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DEVELOPMENT OF A PROTOTYPE LIGNIN CONCENTRATION SENSOR

FINAL REPORT

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PREPARED BY: L. A. JEFFERS

THE BABCOCK & WILCOX COMPANY
RESEARCH AND DEVELOPMENT DIVISION
ALLIANCE, OHIO 44601

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EXECUTIVE SUMMARY

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INTRODUCTION

The ultimate objective of the DOE-sponsored program discussed in this report is to commercialize an instrument for real-time, in-situ measurement of lignin in wood pulp at a variety of locations in the pulp process stream. The instrument will be used as a primary sensor for process control in the pulp and paper industry.

Work done by B&W prior to the initiation of this program had shown:

- there is a functional relationship between the fluorescence intensity and the Kappa number as measured at the pulp mill laboratory. Kappa number is a standard wet chemical method for determination of the lignin concentration.
- the relationship is one of decreasing intensity with Kappa number, indicating operation in the quenched fluorescence regime.
- a great deal of scatter in the data. Because of the preliminary nature of the study, the origin of the scatter was not identified.

This report documents the results of laboratory measurements made on a variety of well defined pulp samples to generate the data necessary to:

- determine the feasibility of an instrument for on-line lignin concentration measurement using laser fluorescence
- identify the preferred measurement strategy
- define the range of applicability of the instrument
- and to provide background information to guide the design of a field-worthy prototype.

TEST PROGRAM

The laboratory measurements made to characterize the fluorescence properties of wood pulps were divided chronologically into two series of tests. The first series concentrated on the fluorescence parameters while the second series explored the effect of various pulp parameters on the preferred fluorescence approach identified in the first series.

Initial Test Series

Objectives of the initial test series were to determine the feasibility of the proposed instrument and to identify the preferred measurement strategy. The testing was carried out on two sets of laboratory prepared pulp, each consisting of eight samples with Kappa numbers ranging from approximately 15 to 55. Pulp set number 1 was prepared from southern pine chips and pulp set number 2 was prepared from northern spruce chips.

To perform the characterization tests, an apparatus was designed and constructed that employed:

- a pulsed nitrogen/dye laser as the excitation source.
- an intensified, diode-array detector capable of rapid (5 nsec) gating.
- an electronically scanned/controlled spectrometer employing digital data acquisition and processing.

Technologies investigated included:

- measurement of the fluorescence emission at various excitation wavelengths
- time-resolved fluorescence
- phase-resolved fluorescence
- multiple wavelength excitation
- diffuse reflectivity

Measurement of the wavelength centroid which is a quantitative measure of the spectral distribution of the fluorescence emission was identified as the preferred approach for use in the second series of tests.

Second Test Series

Tests were conducted to determine the applicability to:

- Measurement at various locations within the process stream - As initially conceived, the target analyzer would be located at the final stage of brownstock washing and would interrogate the pulp mat as it moves past. This is the location where the grab samples used for laboratory measurement of Kappa number are now obtained. At this location, the pulp is well drained of excess moisture and is fully washed. Measurements at various other locations where the pulp is not fully washed and where it exists in a slurry form are also desirable. To determine the applicability to these locations, the effect of consistency and incomplete washing were addressed.
- Various wood species -- Three additional pulp sets, 2 softwoods and 1 hardwood, were procured to supplement the two softwood sets from the initial test series.
- Extremes of lignin concentration -- the new pulp sets extended the range of Kappa numbers from 8 to 140.
- Oxygen delignified pulps -- pulps covering the low range from $\kappa=8$ to 20 were produced by oxygen treatment.
- Pulps at different temperatures.
- Pulps at various values of pH.

RESULTS

Initial Test Series

Determination of the wavelength centroid which is a measure of the shape of the emission spectrum was identified as the preferred approach. Several measurement strategies in addition to the wavelength centroid approach were also shown to provide a suitable control signal although the total fluorescence (the intensity integrated over the entire emission spectrum) was not among them.

Considerations in the choice of the wavelength centroid approach were:

- The relationship between wavelength centroid and Kappa number is nearly linear, providing good sensitivity to concentration over the entire range of interest.
- The centroid is independent of the absolute intensity of the fluorescence, so long-term intensity changes due to window transmission, detector sensitivity, source output, etc., will not present a problem.
- Compared to the other approaches, the required apparatus is simpler and cheaper.

Second Test Series

The wavelength centroid was shown to provide a suitable control signal for all of the 5 wood species tested over the entire range of Kappa numbers from $\kappa = 8$ to 140. For the Kraft pulps in the range up to about $\kappa=50$, the relationship is nearly linear with a slope from +0.3 to +0.4 nm/ κ . The slope decreases slightly above $\kappa=50$. For the oxygen treated pulps, the response is linear, but the slope is negative with a magnitude in the range -0.5 to -0.7 nm/ κ .

The wavelength centroid increases linearly with pulp consistency at a rate that will give an error in the Kappa reading of 1 κ /1% change in consistency. In applications where the consistency varies by more than a percent, a separate measure of the consistency could be used to compensate the analyzer output.

The wavelength centroid decreases linearly with temperature at a rate that will produce an error in the measured Kappa number of 0.06 to 0.08 $\kappa/^{\circ}\text{F}$. Although it is not expected to be necessary, an independent measure of the temperature could be used to compensate the centroid signal.

The pH of the pulps was found to have a significant effect on the wavelength centroid response. The general trend is for the centroid to increase with increasing pH. Variations in the slope of the response curve among the different wood species tend to decrease with increasing pH. Quantification of the effect of pH was hampered by the fact that there were large variations of pH among the as-received pulps and attempts to adjust the pH met with only limited success.

CONCLUSIONS AND RECOMMENDATIONS

The wavelength centroid has been shown to provide a response suitable for use as a control signal over the entire range of conditions tested. Although there are several areas where additional laboratory testing could provide useful information, the most cost effective next step is to develop and evaluate a field prototype. Additional laboratory work should be done to answer specific questions arising from the prototype testing.

Independent measurements of temperature, consistency, and pH should be included in the testing of the prototype to determine whether or not on-line compensation for these parameters is necessary in the commercial instrument.

1.0 INTRODUCTION

LIGNIN CONCENTRATION SENSOR FINAL REPORT

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L. A. JEFFERS

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1.0 INTRODUCTION

1.1 OBJECTIVES

The ultimate objective of the DOE-sponsored program discussed in this report is to commercialize an instrument for real-time, in-situ measurement of lignin in wood pulp at a variety of locations in the pulp process stream. The instrument will be used as a primary sensor for process control in the pulp and paper industry. Prior to the start of the project, laser-induced fluorescence (LIF) was identified as the preferred technological approach.

The objective of the scope of work reported here was to characterize the fluorescence properties of a variety of well defined pulp samples in order to provide the background information necessary to;

- 1) evaluate the practicality of an LIF based lignin sensor, and
- 2) design a prototype for field evaluation.

1.2 BACKGROUND

1.2.1 The Need For a Lignin Concentration Sensor

Although somewhat of an oversimplification, wood can be characterized as consisting of holocellulose (cellulose and hemicellulose), lignin, and extractives [1]. Lignin, a polymer of complex chemical structure which "cements" the cellulose fibers together, must be partially removed in the paper making process. The removal process is referred to as delignification. It can be accomplished through a chemical pulping (digestion) process that converts the lignin to a soluble form using acid (sulfite) or alkaline (kraft) pulping agents.

Depending upon the paper product being produced, as much as 90% (or more) of the lignin may be removed from the wood. At a typical pulp mill, the pulp is sampled and tested for lignin concentration on a regular (usually hourly) basis. The test result is reported in terms of the Kappa number (or K Number depending on the specific procedure). The pulp Kappa number is an approximate measure of the lignin concentration in the pulp and is determined by measuring the consumption of potassium permanganate solution by moisture free pulp by back-titration [2]. Typical Kappa numbers range from 10 or less, for fine white paper, to more than 80 for brown paper and heavier material.

Many pulp mills employ distributed process control to improve digester performance and often use the pulp Kappa number as a feedback parameter, especially on continuous digesters. In such a control system, the results from the hourly Kappa number (titration) tests at the pulp mill lab are used as feedback (via "keypunching" the test results into the process control system) to the digester in which the delignification process is taking place. The delays in obtaining Kappa numbers, the sampling error, and laboratory error result in uncertainty in the data provided to the control system. In addition, the delay of one hour or more between the time at which the sample is obtained and the time at which the Kappa number is determined in the lab, severely restricts the feed-forward control possibilities.

By eliminating the time lag, a real-time, on-line lignin sensor will provide improved control of the digestion process and will, for the first time, make possible feed-forward control of the bleach plant. This will result in a significant reduction in the amount of bleach consumed. In addition to the cost and material savings, reduction in bleach consumed has favorable environmental implications.

1.2.2 Prior Work

The National Institute of Standards and Technology (NIST) has conducted research with the objective of developing measurement science and technology for on-line measurement of process variables in the pulp and paper industry [3,4]. This research, sponsored by the U. S. Department of Energy, included studies of laser excited fluorescence of lignin in solution (e.g. spent liquor). Although the research concluded that this technique could be a strong candidate for in-situ monitoring of the pulping process [5], the method was limited to very dilute solutions whose concentration of lignin was well below the concentrations found in wood pulp at pulp mills. Other DOE sponsored work studied the feasibility of using mass spectroscopy [6] for determining the concentration of lignin in pulp. Although successful in a laboratory environment, this technique is not considered suitable for in-situ monitoring [7].

The motivation for in-situ measurement of lignin in pulp is better control of the delignification process (feedback to digester) and reduced consumption of bleaching chemicals (feedforward to the bleach plant). It is therefore desirable to develop a sensor which measures the lignin in pulp itself rather than in the spent liquor (focus of the NIST investigation), from which the lignin concentration in the pulp can only be inferred.

State-of-the-art instruments for quasi on-line measurement of lignin in spent liquors [8-10] and pulp [11,12] are based on the long known ultraviolet absorption characteristics of lignin [13-19]. Although much improved over automated titrating devices and conductivity probes, these still involve considerable sample preparation, sample handling (including dilution by as much as 10,000:1), and supplementary measurements (such as consistency) which affect instrument accuracy.

Diffuse Reflectance Infrared Fourier Transform (DRIFT) Spectroscopy has also been studied as an off-line method for measuring the lignin in pulp [20]. The DRIFT method's primary advantages are that it is nondestructive, fast, and not highly dependent upon sample

size. The DRIFT method has not, however, resulted in acceptable precision. The precision of the DRIFT method has been reported to be approximately ± 10 Kappa number [20].

After reviewing the technologies available for possible in-situ sensors for measuring lignin in pulp, B&W decided to pursue an extension of the fluorescence work done at NIST [5], (i.e. laser induced fluorescence). Other investigators had also demonstrated the usefulness of fluorescence for detection of lignin in solution [21-25]. B&W reasoned that the device could be relatively inexpensive, rugged, and be mounted at the final stage of the traditional vacuum washer to the end-wash rollers or deckers (where samples are currently obtained for mill lab testing). The device would be truly real-time and eliminate the need for sampling and sample preparation. Since NIST had only worked with black liquor and only in the highly diluted range, it was necessary to study the fluorescence of actual pulp samples without dilution. An internally funded feasibility study was undertaken by B&W in which the fluorescence of undiluted pulp samples was investigated. The results of this feasibility test, which are discussed in Appendix A of this report, were very encouraging and eventually led to the DOE sponsored effort discussed in this report.

1.3 Developmental Strategy

As mentioned above, earlier work by B&W had shown that lignin fluoresces and had suggested the possibility of determining the lignin concentration from an on-line measurement of the fluorescence from pulp with no sample preparation.

The work necessary to bring the desired system to market was planned in the following three consecutive stages:

- Laboratory Tests: An extensive series of tests to characterize the fluorescence properties of a wide range of well-defined pulp samples.
- Prototype Development: The scope of this work includes the design, development, and field evaluation of a prototype instrument.
- Commercialization: This work includes the development of a production prototype, beta site testing, and market development.

The laboratory testing has now been completed and is the subject of this report.

1.4 Project History

Results of the preproject testing discussed in Appendix A demonstrated a functional relationship between fluorescence intensity of wood pulp and Kappa number over a range of Kappa numbers from 10 to 80. The relationship occurs for pulp in the condition at which it exits the last stage of washing at an operating pulp mill, i.e., undiluted and without sample preparation. The relationship is one in which the fluorescence intensity emitted by a pulp sample decreases with increasing Kappa number, i.e. with increasing lignin concentration.

This inverse relationship of fluorescence intensity with lignin concentration results from a fluorescence phenomenon known as "quenching".

The project work covered by this report divides into two parts: an initial series of tests that were completed by the end of 1991 and a second series extending over the time period from early 1992 through June 1994.

For the initial test series, two sets of pulp were manufactured. Each set had eight samples covering a range of Kappa numbers from roughly 15 to 55. One set was made from chips of southern pine and the other was from northern spruce.

The objectives of the initial tests were:

- to develop a laboratory fluorescence apparatus and procedures that would eliminate measurement error as a cause of the data scatter seen in the preproject testing.
- to apply the apparatus/procedures to the two well defined pulp sample sets and determine if the relationship between the fluorescence and the Kappa number is suitable for use as a control signal.
- to conduct a parametric study of the fluorescence properties of the two pulp sets to determine the optimum approach for deriving the desired control signal.

Analysis of the results from the initial test series confirmed that a variety of approaches could provide a suitable control signal. The instrumentally preferred approach was selected for additional study in the second series of tests.

In the first series of tests the strategy had been to vary the fluorescence parameters while restricting the pulp parameters to a narrow range of conditions. In the second series of tests the rolls were reversed, i.e. the fluorescence parameters as defined by the preferred approach identified in the initial test series were restricted and the pulp parameters were varied. The objective of the second series of tests was to determine how far various pulp parameters could be extended while still observing suitable performance from the preferred fluorescence approach.

1.5 Scope of This Report

The purpose of this report is to document the results of both the first (1990-1991) and second (1992-1994) series of laboratory tests.

In Section 2.0, we give an overview of the test program, beginning with a discussion of fluorescence to define the various terms and procedures used in the test program. The background on fluorescence is followed by a discussion and definition of the pulp parameters involved in the tests. With this background, the scope of the test program is outlined.

Results of the test program are presented in Section 3.0, beginning with plots showing the response function of the preferred approach for the various pulp sample sets. The effect of various pulp parameters on the basic response function are then presented. Finally, the response functions provided by various alternative approaches (all fluorescence based) are discussed.

Conclusions and recommendations for future development are presented in Section 4.0.

Preparation of the various pulp sample sets is discussed in Section 5.0. This section includes details of the pulping process as well as a discussion of the rationale for choosing the various sample sets and processing parameters.

The laboratory procedures for preparing individual pulp specimens for fluorescence measurements are discussed in Section 6.0. The method of sample preparation and presentation was different in the second series of tests from what it had been in the first series. The reason for the modification is described along with a discussion of various alternative procedures that were investigated and discarded.

The apparatus constructed for carrying out the fluorescence tests is described in Section 7.0 along with a discussion of various operating procedures.

Section 8.0 describes the custom software developed for reduction of the spectral fluorescence data, while Section 9.0 discusses the results of various tests related to, but outside the mainstream of, the test program.

2.0 OVERVIEW OF PROGRAM

2.0 OVERVIEW OF PROGRAM

2.1 OBJECTIVE

The workscope covered in this report is the first step toward the development of an instrument for the on-line measurement of lignin concentration in wood pulp. This first-step program consisted of a series of laboratory measurements of the fluorescence spectra of well-defined pulp samples. The objective of the program was to develop the data base necessary to:

- design a field-testable prototype instrument.
- define the range of conditions over which the prototype can be expected to provide satisfactory performance.
- provide the background for interpretation of the results obtained when field testing the prototype.

2.2 DISCUSSION OF FLUORESCENCE PARAMETERS

2.2.1 The Fluorescence Process

Fluorescence is a multi-step process shown diagrammatically in Figure 2.1 and consisting of the following steps:

- absorption of a photon with wavelength λ_x which raises the absorbing molecule from the ground state to an excited state.
- transition of the molecule to an intermediate state, with the excess energy being transferred as heat to surrounding molecules by collision.
- return to the ground state by the emission of a photon with wavelength λ_m .

As shown in Figure 2.1, the molecule may alternatively return to the ground state by a non-radiative transition. The non-radiative transition involves transferring the excess energy to surrounding molecules via collisions. The fluorescence efficiency is determined by the ratio of the radiative to non-radiative transition probabilities.

In gases, the energy levels are few and far between as depicted in Figure 2.1. For liquids and solids, however, many individual levels of slightly different energy merge together to form bands rather than discrete levels. As a result, the fluorescence is spread over a range of wavelengths as shown in Figure 2.2. The fluorescence can be excited by a band of excitation wavelengths also, but we can dismiss this complication since our interest is in excitation using a monochromatic laser source.

Figure 2.1 Fluorescence Process Energy Level Diagram

Figure 2.2 Fluorescence Emission Spectrum

2.2.2 Total Fluorescence

We define the total fluorescence intensity as

$$F \equiv \int_0^{\infty} I(\lambda_m) d\lambda_m \quad (2.1)$$

where $I(\lambda_m)$ is the intensity at λ_m as indicated in Figure 2.2.

If there is only a single fluorescing species present, a plot of F as a function of the species concentration will produce a curve as shown in Figure 2.3. At low concentrations, F increases linearly with concentration since more of the incident light is absorbed. This is the range normally employed for analytical purposes. As the concentration increases to the point where 100% of the incident light is absorbed, the fluorescence levels off or begins to decrease as indicated in Figure 2.3. The decrease comes about from the fact that increasing the concentration increases the probability of non-radiative decay through interaction with neighboring molecules. This phenomenon is termed fluorescence quenching.

2.2.3 Species Discrimination

Quantitative measurement is complicated when more than one fluorescing species is present in the sample. In this case it is often possible to discriminate between the species of interest and the interfering species on the basis of differences in various fluorescence characteristics. These include:

- differences in temporal characteristics
- differences in the absorption (excitation) spectrum
- differences in the emission spectrum.

2.2.3.1 Time Resolved Spectroscopy

Figure 2.4 shows the temporal behavior of the total fluorescence intensity when excited by a short duration pulse.

During the excitation pulse, the fluorescence intensity rises rapidly. Once the exciting light is gone, the fluorescence begins an exponential decay with some characteristic time constant. Figure 2.5 shows the pulsed excitation fluorescence from two species with different time constants. In a sample that consists of a mixture of the two species A and B, the resultant signal would be the sum of the two curves in Figure 2.5. In this case, the total fluorescence as defined earlier would be given by the expression

$$F = \int_0^{\infty} F(t) dt \quad (2.2)$$

Figure 2.3 Total Fluorescence vs. Concentration

Figure 2.4 Total Fluorescence vs. Time for Pulsed Excitation

Figure 2.5 Comparison of Temporal Behavior of Two Different Species

Time resolved fluorescence spectroscopy makes use of the knowledge that component B fluorescence decays much more rapidly than does that from A. If the decay time difference is large, one simply waits to turn the detector on until virtually all of the fluorescence from B is gone as shown in Figure 2.5, at the time t_d . The resultant signal, F_d , although smaller than the total, F , can be attributed to A and therefore used to measure the concentration of A. Knowing the concentration of A, the B concentration can then be calculated from a second measurement made with no time delay.

In fact, the difference in decay times need not be so large as to allow the complete decay of B before making the measurement. As long as the time constants are known, any two measurements made over two different time intervals, provide the information necessary to calculate the concentration of both A and B.

2.2.3.2 Phase Sensitive Spectroscopy

Phase sensitive spectroscopy is also based on the differential in decay times. Instrumentally, however, it is altogether different. Instead of pulsing the excitation and making measurements at known time intervals after the pulse, as in the time resolved approach, a continuous source is used. The intensity of the source is then rapidly modulated. This in turn modulates the fluorescence signal. In other words, if you turn the excitation on and off at some rate, the fluorescence signal will turn on and off at the same rate. Because of the time constant, however, the fluorescence signal doesn't shut off at the same time as the source but at some time later, determined by the decay time constant. The fluorescence signal then has the same frequency as the source modulation but is delayed in phase, the phase delay being proportional to the decay time constant. When the sample has two or more components, the fluorescent signal is a sum of two or more signals all having the same frequency but each differing in phase. These signals can be electronically separated on the basis of the phase difference and used separately to determine the concentration of individual components.

2.2.3.3 Absorption (Excitation) Spectrum

Since the process of fluorescence begins with the absorption of the excitation light, differences in the absorption spectrum of two species can be used to separate the fluorescence due to each. Figure 2.6 illustrates the concept. If the two species are simultaneously excited with a pulse having a wavelength λ_1 , the resultant fluorescence will be a mix of fluorescence from the two. If, however, excitation is at λ_2 , only component A will absorb and, hence, contribute to the fluorescence. Likewise, excitation at λ_3 will excite fluorescence from only component B. As in the case of the temporal differences, the absorption differences do not need to be as extreme as discussed in this example in order to separate the effect of two components from two independent measurements.

Figure 2.6 Absorption Spectra of Two Species

2.2.3.4 Emission Spectrum

Each fluorescing species has its own characteristic emission spectrum which is determined by the details of its energy level diagram. When two species are simultaneously present in the sample, the resultant spectrum is a superposition of the two as indicated in Figure 2.7. The total fluorescence, F , which is the total area under the resultant fluorescence curve, gives no information concerning the relative importance of the two species. The spectral distribution, $I(\lambda_m)$, however, contains information concerning the individual components. In cases where the characteristic spectra of the individual components is known, there are mathematical techniques for quantitatively determining the individual concentrations from the emission spectrum.

In the course of our work on pulp fluorescence, we observed that there were variations in the shape of the emission spectrum among the various samples. Figure 2.8 is an example where the spectrum from a low Kappa number pulp is compared to that from a high Kappa number pulp. Rather than try to quantitatively separate the spectra into contributions from individual components, we simply wanted some means of quantifying the observed changes in the spectral distribution. Two methods were evaluated. The first being simply to divide the spectrum into two wavelength ranges; a high and a low. The shape factor was then defined as the total intensity in the high range divided by the total intensity in the low range. The second method for quantifying the shape factor was to calculate the wavelength centroid, λ_c , defined by the expression

$$\lambda_c = \frac{\int_0^{\infty} \lambda_m I(\lambda_m) d\lambda_m}{\int_0^{\infty} I(\lambda_m) d\lambda_m} \quad (2.3)$$

Figure 2.7 Fluorescence Emission Spectrum of Two Species

FIGURE 2.8
COMPARISON OF SPECTRAL DISTRIBUTION
FOR HIGH AND LOW KAPPA SAMPLES
BALSAM FIR PULP AT 9% CONSISTENCY

2.3 DISCUSSION OF PULP PARAMETERS

In this section we consider the various pulp parameters and conditions that must be taken into consideration, both in the conduct of the laboratory studies and later in application of the sensor. These parameters are discussed individually below.

2.3.1 Wood Species

One of the first requirements for the target sensor is that it must be applicable to the wide variety of wood species that are commonly used as feedstock to the pulping process. In our program, pulps from 5 different wood species were investigated; 4 were softwoods and 1 was hardwood. For each species a sample set covering a range of lignin concentrations (as determined by Kappa number measurement) was prepared and characterized. Details on the rationale for the choice of species are given in Section 5.0.

2.3.2 Pulping Recipe

In the initial test series the objective was to study the fluorescence parameters and select a preferred measurement approach. The two pulp sets prepared for use in these tests were prepared using the same pulping chemistry and temperature for all samples in the set. Different Kappa numbers were obtained by varying the cooking time only. The rationale for this approach was to eliminate variable chemistry as a factor. In the second series of tests where the fluorescence approach had been selected and the focus was on the pulp parameters, the sample sets were prepared with pulping conditions more representative of those actually employed in the field, i.e., the pulping conditions being different depending on the desired final Kappa number. Details of the pulping recipes are discussed further in Section 5.0.

2.3.3 Kappa Number

Kappa number measurement according to TAPPI procedure T-236 was used as the independent determination of lignin concentration, i.e., it is the standard against which all of our fluorescence data was plotted.

The two sample sets used in the first series of tests covered the Kappa range from 15 to 55 which was intended to cover the range of most potential applications. The pulp sets prepared for the second series of tests extended the Kappa range to the extremes on both ends, i.e., down to $\kappa=8$ on the low end and $\kappa=140$ on the high end.

Although Kappa number was used as the independent standard by which the lignin concentration of the samples was determined, we found early on that the variability in Kappa number determination from lab to lab was much larger than expected. This variability error is in fact large enough that it becomes the primary limit to the evaluation of the fluorescence measurements accuracy, i.e., the specimen-to-specimen and long-term repeatability of the fluorescence measurements is better than the repeatability from lab-to-lab of the Kappa number determination.

Details of the Kappa number measurements and repeatability are given in Section 5.0.

2.3.4 Heterogeneity

Because of the heterogeneous nature of wood pulp, any measurement technique must deal with the problem of obtaining a representative sample, i.e., how to assure that the concentration measured at the small point irradiated by the laser is the same as the average value for all of the pulp. This is a concern for both the laboratory measurements and in the mill. In the mill application, the pulp will be continuously flowing past the measurement point so each laser pulse will hit a different area. The sensor will average the readings from many sequential pulses to give an output representative of the total pulp stream.

In the laboratory tests the problem was handled by mounting the pulp specimens on a motor driven translation stage that scanned the pulp surface under the incident laser beam. Usually the results of more than 100 individual pulses were averaged together to produce a spectral data file.

In the second series of tests, relatively large aliquots of pulp were whizzed in a blender prior to specimen preparation in order to further average out any local variations of lignin concentrations.

2.3.5 Consistency

At the beginning of the program it was envisioned that the sensor would be located near the end of the last stage of the brownstock washer and view the "drained" pulp passing by on the conveyor screen. During the first series of tests the consistency of the pulp specimens was generally above 15% but was not controlled or measured. In planning the second series of tests it was deemed desirable to have the ability to make measurements at other process locations as well. These other locations would involve in-pipe slurries. Therefore, in the second series of tests a new procedure for specimen preparation was developed and used to determine the effect of consistency variations over the range from 5 to 14%.

2.3.6 Degree of Wash

The interest in measurement at additional locations also raised a question concerning the degree to which the pulp must be washed to remove the residual black liquor before the sensor can provide a valid measurement. Most of the fluorescence measurements made in the course of the program were made on specimens prepared from fully washed pulp samples. To investigate the applicability to partially washed pulp a series of specimens were tested that had been prepared from pulp samples taken directly from the digester with no subsequent washing.

2.3.7 Temperature

Fluorescence is known to be a temperature dependent process. However, preliminary tests showed that the effect on the output of the preferred approach was minimal and would, at most, require a simple linear compensation term. Therefore, any further temperature effect testing was deferred to the prototype testing phase.

2.3.8 pH

At the 337 nm laser excitation wavelength, the absorbance of lignin in aqueous solutions is the resultant of the superposition of 5 individual overlapping absorption bands [18, 26-31]. The intensity of each of these bands is a function of the pH of the solution [18]. It is to be expected, therefore, that the fluorescence characteristics will also depend on pH.

For all of the series two testing, we attempted to control and/or measure the pH of the specimens. In addition, a series of tests were run on both black liquor and pulp specimens as a function of pH. Details of these tests are discussed in Section 3.6 and 9.1.

2.4 FEASIBILITY STUDY RESULTS

Figure 2.9 shows results obtained in a B&W funded study prior to the initiation of the project reported here. In this study the fluorescence was excited by a mercury vapor lamp instead of a laser. The pulp samples were obtained as grab samples from pulp mills operating at three different target Kappa ranges. Additional details of the study are given in Appendix A.

Figure 2.9 shows that:

- there is a functional relationship between the fluorescence intensity and the Kappa number as measured at the pulp mill laboratory.
- the relationship is one of decreasing intensity with Kappa number indicating operation in the quenched fluorescence regime.
- there is a great deal of scatter in the data. Because of the preliminary nature of the study the origin of the scatter was not identified.

2.5 INITIAL TEST SERIES

2.5.1 Objectives

The results of the preproject study presented in Figure 2.9 showed an unacceptable level of scatter among the data points. The first objective of these tests was to determine whether the scatter was due to instrumental error or was inherent in the properties of the pulp.

Fluorescent Intensity vs. Mill Kappa #

Figure 2.9 Fluorescence Intensity vs Mill Kappa Number from PreProject Feasibility Study

If a property of the pulp, the next objective was to explore the fluorescence characteristics, in detail, with the goal of identifying a measurement strategy that could yield a response function suitable for use as a control signal.

2.5.2 Approach

Possible causes of the data scatter were:

- optical instability error (drift of optical alignment, drift of source excitation intensity and wavelength, etc.)
- local variations of Kappa number within the pulp samples (area sampled by the fluorescence probe not representative of the bulk sample).
- bleaching effects (the extent to which exposure to the excitation light caused irreversible chemical changes that effected the fluorescence efficiency were unknown and the total exposure experience during the tests was not controlled).
- Kappa measurement (there was no data concerning the error band associated with the Kappa number measurement. Neither was there any information on how representative the specimens used in the fluorescence tests were of the pulp used in the Kappa testing).
- uncontrolled variables inherent in the pulp (the presence of species whose concentration does not correlate with Kappa number can affect the measured fluorescence either by adding their own fluorescence or by altering the efficiency of the fluorescence from the lignin).

The initial test series was designed to deal with the possible causes of scatter enumerated above. The first three were addressed through the design of the apparatus and testing procedures. A new laser based fluorescence spectroscopy apparatus was developed for the tests. Instrumental error was minimized through careful design and then quantified by the use of on-line standards. To minimize the effect of pulp inhomogeneity and to avoid bleaching problems, the specimens were mounted on a motor driven table that was automatically raster-scanned during the exposure period.

The Kappa number problem was addressed by having two simplified and well-defined sample sets manufactured. Each set consisted of eight samples spanning the range of Kappa numbers from 15 to 55. The range of Kappas was achieved by varying the cooking time. Within each set the samples all came from the same single species parent wood-chip stock, and all had been processed with the same chemistry. The Kappa numbers of the pulp samples were determined at two different labs using Tappi procedure T236.

The final potential source of scatter (inherent to pulp) was addressed by a comprehensive study of the fluorescence characteristics of the two specially prepared pulp

sample sets. The approach in these tests was to keep the pulp parameters constant while exploring all of the fluorescence parameters. For all of the tests:

- the specimens were prepared from fully washed pulp samples.
- the measurements were made at room temperature.
- the specimens were mounted in quartz cuvetts with relatively high ($\approx 15\%$) but unmeasured consistency.
- the pH was unmeasured and uncontrolled.

Various fluorescence parameters investigated included:

- total fluorescence intensity, F , with excitation at 337 nm.
- time resolved fluorescence intensity, F_d , for a range of delay times.
- total fluorescence intensity with excitation at various wavelengths > 337 nm as provided by a dye laser.
- the spectral distribution of the emission intensity as quantified by both the wavelength centroid, λ_c , and by the ratio of the integrated fluorescence in the high range to the integrated fluorescence in the low range.

2.5.3 Outcome

Results of the initial test series showed that the total fluorescence, F , does not provide a suitable control signal. However, a suitable function can be derived from several different alternative approaches. Measurement of the wavelength centroid was chosen as the preferred approach. It provides a suitable control function for each of the sample sets and has the advantage of being independent of absolute intensity which is a great advantage in field application.

2.6 SECOND TEST SERIES

2.6.1 Objective

The objective of the second test series was to provide the background data base necessary for the design of a field prototype and evaluation of the range of conditions/locations over which the prototype can be expected to successfully function.

2.6.2 Approach

The starting point for the second test series was the choice of the wavelength centroid method using excitation at 337 nm as the preferred approach. No time resolved or variable

wavelength excitation tests were included. The test series consisted of a number of individual experiments in which the effect of various pulp parameters on the wavelength centroid response function was determined.

2.6.3 Description of Experiments

The first task in the second series was to develop new procedures for the preparation and presentation of the pulp specimens. For all tests in the second series the specimens were prepared with known consistencies. Rather than using a cuvet, as in the initial test series, the pulp specimens were placed in small (1 oz) glass jars and irradiated from above through the open top of the jar. The jars were scanned beneath the beam to distribute the interrogated surface over a larger area as in the case of the cuvet specimens.

Pulp parameters investigated included:

- **Wood Species:** Three additional sample sets were prepared, bringing the total number of sets to 5. All of the samples within a given set were created from the same single species set of wood chips. One of the sets was from a hardwood while the balance were softwoods.
- **Pulping Process:** Both initial sample sets and most of the samples in the three new sets were produced using a kraft pulping process. Several samples from each of the three new species sets were produced using oxygen delignification of Kraft prepared pulps to achieve the desired low Kappa numbers.
- **Range of Kappa Number:** While the two original sample sets were limited to the range of Kappas from 15 to 55, the new sets extended the range to the extremes on either end, i.e. 8 to 140.
- **Consistency:** The consistency of the pulp specimens was controlled in all of the second series tests. Tests to determine the sensitivity of the centroid response function to consistency investigated the range from 5 to 14. During all of the other experiments, a standard of 9% consistency was used for all specimens.
- **Degree of Wash:** An experiment was run on a series of specimens prepared from pulp that had received varying degrees of rinsing after removal from the digester. This was to assess the applicability of the proposed sensor to measurement points upstream of the final washing stage where there is still considerable residual black liquor mixed in with the pulp.
- **pH:** At most potential measurement points in a pulp mill the pH of the pulp slurry is expected to be above pH = 10. Measurements made on the washed pulp samples as received from the labs where they were produced yielded a wide range of values; all below pH = 9 and some as low as pH = 5.

Since pH is expected to be an important parameter influencing the fluorescence properties, an attempt was made to produce a uniform pH around 10 by soaking the pulps in high pH NaOH solutions. As discussed in Section 9.1, this procedure was only partially successful and pH emerges as the most poorly controlled variable affecting the test results.

In addition to the attempt to produce a standard pH for all test specimens, one experiment was conducted where the pulp was treated to vary the pH to determine the sensitivity of the centroid response function to pH changes.

Additional information about the effect of pH was provided by an experiment on specimens of black liquor produced during the production of the pulp sample sets.

3.0 RESULTS

3.0 RESULTS

3.1 WAVELENGTH CENTROID RESPONSE FUNCTION

Figure 3.1 shows the wavelength centroid as a function of the Kappa number of the pulp for the two softwood species used in the initial test series. This is data taken during the initial test series and was the basis for the selection of wavelength centroid as the preferred approach. In addition to demonstrating the suitability of the wavelength centroid response function for use as a control signal, Figure 3.1 shows that the apparatus and test procedure provided excellent repeatability. Independent readings taken on opposite sides of the specimen cuvetts (designated front and back in Figure 3.1) show excellent agreement.

For the second series of tests, the apparatus and procedures for specimen preparation/presentation were modified. Figure 3.2 compares the wavelength centroid response function obtained in the two difference cases. The slope of the response curve is greater for the second series tests but the data is otherwise in very good agreement. In Figure 3.2 the designation "9% consistency via H₂O" refers to the procedure for specimen preparation. The procedure which is discussed fully in Section 6.0, involved homogenizing the pulp by adding a liter of liquid to 140 ml of as-received pulp, and mixing the resulting slurry in a blender. After mixing, excess liquid was removed to yield pulp with consistency in the range 15 to 20%. The consistency was determined by oven drying a portion, and then 10 ml of the high consistency pulp was placed in a glass jar and brought to the desired 9% consistency by the addition of liquid. The designation "via H₂O" in Figure 3.2 refers to the fact that the liquid used both in the original homogenization and to bring the specimen to 9% was distilled, deionized water.

Figures 3.3 and 3.4 show the wavelengths centroid response function for the two new sample sets prepared from softwoods. The samples prepared by Kraft pulping are shown in Figure 3.3, while those receiving the oxygen delignification treatment are shown in Figure 3.4. Figure 3.3 shows a response function very like that shown for the initial sample sets in Figure 3.1. The oxygen treated pulp behave quite differently, however. The response function is a single valued, nearly liner, function of Kappa number which could be used as a control signal, but the change with Kappa is in the opposite direction from that for the Kraft processed samples.

The centroid response function for the one hardwood sample set is shown in Figure 3.5. It can be seen that the wavelength centroid decreases with Kappa number for both Kraft and oxygen treated samples. For the data in Figures 3.3 - 3.5, the consistency was set to 9% by the addition of distilled deionized water. As a result, the pH of the specimens was determined primarily by the pH of the as-received, washed pulps and was subject to considerable variation as discussed in Section 3.5. Subsequent to the tests reported in Figures 3.2 through 3.5, the specimen preparation procedure was modified in an attempt to provide better control of the pH. The modification was to substitute a solution of NaOH with a pH=10 for the distilled water used both for homogenization and for adjusting the consistency to 9%. Figures 3.6 and 3.7 show the results obtained with the new specimen preparation. Kraft pulp samples from each of the five wood species are shown in Figure 3.6, while those receiving oxygen treatment are shown in Figure 3.7.

Figure 3.1 Wavelength Centroid vs. Kappa Number (Initial Test Series)

FIGURE 3.2
COMPARISON OF INITIAL AND SECOND TEST SERIES RESULTS

FIGURE 3.3
WAVELENGTH CENTROID VS. KAPPA NUMBER - KRAFT SOFTWOODS
(SECOND TEST SERIES)

FIGURE 3.4
WAVELENGTH CENTROID VS. KAPPA NUMBER -
OXYGEN TREATED SOFTWOODS
(SECOND TEST SERIES)

FIGURE 3.5
WAVELENGTH CENTROID VS. KAPPA NUMBER - HARDWOOD
(SECOND TEST SERIES)

FIGURE 3.6
WAVELENGTH CENTROID VS. KAPPA NUMBER
KRAFT PULPS : pH 10 TREATMENT
(SECOND TEST SERIES)

FIGURE 3.7
WAVELENGTH CENTROID VS. KAPPA NUMBER - OXYGEN TREATED PULPS :
pH 10 TREATMENT

In Figure 3.6 it can be seen that all of the softwoods tend to follow the same line, while the hardwood (birch) follows a roughly parallel line that is displaced upward by some 12 nm. In Figure 3.7 the oxygen treated softwoods follow one another but the hardwood is different.

Although the specimens tested in Figures 3.6 and 3.7 were prepared with a pH=10 solution, the resultant 9% slurry did not come to a pH of 10. Rather, the average pH value for all the 21 samples involved in this experiment was just under pH=8.

A second series of specimens was prepared using an NaOH solution with a pH of 12 which resulted in an average specimen pH of just under 10. The measured centroid response function for those specimens is shown in Figures 3.8 and 3.9, where it can be seen that all five wood species tend to follow the same line. The Kraft samples still follow a different curve than the oxygen treated samples, but the birch (hardwood) behaves the same as the softwoods for both pulping processes.

3.2 CONSISTENCY

The Red Spruce sample set, consisting of 14 Kraft pulps and 6 oxygen treated pulps, was used in an experiment to determine the effect of pulp consistency on the wavelength centroid response function. Figure 3.10 shows the centroid response function for Kraft samples measured at consistencies over the range from 9 to 13%. Results for the oxygen treated samples are shown in Figure 3.11. For both pulping processes, the effect of increasing consistency is to shift the wavelength response curve upward. The magnitude of the upward shift is shown in Figures 3.12 and 3.13, where the average of the centroids for the entire sample set are plotted against the consistency. An early experiment using the southern pine sample set where the specimens were prepared with distilled, deionized water instead of the pH=10 NaOH solution, showed a somewhat smaller upward shift over a wider consistency range as shown in Figure 3.14.

3.3 DEGREE OF WASHING

Four pulps from the Red Spruce sample set were selected for an experiment aimed at assessing the effect of residual black liquor on the centroid response function. All of the other experiments reported here involved measurements on pulp samples that were thoroughly washed at the time of their production. This experiment, however, involved measurements on pulps that received no washing at the time of their production. The pulps were removed from the digester, the excess black liquor was drained away and the unwashed pulp placed in sample storage jars. The black liquor was also bottled for subsequent testing.

Beginning with the four totally unwashed pulp samples, specimens were prepared with 9% consistency using the standard blender homogenization procedure. For this procedure, 140 ml of the unwashed pulp was added to one liter of distilled, deionized water and mixed in the blender for one minute. The solution drained from the pulp after mixing was saved for later quantification of the solids content and to adjust the specimen consistency to 9%. The four specimens prepared this way were designated as having received one wash. Another liter

FIGURE 3.8
 WAVELENGTH CENTROID VS. KAPPA NUMBER
 KRAFT PULP : pH 12 TREATMENT

FIGURE 3.9
WAVELENGTH CENTROID VS. KAPPA NUMBER
OXYGEN TREATED PULPS : pH 12 TREATMENT

FIGURE 3.10
EFFECT OF CONSISTENCY ON CENTROID RESPONSE FUNCTION -
KRAFT SAMPLES

FIGURE 3.11
EFFECT OF CONSISTENCY ON CENTROID RESPONSE FUNCTION -
OXYGEN DELIGNIFIED SAMPLES

FIGURE 3.12
AVERAGE CENTROID AS A FUNCTION OF CONSISTENCY - KRAFT SAMPLES

FIGURE 3.13
AVERAGE CENTROID AS A FUNCTION OF CONSISTENCY -
OXYGEN DELIGNIFIED SAMPLES

FIGURE 3.14
AVERAGE CENTROID AS A FUNCTION OF CONSISTENCY -
KRAFT SOUTHERN PINE

of distilled deionized water was then added to the remaining once-washed pulp, mixed in the blender, and then drained creating the twice-washed pulp. Specimens were prepared for 1 through 5 washes.

Table 3.1 shows the solids content of the original black liquor and the various wash waters for the samples whose fully washed pulp has a Kappa number of 46.7.

Table 3.1 Solids Content of Wash Water

Wash #	% Solids
0 (Black Liquor)	15
1	.52
2	.066
3	.049
4	.046
5	.041

The effect of this washing on the centroid response function is shown in Figure 3.15. The same data is presented in Figures 3.16 in terms of centroid as a function of wash number. The centroid decreases with increased washing as would be expected from the fact that the centroid increases with increasing lignin concentration.

The response function as shown in Figure 3.15 is as desired for the first few rinses, i.e., it increases monotonically with Kappa number with about the same slope as the fully washed pulp. As the number of washes increases, however, the high Kappa number pulp's centroid decreases much faster than that of the other pulps, so that by wash #5 the response function becomes double valued. This may be an artifact of the preparation procedure resulting from uncontrolled (and unmeasured) pH changes. Alternatively, it may be due to the fact that the excess liquor is more easily washed from the high Kappa number pulp.

3.4 TEMPERATURE

The effect of pulp temperature on fluorescence intensity was determined using the initial test series set-up and procedure, i.e., mounting the specimen in a quartz cuvet and exposing to multiple pulses while scanning the specimen so that each subsequent pulse hit a new area. During the temperature tests, however, the same specimen was scanned 27 different times. If the scan were over exactly the same area each time, this could introduce a bleaching error on the order of a few percent. Because the laser pulsing was not synchronized with the specimen scanning motors, the bleaching effect is estimated at about 1%.

For the temperature tests, a thermocouple was inserted into a pulp filled quartz cuvet approximately 1 mm from the irradiated surface. The cuvet was held on the translation stage against a large aluminum block. The block was heated by a hot air gun until the thermocouple read 172°F. A series of baffles protected the specimen from direct exposure to the heating air to avoid drying. After heating, the air gun was turned off and the system

FIGURE 3.15
EFFECT OF WASHING ON CENTROID RESPONSE FUNCTION

FIGURE 3.16
CENTROID AS A FUCTION OF WASHING

allowed to equilibrate for five minutes. Then a series of data scans were run as the temperature slowly dropped. The large thermal mass of the aluminum block moderated the rate of decrease in temperature to a few degrees over the period of a data scan.

An earlier attempt to measure the effect at temperatures below room temperature involved putting the specimen in a freezer prior to a series of scans. These tests indicated a general trend consistent with the high temperature results, but were noisy and unreliable due to condensation on the cuvet face.

Figure 3.17 shows the effect of pulp temperature on the total fluorescence. The data was obtained from a southern pine sample with a Kappa number of 15. The total fluorescence intensity decreases linearly with temperature at approximately $0.2\%/^{\circ}\text{F}$.

Figure 3.18 shows the effect of temperature on the wavelength centroid. The effect is a small linear decrease which could be easily compensated. Part, if not all of this decrease may be due to the multiple pulse exposure of the sample. Along with the drop in total fluorescence (bleaching) with continued exposure there is also a shift of the centroid to longer wavelengths. Since total exposure increased with decreasing temperature in the experiment, some of the observed shift may be due to the exposure rather than temperature. The slope of $0.025 \text{ nm}/^{\circ}\text{F}$ ($\approx 0.07 \text{ nm}/^{\circ}\text{C}$) observed in Figure 3.18 should thus be considered an upper limit of the magnitude of the shift with temperature.

3.5 pH

An experiment was run, during the initial test series, to determine how pH would effect the wavelength centroid response function. Samples were prepared for this test by soaking the pulp samples for 24 hours at room temperature in the following solutions; distilled-deionized water, Fisher pH 7 buffer solution, and Fisher pH 10 buffer solution. After the 24 hour soak, the pulp was loaded into Fisher acrylic cuvetts. Standard fluorescence measurements were made on the resultant 48 specimens (2 wood species x 8 Kappa numbers x 3 pH). Litmus paper testing of the prepared slurries showed that those soaked in water had a $\text{pH} = 6.1 \pm 1$, while the buffered slurries were all within 0.1 of the buffer solution pH.

Figures 3.19 and 3.20 show the effect of pH on the wavelength centroid response function for the southern pine and northern spruce samples, respectively. The centroid tends to shift toward longer wavelengths with increasing pH in both wood species, although the effect is smaller for the southern than the northern spruce.

The 48 acrylic cuvetts (2 species x 8 samples x 3 pH's) used in the test were all taken from the same carton. As discussed in Section 7.8, some significant differences in cuvet fluorescence were discovered after the pH tests were completed. Cuvet interference may therefore account for some of the irregularities in the observed response functions. It is clear, however, that pH has a significant effect on the centroid response.

Figure 3.17 Temperature Effect on Total Fluorescence

Figure 3.18 Temperature Effect on Wavelength Centroid

Figure 3.19 Effect of pH on Wavelength Centroid of Southern Pine Samples

Figure 3.20 Effect of pH on Wavelength Centroid of Northern Spruce Samples

To eliminate pH as a variable in the second series of tests, the initial plan was to soak all pulps when received in an NaOH solution. As received pulp pH values around 9 to 10 were anticipated and the pH of the NaOH solution was to be chosen just above the highest pulp value.

Figure 3.21 shows the as-received pH values measured on the first shipment of new pulps. Measurements were made using a ORION model 8-135 Ross pH electrode specifically designed for use on soft moist surfaces of solids and semi-solids. The average value of pH is lower than had been anticipated and there were a number of samples with pH values much lower than expected. Four of the six samples with pH below 7 were samples rejected for fluorescence testing because of the large discrepancy between the Kappa numbers as measured by Miami University and the Institute of Paper Science and Technology (IPST) (see Section 5.0).

Notwithstanding the large pH variations, the pulps were all soaked for 24 hours in a pH=9 solution of NaOH. Measurements made at the end of the soak period indicated that there was still a large variation. The pulps were then subjected to a series of soaks in NaOH solutions that varied from pH = 9 to 12 (depending on the pulp pH) over the next 4 days. Figure 3.22 compares the measured pH values after this treatment to the as-received readings. The objective of uniform pH for all samples was clearly not achieved by this treatment strategy which was therefore abandoned.

The alternative approach which was used for subsequent testing yielded pH variations larger than desired but smaller than those shown in Figure 3.22. This approach was to mix the as-received pulp with the NaOH solution in a blender for 1 minute, remove the excess liquid, and then prepare specimens with the desired consistency by the addition of the NaOH solution.

Figures 3.23 through 3.27 compare the centroid response functions for Kraft specimens prepared using NaOH solutions with pH-10 to those prepared with pH-12 NaOH solutions. Specimens prepared with the pH-10 solution had an average pH of 7.9 ± 0.6 , while those prepared with pH=12 measured pH = 9.9 ± 0.8 . The effect of increasing pH is to shift the centroid response upward for all four softwood species. This is in accordance with the earlier results shown in Figures 3.19 and 3.20. The effect on the one hardwood (birch) species shown in Figure 3.27, however, is just the opposite.

The effect is also reversed for the pulps that had received oxygen delignification treatment as shown in Figure 3.28.

Figure 3.29 shows the results of an experiment using a specimen of black liquor rather than pulp. The liquor was that from the production of the balsam fir pulp with a Kappa number of 18.5. Figure 3.29 plots the wavelength centroid at various liquor dilutions. When the liquor is diluted with water, there is a drop in the centroid beginning at dilutions greater than 128:1 ($\log = -2.11$). When the dilution is with an NaOH solution having the same pH as the undiluted liquor (pH=13) so that the pH remains constant, there is no sharp drop in the centroid at high dilutions. This suggests that the sharp drop is due to a pH change rather than

FIGURE 3.21
pH OF AS-RECEIVED PULP SAMPLES

FIGURE 3.22
COMPARISON OF PULP pH BEFORE AND AFTER
TREATMENT TO EQUALIZE pH

FIGURE 3.23
EFFECT OF pH ON CENTROID RESPONSE FUNCTION - RED SPRUCE

FIGURE 3.24
EFFECT OF pH ON CENTROID RESPONSE FUNCTION - BALSAM FIR

FIGURE 3.25
EFFECT OF pH ON CENTROID RESPONSE FUNCTION -
NORTHERN SPRUCE

FIGURE 3.26

EFFECT OF pH ON CENTROID RESPONSE FUNCTION - SOUTHERN PINE

FIGURE 3.27

EFFECT OF pH ON CENTROID RESPONSE FUNCTION - BIRCH

FIGURE 3.28
EFFECT OF pH ON CENTROID RESPONSE FUNCTION -
OXYGEN TREATED PULPS

FIGURE 3.29
EFFECT OF pH ON WAVELENGTH CENTROID OF DILUTED BLACK LIQUOR
FROM BALSAM FIR

concentration. Figure 3.30 plots the pH of the water diluted liquor as a function of dilution showing that the steep portion of the centroid vs. concentration curve in Figure 3.29 corresponds to pH values below 11.

Figure 3.31 presents the results of this black liquor experiment in terms of the emission spectra.

3.6 ALTERNATIVE APPROACHES

As a result of the initial test series, the wavelength centroid measurement was chosen as the preferred approach. In this section we present the results obtained for various alternative approaches.

3.6.1 Total Integrated Fluorescence

The first and most straightforward approach considered was the measurement of total integrated fluorescence, F . Figure 3.32 shows that F does not provide a suitable control signal. While there is a general downward trend of F with increasing Kappa number, there are a number of irregularities that suggest the presence of some non-correlating component along with the component that decreases monotonically with the Kappa number.

3.6.2 Temporal Behavior of Fluorescence

Because the distribution of fluorescence over time is characteristic of the fluorescing species, it is often possible to discriminate against the effects of an interfering species on the basis of the temporal distribution of the fluorescence. Instrumentally there are two approaches that are commonly used to exploit the temporal behavior. These are called time-resolved and phase-resolved spectroscopy.

Figure 3.33 shows the results obtained using the time-resolved approach. In this set of tests, the detector measures only the fluorescence that occurred more than 12 nsec after the initial laser pulse. Comparison of Figure 3.33 with 3.32 shows that the time-delayed fluorescence provides a "better" response curve, i.e., the disruptions due to the non-correlating components are less severe. Figure 3.33 shows only the results for a 12 nsec delay. As the delay is increased from zero (a delay of zero gives the total integrated fluorescence shown in Figure 3.32) the disruptions gradually decrease up to delays of 20 nsec. As the delay increases, however, the total remaining signal decreases. Delay time much more than 12 nsec results in an impractically low signal level, i.e., the signal becomes dominated by noise.

Although the time-delayed fluorescence shown in Figure 3.33 is an improvement over the basic response shown in Figure 3.32 it is still far from ideal as a control signal, particularly at higher Kappa numbers.

FIGURE 3.30
EFFECT OF WATER DILUTION ON pH OF BLACK LIQUOR
LIQUOR FROM BALSAM FIR WITH KAPPA=18.5

FIGURE 3.31A
LIQUOR FROM BALSAM FIR SAMPLE WITH KAPPA=18.5
DILUTED WITH H₂O
EFFECT OF DILUTION ON NORMALIZED FLUORESCENCE SPECTRA (LQR2)
DATA OF 3/18/94

FIGURE 3.31B
LIQUOR FROM BALSAM FIR SAMPLE WITH $KAPPA=18.5$
DILUTED WITH NaOH pH=13
EFFECT OF DILUTION ON NORMALIZED FLUORESCENCE SPECTRA
DATA OF 3/25/94

Figure 3.32 Total Fluorescence Intensity vs. Kappa Number; Excitation at 337 nm

Figure 3.33 Time Resolved Fluorescence Intensity vs. Kappa Number - 12 ns Delay

In Figure 3.34 we combine the two curves by taking the ratio of the 12 nsec delayed response to the total (delay = 0) response. The resultant response function is much more suitable. It is particularly significant that the species dependence is greatly reduced, i.e., the difference between the northern spruce and southern pine samples is minimal.

Figures 3.35 and 3.36 show results obtained using the phase-resolved approach to temporal discrimination. As in the case of the time-resolved approach, the selection of the proper time response in Figure 3.36 discriminates against the non-correlating component that is present in Figure 3.35.

3.6.3 Excitation Wavelength

Fluorescence is dependent on the wavelength of the source used for excitation. Since the dependence is characteristic of the fluorescing species, this is another approach commonly used to discriminate against interfering species. Figure 3.37 shows the total fluorescence intensity as a function of Kappa number for an excitation wavelength of 442 nm. Clearly the response function is no improvement over that for excitation at 337 nm which was shown in Figure 3.32.

Several excitation wavelengths between 337 and 488 were investigated. The general trend was that the response curve became more erratic as the wavelength was increased. This suggests that the function might improve for excitation wavelengths below 337 nm. Unfortunately the N_2 /Dye laser cannot provide wavelengths shorter than 337 nm. Because of the non-availability of a practical source at shorter wavelengths, we have not pursued testing at excitation wavelengths less than 337 nm.

The 442 nm response shown in Figure 3.37 indicates that the non-correlating component is more of a factor in the total than is the case for the 337 nm response. This suggests the possibility of combining the two measurements. In Figure 3.38 we show the response function obtained as a linear combination of the 337 nm excited response with the 442 nm excited response. The constant 4 (see y-axis in Figure 3.38) was chosen empirically as that which gave the smoothest response curve.

3.6.4 Spectral Distribution

The spectral distribution of the fluorescence emission is another factor commonly used to provide discrimination against an interfering species.

One instrumentally simple but crude way to implement an emission spectrum analysis is to use a pair of broadband filters to separate the fluorescence into a long and a short wavelength component. Figure 3.39A shows the ratio of two wavelength bands as a function of the Kappa number. Although there is some species dependence (the curves for northern spruce and southern pine are different) the resultant response function looks very promising as a potential control signal. Particularly important is the fact that the sensitivity does not appear to drop off at higher Kappa numbers.

Figure 3.34 Ratio of 12 ns Delayed Fluorescence to 0 ns Delayed Fluorescence vs. Kappa Number

Figure 3.37 Total Fluorescence Intensity vs. Kappa Number; Excitation at 442 nm

Figure 3.38 Dual Excitation-Wavelength Response Function vs. Kappa Number

Figure 3.39A Ratio of Fluorescence Intensity Over Two Emission Wavelength Ranges vs. Kappa Number

Figure 3.39B Wavelength Centroid vs. Kappa Number

Figure 3.39B shows the wavelength centroid, as a function of the pulp Kappa numbers. The response function is very similar to that for the band ratios, which is to be expected since the centroid is just an alternative measure of the shape of the emission spectrum. Although somewhat more complex to implement, the centroid approach should provide a more stable measurement since it is unaffected by filter and detector response drift. Figure 3.39B also shows how well the front and back surface agree -- on the order of $\Delta\kappa \approx 1$. The front and back surfaces are essentially two independent specimens.

3.7 KAPPA NUMBERS

3.7.1 Initial Test Series Pulps

Sample sets from two wood species, southern pine and northern spruce, were produced for the initial test series at the laboratory of the Paper Science and Engineering Department of Miami University in Oxford, Ohio.

At the time each species was produced, Kappa number tests according to TAPPI T-236 were performed by Miami University using an automatic Kappa number analyzer. After Kappa analysis, the samples were delivered to the B&W research lab in October 1990 and have been maintained under refrigeration since that time. The time span between the arrival of the pulp samples at B&W (October 1990) and the first meaningful fluorescence test results (January 1991) was a number of months. To assure that the pulp Kappa numbers had not changed during the storage period and to confirm the original Miami test results, portions of the southern pine samples were sent to the Institute of Paper Science and Technology (IPST) in March 1991. The results of the IPST Kappa number testing did not compare well to the Miami test results. This left one to conclude that either the pulp Kappa number had changed, or one, or both of the labs were in error. To eliminate the suspicion that the pulp had changed, portions of the southern pine samples were returned to Miami University for retesting. The second set of Miami results agreed reasonably well with the first.

Although both Miami and IPST measurements were made in accordance with TAPPI procedure T-236, Miami used an automated titrator (Systematix Model SX44090) while manual testing was done at IPST. To determine the extent to which the discrepancy was due to automated vs. manual testing, the southern pine pulps were all tested again at Miami. This time both manual and automated measurements were made. Meanwhile, southern pine samples were sent for measurement to a third testing lab - Econotech Services Ltd. of New Westminster, BC.

Figure 3.40 compares the results of the measurements made at the various laboratories at different times. The data is presented in terms of the difference between the average of all six measurements on a given sample and the value obtained in the specific measurement set. It can be seen that no set of measurements agrees with the average any better than the other sets do. On the basis of this data, there is no evidence to favor one set of measurements over another. Worse yet, the magnitudes of the differences ($\approx \pm 4$) are much larger than the repeatability claimed for TAPPI procedure T-236.

FIGURE 3.40
COMPARISON OF VARIOUS KAPPA NUMBER MEASUREMENTS ON
SOUTHERN PINE SAMPLE SET

Figure 3.41 shows that the agreement between measurements made on the northern spruce samples at Miami University and Econotech is no better.

Two additional experiments were run in an attempt to define the preferred laboratory for Kappa number determination. The first of these involved a pair of paper samples obtained from Union Camp Corp., Savannah, GA. These samples are used at Union Camp as Kappa number control standards. Kappa determinations were made on these samples at Econotech and at Miami University where both manual and automatic measurements were made. As can be seen in Figure 3.42, the results of this experiment do not help identify a preferred laboratory. The Econotech and Miami University measurements agree reasonably well with one another, but not with the measurements performed at Union Camp.

The second experiment involved comparison of measurements made at Miami University and IPST on a pair of Miami University standards. These measurements also resulted in a significant difference among the different measurements as shown in Figure 3.43.

3.7.2 Pulp Sets for Second Test Series

The Kraft pulps for the second series tests were produced at Miami University, Oxford, Ohio. The Kappa numbers were determined at Miami using their automated titrator before the samples were shipped to B&W. Kappa number measurements on these pulps were subsequently repeated at IPST.

The pulps that received oxygen delignification treatment were produced at IPST where the Kappa numbers were measured prior to shipment to B&W. No duplicate Kappa measurements were made on these samples.

Of the 26 pulp samples for which Kappa measurements were made at both Miami University and IPST, five were set aside and not used in the fluorescence tests because the difference in the two Kappa determinations was too great. Figure 3.44 compares the Miami University and IPST values for the remaining 21 pulps. Results for the five rejected pulps are given in Figure 3.45.

The IPST values for Kappa number are used in plotting all of the second series test data because they are available for both Kraft and oxygen treated samples whereas Miami University values are only available for the Kraft pulps.

FIGURE 3.41
 COMPARISON OF MIAMI U. AND ECONOTECH
 MEASUREMENTS OF KAPPA NUMBERS -
 NORTHERN SPRUCE SAMPLE SET

FIGURE 3.42

COMPARISON OF KAPPA MEASUREMENTS ON UNION CAMP STANDARDS

FIGURE 3.43
COMPARISON OF KAPPA MEASUREMENTS ON MIAMI U. STANDARDS

FIGURE 3.44
COMPARISON OF MIAMI U. AND IPST KAPPA NUMBER MEASUREMENTS -
NEW SAMPLE SETS

FIGURE 3.45

COMPARISON OF MIAMI U. AND IPST KAPPA NUMBER MEASUREMENTS -
SAMPLES REJECTED DUE TO MAGNITUDE OF DIFFERENCE

4.0 CONCLUSIONS

4.0 CONCLUSIONS

The purpose of the testing program reported here was to generate the data necessary to:

- determine the feasibility of an instrument for on-line lignin concentration measurement using laser fluorescence
- identify the preferred measurement strategy
- define the range of applicability of the instrument
- and to provide background information to guide the design of a field-worthy prototype.

The first two items above were addressed during the initial test series while the second two were the focus of the second series of tests.

4.1 FEASIBILITY

Work done by B&W prior to the initiation of this program had shown a correlation between the total fluorescence of wood pulp and its lignin concentration as determined by Kappa number measurement. The data was encouraging but noisy and of quite limited scope.

The first activity undertaken when this project began was to develop an apparatus and set of test procedures that would eliminate instrumental error as a significant source of error leading to scatter in the data. As discussed in Section 7.9, this was accomplished. Repeatable, stable fluorescence measurements were made on two sets of specially prepared wood pulp samples and it was found that the relationship between total fluorescence and Kappa number is unsuitable. The Kappa number cannot be unambiguously determined with any useable accuracy from the measurement of total fluorescence. Figure 3.32 shows the problem as measured on the two sample sets used in the initial test series. Although not presented graphically in this report, the relationship between total fluorescence and Kappa number for the additional three pulp sets obtained for the second test series were equally unsuitable.

Although total fluorescence was shown to be unusable, a number of alternative measurement strategies were all shown to be feasible as demonstrated by the data presented in Figures 3.33 through 3.39. These strategies are based on techniques commonly employed in fluorescence spectroscopy to discriminate between the fluorescence from a species of interest and other fluorescing components in the same specimen. Methods that showed promise for Kappa number measurement were:

- The use of time resolved spectroscopy, specifically, determining the ratio of the fluorescence occurring after a time delay of 10 to 15 nsec to the fluorescence with no delay.
- The combination of total fluorescence measurements taken at two different excitation wavelengths.

- The analysis of the shape of the emission spectrum either by ratioing the fluorescence integrated over two different wavelength bands or by measuring the wavelength centroid of the emission spectrum.

4.2 PREFERRED APPROACH

Measurement of the wavelength centroid was identified as the preferred approach based on the following considerations:

- The relationship between the wavelength centroid and Kappa number is nearly linear providing good sensitivity to lignin concentration over the entire range of interest.
- The centroid is independent of the absolute intensity of the fluorescence, so long-term intensity changes due to window/fiber transmission, detector sensitivity, source output, etc., will not present a problem.
- Compared to the other approaches, the required apparatus is simpler and cheaper. It does not require a fast gateable detector, or high-speed response detector as required by the time- and phase-resolved approaches, and it requires excitation by only one wavelength rather than two as in the dual excitation-wavelength approach.
- The response function for the centroid and the "band ratio" approach are nearly identical and the band-ratio approach could eventually be cheaper to implement. However, the centroid approach provides for greater flexibility in adapting to surprises, and can provide supplemental information useful in interpretation of field test results. The band-ratio technique was therefore deferred for potential use at a later stage of development.

4.3 RANGE OF APPLICABILITY

As initially conceived, the target analyzer would be located at the final stage of brownstock washing and would interrogate the pulp mat as it moves past. This is the location where the grab samples used for laboratory measurement of Kappa number are now obtained. At this location, the pulp is well drained of excess moisture and is fully washed. This would be an ideal location for deriving a signal for use in feed forward control of the bleaching process. It could also be used for feedback control to the digester although a location further upstream would be preferable for the feedback signal since it would reduce the time lag between the processing and the measurement. At these upstream locations, the pulp is not fully washed and is normally in slurry form.

Having identified the wavelength centroid as the preferred approach in the initial test series, the focus of activity in the second series was to determine its range of applicability. Specific questions addressed included:

- Could the analyzer be used at a location where the pulp exists in slurry form within a pipe? The effect of consistency and the effect of imperfect washing are relevant to the analyzer location question.
- Can the analyzer be applied to the high and low extremes of lignin concentration? In the initial series, the pulps only covered the mid-range from $\kappa=15$ to 55.
- How does the wavelength centroid response function depend on the wood species? Only two species were tested in the initial series.

4.3.1 Consistency

Measurements made at various consistencies from 5% to 14% showed a linear change of the centroid with consistency. For Kraft pulps, the magnitude of the shift was 0.3 to 0.4 nm/%, as shown in Figures 3.12 and 3.14. Since the shift of centroid with Kappa number is in the range from 0.3 to 0.4 nm/ κ a variation of $\pm 1\%$ in consistency would create an error of about $\pm 1\kappa$. The slope of the curve for the oxygen-treated pulp shown in Figure 3.13 is larger, 0.45 nm/%. However, the sensitivity to Kappa number is also greater (0.5 to 0.7 nm/ κ) so the error due to consistency will be the same as for the Kraft pulps.

In locations where the consistency varies by more than a few percent, a separate determination of consistency could be used to compensate the Kappa readings.

4.3.2 Incomplete Washing

The question of the effect of residual black liquor caused by incomplete washing of the pulp was addressed in a preliminary experiment only. The results which were presented in Figure 3.15 and 3.16 were inconclusive. There is a general trend of centroid increasing with Kappa number regardless of the degree of wash, the effect of residual black liquor being to shift the response curve upward. The behavior of the highest Kappa number specimens is, however, against the general trend. As the number of washes increases, the centroid for the specimen with $\kappa = 125$ decreases more rapidly than that of the others. It is unknown whether this behavior is inherent (due to easier/faster removal of the residual from the high Kappa pulp) or simply an artifact of the experiment, e.g., due to uncontrolled variations of pH.

Further experimentation with a larger sample set is required to answer the questions concerning the degree of wash.

4.3.3 Kappa Range

The new sample sets obtained for the second test series included pulps with Kappas up to 140. As shown in Figures 3.1, 3.3, 3.6, 3.8, and 3.10, the centroid increases over the entire range of Kappas for all the Kraft softwoods. In the range up to about $\kappa=50$, the relationship is roughly linear with a slope in the range from 0.3 to 0.4 nm/ κ . There is a slight roll-off (decrease of slope) above $\kappa=50$.

To extend the Kappa range below $\kappa=15$, a series of pulps were produced using an oxygen delignification step after the Kraft pulping. For the oxygen treated softwood pulps, the centroid response is also linear with Kappa number but the slope is negative rather than positive. As shown in Figures 3.4, 3.9, and 3.11, the slope is in the range from -0.5 to -0.7 nm/ κ .

For the one hardwood sample set, the centroid slope for the oxygen treated samples is the same as for the softwoods when the specimens are prepared with the high pH NaOH solution (Figure 3.11). For other specimen preparations, the slope is positive instead of negative.

The wavelength centroid approach gives a suitable response for use as a control signal over the entire range of Kappas from very small to very large. The fact that the behavior of the oxygen treated pulps is different from that of the Kraft pulps should pose no difficulty. The calibration of the analyzer will simply be dependent upon the application.

4.3.4 Wood Species

For the four softwood species tested, the wavelength centroid response is roughly linear with Kappa number up to about $\kappa=50$ with some roll-off at higher Kappas. Slight differences in the slope and offset of the curves from one species to another tend to be reduced at higher values of pH as shown in Figures 3.8 and 3.9. The one sample set prepared from a hardwood (birch) gave confusing results throughout. The initial data shown in Figure 3.5 shows a general decrease of centroid with Kappa number for both Kraft and oxygen treated samples. There is, however, a great deal of scatter in the data. Subsequent tests run with specimens prepared with the pH 12 NaOH solution showed the hardwood behaving the same as the softwoods as shown in Figures 3.8 and 3.9 for the Kraft and oxygen treated pulps, respectively. Only a few of the birch samples were included in that experiment, however. Many of the birch samples arrived too late to be included in much of the test program. Further experimentation with the entire birch sample set is required.

4.4 DESIGN DATA BASE

In addition to the data discussed above which, of course, is applicable to the design of a prototype analyzer, tests were also run to determine the effect of temperature and pH.

As shown in Figure 3.18, the wavelength centroid shifts linearly with temperature at a rate of 0.025 nm/ $^{\circ}$ F. This translates to an effect in terms of measured Kappa number of 0.06 to 0.08 Kappa/ $^{\circ}$ F. Because the effect was so small, no data beyond this one test involving one pulp with $\kappa=15$ was obtained.

Several experiments demonstrated that pH has a significant effect on the measured centroid. Since the pH of the as-received pulps was quite variable and not easily manipulated, pH was the most poorly controlled variable effecting the test results reported here. Uncontrolled variations of pH not only create uncertainties in the interpretation of the test results but also raise a question concerning how closely our laboratory pulps mimic the

behavior of the pulps that will be encountered in the field. Does the pH of process-pulp vary as widely as our sample sets or is the variability an artifact of the washing procedure used in the production of the laboratory pulps?

Figures 3.8 and 3.9 show that for specimens prepared using the pH=12 solution of NaOH which gave pulp pH = 9.9 ± 0.8 , the centroid response function is nearly independent of wood-species -- even the hardwood (birch) falls in line. If the pH of process pulps at the location of the analyzer is relatively constant and high (pH $\approx$ 10), application of the proposed fluorescence analyzer will be greatly simplified. Contrariwise, if the pH is low and/or highly variable, the analyzer will require compensation for pH which will require additional characterization to implement.

4.5 RECOMMENDATIONS

The wavelength centroid measurement has been shown to provide a response suitable for use as a control signal over a wide range of test conditions.

There are several areas where additional laboratory testing could provide useful insight. Specifically:

- additional testing of the entire birch sample set.
- a more comprehensive test of the effect of incomplete washing.
- second derivative spectral analysis to identify the fluorescing species and provide an understanding of the basic physics behind the observed fluorescence results.

Nevertheless, the data base generated provides sufficient confidence in the capabilities of the wavelength centroid approach to warrant the development and testing of a field prototype as the next step toward the commercialization of the desired lignin analyzer. Prototype development should be the primary activity of the next phase with laboratory testing in the supporting role of providing specific data to answer questions arising in the course of the prototype testing.

5.0 PREPARATION OF SAMPLE SETS

5.0 PREPARATION OF SAMPLE SETS

5.1 SAMPLE SETS FOR INITIAL TEST SERIES

Two pulp sets were produced for the initial test series. Both were produced at the laboratory of Miami University's Paper Science and Engineering Department according to specifications from B&W. The specification for the first pulp set is reproduced below:

" *Specification for Preparation and Delivery of Laboratory
Prepared Pulp and "Bjorkman" Lignin Samples*

5/24/90

The Babcock & Wilcox Co. requires pulp samples for laboratory testing currently being conducted for the U S Department of Energy. The samples will be used as a basis for evaluating alternate methods of determining the lignin content of pulp. It is therefore desirable that the samples provided span a range of KAPPA numbers.

Please provide an estimate of the cost for samples prepared and delivered in accordance with the following requirements:

1. Number and Size of Samples

Eight pulp samples are requested and their volume shall be as large as possible subject to the volume restrictions of the batch digesters at the university pulp lab (approx. 1 liter digester volumes).

2. Wood Species

The wood species used to make the pulp shall be a southern pine (e.g. loblolly pine or slash pine).

3. Lignin Concentration of Samples

The KAPPA numbers of the six batches of pulp shall span a range of KAPPA=15 through KAPPA=50 at approximately equally spaced intervals. For example:

<i>Sample #</i>	<i>Approximate KAPPA #</i>
1	15
2	20
3	25
4	30
5	35
6	40
7	45
8	50

4. KAPPA Number Testing

Each of the above eight pulp samples shall be tested for KAPPA Number in triplicate using the University's Systematix SX4400 Automatic Titrator.

5. Bjorkman Lignin Specimen

In addition to the eight batches of pulp, a quantity of the wood chips shall be ground and the Bjorkman or "milled" wood lignin specimen obtained.

6. Delivery

The eight pulp samples shall be packaged to avoid damage and spoilage and shipped by overnight delivery to

*Babcock & Wilcox Co.
Research and Development Division
1562 Beeson Street
Alliance, Ohio 44601
Attn: Mike Malito "*

In addition to the results of the Kappa number measurements (discussed earlier in Section 3.7) Miami provided the following additional information about the pulps.

"Chips were obtained from Champion International - Canton, NC - Southern Pine. Chips were screened, chips from #4 screen were used for pulp procedure.

Digester Conditions

20% AA
13% Sulfidity
4 To 1 Liquor To Wood Ratio
56% Chip Moisture
1000 gms OD Chips
200 gms AA AS Na₂O
54.5 gms Na₂S Flakes
228 gms NaOH Pellets
4000 gms Water (784 chips - 3215 water)

Cooking Times & Temperatures

<u>Sample</u>	<u>KAPPA No.</u>	<u>Temp.</u>	<u>Time</u>
1	14	175°C	5 hours
2	19.6	175°C	3 hours 26 min.
3	24.4	175°C	2 hours 30 min.
4	28.9	175°C	1 hour 15 min.
5	34.8	175°C	1 hour 6 min.
6	39.8	165°C	2 hours 10 min.
7	46.2	165°C	1 hour 49 min.
8	51.6	165°C	1 hour 28 min.

Chemicals Remained Constant for All Cooks. "

The specification for the second sample set was the same as for the first with the addition of the following:

"4. Disposition of Pulp and Black Liquor

Up to 1 liter of the black liquor drained off the digester during each "cook" shall be collected and saved for delivery to B&W. If more than 1 liter of black liquor is available, the excess may be disposed of.

Upon exiting the digester, the pulp samples shall be separated into two approximately equal volumes. Half shall be packaged "as is" and the other half shall be screened and washed before packaging.

7. Deliverables

8 packages of unwashed pulp
8 packages of washed pulp
8 containers of black liquor
1 package (approx. 1 liter volume) of feed chips
1 Bjorkman lignin specimen (if possible) "

5.2 SAMPLE SETS FOR SECOND SERIES OF TESTS

The general scope of the second series test program was recommended by the DOE/Industry advisory group at their annual meeting in November of 1991. The specific test plan, including the requirements for additional pulp samples, was subsequently developed by B&W and Bailey Controls Co. with significant consulting input from personnel at Miami University and the Institute of Paper Science & Technology (IPST). The primary source of this consulting was a meeting held at Miami University on 1/29/93 to solicit input from Dr. Chris Peterson of Miami University, and Dr. Tom McDonough of IPST. Minutes of this meeting are contained in Appendix B of this report.

One of the key issues discussed at this meeting was the preparation of additional pulp samples. The detailed specification for the new pulp samples that resulted from this discussion is reproduced below. This specification was attached to the purchase orders for the new pulp sets. The Kraft pulps were produced at Miami University while those involving the oxygen delignification treatment were produced at IPST. Additional information on the processing of the oxygen pulps is included in a report supplied with the sample by IPST and reproduced as Appendix C of this report.

" SPECIFICATION FOR PREPARATION AND DELIVERY OF
LABORATORY PREPARED PULP SAMPLES

3/4/93

The Babcock & Wilcox Company requires pulp samples for laboratory testing currently being conducted for the U.S. Department of Energy. The samples will be used as a basis for evaluating alternate methods of determining the lignin content of pulp using the fluorescence of lignin. It is, therefore, desirable that the samples span a range of KAPPA numbers and that the samples not be contaminated with other fluorescing materials, such as plastics. All containers for the processed pulp shall be made of glass. The following provides guidelines for the production of the pulp and any exceptions based on equipment limitations, contrary experience or suggested alternative approaches must be discussed with Babcock & Wilcox prior to the processing of the samples.

1. Number and Size of Batches

At total of thirty (30) batches of pulp are required. Fourteen (14) batches will be obtained from Lot A softwood chips. Eight (8) batches will be

obtained from Lot B softwood chips. Eight (8) batches will be obtained from Lot C hardwood chips. The individual wood species will be dependent upon availability and Lot A and B softwoods are expected to be species which are typically mixed at a mill to obtain the range of Kappa numbers provided in Tables 1 and 2. It is anticipated that the wood chips will be obtained from a mill along with the black liquor and white liquor used at the mill to process the chips. If the white and black liquor cannot be obtained from a mill, then they will be formulated prior to pulp preparation. If the pedigree of the chips which the mill has available is not certain, then a log of the chosen species shall be obtained and chipped to assure that the species is known.

Similarly, the hardwood will be a typical hardwood used in the pulp industry for the range of Kappa numbers presented in Table 3. If possible, the white and black liquor shall be obtained from a mill which processes the chosen hardwood species. Again, if the pedigree of the mill chips cannot be documented with certainty, a log of the desired species shall be obtained and chipped.

The volume of each batch of processed pulp shall be as large as possible subject to the volume restrictions of the digesters at the lab making the pulp. A bomb digester size of 6 liter capacity is preferred. Notify B&W prior to the start of the pulp preparation if this size digester is not available.

2. Wood Species

Note, that previous testing has been performed on Southern Pine from Champion in Canton, South Carolina and Northern Spruce from the Consolidated Mill in Wisconsin. The chosen species for the 30 new batches should be commonly used species but should exclude the southern pine and the northern spruce used for the previous tests. Once the three wood species are selected based on mill availability and typical Kappa ranges, notify Babcock & Wilcox prior to procuring the chosen species.

3. Lignin Concentration of Individual Batches

Table 1 and Table 2 present the target KAPPA numbers, the processing requirements and resulting constituents from the processing of the Lot A and Lot B softwoods. Table 3 supplies the same information for the one batch of the hardwood pulp.

4. Chemistry and Cook Times

The following specifies the processing conditions for producing the pulp batches as outlined in Tables 1, 2 and 3. The objective is to produce

Kraft industry grade pulps from each of the wood species at each of the yields (KAPPA), respectively. In addition, the chemistry and physical properties of the spent cooking media shall closely replicate those found in industry prevailing at each of the yields. This is imperative as the spent pulp carrier media will be studied for fluorescence properties in order to determine feasibility of "insitu" lignin sensor applications. The pulp yields shall be varied as the output of the experiment while the spent liquor concentrations shall be constant.

For the Lot A softwood, fourteen (14) batches of pulp shall be derived from the softwood chips (see Table 1). Batches #A1 through #A4 will be obtained by oxygen treating kraft pulp which has been processed to nominally Kappa 30, washed and screened prior to the oxygen treatment. Batches #A5 through #A10 will be kraft processed pulp. Batches #A11 through #A14 will be kraft processed pulp typical of that used for liner board.

For the Lot B softwood, eight (8) batches of pulp shall be derived from the softwood chips (see Table 2). Batches #B1 and #B2 will be obtained by oxygen treating kraft pulp which has been processed to nominally Kappa 30, washed and screened prior to oxygen treatment. Batches #A3 through #B5 will be kraft processed pulp. Batches #B6 through #B8 will be kraft processed pulp typical of that used for liner board.

For the Lot C hardwood, eight (8) batches of pulp shall be derived from the supplied hardwood chips (Table 3). Batches #C1 through #C4 will be obtained by oxygen treating kraft pulp which has been processed to nominally Kappa 20, washed and screened prior to oxygen treatment. Batches #C5 through #C8 will be kraft processed pulp.

TABLE 1

LOT A SOFTWOOD BATCHES

<i>Batch No.</i>	<i>Target KAPPA</i>	<i>Process</i>	<i>Black Liquor</i>	<i>Kraft Unscreen. Unwashed Pulp</i>	<i>Kraft Screened Washed Pulp</i>	<i>Oxygen Treated Pulp</i>
A1	12	K-O-Unbl.	n	n	n	y
A2	15	K-O-Unbl.	n	n	n	y
A3	18	K-O-Unbl.	n	n	n	y
A4	22	K-O-Unbl.	n	n	n	y
A5	20	K-Unbl.	y	y	y	n
A6	23	K-Unbl.	y	y	y	n
A7	26	K-Unbl.	y	y	y	n
A8	29	K-Unbl.	y	y	y	n
A9	32	K-Unbl.	y	y	y	n
A10	35	K-Unbl.	y	y	y	n
A11	80	K (Liner)	y	y	y	n
A12	80	K (Liner)	y	y	y	n
A13	95	K (Liner)	y	y	y	n
A14	110	K (Liner)	y	y	y	n

y = yes n = no sample K = Kraft O = Oxygen Unbl. = Unbleached

Oxygen treated pulp to start with nominal Kappa 25 - 30 screened stock (or typical plant Kappa).

Drain black liquor sample from cooked chips on removal from bomb.

Kraft, unscreened, unwashed sample not to be refined, washed or screened.

TABLE 2

LOT B SOFTWOOD BATCHES

<i>Batch No.</i>	<i>Target KAPPA</i>	<i>Process</i>	<i>Black Liquor</i>	<i>Kraft Unscreen. Unwashed Pulp</i>	<i>Kraft Screened Washed Pulp</i>	<i>Oxygen Treated Pulp</i>
<i>B1</i>	<i>12</i>	<i>K-O-Unbl.</i>	<i>n</i>	<i>n</i>	<i>n</i>	<i>y</i>
<i>B2</i>	<i>22</i>	<i>K-O-Unbl.</i>	<i>n</i>	<i>n</i>	<i>n</i>	<i>y</i>
<i>B3</i>	<i>20</i>	<i>K-Unbl.</i>	<i>y</i>	<i>y</i>	<i>y</i>	<i>n</i>
<i>B4</i>	<i>26</i>	<i>K-Unbl.</i>	<i>y</i>	<i>y</i>	<i>y</i>	<i>n</i>
<i>B5</i>	<i>35</i>	<i>K-Unbl.</i>	<i>y</i>	<i>y</i>	<i>y</i>	<i>n</i>
<i>B6</i>	<i>70</i>	<i>K (Liner)</i>	<i>y</i>	<i>y</i>	<i>y</i>	<i>n</i>
<i>B7</i>	<i>95</i>	<i>K (Liner)</i>	<i>y</i>	<i>y</i>	<i>y</i>	<i>n</i>
<i>B8</i>	<i>110</i>	<i>K (Liner)</i>	<i>y</i>	<i>y</i>	<i>y</i>	<i>n</i>

y = yes n = no sample K = Kraft O = Oxygen Unbl. = Unbleached

Oxygen treated pulp to start with nominal Kappa 25 - 30 screened stock (or typical plant Kappa).

Drain black liquor sample from cooked chips on removal from bomb.

Kraft, unscreened, unwashed sample not to be refined, washed or screened.

TABLE 3

LOT C HARDWOOD BATCHES

<i>Batch No.</i>	<i>Target KAPPA</i>	<i>Process</i>	<i>Black Liquor</i>	<i>Kraft Unscreen. Unwashed Pulp</i>	<i>Kraft Screened Washed Pulp</i>	<i>Oxygen Treated Pulp</i>
<i>C1</i>	<i>7</i>	<i>K-O-Unbl.</i>	<i>n</i>	<i>n</i>	<i>n</i>	<i>y</i>
<i>C2</i>	<i>10</i>	<i>K-O-Unbl.</i>	<i>n</i>	<i>n</i>	<i>n</i>	<i>y</i>
<i>C3</i>	<i>12</i>	<i>K-O-Unbl.</i>	<i>n</i>	<i>n</i>	<i>n</i>	<i>y</i>
<i>C4</i>	<i>15</i>	<i>K-O-Unbl.</i>	<i>n</i>	<i>n</i>	<i>n</i>	<i>y</i>
<i>C5</i>	<i>10</i>	<i>K-Unbl.</i>	<i>y</i>	<i>y</i>	<i>y</i>	<i>n</i>
<i>C6</i>	<i>14</i>	<i>K-Unbl.</i>	<i>y</i>	<i>y</i>	<i>y</i>	<i>n</i>
<i>C7</i>	<i>18</i>	<i>K-Unbl.</i>	<i>y</i>	<i>y</i>	<i>y</i>	<i>n</i>
<i>C8</i>	<i>22</i>	<i>K-Unbl.</i>	<i>y</i>	<i>y</i>	<i>y</i>	<i>n</i>

y = yes n = no sample K = Kraft O = Oxygen Unbl. = Unbleached

Oxygen treated pulp to start with nominal Kappa 20 screened stock (or typical plant Kappa).

Drain black liquor sample from cooked chips on removal from bomb.

Kraft, unscreened, unwashed sample not to be refined, washed or screened.

For Kraft cooking, the white and black liquor shall, if possible, be obtained from a pulp mill which typically processes the chosen wood species to the nominal Kappa range desired for the pulp batches. Alternatively, the following general guidelines should be used to formulate the kraft chemistry. An alkaline solution of sodium hydroxide and sodium sulfite (white liquor) shall be applied as the delignification agent. The liquor shall be 22% to 30% sulfidity and 5.4 to 6.0 lb/ft³ of effective alkali (NaOH + Na₂S) as Na₂O. Spent, or black liquor, shall be used to supplement the cooking liquor raising the liquor-to-wood ratio to between 3.5 and 4.0. This supplemental black liquor may be obtained by a separate hardwood and a softwood cook operation in another digester. Both liquors shall be blended evenly throughout the batch meeting the targeted liquor to wood and alkali-to-wood ratios. The alkali-to-wood ratio shall be adjusted for each lot, however, the liquor-to-wood ratio shall be held constant. Record in a log book the actual chemistries used or the mill supplied information if the white and black liquors are obtained from a mill.

Subsequent to filling the vessel with wood chips and liquor, the cooking process shall comprise a constant heating, or rise-to-temperature, period of sixty (60) to seventy-five (75) minutes followed by a variable cooking period at a temperature of 340°F. The cooking period and alkali-to-wood ratio shall be adjusted for each batch which simulates a specified process. Those batches within a relatively narrow range of Kappa can use the same chemistry and only vary the time. For example for the Lot A softwood, batches #A1 through #A10 can use the same initial chemistry. Batches #A11 through #A14 would use a different chemistry to obtain the higher Kappa range. The pulp discharge shall be of 10% - 12% stock consistency and 25% - 30% spent liquor solids.

5. Washing

It is desirable that the washed pulp receive at least the amount of washing normally seen at the end washer location and that the individual batches receive approximately the same degree of washing. If these two items can be accomplished through the rinsing and washing which occurs during the screening process, then no additional washing operation is necessary. If not, then the following procedure should be used to provide for consistent, well-washed pulp samples.

- 1. Drain off any free liquid from the pulp - i.e. put it in a bucket or funnel and suck off the liquid into a vacuum flask until the pulp is about 20% consistency.*
- 2. Take the 20% consistency pad and re-suspend it in water until its about 2% consistency.*
- 3. Stir thoroughly for about 5 minutes.*

4. Drain it again using the step 1 procedure.
5. Repeat steps 2, 3 and 4.

6. Disposition of Pulp and Black Liquor

Approximately 250 ml samples of the black liquor drained off the digester during each "cook" identified in Tables 1 through 3 shall be collected in glass jars with metal lids and saved for delivery to B&W. All of the black liquor obtained shall be collected and labeled to indicate the origin (e.g. the "cook", the wood species, the batch no., date, etc.).

Upon exiting the digester, the pulp samples which will not be further processed with an oxygen treatment, shall be separated into two (2) approximately equal volumes. Half shall be placed in glass jars "as is" and the other half shall be screened, washed and placed in glass jars (not plastic) before packaging. Portions of the washed and screened samples shall be removed and triplicate Kappa number testing performed. The oxygen treated batches will have already been washed and screened prior to oxygen treatment and need only be stored in jars after removal of samples for triplicate Kappa testing. All jars with the individual batches shall be labeled with the wood species, batch number, "washed-screened" or "unwashed-unscreened", "oxygen treated" or "kraft", date, "Project No. 40400" and the words "Babcock & Wilcox Pulp Samples".

7. KAPPA Number Testing

Screened and washed samples from each of the 30 batches (14 Lot A softwood, 8 Lot B softwood and 8 Lot C hardwood) shall be tested in triplicate for KAPPA number using TAPPI T 236 hm-85. The use of automatic titration equipment is acceptable. Samples of the pulp will in all probability be sent to a second lab for Kappa verification tests. The Kappa number results from the individual runs shall be tabulated and the average and standard deviation of the three runs shall be calculated and sent with the pulp samples and also presented in the final report. The pulp samples should, as a minimum, be delivered as groups of batches are completed or preferably on a weekly basis as batches are completed. The following are considered groups of batches:

- Group 1: #A1 through #A4*
- Group 2: #A5 through #A10*
- Group 3: #A11 through #A14*
- Group 4: #B1 and #B2*
- Group 5: #B3 through #B5*
- Group 6: #B6 through #B8*
- Group 7: #C1 through #C4*
- Group 8: #C5 through #8*

8. Deliverables

- 4 jars of **oxygen treated** pulp (kraft processed, washed & screened) from Lot A softwood (#A1 through #4A).
- 10 jars of **washed and screened** pulp obtained from the kraft-only processed Lot A softwood (Half of #A5 through #A14).
- 10 jars of **unwashed and unscreened** pulp obtained from the kraft-only processed Lot A softwood (Half of #A5 through #A14).
- 10 jars of black liquor from the 10 batches of kraft-only processed Lot A softwood (#A5 through #A14).
- 2 jars of **oxygen treated** pulp (kraft processed, washed & screened) from Lot B softwood (#B1 and #B2).
- 6 jars of **washed and screened** pulp obtained from the kraft-only processed Lot B softwood (Half of #B3 through #B8).
- 6 jars of **unwashed and unscreened** pulp obtained from the kraft-only processed Lot B softwood (Half of #B3 through #B8).
- 6 jars of black liquor from the 6 batches of kraft-only processed Lot b softwood (#B3 through #B8).
- 4 jars of **oxygen treated** pulp (kraft processed, washed & screened) from Lot C hardwood (#C1 through #C4).
- 4 jars of **washed and screened** pulp obtained from the kraft-only processed Lot C hardwood (Half of #C5 through #C8).
- 4 jars of **unwashed and unscreened** pulp obtained from the kraft-only processed Lot C hardwood (Half of #C5 through #C8).
- 4 jars of black liquor from the 4 batches of kraft-only processed Lot C hardwood (#C5 through #C8).
- 1 package (approx. 4 liter) of the Lot A softwood feed chips (no processing).
- 1 package (approx. 4 liter) of the Lot B softwood feed chips (no processing).
- 1 package (approx. 4 liter) of the Lot C hardwood feed chips (no processing).
- 1 report on the above process, including:
 - types of wood species used
 - the source of the wood species
 - the processing steps (cooks, chemistry, washing operation, etc.) for each batch
 - the measured KAPPA numbers for each sample including average & standard deviation)

The samples (pulp and black liquor) and the KAPPA number values for the groups of batches identified above are to be delivered as soon as possible after manufacture. The report of the process shall follow within three weeks of completion of the group of batches. After manufacture and prior to shipment of the individual batches shall be stored in a cool environment so as to prevent any degradation in the pulp samples. The

samples shall be prepared for shipment so as to prevent degradation during shipping. the samples of pulp and black liquor shall be delivered to the following address using overnight delivery and scheduled to arrive on a weekday:

***Babcock & Wilcox
Research and Development Division
1562 Beeson St.
Alliance, Ohio 44601
Attn: Garry W. Roman***

"

5.3 SUMMARY OF SAMPLES

Table 5.1 is a listing of all the samples prepared for this project.

Table 5.1 Summary of Wood Pulps

WOOD SPECIES	SAMPLE I.D.	KAPPA #	COMMENTS
Southern Pine	SP1	15.6	Kraft-Miami, Fall 1990
	SP2	21.2	
	SP3	25.6	
	SP4	31.8	
	SP5	43.1	
	SP6	49.4	
	SP7	51.0	
	SP8	58.5	
Northern Spruce	NS1	15.1	Kraft-Miami, Spring 1991
	NS2	21.8	
	NS3	24.7	
	NS4	27.7	
	NS5	33.9	
	NS6	42.9	
	NS7	47.1	
	NS8	51.0	
Red Spruce	A1	12.3	Oxygen Delig. - IPST, 1994
	A2	15.5	Oxygen Delig. - IPST, 1994
	A3	18.6	Oxygen Delig. - IPST, 1994
	A4	21.8	Oxygen Delig. - IPST, 1994
	A5	22.5	Kraft - Miami, 1993
	A6	29.3	Kraft - Miami, 1993
	A8	32.5	Kraft - Miami, 1993
	A9	36.3	Kraft - Miami, 1993
	A10	46.4	Kraft - Miami, 1993
	A11	42.5	Kraft - Miami, 1993
	A12	121.0	Kraft - Miami, 1993
	A13	139.0	Kraft - Miami, 1993
	AA1	15.7	Kraft - Miami, 1993
	AA2	18.4	Kraft - Miami, 1993
	AA3	46.2	Kraft - Miami, 1993
	AA4	49.9	Kraft - Miami, 1993
	AA5	46.7	Kraft - Miami, 1993
	AA6	50.9	Kraft - Miami, 1993
	AA7	125.0	Kraft - Miami, 1993
	AA8	8.6	Oxygen Delig. - IPST, 1994
	AA9	19.9	Oxygen Delig. - IPST, 1994
	AA10	27.4	Kraft - IPST, 1994

Table 5.1 Summary of Wood Pulps (Continued)

WOOD SPECIES	SAMPLE I.D.	KAPPA #	COMMENTS
Balsam Fir	B1	12.7	Oxygen Delig. - IPST, 1994
	B2	22.4	Oxygen Delig. - IPST, 1994
	B3	18.5	Kraft - Miami, 1993
	B4	25.4	Kraft - Miami, 1993
	B5	36.8	Kraft - Miami, 1993
	B6	76.0	Kraft - Miami, 1993
	B7	70.1	Kraft - Miami, 1993
	B8	128.0	Kraft - Miami, 1993
	BB1	50.0	Kraft - Miami, 1993
	BB2	104.0	Kraft - Miami, 1993
	BB3	29.2	Kraft - IPST, 1993
	BB4	34.4	Kraft - IPST, 1993
Birch	C1	8.1	Oxygen Delig. - IPST, 1994
	C2	9.8	Oxygen Delig. - IPST, 1994
	C3	12.2	Oxygen Delig. - IPST, 1994
	C4	13.9	Oxygen Delig. - IPST, 1994
	C5	10.5	Kraft - Miami, 1993
	C6	11.1	Kraft - Miami, 1993
	C7	16.9	Kraft - Miami, 1993
	C8	25.8	Kraft - Miami, 1993
	CC1	8.4	Oxygen delig. - IPST, 1994
	CC2	8.7	Oxygen Delig. - IPST, 1994
	CC3	12.9	Oxygen Delig. - IPST, 1994
	CC4	19.1	Kraft - IPST, 1993

The Kappa numbers listed on Table 5.1 are from the measurements made at IPST except for the northern spruce pulps which were not tested at IPST. The northern spruce values are from Miami measurements.

6.0 SPECIMEN PREPARATION AND PRESENTATION

6.0 SPECIMEN PREPARATION AND PRESENTATION

6.1 INITIAL TEST SERIES

The pulps produced for the initial test series were received in plastic zip-lock bags. They were damp but well drained with consistencies on the order of 15%. These samples were kept under refrigeration when not in use.

The procedure for sample preparation consisted of loading the pulp into standard laboratory cuvetts. Tweezers were used to pull pulp from the sample bags and stuff it into the cuvet. In preliminary tests, plastic (acrylic) cuvetts were used, but for the final tests, quartz cuvetts were used to eliminate the effect of cuvet fluorescence discussed in Section 7.8.

The wood pulp samples were inhomogeneous and damp. A natural question arose as to the optimum way to obtain a "full" cuvet, i.e., the total mass of pulp in a "full" cuvet can vary by a factor of more than three, depending on how tightly it is packed. To determine the importance of the packing density, the following experiment was run. Five cuvetts were "filled" with very loose packing and four others with very dense packing. For the dense packing, the pulp was periodically compressed and the excess liquid removed as the cuvet was being filled. After filling and allowing to equilibrate to room temperature, the fluorescence was measured with excitation on first the front and then the back surfaces. This resulted in 10 samples of the loose-packed and 8 samples of the dense packed. Table 6.1 summarizes the results of this test.

Table 6.1 Results of Cuvet Packing Tests

	Average Fluorescent Intensity	Standard Deviation
Loose Packed Samples	960	± 50
Dense Packed Samples	1022	± 42
All Samples	989	± 56

Although the results indicate that the packing density is relatively unimportant, there is a somewhat lower deviation among the dense-packed samples. In subsequent testing, therefore, the samples were compressed into the cuvetts, but not to the maximum possible density. The consistency was typically above 25%.

For measurement, the cuvet specimens were mounted to an x-y motor driven table and raster scanned during the measurement so that a significant area of the pulp surface was interrogated rather than a single spot.

The cuvet packing and scanning procedure used throughout the first test series provided relatively good repeatability as shown in Table 6.1 and discussed further in Section 7.9. However, there were a number of drawbacks that led to the development of a new procedure for the second test series, e.g.:

- there was no way to control and/or vary the consistency of the specimen,
- there was a question about how representative the small quantity of pulp pulled from the storage bags for a specimen was of the average contents of the bag,
- and finally, the cuvet loading procedure was time consuming and tedious.

6.2 SECOND TEST SERIES

6.2.1 Objectives

For the second series of tests, a new specimen preparation procedure was required to

- address the question of representative sampling of the inhomogeneous pulps,
- allow control of the specimen consistency,
- allow control of the specimen pH.

6.2.2 Inhomogeneity and Consistency

The procedure developed to deal with the "representative sampling" question and consistency control involved the following steps:

- a relatively large (140 ml) aliquot of pulp was placed in a blender along with 1 liter of liquid. In early tests, the liquid used was distilled deionized water. For later tests a solution of NaOH with a specified pH was used. Since the total volume of pulp in each sample was on the order of 1 liter, the 140 ml aliquot represented a sizeable fraction of the total.
- the pulp and liquid were mixed in the blender for one minute.
- the homogenized slurry was poured into a 5-compartment mold mounted in a Buchner funnel to remove the liquid from the pulp by vacuum assisted filtration through a 104 μ m mesh stainless steel screen.
- After the liquid was separated, the mold was removed from the funnel and disassembled to release the 5 pulp "pellets" that had been formed in the dewatering process. Each pellet was a circular cylinder with a diameter of 3/4" and length of 2".
- One of the 5 pellets was taken and used to determine the consistency usually in range 15 to 20% while the others were stored in the refrigerator in sealed glass jars to prevent loss of moisture. The consistency was measured by weighing the "test-pellet" before and after overnight drying in an oven at 96°C.

- To prepare a test specimen, a nominal 10 gm piece of one of the four remaining pellets was weighed, placed in a 1 oz wide-mouth glass jar, and brought to the desired consistency by the addition of liquid. The required amount of liquid was calculated from the weight of the pulp and the assumption that its consistency was the same as that of the "test-pellet".
- After addition of the liquid, the slurry was gently mixed and the surface manipulated using a stainless steel spatula to smooth the surface so that the depth variations were less than ± 3 mm.
- The glass specimen jars were mounted on the x-y motor-driven translation stage which was raster scanned during the fluorescence measurements. The top surface of the pulp slurry was directly illuminated through the open top of the jar from above.

This method of specimen preparation gave good repeatability of the fluorescence measurements, both total intensity and wavelength centroid, and allowed control of the consistency to $\pm 0.5\%$.

6.2.3 pH Control

As discussed in Section 3.5, the original plan to bring all of the pulp samples to the same nominal pH by soaking them in a NaOH solution prior to the fluorescence testing was abandoned as impractical. Table 6.2 summarizes the experiment undertaken to equalize the pH via NaOH soaking. The values of pH measured after each treatment are listed. The values in the first and final columns are those compared graphically in Figure 3.22.

Figure 6.1 compares the wavelength centroid response of specimens prepared from the pulps that went through the treatment outlined in Table 6.2 to that of specimens prepared from as-received pulps. Although the pH treatment clearly shifts the centroid upward, the shift is about the same for all samples. The treatment does not tend to reduce the data scatter by selectively shifting certain points. Following the test shown in Figure 6.2, the "treatment" routine was abandoned, since the treatment: 1) did not reduce the data scatter, 2) was not very successful at equalizing the pH's and 3) involved a long, time-consuming process.

In subsequent specimen preparations the blender mixing procedure described above was slightly modified in an attempt to minimize the pH variations among the various pulps. The modification was to use an NaOH solution instead of water as the liquid during the pulp homogenization process in the blender. Table 6.3 shows the extent of equalization attained with this approach for the case where the pH of the NaOH solution was 10. All of the specimens were brought to a 9% consistency.

Table 6.2 Pulp pH After Various Soaks in NaOH Solution

PULP #	INITIAL	A	B	C	C'	C''	D	E	E'	F	G
A10	5.1	6.6	6.8			11	10.5	9.8		10	9.1
AA5	5.6	6.6	6.9			11.2	10.5	9.9		10	9.2
A11	4.7	6.4	6.9			11	10.4	9.9		9.9	9.4
AA6	4.3	4.8	6			10.8	10.3	9.8		10	9.4
AA3	5.5	6.3	6.6			11	10.4	10		10.1	9.5
AA4	6.5	7.3	7.9		8.5		8.5	8.3		8.3	8.2
A9	7	7.6	8.1		8.3		8.4	8.5		8.5	8.2
AA2	7.4	7.9	8.4		8.5		8	8.4		8.5	8.3
AA1	7.7	8	8.4		8.4		8.1	8.6		8.5	8.2
A5	7.9	7.9	8.4		8.4		8.2	8.3		8.4	8.3
A6	8.1	8.4	8.7		8.8		8.4	8.6		8.6	8.2
A8	8	8.2	8.4		8.6		8.3	8.5		8.4	7.9
A12	7.7	7.8	8.3		8.5		8.4	8.6		8.5	7.8
AA7	7.9	8.3	8.3		8.6		8.4	8.7		8.6	8
A13	7.9	8.1	8.3		8.6		8.5	8.3		8.5	8
B3	8.1	8.9	9.1	9.1			9		8.8	8.9	8.8
B5	8	8.7	9	8.9			9		8.9	8.9	8.7
BB2	8	8.6	8.9	8.9			9		8.9	8.9	8.9
BB1	8.1	8.8	9	9			9.1		8.9	9	9
B4	8.1	8.8	8.9	9			8.8		8.7	8.9	8.8
B6	8.1	8.8	9	9			9.2		8.8	8.9	8.7
B7	8.2	8.8	9.1	9.1			9.1		9.1	9.2	9
B8	7.8	8.6	8.6		9.2		9		9.1	9	8.8
C5	7.8	8.4	8.8	8.6			8.6	8.9		8.8	8.2
C6	7.4	7.2	7.3		7.3		7	6.8		7	7.3
C7	7.6	8.1	8.4		8.4		8.1	8		8.1	7.6
C8	7.6	7.9	8.1		8.3		8.1	8.2		8.2	8.4

INITIAL : The pH measured in the as received state. 140 ml sample

A : Added 140 ml of pH 10 NaOH solution to the 140 ml pulp sample and soaked overnight

B : Added 140 ml of pH 10 NaOH solution to the jars and allowed to soak for two hours

C : No change made to samples

C' : Added an additional 140 ml of pH 10 solution to samples

C'' : Added an additional 140 ml of pH 12 solution to samples

D : Drained the solution (added above) from the pulp samples and then added 750 ml of pH 9 solution and allowed to set over the weekend

E : Drained the liquid, rinsed with distilled water and then added 750 ml pH 9 NaOH

E' : No change made to samples

F : No change made to samples. Readings made after sitting overnight

G : Drained, refilled with pH 9 solution, and soaked for two hours. Repeated three times

EFFECT OF pH TREATMENT ON CENTROID RED SPRUCE SAMPLES (10/21 & 10/27/93)

EFFECT OF pH TREATMENT ON CENTROID BALSAM FIR SAMPLES (10/21 & 10/27/93)

Figure 6.1 Effect of pH Treatment of Wavelength Centroid

Table 6.3 pH of Specimens Prepared by Blending in pH=10 NaOH Solution

Pulp #	Specimen pH (measured 3/24/93)
AA1	6.76
A5	7.72
AA5	6.64
A12	7.59
AA8	8.39
A2	8.22
A4	8.18
AA10	8.1
B1	8.19
B8	7.54
BB3	7.93
B2	8.4
B3	8.08
C1	8.77
C6	6.8
C3	8.19
C8	7.37
CC4	8.03
SP1	8.33
SP8	8.1
NP1	8.19
NP8	8.22

7.0 APPARATUS

7.0 APPARATUS

7.1 SYSTEM OVERVIEW

Figure 7-1 is a block diagram showing the major components of the fluorescence spectroscopy system used in the laboratory test program.

A Laser Science, Inc., Model VSL-337 pulsed nitrogen laser is used to either directly excite the fluorescence in the wood pulp, or to optically pump a tunable dye laser (Laser Science, Inc. Model DLM-120) which is then used to excite the fluorescence. The nitrogen laser provides peak power of 40 kilowatts with a pulse width of 3 nsec, and pulse rate from 1 to 20 pulses per second at a wavelength of 337 nm. The dye laser provides output at any wavelength from the near UV through the visible spectrum. The power level of the dye-laser output is reduced by a factor of 4 to 20 from the nitrogen laser depending on the wavelength of operation.

The collection/excitation optics consists of a set of lenses and mirrors that:

- focus the laser beam to a small spot on the sample. During the first series of tests, the spot size was less than 1 mm. For the second series, it was expanded to 5 mm diameter.
- focus the resultant fluorescent light onto a long fiber optic bundle, FB1, that delivers it to the monochromator.
- focus a portion of the original laser light onto an optical fiber, FB2, that delivers it to the gate pulse generator as a trigger signal.

The pulp specimen is mounted on an X-Y-Z translation stage. The Z-axis is manually adjusted to put the sample surface at the focus of the laser. The X and Y axes are stepper-motor driven to provide a raster scan of the pulp surface during data acquisition.

The function of the gate pulse generator (Princeton Instruments Model FG-100) is to provide a voltage pulse that rapidly turns the detector on and off. The detector is turned on for the duration of the gate pulse which can be varied from 5 nsec to 2000 nsec. The beginning of the gate pulse can be varied from about 25 nsec to 1700 nsec after the arrival of the trigger pulse to the gate pulse generator from the laser light through fiber FB2. The ability to turn the detector on and off in sync with the pulsing of the laser provides a very high degree of discrimination against background light. For example, if the laser is pulsed once per second and the detector is turned on for only 10 nsec, it will only "see" $10^{-8}B$, where B is the intensity of the constant background light. As a result, it is possible to perform all measurements with room lights on and no detectable interference. In addition to background light rejection, the gating provides the means to obtain time-resolved data.

The oscilloscope is used to monitor the time delay (at sub-nanosecond resolution) between the laser firing and the detector gating. It enables the time delay to be adjusted precisely for experiments employing "time-resolved fluorescence".

Figure 7.1 Block Diagram of Fluorescence Spectroscopy System

The function of the monochromator is to spread the incoming fluorescent light into a spectrum and focus that spectrum onto the 700 individual elements of the detector array such that each detector element receives light of a different wavelength. The detector array actually contains 1024 elements, but only the center 700 are used due to size limitations of the intensifier stage.

The detector (Princeton Instruments Model IRY-690G/B/PAR) consists of a thermoelectrically cooled array of silicon photodiodes equipped with an image intensifier (microchannel plate). The intensifier provides the gating capability as well as very high sensitivity.

The detector controller (Princeton Instruments Model ST120) provides periodic readout of the detector under software control through a 386 computer. The readout of the detector array is synchronized with the laser pulses via a readout pulse that is derived from the gate pulse. Readout consists of:

- performing an A/D conversion of the signal from each of the 1024 individual elements of the detector array.
- storing the results of the conversions to the computer's hard disk.
- resetting the photodiodes for the next reading.

The computer provides:

- operator interface
- storage of results
- real-time display of the results
- post-test display and analysis of the results.

7.2 SYSTEM TIMING

As discussed above, the laser, detector gating, and readout are all synchronized. Figure 7-2 shows the timing involved. The 3 nsec laser pulse is the reference event.

The fluorescent signal begins a few nsec after the beginning of the laser pulse (the time required for the light to travel from the laser to the sample) and rises very quickly to a peak that coincides with the arrival of the end of the laser pulse. The fluorescence then decays over a period of less than 200 nsec.

There is a delay of roughly 35 nsec between the start of the laser pulse and the time when the gate pulse arrives at the detector. Part of this delay is due to the time required for the trigger pulse to travel to the gate pulse generator but most of it is due to inherent speed-of-response limitations in the electronic circuitry of the gate pulse generator itself. Note that this delay means that, unless special provisions are taken, the detector will not be turned on until after the bulk of the fluorescent light has been emitted.

Figure 7.2 Timing Diagram

To circumvent this problem, the fiber optic bundle, FB1, used to carry the light to the monochromator, was selected to be 10 meters long. The transit time through the bundle is approximately 50 nsec and the light arrives on the detector after the gate pulse has turned on the detector. The combination of the FG100 gate pulse generator and the IRY microchannel plate allows "gate on" or "gate off" speeds of approximately 7 ns.

7.3 DATA ACQUISITION PARAMETERS

The detector readout trigger, which is generated by the transition at the end of the gate pulse, triggers a read and reset of the detectors. A readout of the detector array occurs, therefore, for each pulse of the laser. During setup of the equipment, via the software running on the computer, the user can specify that several readouts be automatically added together to produce a final result which is then saved as a spectrum. This accumulation improves the signal-to-noise ratio in the resultant spectrum by roughly the square root of the number of pulses accumulated. Another feature of the setup software is the ability to specify that a given number of consecutive spectra be recorded, each consisting of the addition (accumulation) of multiple pulses. One can, for example, set an experiment where 100 spectra are recorded, each one being the result of 50 laser pulses.

For the majority of the tests, the system was set to accumulate the results of 90 to 100 laser shots to provide a single spectrum. The only data obtained with different setup parameters was taken to determine the extent to which the pulp samples are sensitive to bleaching. In the bleaching tests, the sample was held stationary, the accumulation was set to 10, and 10 spectra were recorded. Data recording was, however, not continuous. Each spectra was recorded 1000 pulses after the preceeding one, giving data over a 10,000 pulse exposure. These bleaching tests provided a measurement of the drop in fluorescence intensity as a function of successive laser pulses.

7.4 ELECTRONICS

Figure 7-3 shows the interconnection of the electronic system. Fiber, FB2, delivers a trigger pulse from the laser into the optical trigger input on the back of the FB-100 gate pulse generator. The gate pulse to the detector is taken from the output labeled VARIABLE. None of the other back panel connectors are used in the present mode of operation. The front panel connector labeled INPUT is intended for the input of an electronic trigger signal. Because it is internally connected to the signal generated by the optical trigger input, it is used to monitor the arrival of the optical trigger through the front panel "INPUT" connector. This signal is displayed on channel 1 of the high-speed oscilloscope (Hewlett Packard Model 54510A) and the gate pulse is monitored on channel 2 using the PULSE MONITOR output on the front of the FG-100.

Displaying the laser pulse and the gate pulse on the oscilloscope allows quantitative determination of the pulse delay and pulse width, both of which are adjustable by the use of 10 turn potentiometers on the front panel of the FG-100. The third potentiometer labeled REP RATE is used to set the frequency of an internally generated trigger signal which is not used in the present mode of operation. For the testing reported here, the internal trigger on the laser was used (adjustable from 1-20 pulses/second).

Figure 7.3 Interconnection of Electronics

The signal from the pulse monitor output is split and used, not only for the scope display, but also to generate the readout trigger pulse which is connected to the EXT-SYNC port on the back of the ST-120 controller.

7.5 OPTICS

7.5.1 Initial Test Series

Figure 7-4 shows the layout of the optical system used for this first series of tests. The specimens (samples) were contained within standard 10 mm cuvetts which mount on a precision X,Y,Z translation stage. During a standard 100 pulse data run, the laser was pulsed at a rate of 2 pulses/sec and the stepper motors provided a raster scan of the cuvet at a rate of 2 mm/sec. The focused laser spot is less than 1 mm in diameter, so each pulse hit the pulp at a previously unexposed point. This provided two important functions. First, it assured that the resultant data was independent of bleaching effects. Second, it distributed the exposure over an extended area to minimize the effect of localized variations in the pulp properties.

Both acrylic and quartz cuvetts were employed to hold pulp specimens during fluorescence tests. The quartz cuvetts were more uniform and had much less background fluorescence than the acrylic cuvetts. Throw-away acrylic cuvetts were used extensively during early testing for convenience in testing large numbers of samples. Since the acrylic cuvetts did introduce some aliasing and data scatter (see Section 7.8), the most critical tests were repeated using only quartz cuvetts.

The fluorescence delivery bundle, FB1, consists of seven fibers each with a 365 micron core diameter. At the pick-up end, they are arranged in a circular pattern approximately 1.2 mm in diameter which is the same as the nominal diameter of the spot to which the fluorescent light is focused by the spherical mirror, M4. At the output end of the bundle, the seven fibers are aligned in a single file row to provide a good geometrical match to the entrance slit of the monochromator. A set of relay lenses focuses an image of the 1x7 fiber array onto the monochromator's entrance slit. The monochromator's entrance slit is continuously adjustable and was not necessarily set to the same opening each time a set of tests were conducted. Therefore, comparison of absolute values of fluorescence intensity from one test period to another may not be valid.

The laser beam, which exits the laser with a rectangular cross sectional area ($\approx 2 \times 8$ mm), is diverged by lens L1, and then focused by lens L2 to a spot on the specimen less than 1 mm in either dimension. The absorbance of the pulp sample is high, so the laser beam is essentially absorbed at the pulp surface.

The fluorescent light is focused by the spherical mirror onto the end of the fiber bundle FB1 with a slight ($\approx 1.2X$) magnification. A 380 nm long pass filter, F, just in front of FB1 absorbs most of the scattered 337 nm laser light to prevent it from entering the fiber where it could produce noise fluorescence in the fiber material and scatter in the monochromator.

Figure 7.4 Optical System Layout

The beam splitter, BS, reflects about 8% of the laser beam towards lens L3 which focuses it onto the end of the trigger fiber FB2.

All of the components, with the exception of the monochromator and detector, shown in Figure 7-4 are attached firmly to an optical breadboard.

7.5.2 Second Test Series

For the second series of tests, a new method of specimen preparation was required both to reduce the time required and, more importantly, to allow the preparation of specimens with controlled consistencies. As discussed in Section 6.0, the specimen preparation technique adopted for use throughout all of the second series tests involved placing the pulp in a glass jar and illuminating it from above through the open top.

The new specimens created the need to consider the depth-of-field of the optical system. In the initial test series the cuvet specimens were always located at the laser focus with the cuvet face perpendicular to the incident beam. There was never any variation of the axial position of the specimen, so depth of field was not an issue. With the new specimens, however, the axial position of the illuminated surface could vary either due to differences in the amount of specimen material or due to surface irregularities.

The optical system was modified as shown in Figure 7.5 in order to provide a large depth of field to accommodate these variations. In addition to solving the problem of field depth, the new optical setup has the advantage of closely simulating the design envisioned for the field prototype.

The new optics incorporates three significant changes:

- the numerical aperture of collection is reduced from .17 to .035. This provides the desired depth of field. Although it reduces the signal level by more than 20X, there is still abundant signal to work with.
- Rather than focus the collected light directly on the end of the seven fiber collection bundle there is an intermediate section of large diameter acrylic fiber. Changes in the axial distance from the pulp surface to the collection mirror result in a small lateral shift of the image of the laser spot focused onto the pick-up fiber. A ± 10 mm difference in axial distance results in a ± 2 mm lateral shift. Since the image of the laser spot is about 1.1 mm diameter, the entire spot stays within the core of the 1.5 mm diameter pick-up section as shown in Figure 7.6A. The spatial distribution of the light is "scrambled" as it passes through the acrylic fiber so that the portion coupled into the seven fiber bundle is independent of the position at the entrance. Compare this to the case where the laser spot is focused directly onto the seven fiber bundle as shown in Figure 7.6B. In this case, the coupling efficiency is very dependent on lateral movement of the image.

Figure 7.5 Top View of Excitation/Collection Optics Used After November, 1992

- The size of the incident beam is increased. The two lenses expand the beam diameter and a circular aperture passes a collimated beam 5 mm in diameter. This change was adopted in response to an observation made in the course of testing to evaluate the depth-of-field. A section of manila file folder was being used as a fluorescence generating target and it was found that the fluorescence was not linearly related to the laser intensity. Figure 7.7 shows the response as a function of laser beam intensity. The roll-off at high intensity was hypothesized to be due to a saturation effect, e.g., the photon density becoming comparable to the number of available fluorescing molecules. To confirm this hypothesis, the laser spot size was increased providing a reduction of the photon density by more than a factor of 25. As shown in Figure 7-8, the response with this lower photon density is linear.

What effects the non-linear effect might have on the wavelength centroid is unknown. The comparison shown in Figure 3.2 between the response function measured with the old setup and with the new suggests no problem. Nonetheless, the 5 mm spot size was adopted to avoid any potential complications. Side benefits of the large diameter are: an increase of more than 4X in the total fluorescence and a slower rate of "bleaching".

To evaluate the performance of the new excitation/collection optics, a manila folder target was set on the xyz translation stage and the axial position (z) varied over a range of 20 mm. Figure 7.9 shows the measured total fluorescence, F, as a function of axial position. In the majority of subsequent pulp tests the axial position varied less than ± 5 mm which can be seen to effect the measured F by less than 5%. In some experiments the axial position varied by as much as ± 10 mm for which the effect on F is still less than 15%. Of course, the effect of axial position on the wavelength centroid is the question of primary importance. Figure 7.10 shows the centroid variation for the same experiment. Although there is a gradual upward drift of the centroid with time, there is no measurable dependence on axial position. The shift upward is due to the continued exposure of the same point on the target. The diffuse reflectance of the laser beam plotted in Figure 7.11 gives additional evidence that the exposure physically changes the target with time. the entire test resulted in exposing the target to approximately 5000 laser pulses. Over this period, the fluorescence decreased by about 1.5%, the reflectance increased by 8% and the centroid shifted by 1.4 nm.

7.6 REFLECTION TESTS

Not shown in Figures 7-1 or 7-4 are a pair of He-Ne lasers (one with output at 633 nm and the other at 543 nm) and their associated beam steering optics that were used in the series of diffuse reflection tests. In these tests both lasers were focused simultaneously to a spot about 1 mm in diameter that coincided at the sample surface with the position of the fluorescence excitation laser spot. The scattered (diffusely reflected) light was collected and input to the monochromator/detector with the same optical collection system used for the fluorescence tests.

Figure 7.6 Laser Spot Capture Efficiency With and Without Acrylic Scambler

Figure 7.7 Nonlinear Fluorescence Response

Figure 7.8 Response Linearity

FIGURE 7.9
FLUORESCENCE AS A FUNCTION OF AXIAL POSITION - DEPTH OF FIELD

FIGURE 7.10
WAVELENGTH CENTROID VS. AXIAL POSITION

FIGURE 7.11
DIFFUSE REFLECTANCE AS A FUNCTION OF AXIAL POSITION

7.7 PHASE-RESOLVED FLUORESCENCE

The phase-resolved fluorescence tests were conducted at Duke University, Department of Chemistry, using an SLM-48000 system and a Liconix model 4240 NB HeCd CW laser with 15 mW of power at 325 nm. A front surface adapter was employed. All phase-resolved testing was conducted with quartz cuvetts.

7.8 FLUORESCENCE OF EMPTY CUVETS

Figure 7-12 shows the fluorescence intensity spectra for a typical empty quartz cuvet and a typical acrylic (Fisher brand) cuvet. The empty quartz cuvet intensity is not appreciably higher than the detector background signal, while the empty acrylic cuvet has a peak intensity of approximately 6000 counts. This compares to the peak intensity of 130,000 counts for an acrylic cuvet filled with southern pine sample #1, as shown in see Figure 7.13 (note that both the empty cuvetts and the pulp filled cuvetts were tested at the same conditions; e.g. number of laser pulses per spectra, entrance slit opening, etc.). The empty cuvet fluorescence spectra depicted in Figure 7.12 is typical of the majority of all cuvetts used. Many hundreds of acrylic cuvetts were used in the course of the test program and approximately 30 empty cuvetts were tested at random during the course of the program. Until August of 1991, all empty cuvetts tested displayed fluorescence spectra nearly identical to that shown in Figure 7.12. In August 1991, during a pH test series, tests on six empty acrylic cuvetts from a cuvet carton of 50 were tested. The results of these tests are presented in Figure 7.14. As can be seen, three of the cuvetts produced spectra nearly identical to that shown on Figure 7.12, while the others displayed significantly different spectra (significantly higher in intensity and shape). The pH testing had already been completed on acrylic filled cuvetts and was not repeated. The peak intensity from the "worst" empty cuvet in Figure 7.14 is approximately 37,000 counts. This is a significant portion of the 130,000 counts for southern pine pulp sample #1 and approaches the intensity of southern pine sample #8. Although the pH tests already completed were not repeated, subsequent testing was conducted in quartz cuvetts.

7.9 SYSTEM PERFORMANCE

7.9.1 Summary

The procedures and apparatus developed for the tests reported here provided true characterization of the pulp fluorescence properties free of instrumental artifacts. Specifically:

- The apparatus exhibited repeatability on the order of $\pm 5\%$ as discussed in Section 7.9.2.
- The procedure for scanning the excitation beam over an extended area of the sample surface provided good representative sampling. This was evidenced by the fact, shown in Figure 3.1, that the measurements taken by exposing the front surface of the sample cuvet matched those from back surface exposure within about 5%.

Figure 7.12 Typical Fluorescence From Quartz and Acrylic Cuvets

Figure 7.13 Fluorescence of S. Pine Sample #1 in Acrylic Cuvet

Figure 7.14 Fluorescence of Six Different Empty Acrylic Cuvets

- The pulp samples were subject to bleaching such that the total fluorescence decreased about 0.1%/laser pulse. Since the testing procedure insured that no spot would receive more than two laser pulses the effect of bleaching on the reported data is negligible.
- The total fluorescence from the quartz cuvetts used to hold the samples was negligible, being less than 0.3% of the fluorescence from the pulp samples. In the second series tests, the specimens were illuminated directly, i.e., no intervening window material that could add to the observed fluorescence.
- The fluorescence properties of the pulp samples remained stable over a three-year period of refrigerated storage as discussed in Section 7.9.3.
- The main factors limiting the accuracy and repeatability of the results reported here are the pH of the specimens (see Section 9.1) and the true Kappa numbers of the pulps (see Section 3.7).

7.9.2 Apparatus Stability

The data from the initial test series presented in Section 3.0 was all taken during a series of tests run 10/31/91 through 11/1/91. Table 7.1 shows the analysis file from those tests dealing with fluorescence excitation at 337 nm. A similar set of files were generated for excitation at 442 nm and 488 nm. In addition, there were a series of files dealing with the measurement of diffuse reflection. To insure that the system sensitivity was stable throughout the series of tests, a number of "standards" were measured periodically throughout the tests. The standards were:

- an NSG Precision Cells plastic cuvet filled with distilled-deionized water. Designated as Code H.
- a Fisher Scientific plastic cuvet filled with distilled-deionized water. Designated as Code F.
- the face of the aluminum mounting block used to hold the cuvet on the translation table. Designated as Code A.

The results of the measurements on the Standards are shown in Figures 7.15A and 7.15B. It can be seen that the readings all are repeatable within $\pm 5\%$ with the exception of the third and fourth readings on the Code F (Fisher acrylic) standard. The reason for these high readings is unexplained but appears to be some artifact rather than a real response change, since the Code A (aluminum) and Code H (NSG plastic) readings do not show the change. The sequence of readings was:

High	F(3) @ 49 minutes elapsed
Normal	H(3) @ 50 minutes elapsed
Normal	A(2) @ 54 minutes elapsed
High	F(4) @ 121 minutes elapsed
Normal	H(4) @ 122 minutes elapsed

The fact that the H and A readings taken between the two high F readings were normal, strongly suggests that the change was related just to the Code F standard rather than the system.

Table 7.1 Analysis File from 10/31/91 Test of 337 nm Excitation

FILE TIMERS.WK1 ON DISK 103191-02 TIME RESOLVED FLUORESCENCE ON S. PINE AND N. PINE EXCITATION - 337 NM ALL PULP SAMPLE IN QUARTZ CUVETS													
FILE NAME	M O N T H	D A Y	H O U R	M I N U T E S	S P E C I E S	S A M P L E	S U F F I X	S C E N T R O I D OF DIODES	PEAK INTENSITY BETWEEN DIODES	A1 AREA BETWEEN DIODES 25-140	A2 AREA BETWEEN DIODES 173-708	A3 AREA BETWEEN DIODES 300-320	A4 AREA BETWEEN DIODES 732-772
AFIA00	10	31	14	38	SP	FF	1 00	370.6	543263	20922	1 1E+08	11090198	395460
AFIB00	10	31	14	40	SP	FF	1 00	373.7	353379	11505	72881067	7215069	287984
AFIC00	10	31	14	41	SP	FF	3 00	379.6	266846	77748	575033628	5504359	273201
AFID00	10	31	14	42	SP	FF	4 00	386.3	270520	8279	61844368	5602096	325298
AFIE00	10	31	14	43	SP	FF	5 00	390.3	265368	8626	61628545	5483022	372380
AFIF00	10	31	14	44	SP	FF	6 00	393.2	183996	4628	44105776	3828327	285569
AFIG00	10	31	14	46	SP	FF	7 00	395.5	166320	3108	40152830	3438784	276579
AFIH00	10	31	14	47	SP	FF	8 00	398.4	159214	3243	39861918	3316134	282375
ABIA00	10	31	14	59	SP	B	1 00	370.1	533598	20431	1 1E+08	10832518	387290
ABIB00	10	31	15	0	SP	B	2 00	374.6	243415	10079	71796857	7056447	294562
ABIC00	10	31	15	1	SP	B	3 00	379.9	251312	6970	52725334	5182744	263528
ABID00	10	31	15	3	SP	B	4 00	387	260656	8175	59552946	5387090	319380
ABIE00	10	31	15	4	SP	B	5 00	390.4	260604	8141	60793396	5400099	371093
ABIF00	10	31	15	5	SP	B	6 00	393.1	174027	3492	41593733	3608935	270151
ABIG00	10	31	15	6	SP	B	7 00	395.9	168405	3713	40774474	3478950	288812
ABIH00	10	31	15	7	SP	B	8 00	398.5	156223	3145	38946924	3239757	276183
AFIA06	10	31	15	55	SP	FF	1 06	369.5	73995	-2638	15275814	1511750	36624
AFIB06	10	31	15	56	SP	FF	2 06	371.8	40701	-3733	8524582	828089	18903
AFIC06	10	31	15	57	SP	FF	3 06	375.1	32078	-4841	6868947	657925	15880
AFID06	10	31	15	58	SP	FF	4 06	380.1	28731	-4707	6426870	587212	15976
AFIE06	10	31	15	59	SP	FF	5 06	382.3	26282	-5232	5957408	540359	15364
AFIF06	10	31	16	0	SP	FF	6 06	382.3	17036	-5220	3904177	350992	9816
AFIG06	10	31	16	1	SP	FF	7 06	382.3	14653	-6200	3348782	350964	8401
AFIH06	10	31	16	2	SP	FF	8 06	385.1	13227	-5871	3077718	272319	7690
ABIA06	10	31	15	27	SP	B	1 06	369	72368	-2776	14952999	1483405	33184
ABIB06	10	31	15	28	SP	B	2 06	372.8	43763	-4325	9218638	892962	22160
ABIC06	10	31	15	29	SP	B	3 06	374.8	29992	-5240	6437097	617224	15231
ABID06	10	31	15	31	SP	B	4 06	380.5	27149	-7596	6132194	560543	15129
ABIE06	10	31	15	32	SP	B	5 06	381.7	27455	-4498	6225143	563599	17265
ABIF06	10	31	15	43	SP	B	6 06	381.7	14896	-5450	3355327	305766	8797
ABIG06	10	31	15	43	SP	B	7 06	383.3	10644	-3855	2409872	214978	6218
ABIH06	10	31	15	44	SP	B	8 06	384.5	13807	-5476	3250253	286379	8438
AFIA12A10	10	31	16	41	SP	FF	12 A	385	13335	-7775	3009316	274748	6184
AFIB12A10	10	31	16	42	SP	FF	12 A	387	7925	-6799	1800104	161990	1827
AFIC12A10	10	31	16	43	SP	FF	12 A	389.7	5628	-6841	1262870	110111	1058
AFID12A10	10	31	16	44	SP	FF	12 A	394.7	4795	-7939	1150976	94051	1147
AFIE12	10	31	16	45	SP	FF	12 A	397	4601	-7672	1103519	90089	1292
AFIF12	10	31	16	46	SP	FF	12 A	396	2989	-7357	701647	56948	-440
AFIG12	10	31	16	47	SP	FF	12 A	396.6	2376	-7546	575042	46028	-1176
AFIH12	10	31	16	48	SP	FF	12 A	395.7	2365	-7718	557536	44661	-699
ABIA12	10	31	17	0	SP	B	12	384.7	13157	-6573	2937534	271671	4752
ABIB12	10	31	17	1	SP	B	2 12	386.5	5086	-6459	1713778	153975	2484
ABIC12	10	31	17	2	SP	B	3 12	389.1	5000	-7617	1170263	101891	235
ABID12	10	31	17	4	SP	B	4 12	396.4	4833	-6299	1175430	95183	922
ABIE12	10	31	17	5	SP	B	5 12	398.8	4390	-6593	1102005	88112	905
ABIF12	10	31	17	6	SP	B	6 12	398.9	2835	-7034	165780	547138	-719
ABIG12	10	31	17	7	SP	B	7 12	397.6	2542	-6471	594205	47136	-668
ABIH12	10	31	17	8	SP	B	8 12	390.7	2728	-6329	660604	53508	-839

Table 7.1 Analysis File from 10/31/91 Test of 337 nm Excitation (Continued)

FILE NAME	M O N T H	D A Y	H O U R	M I N U T E S	S P E C I E S	S U R F A C E	S A M P L E	S U R F A C E	S U P P L Y	C E N T R O I D OF DIODES 173-708	PEAK I N T E N S I T Y B E T W E E N 173-708	A1 AREA BETWEEN DIODES 25-140	A2 AREA BETWEEN DIODES 173-708	A3 AREA BETWEEN DIODES 300-320	A4 AREA BETWEEN DIODES 732-772
AF1I00	10	31	14	48	NP	FF	1	00	00	369.3	719902	28919	1.4E+08	14763113	471372
AF1J00	10	31	14	49	NP	FF	2	00	00	375.4	502742	19039	1.1E+08	10310074	415642
AF1K00	10	31	14	51	NP	FF	3	00	00	376.6	531620	20061	1.1E+08	10917733	464229
AF1L00	10	31	14	52	NP	FF	4	00	00	378.2	461525	17189	73560103	9538776	435967
AF1M00	10	31	14	53	NP	FF	5	00	00	383.8	334777	10837	73560103	6886078	371253
AF1N00	10	31	14	54	NP	FF	6	00	00	387.7	354172	13035	80020035	7387919	437370
AF1O00	10	31	14	55	NP	FF	7	00	00	388.4	333298	11885	75869801	6894515	427914
AF1P00	10	31	14	56	NP	FF	8	00	00	390.4	317833	10922	73775737	6602568	438481
AB1I00	10	31	15	8	NP	B	1	00	00	369.1	684227	26871	1.4E+08	14004796	440709
AB1J00	10	31	15	9	NP	B	2	00	00	374.3	460429	16885	95476782	9445445	361008
AB1K00	10	31	15	10	NP	B	3	00	00	376.7	472847	17935	92425455	8741677	421896
AB1L00	10	31	15	11	NP	B	4	00	00	379.8	396973	13876	95089721	8151079	390208
AB1M00	10	31	15	12	NP	B	5	00	00	383.1	297812	9572	65892283	6147013	342114
AB1N00	10	31	15	13	NP	B	6	00	00	387.6	301577	10017	68337249	6243072	378980
AB1O00	10	31	15	14	NP	B	7	00	00	388.9	299055	10445	68570017	6196664	396336
AB1P00	10	31	15	15	NP	B	8	00	00	390.9	281860	9201	65957638	5865696	398279
AF1I06	10	31	16	4	NP	FF	1	06	06	370	91070	-1509	18801778	1866854	41008
AF1J06	10	31	16	5	NP	FF	2	06	06	373.9	55852	-3317	11880742	1135571	27346
AF1K06	10	31	16	6	NP	FF	3	06	06	375.5	58493	-3317	12637662	12015914	30314
AF1L06	10	31	16	7	NP	FF	4	06	06	378.4	47715	-4440	10340329	682171	25325
AF1M06	10	31	16	8	NP	FF	5	06	06	380.7	333625	-5128	74032367	68517	17888
AF1N06	10	31	16	9	NP	FF	6	06	06	382.6	300610	-5562	75592247	690434	21099
AF1O06	10	31	16	10	NP	FF	7	06	06	382.8	26510	-5473	67796329	618058	18730
AF1P06	10	31	16	11	NP	FF	8	06	06	382.8	26510	-5473	67796329	548488	16664
AB1I06	10	31	15	46	NP	B	1	06	06	369.4	94922	-1723	19502135	1942889	41762
AB1J06	10	31	15	47	NP	B	2	06	06	373.1	61020	-3126	13003840	1246264	29422
AB1K06	10	31	15	48	NP	B	3	06	06	375.7	57915	-3275	12491152	1189984	30511
AB1L06	10	31	15	49	NP	B	4	06	06	376.8	45118	-4222	9864905	930078	24296
AB1M06	10	31	15	50	NP	B	5	06	06	378.6	32736	-4407	7284905	675254	17204
AB1N06	10	31	15	51	NP	B	6	06	06	381.7	30365	-4932	76849725	622226	17754
AB1O06	10	31	15	52	NP	B	7	06	06	381.7	29420	-4262	6643471	603258	16494
AB1P06	10	31	15	53	NP	B	8	06	06	383.4	27458	-4401	6240522	561880	17277
AF1I12	10	31	16	49	NP	FF	1	12	12	384.7	16471	-6032	3658731	335023	7255
AF1J12	10	31	16	50	NP	FF	2	12	12	390.1	9253	-6362	2209836	190155	4336
AF1K12	10	31	16	51	NP	FF	3	12	12	391.1	10101	-6542	2373117	199980	4370
AF1L12	10	31	16	52	NP	FF	4	12	12	393.1	7805	-6854	1862947	1562774	3390
AF1M12	10	31	16	53	NP	FF	5	12	12	394.8	5439	-6634	1314661	108784	1512
AF1N12	10	31	16	54	NP	FF	6	12	12	397.6	5107	-6807	1291107	103250	2291
AF1O12	10	31	16	55	NP	FF	7	12	12	398.8	4916	-6627	1198309	97334	1479
AF1P12	10	31	16	56	NP	FF	8	12	12	399.1	4484	-7018	1112016	88211	1518
AB1I12	10	31	17	9	NP	B	1	12	12	384.7	17015	-6038	3768469	347070	7438
AB1J12	10	31	17	10	NP	B	2	12	12	389.5	9627	-6148	2294613	197094	3675
AB1K12	10	31	17	11	NP	B	3	12	12	391.5	10012	-6744	2352064	202373	4913
AB1L12	10	31	17	12	NP	B	4	12	12	392.8	7641	-6402	1840467	154482	3258
AB1M12	10	31	17	13	NP	B	5	12	12	394.6	5296	-6710	1293203	106907	1320
AB1N12	10	31	17	14	NP	B	6	12	12	397.7	5084	-6234	1243682	99038	1371
AB1O12	10	31	17	15	NP	B	7	12	12	398.3	4830	-6390	1213271	97038	1792
AB1P12	10	31	17	16	NP	B	8	12	12	400.1	4508	-6654	1107496	86143	1306

INTEGR. INTENSITY OVER DIODES 173-708

Figure 7.15A Fluorescence of Standards During Test Program on 10/31/91 and 11/01/91 - 337 nm Excitation

Figure 7.15B Fluorescence of Standards During Test Program on 11/01/91 - Excitation at 42 nm

In May 1991, a series of tests were conducted on eight southern pine samples in acrylic cuvetts at various time delays ranging from -6 ns to 12 ns (note -6 ns is essentially the same as 0 ns). the time delay of -6 ns was executed twice and the 0 ns was executed once. These tests were carried out over a period of seven hours, thus providing an opportunity to observe the repeatability of the laboratory setup on pulp fluorescence over three trials. Each trial was executed on the front face of the cuvetts as well as the back face of the cuvetts, which constitutes two separate specimens for each sample. All tests were conducted at an excitation wavelength of 337 nm.

The sequence of the tests is presented in Table 7.2 and the results are plotted in Figure 7.16. Figure 7.16 contains the results of all six trials (three on the front face and three on the back face). The maximum difference between any two trials is 10.8 % ($\pm 5.2\%$) and occurs for sample number 2 (KAPPA = 21). For all other samples the error is less than $\pm 3\%$.

7.9.3 Pulp Stability - Storage

All pulp samples were stored in a refrigerator when not in use. The earliest sample set has been kept for over four years. There is no evidence of deterioration or "growth" on any of the sample pulps. The comparison of measurements made on the southern pine sample set in initial and second test series as shown earlier in Figure 3.2 suggests that the fluorescence characteristics also remain stable over extended periods of storage.

Directly comparable test results are presented in Figure 7.17. The two data sets were both taken with the same setup of the apparatus (initial test series configuration) but were obtained 5 months apart. It can be seen that the general response is quite similar, indicating good long-term stability of the samples. Also, the repeatability from sample to sample with the same Kappa number is very good. The y-axis of Figure 7.17 is normalized to allow comparison. The absolute intensities of the two test series are approximately 30% different owing to differences in the test setup (e.g., monochromator slit opening and optical alignment efficiency).

7.9.4 Pulp Stability - Illumination

When the laser is allowed to continually irradiate the same spot on the pulp sample, the fluorescence intensity decreases and the spectral distribution drifts toward the red due to photochemical bleaching. Figure 7.18 shows the results of an experiment where a fixed spot on the pulp sample received 10^4 laser pulses. The spectra in Figure 7.18 were taken at intervals of 1000 pulses. The total fluorescence intensity drops by 27% from the first spectrum to the second which, if the drop were linear with exposure, would indicate a bleaching effect of .027%/pulse. The effect is in fact not linear with exposure. The percentage of decrease in fluorescent intensity is less for each successive curve. The effect during the first few pulses is, therefore, more than .027% which is the average over the first 1000 pulses. The rate of change of the bleaching effect with total exposure seen in the Figure 7.18 data suggests that the initial bleaching rate may be as high as 0.1%/pulse.

Table 7.2 Sequence Testing on 5/29/9

TRIAL	SAMPLE	CUVET FACE	TIME.... (HR) (MIN)	TRIAL	SAMPLE	CUVET FACE	TIME.... (HR) (MIN)
1	2	F	9 25	1	2	B	14 31
1	5	F	9 29	1	5	B	14 33
1	1	F	9 33	1	1	B	14 35
1	8	F	9 35	1	8	B	14 36
1	4	F	9 37	1	4	B	14 37
1	3	F	9 39	1	3	B	14 38
1	7	F	9 40	1	7	B	14 40
1	6	F	9 42	1	6	B	14 41
3	2	B	9 44	3	2	F	15 59
3	5	B	9 47	3	5	F	16 2
3	1	B	9 48	3	1	F	16 4
3	8	B	9 49	3	8	F	16 5
3	4	B	9 51	3	4	F	16 6
3	3	B	9 52	3	3	F	16 7
3	7	B	9 54	3	7	F	16 9
3	6	B	9 55	3	6	F	16 10
2	2	F	14 19	2	2	B	16 12
2	5	F	14 21	2	5	B	16 15
2	1	F	14 23	2	1	B	16 16
2	8	F	14 24	2	8	B	16 17
2	4	F	14 25	2	4	B	16 18
2	3	F	14 27	2	3	B	16 20
2	7	F	14 28	2	7	B	16 21
2	6	F	14 29	2	6	B	16 22

Figure 7.16 Repeatability of S. Pine Fluorescence Two Specimen Sets
(Front and Back) 3 Trials Each

Figure 7.17 Repeatability of Total Fluorescence Over a Five Month Period (S. Pine Only)

Figure 7.18 Bleaching Effect During 10,000 Pulse Exposure

8.0 ANALYSIS

8.0 ANALYSIS

8.1 DATA FORMAT

The detector located at the exit plane of the monochromator consists of a 1024 element silicon-photodiode array behind a gateable intensifier section. All 1024 elements of the array are read out sequentially when the controller receives a synch-pulse. Each element of the resultant 1024 element data array gives a measure of the intensity over a small wavelength band, $\Delta\lambda$. Because of the limited size of the intensifier section, only the central 700 elements of the 1024 array are intensified and therefore useful. The raw data stored during an experiment is an array of intensities measured in counts, as a function of diode number.

Using a discharge lamp with a series of narrow spectral lines of known wavelength, the relationship between diode number and wavelength was determined so that the raw data could be converted to counts as a function of wavelength. In this form, the data is dependent on the spectral characteristics of the system as well as of the pulp sample. In order to obtain results independent of the system the measured spectra would need to be corrected for the system response which is shown in Figure 8.1. Since the interest here was primarily in the relative response among the various pulps, the complication of putting the results into absolute terms was avoided. If the spectral sensitivity of the prototype system is very different from the laboratory system the effect would be to create an offset and perhaps minor slope change to the centroid response function.

In Section 2, the total fluorescence and wavelength centroids are defined in terms of integrals. Because of the discrete rather than continuous nature of the detector used the integrals need to be replaced by the summations

$$F = \sum_{n=1}^{1024} I_n \quad 8.1$$

where I_n is the intensity in counts, measured by the n^{th} diode in the detector array, and

$$\lambda_c = \frac{\sum_{n=1}^{1024} \lambda_n I_n}{\sum_{n=1}^{1024} I_n} \quad 8.2$$

where λ_n is the wavelength at the n^{th} diode.

The limits of summation in Equations 8.1 and 8.2 correspond to the integration limits 0 to ∞ .

Figure 8.1 Sensitivity/Transmission Curve of Lab Setup - Detector, Grating & Filter

8.2 REDUCTION PROGRAM

A c language program was written to facilitate the reduction/manipulation of the data files. It provides an easy and rapid means of calculation F , λ_c , and other parameters. When the program is run, the screen shown in Figure 8.2 is displayed. We shall discuss each of the menu selections in turn.

8.2.1 Wavelength Conversion

Selection of the wavelength conversion option of the main menu brings up the screen in Figure 8.3 which allows the user to input the wavelength calibration constants. Over the limited wavelength range covered by the detector a linear relationship between wavelength and diode number is sufficient to specify the wavelength within ± 0.2 nm. To provide the wavelength calibration information, the known wavelength at two diode numbers is input to the screen shown in Figure 8.3. The computer then determines and displays the linear relationship that it will use to convert the diode numbers of the raw data file to wavelength.

8.2.2 Default Paths

Selection of the second item from the main menu of Figure 8.2 brings up the screen shown in Figure 8.4. The first line allows the user to specify where the raw data files (identified by the extension .SPE) are to be found. In the example of Figure 8.4, the A drive is specified but any location can be specified by simply typing in the appropriate path name.

The second line allows the user to specify where the files that result from the data reduction are to be stored. Again, the choice is made simply by typing in the desired path.

There are two main types of reduced data files generated by the program. Lines 3 and 4 of the screen shown in Figure 8.4 allow the user to specify any three character extension by which these files can be identified. As before, the desired extensions are typed in on the appropriate lines.

8.2.3 Select Wavelengths

The third selection from the menu of Figure 8.2 brings up the screen shown in Figure 8.5. The user can specify four different wavelength ranges by typing in the wavelengths of the low and high limits of the desired range. The ranges specified in the example of Figure 8.5 are the ranges that were normally used in the course of the work reported here.

In subsequent data reduction, the program computes the total fluorescence in each of the specified areas using the equations:

Figure 8.2 Main Menu of the Data Reduction Program

Diode to Wavelength Conversion Parameters

Diode(min):	252	Wavelength(min):	400.2
Diode(max):	617	Wavelength(max):	600.0

Calculation: $\text{Wavelength} = 400.200 + (\text{Diode} - 252) * 0.547$

<TAB/ARROWS=Next> <ALT_A=Accept> <ESC=Cancel>

Figure 8.3 Wavelength Calibration Screen

Path for SRE Files	AN
Path for Area 3 Plot Files	AN
Extension for Area Files	PRN
Extension for Plot Files	PRN

<ALT-A> Accept <ESC> Cancel

Figure 8.4 Screen for Inputting File Paths and Extensions

Figure 8.5 Wavelength Range Specification Screen

$$A_1 = BASE = \sum_{\lambda=Low(1)}^{High(1)} I_{\lambda} \quad 8.3$$

$$A'_2 = \sum_{\lambda=Low(2)}^{High(2)} I_{\lambda} \quad 8.4$$

$$A'_3 = \sum_{\lambda=Low(3)}^{High(3)} I_{\lambda} \quad 8.5$$

$$A'_4 = \sum_{\lambda=Low(4)}^{High(4)} I_{\lambda} \quad 8.6$$

where I_{λ} is the intensity measured by the array diode located at wavelength, λ , and Low(n) and High (n) are the wavelength limits input to the screen in Figure 8.5.

The first range, A_1 , is designated base because it is used as a noise correction term for the other three ranges. The detector array has 1024 diodes but only the central 700 are intensified. The wavelength range specified for the "base" range in Figure 8.5 corresponds to unintensified diodes. Furthermore, filters in the optical system block light with these wavelengths from reaching the detector. As a result, the summation over the base range gives a measure of the dark noise level which is a combination of electronic noise and light scattered in the monochromator.

The total fluorescence summations recorded in the data files are corrected for the dark-noise using the equations

$$A_2 = A'_2 - A_1 * \frac{\Delta\lambda(2)}{\Delta\lambda(1)} \quad 8.7$$

$$A_3 = A'_3 - A_1 * \frac{\Delta\lambda(3)}{\Delta\lambda(1)} \quad 8.8$$

$$A_4 = A'_4 - A_1 * \frac{\Delta\lambda(4)}{\Delta\lambda(1)} \quad 8.9$$

where $\Delta\lambda(i) = \text{High}(i) - \text{Low}(i)$ is the range of wavelengths covered by the i^{th} range.

The ratios in Equations 8.7 through 8.9 are to put the noise on a per diode basis.

8.2.4 Select SPE Files

The menu selection titled "Select SPE Files" in Figure 8.2 brings up a screen as shown in Figure 8.6 that lists all of the raw data files in the location specified in the Default Path screen discussed above.

As prompted at the bottom of the screen, the user can select one or any number of the listed files for reduction. The procedure is to move the highlight cursor to the desired file and then press the F1 function key. This causes the background color behind the selected file to change so the user can easily track which files have been chosen.

Once all desired files have been highlighted, the user presses enter to return to the main menu where he can then select one of three processing options.

8.2.5 Convert to ASCII

The first processing option does no reduction, other than the wavelength calibration, but merely converts the raw data file to an ASCII format. For each SPE file designated in the previous screen, a separate ASCII file is created having the same filename as the original SPE file, but with an extension as specified earlier in the Default Paths screen.

8.2.6 Create Plot File

This function is much like the convert to ASCII function. The difference being that all of the specified SPE files are placed together in a single ASCII file that is formatted for direct import to LOTUS 1-2-3 and other spreadsheet programs. When this menu option is chosen, a screen first comes up prompting the user to specify the name desired for the resultant file. Again the extension specified earlier is automatically appended to the specified name.

This option is used whenever plots of intensity vs wavelength are desired. The plotting is then done through LOTUS 1-2-3, or other spreadsheet program.

BRCH3-09.SPE
FIR1-09.SPE
BRCH5-09.SPE
SPRC2-09.SPE
BRCH6-09.SPE
SPRC1-09.SPE
BRCH1-09.SPE
SPRC6-09.SPE
SPRC5-09.SPE
FIR2-09.SPE
BRCH8-09.SPE
BRCH4-09.SPE
SPRC4-09.SPE
SPRC3-09.SPE
BRCH2-09.SPE
TESTX.SPE

<F1=Select> <F2=De-Select> <ARROWS=Position> <←=Exit>

Figure 8.6 Listing of Available Raw Data Files (SPE Files)

8.2.7 Calculate Areas

When the item Calculate Areas is selected from the main menu, the monitor first prompts the user to input the filename desired. Again, the extension specified earlier through the Default Path screen is automatically appended to the specified filename.

Once the filename is entered, the program goes through each of the specified SPE files in sequence, making calculations and displaying the results on the monitor as shown in Figure 8.7.

The graph of Figure 8.7 shows the various specified wavelength ranges. The base area can be seen as the small flat area beginning at the left of the graph. The large central area covers nearly all of the fluorescence range and is both area 2 and area 3 in this example, since both were specified with identical wavelength limits. This is because, for the majority of the cases, there was no need for all of the areas. This feature was used only during the tests on ratioing various wavelength range responses.

The final area on the right-hand side of the graph which includes the sharp peak is area 4. The peak is due to diffusely reflected laser light having a wavelength of 337 nm. This light shows up in the second-order monochromator spectrum at a position corresponding to 2×337 nm. The prefilter used in front of the optical pick-up fiber was chosen to reject the vast majority of the reflected laser light but pass just enough that it could be measured. The limits of area 4 were chosen to cover just the laser peak so that A_4 can be used as a measure of reflectance.

In addition to the A terms, the wavelength centroid of the area 3 range is calculated using Equation 8.2 with the limits of summation changed to correspond to the limits specified for area 3.

When the calculations are complete, the data is automatically stored as a disk file. Table 8.1 shows the format of the data stored in the file. For the file shown in Table 8.1 there were 8 SPE files specified. There is, however, no limit to the number that can be included. The resultant file would simply have more rows. As can be seen in Table 8.1, the specified limits of the four wavelength ranges are listed at the top. The columns listed below the area limits have the following significance:

- Filename : this gives the name of the raw data file used to generate the data in the other columns of the row.
- PKWAVE : this specifies the wavelength at which the signal intensity (in counts) was the highest. The entire range of the spectrum is included in the search for PKWAVE, i.e., it is not restricted to any of the specified ranges.
- PEAK : this gives the intensity at the peak wavelength.

Figure 8.7 Display Screen for Calculation of Area Files

- **CENTROID** : this is the wavelength centroid calculated over the range designated as area 3.
- **A1** : this is the integrated intensity over the base range calculated from Equation 8.3.
- **A2,A3,A4:** : these are the integrated intensities (total fluorescence) calculated for each of the areas using Equations 8.7, 8.8, and 8.9.

Table 8.1 Format of a Typical Area File

Area 1	268.6	349.0					
Area 2	349.0	648.2					
Area 3	349.0	648.2					
Area 4	668.4	681.0					
FILENAME	PKWAVE	PEAK	CENTROID	A1	A2	A3	A4
14SP1A	423.3	1934	464.4	12543	388074	388074	6048
14SP6A	437.0	540	476.3	12001	103409	103409	2697
14SP4A	433.7	922	473.1	11138	185979	185979	4297
14SP3A	432.1	914	466.9	10228	173534	173534	3993
14SP5A	433.2	896	478.0	9575	177666	177666	3718
14SP8A	433.2	626	484.5	10100	136441	136441	3749
14SP2A	432.1	1209	464.9	9935	244133	244133	4544
14SP7A	426.6	740	479.6	9761	161760	161760	4294

9.0 SUPPLEMENTAL TESTING

9.0 SUPPLEMENTAL TESTING

9.1 EFFECT OF pH ON TOTAL FLUORESCENCE

According to Reference 18, the UV absorption spectrum of lignin can be described by a model of 13 overlapping gaussian absorption bands, whose relative intensities are dependent on pH. To explore how this pH dependent absorption effects the fluorescent properties, an experiment was run with pH buffered pulp samples during the initial test series.

Samples were prepared for this test by soaking washed and screened pulp samples for 24 hours at room temperature in the following solutions; distilled-deionized water, Fisher pH 7 buffer solution, and Fisher pH 10 buffer solution. After the 24 hour soak, the pulp was loaded into fisher acrylic cuvetts using the standard technique of compressing the pulp and removing the excess solution. Standard fluorescence measurements were then made on the resultant 48 specimens (2 wood species x 8 Kappa numbers x 3 pH). Results of this experiment have been discussed earlier (Section 3.5) in terms of the effect of pH on the wavelength centroid. Figure 9.1 presents the results in terms of the effect on the total fluorescence. For both species, the trend is for F to increase with increasing pH. It can be seen, however, that bringing the pulp all to a uniform pH does not improve the prospects for using F as a control signal.

Section 3.5 also discusses the results of a pH experiment conducted during the second test series. Figures 3.23 through 3.28 show the difference in the wavelength response function for samples prepared in NaOH solutions of pH=10 and pH=12, respectively. In Figure 9.2 the results of that same experiment are shown in terms of the effect on the total fluorescence, F.

9.2 PULP CHARACTERIZATION

Characterization of the pulp samples in terms of their Kappa number and pH have been discussed earlier in Sections 3.7 and 3.5, respectively. The Klason lignin and extractives content of the two pulp sets produced for the initial test series were also determined.

9.2.1 Klason Lignin

At the time that the southern pine pulp samples were sent to the IPST for confirmatory Kappa testing, samples were also provided for Klason lignin testing according to TAPPI T 222. It was thought that Klason lignin may correlate better with the fluorescence tests conducted by B&W. Klason lignin is defined as the percent, by weight, of lignin in the pulp which is insoluble in an acid solution. The TAPPI procedure states that, for undigested pulps, the extractives must first be removed and the wood disintegrated mechanically prior to adding it to an acid solution. The TAPPI procedure does not require extractive removal and disintegration for pulps with Kappa numbers less than 75 since the digestion procedure generally removes almost all extractives. IPST therefore did not remove extractives or disintegrate the pulp prior to dissolving the pulp in acid.

Figure 9.1 Effect of pH on Total Fluorescence - Initial Test Series

Figure 9.2 Effect of pH on Total Fluorescence, F - Second Test Series

During the Klason lignin tests, IPST noticed that the solute was tackier than normal and they had much difficulty in filtering the acid solution. This difficulty manifested itself in essentially unusable Klason lignin results. The TAPPI procedure gives an approximate expression for the relationship between Klason lignin and Kappa number as:

$$\% \text{ Klason lignin} \approx 0.15 \times \text{Kappa number}$$

The results of the IPST Klason lignin testing along with the results of the IPST Kappa number testing on the same specimens are:

SOUTHERN PINE KLASON LIGNIN, EQUIVALENT LIGNIN, AND KAPPA

SAMPLE NUMBER	LAB	IPST	IPST	IPST
	DATE	04/91	04/91	04/91
	# OF TRIALS	1	1	2
	TYPE	KLASON	EQUIV.KLASON	KAPPA
	MEASURED OR CALCULATED	MEAS.	CALC.	MEAS.
		(%)	0.15xKappa	Kappa
1		24.1	2.34	15.6
2		14.4	3.18	21.2
3		23.1	3.83	25.6
4		7.2	4.79	31.9
5		18.8	6.47	43.1
6		12.4	7.43	49.5
7		27.7	7.65	51.0
8		25.9	8.78	58.5

Comparison of percent insoluble lignin (i.e., Klason lignin) to the equivalent % lignin from Kappa numbers reveals that the Klason lignin results are seriously in error. Upon advice from IPST that Kappa number testing is much more repeatable and accurate than Klason lignin testing, the expense of further Klason lignin testing could not be justified.

9.2.2 Extractives in Pulp Samples

The extractives content of wood pulp can be determined according to TAPPI procedure T204 om-88. The least digested sample of each of the two pulp species, sample number 8, was subjected to the TAPPI extractives test. The least digested of the pulps should contain the highest concentration of extractives.

The extractives test was conducted at the B&W chemistry lab and the TAPPI procedure was followed, with the exception that the size of the glassware recommended was not available. This necessitated that the sample size tested be reduced from 10 g to 1.8 g. The tests were conducted in duplicate and the results are:

SPECIES	SAMPLE	TRIAL	% EXTRACTIVES
S PINE	8	1	0.64
S PINE	8	2	0.88
N SPRUCE	8	1	1.54
N SPRUCE	8	2	0.46

After the extractives were determined, a portion of the solution into which the extractives were dissolved was placed in a quartz cell and subjected to absorbance testing over the wavelength range 250 nm to 500 nm. The presence of compounds in this solution which exhibited absorbance much different from that of lignin would be an indication that non-lignins were absorbing UV light and, therefore, could be the cause of the non-Kappa correlating fluorescence. However, the observed absorbance spectrum was not different from that of lignin, probably due to a slight carryover of lignin.

These results lead to the conclusion that, in comparison to lignin, the extractives are not strong absorbers of UV light and are therefore not likely to interfere with the lignin fluorescence.

9.2.3 pH of As-received Initial Series Pulps

The pH readings on the as-received pulps prepared for the second test series are presented in Figure 3.21. The results of measurements on the initial series pulps are presented in Table 9.1. The variation among pulps is much less for these sets than for the new sets.

Table 9.1 Results of pH Testing of Pulp Samples
Per TAPPI T252 om-90 @ 25C

SPECIES	SAMPLE #	SPECIMEN LABEL	Ph
S PINE	1	F-4784	9.12
S PINE	2	F-4785	9.04
S PINE	3	F-4786	9.05
S PINE	4	F-4787	8.94
S PINE	5	F-4788	8.28
S PINE	6	F-4789	8.71
S PINE	7	F-4790	8.91
S PINE	8	F-4791	8.91
N SPRUCE	1	F-4792	7.95
N SPRUCE	2	F-4793	7.72
N SPRUCE	3	F-4794	7.93
N SPRUCE	4	F-4795	8.34
N SPRUCE	5	F-4796	8.32
N SPRUCE	6	F-4797	8.16
N SPRUCE	7	F-4798	7.87
N SPRUCE	8	F-4799	7.85

9.3 DIFFUSE REFLECTION

In the phase-resolved data taken at Duke University, reflected light from several non-lasing plasma lines from the He-Cd laser were superimposed on the fluorescence spectrum. A plot of the intensity of the strongest of these reflected lines vs Kappa number is shown in Figure 9.3 for 40 MHz modulation and in Figure 9.4 for 60 MHz modulation. There seems to be a good correlation between the reflection at 40 MHz and Kappa number, whereas the reflection at 60 MHz is erratic. This is in contrast to the fluorescence results shown in Figures 3.33 and 3.34, where the 60 MHz results correlate better with lignin concentration than the 40 MHz results.

To explore the reflection properties further, two He-Ne lasers were added to the B&W apparatus shown in Figure 7.4. One of these emitted at 633 nm while the other's output was at 543 nm. Both beams were brought to focus at the same point on the cuvet samples as the fluorescence excitation laser. The size of the focused spots was comparable to the size of the excitation laser spot. A series of files were recorded with the samples being scanned over the same area as for the fluorescence tests. The resultant files consisted of two peaks corresponding to the reflected light at the two laser wavelengths.

The results of these tests are presented in Figures 9.5 through 9.8. The repeatability from front to back surface is not good. This is most likely due to the fact that reflection depends strongly on the morphology of the surface. Although the scanned area is large

S. PINE, PHASE RESOLV. AT 40 MHz

REFL. INTENS. AT 442 nm "PH40442"

Figure 9.3 Intensity of 442 nm Reflected Light as a Function of Kappa Number for 40 MHz Modulation

S. PINE, PHASE RESOLV. AT 60 MHz

REFL. INTENS. AT 442 nm "PH60442"

Figure 9.4 Intensity of 442 nm Reflected Light as a Function of Kappa Number for 60 MHz Modulation

S PINE TESTS 11/1/91

633 nm

"SPFB633"

Figure 9.5 Intensity of 663 nm Reflection vs Kappa Number for Southern Pine Samples

S PINE TESTS 11/1/91

543 nm

"SPFB543"

Figure 9.6 Intensity of 543 nm Reflection vs Kappa Number for Southern Pine Samples

Figure 9.7 Intensity of 633 nm Reflection vs Kappa Number for Northern Spruce Samples

Figure 9.8 Intensity of 543 nm Reflection vs Kappa Number for Northern Spruce Samples

enough to give representative sampling of the fluorescence, the variability of reflection with position is too large to provide adequate averaging with the scanned area used. The results at both wavelengths show the same variability, which is consistent with the interpretation that the results are dominated by local variability that is not averaged out.

If there is a correlation between the reflection and Kappa number similar to that seen in the phase-resolved data, it is masked by the non-repeatability of the reflection data.

9.4 DERIVATIVE SPECTROSCOPY

A technique, commonly employed in UV spectroscopy to separate the absorption effects due to species with overlapping spectral bands, is to take the second and sometimes higher order derivatives of the measured spectrum. Peaks occur in the second derivative spectrum at the same wavelengths as the overlapping bands in the original spectrum.

Figure 9.9 shows the fluorescence spectra and the first three derivatives for southern pine samples #1 through #6. Three negative going peaks can be seen in the second derivative spectrum, showing that the smooth appearing curves of the original spectrum are made up of three bands having peaks at roughly 400 nm, 420 nm, and 450 nm. Note that the plots in Figure 9.9 are in terms of diode number which must be converted to wavelength using the expression:

$$\text{wavelength} = .547 * \text{diode number} + 262.$$

Although the second derivative separates the effects of the various lines contributing to the spectrum, the magnitudes of the dips do not provide a suitable control signal when plotted against Kappa number.

9.5 BLACK LIQUOR

An experiment was run during the second test series to determine the fluorescence response of various black liquor samples. The black liquor was that saved from the production of the pulp samples.

The liquor specimens were held in plastic cuvetts and illuminated through the open end so that fluorescence of the cuvet was not an issue. The specimens were held stationary during the data collection rather than being scanned as the pulp specimens were. Preliminary tests had shown that the liquor specimens exhibited negligible "bleaching", perhaps because of natural circulation of the liquid.

Results of the experiment are presented in Figures 9.10 and 9.11, where the total fluorescence and wavelength centroid are plotted against the Kappa number of the pulp from which the liquor was drained. Since the liquor contains the lignin removed from the pulp during the processing, the pulp Kappa is an inverse measure of the lignin concentration in the liquor, e.g., most of the lignin has been removed from a $\kappa=10$ pulp so the corresponding liquor should have a high lignin concentration.

DIODE NUMBER
 — SAMPLE 1 — SAMPLE 2 — SAMPLE 3 — SAMPLE 4 — SAMPLE 5
 — SAMPLE 6

DIODE NUMBER
 — SAMPLE 1 — SAMPLE 2 — SAMPLE 3 — SAMPLE 4 — SAMPLE 5
 — SAMPLE 6

DIODE NUMBER
 — SAMPLE 1 — SAMPLE 2 — SAMPLE 3 — SAMPLE 4 — SAMPLE 5
 — SAMPLE 6

DIODE NUMBER
 — SAMPLE 1 — SAMPLE 2 — SAMPLE 3 — SAMPLE 4 — SAMPLE 5
 — SAMPLE 6

Figure 9.9 Fluorescence Emission Spectrum and Its First Three Derivatives for Southern Pine Samples #1 through #6

BLACK LIQUOR – CENTRIOD RESPONSE

UNDILUTED : MARCH 1994

Figure 9.11 Wavelength Centroid for Black Liquor Samples

BLACK LIQUOR – TOTAL FLUORESCENCE

UNDILUTED : MARCH 1994

Figure 9.10 Total Fluorescence of Black Liquors

Keeping in mind that the lignin concentration decreases to the right in Figure 9.10 it can be seen that for the two softwood species the fluorescence decreases with increasing lignin concentration while the opposite is true for the birch (hardwood). This is the same behavior noted previously for the pulps.

Likewise, the wavelength centroid increases (for all three wood species) with increasing lignin concentration as was the case for the pulps (see Figures 3.8 and 3.9).

10.0 REFERENCES

10.0 REFERENCES

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APPENDIX A

B&W'S INITIAL FEASIBILITY STUDY

APPENDIX A

B&W'S INITIAL FEASIBILITY STUDY

During the second half of calendar year 1988, B&W conducted an in-house research effort into the feasibility of measuring lignin concentration in wood pulp using the fluorescence resulting from narrowband ultraviolet excitation of the pulp. This research effort was performed at the Babcock & Wilcox Alliance Research Center in Alliance, Ohio, using the laboratory instrumentation shown in Figure A-1. The pulp used in the research was obtained from the Weyerhaeuser Plymouth, N.C. plant and included a total of 43 specimens from three mills operating at target Kappa numbers of 12, 24, and 80 respectively, as shown in Table A-1.

NARROW BAND EXCITATION OF FLUORESCENCE OF PULP USING BROAD BAND LIGHT SOURCE

Figure A-1 Apparatus for Feasibility Study Fluorescence Measurements

TABLE A-1 FEASIBILITY STUDY SAMPLES

<u>TARGET KAPPA #</u>	<u># OF SAMPLES</u>	<u>TYPE OF WOOD PULP</u>
80	6	Southern Pine
22	21	Southern Pine
12	23	Mixed Hardwoods

$$\text{Percent Lignin} \approx [\text{Kappa \#}] \times 0.15$$

The results of the research indicated that the fluorescence intensity decreased with increasing Kappa number as shown in Figure A-2. To verify this unexpected result, a single sample of black liquor was diluted with high purity water to various concentrations and excited in the same manner as the pulp samples. The results of the black liquor tests are presented in Figures A-3 and A-4. At very low concentrations, the fluorescence intensity increases with increasing lignin concentration. At concentrations of approximately 2,000 - 20,000 ppm solids ($\approx$ 1,000 - 10,000 ppm lignin), the fluorescence intensity peaks. Beyond concentrations of 20,000 ppm solids, the fluorescence intensity decreases nonlinearly with increasing concentration.

The fluorescence intensity of the pulp was demonstrated to be very repeatable, as indicated in Figure A-5. The independent variable (Kappa number) was obtained from the pulp mill lab results and no statistical sampling within the specimens was performed. Therefore, it could not be determined if the fluorescence was due solely to lignin or to a combination of lignin and other fluorescing species, which might be present in concentrations not related to the concentration of lignin.

Specific feasibility study results included:

- The fluorescence intensity is very repeatable despite a laboratory set-up which was not optimum.
- Washing the mill supplied pulp in distilled water had little or no effect on it's fluorescence intensity.
- Maximum fluorescence occurred in the region of 420 - 450 nm (see Figure A-6).
- A functional relationship between fluorescence intensity and Kappa number was shown to exist (see Figure A-2). The fluorescence intensity decreases with increasing Kappa number. This inverse relationship is due to "fluorescence quenching". The quenching behavior of lignin was not previously investigated or reported in the literature.

FLUORESCENCE INTENSITY vs. MILL KAPPA NUMBER

Figure A-2 Fluorescence Intensity vs Mill Kappa Number

FLUORESCENCE OF BLACK LIQUOR SPECIMEN # F-3656 EXCITATION WAVELENGTH = 334 nm

Figure A-3 Fluorescence Intensity vs Solids Concentration for Diluted Black Liqueur Samples -- Low Concentration Range

FLUORESCENCE OF BLACK LIQUOR SPECIMEN # 3656 (BL3)
 (SAME AS FIG. A-3 BUT WITH EXPANDED SCALE)

Figure A-4 Fluorescence Intensity vs Solids Concentration for Diluted Black Liqueur Samples -- High Concentration Range

REPEATABILITY OF FLUORESCENCE INTENSITY vs. SPECIMEN #

Figure A-5 Repeatability of Fluorescence Intensity

FLUORESCENCE INTENSITY OF SAMPLE #6 FROM MILL #4

Figure A-6 Spectral Distribution of Fluorescence Intensity

Some of the questions which remained outstanding at the end of the effort included:

- What is the source of the data scatter? Possible answers include:
 - 1) Inaccuracy in the pulp mill Kappa numbers.
 - 2) Fluorescence of non-lignins which could be interfering with the lignin fluorescence (i.e., aliasing).
 - 3) Effect of temperature on the fluorescence.
 - 4) Inaccuracies due to the Phase I laboratory apparatus.
 - 5) Local variations within individual pulp samples.
- How does the fluorescence intensity vs. Kappa number vary from wood species to wood species?
- What is the effect of other excitation frequencies on the fluorescence intensities?
- Could phase-resolved and/or time-resolved techniques be used to eliminate scatter?
- Could information from the emission spectra, other than intensity, be used to eliminate scatter?

APPENDIX B

MEETING MINUTES

To

DISTRIBUTION

From

G. W. ROMAN, STRUCTURAL MECHANICS, ARC

Customer

DOE

File No.

40400-013

SubjectMEETING MINUTES - 1/29/93 MEETING AT MIAMI UNIVERSITY
ON DEVELOPMENT OF A PROTOTYPE LIGNIN CONCENTRATION SENSOR

Date

February 8, 1993

This letter to cover one customer and one subject only

On January 29, 1993 a meeting was held at Miami University in Oxford, Ohio. The purpose of the meeting was to discuss Babcock & Wilcox's (B&W) approach for the add-on laboratory tests which were added to the Development of a Prototype Lignin Concentration Sensor program in October 1992. The general scope of the add-on tests were recommended by the DOE/Industry advisory group in November 1991. The add-on test plan was developed jointly by B&W and Bailey Controls Company (BCC). At a January 12, 1993 review meeting at the B&W Alliance Research Center, Elmer Fleischman, a DOE representative who is assisting Stan Sobczynski, the DOE program manager, suggested that B&W obtain input from some pulp and paper science experts on the approach being taken in the add-on testing. To this end a meeting was arranged at Miami University with Dr. Chris Peterson, a professor at the University who has been working with B&W in preparing pulp samples, and Dr. Tom McDonough, a professor working with the Institute of Paper Science and Technology (IPST). These two individuals have extensive experience in pulp and paper science and were asked to provide input on the approach being taken in the add-on testing program. The following were in attendance at the meeting:

ATTENDEES

Chris Peterson - Professor - Miami University - (513)-529-2202
Dick Kling - Research Associate - Miami University - (513)-529-1227
Doug Hart - Research Associate - Miami University - (513)-529-2530
Tom McDonough - Professor - IPST - (404)- 853-9707
Larry Jeffers - Principal Investigator - B&W - (216)-829-7232
Garry Roman - Project Manager - B&W - (216)-829-7484
Taryl Vertal - Supervisor - Bailey Controls - (216)-585-6618

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Attendees

J. A. Beller - Bailey Controls
R. W. Haggard - CRD
M. L. Malito

There was a list of 10 questions which were prepared prior to the meeting which addressed the major areas where input was required. In addition, a program overview and technical results overview were presented and these triggered additional questions. The following meeting minutes are presented in terms of the consensus arrived at for each of the questions, including an "other" category. I have asked Dr. Peterson and Tom McDonough to review and sign-off on the meeting minutes to assure that what is presented faithfully represents their opinions. Attached to these minutes are the handouts supplied to the attendees.

QUESTIONS AND RESPONSES FOR 1/29/93 MEETING

QUESTIONS RELATED TO PREPARATION OF PULP SAMPLES

QUESTION #1. CHEMISTRY:

- Constant chemistry with variable time?
- Constant time with variable chemistry?
- Combination?
- Bleaching for mid-range Kappa - CE or O?

RESPONSE:

A mill would not use a fixed alkali charge (black liquor and white liquor) and variable time of the cook to obtain a wide range of Kappa numbers. They would vary the proportions of the white and black liquor depending on the desired Kappa number. However, based on other discussions in which it now appears B&W will request groups of pulp over a relatively narrow range of Kappa numbers, **it was agreed that it was a reasonable approach to fix the chemistry for a given range and use variable H-factor to obtain a range of Kappa numbers. Furthermore, it would be more representative and easier to make the new pulp samples if we obtain not only the wood chips from a pulp mill but the black and white liquor also.** On the issue of bleached pulp it was agreed that for mid-range Kappa numbers, say 12 to 22, oxygen treatment should be used rather than a C/E sequence. Use the C/E sequence for the low Kappa numbers around 3 to 6. **It was concluded that the pursuit of applications for the lignin sensor in the bleach stages should be a lower priority** since existing whiteness measurement instrumentation seems to be doing an adequate job of controlling this stage of the process. **Unless Bailey Controls Marketing personnel object, an investigation of C/E sequence bleached pulps will be not be performed during the current add-on tests. A number of samples in the Kappa 12 to 22 range will be obtained using an oxygen treatment.** During the later stages of the program, B&W may, however, obtain samples of bleached pulp from a mill to determine if there is a problem in applying the sensor to this material. Although Miami can inject oxygen into a batch digester and agitate the pulp with air, they do not have any equipment which operates like a commercial oxygen reactor. The consensus was, however, that for the manufacture oxygen bleached pulp samples, the Miami setup should provide an adequate simulation of the actual process.

QUESTION #2. SELECTION OF SPECIES TYPE:

- one hardwood, one softwood?
- two hardwood?
- mixed hardwoods?
- how variable is mix at plant? (lab test $\neq$ field test?)
- what species?

RESPONSE:

There was considerable discussion on the types of wood and the areas of the country which might use some of the species. It was not recommended that mixed species be tested since it would not be repeatable and lab test versus field test results could be considerably different due to the frequent changes in the mix at most pulp mills. For hardwoods it was suggested that there might be southern mills making bleachable grades using primarily gum and oak, perhaps Champion in Pensacola. The southern bleach mills may not have the wide variety of hardwoods passing through the plant that the northern hardwood mills have. Dr. Peterson thought that in the Chillicothe area alone there are about 20 different hardwoods in use, maybe 30% to 40% oak/hickory mixtures - but several different oaks and several different hickories. The mixtures being used in the plant can change by the hour. Other hardwoods in use include red maple, sycamore and yellow poplar. Dr. Peterson will call some southern plants to determine the types of woods being processed. These may include Cortland, Pensacola and East Tex. B&W may test just one hardwood or possibly two hardwoods that would normally be processed together. Data from the hardwood is important since only softwoods have been tested to date.

For the softwoods, the use of woods commonly processed in the northwest was discussed. Dr. Peterson said the previous pulp samples prepared for B&W by Miami were a southern pine from Champion in Canton, South Carolina and a northern spruce from the Consolidated Mill in Wisconsin - both eastern woods. Western Hemlock and Douglas Fir were mentioned as common woods used in the northwest. However, after discussion about potential difficulties in obtaining fast delivery from the northwest and a discussion about the uncertainty of future wood supplies in this area of the country, it was decided that it may be best to obtain new softwood species from the Lake States or Eastern Canada. From this area two possible softwood species would be white spruce and balsam fir. These are common in this area and likely to be typically mixed. Dr. Peterson will call some plants to determine which plants may be using this mix. The intent would be to test two softwoods that are typically mixed in a plant, but perform the tests on the individual pure species. It was also agreed that, if possible, it may be better to obtain a log and to have it chipped rather than wood chips from the mill. This would help assure that you have a known, pure species.

QUESTION #3. INDUSTRY GROUP RECOMMENDED K = 3 to 100:

- Is this realistic for hardwood (i.e. is hardwood ever processed to K = 100?)
- Maybe two hardwoods (7 samples each) over more realistic range?
- Is this realistic for softwood?

RESPONSE:

There was a discussion about what are realistic Kappa numbers for the various wood species. Tom McDonough suggested that we think about not only species specific ranges but end product specific ranges. To that end he outlined processes and typical Kappa ranges for both softwoods and hardwoods. The following is the final form of that table.

<u>PROCESS</u>	<u>SOFTWOOD KAPPA</u>	<u>HARDWOOD KAPPA</u>
1. Kraft - Liner	70 - 110	No need for Kappa
2. Kraft - Unbleached	20 - 35	10 - 22
3. Kraft - Oxy - Unblch	12 - 22	7 - 15
4. Kraft - O - D - E ₀	2 - 5	----

(#4 is low priority)

If process #4 (Kappa 2 to 5) is considered a low priority because it involves bleaching (see the response to question #1), then there are three (3) softwood processes and two (2) hardwood processes which taken together cover a range of Kappa numbers from about 12 to 110. We must still decide which species would be used for the softwood and the hardwood. Chris Peterson also suggested that another possible way of looking at a wide range of Kappa numbers would be to use a commercial lignin product called Inulin. This material could be diluted to obtain a range of Kappa numbers and then possibly used to saturate pure cellulose (e.g. cotton linters) to obtain a very repeatable, laboratory standard. B&W will consider this as a possible separate investigation.

QUESTION #4. REQUIRED RESOLUTION:

- Is trend across a wide range of Kappa important or is it more important to resolve changes over a very narrow range of Kappa? (since a given plant may operate over a relatively small range of Kappa). If this is important should we have many samples over a small range and can we know Kappa number accurately enough to even make use of this approach?

RESPONSE:

The general consensus was that covering the bands of Kappa numbers (see response to question #3) with a number of relatively evenly spaced samples was a suitable approach for verifying the lignin sensor's potential. In an ideal situation, an investigation of sensor resolution over a very narrow range of Kappa number would provide information which would be more directly comparable to the situation in a mill - where the Kappa range is typically narrow. However, it may not be practical, within the scope of this program, to generate pulp samples with very accurately known Kappa values (say within 0.2 Kappa) to use for fluorescence testing and still try to cover the entire range of Kappa

numbers. Dr. Peterson again mentioned the potential for using Inulin to generate a small range of Kappa numbers.

QUESTION #5. SHIVES AND KNOTS:

- Should these be removed from samples or ground up?
- Is the answer a function of Kappa number?
- What best simulates pulp mill procedures?

RESPONSE:

It was agreed that at high Kappa numbers the shives are usually ground up in the pulp. Tom McDonough suggested that the criteria may be whether the application is before or after the screen room. **But for simplification of this experiment, he thought it may be better to use pulp with the knots and shives removed. It may be worthwhile somewhere along the line to test some samples both with and without shives to see the effect.** Obtaining samples from an actual mill before and after the screen room might be a possible way of looking at the effect. A good time to do that may be during the prototype debugging.

QUESTION #5a. HOMOGENEITY:

- In actual on-line operation, we should have the luxury of sampling or averaging a significant sample area so that we can average out local variations.
- In the lab, the samples are small.
- Should we use a blender to assure lab samples are homogeneous?
- Will a blending operation result in changes in the pulp?

RESPONSE:

The consensus was that chopping up the pulp in a blender would be a way to increase uniformity. The blending operation would not be expected to significantly change the lignin fluorescence signal.

QUESTION #6. WASHING:

All of our earlier results were obtained on washed samples (but there was no quantitative definition of "washed"). Could our non-monotonicity in some of the plots be due simply to variation in washing?

- How should we define washing?
- What kind of quantitative or qualitative measure of washing should we use?
 - No change with further washings
 - Analysis of the washed water - chemical, ionic, transmission
- We could check on the idea that irregularities are due to washing variations by overwashing - and this will probably be done for information. However, in the actual process, we won't have ultimate washing, i.e. infinite time with DD water. We need input on the actual wash water purity and expected variations in the plant.

RESPONSE:

This discussion centered on the concept of a how to define "washing" such that we have a repeatable procedure. Tom McDonough stated that the Kappa value will continue to reduce as you continue to wash. This is due to diffusion of the lignin from the fiber wall. He stated that one way to at least obtain more consistent results would be to wash the pulp to some arbitrary point and then to remove all the free water to obtain about a 35% consistency (percent solid by weight). Once the free water is removed you measure the Kappa and any diffusion after that point is just from one part of the cell wall to another - but it is still inside the cell wall.

During a later discussion, Tom suggested a typical "washing" procedure used at IPST. This was:

1. Drain off any free liquid from the pulp - i.e. put it in a bucket or funnel and suck off the liquid into a vacuum flask until the pulp is about 20% consistency.
2. Take the 20% consistency pad and re-suspend it in water until its about 2% consistency.
3. Stir thoroughly for about 5 minutes.
4. Drain it again using the step 1 procedure.
5. Repeat steps 2, 3 and 4.
6. Declare the pulp "washed".

B&W will likely include this procedure in the pulp preparation specification so that "washing" is defined.

There was discussion that the pulp undergoes additional washing during screening. Tom cautioned that the water quality for screening was very important and he recommended distilled, de-ionized water for this step to avoid contamination. He also said to be sure there were no copper pipes used in the process.

QUESTIONS RELATED TO TESTING

QUESTION #7. pH:

Prior work has shown significant variations with pH (overnight soak in buffer).

- Black liquor setting in cuvette (plastic) changed pH overnight due to:
 - interaction with plastic?
 - interaction with air?
 - other possibilities?

RESPONSE:

It was generally agreed that it was not surprising that the pH affected the fluorescence. Tom mentioned that the ionization of the phenolic hydroxyls in the lignin has an effect on the UV and therefore would be expected to effect the fluorescence. There should, however, be a systematic effect. Also, the consensus was that a change in the pH overnight for black liquor would probably be due to a combination of CO₂ pickup from the atmosphere and oxidation of the sulfide.

Relative to the question of how to handle the effect of the pH, Tom suggested that ideally you should run all tests at a constant pH or at least measure the pH. However, to run all tests at a constant pH you would have to suspend the pulp in a buffer and this would introduce another variable. Alternatively, you could measure the pH and if it

deviated from some arbitrary value (10 was suggested - as this is about what would be expected at the end washer) by more than, say ± 0.5 , then adjust it. **We did not resolve the question on how to adjust it without adding an additional variable.**

There was a brief discussion of possible ways to measure the pH. The obvious way was to dilute the pulp and measure the suspension. Dick Kling suggested that a surface pH meter might work on the pulp sample. **B&W will have to determine how to handle the pH issue.**

QUESTION #8. BLACK LIQUOR EFFECT TESTS:

- In washing steps - how should we quantify the washing operation?
 - Chemical tests? Which?
 - Ionic?
 - Light transmission?
 - Number of rinses?
 - Other

RESPONSE:

Two issues were discussed relative to the black liquor tests. These were (1) the effects of consistency and; (2) how to quantify the squeeze.

There was some general discussion about the measurement of the effect of black liquor in order to better define the potential of the sensor for use in-pipe. Dr. Peterson questioned the priority for measuring in-pipe. His rationale was that if you have a good lignin sensor and a good material balance, you should be able to calculate conditions down line. Tom McDonough thought things might be too complicated to have a reliable calculation primarily because of the presence of liquid phase dissolved lignin. Tom stated that there were three things factors which effect the rest of the system. These are:

1. The Kappa number of the pulp in the slurry.
2. The consistency.
3. The concentration of the solid material in the liquid.

Taryl Vertal will discuss the Bailey Controls interest in the in-pipe application with Jeff Beller, who heads the Bailey Controls Marketing in this area. Tom did state that you need to look at the effect of black liquor even at the end washer location because, even though the pulp is washed, there will be carry-over.

Relative to the effects of consistency, Chris Peterson suggested that a factorial experiment could be performed with consistencies ranging from about 5% to 15% and Kappa from 20 to 75. You could mix the black liquor into the pulp but there is a question of how long it would take to diffuse into the cell wall. **This is essentially the experiment that B&W had designed.** It starts with washed pulp and would add black liquor to obtain a range of consistencies for a range of Kappa numbers. There is a question about how long to let the pulp soak before starting the experiment and this may have to be investigated by looking at how the fluorescence on one or two samples changes with time. Chris suggested that the rate of absorption would probably depend on temperature and that typically the process operates at about 40°C to 50°C.

Relative to a quantitative measure when squeezing black liquor from pulp, Tom suggested measurement of UV absorbance at 280 nm or a measure of the chemical oxygen demand of the effluent. **B&W will have to find a cost effective way to track the squeeze.**

QUESTION #9. FOR BLACK LIQUOR AND IN-PIPE TESTS:

- Is there concern over using old pulp samples or is it best to wait on new pulp samples?

RESPONSE:

The consensus was that if the pulp has been kept cold (near 4°C to 5°C, in sealed bags and there is no indication of biological growth, then using the existing pulp samples for some of the in-pipe and black liquor tests was not of significant concern. Tom recommended that new Kappa results be run. B&W confirmed that the pulp had been kept sealed, cold and did not exhibit any biological growth. Also, Kappa number tests have recently been run. B&W would expect to repeat a sub-set of the tests when the new pulp samples are available.

#10. MISCELLANEOUS:

A number of other discussions came up during the meeting and these are briefly presented here.

Tom mentioned that there is a real need to determine fiber-to-fiber uniformity of lignin content and he asked how fine of focus could be obtained on the laser beam. Larry said that even though a nitrogen laser is not as collimated as some lasers, there was plenty of illumination and the beam could be trimmed and focused to about 5 microns. Tom said the collapsed fiber is about 30 to 35 microns so a 5 micron spot may be alright.

At some point it may be worth looking at the effect of extractives on fluorescence. Pulp samples could be examined before and after extractive removal.

It was decided that Miami would use the auto-titration equipment to obtain Kappa number for the pulp samples and the additional Kappa number tests would be run as verification, probably at IPST.

G. W. Roman

The following have read the above meeting minutes and feel that it faithfully represents the comments and direction given during the subject meeting.

Chris Peterson

Tom McDonough

APPENDIX C

PREPARATION OF PULPS

*Company confidential
paper removed.*