AN ABSTRACT OF THE THESIS OF

DENNIS CLELAN WADE for the degree of MASTER OF SCIENCE

in FOREST PRODUCTS presented on March 16, 1977

Title: THE APPLICATION OF FLUORESCENCE OF PULPING WASTE LIQUORS TO THE CONTROL OF LABORATORY AND COMMERCIAL PULPING OPERATIONS

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Abstract approved: _____
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Samples of Douglas-fir chips and western hemlock/true fir chips were pulped by the kraft and sulfite processes respectively. The spent liquors were analyzed for fluorescent response, and the fluorescent intensities of each liquor sample correlated with yields, Kappa numbers, and lignin contents of the pulps.

Linear relationships were seen between fluorescent intensities and the pulp properties of kraft samples, while the sulfite samples demonstrated a maximum fluorescent intensity in the region of a 40% yield. It is postulated that the nonlinear relationship between fluorescence and sulfite pulp properties is due to lignin condensation reactions.

Industrial samples were obtained from one sulfite and three kraft pulp mills. Nonlinear relationships were found between liquor fluorescences and Kappa numbers for the kraft mill samples, due to alterations in production parameters between samples. The results from the analysis of the sulfite mill samples verify the laboratory findings that

a maximum fluorescent intensity is attained near the end of a normal sulfite cook.

A comparison was made between a Turner model 111 filter fluoromter and a Turner model 210 spectrofluorometer, to determine whether the less expensive filter fluorometer would suffice for the monitoring of delignification in a mill. The results suggest that with the correct filters and light source, the model 111 is an accurate tool for the measurement of spent pulping liquor fluorescence.

THE APPLICATION OF FLUORESCENCE OF PULPING WASTE LIQUORS TO THE CONTROL OF LABORATORY AND COMMERCIAL PULPING OPERATIONS

by

Dennis Clelan Wade

A THESIS

submitted to

Oregon State University

in partial fulfillment of
the requirements for the
degree of

Master of Science

June 1977

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Date thesis is presented March 16, 1977

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TABLE OF CONTENTS

	Page
INTRODUCTION	1
LITERATURE REVIEW	3
Nature of Fluorescence	3
Raman Spectra	5
Ultraviolet Spectra of Waste Liquors	5
Waste Liquor Fluorescence	6
Molecular Weight	7
Sample pH	8
Temperature	8
Concentration	9
Pulping Processes and Species	10
Effects of Time	11
Photodecay	11
Presence of Other Organics	11
EXPERIMENTAL PROCEDURE	12
Sample Preparation	12
Pulping Processes	12
Dilution Procedure	15
Spectral Conditions	16
Pulp Preparations	18
Pulp Testing	18
Statistical Analysis	19
Mill Sampling	19
RESULTS AND DISCUSSION	22
Optimum Wavelengths for Fluorescent Analysis	22
Optimum Bandwidths for Fluorescent Analysis	22
Kraft Pulping Results	31
Lignin Content versus Pulp Yield	31
Kappa Number versus Kraft Lignin Content	31
Kappa Number versus Yield	34
The Fluorescent Characteristics of Kraft Waste Liquor	34
Corrected Fluorescent Intensity versus Lignin Content of Kraft Pulps	34
Corrected Fluorescent Intensity versus Kappa Number	38
Corrected Fluorescent Intensity versus Pulp Yield	40
Effects of Sample Age on Kraft Liquor Fluorescence	40
Fluorescent Characteristics of Kraft Mill Spent liquors	45
Sulfite Pulp Properties	48
Lignin Content as a Function of Total Yield	48
Kappa Number versus Lignin Content	48
Kappa Number as a Function of Pulp Yield	52

Fluorescent Characteristics of Spent Sulfite Liquor 52
Fluorescent Intensity versus Lignin Content 52
Fluorescent Intensity versus Kappa Number 52
Sulfite Liquor Fluorescence as a Function of Pulp Yield 52
Aging and Spent Liquor Fluorescence 57
Fluorescent Characteristics of Industrial Spent Sulfite Liquor 57
Fluorescent Intensity as a Function of Cooking Time 59
A Comparison Between a Corrected Spectrofluorometer and a Filter Fluorometer 61
Turner model 210 Spectrofluorometer 61
Turner model 111 Filter Fluorometer 62
Filter Fluorescence as a Function of Corrected Fluorescent Intensity 64

SUMMARY 69

CONCLUSIONS 72

LITERATURE CITED 75

APPENDICES 77

LIST OF FIGURES

Figure		Page
1	Effect of Excitation and Emission Bandwidths on the Relationship: Corrected Fluorescent Intensity = f(Kappa no.) for Kraft Laboratory Experiments	24
2	Effect of Excitation and Emission Bandwidths on the Relationship Corrected Fluorescent Intensity = f(Kappa no.) for Sulfite Mill Samples	28
3	Lignin Content on wood = f(Yield) for Kraft Laboratory Samples	32
4	Lignin Content on pulp = f(Yield) for Kraft Laboratory Pulps	33
5	Kappa number = f(Lignin Content) for Kraft Laboratory Samples	35
6	Kappa number = f(Yield) for Kraft Laboratory Samples	36
7	Corrected Fluorescent Intensity = f(Lignin Content) for Kraft Laboratory Samples	37
8	Corrected Fluorescent Intensity = f(Kappa no.) for Kraft Laboratory Samples	39
9	Corrected Fluorescent Intensity = f(Yield) for Kraft Laboratory Samples	41
10	Affect of Age on Corrected Fluorescent Intensity = f(Kappa no.) for Kraft Laboratory Samples	42
11	Corrected Fluorescent Intensity = f(Time in days) for Kraft Laboratory Samples	43
12	Affect of Aging on Corrected Fluorescent Intensity = f(Kappa no.) for Kraft Laboratory Samples	44
13	Corrected Fluorescent Intensity = f(Kappa no.) for Kraft Mill Samples	47
14	Lignin Content on Wood = f(Yield) for Sulfite Laboratory Pulps	49
15	Lignin Content on Pulp = f(Yield) for Sulfite Laboratory Pulps	50

Figure		Page
16	Kappa number = f(Lignin Content) for Sulfite Laboratory Samples	51
17	Kappa number = f(Yield) for Sulfite Laboratory Samples	53
18	Corrected Fluorescent Intensity = f(Lignin Content) for Sulfite Laboratory Samples	54
19	Corrected Fluorescent Intensity = f(Kappa number) for Sulfite Laboratory Samples	55
20	Corrected Fluorescent Intensity = f(Yield) for Sulfite Laboratory Samples	56
21	Corrected Fluorescent Intensity = f(Age) for Sulfite Laboratory Samples	58
22	Corrected Fluorescent Intensity = f(Cooking Time) for Sulfite Mill Samples, Digester #1	60
23	Schematic representation of the Turner model 210	63
24	Schematic representation of the Turner model 111	63
25	Filter Fluorescent Intensity = f(Corrected Fluorescent Intensity) for Kraft Laboratory Samples	65
26	Filter Fluorescent Intensity = f(Corrected Fluorescent Intensity) for Sulfite Laboratory Samples ex 10/em 10	66
27	Filter Fluorescent Intensity = f(Corrected Fluorescent Intensity) for Sulfite Laboratory Samples ex 15/em 25	68

LIST OF TABLES

Table		Page
1	Kraft Pulping Conditions	14
2	Sulfite Pulping Conditions	14
3	Spectral Conditions Turner model 210	15
4	Spectral Conditions Turner model 111	16
5	Kraft Statistical Data	24
6	Sulfite Statistical Data	28

LIST OF APPENDIX TABLES

Table		Page
1	Comparison of Excitation and Emission Bandwidths, Kraft Laboratory Data	77
2	Comparison of Excitation and Emission Bandwidths, Sulfite Laboratory Data	78
3	Kraft Pulping Results for Laboratory Samples	79
4	Kraft Liquor Fluorescence for Laboratory Samples	80
5	Sulfite Pulping Results for Laboratory Samples	81
6	Sulfite Liquor Fluorescence for Laboratory Samples	82
7	Kraft Mill Data	83
8	Sulfite Mill Data	84

THE APPLICATION OF FLUORESCENCE OF PULPING WASTE LIQUORS TO THE CONTROL OF LABORATORY AND COMMERCIAL PULPING OPERATIONS

INTRODUCTION

Paper is a mat of wood fibers, which are produced from wood by a chemical process. This process is designed to dissolve enough of the natural adhesive (lignin) which holds the fibers together in wood so that the fibers may come apart with minimal physical damage. Normally this occurs at about 50% yield (50% of the original wood remains as fiber, and the rest has been dissolved in the pulping liquor). However, the pulping processes presently in use dissolve a substantial amount of carbohydrate material (the part of the fiber that is desirable to recover) along with the lignin to reach this point (1). As an example, of the 50% dissolved material, 30% is carbohydrate, and 20% is lignin (all values based on original wood substance). This loss of potentially useful carbohydrate material illustrates the basic inefficiency of pulping operations, due in part to an incomplete understanding of the reactions of lignin in a digester.

The normal method for controlling the pulping process is the regulation of cooking time, temperature, and chemical charge. Under the best of commercial conditions, however, variations in pulp quality occur due to uncontrolled variations in raw material input and/or undetected variations in process control. These variations can affect the rate of delignification, but this cannot be readily detected in commercial practise. Pulp mills have developed a post-facto measure of delignification (Kappa number) which is used to adjust the pulping conditions

of subsequent cooks. It is difficult to remove wood from the digester as it is being pulped, and therefore the Kappa number test cannot be used to monitor an ongoing cook. The development of a system to monitor the ongoing delignification reaction would be a great benefit to the pulping industry, as well as an aid to pulping research.

A new tool has recently appeared, which shows promise regarding the measurement of lignin in solution. This method, based on the property of lignin to fluoresce when excited with ultraviolet light, was first used to monitor pulp mill effluents, where it proved that it can detect minute quantities of lignin in aqueous solution (2-6). Since fluorometry can detect lignin in effluent streams, it is reasonable to assume that this technique can also detect lignin in pulping liquors. This analysis may be performed on pulping liquor during a cook, and thus it should be possible to determine the rate of delignification of a cook in progress.

The objectives of this thesis were:

1) To correlate the fluorescence of spent pulping liquors with total yields, lignin contents, and Kappa numbers of kraft and sulfite pulps.
2) To evaluate a filter fluorometer as a control tool for testing pulping liquor fluorescence.
3) To initiate mill scale trials for correlation of pulp liquor fluorescence and other control variables.

The Nature of Fluorescence

The phenomenon of fluorescence can be described as being the essentially instantaneous emission of light from a molecule which has absorbed light(7). A photon, which is a discrete packet of energy, is absorbed by a molecule, and the increased energy content of the molecule serves to excite certain electrons and shift them from the ground state (S_0) to higher energy levels (S_1, S_2,...S_N) (8). However, the energy which a molecule gains upon absorption of a photon does not remain in that molecule, but is lost through any of a number of mechanisms. Of particular importance to fluorescence is the loss of energy through heat. Excited molecules acquire extra vibrational energy as well as electronic energy, and these molecules will collide, generating heat through friction, and lower the energy of the molecule to the lowest vibrational state within the same electronic (singlet) level(8). This radiationless loss of energy leaves the molecule in an excited electronic state, and the molecule will then return to the ground state (S_0) by radiating the remainder of the energy through the emission of a photon. This photon contains less energy than that which initially excited the molecule, and the radiation is emitted at a longer wavelength. (8). The emerging photons are scattered in all directions. To measure fluorescense a photocell generally is placed at an angle normal to the excitation radiation to differentiate between excitation and emission(8,9).

Any given fluorescent molecule in a given environment has two characteristic spectra, the excitation spectrum (the relative efficiency of different exciting wavelengths to cause fluorescence) and the emission spectrum (the relative intensity of light emitted at various wavelengths).

The shape of the excitation spectrum is that of the absorbance curve of the molecule and is independent of the wavelength at which fluorescence is measured (9).

Fluorometry is often compared with absorption spectroscopy, which is the measurement of absorbed light by a spectrophotometer (9). This comparison is made because, in order to fluoresce, a molecule must first absorb energy. Fluorometry, however, allows for greater sensitivity and specificity than is possible with measurements of absorbance alone (7,8,9). A spectrophotometer can detect absorbant materials in concentrations as low as one part per ten million, whereas a spectrofluorometer can detect fluorescent materials in concentrations as low as one part per ten billion, thus exhibiting 1000 times greater sensitivity (8,9).

According to Turner:

"If the exciting light is of a wavelength which is different from the wavelength of the absorption peak, a smaller portion of the light will be absorbed and proportionally less light will be emitted" (7). This illustrates an important characteristic of fluorometry: The ratio of total absorbed light to total emitted light is constant (8). This means optical measurements need not be made at spectral maxima, or even at a flat region of the emission wave, as required by absorptiometry (7,8,9). It is often possible to avoid interference from other substances by using wavelengths removed from the emission maxima (9). The ratio of total absorbed energy to total emitted energy is termed quantum efficiency, and is a property of each fluorescent species (within a strict range of concentrations) (8).

Other factors contributing to the specificity of fluorometry are: first, not all compounds which absorb energy will fluoresce, and there-

fore there are fewer fluorescent compounds than absorbing ones (9). Second, fluorescent compounds which absorb at the same wavelength will not necessarily have the same emission peak wavelength (8,9).

Raman Spectra

A phenomenon bearing some relation to fluorescence, and which must be considered before fluorescent analysis can be performed, is the Raman effect, or Raman scattering (10). Like fluorescence, the Raman effect is characterized by the emission of light from a sample with a change in wavelength from that of the exciting light. Whereas fluorescence is characterized by the absorption of the exciting radiation, followed by a brief delay of 10^{-8} seconds before the emission of a new photon, the Raman effect is characterized by no absorption of the incident radiation (8,9). A collision between a molecule and a high energy photon results in extraction of energy from the photon and an increase in the vibrational state of the molecule. However, the emerging photon is the same one that entered, but with less energy and therefore a longer wavelength (8). The Raman effect is thus a scattering of the photons at a longer wavelength, and is therefore easily confused with fluorescence. (10). The problem this phenomenon presents can be seen when this scattering occurs with an otherwise nonfluorescent solvent (such as distilled water) thereby increasing the apparent fluorescence of the sample. It is thus important to measure the spectral response of the solvent to determine whether such interference exists (10).

Ultraviolet Spectra of Waste Liquors

The spectral properties of pulping waste liquors, particularly the ultraviolet absorbance and fluorescence, have been the subject of extensive research. These liquors are solutions of lignin and car-

bohydrates in various stages of degradation, as well as much of the original chemicals used in the pulping operation (1). All of these components will absorb ultraviolet light in varying degrees and at characteristic wavelengths (1,10-19).

Several investigators have sought to correlate ultraviolet absorption of waste liquor with the lignin content of the liquor (11-19) but comparisons of liquor absorbance with wood residue analysis (i.e. Kappa number and pulp viscosity) have received less attention (16,19). In a series of studies performed on the spectral properties of lignin, all lignin preparations demonstrated the same absorbance characteristics, specifically a peak absorbance in the region of 205 to 215 nm and a secondary peak at 280 nm, both of which are characteristic of an aromatic nucleus (11-19). The 280 nm peak also corresponds with the absorbance maxima of certain carbohydrate hydrolysis products, namely furfural and hydroxymethylfurfural, which precludes the use of this wavelength as a specific measure of pulping delignification via absorptiometry (12-19).

Waste Liquor Fluorescence

Of the three types of components which make up pulping waste liquor (lignin-like material, degraded carbohydrates, and inorganic chemicals), only the lignin-like materials which contain an aromatic nucleii are known to fluoresce. Certain extractives of a phenolic nature (i.e. dihydroquercetin) may fluoresce (1), and their effect on pulping waste liquor fluorescence will be discussed subsequently.

Within spent liquor, by far the predominant molecular species of an aromatic nature is dissolved lignin (20). The ability of fluorometry to differentiate between the components of spent liquor, measure the

concentration of such aromatics, and thus give a fairly accurate representation of dissolved lignin content, has provided a powerful tool for analysis of pulp mill effluents (2-6). Fluorometric analysis of spent liquors is both easier to apply and more sensitive to the presence of lignin than the former standard procedures for the determination of lignin content, the Pearl-Benson Index (in which test color complexes are formed by reacting lignin with nitrous acid, and then measured by a colorimeter) (21) or the alkaline hydrolysis method of Felicetta and McCarthy (22) (the hydrolysis of lignin sulfonates to vanillin followed by the determination of vanillin by gas chromatography) (2,3).

The fluorescent intensity of pulping waste liquor and the wavelengths of maximum intensity radiation for excitation and fluorescence are dependent upon several factors. These include: the concentration and the average molecular weight of the degraded lignin molecules within the sample being tested, the pH of the sample, the temperature of the sample, and various pulping parameters, such as pulping process and wood species pulped (1-10,23). Other factors that may affect spent pulping liquor fluorescence are the amount of time that has elapsed from the collection of the sample to its measurement, possible exposure to ultraviolet light before measurement of fluorescence, and possible contamination with other organic compounds of an aromatic nature (2, 16,18,20,21).

Molecular Weight

Christman and Minear (2,3), in their pioneering work on the fluorescent properties of lignin sulfonates (LS) and spent sulfite liquor (SSL), reported that the fluorescent intensity of LS in solution

decreased with increasing molecular weight, at equal concentration. This was attributed to an inability of the phenolic nucleii to resonate freely when additional bonds exist between the aromatic ring and other molecular units (2,3).

Sample pH

The affects of sample pH have been studied by several investigators. It was noted by Christman and Minear (2,3) that a significant decrease in fluorescent intensity for LS and SSL was associated with extremes in pH. For a range of pH4-7, fluorescent intensity was insensitive to changes in pH. They also found that a change in pH from neutral to alkaline shifted the location of the excitation and emission peaks to longer wavelengths (2,3). Thurston (23) found that a variation in pH from 5 to 9 did not affect LS fluorescent intensity. Bublitz and Meng (10) found that the fluorescent behaviors of both kraft and sulfite liquors are pH dependent. They reported that changing the pH of a dilute SSL solution from 6.5 to 12 caused a shift in the location of the fluorescent maximum from 400 nm to 430 nm. This phenomenon is reportedly reversible and affects kraft liquors as well. In the case of kraft liquor, a shift in pH from 12 to 6-7 produced a shift in the fluorescent maximum wavelength from 430 nm to 400 nm (10).

Temperature

The temperature of the sample will also affect fluorescence, as reported by Christman and Minear (2,3). They noticed a linear decrease in fluorescent intensity between 5°C and 30°C, but above 30°C the decrease in fluorescent intensity was non-linear. They attribute this to an increase of the collisional deactivation of the excited molecules, due to an increase in kinetic energy (2,3).

Concentration

Sample concentration is an important factor in all fluorescent studies, due to the great sensitivity of fluorometric devices (2, 3,8,9). This can be illustrated by the governing equation of the simplest fluorescent system, which is a single absorbing and fluorescing compound in solution:

$$F = (P) \times (K) \times (1 - 10^{-A}) \qquad \text{(Eq. 1)}$$

where F is the fluorescent intensity which reaches the photocell, P is the intensity of the exciting radiation, and K is a factor for converting the amount of absorbed energy to the amount of fluorescence that reaches the detector (which is a function of instrument design and is a constant for a given instrument). A is the absorbance of the solution (synonomous with optical density) at the wavelength of excitation, and is equal to $\log {}^{I_o}/_{I,}$ where I_o is the intensity of radiant energy as it enters the sample cell, and I is the intensity of radiation leaving the cell (8). At low concentrations of fluorescing material F is linearly related to A. Since A is linear with concentration and follows Beer's law, at low concentration, F (fluorescent intensity) is also linearly related to concentration (8).

Equation 1 will predict linearity only for very small values of A, in the vicinity of 0.01, which necessitates low sample concentrations. At higher concentrations, Eq. 1 predicts a non-linear relationship, and K may no longer be constant. Bublitz and Meng (10) have reported that the sample must be sufficiently dilute to allow a percent transmission of 95% or above (A = .022) to insure linearity between fluorescent intensity and concentration. Thurston (23) has reported that the relationship of fluorescent intensity to concentration of SSL solutions

deviates from linearity in concentrations above 50 mg/l solids (23). Christman and Minear (2,3) have found that the region in which fluorescent intensity increases linearly with increased concentration lies below a concentration of approximately 10 ppm SSL. They reported an excitation peak in the region of 290 nm which disappeared with increased concentration. This phenomenon was true for both LS and SSL solutions, and was described as "concentration quenching" (2,3).

Pulping Processes and Species

Differences in fluorescence due to pulping processes and species of wood have been studied by several investigators. The initial studies were performed on SSL and LS, establishing that characteristic spectral responses for both included an excitation peak at 293 nm, and fluorescent peak at 400 nm (2,3). Wilson (4) followed the work of Christman and Minear with a study of kraft black liquor, reporting that significant differences existed between the fluorescence spectra of western hemlock and Douglas-fir kraft liquors. These differences were found both in the fluorescent intensities and the wavelengths of the excitation and emission maxima. Wilson's findings were not verified by Bublitz and Meng, who report that no difference in the location of wavelengths of peak intensity could be found between western hemlock and Douglas-fir woods pulped by the same process, and at the same liquor sample pH (10). They noted differences in fluorescent intensities, at equal lignin concentrations, between the two liquors, with the greater intensity of the Douglas-fir solutions attributed to the presence of additional aromatic compounds, such as dihydroquercetin or other extractives. They also found little difference between the fluorescent behavior of kraft pulping liquor and sulfite pulping liquor obtained

from the same wood species, western hemlock, when the liquor samples were adjusted to equal pH.

Effects of Time

Baumgartner et al (5), reported the fluorescent intensity of a sample decreases with time. This particular study of kraft mill effluent showed a substantial decrease in 430 nm fluorescent intensity after a 48 hour period, possibly due to chemical or physical alteration of the fluorescent species. They suggested that fluorescent analyses be performed within 48 hours of sampling.

Photodecay

Decreased fluorescent intensity has also been reported with samples receiving repeated irradiation with utraviolet light (4). This was attributed to photodecay of the lignin sulfonates in solution. Thurston (23) reported the same phenomenon with samples left in bright sunlight for an extended period.

Presence of Other Organics

Thurston (23) noted that other organics containing an aromatic nucleus may increase the fluorescent intensity of a water sample beyond the fluorescence attributable to lignin, and this has presented an obstacle to the use of fluorometry to monitor pulp mill effluents in receiving waters. Almgren and Josefsson (6), however, developed a standard addition technique, using known quantities of LS to determine the amount of fluorescence within water samples attributable to SSL. The authors claim this method can overcome the problem presented by contamination with humic substances.

In summary, fluorometry is a technique which promises to be applicable to the study of delignification in pulping processes. It is

both more sensitive and more specific than absorptiometry, although to ensure a linear relationship between fluorescence and lignin concentration the sample must be diluted several thousand times (2,3, 8,10). Due to the sensitivity of fluorescent behavior to the many factors already discussed, it is of paramount importance that a set of standard procedures be developed and maintained for any fluorescent analysis undertaken.

EXPERIMENTAL PROCEDURE

Sample Preparation

Samples of Douglas-fir chips for kraft pulping were obtained from the Western Kraft Corp. mill in Albany, Oregon, and stored in a cold room at $3^{o}C$ until screened. One kilogram samples were run through a Williamson chip screen (a round hole screen) for 5 minutes and the -5/8 inch + 3/8 inch fraction was separated from the remainder. This fraction was then hand sorted to remove bark, rot and knots; it was then thoroughly mixed, bagged in plastic, and stored in the cold room for a week to allow equilibration of moisture throughout the sample.

For sulfite pulping, samples of hemlock/true fir chips were obtained from the Publishers' Paper Co. mill in Oregon City, Oregon. These chips received the same preparation as the samples for kraft pulping previously described.

In addition to the chip samples, a sample of Magnefite cooking liquor was obtained from the Publishers' Paper Co. mill for the pulping of the hemlock/true fir chips by the sulfite process. It was tested for pH and total, free, and combined SO_2 using Tappi Standard T 604.

Pulping Procedures

Eight kraft cooks and four sulfite cooks were performed in the 1 kg stainless steel digesters. Forced circulation of the liquor through an external heat exchanger supplied heat to the digester, and the heating cycle was controlled by use of an electronic cam which regulated steam flow to the exchanger.

Prior to charging the digester, the chip moisture content was measured in order to calculate the appropriate sample size. This amount of chips was placed in a wire basket and sealed in the digester. One

thousand gram (o.d.) samples were used in the kraft cooks, while 900 gram (o.d.) samples were used for the sulfite cooks.

Table 1 Kraft Pulping Conditions

Active Alkali (as Na_2O)	32 gpl in white liquor
	24.4% on o.d.wood
Sulfidity	25%
Liquor to wood ratio	8:1
Time to temperature	45 minutes
Time at temperature	0 to 3 hours
Final temperature	170°C (338°F)

Both active alkali and sulfidity were measured by Tappi Standard T 624. While all other parameters were held constant between kraft cooks, time at final temperature was varied to achieve varying degrees of delignification.

Table 2 Sulfite Pulping Conditions

Total SO_2	5.2% (52 gpl)
Free SO_2	2.6% (26 gpl)
Combined SO_2	2.6% (26 gpl)
Liquor to wood ratio	9:1
Time to 90°C(194°F)	10 minutes
Impregnation time (time at 90°C)	2 hours
Time from 90°C to final temperature	15 minutes
Time at final temperature	0 to 3 hours
Final temperature	166°C (330°F)

The mechanics of sulfite pulping require substantial impregnation time below the boiling point of water (in this case two hours) to allow for sufficient impregnation of the chips via the exposed end grain. Once this impregnation period is complete, the charge is heated to its final temperature. Time at final temperature was also varied between 0 and 3 hours, while the other parameters were held constant.

At the end of the cooking cycle, the digester blow valve was opened and liquor samples were collected. For the sulfite cooks, a condenser was attached to the blow valve to cool the escaping spent liquor and prevent loss of SO_2. Since this attachment could not be made with the kraft digester, the spent kraft liquors "flashed" upon release from the digester, and are of higher solids content than is actually the case within the digester. Due to the fact that digester temperature and pressure were constant for all kraft cooks, this "flashing" should have affected all liquor samples equally.

Dilution Procedure

Spent liquor samples were immediately placed in the freezer to cool to 25°C before dilution. A 1.0 ml aliquot was pipeted from each sample of spent liquor, placed in a 25 ml volumetric flask for sulfite liquor or a 50 ml volumetric flask for kraft liquor. These were then diluted to the mark using as solvents glass-distilled water for the sulfite liquor, and .01 N NaOH for kraft liquor. This maintained the pH of diluted samples at 3.9 to 4.5 for SSL and 11.6 to 12.3 for spent kraft liquors. One ml samples were again taken from the now dilute liquor, placed in a 100 ml volumetric flask and again diluted to the mark. The final dilutions thus were 1:2500 for sulfite liquor and 1:5000 for kraft. These ratios were determined as optimum as they required the

least dilution and yet still met the required UV transmission value of 95% or above.

The diluted samples were placed on ice and cooled to 5°C. Upon final cooling, the samples were taken to the EPA Corvallis Environmental Research Laboratory in Corvallis, Oregon for spectral analysis.

Spectral Conditions

A Turner model 210 absolute spectrofluorometer was used for fluorescent examination, due to its high sensitivity and versatility. Quartz cuvets (10 x 10 x 45 mm) were filled with samples of the diluted liquor and the cuvets placed in the sample compartment of the fluorometer for measurement.

Table 3 Spectral Conditions Turner model 210

Excitation wavelength	280 nm
Emission wavelength	400 nm for sulfite liquors 430 nm for kraft liquors
Fluorescent sensitivity	10x and 30x
Excitation bandwidths	10 nm and 15 nm
Emission bandwidths	10 and 25 nm
Dilution ratios	1:2500 sulfite 1:5000 kraft
Pen damping	100
Scan rate	1 nm/second
Scan range	250 nm (250-500)
Scan mode	single
Zero knob reading	000

Fluorescent analysis was performed on both the diluted liquor and its diluent. If I_s (sample intensity) is equal to the height of the sample curve from the baseline in millimeters, and I_0 (reference intensity) is equal to the height of the blank curve from the baseline in millimeters, fluorescent intensity is determined by the formula:

$$\text{Fluorescent Intensity in mm} = \frac{I_s - I_0}{\text{fluorescent sensitivity}}$$

In addition to the fluorescent studies made using the Turner model 210, a series of measurements were also performed using a Turner 111 filter fluorometer. This instrument is somewhat simpler than the model 210, using optical filters to control excitation and emission wavelengths rather than a grating monochromator.

The model 111 filter fluorometer automatically subtracts the fluorescent intensity of the diluent from that of the sample and reads out this corrected fluorescent intensity on a dial (scale 0-100). A Turner model 110-855 U.V. lamp was used to provide excitation energy in the region of 280 nm.

Table 4 Spectral Conditions	Turner model 111
Excitation wavelength	280 nm
Emission wavelength	400 nm for sulfite liquors
	430 nm for kraft liquors
Fluorescent intensity	3x and 10x
Excitation bandwidths	9.5 nm
Emission bandwidths	12 nm, 24 nm and 35 nm
	for both kraft and sulfite
Dilution ratio	1:2500 sulfite
	1:5000 kraft

All samples were tested for percent transmission using a Beckman DB spectrophotometer before fluorescent examination. This instrument was also used to determine acid-soluble lignin via U.V. absorption.

Pulp Preparations

Immediately after blowing the digester, the cooked wood was quantitatively withdrawn and bagged, and allowed to cool overnight. The contents were weighed the next day and 100 grams (wet weight) of material was removed for subsequent washing and testing following Tappi sampling procedure T 605.

This 100 gram sample was placed in a large plastic bucket, diluted with 10 liters of water and stirred with a mixer to defiber and wash the pulped wood. This slurry was then dewatered through a 150 mesh screen, the recollected material rinsed, and then replaced in the bucket for further dilution and mixing.

Following the second mixing, the pulp was screened, rinsed, and placed in a PFI refiner and beaten 100 revolutions. The beaten pulp was diluted again with 10 liters of water, mixed for five minutes, and poured directly into a British sheet mold to form thick pads for testing.

The pads were placed in an oven ($100^{o}C$) overnight, cooled in a desiccator, and weighed. The solids content (consistency) was calculated using the formula:

$$\% \text{ Solids} = \frac{(\% \text{ solids}) \times (\text{wet weight of pulp})}{100}$$

This value was used to calculate pulp yield in the following manner:

$$\text{Yield in grams (OD)} = \frac{(\% \text{ solids}) \times (\text{wet weight of pulp})}{100}$$

$$\% \text{ Yield} = \frac{\text{Yield in grams (OD)}}{\text{grams wood input (OD)}} \times 100$$

Pulp Testing

In order to estimate the amount of lignin present in the pulp samples, Kappa number tests were performed on the samples according to Tappi standard T 236. In addition, more direct determinations of pulp lignin content were made using the Klason lignin method.

The acid-insoluble lignin content of the wood and pulp samples was determined using Tappi standard T 222, and reported as Klason lignin. The ash content of the Klason lignin was established according to Tappi standard T 211. Finally, the amount of acid-soluble lignin was estimated for each sample, using Tappi useful method UM 250 and a Beckman DB spectrophotometer. Total lignin was determined by the addition of Klason lignin (corrected for ash) and acid-soluble lignin, and was reported both as a percent of the original wood (o.d.) and as a percent of the pulp.

Statistical Analysis

The linear regression equation ($Y = a + bX$), coefficient of determination (r^2), standard error of regression ($S_{y.x}$), and F statistic were calculated for each relationship considered in Results and Discussion. These statistics are presented in Table 5, for Kraft data, and Table 6, for sulfite data. The F statistic was used to determine the level of statistical significance using 1 and n-2 degrees of freedom.

Mill Sampling

Several pulp mills cooperated in this experiment by providing the opportunity to acquire pulp and liquor samples. Kraft samples were obtained from: Western Kraft Corp., in Albany, Oregon, the American Can Co. in Halsey, Oregon, and Weyerhaeuser Co. in Springfield, Oregon. Publishers' Paper Co. in Oregon City, Oregon, supplied the sulfite samples used in this study.

The first mill visited was Western Kraft Corp. This mill uses several batch digesters, and produces unbleached linerboard from Douglas-fir chips. Two one liter samples of pulp and liquor were

obtained at the brown stock washers.

The American Can Co. provided the next source of samples. Continuous digesters are used at this mill to produce a bleachable pulp from Douglas-fir sawdust and chips. This pulp is used for tissue and paper towel products. Three samples were obtained from a sampling port located at the end of the cooking cycle, before the pulp reaches the brown stock washers.

Three kraft samples were obtained from the Weyerhaeuser Co. This mill uses several batch and one continous digester to pulp a mixture of primarily Douglas-fir and some lodgepole pine for the production of unbleached linerboard. The samples were taken at the extraction zone of the continuous digester, just before the washing of the pulp.

Spent liquor for fluorescent analysis was hand squeezed from the stock samples obtained from both Western Kraft Corp. and the American Can Co., whereas the liquor samples were obtained from a different sampling port than the pulp samples at Weyerhaeuser. The pulp samples were washed as previously described, and tested for Kappa number.

A series of sulfite pulp and spent liquor samples was obtained at Publishers' Paper Co. This mill uses several batch digesters to produce a bleachable pulp for bond papers and printing purposes. The liquor samples were taken from a central sampling location in the digester house, while pulp samples were obtained from a pipe transporting the stock from the blow pit to the surge bin. One set of SSL samples corresponds with the final pulping conditions of five separate cooks. These samples were used with corresponding pulp samples to establish the relationship of spent liquor fluorescence

to Kappa number A second set of liquor samples was taken from one digester at half hour intervals from the beginning to the end of the cook. These samples were used to establish the effects of cooking time on spent liquor fluorescence.

RESULTS AND DISCUSSION

Optimum Wavelengths for Fluorescent Analysis

Previous investigators have established that the most useful excitation wavelengths for the fluorescent analysis of spent pulping liquors correspond to the ultraviolet absorption peaks of lignosulfonates in solution (205-215 nm, and 280 nm), while the fluorescent emission peaks are located at 400 nm for SSL and 430 nm for spent kraft liquor (1-6,10,23).

The wavelength of excitation for this study was arbitrarily chosen to be 280 nm, and the first samples of each type of spent liquor were examined by scanning the excitation spectrum from 250 nm to 400 nm to determine whether this wavelength corresponded with any absorption peak of the liquor. It was found that all liquor samples studied had excitation peaks in the range of 279-282 nm. The excitation monochromator was then set at 280 nm and held constant throughout the remainder of the study.

It was found that some samples of both kraft and sulfite spent liquor did not produce emission peaks exactly at the 400 and 430 nm wavelengths as had been established by Bublitz and Meng (10). However, fluorescent intensity was measured at 400 nm for SSL and 430 nm for kraft liquor, regardless of the exact location of the peak.

Optimum Bandwidths for Fluorescent Analysis

Samples of each type of spent pulping liquor were studied to determine the optimum bandwidth settings of excitation and emission. The

bandwidth combinations used were: excitation (ex) 10 nm/emission (em) 10 nm, ex 15 nm/em 10 nm, and ex 15 nm/em 25 nm. The fluorescent intensities recorded at each of these combinations were then plotted as functions of Kappa numbers and analyzed statistically to determine which combination of bandwidths provided the best relationship between fluorescent intensity and Kappa number.

The results of the kraft study are presented in Figure 1, with the statistical data in Table 5. Of the bandwidths tested, the combination of ex 15/em 25 gave the best results, with a coefficient of determination (r^2) equal to 0.99, a level of statistical significance $\geq$ 95%, and a standard error of regression ($S_{y.x}$) of 0.01.

The superior statistical significance and the steeper slope of the regression line, which would improve the ability to differentiate between samples, suggests that the combination of bandwidths ex 15/em 25 would be optimum for the subsequent fluorometric analysis of kraft waste liquor.

The results of the bandwidth comparison for spent sulfite liquor are presented in Figure 2, with supporting statistics in Table 6. Unlike the kraft waste liquor, which gave the most linear results with the widest bandwidth settings, the samples of spent sulfite liquor provided the best relationship between corrected fluorescent intensities and Kappa numbers with the combination of narrowest bandwidths, ex 10/em 10. This particular combination provided a regression equation with an r^2 of 0.90, and a $\geq$ 95% level of significance, and was therefore used for the subsequent analysis of spent sulfite liquor.

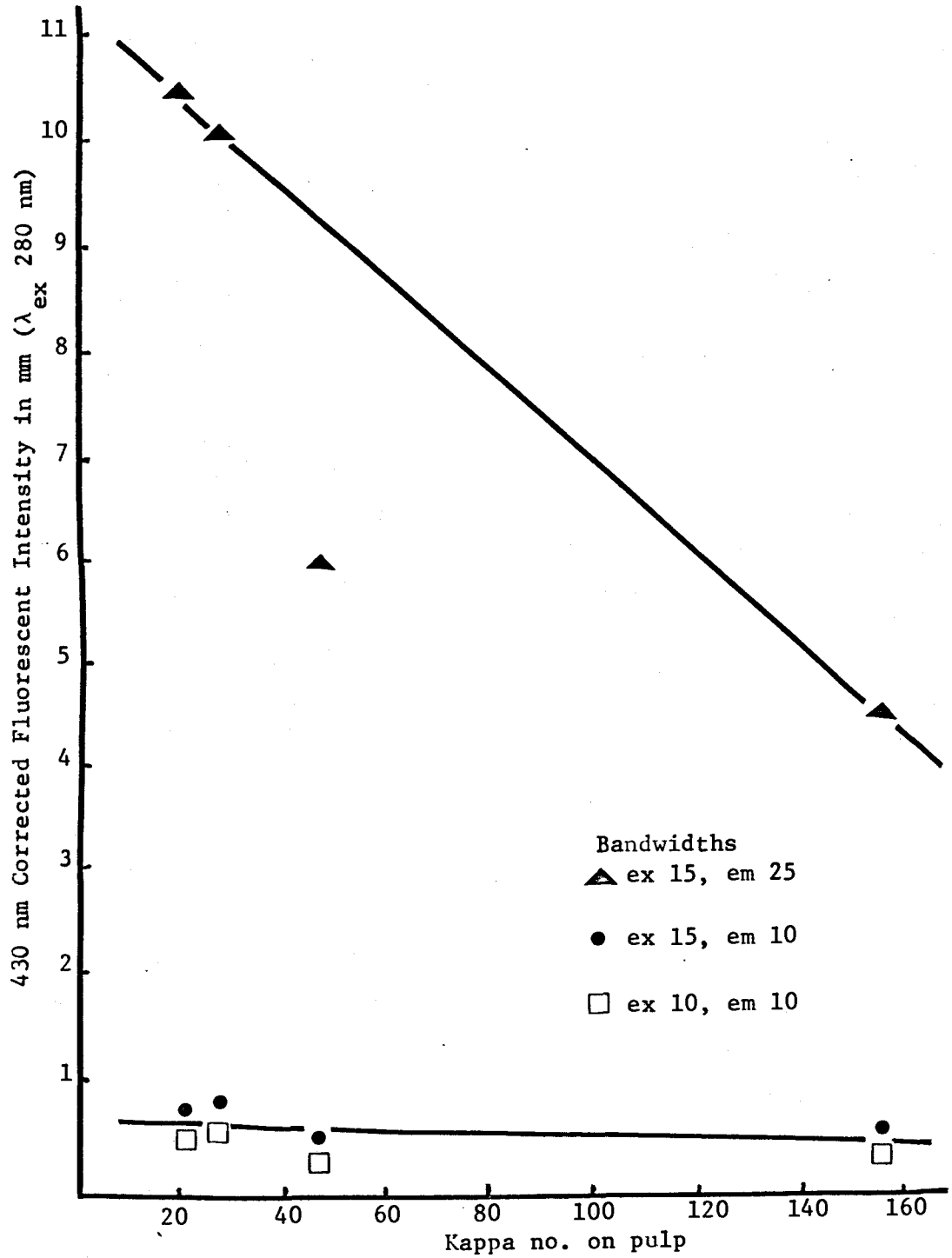

Fig. 1 Effect of Excitation and Emission Bandwidths on the Relationship: Corrected Fluorescent Intensity = f(Kappa no.) for Kraft Laboratory Experiments

Table 5 Kraft Statistical Data

Relationship	Regression coefficients[1/] a	b	r^2	F statistic[2/]	$S_{y \cdot x}$
Fig. 1					
Corrected F.I.[3/] = f(Kappa no.)					
ex 15/em 25	11.18	-0.04	0.99	124350 (2)	0.01
ex 15/em 10	0.70	0.00	0.92	12 (1)	0.08
ex 10/em 10	0.55	0.00	0.80	4 (1)	0.08
Fig. 3					
Total lignin (% on wood) = f(Yield	-14.87	0.44	0.97	227 (3)	1.66
Klason lignin (% on wood) = f(Yield)	-14.99	0.44	0.96	221 (3)	1.68
Fig. 4					
Total lignin (% on pulp) f(Yield)	-29.09	0.88	0.94	106 (3)	2.15
Klason lignin (% on pulp) = f(Yield)	-30.74	0.89	0.95	114 (3)	2.11
Fig. 5					
Kappa no. = f(Total lignin on pulp)	-8.82	6.65	0.98	468 (3)	7.01
Kappa no. = f(Klason lignin on pulp)	-2.14	6.56	0.98	486 (3)	6.88
Fig. 6					
Kappa no. = f(Yield)	-207.63	6.00	0.98	299 (3)	8.74
Fig. 7					
Corrected F.I. = f(Total lignin on pulp)	11.36	-0.28	0.97	162 (3)	0.50
Corrected F.I. = f(Klason lignin on pulp)	11.05	-0.04	0.97	169 (3)	0.49
Fig. 8					
Corrected F.I. = f(Kappa no.)	10.98	-0.04	0.99	538 (3)	0.28

(Table 5 continued)

Relationship	Regression coefficients[1/] a	b	r^2	F statistic[2/]	$S_{y \cdot x}$
Fig. 9					
Corrected F.I. = f(Yield)	19.82	-0.25	0.97	244 (3)	0.41
Fig. 10					
Corrected F.I. = f(Kappa no.)					
day 1 = day of cook	10.98	-0.04	0.99	528 (3)	0.28
day 2	10.78	-0.04	0.99	936 (3)	0.20
day 3	11.21	-0.03	0.68	11 (2)	1.52
day 16	4.23	0.00	0.11	1 (1)	17.20
Fig. 11					
Corrected F.I. - f(Age in days)	-	-	-	-	-
Fig. 12					
Corrected F.I. = f(Kappa number)					
Day 1 (diluted day 1)	10.98	-0.04	0.99	528 (3)	0.28
Day 40 (diluted day 40)	8.52	-0.03	0.76	20 (2)	1.26
Fig. 13					
Corrected F.I. = f(Kappa)					
Weyerhaeuser	20.19	-0.13	0.90	9.44 (1)	1.37
American Can	37.05	-0.26	0.84	5.54 (1)	1.89
Western Kraft	-	-	-	-	-
Fig. 25					
Filter F.I. = f(Corrected F.I.)					
440 cut off filter	0.21	0.34	0.96	140 (3)	0.18
405 + 436 band pass filter	0.04	0.15	0.69	14 (2)	0.26
436 band pass filter	0.00	0.07	0.78	21 (2)	0.10

(Table 5 continued)

1/ Linear regression equation $Y = a + bX$

2/ (1) F test $\leq$ 95% significance

(2) 95% $\leq F_{test} \leq$ 99.9%

(3) 99.9 $\leq F_{test}$

3/ F.I. = fluorescent intensity

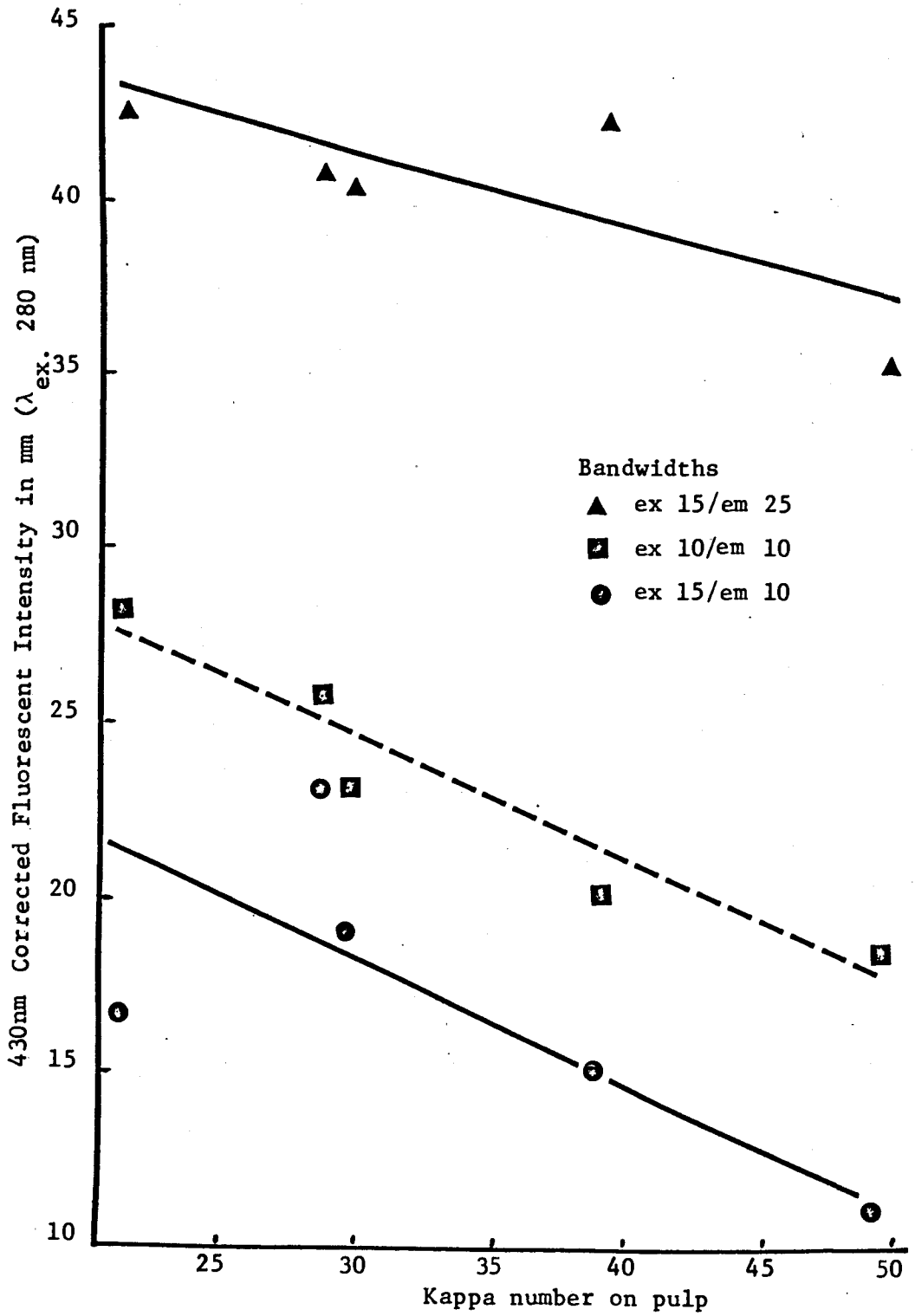

Fig. 2 Effect of Excitation and Emission Bandwidths on the Relationship: Corrected Fluorescent Intensity = f(Kappa no.) for Sulfite Mill Samples.

Table 6 Sulfite Statistical Data

Relationship	Regression coefficients[1] a	b	r^2	F statistic[2]	$S_{y \cdot x}$
Fig. 2					
Corrected F.I.[3] = f(Kappa no.)					
ex 15/em 25	48.18	-0.23	0.61	28.62 (2)	2.31
ex 15/em 10	27.75	-0.32	0.53	3.50 (1)	3.52
ex 10/em 10	35.82	-0.38	0.90	25.93 (2)	1.52
Fig. 14					
Total lignin on wood = f(Yield)	-15.56	0.47	0.98	253 (3)	1.73
Klason lignin on wood = f(Yield)	-15.99	0.46	0.98	258 (3)	1.68
Fig. 15					
Total lignin on pulp = f(Yield)	-9.63	0.44	0.81	8.87 (1)	5.95
Klason lignin on pulp = f(Yield)	-10.92	0.43	0.90	20.0 (2)	3.89
Fig. 16					
Kappa no. = f(Total lignin on pulp)	-5.50	5.64	0.99	202 (3)	7.80
Kappa no. = f(Klason lignin on pulp)	-0.43	6.15	1.00	1570 (3)	2.81
Fig. 17					
Kappa no. = f(Yield)	-76.6	2.78	0.89	24.15 (2)	23.67
Fig. 18					
Corrected F.I. = f(Total lignin on pulp)	5.96	-0.15	0.51	2.09 (1)	2.13
Corrected F.I. = f(Klason lignin on pulpP	5.09	-0.18	0.60	3.09 (1)	1.91
Fig. 19					
Corrected F.I. = f(Kappa no.)	5.79	-0.02	0.58	4.19 (1)	1.70

(Table 6 continued)

Relationship	Regression coefficients[1/] a	b	r^2	F statistic[2/]	$S_{y \cdot x}$
Fig. 20					
Corrected F.I. = f(Yield)	8.66	-0.09	0.77	10.05 (1)	1.23
Fig. 21					
Corrected F.I. = f(Age)	-	-	-	-	-
Fig. 22					
Corrected F.I. = f(Cooking ime)	-	-	-	-	-
Fig. 26					
Filter F.I. = f(Corrected F.I.)[4/]					
440 cut off filter	-	-	-	-	-
405 + 436 nm filter	4.04	1.53	0.59	2.86 (1)	3.94
405 nm filter	0.78	0.32	0.68	4.28 (1)	0.68
Fig. 27					
Filter F.I. = f(Corrected F.I.)[5/]					
440 cut off filter	-	-	-	-	-
405 + 436 nm filter	0.84	0.15	0.99	793.26 (3)	0.31
405 nm filter	0.28	0.03	0.99	317.27 (3)	0.10

1/ Linear regression equation $Y = a + bX$

2/ (1) F test ≤ 95% significance (2) 95 % ≤ F_{test} ≤ 99.9% (3) 99.9% ≤ F_{test}

3/ F.I. = fluorescent intensity

4/ ex 10/em 10

5/ ex 15/em 25

Kraft Pulping Results

Lignin Content versus Pulp Yield

The lignin content of wood pulps may be considered in two ways: as a percentage of the original wood substance or as a percentage of the pulp. The first method of considering lignin content provides an overview of the pulping process. Given 100 pounds of wood input, for example, about 28 pounds is lignin (Figure 3); as this wood is pulped by the kraft process to a total yield of 50%, approximately seven pounds of lignin remains in the pulp, or 7% of the original wood. This concept of lignin content is valuable for material balances. The second method of considering lignin content (as a percentage of the pulped wood) pertains to the quality of the finished pulp, by describing the amount of lignin actually remaining in it.

Figure 3 represents the relationship of lignin content (as a percent of the original wood) to total pulp yield. A linear relationship exists between these variables which explains 97% of the observed variation ($r^2 = 0.97$), with a 99.9% level of significance (Table 5).

The relationship between lignin content (as a percentage of the remaining pulp) and pulp yield is also linear (Figure 4). The regression equation for this relationship has an $r^2 = 0.94$, and a 99.9% level of significance (Table 5).

Kappa Number versus Kraft Lignin Content

The determination of the Kappa number is an industrial test made on pulp samples to estimate the lignin content of the pulp. The test, which is a measure of the oxidizable material present in the pulp sample, may be conducted in a matter of minutes, compared with a minimum of eight hours for the Klason lignin method. Kappa number, or a similar test called permanganate number (K number), is a standard control test in

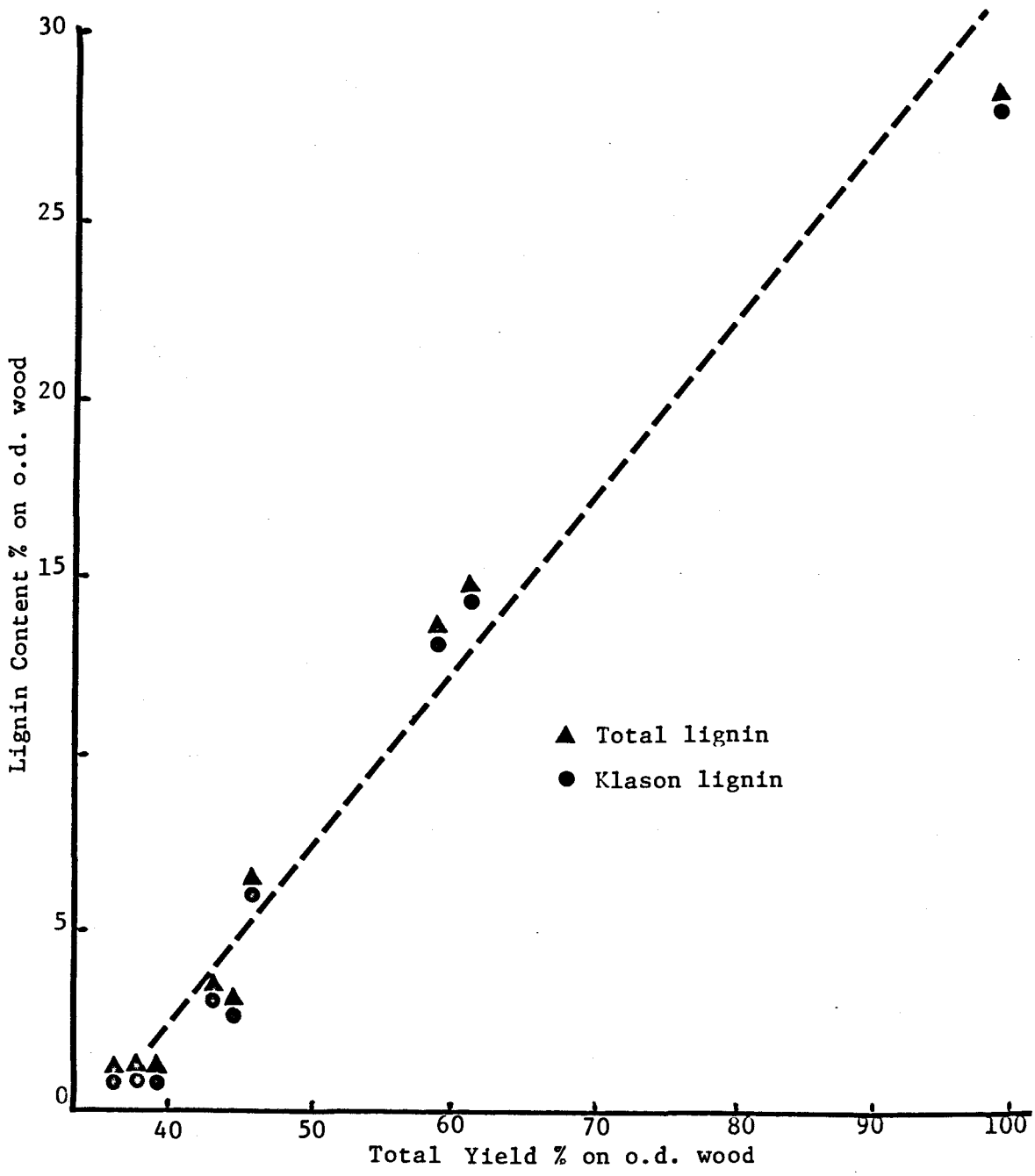

Fig. 3 Lignin Content = f(Yield) for Kraft Laboratory Samples

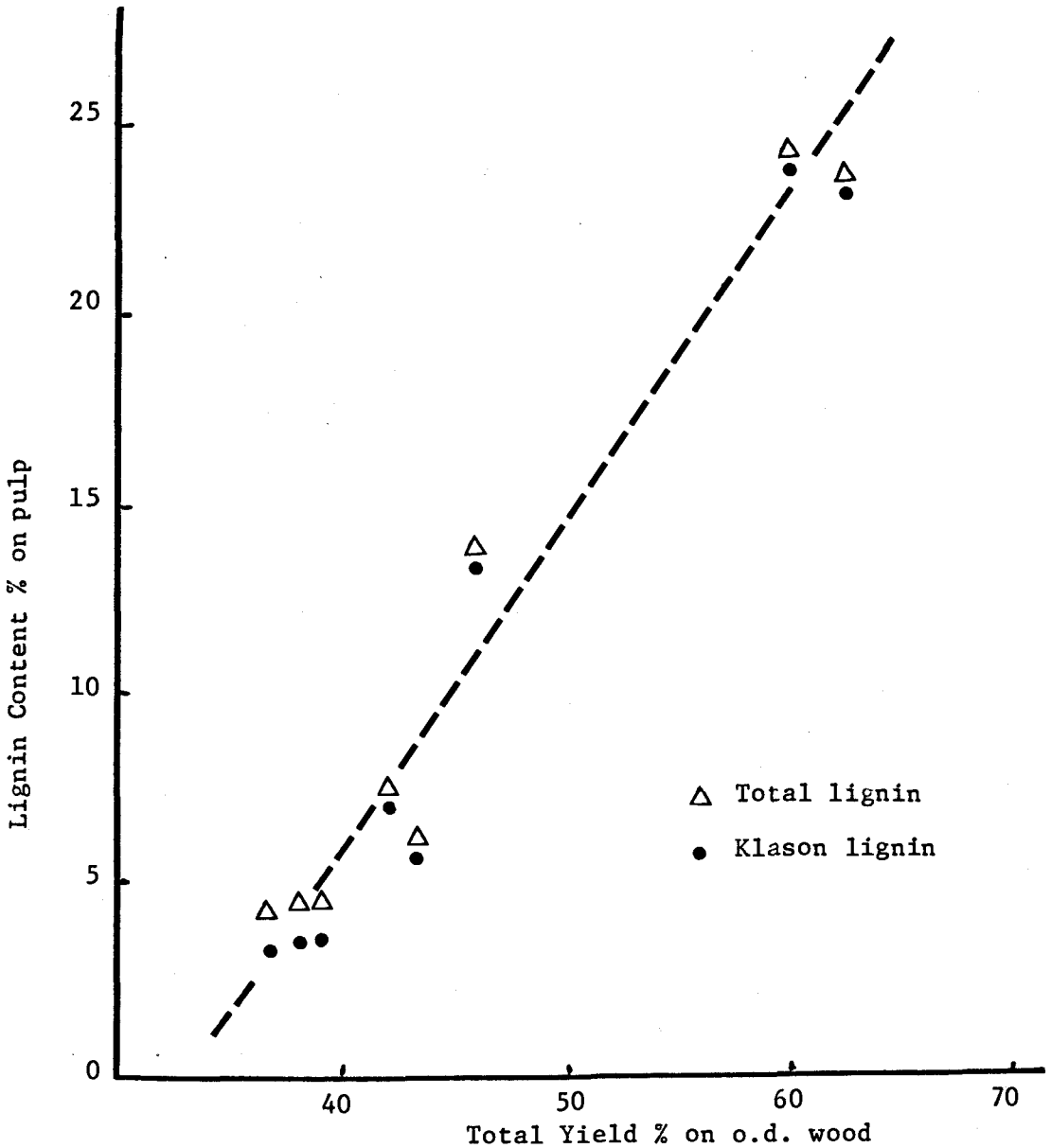

Fig. 4 Lignin Content on pulp = f(Yield)
for Kraft Laboratory Pulps

the pulp industry.

The relationship of pulp Kappa number to pulp lignin content is depicted graphically in Figure 5, with supporting statistics in Table 5. The relationship is linear, with an r^2 of 0.98 for both Kappa vs. total lignin and Kappa vs. Klason lignin, and F statistics for both are of $\geq$ 99.9% significance. It appears from this data that Kappa number may be used as an accurate approximator of lignin content in kraft pulps, and verifies the findings of Hinrichs (24) that the Kappa number test is a suitable procedure for the estimation of lignin content in industrial pulps.

Kappa Number versus Yield

The relationship of Kappa numbers to pulp yields is also linear for the laboratory samples, with an r^2 of 0.98 and a significance level of $\geq$ 99.9% (Figure 6, Table 5). This relationship is of commercial importance, due to the difficulty of determining pulp yield in a mill.

The Fluorescent Characteristics of Kraft Waste Liquor

Corrected Fluorescent Intensity versus Lignin Content of Kraft Pulps

This relationship is presented in Figure 7. The regression line has a coefficient of determination equal to 0.97 for both corrected fluorescent intensity vs. total lignin and corrected fluorescent intensity vs. Klason lignin. Both equations have significance levels $\geq$ 99.9%, and almost equal $S_{y \cdot x}$ values (Table 5).

These results encompass the heart of this research. Within a closed digester, the bulk of the lignin removed from the wood will be contained in the cooking liquor, and by the fluorometric measurement of the lignin content with the liquor (under constant conditions) an estimation may be made of the lignin remaining in the pulp. This knowledge

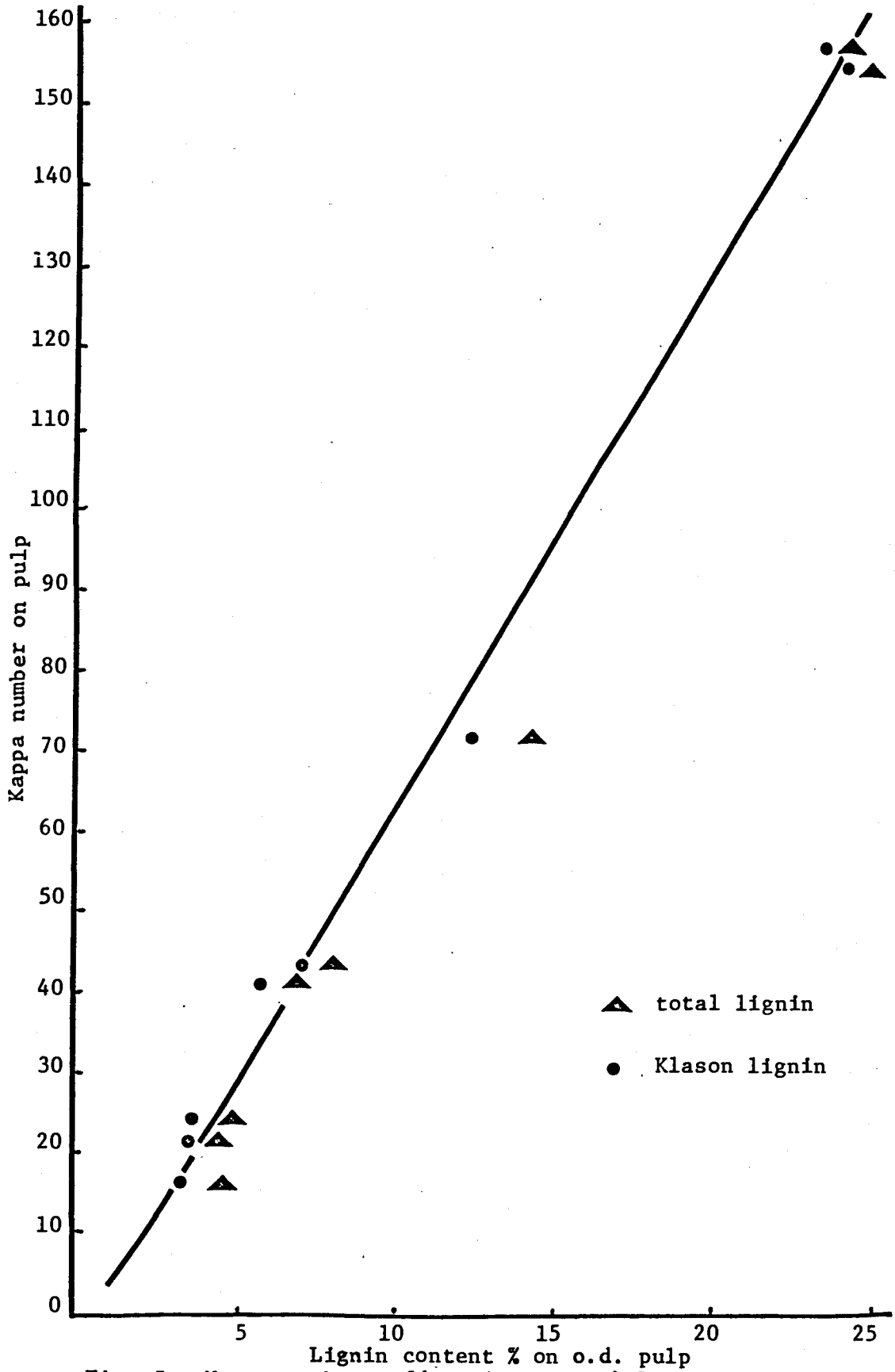

Fig. 5 Kappa number = f(Lignin Content) for Kraft Laboratory Samples

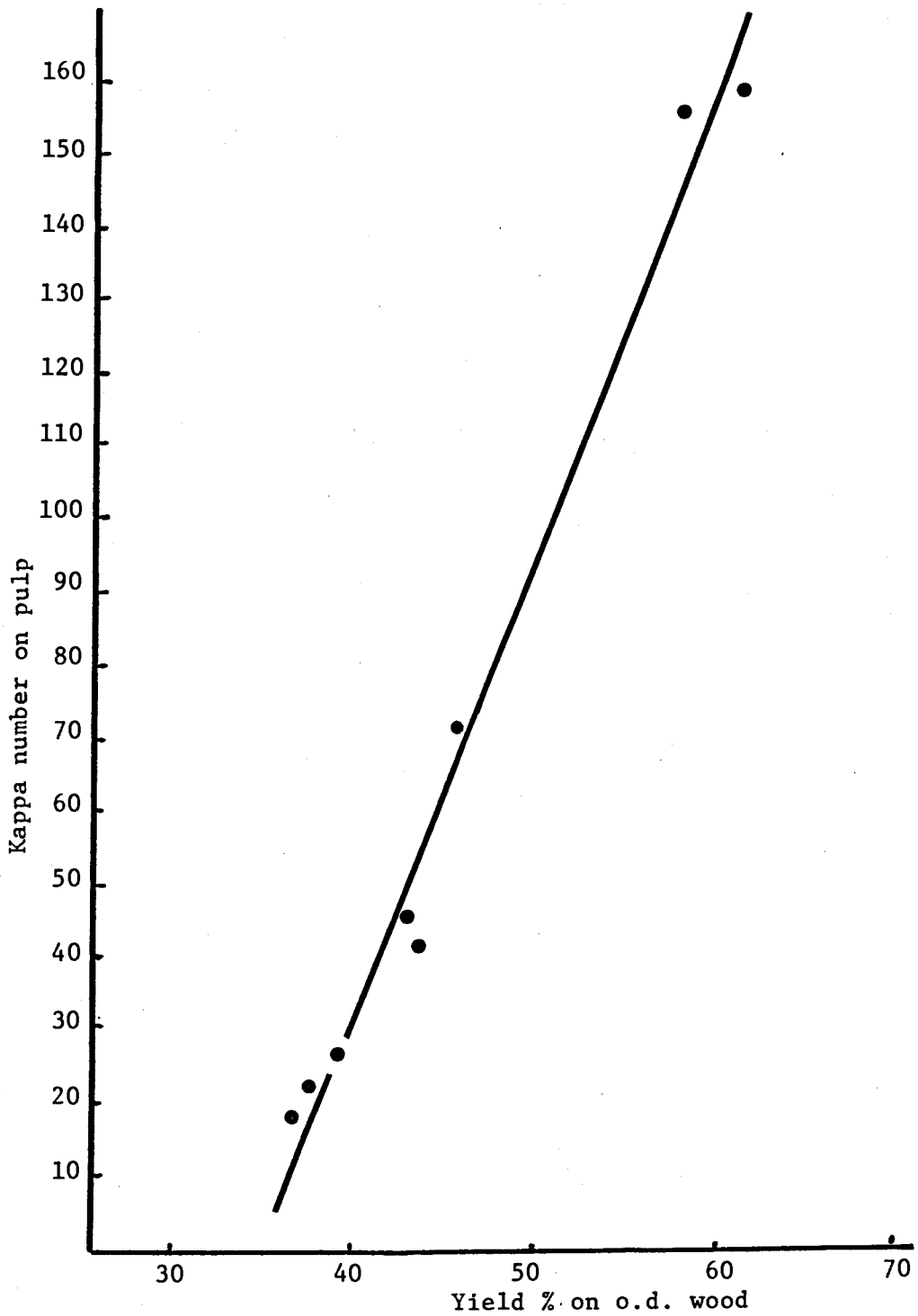

Fig. 6 Kappa number = f(Yield)
for Kraft Laboratory Samples

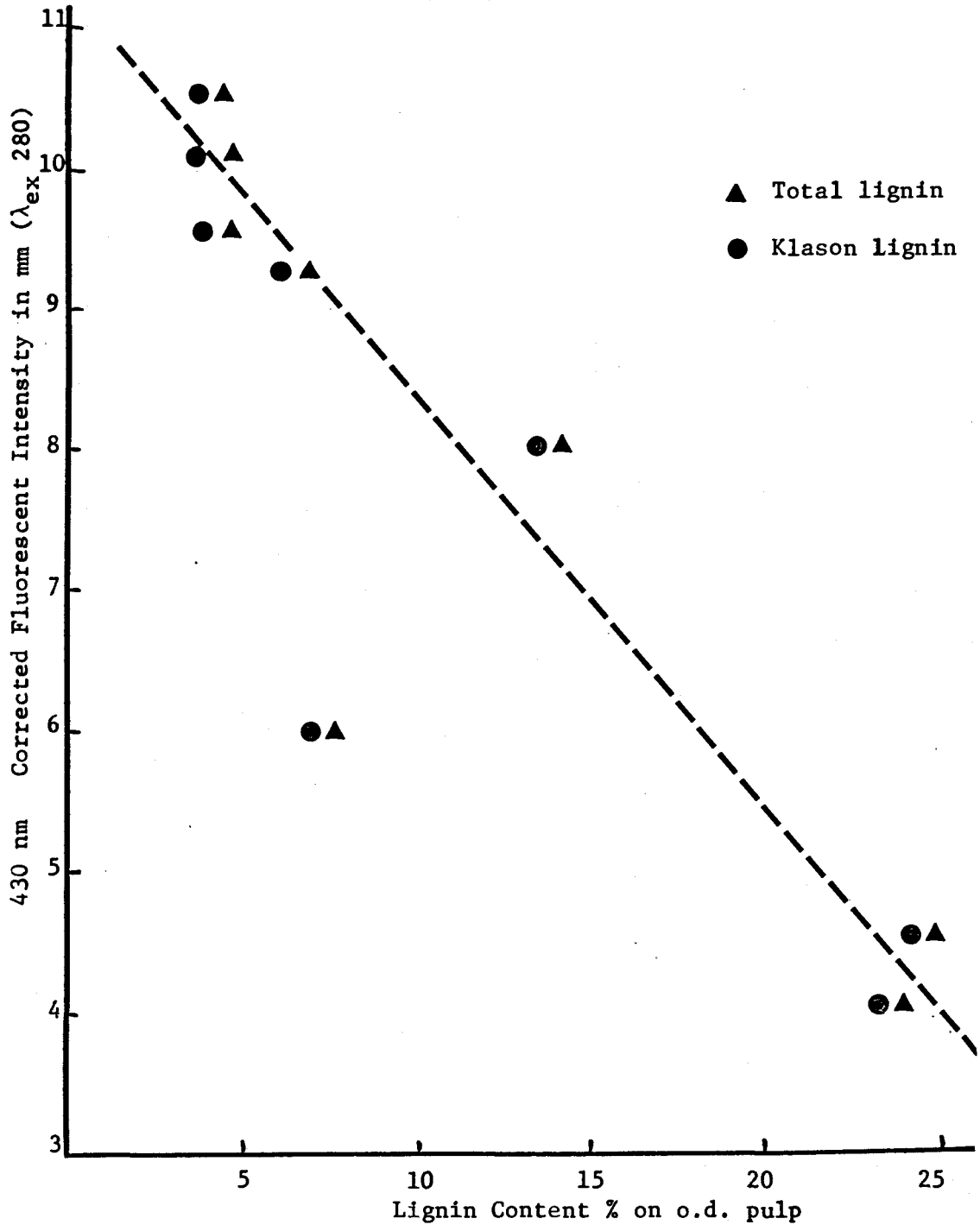

Fig. 7 Corrected Fluorescent Intensity = f(Lignin Content) for Kraft Laboratory Samples

may then be used to determine the progress of the pulping reaction and thus ultimately to establish when the desired amount of delignification has been achieved.

Corrected Fluorescent Intensity versus Kappa Number

Due to the linearity existing between Kappa numbers of pulps and pulp lignin content, as well as between corrected fluorescent intensity and kraft lignin, it is not surprising that the relationship of corrected fluorescent intensity = f(Kappa number) is also linear in nature (Figure 8).

The regression equation for this relationship explains somewhat more of the sample variation than did the equation for corrected fluorescent intensity = f(lignin content), (r^2 = 0.99 compared with 0.97). Fluorescent intensity as a function of pulp Kappa number has a level of statistical significance $\geq$ 99.9% (Table 5).

The linear nature of this relationship means that it should be possible to use the fluorescent intensity of kraft liquor as an indirect measure of pulp Kappa number, the present industrial standard. Even though the determination of Kappa number is a fairly short procedure, the test cannot be made until the pulping process has been completed for the sample in question. This means that any changes in pulping control parameters based upon the Kappa number of the pulp are made after the fact, and may not represent the optimum conditions for delignification for the next digester cycle. Measurement of liquor fluorescence, however, can be done during the actual cooking operation by removing a small quantity of cooking liquor from the liquor circulation system, diluting it to the proper degree, and inserting it into a fluorometer for analysis. This would allow continual monitoring of the ongoing pulping process, and therefore should improve the precision and accuracy

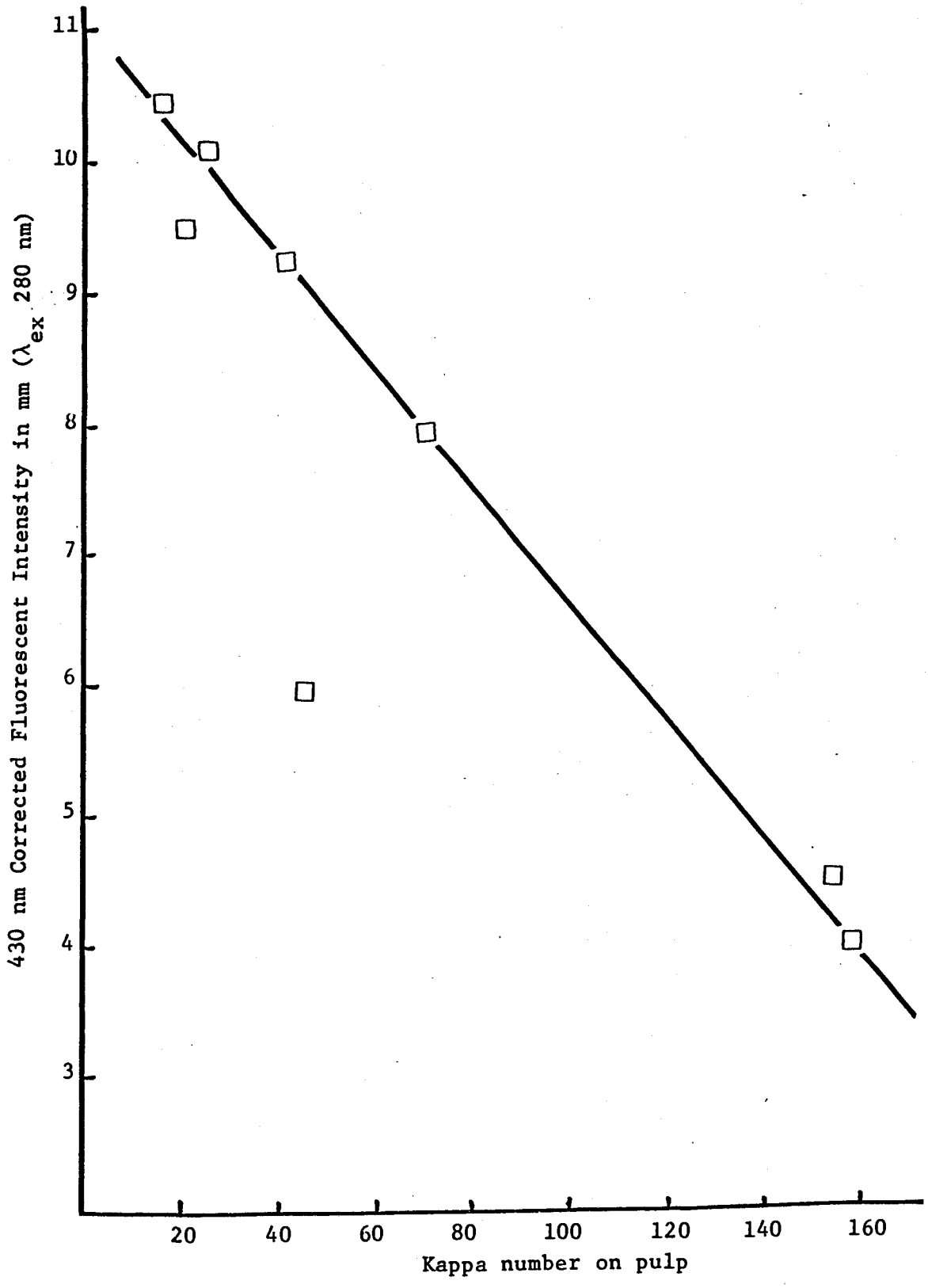

Fig. 8 Corrected Fluorescent Intensity = f(Kappa no.) for Kraft Laboratory Samples

of estimating the desired endpoint of the cook. This increased control over the pulping process should provide a savings in raw material, cooking liquor, and in the energy required to heat the digester.

Corrected Fluorescent Intensity versus Pulp Yield

The relationship of fluorescent intensity to total pulp yield is linear, with an r^2 of 0.97, and is significant at the 99.9% level (Figure 9, Table 5). According to these results, spent liquor fluorescence may thus serve as a tool for the estimation of kraft pulping yields.

Effects of Sample Age on Kraft Liquor Fluorescence

The relationship between kraft liquor fluorescence and Kappa number appears to be time dependent (Figures 10 and 12). Table 5 shows that the variation in fluorescent intensity that is explained by the regression equation, Corrected fluorescent intensity = f(Kappa number), decreases within two days following pulping. Values of r^2 dropped from 0.99 to 0.68 within a three day period, followed by a further decrease from 0.68 to 0.11 between days 3 and 16. There is a corresponding decrease in the significance level during this period, as well. These results are shown in Figure 10, and represent a study performed on samples which were diluted immediately following the pulping operation, and stored under refrigeration in the dilute form for 16 days.

Figure 11 shows other effects of aging on spent liquor fluorescence. This graph depicts the changes in fluorescent intensity that occur each day following the cook, and shows a two day period during which the fluorescent response of each sample appears stable. From Table 5 it can be seen that there is no change in r^2 or significance

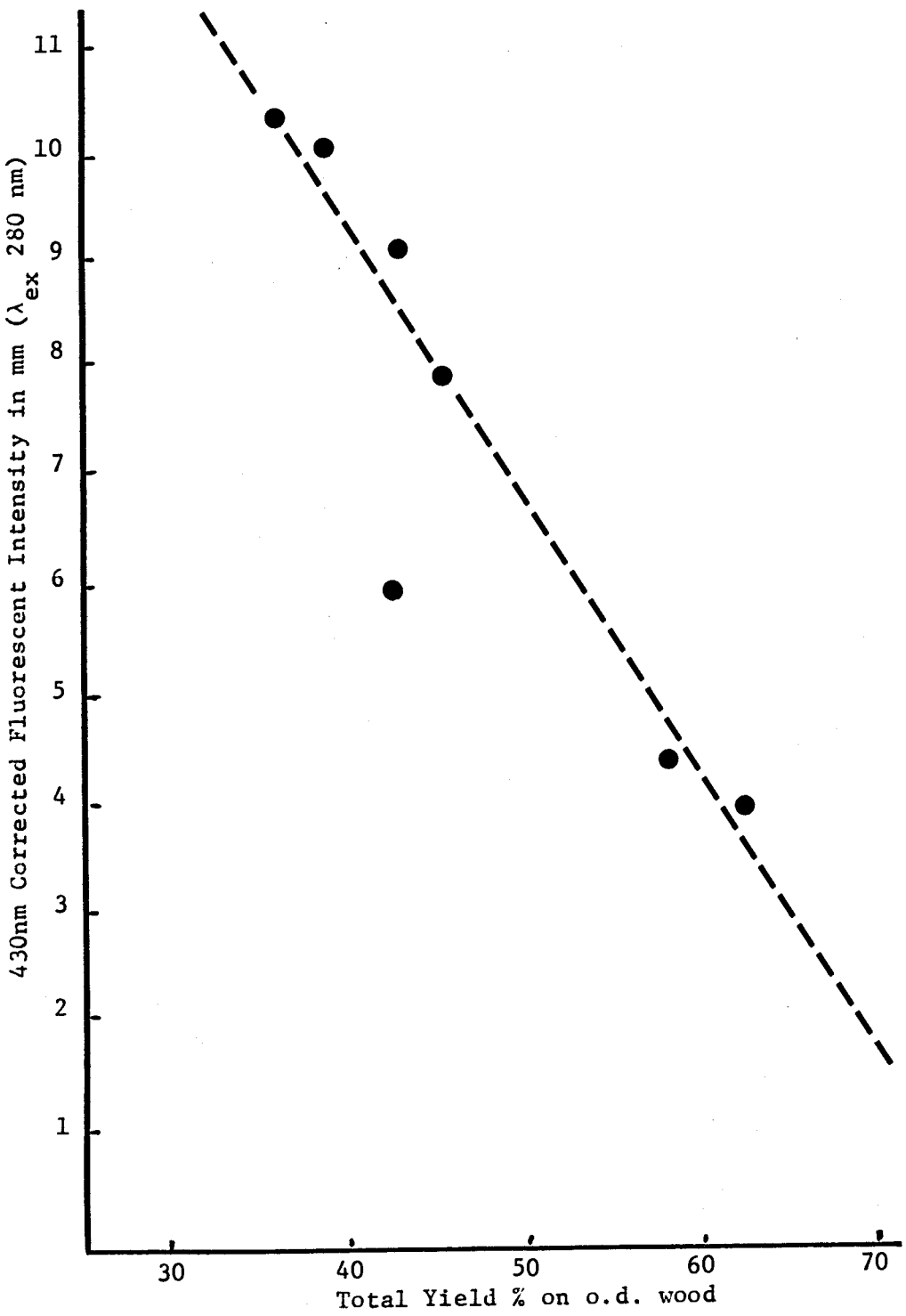

Fig. 9 Corrected Fluorescent Intensity = f(Yield) for Kraft Laboratory Samples

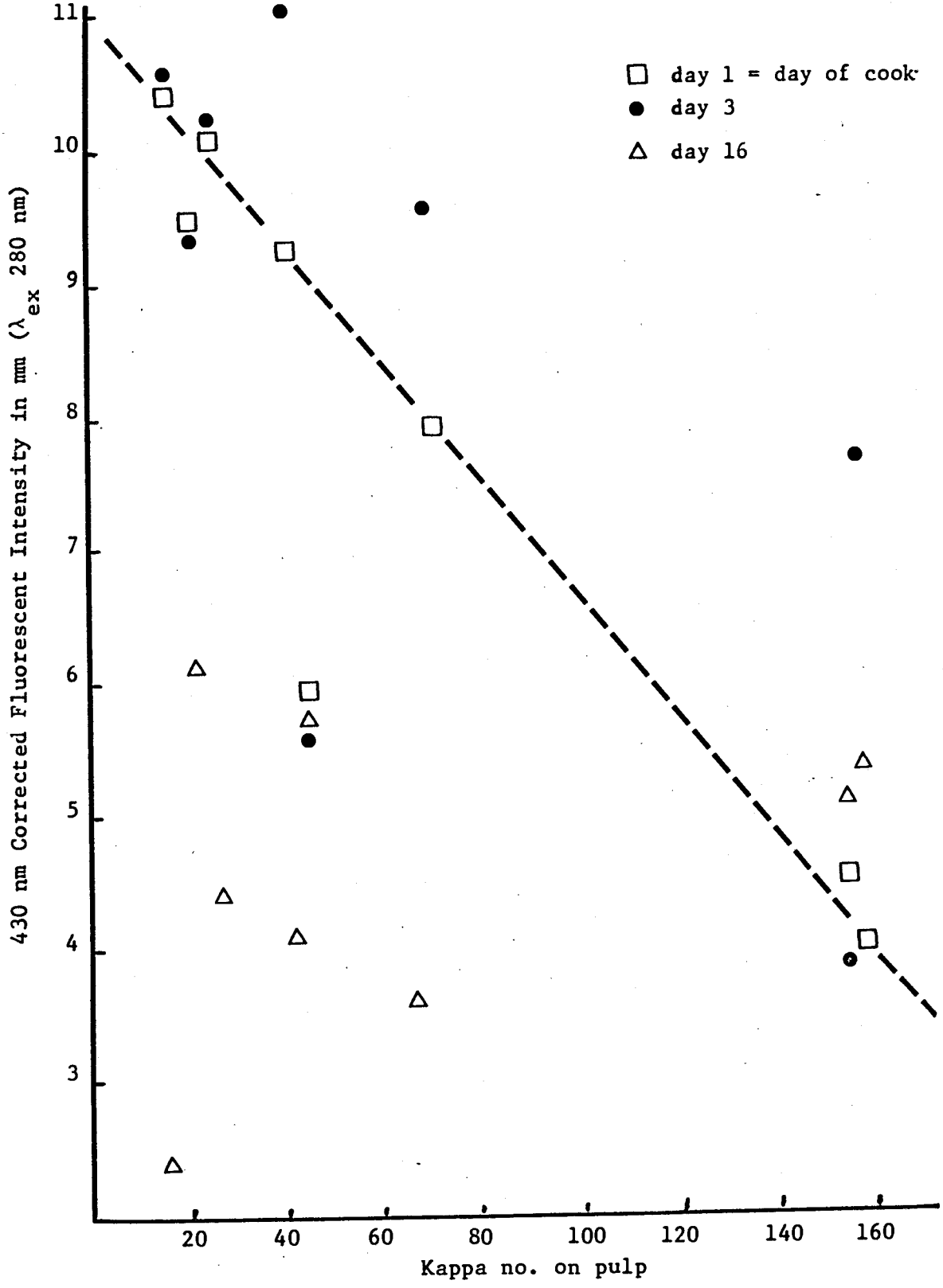

Fig. 10 Affect of Age of Corrected Fluorescent Intensity = f(Kappa no.) for Kraft Laboratory Samples

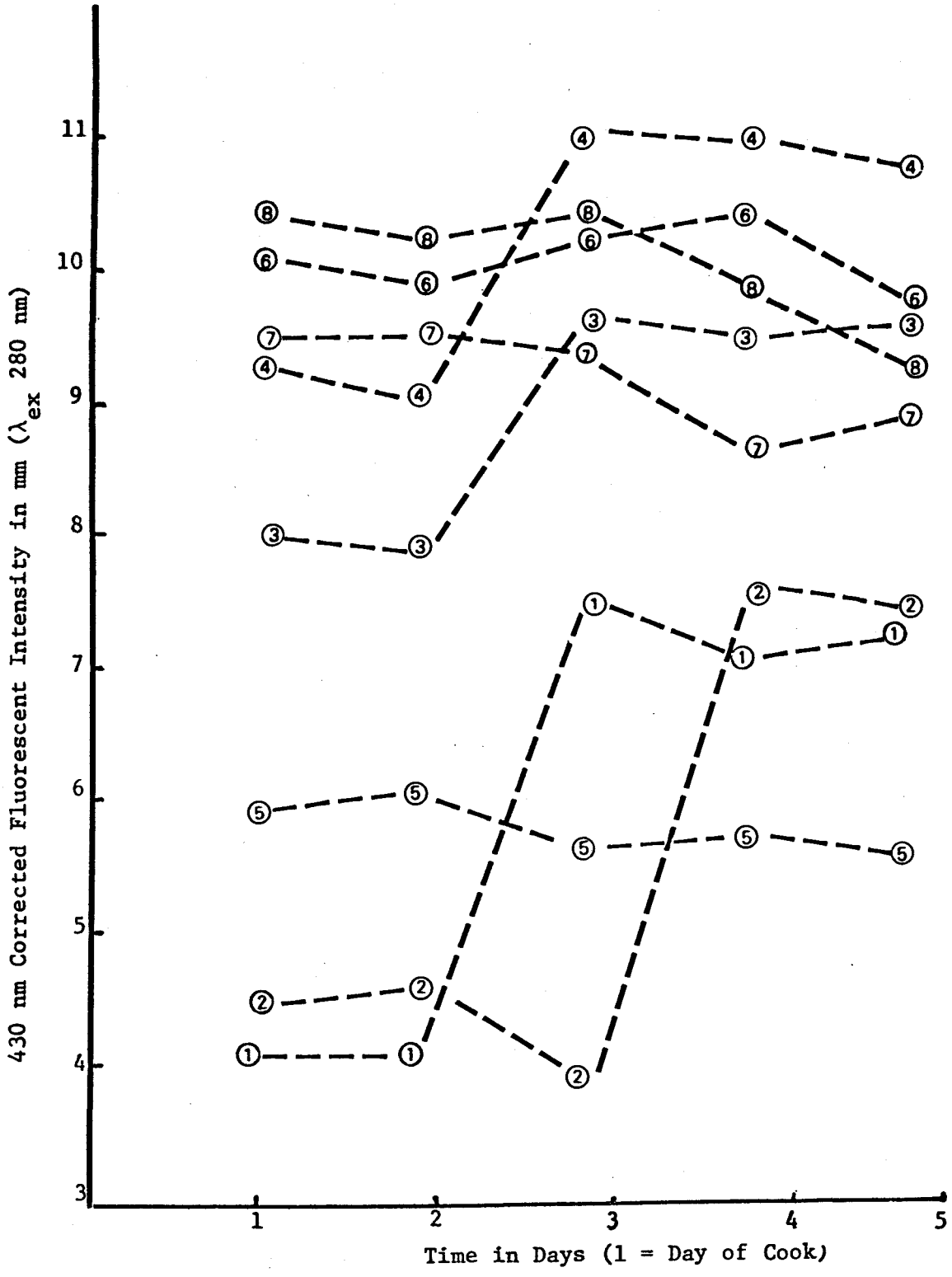

Fig. 11 Corrected Fluorescent Intensity = f(Time in days) for Kraft Laboratory Samples, Diluted day 1

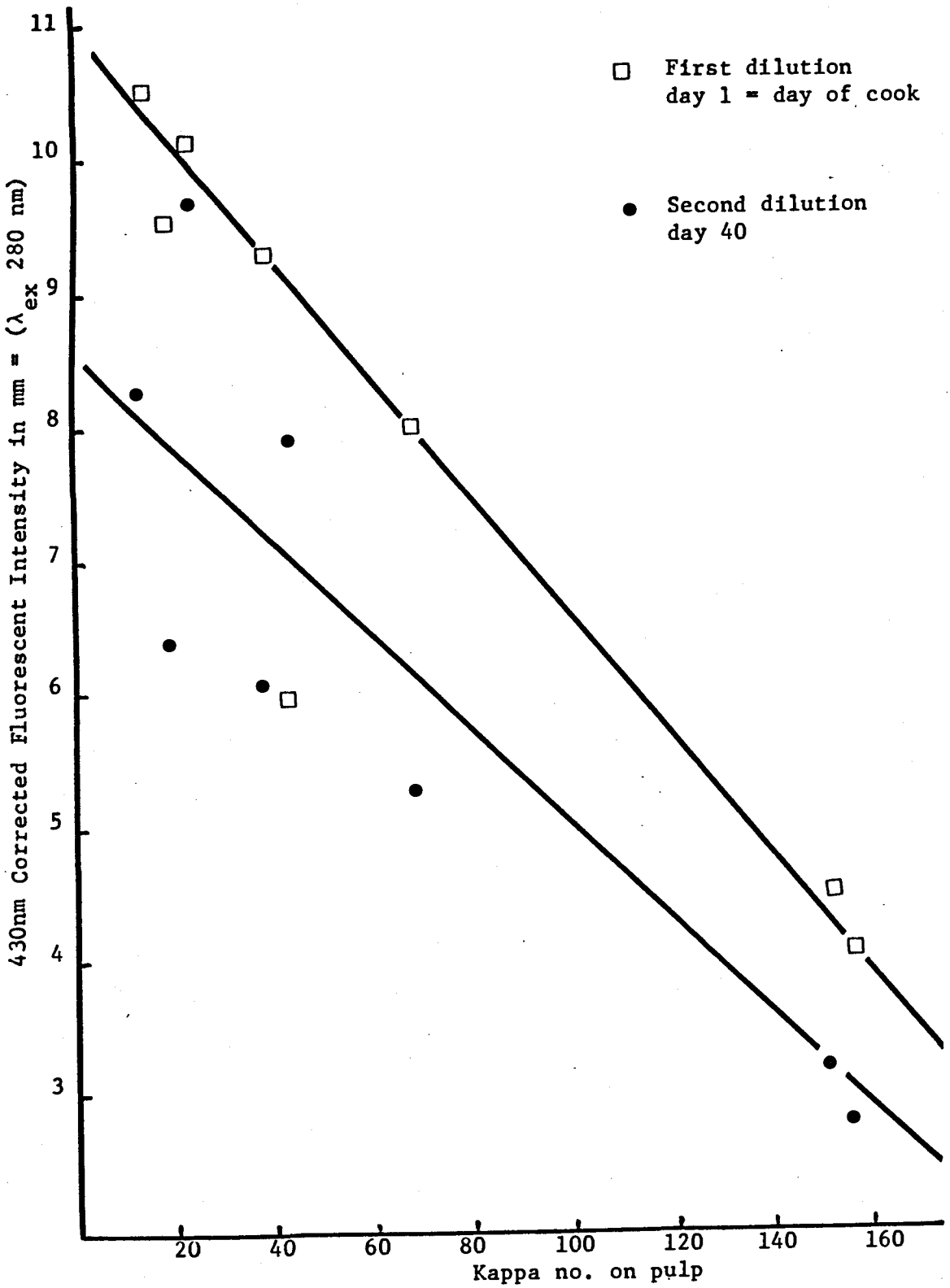

Fig. 12 Affect of Aging on Corrected Fluorescent Intensity = f(Kappa no.) for Kraft Laboratory Samples

level of the relationship of fluorescence to Kappa numbers for days 1 and 2 (day 1 = day of cook). These findings support the contention of Baumgartner et al (5) that fluorescent analysis of kraft pulping wastes must be conducted within 48 hours of sample collection. However, these investigators noticed only a decrease in fluorescent output, whereas the samples of kraft liquor studied in this experiment show no uniform response with age (Figure 11).

A subsequent study performed on freshly diluted samples of kraft liquor indicates a lessened effect of aging when the samples are stored at the original concentration (undiluted). This study was performed 40 days after pulping, using the same liquor sample as was used for the study of dilute liquor aging, and the decreases in r^2 and significance level were not as great for these samples as for the samples which were diluted first and then stored (Figure 12, Table 5). This suggests that samples of kraft mill waste which are being held for fluorescent analysis should not be diluted until tested, in order to minimize the effect of aging upon fluorescence.

Fluorescent Characteristics of Kraft Mill Spent Liquors

As noted, the first mill visited to obtain kraft pulp and liquor samples was Western Kraft Corp. in Albany, Oregon. At this mill, when the cooking cycle has been completed, a valve at the base of the digester is opened, and the pressure within the digester blows the pulped wood and liquor into a common blow pit. The pulp and liquor of several preceding cooks is mixed at this point, and this stock is then further diluted with more waste liquor in order to achieve a low enough consistency to allow the blow pit to be pumped out. This means that any pulp and liquor samples not obtained directly from a digester will be a

mixture of several cooks, and no longer representative of the pulping conditions which have just occurred.

Unfortunately, the first readily available sampling location after the digesters was at the brown stock washers, and therefore no samples could be obtained until after stock from different digester batches had already been mixed. This mixing resulted in a relationship between fluorescent intensity and Kappa number that was inverse to that exhibited by the laboratory samples (Figure 13).

The other kraft mill samples were obtained from the American Can Co. mill in Halsey, Oregon, and the Weyerhaeuser Co. mill in Springfield, Oregon. Both samples were obtained from continuous digesters after the pulping zone, and preceding the washing of the pulp. Therefore, the liquor samples were uncontaminated, and should correspond with the pulp samples which were obtained at the same sampling port.

Figure 13 depicts a non-linear relationship between fluorescent intensity and Kappa number, for the samples obtained from American Can Co. Two of three samples obtained at this mill correspond to a period when chips were being pulped. The third sample, which had by far the highest fluorescent intensity, as well as the lowest Kappa number, was taken when the mill was pulping sawdust. The difference in fluorescent intensity of this last sample could be due to a difference in the delignification rate between sawdust and chips.

A non-linear relationship also exists between fluorescent intensity and Kappa number for the Weyerhaeuser Co. samples (Figure 13). This mill uses predominantly Douglas-fir chips with a lesser amount of lodgepole pine (usually 20-25%). The sample which exhibited the greatest fluorescent intensity, as well as the lowest Kappa number, had been withdrawn from a cook composed of 30-40% pine, and it had been over-

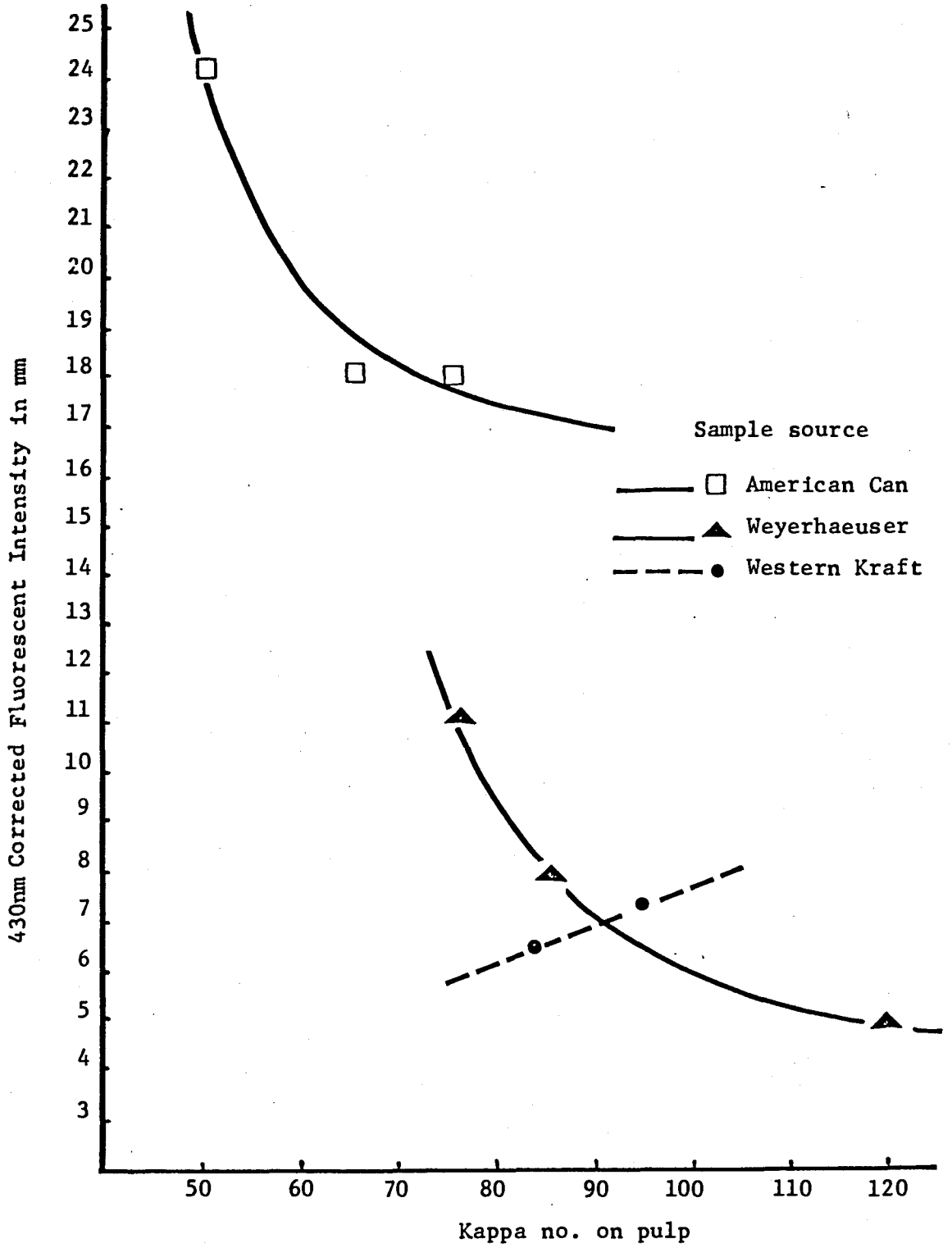

Fig. 13 Corrected Fluorescent Intensity = f(Kappa no.) for Kraft Mill Samples

cooked. The difference in fluorescence between these samples may be due in part to the change in species mix, and in part to the longer cooking time, which would increase the total delignification and thus the total amount of lignin in the liquor.

It is interesting to note that the liquor samples from the two mills producing linerboard had similar fluorescent intensities. Kappa numbers of the pulp samples were also similar. The Kappa numbers of the American Can Co. samples are much lower, reflecting the needs of a mill producing bleached tissue products for a pulp containing less lignin.

Sulfite Pulp Properties

Lignin Content as a Function of Total Pulp Yield

The relationship of lignin content (as a percent of the original wood) to sulfite laboratory pulp yield is presented in Figure 14. The linear regression equation has an r^2 of 0.98, with a $\geq$ 99.9% level of significance (Table 6). This graph represents an overview of the delignification process.

When lignin content is measured as a percent of the remaining pulp, its relationship to pulp yield is nonlinear (Figure 15).

Kappa Number versus Lignin Content

According to the data presented in Table 6, Kappa number is an accurate measure of the lignin content of sulfite pulps. The regression equation for the relationship Kappa number = f(Total lignin) explains 99% of the observed variation (r^2 = 0.99), while the equation for Kappa number = f(Klason lignin) also explains 99% of the observed variation between pulp samples (r^2 = 0.99). Both equations exceeded the 99.9% level of statistical significance (Figure 16, Table 6).

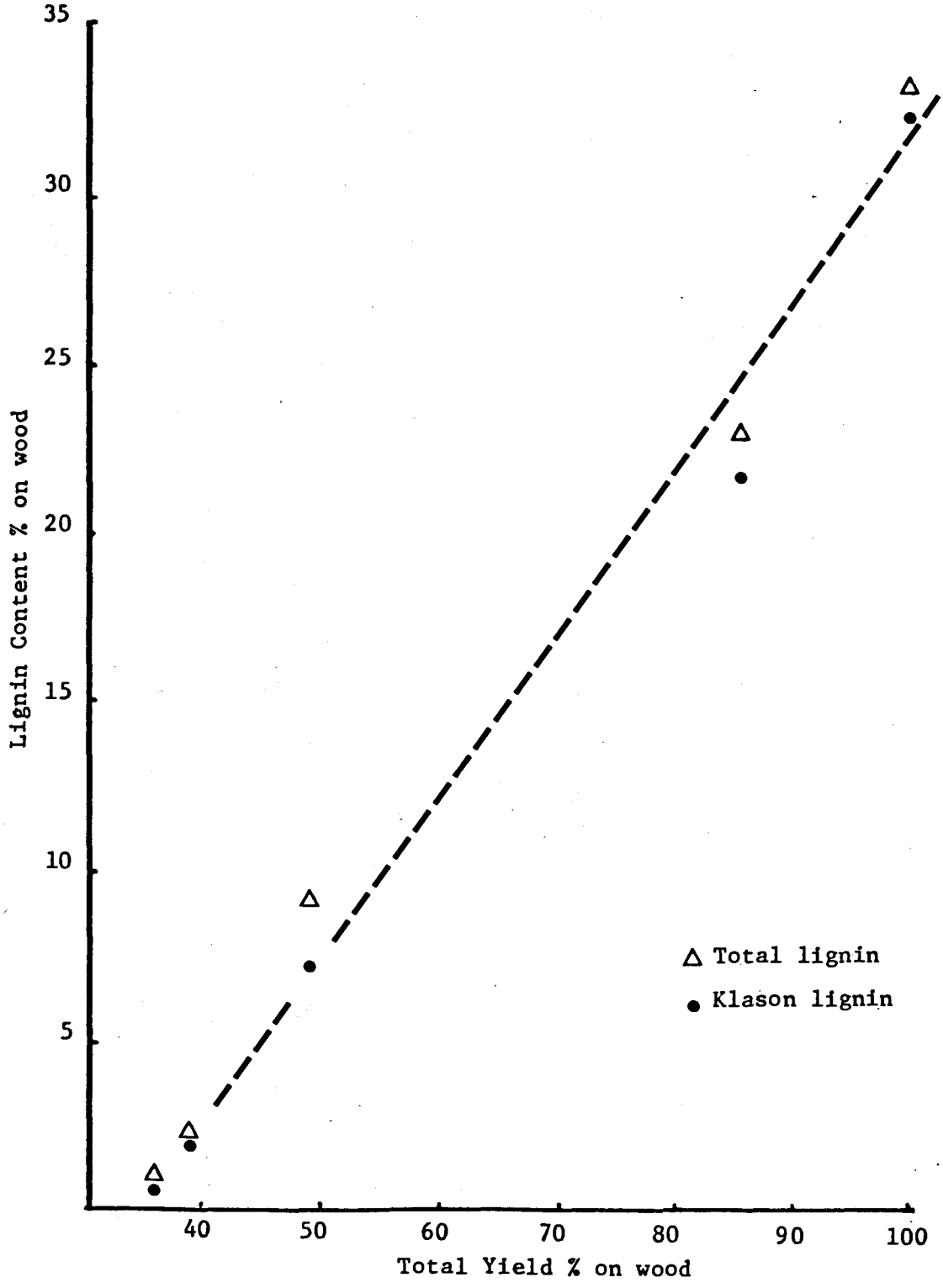

Fig. 14 Lignin Content on wood = f(Yield) for Sulfite Laboratory Pulps

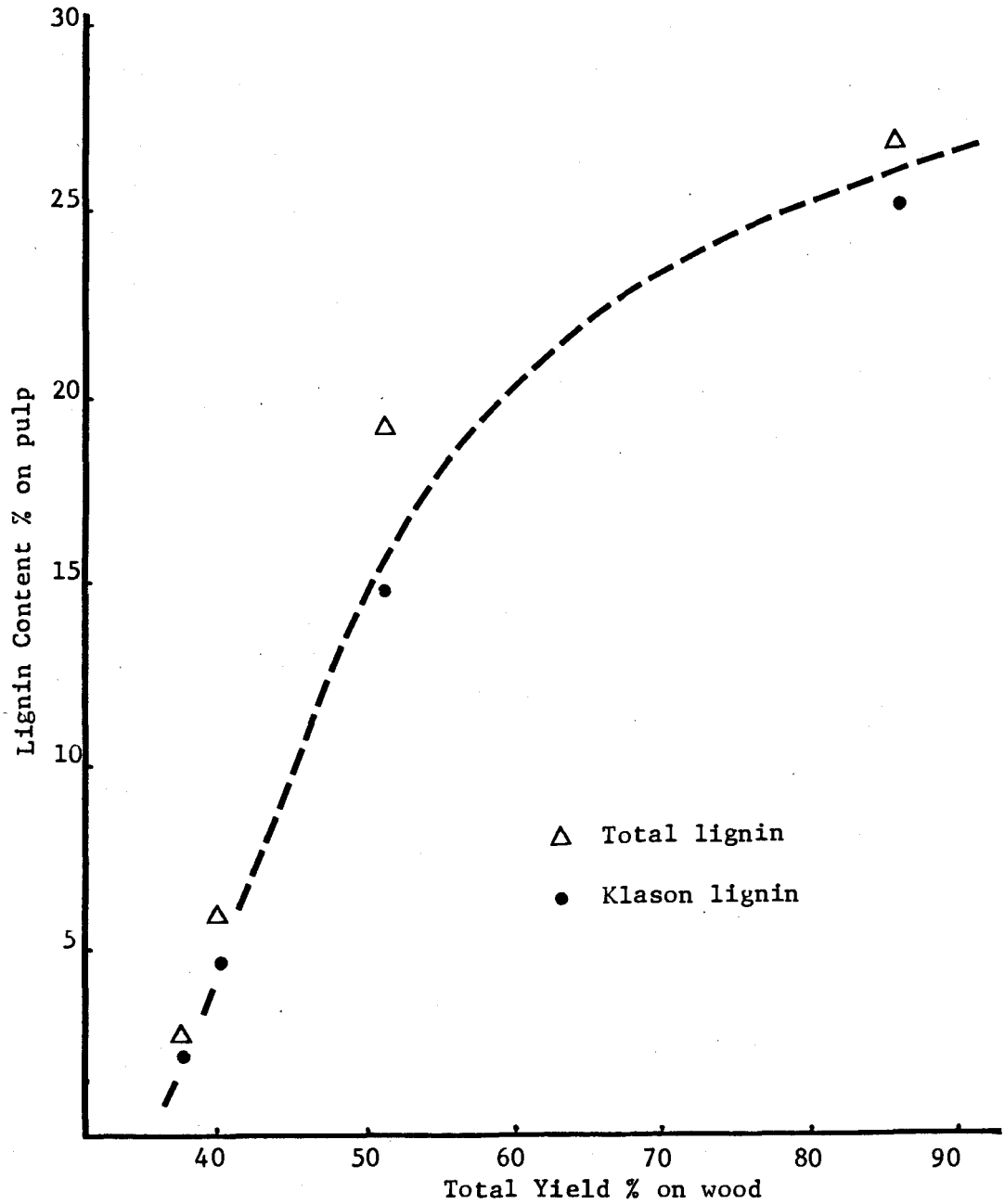

Fig. 15 Lignin Content on Pulp= f(Yield) for Sulfite Laboratory Pulps

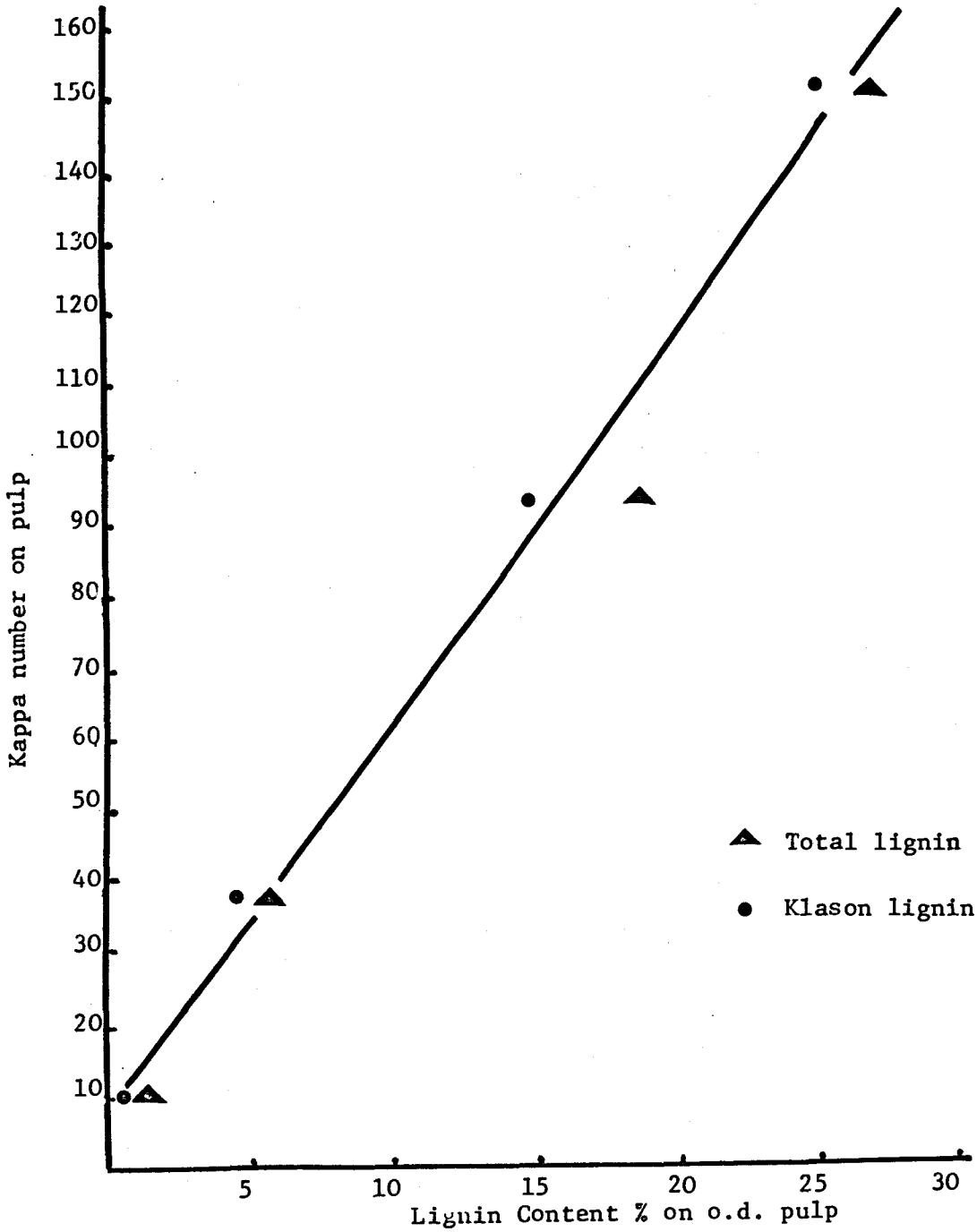

Fig. 16 Kappa number = f(Lignin Content) for Sulfite Laboratory Samples

Kappa Number as a Function of Pulp Yield

Much like pulp lignin content, Kappa number does not appear to bear a linear relationship with pulp yield (Figure 17).

Fluorescent Characteristics of Spent Sulfite Liquor

Fluorescent Intensity versus Lignin Content

Unlike the results of the kraft pulping study, the correlation of fluorescent intensity to lignin content of sulfite pulp is nonlinear, reaching a maximum fluorescent intensity in the region of 5-10% lignin content on pulp (Figure 18, Table 6). This corresponds with approximately 40% yield (Figure 15). When a sufficient amount of lignin is extracted from the wood, the fluorescent species (lignin) apparently undergoes a reaction which sharply decreases the fluorescent activity of the waste liquor.

Christman and Minear (2,3) established that increases in the molecular weight of lignosulfonates decreases their fluorescent activity. It is possible that, after a sufficient amount of lignin has been dissolved into the cooking liquor, a condensation reaction occurs between the lignin molecules, resulting in larger lignin molecules which are less fluorescent by nature.

Fluorescent Intensity versus Kappa Number

Fluorescent intensity goes through a maximum at a Kappa number of 40 followed by a sharp decrease in fluorescent output as more lignin is brought into solution (Figure 19).

Sulfite Liquor Fluorescence as a Function of Pulp Yield

This relationship presents the same fluorescent maxima in the neighborhood of 40% yield, as noted earlier (Figure 20).

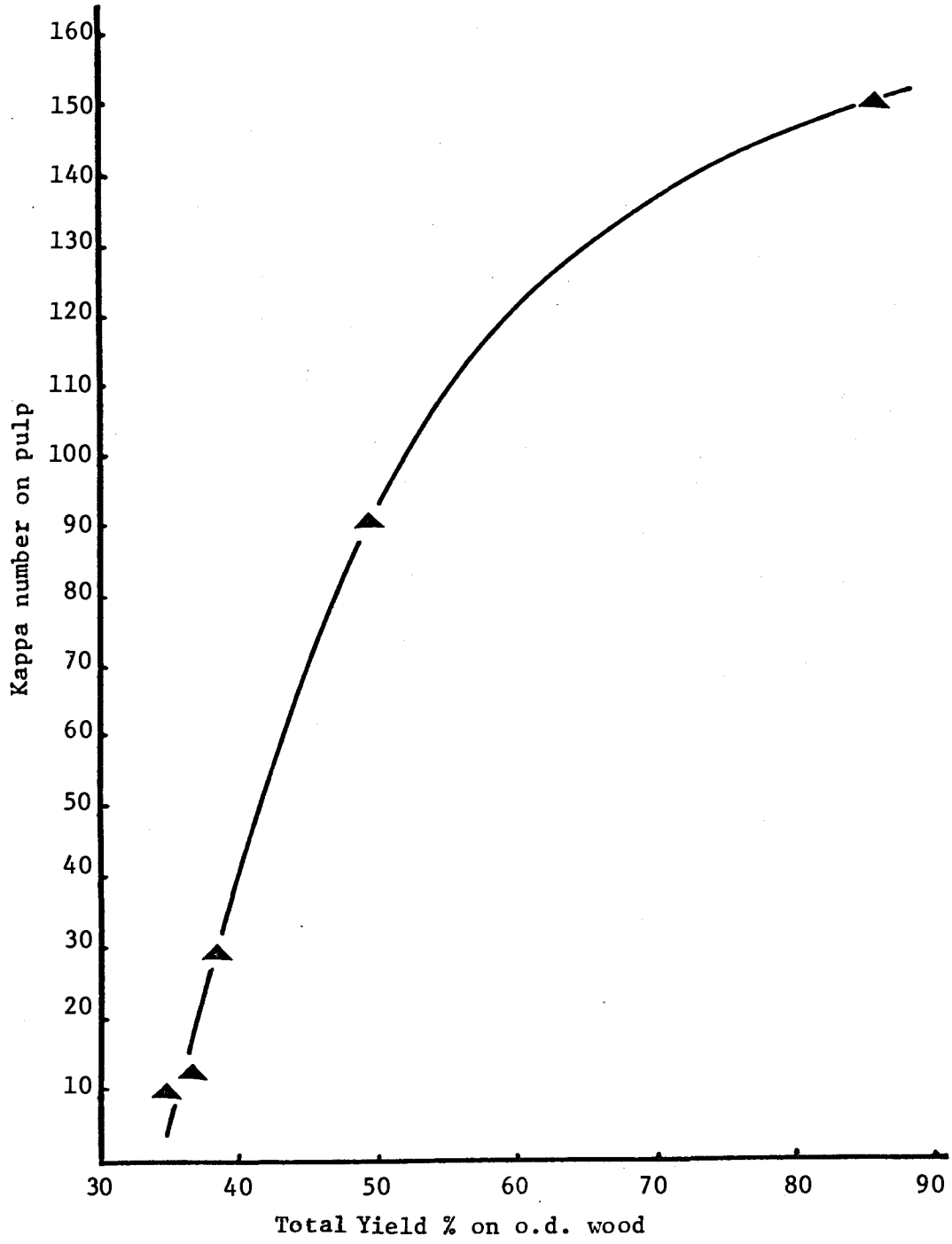

Fig. 17 Kappa number = f(Yield) for Sulfite Laboratory Samples

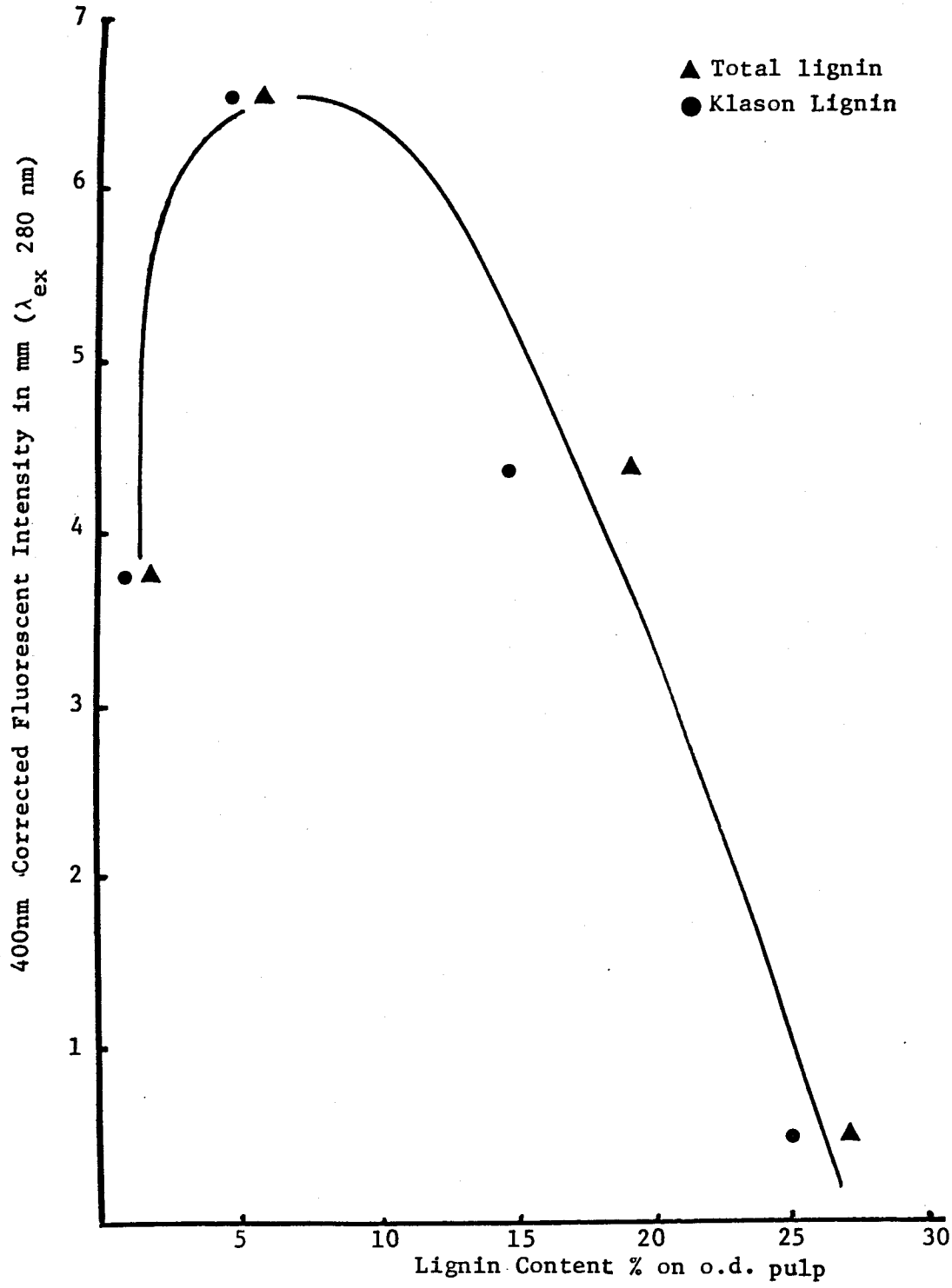

Fig. 18 Corrected Fluorescent Intensity = f(Lignin Content) for

Sulfite Laboratory Samples

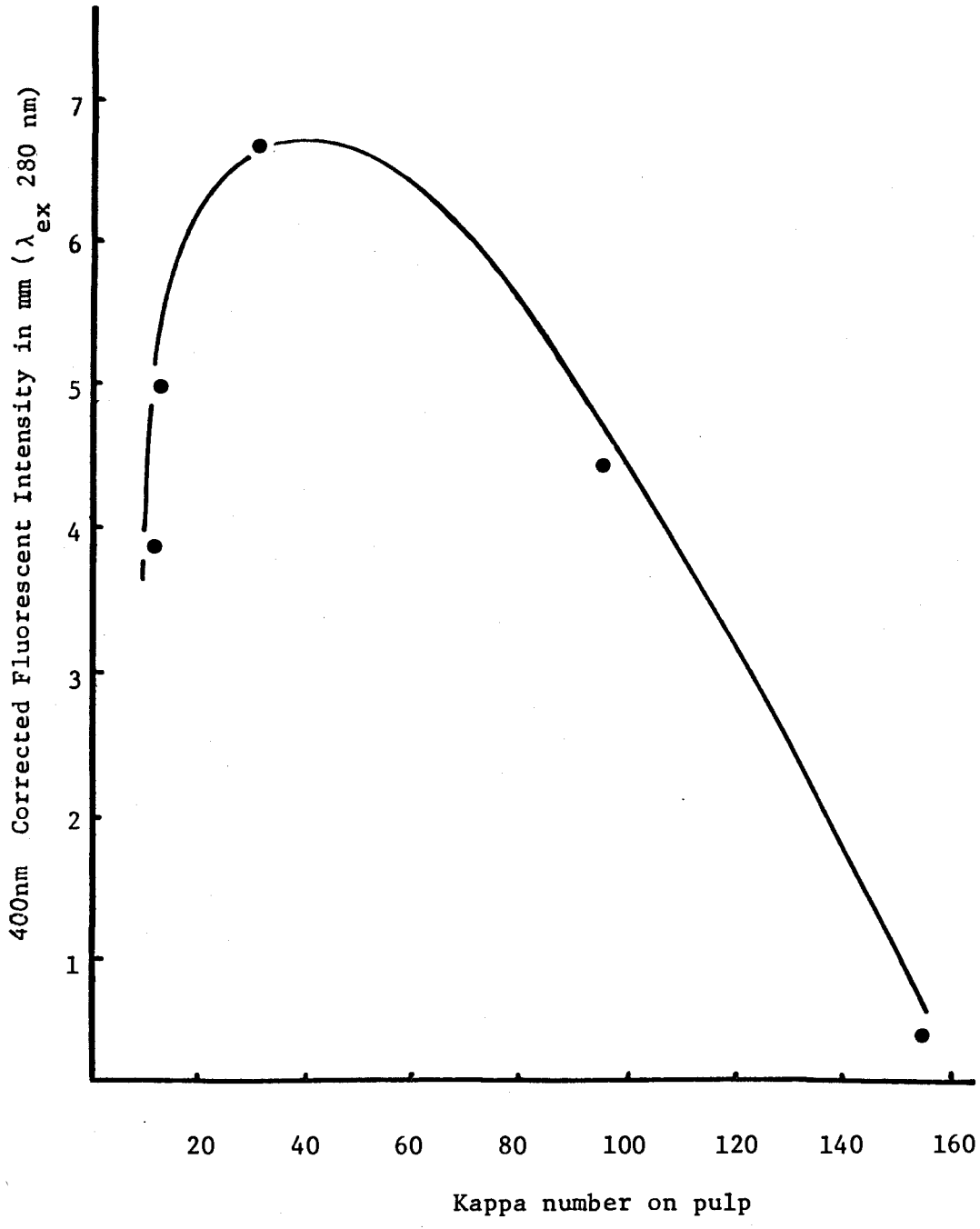

Fig. 19 Corrected Fluorescent Intensity = f(Kappa number) for

Sulfite Laboratory Samples

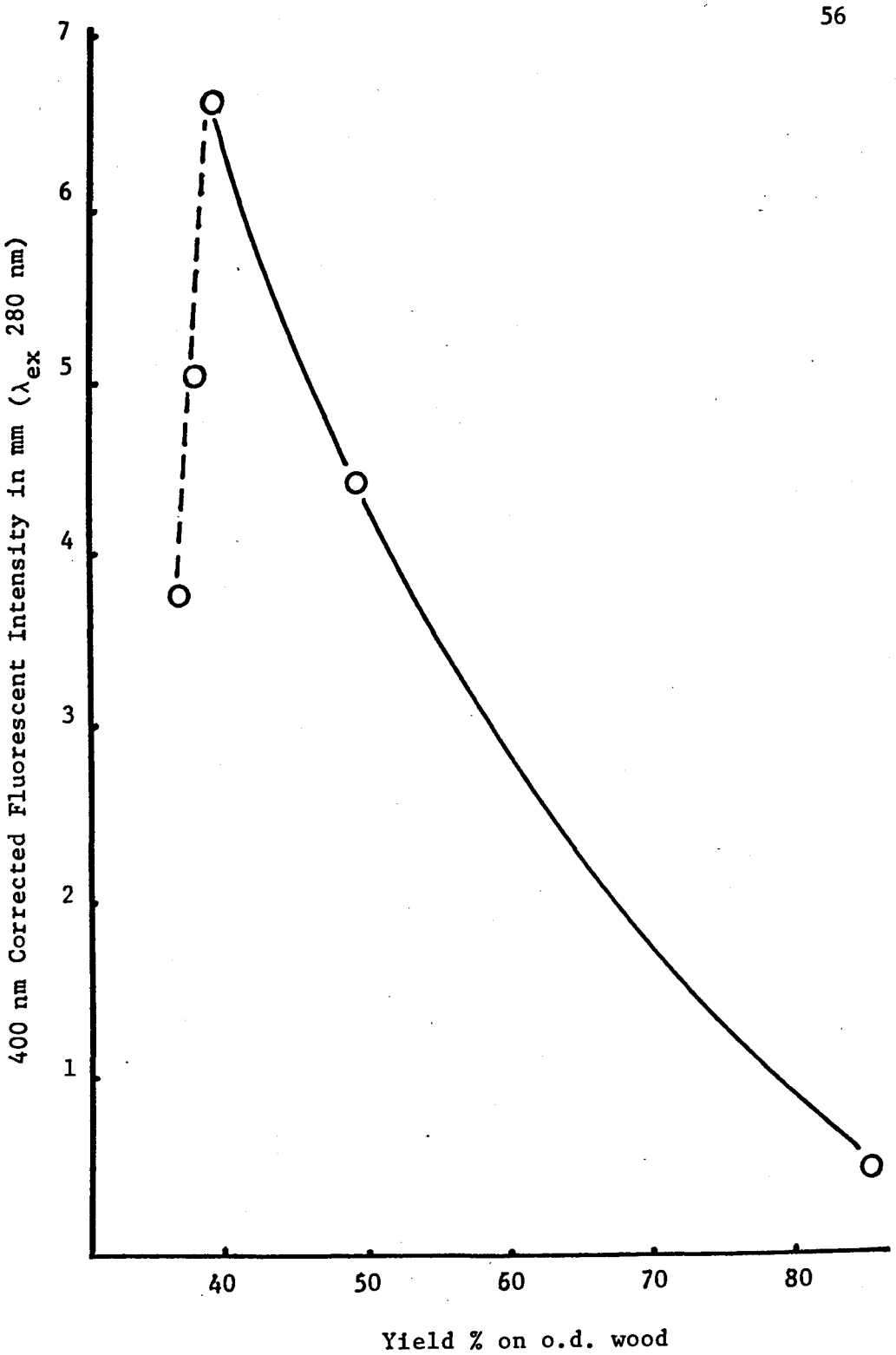

Fig. 20 Corrected Fluorescent Intensity = f(Yield) for Sulfite Laboratory Samples

Aging and Spent Sulfite Liquor Fluorescence

The relationship of corrected fluorescent intensity to age of the spent sulfite liquor is presented in Figure 21 and Table 6. Apparently the fluorescent response of lignin in SSL is not as stable over time as dissolved lignin from the kraft process. The fluorescent intensity of the SSL samples had changed substantially by the second day, whereas the kraft samples had an initial two day period during which little change in fluorescent intensity was noted.

Fluorescent Characteristics of Industrial Spent Sulfite Liquor

Samples of sulfite pulp and SSL were obtained from Publishers' Paper Co. in Oregon City, Oregon. Because the end of cook determinations used by sulfite pulp mills (titration for total SO_2 and visual inspection of the cooking liquor) require frequent sampling of the liquor, tap lines have been placed to run from the liquor circulation system of each digester through a condenser to the digester control room, thus facilitating the withdrawal of a representative liquor sample. When the liquor sample indicates that the level of total SO_2 is less than one percent of the cooking liquor, the digester operator will visually inspect the liquor for increases in color (an estimation of delignification) and the presence of short fibers (an indication of the breaking apart of the chip). The total SO_2 content of the liquor is an important parameter because when sufficient SO_2 has been withdrawn from solution by reactions with lignin, and the pulping process continues, lignosulfonic acids are formed, decreasing the pH of the cooking liquor, to the point of burning the cook (25). This breakdown of the liquor produces a dark, low quality pulp that is unusable in many products.

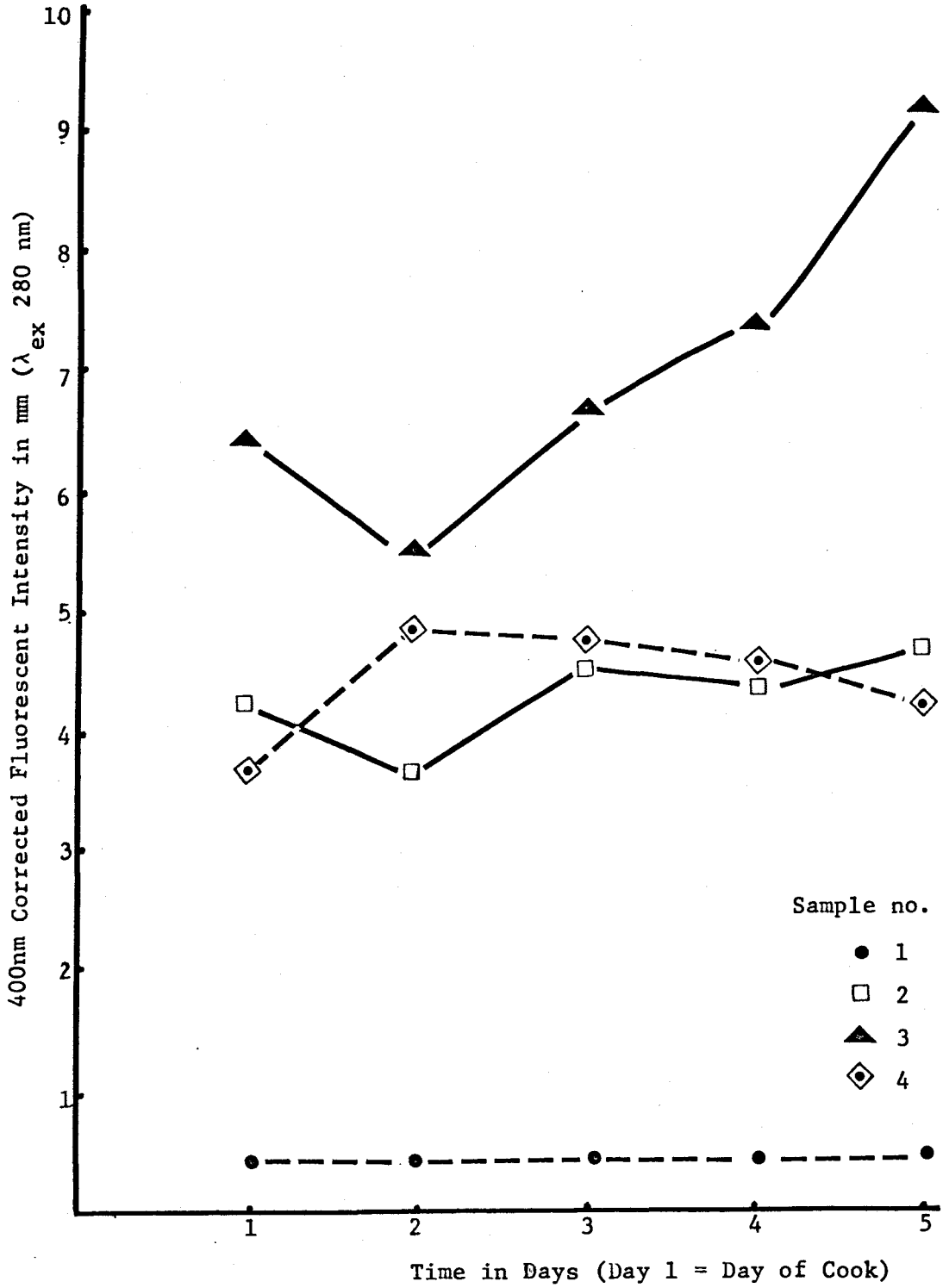

Fig. 21 Corrected Fluorescent Intensity = f(Yield) for Sulfite Laboratory Samples

When the digester operator decides that the proper amount of delignification has occurred, dilute SSL is pumped into the digester to cool the charge and stop the pulping reaction. More liquor from previous cooks is then used to pump the stock out of the digester into the blow pit. This procedure is different from what was done formerly. Prior to air quality controls, the digesters were merely opened and the pressure within them allowed to force the contents into a common blow pit. This practise allowed the escape of SO_2 into the atmosphere, and has been replaced with the method of pumping out the digesters just described.

The relationship of fluorescent intensity to Kappa number was presented earlier in Figure 2. The most linear relationship was found to exist with the bandwidth combination of ex 10/em 10. The linear regression equation explains 90% of the observed variation, over a range of Kappa numbers from 22 to 50.

Fluorescent Intensity as a Function of Cooking Time

Liquor samples were withdrawn from digester no. 1 every half hour beginning with the addition of the cooking liquor to the digester to the end of the cook. Figure 22 represents the relationship of fluorescent intensity to cooking time. Values of fluorescent intensity increased throughout the majority of the cooks as more lignin was dissolved by the pulping process. At the very end, however, a drop in fluorescence was noted. This decrease was also seen in the laboratory samples of SSL, as the concentration of lignin in solution increased beyond a certain point, and may be due to a condensation of the lignin, resulting in larger molecules with less ability to fluoresce (2,3). The mill samples obtained from Publisher's Paper Co. appear to have been

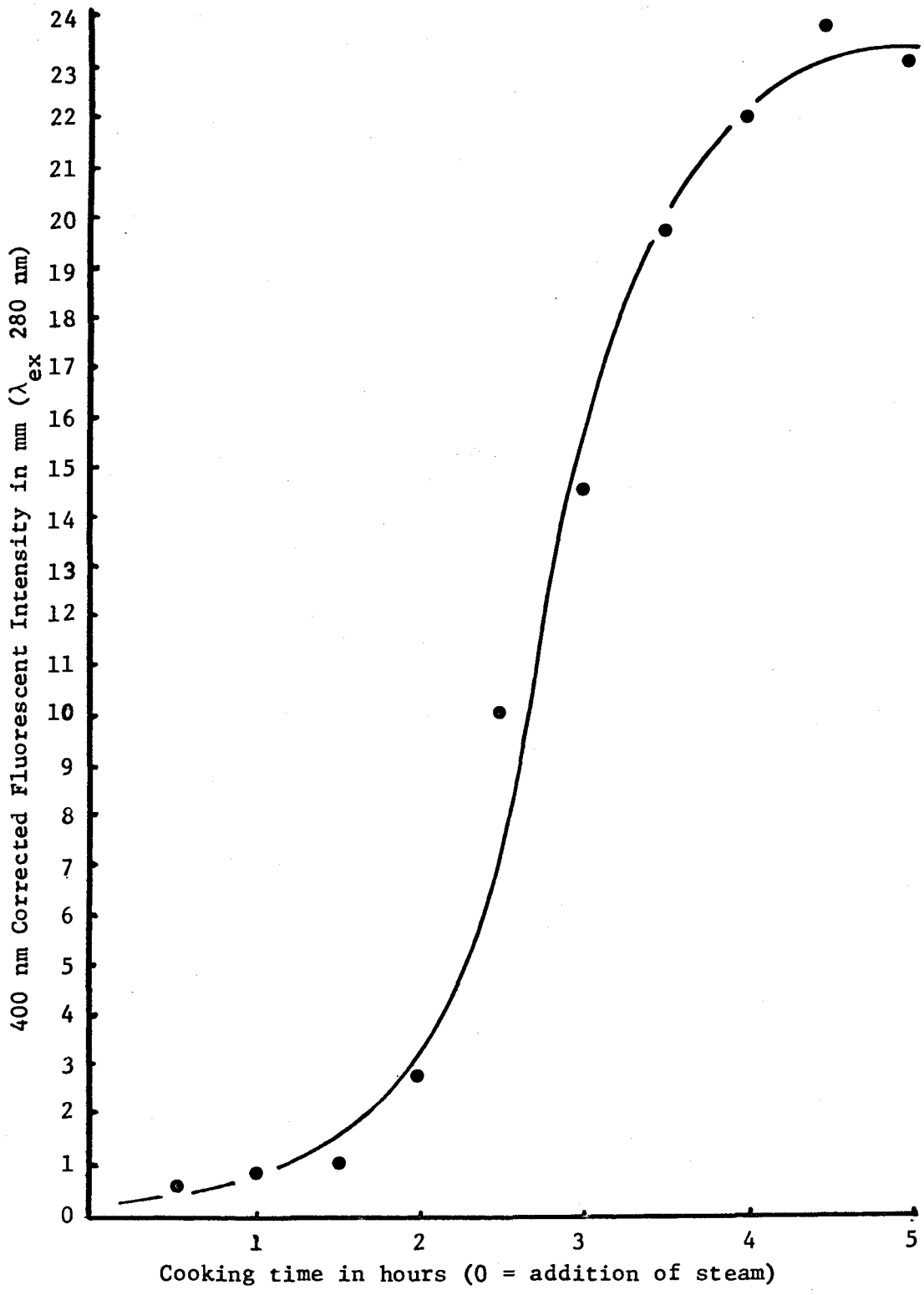

Fig. 22 Corrected Fluorescent Intensity = f(Cooking Time) for Sulfite Mill Samples, Digester #1, 12/3/76

pulped to the point where possible lignin condensation is just beginning to take place.

Spent liquor fluorescence, as a measure of delignification, may be more fundamental to the pulping process than is the determination of total SO_2, and also is more meaningful than a visual colorimetric test for lignin. The apparent sensitivity of fluorescent analysis to lignin concentration and condensation reactions may serve the sulfite pulping industry as an aid in pulping end point determinations.

A Comparison Between a Corrected Spectrofluorometer and a Filter Fluorometer

Turner Model 210 Spectrofluorometer

This model spectrofluorometer uses monochromators to select both the wavelengths and bandwidths of the incident and emitted radiation. Each monochromator contains a fine-line grating (or prism) to diffract the entering light into a continuous distribution of wavelengths. The grating is rotated to bring the dispersed radiation past a slit in order to select the primary wavelength of light leaving the monochromator. The width of the slits may be adjusted, which alters the distributions of light around the central wavelengths (bandwidths) for both monochromators. Adjusting the height of the slit of the excitation monochromator alters the amount of total energy leaving this monochromator, and allows for the selection of the desired magnification of fluorescent intensity.

The Turner model 210 is termed a corrected or absolute spectrofluorometer, because the fluorescent spectra is corrected for instrumental artifacts, such as monochromator efficiency, and the spectral

distribution of the lamp output. Monochromator efficiency (the ratio of energy leaving the monochromator to the energy entering it) is maintained by the use of a reference lamp (Figure 23) whose output intensity is automatically adjusted to match the amount of energy leaving the excitation monochromator and falling on the sample. This reference lamp directs some radiation through an attenuator to a time sharing photomultiplier tube. This attenuator adjusts the intensity of the reference beam to match the efficiency of the emission monochromator. The adjustment is necessary because the monochromator efficiency varies with wavelength (7). This instrument uses a xenon lamp, (model 210-002) which provides a continuous spectral distribution from 200 nm to 1100 nm. Due to the corrections made within the instrument for monochromator efficiency, and the use of a xenon lamp, only the true excitation and emission spectra of a compound are measured (7).

Turner Model 111 Filter Fluorometer

This fluorometer relies upon optical filters to control both central wavelengths and bandwidths of excitation and emission. There is only one light source divided into three light paths which allow for: (1) excitation of the sample, (2) zeroing the blank shutter, and (3) adjusting measurements of fluorescent intensity for fluctuations in the light source (Figure 24). By setting the blank shutter the fluorescent output of the solvent (blank) is automatically subtracted from the fluorescence of the sample, and the difference between the two intensities is expressed on a unitless scale of 0-100. This automatic subtraction of the blank fluorescence is unlike the Turner model 210 operation, which requires that the fluorescence of the solvent be subtracted graphically.

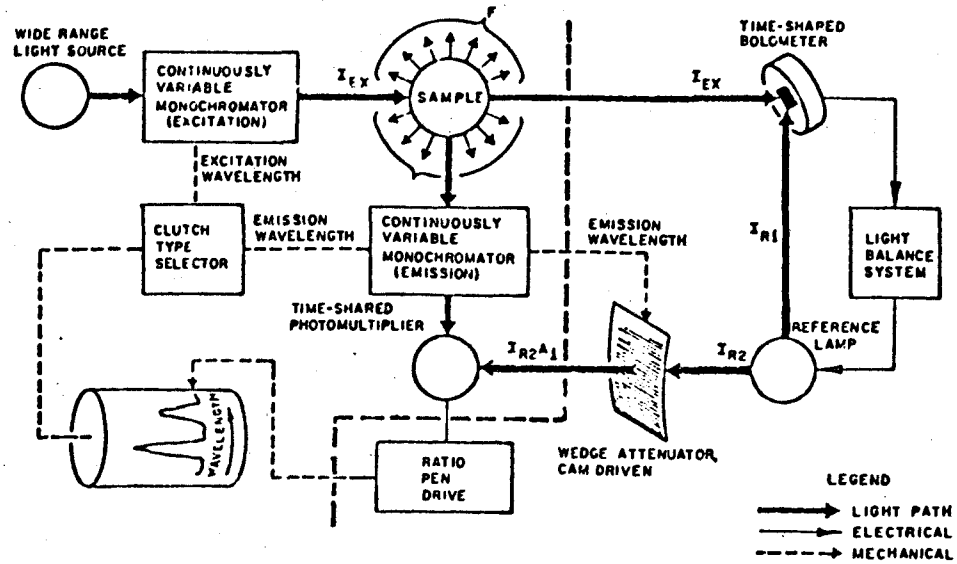

Figure 23 Schematic representation of the Turner model 210 (7)

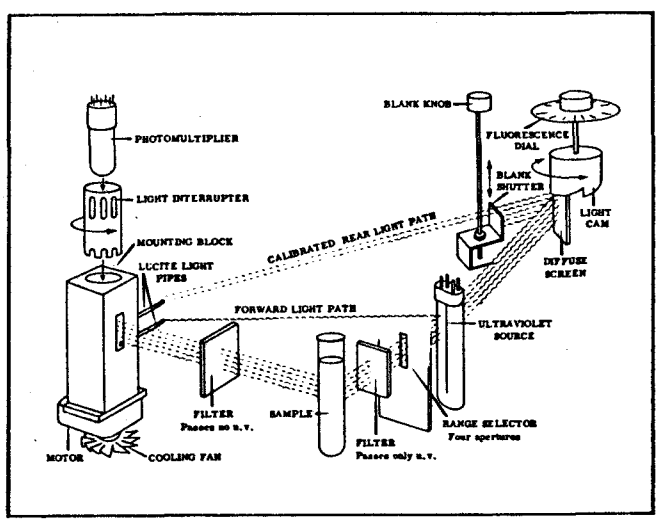

Figure 24 Schematic representation of the Turner model 111 (9)

The Turner model 111 also differs from the model 210 in that the light source is not wide range, and therefore must be changed on occasion to insure the proper wavelengths of excitation. The lamp used in this experiment (Turner #110-855) provided a range of wavelengths from 270 nm to 350 nm. A 280 nm bandpass filter from Ditric Optics, Inc., (effective bandwidth 9.5 nm) provided the necessary selection of excitation wavelength.

Filter Fluorescence as a Function of Corrected Fluorescent Intensity

Four emision filters were used in this study, a 440 nm cut off filter from Ditric Optics, Inc., with an effective transmission range of 400 to 435nm, a 405 nm narrow bandpass filter (Turner #110-812), a dual bandpass filter (Turner model 47B) which allows transmission peaks at both 405 and 436 nm, and a 415 nm cut on filter (Turner model 2A). The 415 nm cut on filter was used in conjunction with the dual bandpass filter, to block out the 405 emission peak.

The relationship of filter fluorescence to the corrected fluorescent intensity (ex15/em 25) of the laboratory kraft liquor samples is presented in Figure 25. It can be seen from this graph, as well as from Table 3, that the 440 nm cut off filter provides the most linear relationship between the two variables, and better utilizes the usable range of both instruments.

This comparison of fluorescent intensities was then conducted on samples of laboratory SSL, using the filters already described in the model 111 and the bandwidth combination of ex 10/em 10 in the model 210. It can be seen from Figure 26 that a nonlinear relationship exists between fluorescent measurements made by the two instruments.

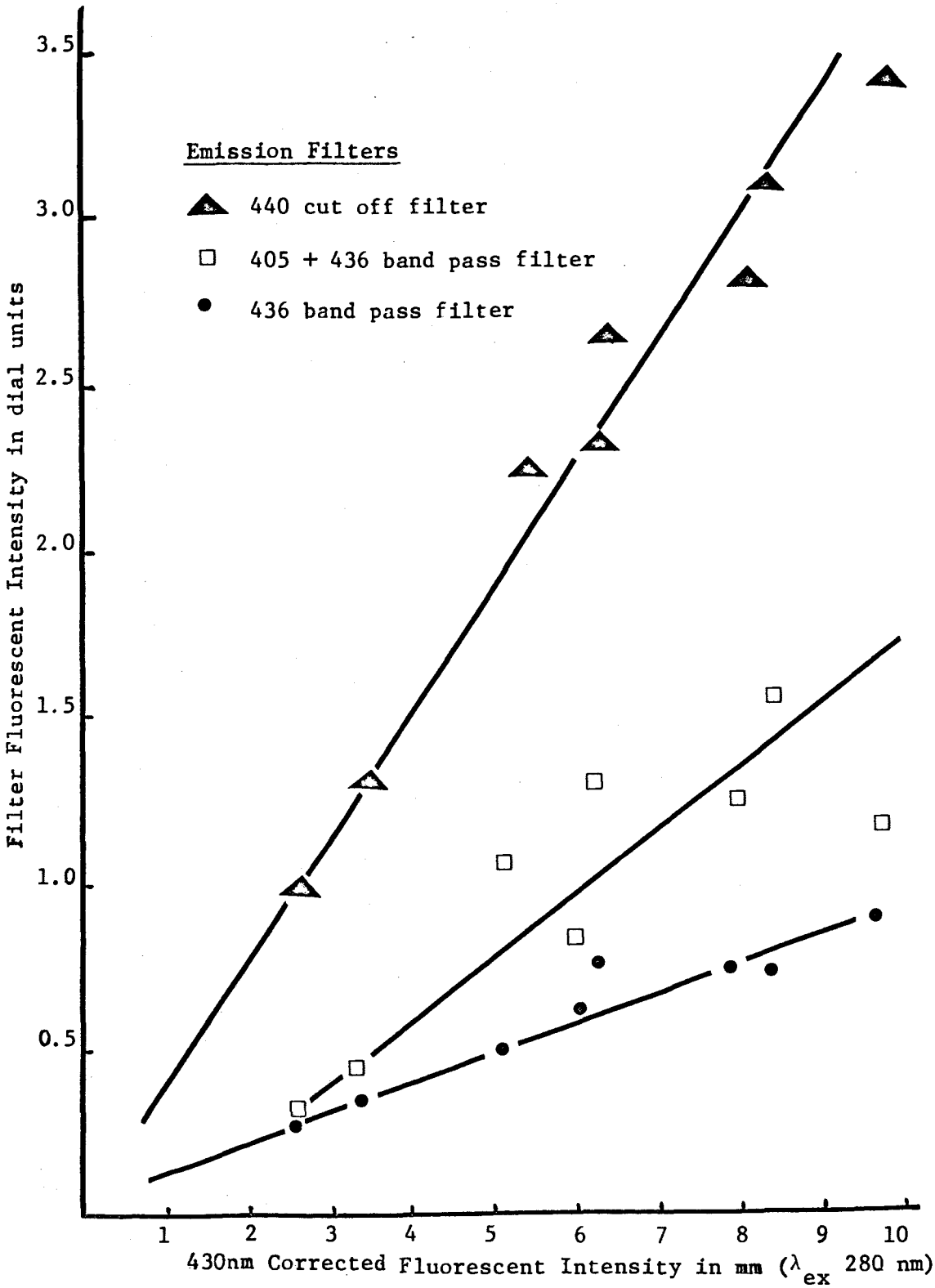

Fig. 25 Filter Fluorescent Intensity = f(Corrected Fluorescent Intensity) for Kraft Laboratory Samples

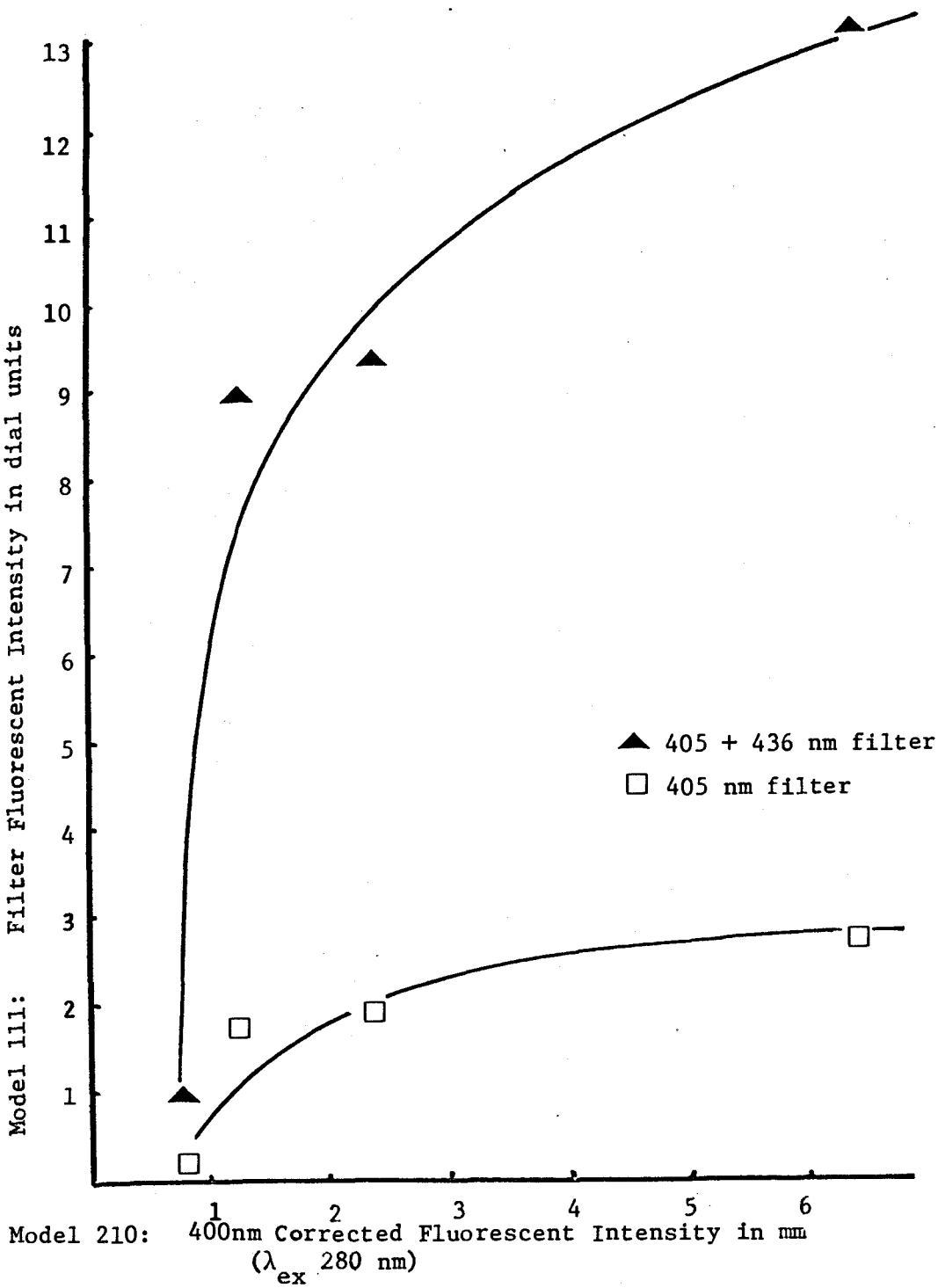

Fig. 26 Filter Fluorescent Intensity = f(Corrected Fluorescent Intensity) for Sulfite Laboratory Samples, ex 10/em 10

Next, a comparison was made using the corrected fluorescent intensity of the laboratory SSL at ex 15/em 25 (Figure 27). This resulted in a linear relationship, with an r^2 of 0.99 for the dual band pass filter, and an r^2 of 0.99 for the 405 nm single bandpass filter. The 405 nm narrow bandpass filter utilizes more of the usable range of both instruments, thus increasing the ability to differentiate between samples.

It should be noted that all SSL samples analyzed using the 440 nm cut off filter were off scale (over 100), even when the liquor samples were further diluted from 1:2500 to 1:5000 with glass distilled water. Therefore, the 440 nm cut off filter was not considered further in this study.

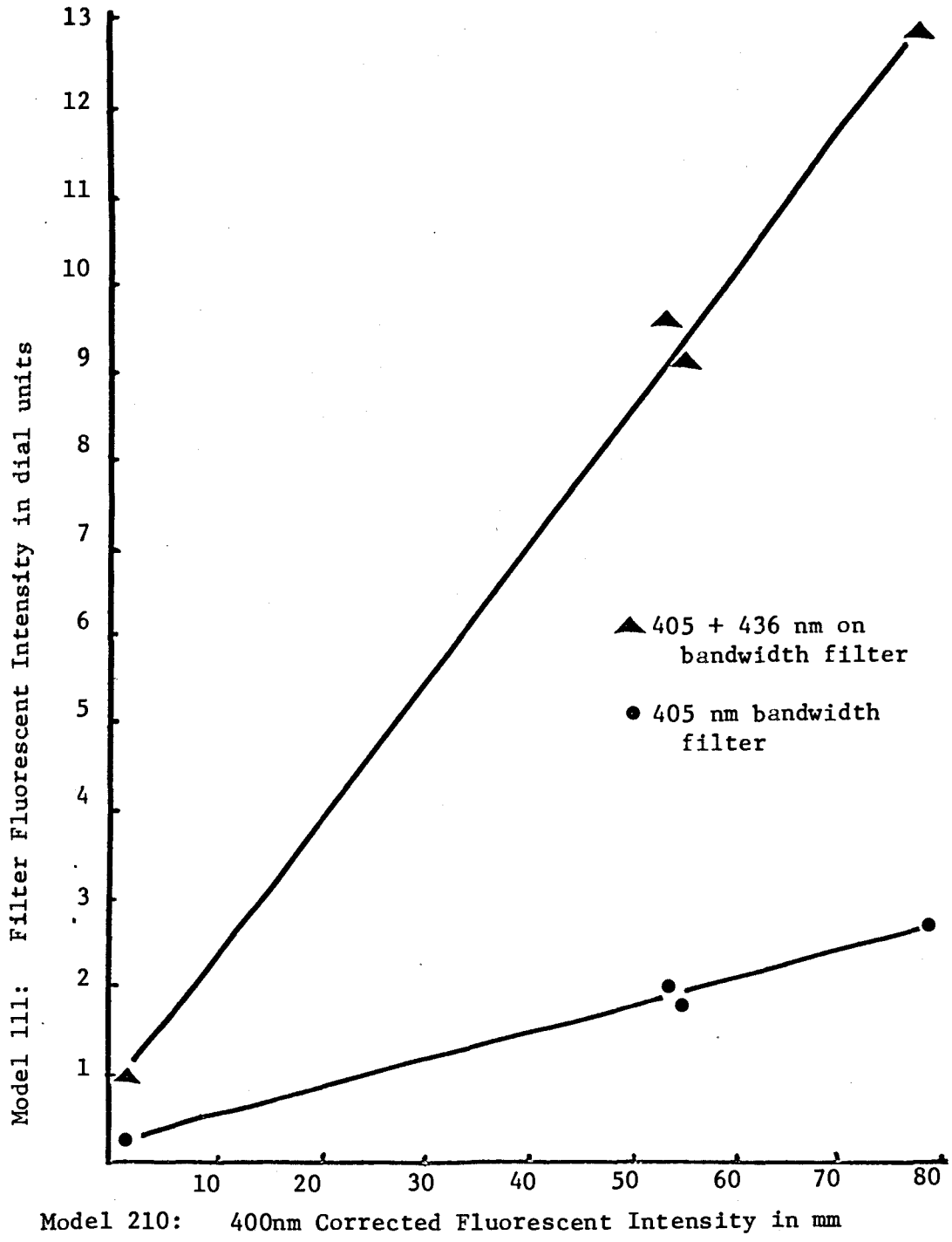

Fig. 27 Filter Fluorescent Intensity = f(Corrected Fluorescent Intensity) for Sulfite Laboratory Samples, ex 15/em 25

Summary

Optimum Spectral Conditions

The 280 nm absorbance peak was characteristic of all spent liquors tested, and was used as the excitation wavelength of this study. Emission wavelengths of 400 nm for spent sulfite liquor and 430 nm for kraft waste liquor were used.

The combination of the widest bandwidths (ex 15/em 25) provides the best results with kraft liquor samples, whereas the combination of the narrowest bandwidths tested (ex 10/em 10) provides the best fluorometric results with SSL.

Kraft Pulping Properties

The lignin content of the laboratory pulps (when considered as either a percent of the original wood or as a percent of the pulp) is linearly related to total pulp yield.

Kappa number is directly related to both pulp lignin content and pulp yield. This test provides the pulping industry with an accurate method of estimating these parameters after the pulping operation.

Laboratory Kraft Spent Liquor Fluorescence

The fluorescent intensity of kraft liquors is dependent upon the lignin content of the liquor. Within a closed digester, the delignification of wood adds more lignin to the cooking liquor, causing an increase in fluorescence.

A linear, inverse relationship exists between the fluorescence of spent kraft liquor and the pulp properties of lignin content, Kappa number, and pulp yield. This suggests that fluorometry may serve as a method of measuring the progress of a kraft cook.

Sulfite Pulping Results

A positive correlation exists between the lignin content of the laboratory samples (as a percent of the original wood) and total pulp yield. However, less of the observed variation is explained by the relationship between lignin content (as a percent of the pulp) to total yield when lignin content is measured as a percent of the pulp.

Kappa number is directly related to pulp lignin content, and provides an accurate estimator of this pulp property. Unlike the kraft samples, however, the Kappa number test on sulfite pulp does not provide a linear relationship with pulp yield.

Laboratory Spent Sulfite Liquor Fluorescence

Fluorescent intensity goes through a maximum as the cook progresses (toward the end of a normal sulfite cook), and the resulting relationships of spent liquor fluorescence to the pulp properties are non-linear. This decrease in fluorescence may be attributed to lignin condensation reactions within the liquor.

Effects of Sample Age on Spent Liquor Fluorescence

The fluorescent intensity of the diluted kraft liquor samples showed an initial period of stability. After the second day, the relationship of fluorescence to Kappa number became less meaningful. Undiluted samples appear less affected by aging. The fluorescent intensity of spent sulfite liquor appears to be less stable with time than kraft liquor.

Results of Mill Studies

The samples obtained from Western Kraft Corporation gave an inverse relationship of fluorescence to Kappa number than that obtained with the laboratory kraft cooks. This was attributed to an inability to obtain samples before the pulp and spent liquor from one cook had been mixed

with liquor from preceding cooks.

The kraft samples obtained from American Can Co. showed a nonlinear relationship between fluorescence and Kappa no. This may have been due to a change from pulping sawdust to pulping chips which was taking place at the time of sampling, which may have caused an increase in the lignin content of the waste liquor.

A nonlinear relationship is also evident in the kraft pulp and liquor samples obtained from the Weyerhaeuser Co. Changes in wood species were encountered which could account for the difference in fluorescent intensitites between the samples.

Spent sulfite liquor and sulfite pulp samples were obtained from several cooks at Publishers' Paper Co. A linear relationship was noted between fluorescence and Kappa number, over the range of Kappa numbers studied. A second study, comparing cooking liquor fluorescence and cooking time for a single cook, shows the progress of the pulping reaction as more lignin is dissolved from the wood into the liquor. Florescent intensity went through a maximum near the end of the cook which may have signified the beginning of lignin condensation within the liquor.

Comparison of the Turner Model 111 Filter Fluorometer and the Turner Model 210 Spectrofluorometer

The Turner model 111 filter fluorometer appears to be a valid tool for the monitoring of spent liquor fluorescence in a mill. In a comparison of kraft liquor fluorescence between the two instruments, the emission filter providing the widest bandwidth (440 nm cut off filter) gave the best results. Conversely, the emission filter with the narrowest bandwidth (405 nm bandpass filter) gave the best results with spent sulfite liquor.

Conclusions

I) The fluorescence of kraft spent liquors is linearly related to total yield, Kappa number, and lignin content of laboratory pulps. The correlations which exist between the fluorescent intensity of the liquor and the pulp properties mentioned suggests that fluorescence may be used as an accurate method of estimating the progress of the pulping reaction. Since liquor fluorescence may be measured during the pulping process, it should be possible to establish the rate of delignification of a cook in progress, and determine the optimum degree of pulping for each cook. This will provide the pulping industry with an ongoing test of pulp quality, which will allow a more immediate response to changes in pulping conditions than is possible with the Kappa number test.

II) The fluorescent intensity of spent sulfite liquor is linearly related to Kappa number up to the point of apparent lignin condensation in the liquor. A maximum in fluorescent intensity is reached toward the end of a normal sulfite cook.

III) The Turner model 111 filter fluorometer can provide an accurate estimation of the corrected fluorescent intensity of spent liquors, as measured by the Turner model 210. Care should be taken to choose the set of filters which best suit the sample to be analyzed, as the emission filter with the widest bandwidth (440 nm cut off filter) gave the best results with spent kraft liquor, while the emission filter with the narrowest bandwidth (405 nm bandpass filter) provided the best correlation between the filter fluorescence and the corrected fluorescence of spent sulfite liquor.

IV) Diluted kraft liquors are stable, with regards to fluorescent intensity, for a two day period. The effects of aging appear to be minimized by not diluting the samples until testing. Sulfite spent liquor fluorescence appears to be less stable with time than that of kraft liquor. It is therefore important that fluorescent analysis be undertaken as soon after sampling as possible.

V) The results from the kraft mill trials show that the fluorescent intensity of spent liquor is sensitive to changes in pulping parameters, such as species mix, or a change in the form of wood being pulped. This is due to the direct relationship between fluorescent intensity and the concentration of lignin in the liquor. Changes in pulping parameters which alter the concentration of lignin in the liquor, such as a change in the liquor-to-wood ratio in the digester, or a change in the lignin content of the raw material, will cause a change in the fluorescent response of the liquor. Therefore, any mill using fluorescence as an analytical tool must develop a calibration curve of fluorescent intensity to pulp properties that is appropriate for the range of conditions the mill expects to encounter.

VI) The results of the sulfite mill study show that spent liquor fluorescence can be used as an estimator of Kappa number within the range of Kappa numbers encountered. In the study of liquor fluorescence as a function of cooking time, a maximum fluorescent intensity was found near the end of the cook. These findings verify the results of the laboratory sulfite study. The sensitivity of fluorometry to apparent lignin condensation could serve

the sulfite pulping industry as an end of cook determination that is more meaningful with regards to the delignification of wood than either of the tests presently in use (the titration for total SO_2, or the visual inspection for changes in color).

VII) The fluorescent characteristics of spent pulping liquor can be used for improved process control in the pulping industry, as well as an aid in research to better understand the reactions of lignin in pulping. Fluorometry is proving itself to be a powerful tool for the study of lignin in solution.

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APPENDICES

Appendix Table 1 Comparison of Excitation and Emission Bandwidths, Kraft Laboratory Data

Sample no.	Kappa no. on pulp	Corrected fluorescent intensity in mm[1/] excitation bandwidths/emission bandwidths in nm		
		ex 15/em 25	ex 15/em 10	ex 10/em 10
2	154.7	4.51	0.27	0.30
5	44.5	5.98	0.11	0.23
7	25.3	10.10	0.70	0.58
8	17.2	10.43	0.58	0.47

1/ Spectral conditions
excitation wavelength 280 nm
emission wavelength 430 nm

Appendix Table 2 Comparison of Excitation and Emission Bandwidths, Sulfite Laboratory Data

Sample no.	Kappa no. on pulp	Corrected fluorescent intensity in mm 1/ excitation bandwidths/emission bandwidths in nm		
		ex 15/em 25	ex 15/em 10	ex 10/em 10
1	29.5	40.6	19.7	23.0
2	22.0	42.5	17.3	27.8
3	27.1	41.0	23.2	25.8
4	38.0	42.3	15.7	21.0
5	48.2	35.8	11.9	20.1

1/ Spectral conditions
excitation wavelength 280 nm
emission wavelength 430 nm

Appendix Table 3 Kraft Pulping Results for Laboratory Samples

Sample	Yield % on o.d. wood	Kappa no. on pulp	Klason lignin % on o.d. wood	Ash % on Klason lignin	Acid-soluble lignin % on o.d. wood	Total lignin % on o.d. wood	Klason lignin % on pulp	Ash % of Klason lignin	Acid-soluble lignin % on pulp	Total lignin % on pulp
wood	100.00	-	27.62	0.80	0.45	27.85	-	-	-	-
1	62.45	157.8	14.58	0.47	0.48	14.59	23.34	0.75	0.77	23.94
2	58.40	154.7	13.63	0.41	0.58	13.80	24.01	0.71	1.00	24.84
3	45.75	71.8	6.13	0.35	0.38	6.16	13.39	0.76	0.84	14.13
4	43.45	41.4	2.54	0.30	0.40	2.64	5.84	0.68	0.91	6.71
5	42.91	44.5	3.00	0.28	0.32	3.04	6.99	0.66	0.74	7.68
6	39.20	25.3	1.42	0.27	0.43	1.58	3.62	0.70	1.10	4.69
7	38.20	22.4	1.35	0.24	0.40	1.51	3.54	0.62	1.05	4.57
8	36.74	17.2	1.19	0.10	0.46	1.55	3.24	0.31	1.26	4.49

Appendix Table 4 Kraft Liquor Fluorescence for Laboratory Samples

Sample	Corrected fluorescent intensity in mm[1/] day 1 (day of cook)	day 2	day 3	day 4	day 5	day 30
1	4.05	4.17	7.69	7.10	7.23	5.42
2	4.51	4.61	3.84	7.68	7.48	5.13
3	8.05	7.89	9.67	9.01	9.19	3.65
4	9.23	9.05	11.10	10.68	10.51	4.09
5[2/]	5.98	6.03	5.63	5.73	5.55	5.72
6	10.10	9.91	10.23	10.42	9.75	4.44
7	9.53	9.55	9.31	8.67	8.85	6.19
8	10.43	10.23	10.40	9.83	9.30	3.39

1/ Spectral conditions: excitation wavelength = 280 nm; emission wavelength = 430 nm; excitation bandwidth = 15 nm; emission bandwidth = 25 nm

2/ Discarded as outlier

Appendix Table 5 Sulfite Pulping Results for Laboratory Samples

Sample	Yield	Kappa no. on pulp	Klason lignin % on o.d. wood	Ash % of Klason lignin	Acid-soluble lignin % on o.d. wood	Total lignin % on o.d. wood	Klason lignin % on pulp	Ash % of Klason lignin	Acid-soluble lignin % on pulp	Total lignin % on pulp
wood	100.00	-	32.11	0.10	0.94	33.02	-	-	-	-
1	85.60	151.83	21.43	0.05	1.52	22.88	25.04	0.06	1.78	26.80
2	48.64	93.49	7.20	0.24	2.15	9.11	14.80	0.50	4.42	19.15
3	38.31	29.32	1.81	0.02	0.50	2.29	4.72	0.04	1.30	6.02
4	37.10	12.08	-	-	-	-	-	-	-	-
5	36.09	10.90	0.78	0.02	0.13	0.89	2.16	0.05	0.37	2.53