permanganate number of a cook are related directly to the liquor color, independently of the cooking conditions. The pressure has been shown to be a major variable in cooking, but here the yield and permanganate number of the pulp and the liquor color of cooks at 75-pound pressure agree with the results of cooks at 100- and 110-pound pressure, with compensating lower maximum temperature. This is the logical result, namely, that the liquor color is a measure of the degree of cooking, independently of the variables in the cook.

The duplicate cooks did not agree in liquor color as well with small scale equipment as with commercial equipment. The cooks at excessive conditions were particularly difficult to duplicate because of the extremely rapid color increase at the high temperature range.

2. The Variation in the Color of Sulfite Liquor with Various Species of Wood

The previous phases of this investigation have been concerned only with spruce as the raw material. Many other species of hardwoods and softwoods are pulped commercially by the sulfite process, either individually or in mixture. The hardwoods are very different from softwoods in wood constituents, and a wide variation in the

Figure 27


The Relation of the Depth
of Color of Sulfite Cooking
Liquor to other Variables
KMnO4 number
131-143°C.
75-133.5 #
Yield
131-143°C.
75-133.5 #
Maximum
Temperature
Pressure dependent
75# max
Absorption coefficient K at 600 mμ
0
1.0
2.0
3.0
4.0
5.0
131
134
137
140
143
50
46
42
18
16
14
12
10
8
6
Maximum Temp °C
Total Yield %
KMnO4 number

liquor color would be expected. The composition of sprucewood has been discussed in some detail, and it has been pointed out that softwoods in general contain 8 to 11 per cent pentosans. Hardwoods are very rich in pentosans, containing 22 to 26 per cent; this fraction is important in a discussion of liquor color because of the production of furfural from pentosans on acid treatment. The lignin content of hardwoods varies from 18 to 22 per cent, in contrast to 26 to 30 per cent for softwoods. Hardwood lignin is definitely different in nature from that of sprucewood; it has a higher methoxyl content, and the ultraviolet spectral absorption curves are different.

The woods used for this comparison were spruce, balsam fir, western hemlock, beech, and white birch. The physical tests on the woods used are summarized in Table XXVII.

TABLE XXVII

PHYSICAL ANALYSIS OF WOODS USED

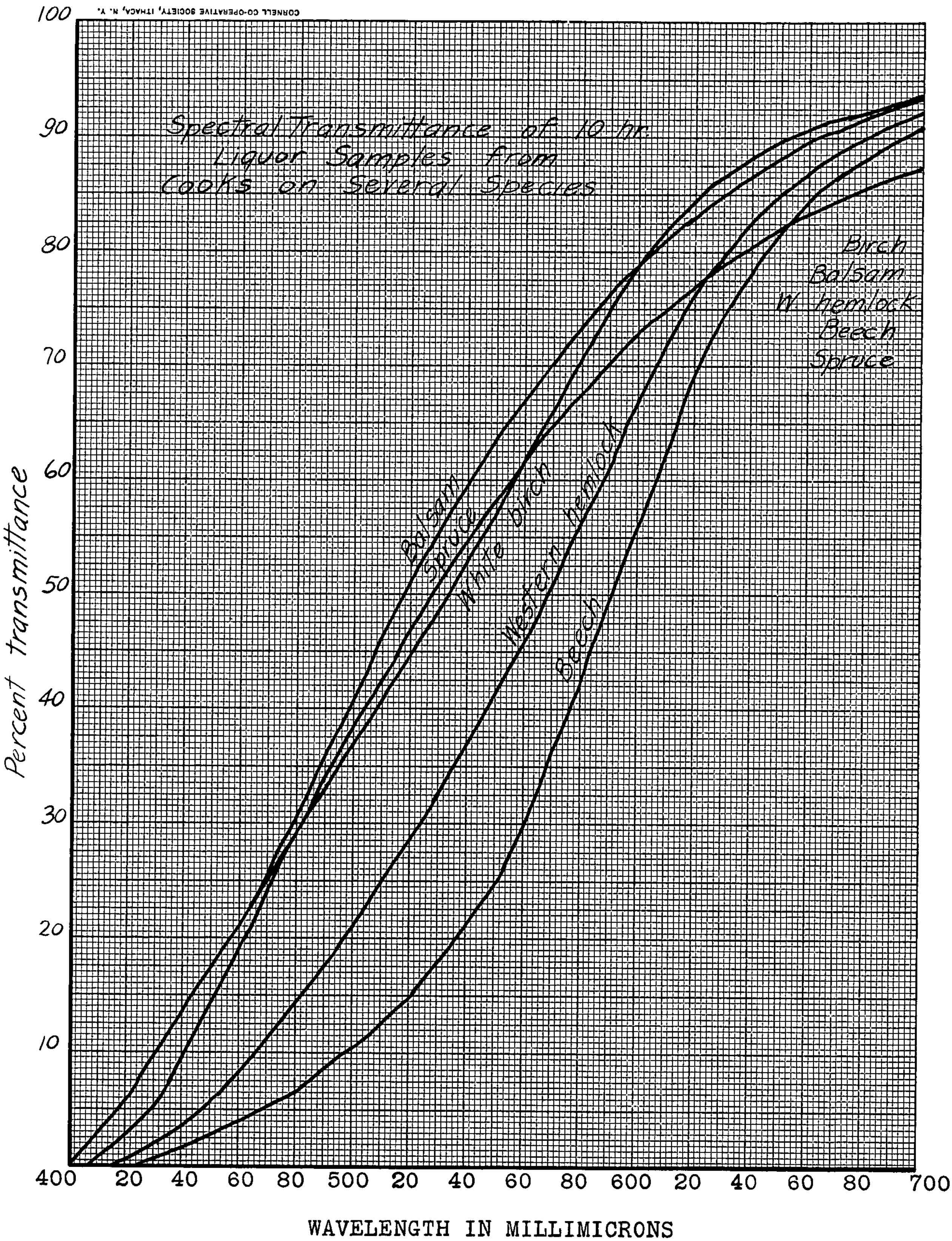
Wood	Age in Years	Diameter inches	Density in Pounds per Cubic Foot	Moisture %
Spruce	86	6.0	28.6	39.9
Balsam fir	70	6.8	23.7	21.1
Western hemlock	458	21.2	29.0	15.0
Beech	52	7.9	43.0	41.1
White birch	50	7.2	40.2	42.9

These woods were barked and chipped by the same procedure as was used for spruce; 5940 grams (oven-dry equivalent) of each was cooked with 26 liters of 6.20 per cent total and 1.20 per cent combined sulfur dioxide by the standard 10-hour schedule. Cook 15A of the previous section was used for the spruce comparison cook. Liquor samples were taken at seven and ten hours; the pulp was washed and prepared for analysis by the standard procedure. The spectral transmittance curves and the log k curves are presented in Figures 28 and 29, respectively, with the absorption coefficients in Table XXXVIII in the Appendix. From the transmittance spectra of Figure 28 it is evident that the cooking of beech produces the darkest liquor, followed by western hemlock, spruce, white birch, and balsam, in that order. The curves of log k plot indicate that the actual hue varies widely with the wood species and that the colors produced are not simple. Western hemlock and beech in particular produce liquors which contain color components not present in spruce liquor. The possibility exists that extractives, lignin, and the hemicellulose fraction of the woods are all concerned.

The conclusions reached from the transmittance spectra concerning the severity of the cook on each wood are tested by chemical analysis of the liquor and pulp produced. The data are presented in Table XXVIII.

The balsam fir used in this study produced a hard cook, with light liquor, high yield, and high permanganate number. The beech gave the lowest yield, a high permanganate number, and the deepest

Figure 28


CORNELL CO-OPERATIVE SOCIETY, ITHACA, N. Y.
Spectral Transmittance of 10 hr. Liquor Samples from Cooks on Several Species
Birch
Balsam
W. hemlock
Beech
Spruce
Balsam
Spruce
White birch
Western hemlock
Beech
Percent transmittance
100
90
80
70
60
50
40
30
20
10
400
20
40
60
80
500
20
40
60
80
600
20
40
60
80
700
WAVELENGTH IN MILLIMICRONS

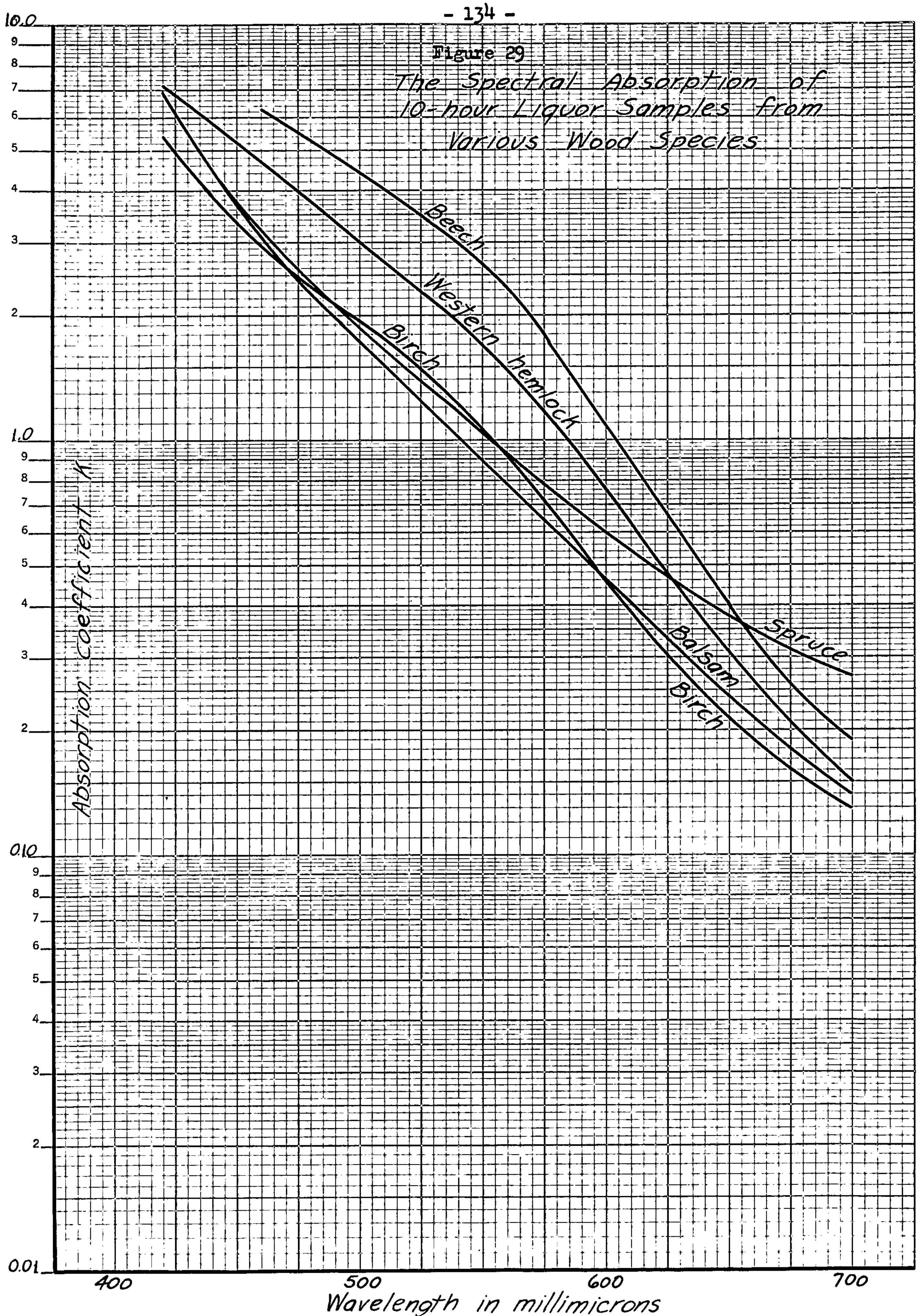


Figure 29
The Spectral Absorption of
10-hour Liquor Samples from
Various Wood Species
Beech
Western hemlock
Birch
Spruce
Balsam
Birch
10.0
1.0
0.10
0.01
400
500
600
700
Absorption Coefficient K
Wavelength in millimicrons

TABLE XXVIII

COMPARISON OF PULP AND LIQUOR FROM SEVERAL SPECIES OF WOOD

	7-Hour Samples				10-Hour Samples				
	Balsam	Western Hemlock	Beech	Birch	Spruce	Balsam	Western Hemlock	Beech	Birch
Pulp {Total Yield, %					46.6	49.1	47.0	44.3	46.8
Pulp {$KMnO_4$ Number					12.2	14.5	11.2	13.5	6.6
pH	1.48	1.42	1.42	1.37	——	1.37	1.40	1.25	1.20
Total SO_2, %	2.51	2.25	2.50	2.90	——	1.09	0.85	0.83	0.73
Total Solids	102.9	113.8	101.4	97.3	——	143.1	148.4	121.0	121.4
Methoxyl from Solids	5.98	6.86	7.57	8.03	——	10.5	11.1	10.3	10.6
Benzidine Precipitate	27.3	35.4	17.0	12.5	——	66.6	74.0	30.4	21.4
Methoxyl of Precipitate, %	10.8	10.8	12.3	16.7	——	10.8	10.8	14.4	16.3
Methoxyl from Benzidine Precipitate	2.94	3.83	2.09	2.09	——	7.22	8.04	4.37	3.50
Methoxyl Precipitated by Benzidine, %	49.1	55.8	27.6	26.0	——	68.7	72.2	42.4	33.0
Reducing Sugars from Benzidine Precipitate	22.9	23.1	28.4	26.4	——	27.7	29.6	30.2	34.5
Total Sugars in Raw Liquor	24.6	26.3	30.0	29.1	——	29.3	29.5	33.5	36.3
Sugar not Precipitated, %	93.1	87.8	94.8	90.7	——	94.8	100	90.1	95.1

All concentrations in grams per liter.

liquor color. The birch was very satisfactory from the practical viewpoint, with high yield, low permanganate number, and a very light-colored pulp.

The analyses of the liquor samples indicated again that the liquor constituents are of little use in the attempt to determine the chromophoric groups present. The hardwoods produced more reducing sugars calculated as glucose and, if the reducing power of the pentoses is taken into account, this difference is even greater. The total solids content in the 10-hour liquors of the softwoods was 20 per cent higher than that of the hardwoods, with the same or lower yield. The volume of liquor and weight of oven-dry wood charged were identical, and the low solids content of the hardwood liquors indicates that considerably more material is removed from the fibers during the washing of the hardwood pulp or, less likely, that a high percentage of the total solids content of the liquor is volatile at 105° C. under the conditions of the total solids determination.

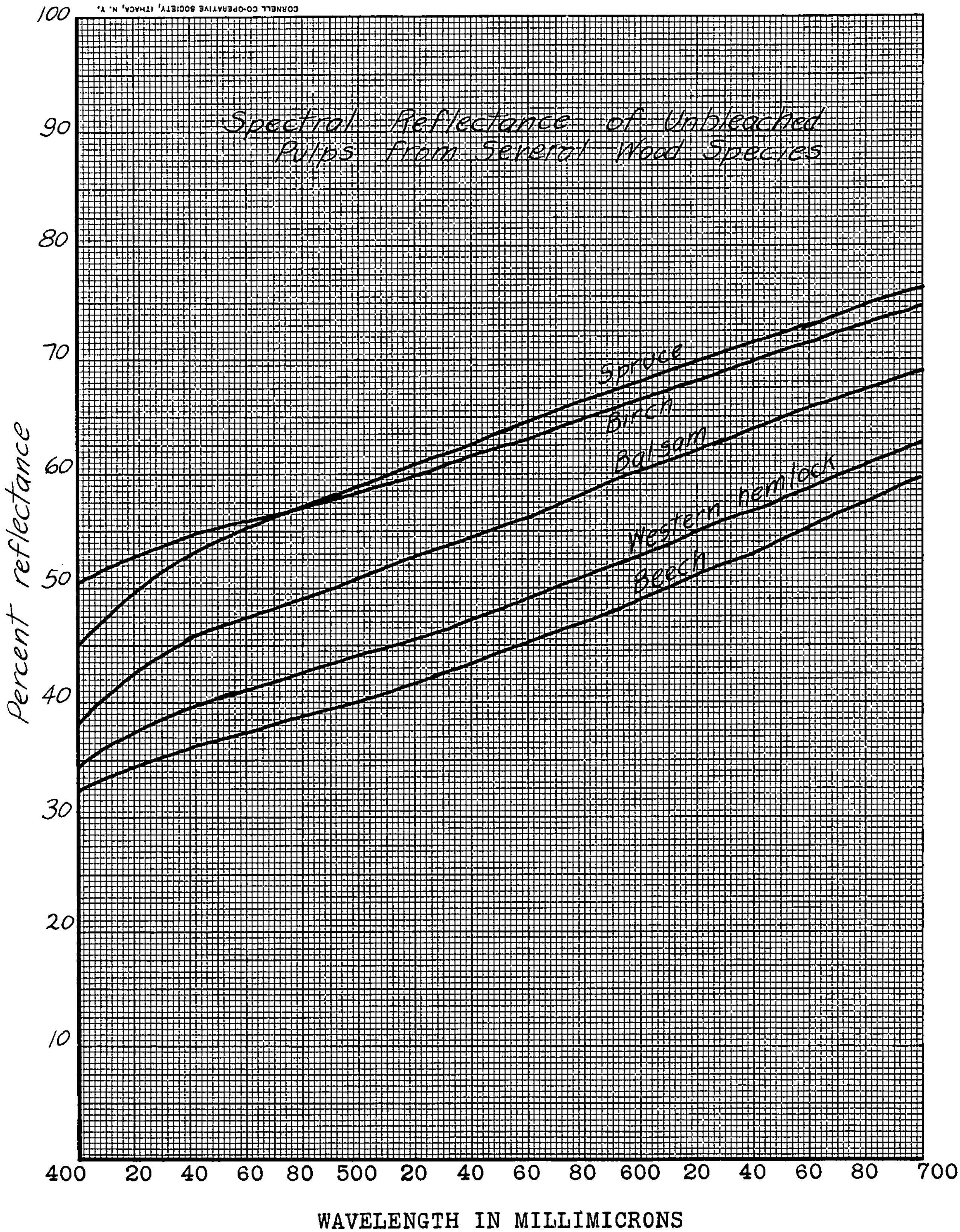
The lignin fractions of these woods are definitely different; whereas those of balsam, western hemlock, and spruce are very similar, that of the hardwoods has a higher methoxyl content. The benzidine procedure for the determination of lignin in sulfite liquor is almost a complete failure for hardwood liquors. Only a maximum of 40 per cent of the methoxyl content was precipitated, as contrasted with the 75 per cent recovery from spruce liquors. The balsam and western hemlock lignin salts were only fair in this respect, with 69 and 72 per cent recovery of methoxyl. The methoxyl content of the softwood lignin-benzidine precipitates indicated that the lignins of balsam and western hemlock are similar to and contain approximately the same amount of methoxyl as does spruce. The methoxyl content of the hard-wood lignin-benzidine precipitates was appreciably higher than that of spruce, in agreement with the higher methoxyl content of these hard-wood lignins.

The color of unbleached pulp may come from three sources, (a) the residual lignin, (b) coloring matter of the wood not removed by the pulping process, and (c) coloring matter absorbed from the cooking liquor during the last part of the digestion. The bleaching problem is the removal of all of these.

The unbleached pulps from this series of cooks of different species show a wide range of color. These colors are shown in Figure 30 in the form of spectral reflectivity curves.

The depth of color corresponds fairly well with the depth of liquor color as shown in Figure 28. The beech pulp and liquor have definitely the lowest color, and bleaching experiments have shown that beech has a bleaching requirement far higher than the lignin content and permanganate number indicate. The balsam cook of this series produced a fairly raw pulp and, consequently, a dark pulp, in contrast to the light liquor. The spruce and birch are definitely superior woods for sulfite pulping, and this work only confirms commercial practice.

Figure 30


CORNELL CO-OPERATIVE SOCIETY, ITHACA, N. Y.
Spectral Reflectance of Unbleached Pulps from Several Wood Species
Percent reflectance
100
90
80
70
60
50
40
30
20
10
Spruce
Birch
Balsam
Western hemlock
Beech
400
20
40
60
80
500
20
40
60
80
600
20
40
60
80
700
WAVELENGTH IN MILLIMICRONS

IV

SUMMARY

The course of the sulfite cook cannot be divided into two or three arbitrary stages on the basis of the evidence obtained in this work, that is, the optical and chemical analyses of the liquor. On the contrary, the rate of increase of the major constituents, lignin and sugar, is practically linear after a temperature of 100° C. is reached, almost to the point of satisfactory delignification and blowing of the cook. A maximum is reached at about nine and one-half hours' time in the cooking schedule used; continuing the cook to actual degradation of the pulp by burning did not affect the concentration of the major constituents of the liquor.

The rate of increase of the coloring matter of the liquor is entirely different from that of the major constituents in the entire cook. However, a practically linear relationship has been established between color and the lignin content of the liquor from three to seven hours, corresponding to the temperature range of 110° to 140° C. This correlation is true only for lignin and color and is not valid for the sugar-color concentration relationship, because an appreciable color is present before sugar can be detected and because the weight of evidence is against the possibility of much sugar degradation at the low temperature in this period. The concentration of calcium lignosulfonate, known to be strongly chromophoric, is two

to four times greater during this period than the concentration of the undegraded sugar.

The character of the color changes through the course of the cook from light yellow brown to deep red brown. In the early hours of the cook, some chromophoric material is dissolved and absorbs strongly at 500 to 700 mμ; with increasing temperature and sulfonation conditions, this color is destroyed, but only in the red end of the spectrum. Other coloring material is dissolved at about the sixth hour of the cook and masks this reversion. The exact mechanism of this color reversion cannot be explained, but it is undoubtedly concerned with either the water-soluble material of spruce or with the progress of sulfonation of lignin.

The major change in the color of the liquor, however, takes place in the 6-1/2- to 8-hour period, in which the color characteristic, the log k curve, changes from a decided curve to a straight line. This change is explained by assuming that the lignin color with curved characteristic is being masked by the color of the carbohydrate degradation products, the caramel, which has the linear color characteristic. The weight of the evidence is in support of this color difference, but there are a few cases of lignin and caramel color which do not conform to this classification.

Isolated calcium and sodium lignosulfonates and the soda base liquor produced by digestion of native lignin all have approximately the same color, with the curved characteristic and appreciable absorption in the red end of the spectrum, producing a yellow brown rather than a yellow or red brown liquor. The color of the isolated lignin compounds is appreciably affected by the cooking conditions; those produced from highly heated liquors are much darker and approach the color of burnt carbohydrate material. This is probably only the physical effect of adsorption of caramel color on the colloidal lignin compound.

The colors produced by heating pure sugars in acid solution are, in general, of the straight line characteristic. However, xylose and mannose do not produce this color in sulfite liquor on mild heating, although in hydrochloric acid they both give deep-colored solutions which have the linear log k characteristic. The slope of the linear log k characteristic is apparently a function of the severity of the sugar degradation. The early stages of acid attack on sugars, with low temperature, hydrogen-ion concentration, and time, develop strong yellow colors with no red absorption and consequently no brown tint. Lignin solutions under all conditions of treatment absorb comparatively strongly in the red end of the spectrum and so are definitely brown.

As the sugar degradation proceeds, the slope of the linear log k characteristic becomes less, a result of the increased red light absorption, and the solution becomes the typical deep red brown. There is a strong resemblance between the color in some stages in this sugar degradation and the color of calcium lignosulfonate, and it is impossible to identify an unknown solution by color alone, either visually or by spectral absorption data, in the range of the spectrum from 400 to 700 mμ.

The course of acid degradation of carbohydrates, from cellulose and hemicelluloses to colored solution, is as follows:

Cellulose Hexosans Pentosans	⟶	Hexoses Pentoses	⟶	Hydroxymethylfurfural Methylfurfural Furfural Humic substances	⟶	Highly colored condensation products, from water-soluble of colloidal material to insoluble humic substances

The condensation of furfural takes place with age alone and is accelerated greatly by acid and heat. The colors produced follow the same course as those found for pure sugars, from very yellow solutions with steep, linear log <u>k</u> color characteristic to deep red brown colors, still with the linear characteristic. Furfuryl alcohol, methylfurfural, and hydroxymethylfurfural have the same color.

An attempt to explain the color of sulfite liquor during wood digestion up to seven hours has already been made. From the seventh hour to the end of the cook the color increases at a rate far out of proportion to the increase in concentration of any of the chemically measurable liquor components. On the basis of the preceding discussion, the assumption is now made that this great color increase is due in most part to the degradation of carbohydrate material, pentosans and hexosans. This theory is based on experiments in which isolated waste liquor, free from the buffering action of fiber, was observed to increase 4600 per cent in color concentration, while the sugar content decreased 44 per cent and the lignin decreased only 4.7 per cent. Calcium lignosulfonate is almost absolutely stable to sulfite acid digestion, with a very slight color increase on prolonged heating, in marked contrast to the great amount of color produced by acid digestion of pure sugars. The liquor sampled at the seventh hour had the lignin color, which changed to that of burnt sugar on heating. This color change and increase was much more marked than that taking place in liquor in contact with fiber; for comparable time and temperature the effect was ten times as great. A part of the carbohydrates of the 7-hour liquor sample were nonreducing and are apparently present as polysaccharides with reducing power lower than that of the simple molecule. These sugars were completely hydrolyzed by further heating.

The effect of age on the color of liquor samples from all stages of the cook was observed and carefully checked. It was thought possible that a color increase and reddening might start as soon as the liquor samples were exposed to the air, an action analogous to that of the reddening of unbleached sulfite pulp on exposure to air. There was absolutely no indication that this occurred in any stage of cooking of five species of wood. The spectral transmittance curves of all these liquors were identical to 0.5 per cent or less, up to several days after sampling, on liquors kept in ordinary glass bottles with rubber stoppers. Aging tests up to seventy days indicated that no change in color occurs in this period, but another test indicated a slight increase in color. Calcium sulfite settles out of these samples, the reducing sugar content decreases greatly, and the methoxyl content drops, but the color is very stable. This indicates that the caramel color is a stable aldehydic resinous condensation product.

The scheme of analysis of the liquor samples was not entirely satisfactory, but with some interpretation the values obtained for lignin and sugar content are not too obscure. The problem in this analysis is the quantitative separation of sugar and lignin and the measurement of each. Two determinations of the lignin content, the methoxyl content of the total dried solids, and the amount of the benzidine precipitate were always carried out. The methoxyl content of the solids indicates more than the actual amount of the lignin present, because the native lignin contains only about 85 per cent of the methoxyl content. The benzidine precipitate, on the other hand, contains only about 75 per cent of the total methoxyl content, and therefore all of the lignin is not precipitated.

Two sugar analyses were also run, on the original liquor and on the filtrate from the benzidine precipitation, which gave values of about 95 per cent of those on the raw liquor. This raised the question of the reducing power of calcium lignosulfonate. Native lignin undoubtedly does reduce Fehling's solution, but the reducing power of the salt is still undecided. The weight of evidence is against any reducing power, for preparations have been made with none. The dialyzed product prepared in this study contained 1 per cent reducing sugars as glucose, but this could easily result from adsorption. The 5 per cent loss in the benzidine precipitation procedure could also be mechanical entrainment or adsorption by the flocculent benzidine-lignin precipitate, and the analysis of raw liquor, considering these factors, is probably the best method of determining the sugar content of sulfite liquor. The cuprous oxide is more difficult to wash in the presence of the lignin, but the procedure is still very accurate.

It is very difficult to obtain accurate absorption coefficients on dark, highly colored liquors, using a fixed optical system. Sulfite liquor does not obey Beer's law on dilution with water, fresh sulfite liquor, or dilute hydrochloric acid. It is probable, however, that a buffered solution could be found that would be a satisfactory diluent for this phase of the analysis.

All of the important constituents of sprucewood were isolated and cooked separately. The ether-soluble material was light yellow in color and not appreciably attacked by sulfite acid. The alcohol-benzene-soluble material, on the other hand, was dark red brown and dissolved almost completely in sulfite acid when digested. The water-soluble fractions are all dark red brown as isolated and increase/in color on acid degradation. The hemicellulose was the greatest source of color, as was expected, the holocellulose was attacked in proportion to the hemicellulose content, and the resistant cellulose fraction was little affected.

The hemicellulose fraction degradation was further investigated by cooking the pure sugars which have been isolated from spruce and which come mainly from the hemicellulose. The results indicate that the pentoses, xylose and arabinose, produce the most color and are attacked first. The aldohexoses, glucose, mannose, and galactose, are all similar in behavior, and the ketohexose, levulose, is attacked least and produces the least color.

The effect of pH was investigated on sulfite waste liquor and on the two major chromophoric components, calcium lignosulfonate and caramel. The lignin compound alone (not the caramel) is responsible for the color shift, with increasing pH, from yellow brown to red brown. The color of all three substances is unaffected by acidity below about pH 3.0. The lignin compound and the caramel are both greatly increased in depth of color by the addition of alkali. The increase in color was only about 200 per cent for the isolated caramel and lignin but averaged 600 per cent in the raw liquor.

The important commercial variables in the sulfite process are the wood and the temperature schedule. The effect of varying the maximum temperature produced smooth curve relationships between liquor absorption coefficients and the maximum temperature, and, with the other dependent variables, pulp yield and permanganate number. With the two variables of temperature and pressure it was found that yield, permanganate number, and liquor color correlated perfectly, no matter how the operating variables were changed. In other words, a given liquor color will always result from a cook to certain yield and permanganate number, within the operating limits used here.

The variation within a single species and within the range of species of wood used for sulfite pulping produced a variety of liquor colors. The liquor colors from beech and western hemlock are entirely different from that of spruce, but those of birch and balsam are fairly close to that of spruce. These colors are not simple and probably result from the entirely different nature of wood extractives, sugars, and lignin. The color of the unbleached pulp and the bleachability are to some extent a function of the liquor color. Beech, for example, produced a very dark liquor and an equally dark pulp.

V

CONCLUSIONS

1. The color of sulfite liquor during the course of the digestion increases steadily and smoothly past the burning stage, with one minor reversion in the early stages.

2. The color of the liquor from the third to the seventh hour is practically all due to the calcium lignosulfonate in solution. Up to the third hour the slight color present is thought to be due to water-soluble material and, to some extent, to lignin.

3. The color of the liquor after a temperature of 140° C. has been reached (after the seventh hour in the schedule used here) is mostly due to carbohydrate degradation material. The lignin in solution is stable and contributes a small amount of color, but this contribution is slight as compared with that of the burned sugars.

4. The pitch and resin in spruce are highly colored and are removed to the extent of 80 per cent by the sulfite digestion. The effect on the total color at the end of the cook is probably slight.

5. The character of the liquor color (hue) changes in the course of the cook, corresponding to the above theory of the course of the dominant chromophoric material present at any stage of the cook.

6. The effect of age up to seventy days on sulfite liquor samples from all stages of the cook is very slight, if it exists at all.

7. Sulfite liquor does not accurately obey Beer's law on dilution.

8. The indicator effect of change of color of sulfite liquor with change of pH has been shown to be due probably entirely to the calcium lignosulfonate. The great increase of depth of color with increase of pH from acid to alkaline is due to both sugar degradation products and to the lignin compound.

9. The hemicellulose fraction is the source of most of the sugars which burn to give the greatest amount of the color present in sulfite liquor at the end of the cook. The pentosans of the hemicellulose fraction are easiest to hydrolyze and are degraded fastest by acid treatment, and the ketohexose, levulose, is least affected. The aldohexoses, i.e., glucose, galactose, and mannose, are average and all give about the same result.

10. The color produced from carbohydrates by acid treatment is a function of the time, temperature, concentration, and type of sugar and acid present. The character of the color produced is best shown by the log k curve; in general, sugars have a linear log k curve of varying slope, depending upon the cooking conditions.

11. The wood constituents, cellulose, hexosans, and pentosans, hydrolyze to the simple sugars and then break down to form insoluble humus and furfural and furfural derivatives. These furfural derivatives condense to colloidal coloring matter and insoluble

resins or humic materials, all making up the caramel system. The log k color characteristics of the heated and naturally aged furfural and furfural solutions are linear, agreeing with those colors obtained by heating various sugars directly.

12. All of the lignin preparations examined have a curved log k color characteristic in contrast to the linear nature of that of the degraded carbohydrate material.

13. In a study of the effect of maximum temperature, smooth curve relationships have been established between liquor color as measured by the absorption coefficient and the maximum temperature and between the liquor color and the dependent variables of pulp yield and permanganate number.

14. Five species of wood have been compared as to liquor color--spruce, balsam fir, western hemlock, beech, and white birch. The log k color characteristics indicate that, while balsam liquor color closely resembles that of spruce, the western hemlock and beech are particularly different. These liquor colors are complex and result from entirely different wood extractives, lignin, and sugars, than are present in spruce.

15. The color of the unbleached pulp from these species is to some extent related to the liquor color and may be important in bleaching. The beech liquor and unbleached pulp are the best example of dark liquor and dark pulp, with excessive bleach requirement.

VI

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VII

APPENDIX

TABLE XXIX

ABSORPTION COEFFICIENTS k FOR COOK 1

Liquor Sample hr.	Wavelength--mmu 420	460	500	540	580	620	660	700
3	0.295	0.170	0.126	0.100	0.086	0.070	0.060	0.058
3.5	0.334	0.181	0.118	0.093	0.077	0.056	-----	-----
4	0.368	0.147	0.098	0.071	0.056	0.036	-----	-----
4.5	0.474	0.198	0.109	0.073	0.056	0.036	-----	-----
5	0.619	0.275	0.168	0.118	0.088	0.068	0.064	-----
5.5	0.752	0.318	0.177	0.117	0.077	0.059	-----	-----
6	0.938	0.388	0.215	0.133	0.090	0.070	0.058	-----
6.5	1.23	0.511	0.287	0.189	0.126	0.086	0.069	0.066
7	1.70	0.708	0.426	0.274	0.189	0.135	0.108	0.097
7.5	2.18	0.911	0.528	0.332	0.218	0.147	0.108	0.097
8	2.92	1.23	0.730	0.462	0.296	0.201	0.152	0.124
8.5	3.76	1.63	0.990	0.625	0.400	0.267	0.195	0.149
9	4.27	2.06	1.26	0.797	0.488	0.320	0.222	0.165
9.5	5.60	2.83	1.72	1.09	0.665	0.422	0.271	0.189
10	6.80	3.50	2.11	1.34	0.828	0.524	0.344	0.245

TABLE XXI

ABSORPTION COEFFICIENTS k FOR COOK 2

Liquor Sample hr.	Wavelength—mμ 420	460	500	540	580	620	660	700
0	0	0	0	0	0	0	0	0
1	0.165	0.094	0.068	0.059	0.059	0.059	0.055	0.058
2	0.256	0.142	0.097	0.085	0.079	0.058	0.055	0.055
3	0.563	0.270	0.175	0.136	0.118	0.106	0.095	0.092
4	0.868	0.350	0.189	0.133	0.104	0.084	0.077	0.079
5	1.50	0.530	0.238	0.136	0.097	0.073	0.066	0.062
6	2.42	0.866	0.397	0.231	0.159	0.122	0.101	0.099
7	3.54	1.30	0.643	0.375	0.242	0.175	0.138	0.118
7.5	4.87	1.86	0.937	0.541	0.337	0.228	0.170	0.135
8	6.70	2.59	1.40	0.823	0.510	0.333	0.223	0.168
8.5	----	3.62	1.95	1.19	0.745	0.478	0.311	0.213
9	----	5.02	2.86	1.76	1.11	0.710	0.448	0.284
9.5	----	7.12	4.22	2.60	1.66	1.05	0.647	0.410
10	----	----	6.15	3.90	2.49	1.61	0.990	0.612
10.5	----	----	----	5.72	3.72	2.36	1.46	0.903
10.83	----	----	----	6.96	4.59	2.94	1.84	1.14
11.17	----	----	----	----	5.96	3.95	2.47	1.55
11.5	----	----	----	----	8.01	5.35	3.43	2.21
11.75	----	----	----	----	----	6.58	4.31	2.77
12	----	----	----	----	----	8.15	5.52	3.60

TABLE XXXI

ABSORPTION COEFFICIENTS $\underline{k}$ FOR COOK 3

Liquor Sample hr.	Wavelength--mμ							
	420	460	500	540	580	620	660	700
2	0.275	0.134	0.086	0.059	0.053	――	――	――
3	0.502	0.246	0.153	0.118	0.097	0.084	0.079	0.077
4	0.897	0.367	0.184	0.120	0.097	0.086	0.070	0.070
5	1.58	0.563	0.248	0.138	0.101	0.074	0.068	0.065
6	2.37	0.792	0.333	0.180	0.118	0.086	0.070	0.070
7	3.59	1.25	0.576	0.319	0.206	0.147	0.118	0.101
7.5	4.32	1.59	0.788	0.444	0.285	0.199	0.155	0.130
8	5.80	2.18	1.10	0.628	0.386	0.245	0.178	0.138
8.5	6.90	2.80	1.51	0.892	0.546	0.356	0.244	0.181
9	――	3.75	2.09	1.27	0.780	0.493	0.325	0.220
9.5	――	4.97	2.90	1.80	1.12	0.708	0.453	0.292
10	――	6.88	4.20	2.68	1.69	1.07	0.692	0.458

TABLE XXXXI

ABSORPTION COEFFICIENTS k FOR SODA BASE LIQUOR COOKS
ON WOOD CONSTITUENTS AT 5 HOURS' TIME AND 140° C.

Substance		Wavelength—mμ							
		420	460	500	540	580	620	660	700
Wood, 65-mesh		1.17	0.440	0.242	0.151	0.097	0.065	0.038	———
Wood, extracted		1.04	0.380	0.201	0.117	0.068	0.037	———	———
Ether-soluble		0.286	0.065	0.038	———	———	———	———	———
Alcohol-benzene soluble		2.90	1.26	0.713	0.393	0.212	0.117	0.067	0.044
Water-soluble		———	5.11	3.45	2.46	1.81	1.39	1.11	0.930
Water soluble-alcohol insoluble		2.18	1.12	0.678	0.453	0.335	0.272	0.236	0.212
Water soluble-alcohol soluble		5.37	2.54	1.39	0.805	0.484	0.297	0.204	0.147
d-glucose		0.910	0.252	0.082	———	———	———	———	———
d-levulose		0.088	———	———	———	———	———	———	———
d-mannose		0.660	0.226	0.132	0.108	0.097	0.090	0.088	0.084
d-galactose		1.13	0.338	0.134	0.068	0.038	———	———	———
d-arabinose		1.53	0.467	0.191	0.077	0.038	———	———	———
d-xylose		4.31	1.78	0.897	0.497	0.321	0.231	0.170	0.134
Cellobiose		0.389	0.108	0.061	0.049	0.047	0.044	0.038	0.038
Sucrose		1.71	0.571	0.159	0.059	———	———	———	———
Ca lignosulfonate		6.57	3.10	1.92	1.26	0.850	0.597	0.416	0.312
Ca lignosulfonate	Commercial	6.71	2.93	1.63	0.965	0.546	0.297	0.159	0.082
Na lignosulfonate	Commercial	7.15	3.07	1.74	1.01	0.560	0.297	0.159	0.082
Ca lignosulfonate	Dr. Brauns	2.12	0.828	0.462	0.277	0.166	0.095	0.051	0.029
Na lignosulfonate	Dr. Brauns	1.80	0.748	0.426	0.289	0.210	0.140	0.090	0.059
Native lignin, Na base	Dr. Brauns	4.35	1.85	1.02	0.537	0.311	0.206	0.146	0.108
Cotton cellulose		0.086	———	———	———	———	———	———	———
Corn starch		2.01	0.740	0.365	0.191	0.110	0.068	0.047	0.029
Tannic acid		1.70	0.345	0.108	0.051	———	———	———	———
Lemon pectin		1.28	0.585	0.323	0.182	0.090	0.038	———	———

TABLE XXXIII

ABSORPTION COEFFICIENTS k FOR HCl-COOKED SUGARS

Sugar	Wavelength—mμ 420	460	500	540	580	620	660	700
d-arabinose	1.43	0.960	0.780	0.643	0.568	0.510	0.462	0.423
d-xylose	1.62	1.07	0.872	0.740	0.677	0.625	0.576	0.524
d-glucose	2.18	1.03	0.642	0.427	0.287	0.211	0.157	0.127
d-galactose	2.82	1.61	1.07	0.735	0.537	0.440	0.368	0.319
d-mannose	1.04	0.480	0.298	0.181	0.108	0.065	0.041	0.030
d-levulose	4.68	2.14	1.21	0.770	0.567	0.455	0.392	0.354
Cellobiose	1.13	0.585	0.365	0.242	0.170	0.128	0.108	0.097
Sucrose	3.40	2.19	1.59	1.08	0.850	0.748	0.700	0.642

TABLE XXXIV

ABSORPTION COEFFICIENTS k FOR FURFURAL COMPOUNDS

Compound	Wavelength—mμ 420	460	500	540	580	620	660	700
Furfural, 1 day old	2.65	0.339	0.0	——	——	——	——	——
Furfural, aged	5.03	2.80	0.179	0.118	0.792	0.536	0.365	0.255
Furfuryl alcohol	2.88	1.57	0.942	0.598	0.369	0.220	0.136	0.088
5-Methylfurfural	1.92	0.902	0.453	0.242	0.125	0.075	0.047	0.028
Hydroxymethyl-furfural	1.12	0.502	0.273	0.148	0.074	0.041	0.020	0.010

TABLE XXXV

ABSORPTION COEFFICIENTS k FOR FURFURAL COOKS OF TABLE XXII

Sample	Wavelength—mμ 420	460	500	540	580	620	660	700
A	——	5.47	3.73	2.69	2.02	1.58	1.25	1.02
C	2.20	0.084	——	——	——	——	——	——
D (4%)	4.67	4.23	3.78	3.21	2.62	2.15	1.78	1.49
E	3.31	1.30	0.510	0.206	0.086	0.037	——	——
F	5.55	1.99	0.717	0.269	0.110	0.049	0.019	0.0

TABLE XXXVI

ABSORPTION COEFFICIENTS *k* FOR FIGURE 22; THE EFFECT OF *p*H ON CALCIUM LIGNOSULFONATE

Sample	*p*H	Wavelength--mμ 420	460	500	540	580	620	660	700
A	10.25	----	4.32	2.81	2.04	1.44	0.98	0.66	0.43
B	9.20	5.23	3.38	2.54	1.94	1.38	0.95	0.64	0.41
C	7.60	4.18	2.85	2.27	1.79	1.29	0.90	0.62	0.40
D	6.40	3.69	2.51	2.02	1.64	1.26	0.96	0.71	0.52
E	5.75	3.69	2.51	2.02	1.64	1.26	0.96	0.71	0.52
F	5.24	3.38	2.86	1.78	1.43	1.11	0.86	0.67	0.51
G	4.05	2.98	1.87	1.36	1.01	0.72	0.53	0.41	0.32
H	2.45	2.80	1.71	1.18	0.81	0.52	0.34	0.21	0.14
I	1.50	2.69	1.67	1.14	0.76	0.49	0.32	0.20	0.13

TABLE XXXVII

ABSORPTION COEFFICIENTS *k* FOR FIGURE 24; THE EFFECT OF *p*H ON SUCROSE CARAMEL

Sample	*p*H	Wavelength--mμ 420	460	500	540	580	620	660	700
A	11.10	----	5.24	3.17	1.89	1.14	0.709	0.445	0.287
B	10.80	7.38	4.66	2.85	1.70	1.02	0.621	0.388	0.246
C	9.10	5.88	3.65	2.27	1.35	0.792	0.475	0.298	0.191
D	7.15	4.73	2.82	1.73	1.02	0.590	0.356	0.222	0.146
E	6.50	4.40	2.52	1.51	0.876	0.511	0.300	0.191	0.123
F	4.45	4.12	2.17	1.21	0.691	0.391	0.229	0.144	0.095
G	3.06	3.95	2.05	1.11	0.638	0.356	0.229	0.144	0.088
H	2.75	3.95	2.05	1.11	0.638	0.356	0.229	0.144	0.088
I	2.40	3.95	2.05	1.11	0.638	0.356	0.229	0.144	0.088

TABLE XXXVIII

ABSORPTION COEFFICIENTS k FOR 7- AND 10-HOUR LIQUORS ON COMPARISON OF WOOD SPECIES

Wood	Wavelength—mμ							
	420	460	500	540	580	620	660	700
7 hours								
Balsam fir	3.85	1.42	0.68	0.37	0.21	0.13	0.088	0.068
Western hemlock	5.48	2.32	1.29	0.80	0.45	0.20	0.097	0.058
Beech	4.69	2.19	1.36	0.98	0.57	0.23	0.117	0.077
10 hours								
Spruce	6.97	3.12	1.83	1.17	0.75	0.51	0.35	0.27
Balsam fir	7.12	3.07	1.71	0.99	0.59	0.35	0.21	0.14
Western hemlock	----	4.66	2.97	1.90	1.12	0.52	0.26	0.15
Beech	----	6.20	4.32	3.02	1.63	0.71	0.33	0.19
Birch	5.51	2.95	1.93	1.23	0.66	0.33	0.19	0.13