DEVELOPMENT OF A PROTOTYPE LIGNIN CONCENTRATION SENSOR

Prepared by:

M. L. Malito and L. A. Jeffers
The Babcock & Wilcox Company
Research and Development Division
Alliance Research Center
1562 Beeson Street
Alliance, OH   44601

MASTER

RDD:92:4030-03-01:01   RECEIVED   January 1993

M?? 2 /. 1993

DOE/CE/40905--32

DE93 009767

TABLE OF CONTENTS

EXECUTIVE SUMMARY

INTRODUCTION

The U.S. Department of Energy, Office of Industrial Technologies, is sponsoring a research and development program for the development of a real-time, in-situ sensor to measure the concentration of lignin in wood pulp. The program is composed of three phases:

- Phase I - Feasibility -- complete
- Phase II - Development and Testing of a Field Prototype --
        in progress
- Phase III - Commercialization -- future.

The Phase I work (funded entirely by B&W) demonstrated a correlation between the fluorescence intensity and lignin concentration (as measured by TAPPI procedure, T 236 hm-85 "Kappa Number of Pulp") for undiluted wood pulp samples.

In Phase II, a laboratory test program directed at characterizing the fluorescence of wood pulp has been conducted as a prelude to the design of a prototype sensor. The current report summarizes the testing completed in Phase I and documents the Phase II laboratory testing completed through December 1991.

Future Phase II efforts include additional laboratory testing, design and fabrication of a prototype sensor, and field testing of the prototype sensor. Phase III of the program will concentrate on the incorporation of the sensor into a control system and commercialization of the sensor.

TEST PROGRAM

Very little data on the fluorescence characteristics of lignin exists in the open literature. What data does exist is on lignin in liquid form in very dilute concentrations. The research performed under the current program is the first attempt known to the authors to characterize the fluorescence of lignin in pulp. Since the purpose of the current program is to develop an instrument for industrial process control, the work reported here is not intended to be comprehensive.

The research was carried only to the point which would permit the design of a field testable prototype sensor for industrial process control.

The Phase II testing was carried out on two sets of laboratory prepared pulp, each consisting of eight samples with Kappa numbers ranging from approximately 15 to 50. Pulp set number 1 was prepared from southern pine chips and pulp set number 2 was prepared from northern pine 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 total fluorescence at various excitation wavelengths
- time-resolved fluorescence
- phase-resolved fluorescence
- multiple wavelength excitation
- diffuse reflectivity

A variety of post-test processing approaches were applied to the data in an attempt to determine the technique/processing combination most suitable for use in deriving a usable control function. The processing techniques included:

- integration of the fluorescence emission spectrum over the entire wavelength range to give the total fluorescent intensity.
- linear combination of the total fluorescence excited by two different excitation wavelengths.
- ratios of the fluorescence integrated over two different wavelength ranges.

- calculation of the wavelength centroid of the emission spectrum.
- differentiation of the emission spectrum.

Tests were also conducted to investigate the effect of temperature and pH on the fluorescence.

RESULTS AND CONCLUSIONS

The results of the steady-state fluorescence tests confirmed the earlier feasibility results - namely that an inverse functional relationship exists between fluorescence intensity and Kappa number. The relationship is not monotonic over the entire range of Kappa numbers of interest and has poor resolution at high Kappa numbers. The non-monotonic nature of the relationship is suspected to be caused by the presence of an interfering compound.

A variety of approaches were identified that minimize the effects of the interferant and provide response functions more promising for control purposes. These approaches included using:
- time-resolved and phase-resolved techniques.
- multiple excitation wavelengths.
- shift of the emission spectral distribution as measured by the wavelength centroid or ratio of intensities over two wavelength ranges.

Of these three general approaches, the emission spectral distribution shift is the most promising for use in a field instrument. Advantages include:
- shift is independent of absolute intensity of the fluorescence so compensation for drift of the source, detector, or collection efficiency is not required.
- the equipment is less complex. It does not require high-speed, gateable detector/electronics as does the time or phase resolved approach and it requires only a single excitation wavelength.

1.0 INTRODUCTION

1.1 PROJECT OBJECTIVES

The long-term objective of this DOE-sponsored program is to provide an instrument for real-time, in-situ measurement of lignin in pulp at a variety of locations in the pulp process stream. The instrument would ultimately be used as a primary sensor for process control in the pulp and paper industry. The program is composed of three phases:

- Phase I - Feasibility Demonstration
- Phase II - Development and Testing of a Field Prototype
- Phase III - Commercialization

This report summarizes the work to date on Phase II. The objectives of Phase II are to:

- Perform a carefully controlled set of laboratory experiments that characterize the fluorescent properties of wood pulp in order to answer various questions raised in Phase I and to provide the background data required to design a field testable prototype.

- Design and fabricate a field testable prototype system for measurement of the lignin concentration in undiluted pulp at the last stage of a brownstock washer.

- Evaluate the performance of the prototype in actual field conditions.

1.2 BACKGROUND - THE NEED FOR CONTROL OF LIGNIN CONCENTRATION

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.

1.3 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 at a pulp mill (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. A feasibility study (Phase I of this program) was undertaken by B&W in which the fluorescence of undiluted pulp samples was investigated. The results of the Phase I feasibility tests, which are discussed in Section 2 of this report, were very encouraging and led to the current Phase II effort.

1.4 SCOPE OF THIS REPORT

The first objective of Phase II was to provide the background data required for the design of a field testable prototype. The workscope planned to meet that first objective has been completed. The purpose of this report is to document the results of that study. To provide background for understanding the approach taken in the laboratory characterization study, the results of the Phase I feasibility tests and questions outstanding at the end of Phase I are reviewed in Section 2.0. The work plan for the characterization study is outlined in Section 3.0. Details of the characterization study in Sections 4.0 through 9.0 form the bulk of this report.

2.0 PHASE I RESULTS AND OPEN QUESTIONS

2.1 STATUS AT CONCLUSION OF PHASE I

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 Phase I research effort was performed at the Babcock & Wilcox Alliance Research Center in Alliance, Ohio, using the laboratory instrumentation shown in Figure 2-1. The pulp used in the research was obtained from the Weyerhauser 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 2-1.

TABLE 2-1   PHASE I SAMPLES

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

Percent Lignin $\simeq$ [Kappa #] x 0.15

The results of the research indicated that the fluorescence intensity decreased with increasing Kappa number as shown in Figure 2-2. 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 2-3 and 2-4. 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 2-5. 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 Phase I 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 2-6).

- A functional relationship between fluorescence intensity and Kappa number was shown to exist (see Figure 2-2). 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.

Some of the questions which remained outstanding at the end of the Phase I 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?

2.2 INITIATION OF PHASE II

Although very encouraging, the Phase I results were based on limited testing with a relatively crude laboratory apparatus. In preparation for Phase II of the project, B&W procured a "state of the art" intensified optical multi-channel analyzer capable of being gated down to 5 ns, a pulsed nitrogen laser, and a gigahertz oscilloscope. Additionally, B&W arranged for phase-resolved fluorescence tests to be conducted at Duke University, Department of Chemistry (Duke owns an SLM 48000 fluorescence analyzer capable of phase-resolved fluorescence).

Arrangements were also made with Miami University (Ohio) Paper Science and Engineering Department to have two sets of pulp samples prepared from two different wood species. Each set spanned a range of Kappa numbers from approximately 15 - 50. Miami measured Kappa number on each sample in triplicate. Arrangements were also made with the Institute of Paper Science and Technology for duplicate Kappa number tests and Klason lignin tests on one of the two sets of pulp.

Phase II of the project was then initiated to investigate the pulp fluorescence phenomena more thoroughly and to design, fabricate, and field test a prototype sensor.

NARROW BAND EXCITATION OF FLUORESCENCE OF PULP USING BROAD BAND LIGHT SOURCE
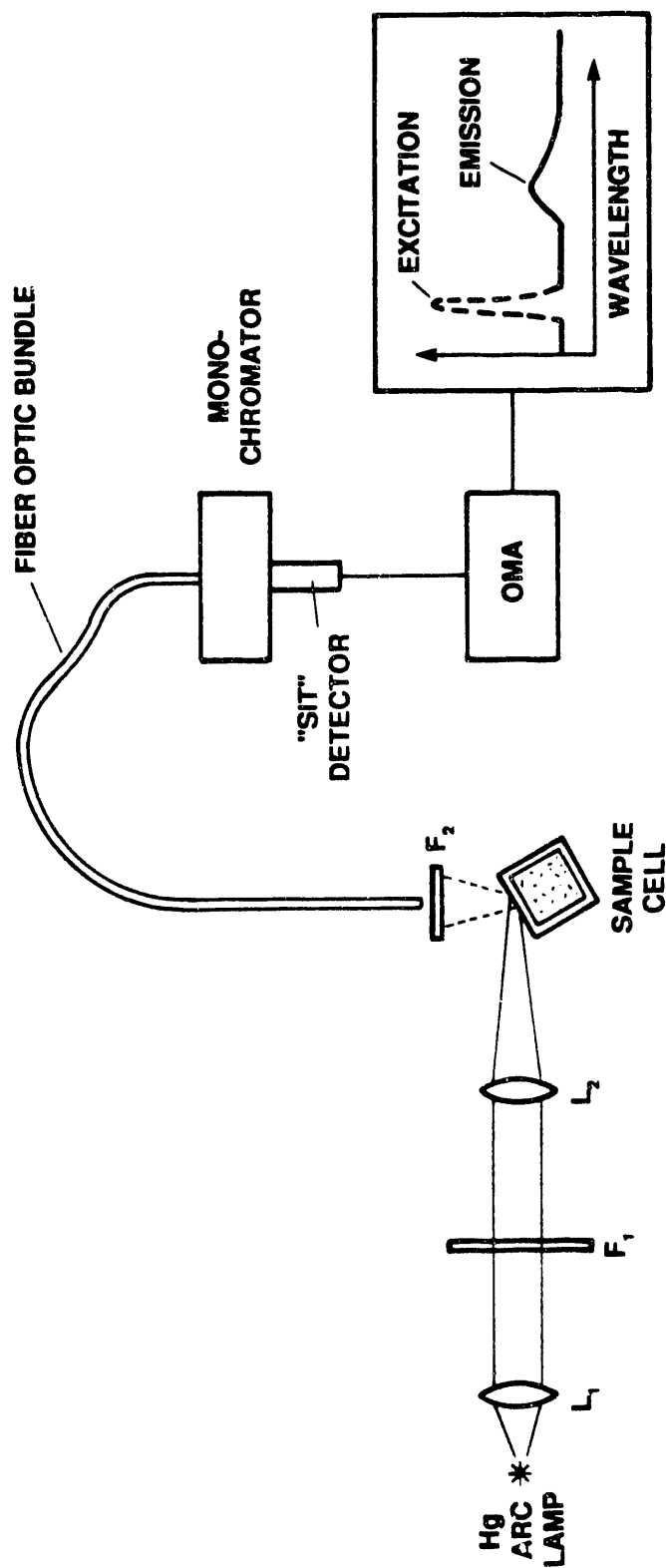
Figure 2-1   Apparatus for Phase I Fluorescence Measurements

FLUORESCENCE INTENSITY vs. MILL KAPPA NUMBER
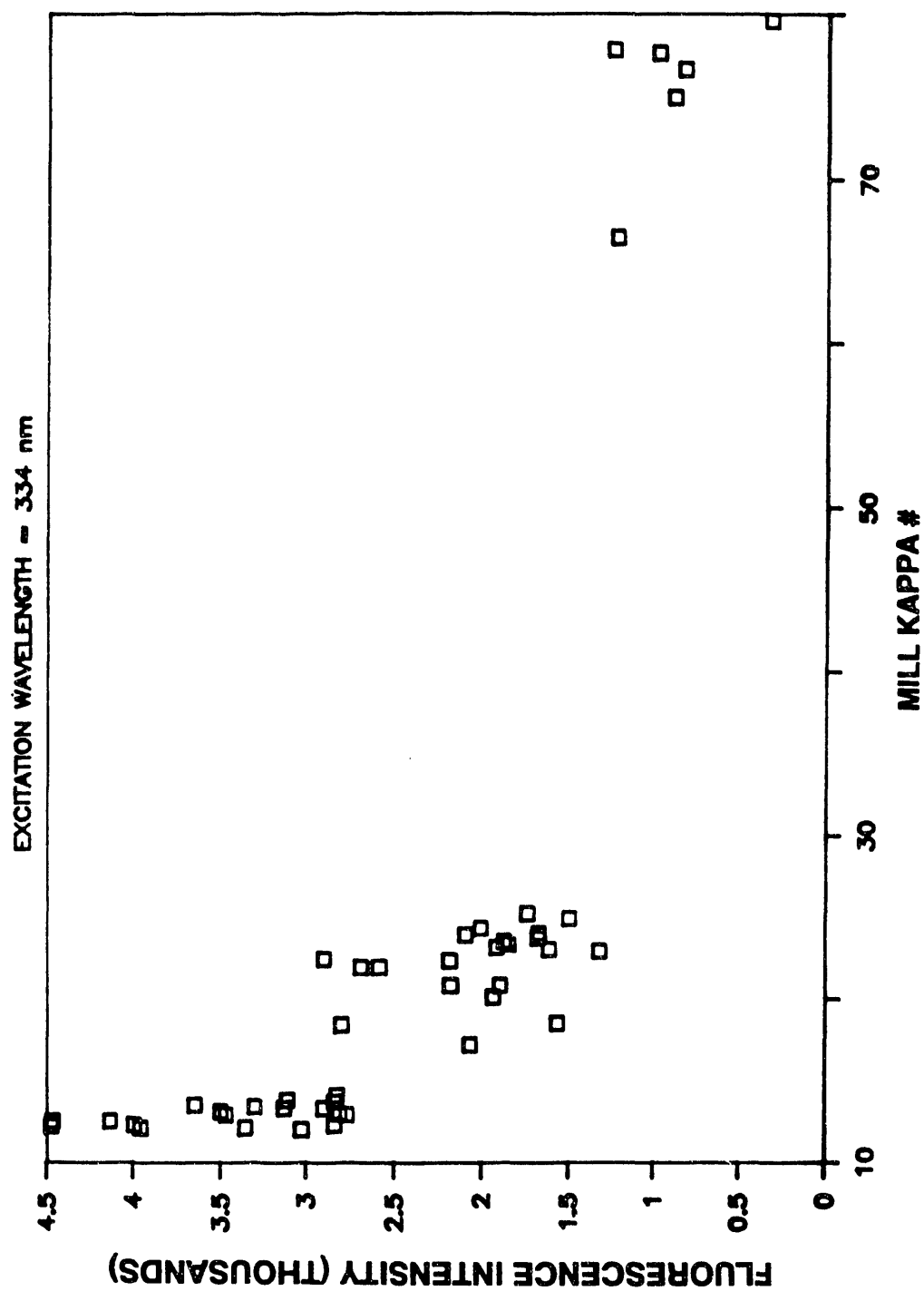
Figure 2-2 Fluorescence Intensity vs Mill Kappa Number
for Phase I Samples

FLUORESCENCE OF BLACK LIQUOR SPECIMEN # F-3656
EXCITATION WAVELENGTH = 334 nm
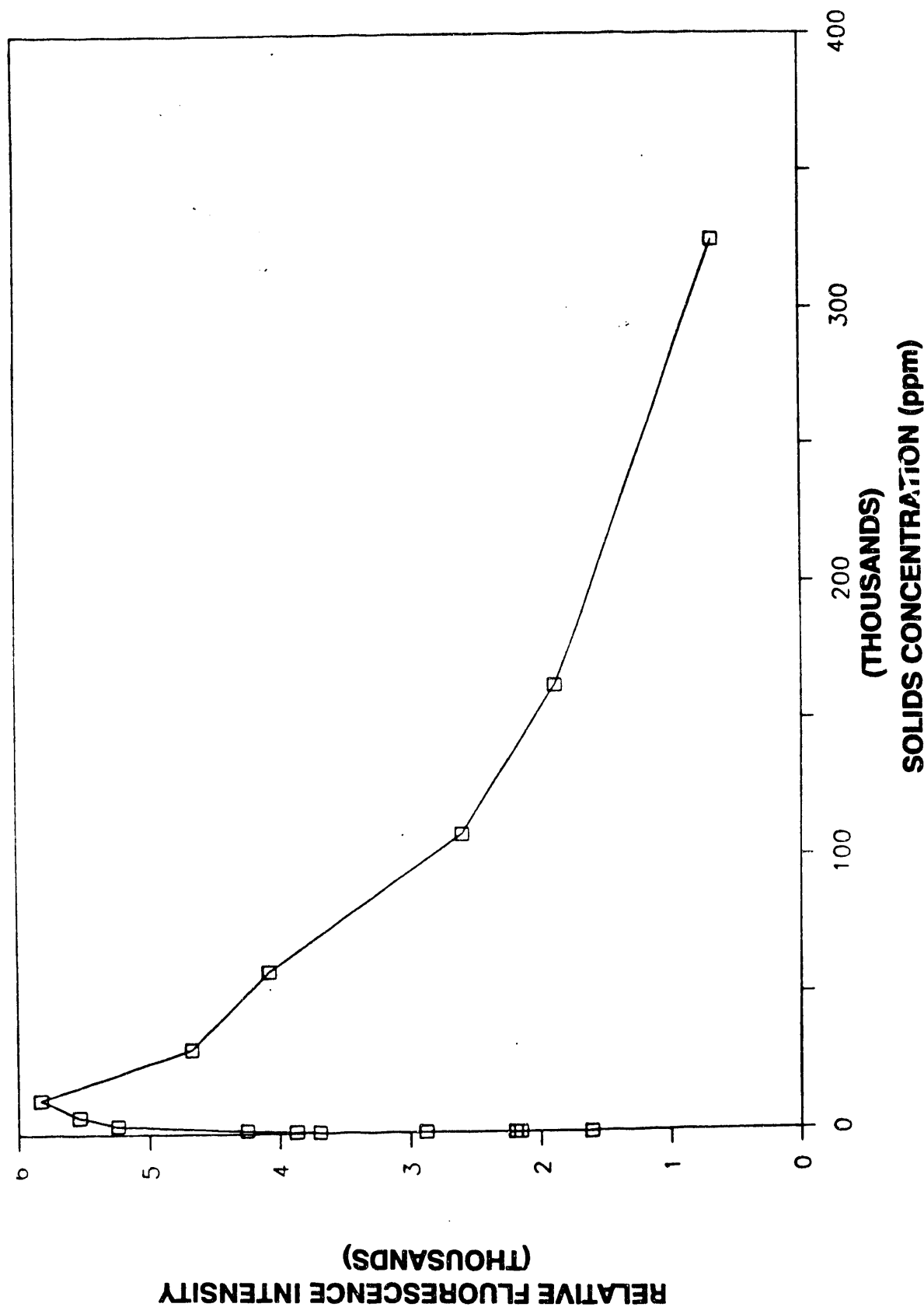
Figure 2-3   Fluorescence Intensity vs Solids Concentration for Diluted
Black Liquor Samples -- Low Concentration Range

FLUORESCENCE OF BLACK LIQUOR SPECIMEN # 3656 (BL3)
(SAME AS FIG. 2-3 BUT WITH EXPANDED SCALE)
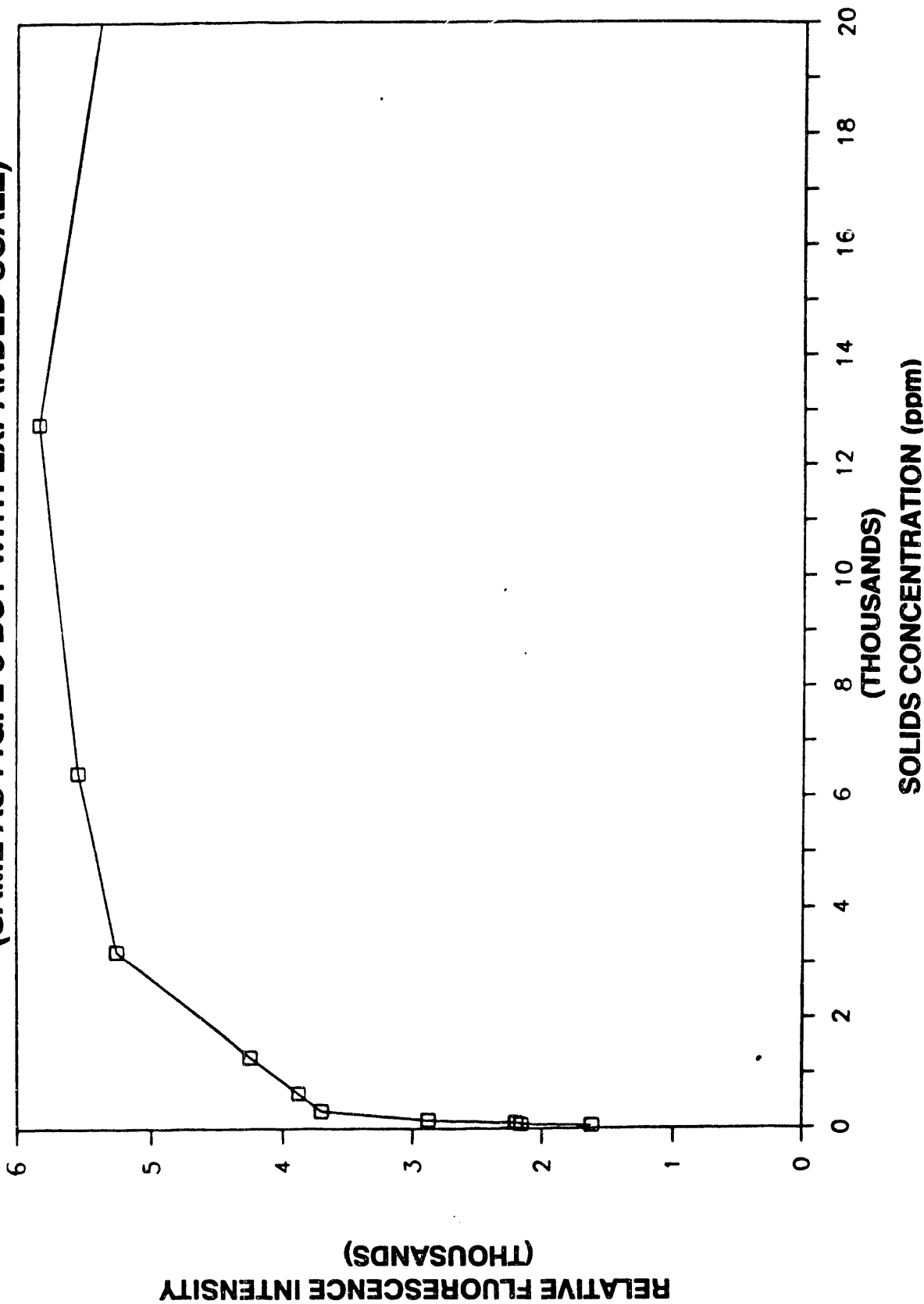
Figure 2-4   Fluorescence Intensity vs Solids Concentration for Diluted
Black Liquor Samples -- High Concentration Range

Figure 2-5   Repeatability of Fluorescence Intensity for Phase I Samples

FLUORESCENCE INTENSITY OF SAMPLE #6 FROM MILL #4

FLUORESCENCE

EXCITATION
334 nm

WAVELENGTH nm →
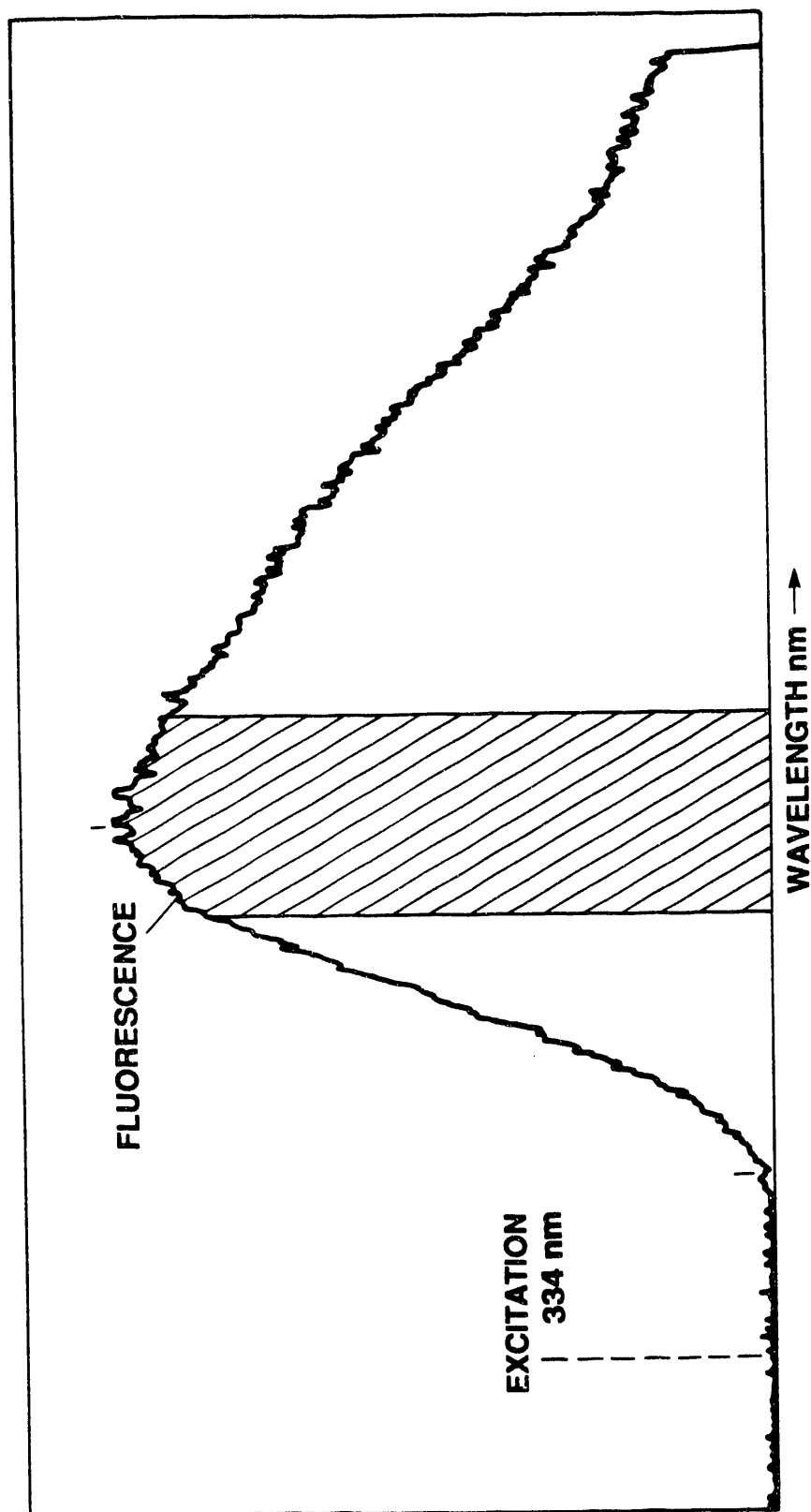
Figure 2-6   Spectral Distribution of Fluorescence Intensity (Phase I)

3.0 OVERVIEW OF PHASE II LABORATORY CHARACTERIZATION STUDY

During Phase I of the project, B&W demonstrated that a functional relationship exists 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".

3.1 ORIGIN OF SCATTER

The Phase I test results, as can be seen in Figure 2-2, exhibited a good deal of noise or data scatter. The Phase II tests were designed to eliminate this scatter or at the very least identify the cause. Possible causes considered were:

1) instrumentation error (drift of optical alignment, drift of source excitation intensity and wavelength, etc.)

2) local variations of Kappa number within the pulp samples (area sampled by the fluorescence probe not representative of the bulk sample).

3) 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 experienced during the tests was not controlled.

4) temperature effects (neither the sensitivity of the fluorescence to temperature changes, nor the magnitude of temperature variations during the tests were known).

5) uncertainties in the measured values of Kappa number.

6) variations in fluorescence properties of lignin dependent on the wood type (fluorescence efficiency is commonly affected by interaction with non-fluorescing molecules in the sample).

7) fluorescence interference of non-lignins (the presence of species whose concentration does not correlate with Kappa number can affect the measured fluorescence either by adding a non-lignin fluorescence or by altering the efficiency of the fluorescence from the lignin.

3.2 STRATEGY FOR DEALING WITH SCATTER

The Phase II characterization tests were designed to deal with the possible causes of data scatter enumerated above in the manner described below.

The first four causes listed above were addressed through the design of the apparatus and testing procedure.

1) Instrumental error was minimized through careful design and then quantified by the use of on-line standards.

2) To minimize the effect of sample inhomogeneity, the sample cuvets were mounted on a motor driven table that was automatically scanned during the exposure period.

3) Not only did this spread the exposure over a wide area but it also avoided bleaching problems that would occur if the exposure was confined to a single small area.

4) The effect of sample temperature on fluorescence was quantified and, to minimize variations due to temperature, the samples (which were normally stored in a refrigerator) were allowed to set out long enough to come to room temperature before any data was taken.

5/6) The questions concerning the Kappa number measurement and variations caused by wood species were addressed by having

two controlled sample sets prepared for the test program. One set was made from a southern pine and the other from a northern pine. Each set consisted of eight samples spanning the range of Kappa numbers from approximately 15 to 55. The range of Kappa numbers was achieved by removing samples from the digester at different times so that within a set, each of the samples came from the same parent wood-chip stock, and all had been processed with the same chemistry. The sample sets were prepared by the Paper Science and Engineering Department at Miami University in Oxford, Ohio. Miami University made Kappa number measurements, in triplicate, on each of the samples at the time of the preparation. In the case of the southern pine samples, Miami University repeated the Kappa measurements seven months later to insure that the samples were not changing with time. An independent set of Kappa number measurements were made on the southern pine samples by the Institute of Paper Science and Technology.

7)   A wide range of testing techniques and data reduction approaches were used in the characterization of the lignin fluorescent properties. The objective was to determine the approach most suitable for incorporation in the field prototype. Early testing indicated that there were "interfering" components in the pulp samples that would preclude the straightforward use of a simple total fluorescence signal. The objective of the test program was to identify an approach that could give a measure of the Kappa number in the presence of the interfering components.

In fluorescence spectroscopy there are several parameters that can be manipulated. These are listed and discussed below:

•   <u>Amplitude of the total fluorescence emission</u> – This is the most straightforward measurement, instrumentally. The sample is illuminated and the detector produces a signal proportional to the total amount of resultant emission. The first set of experiments involved measurement of total fluorescence emission.

- **Temporal behavior** - Interference due to other fluorescing species can often be suppressed if the time ccnstant for fluorescent decay is significantly different for the two species. There are t·· general methods for achieving discrimination based on time constant differences. Instrumentally they are quite different but they supply equivalent information about the sample. The first method is that of time-resolved fluorescence which was investigated using the apparatus described in Section 6.0. The second method is that of phase-resolved fluorescence spectroscopy which was employed on the southern pine samples under subcontract to the Department of Chemistry at Duke University using a state-of-the-art SLM4800 fluorescence analyzer system.

- **Excitation spectrum** - The amount of fluorescence from a given species is dependent on the spectral distribution of the light used to excite the fluorescence. Two interfering species can often be separated by observing differences due to excitation spectrum changes. This possibility was investigated by obtaining fluorescence response for several different wavelengths of excitation using a tunable dye-laser as the source.

- **Spectral distributions of fluorescence emission** - Additional information about the fluorescing species can be obtained by analyzing the spectral distribution of the emission, since each species has its own characteristic emission spectrum. The spectral distribution of the fluorescence emission was recorded during the time-resolved and variable excitation wavelength tests discussed above, and analyzed in three ways. The first was simply to calculate the total fluorescence over all wavelengths - which is the approach discussed above that makes no use of the spectral distribution. The second method involved taking the ratio of the intensities in two different spectral bands. The third method was to determine the centroid wavelength of the spectral distribution. To understand the way either of these methods might discriminate between two interfering

species, consider the case where we have two species: one which fluoresces in the blue and one in the red portion of the spectrum. For an equal mix of the two, the resultant emission spectrum would "peak" at some point between red and blue. As the relative concentration of the red emitter increases the distribution and peak wavelengths will shift toward the red. Thus, the peak wavelength or the centroid of the distribution provides a measure of the concentration of the red fluorescing species.

4.0 RESULTS

4.1 TOTAL INTEGRATED FLUORESCENCE

The fluorescence resulting from excitation by a pulsed source is distributed over both time and wavelength in a manner characteristic of the fluorescing species. The most straightforward and instrumentally simplest approach would be to take the total fluorescence integrated over the entire wavelength range and all time. Unfortunately the relationship between this "total integrated fluorescence" and the measured Kappa number is not suitable, as can be seen in Figure 4-1. While there is a general downward trend of the fluorescence with increasing Kappa number, the irregularities suggest the presence of a non-correlating component along with the component that correlates as a monotonically decreasing function with the Kappa number.

As discussed in Section 7.0, the Kappa numbers of the southern pine samples were measured at both Miami University and at the Institute of Paper Science and Technology (IPST) with differing results. The results presented in this section are plotted against Miami Kappa for northern pine data and IPST Kappa for southern pine data.

Most of the results presented in this section (4.0) are from a series of tests conducted over the two-day period from October 31 to November 1, 1992. Several test series had been performed during the months preceding this definitive series, which was intended as a confirmation of the results already obtained. This final series incorporated all of the instrumental and procedural improvements developed over the course of the earlier tests. Figure 4-2 compares the results of this final test series to those of a previous series (5 months earlier). 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 4-2 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, optical alignment, etc.).

4.2 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 4-3 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 4-3 with 4-2 shows that the time-delayed
fluorescence provides a "better" response c"rve, i.e., the disruptions
due to the non-correlating components are less severe. Figure 4-3
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 4-1) the disruptions gradually decrease up to delays
of 12 nsec. As the delay increases 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 4-3 is an
improvement over the basic response shown in Figure 4-1 it is still
far from ideal as a control signal, particularly at higher Kappa
numbers.

In Figure 4-4 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 and southern pine samples is minimal.

Figures 4-5 and 4-6 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 4-6 discriminates against the non-correlating component that is present in Figure 4-5.

4.3 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 4-7 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 is shown in Figure 4-1.

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 4-7 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. In Figure 4-8 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 4-8) was chosen empirically as that which gave the smoothest response curve.

4.4 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

4-3

the fluorescence into a long and a short wavelength component. Figure 4-9 shows the ratio of two wavelength bands as a function of the Kappa number. Although there is some species dependence (the curves for northern 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 4-10 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 4-10 also shows how well the front and back surface agree -- on the order of $\Delta\kappa\approx1$. The front and back surfaces are essentially two different samples.

4.5 THERMAL RESPONSE

Figure 4-11 shows the effect of pulp temperature on the total fluorescence. The data was obtained from a sample with a Kappa number of 15. The total fluorescence intensity decreases linearly with temperature at approximately 0.2%/°F. This corresponds to approximately 0.03 Kappa/°F for low Kappa numbers (e.g., 15). No temperature tests were conducted at higher Kappa numbers, but the effect on Kappa number is expected to be much higher due to the flatness of the intensity curve at high Kappa numbers. The effect is large enough that a Kappa number measurement approach based on the intensity of the fluorescence may need to be compensated for temperature, depending on the natural range of temperature variation at the measurement location. An approach such as that shown in Figure 4-4 might be self-compensating, i.e., the temperature effect may be the same on both the numerator and denominator of the ratio. At this point we do not have the data required to answer this question.

Figure 4-12 shows the effect of temperature on the wavelength centroid. The effect is again a linear decrease which could be easily compensated. The magnitude of the effect on Kappa in this case is

4-4

nearly independent of Kappa number. The slope of the curve is approximately 0.025 nm/°F (see Figure 4-10). Since the centroid change with Kappa number is on the order of 0.37 nm/Kappa, the temperature effect on measured Kappa is approximately 0.07 Kappa/°F.

FIGURE 4-1 TOTAL FLUORESCENCE INTENSITY vs. KAPPA NUMBER; EXCITATION AT 337 nm

SPECIES: S. PINE & N. PINE
TEST DATE: 10/31/91
CUVETS: QUARTZ
EXCIT. WAVELENGTH: 337 nm
TIME DELAY: 0 ns

(DATA POINTS ARE AVERAGE OF
FRONT & BACK MEASUREMENTS)

KAPPA NUMBER

■ S. PINE   + N. PINE

TOTAL FLUORESCENCE INTENSITY
(Millions)
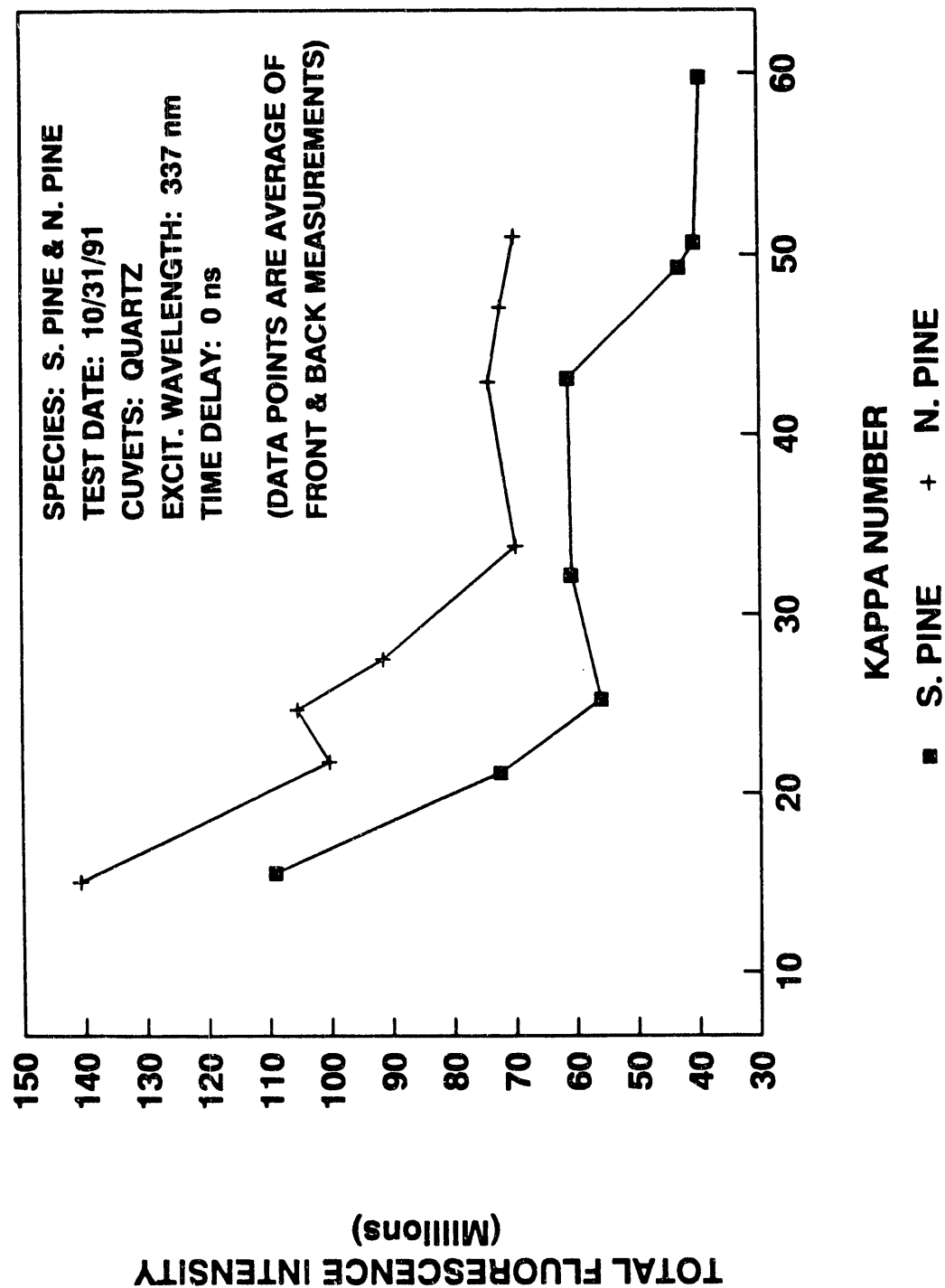
FIGURE 4-2   REPEATABILITY OF TOTAL FLUORESCENCE OVER A FIVE MONTH PERIOD (S. PINE ONLY)
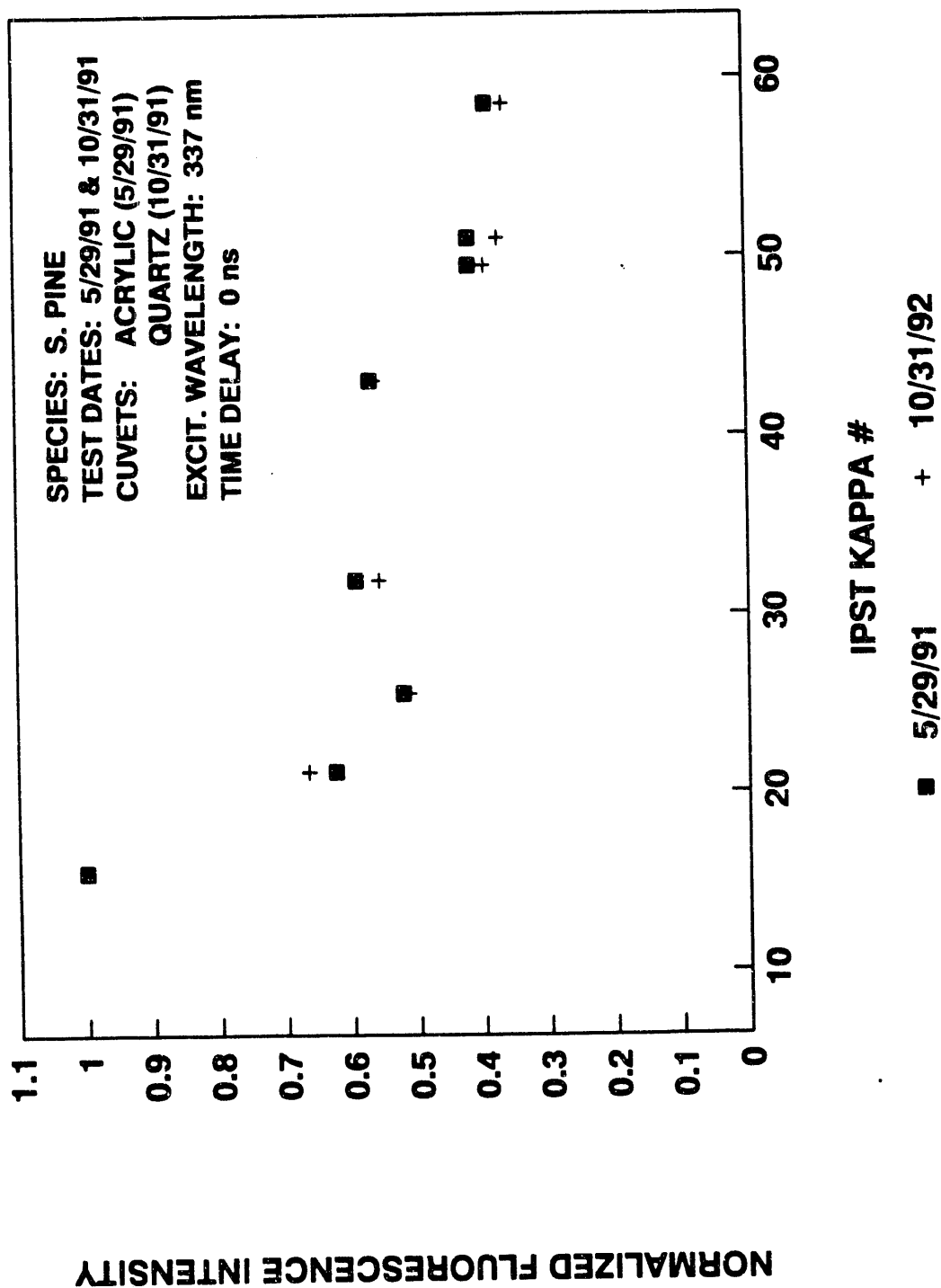
FIGURE 4-3   TIME RESOLVED FLUORESCENCE INTENSITY VS. KAPPA NUMBER - 12 ns DELAY

SPECIES: S. PINE & N. PINE
TEST DATE: 10/31/91
CUVETS: QUARTZ
EXCIT. WAVELENGTH: 337 nm
TIME DELAY: 12 ns
(DATA POINTS ARE AVERAGE OF FRONT AND BACK MEASUREMENTS)

■ s pine   +   n pine

TOTAL FLUORESCENCE INTENSITY (Millions)
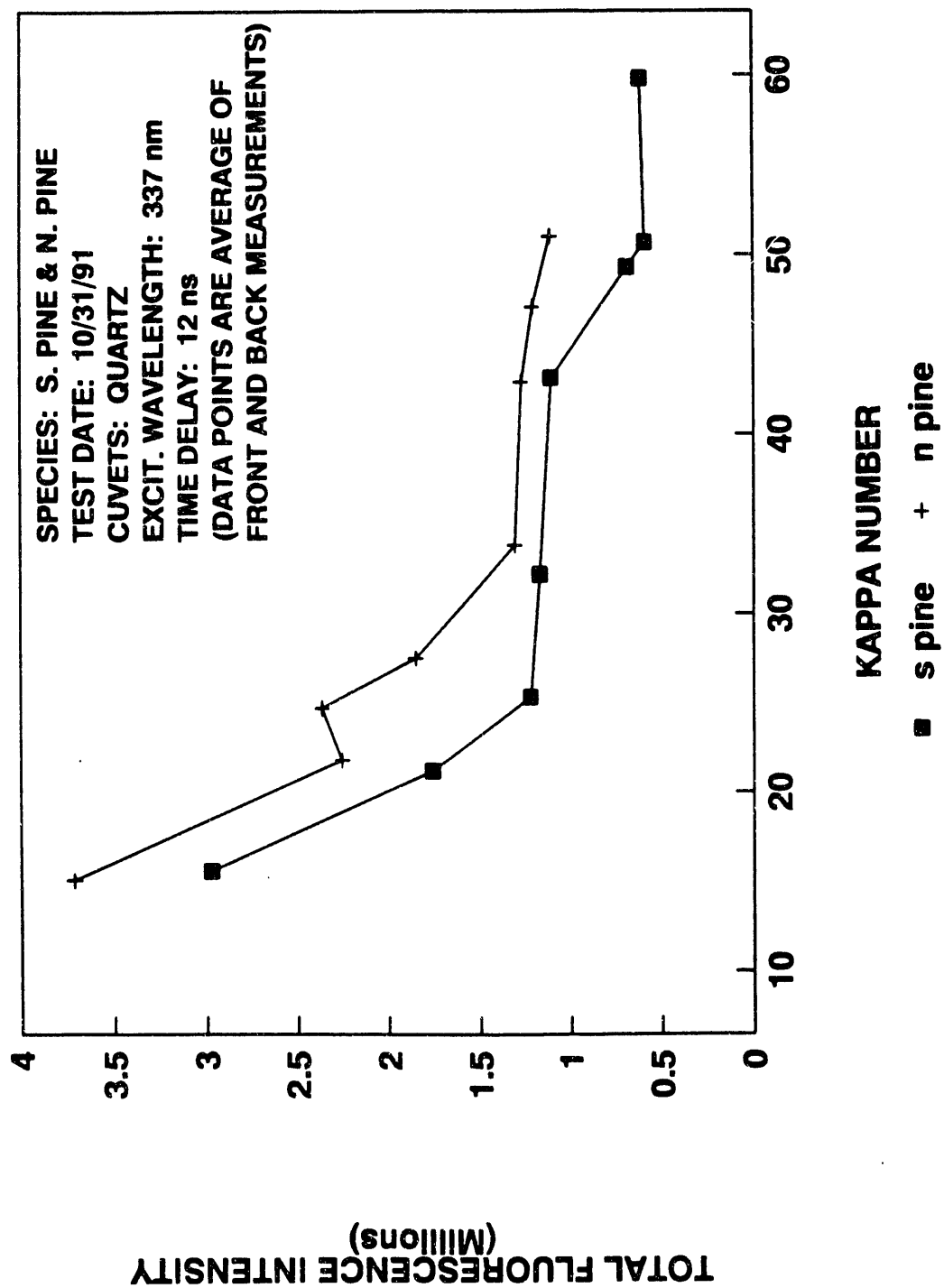
KAPPA NUMBER

FIGURE 4-4   RATIO OF 12 ns DELAYED FLUORESCENCE
TO 0 ns DELAYED FLUORESCENCE
VS. KAPPA NUMBER

SPECIES: S. PINE & N. PINE
TEST DATE: 10/31/91
CUVETS: QUARTZ
EXCIT. WAVELENGTH: 337 nm
TIME DELAY: 0 ns & 12 ns
(DATA POINTS ARE AVERAGE OF
FRONT AND BACK MEASUREMENTS)

KAPPA NUMBER

■ s pine   +   n pine

4-9
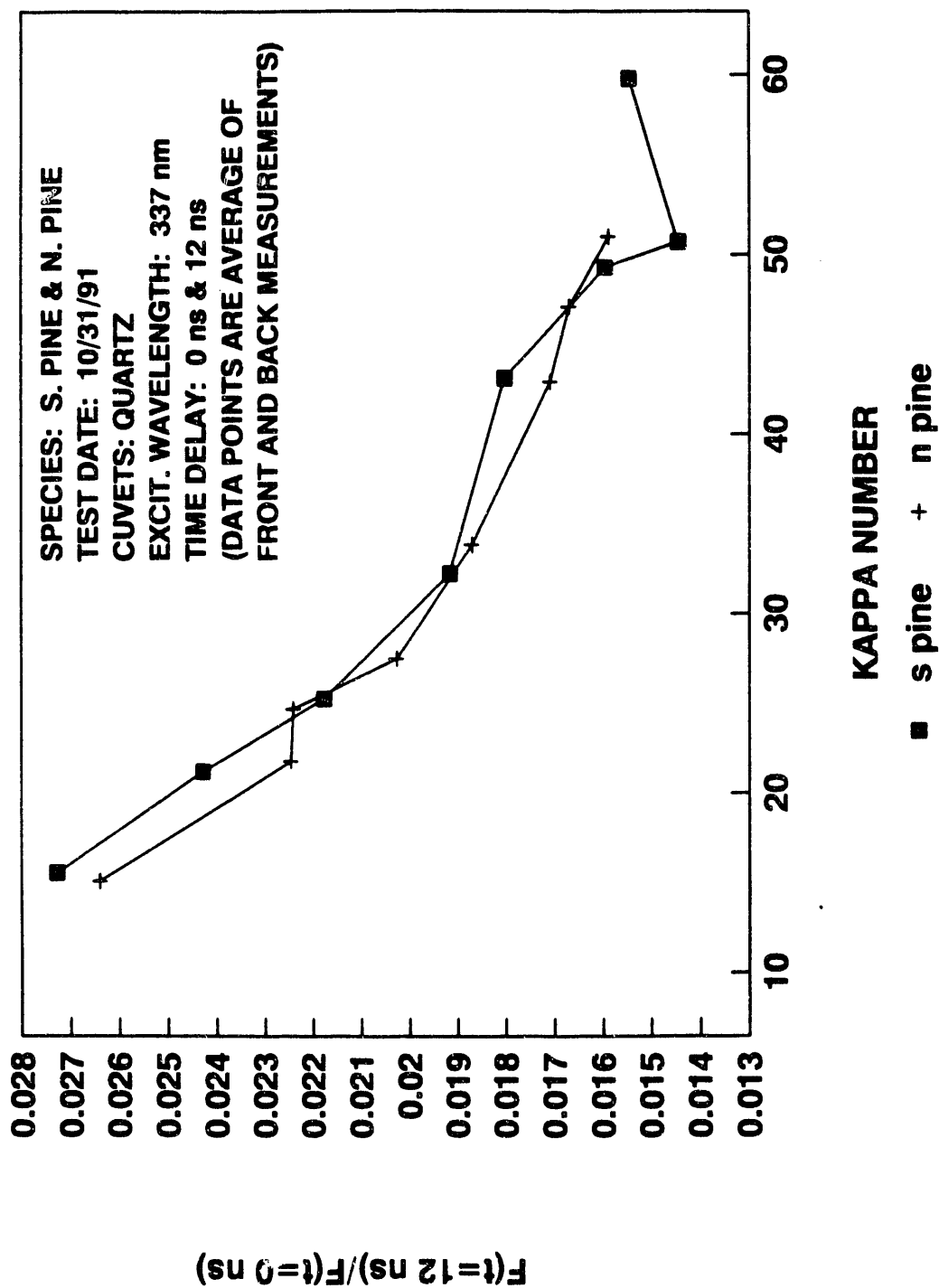
FIGURE 4-5   40 MHz PHASE RESOLVED FLUORESCENCE
RESPONSE VS. KAPPA NUMBER

SPECIES: S. PINE
CUVETS: QUARTZ
EXCIT. WAVELENGTH: 325 nm
MODULATION FREQ.: 40 MHz
EMISSION WAVELENGTH: 410 nm
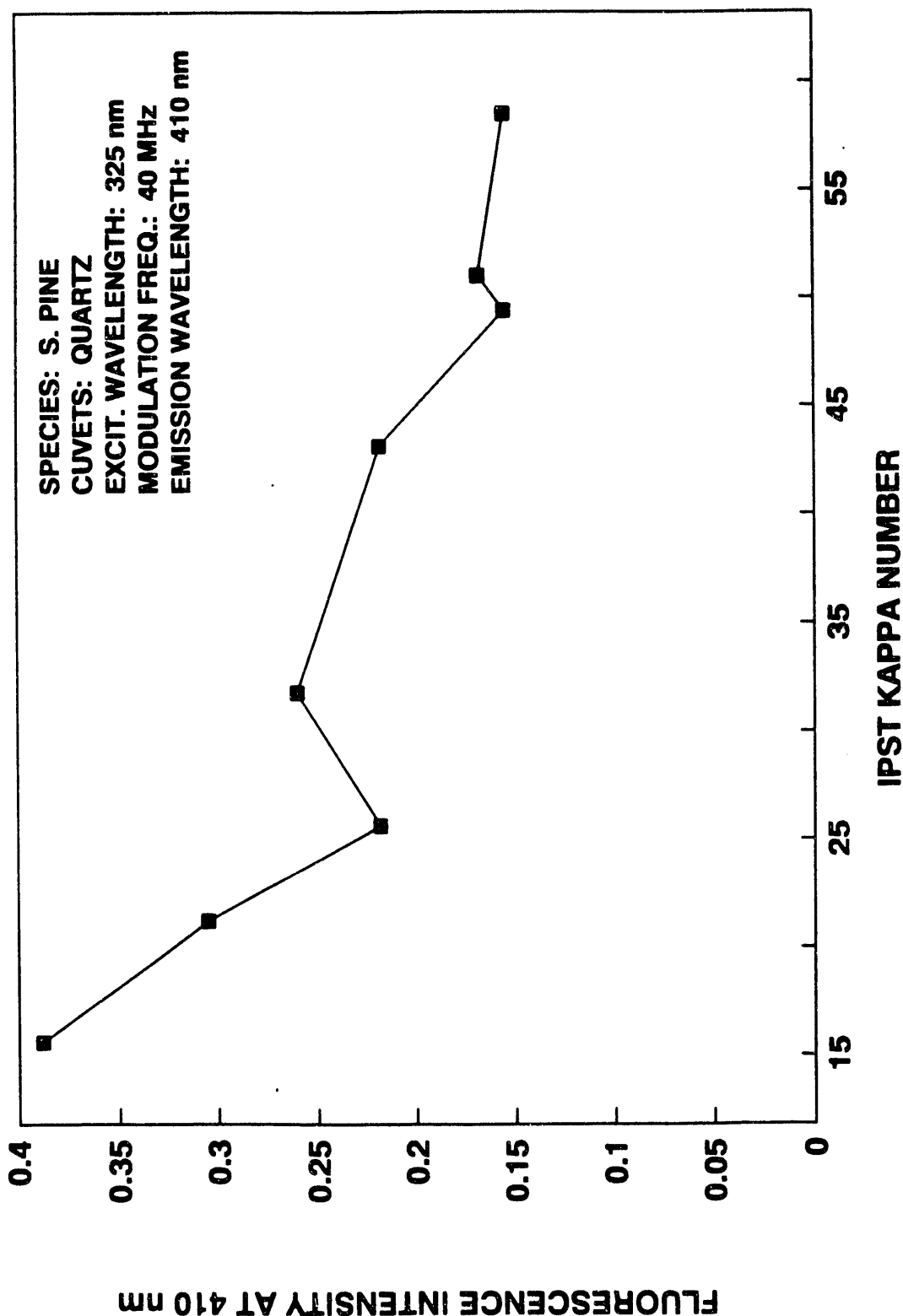
FIGURE 4-6   60 MHz PHASE RESOLVED FLUORESCENCE RESPONSE VS. KAPPA NUMBER

SPECIES: S. PINE
CUVETS: QUARTZ
EXCIT. WAVELENGTH: 325 nm
MODULATION FREQ.: 60 MHz
EMISSION WAVELENGTH: 410 nm

FLUORESCENCE INTENSITY AT 410 nm
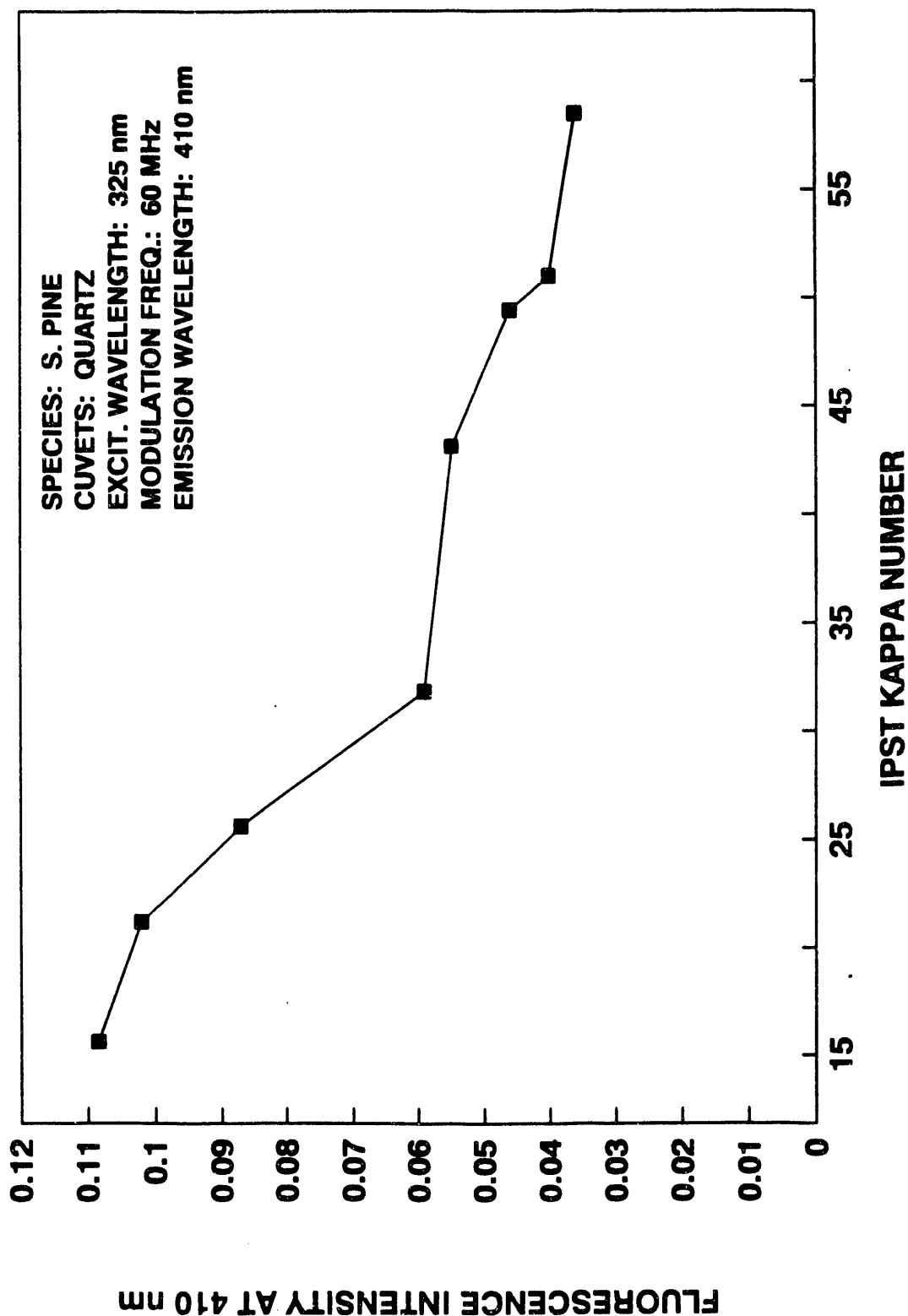
IPST KAPPA NUMBER

FIGURE 4-7   TOTAL FLUORESCENCE INTENSITY
VS. KAPPA NUMBER; EXCITATION AT 442 nm

SPECIES: S. PINE & N. PINE
TEST DATE: 11/1/91
CUVETS: QUARTZ
EXCIT. WAVELENGTH: 442 nm
TIME DELAY: 0 ns

KAPPA NUMBER

■   S. PINE PULP   +   N. PINE PULP

TOTAL FLUORESCENCE INTENSITY
(Millions)
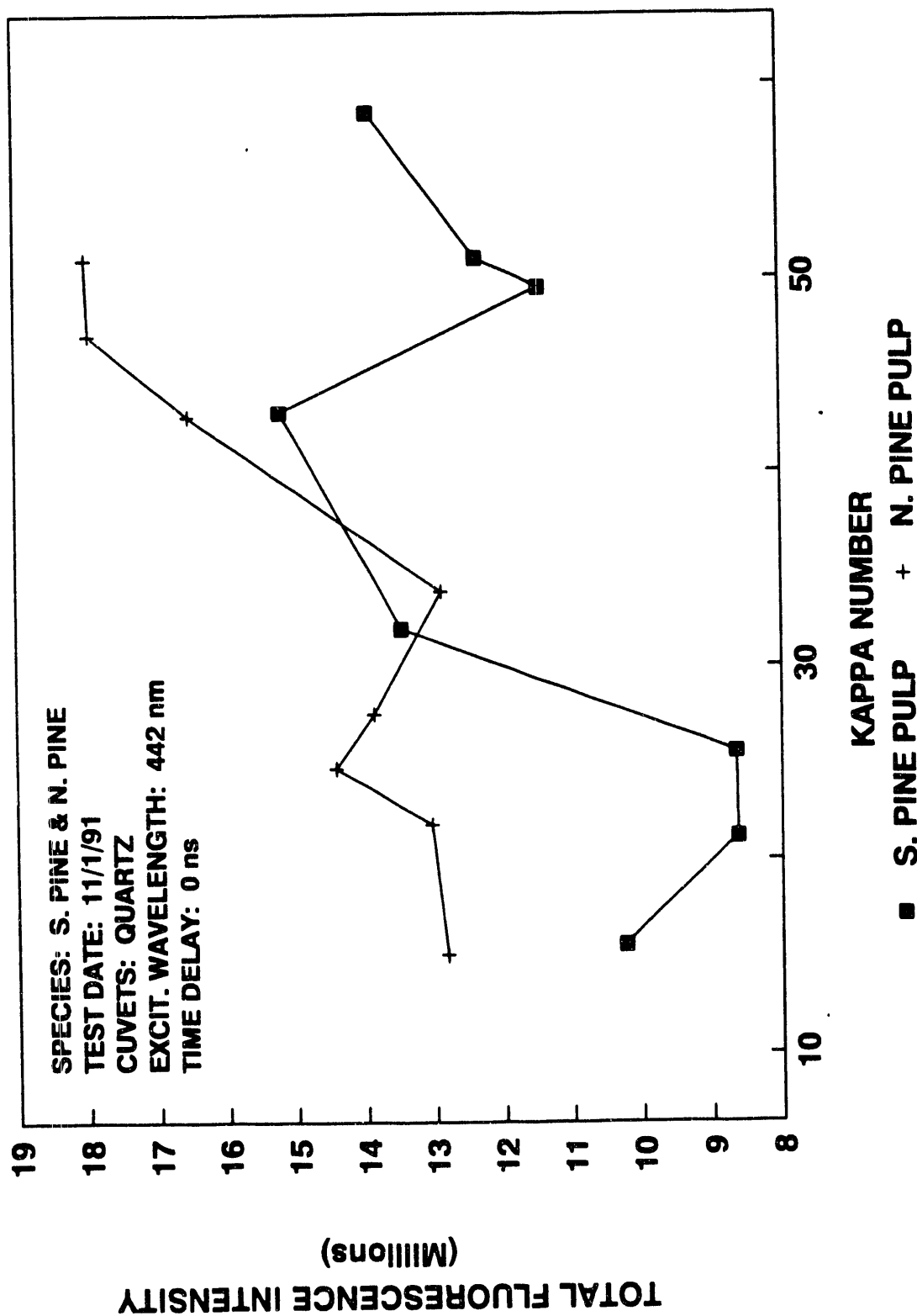
FIGURE 4-8   DUAL EXCITATION-WAVELENGTH RESPONSE FUNCTION VS. KAPPA NUMBER

SPECIES: S. PINE & N. PINE
TEST DATE: 11/1/91
CUVETS: QUARTZ
EXCIT. WAVELENGTHS: 337 nm and 442 nm
TIME DELAY: 0 ns

KAPPA NUMBER

■ S.PINE   +   N.PINE

F(337)-4*F(442) (Millions)
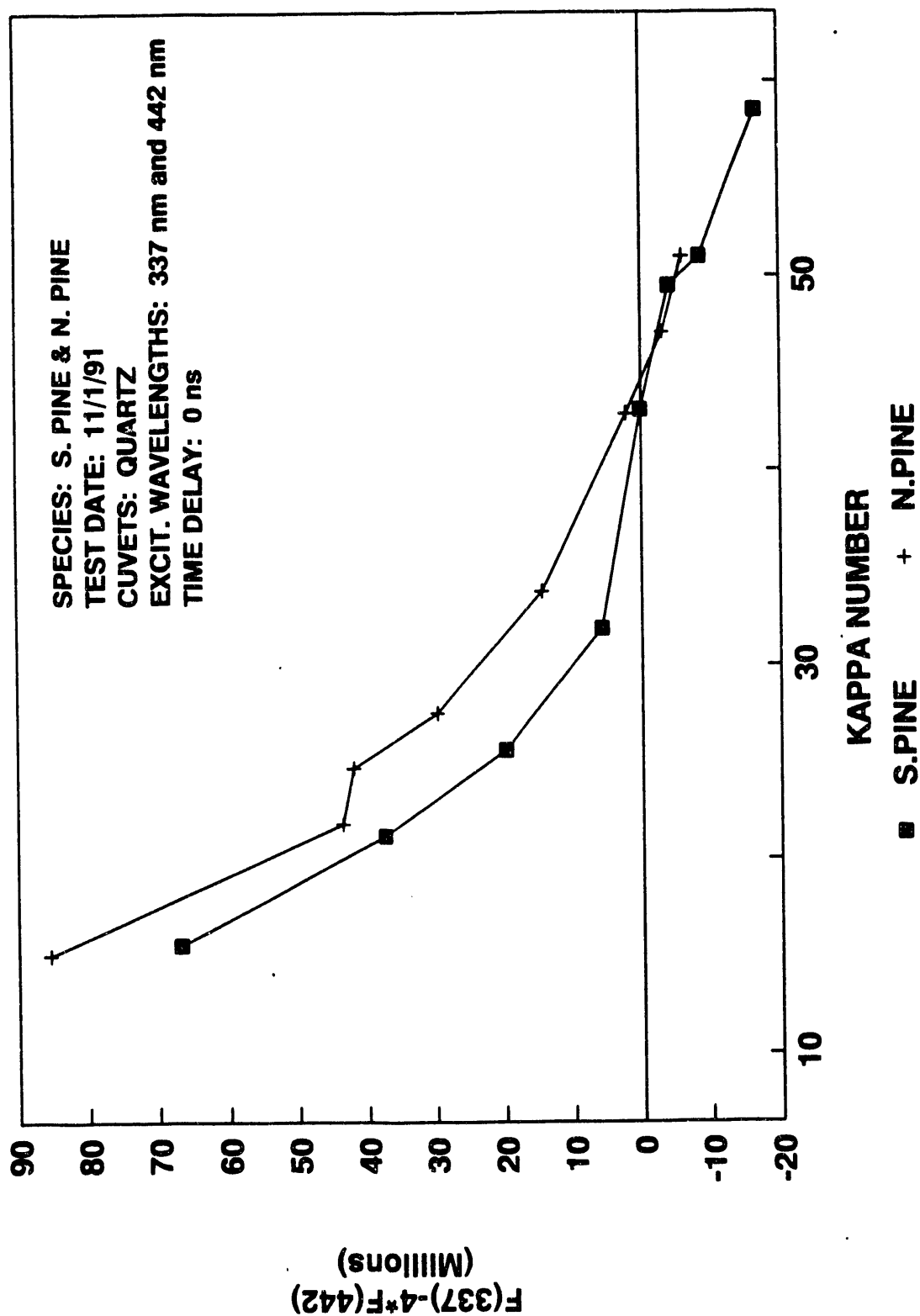
FIGURE 4-9   RATIO OF FLUORESCENCE INTENSITY
OVER TWO EMISSION WAVELENGTH RANGES
VS. KAPPA NUMBER

SPECIES: S. PINE & N. PINE
TEST DATE: 10/31/91
CUVETS: QUARTZ
EXCIT. WAVELENGTH: 337 nm
TIME DELAY: 0 ns
RATIO: LONG TO SHORT WAVELENGTH BAND

KAPPA NUMBER

■ S. PINE   + N. PINE

INTENSITY(509-564)/INTENSITY(371-427)
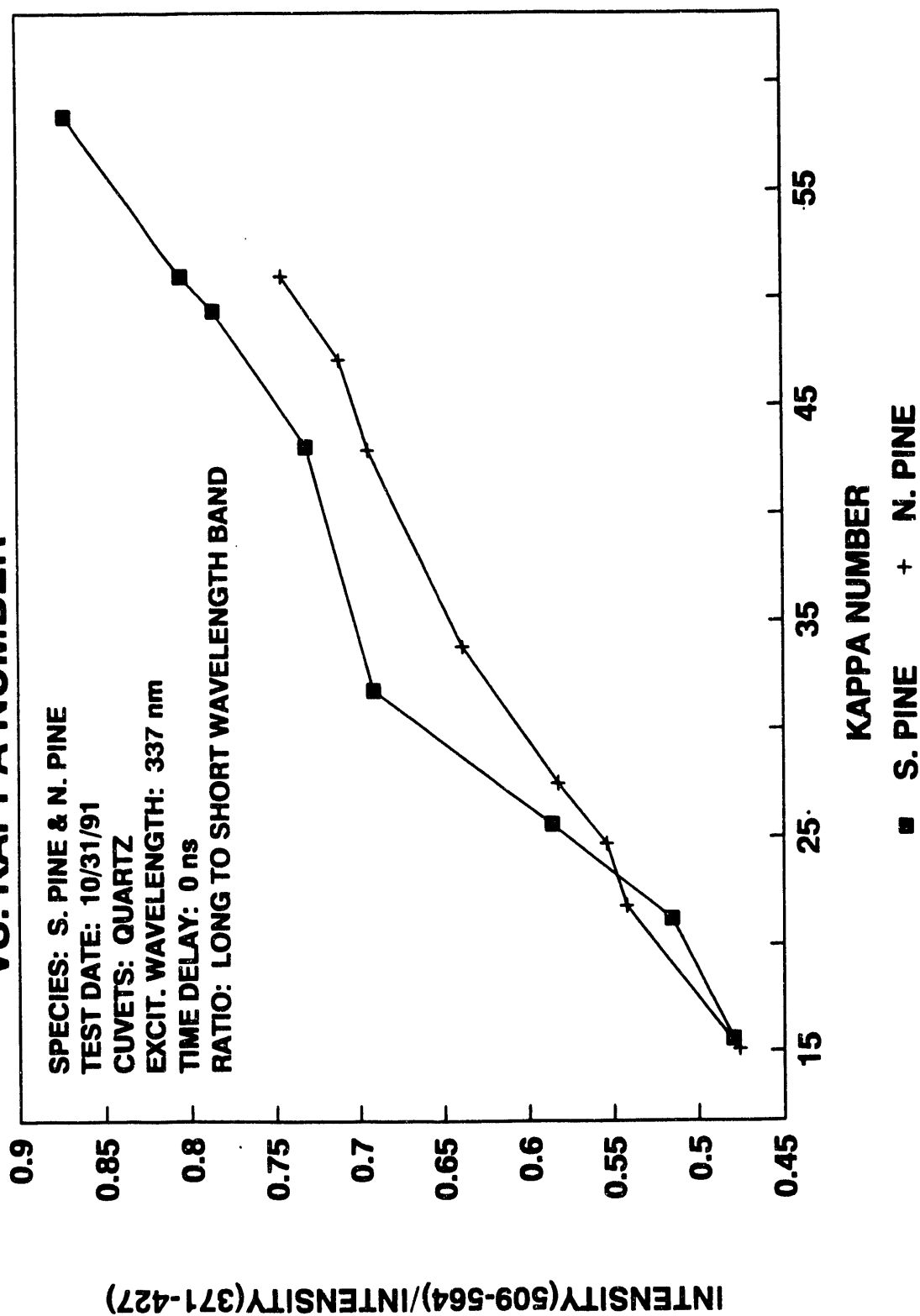
FIGURE 4-10 WAVELENGTH CENTROID VS. KAPPA NUMBER

SPECIES: S. PINE & N. PINE
TEST DATE: 10/31/91
CUVETS: QUARTZ
EXCIT. WAVELENGTH: 337 nm
TIME DELAY: 0 ns

■ S.P. FRONT   + S.P. BACK   ◇ N.P. FRONT   △ N.P. BACK
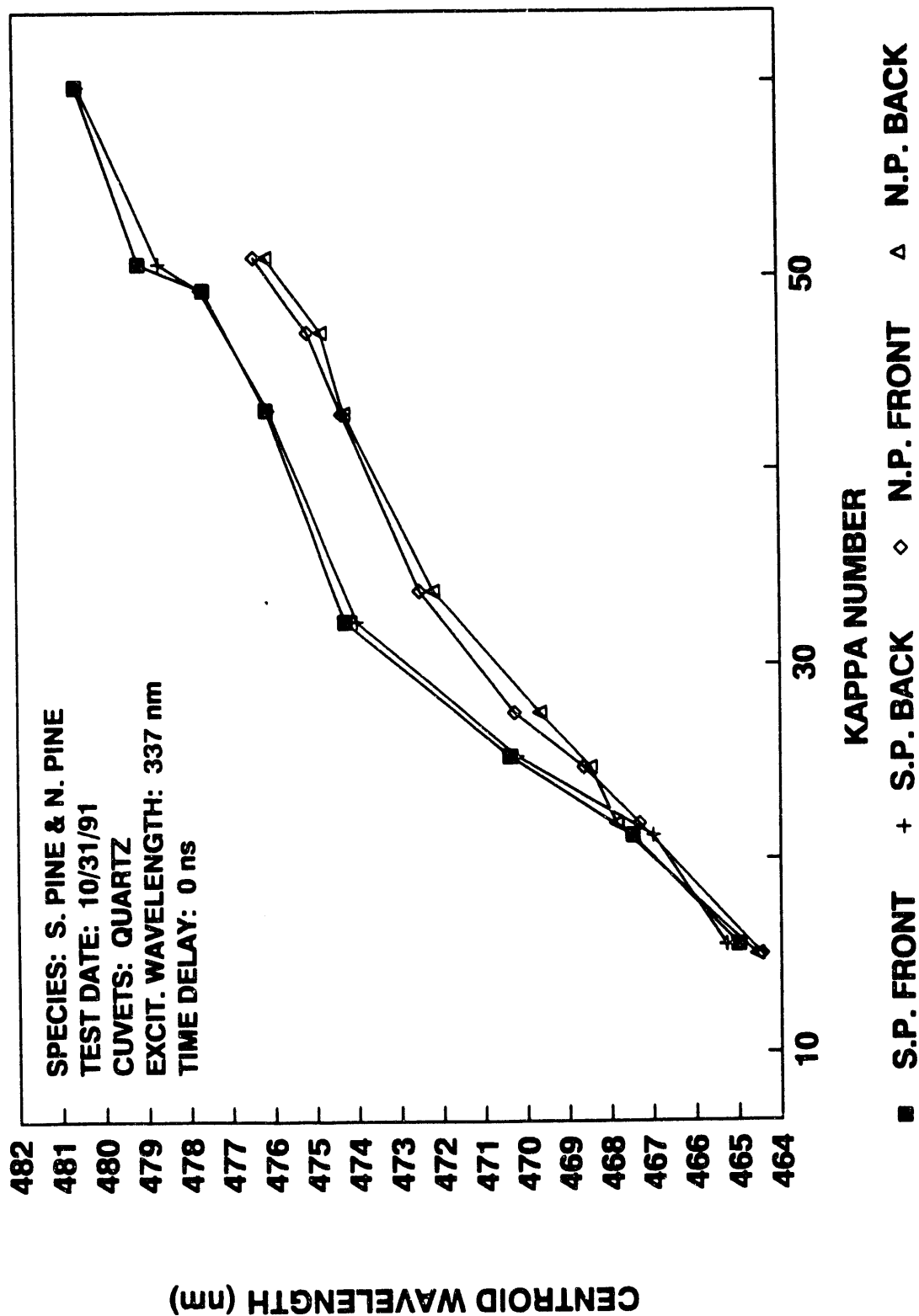
FIGURE 4-11   TEMPERATURE EFFECT ON
TOTAL FLUORESCENCE

SPECIES: S. PINE
TEST DATE: 9/5/91
CUVET: QUARTZ
S. PINE SAMPLE 1 ONLY
EXCIT. WAVELENGTH: 337 nm
TIME DELAY: 0 ns

TEMPERATURE (F)

■ S.P. SAMPLE #1 DATA   ── LINEAR REGRESSION

TOTAL FLUORESCENCE INTENSITY
(Millions)
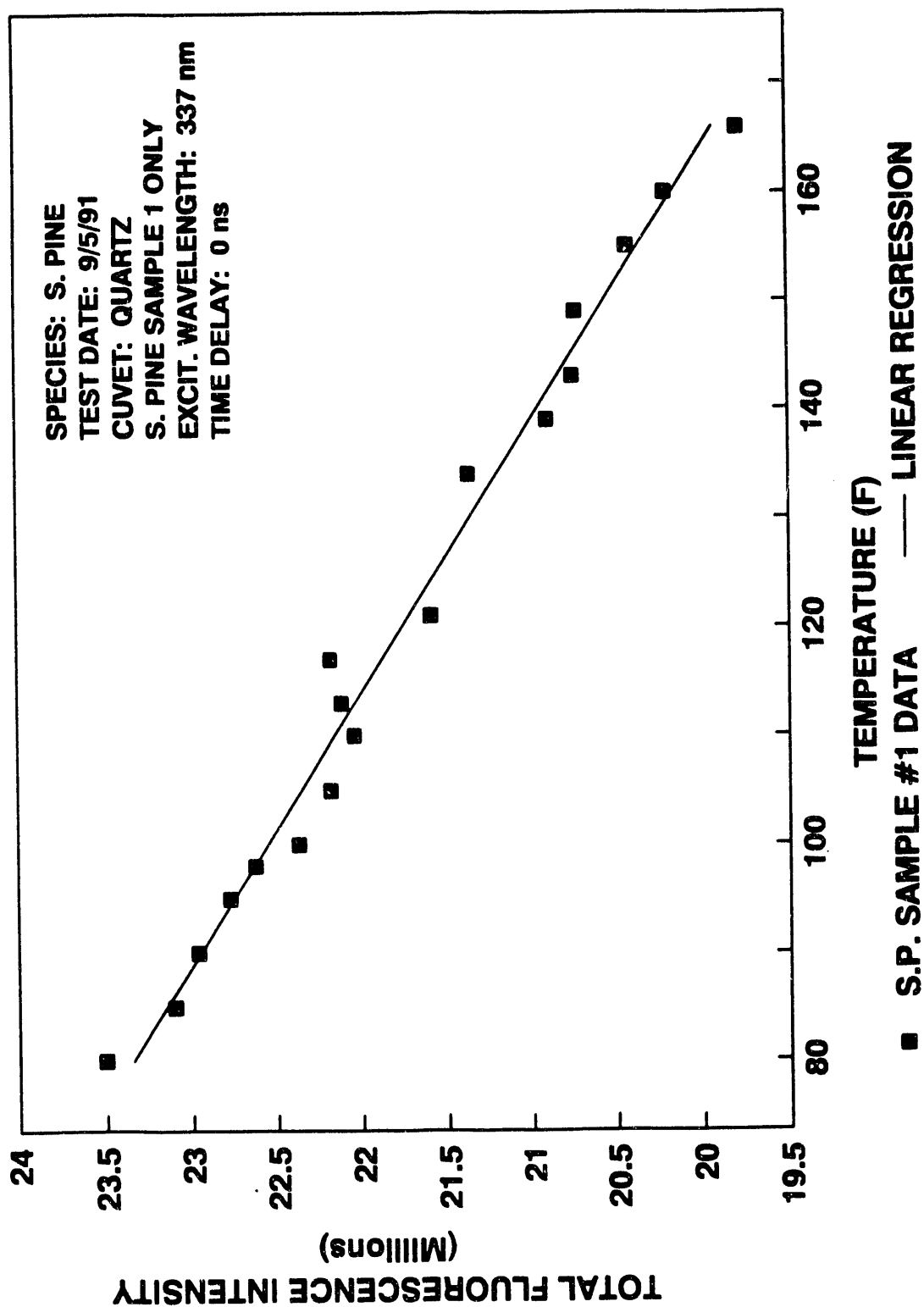
FIGURE 4-12   TEMPERATURE EFFECT ON WAVELENGTH CENTROID

SPECIES: S. PINE
TEST DATE: 9/5/9?
CUVET: QUARTZ
S. PINE SAMPLE 1 ONLY
EXCIT. WAVELENGTH: 337 nm
TIME DELAY: 0 ns

■ S.P. SAMPLE #1 DATA   —— LINEAR REGRESSION
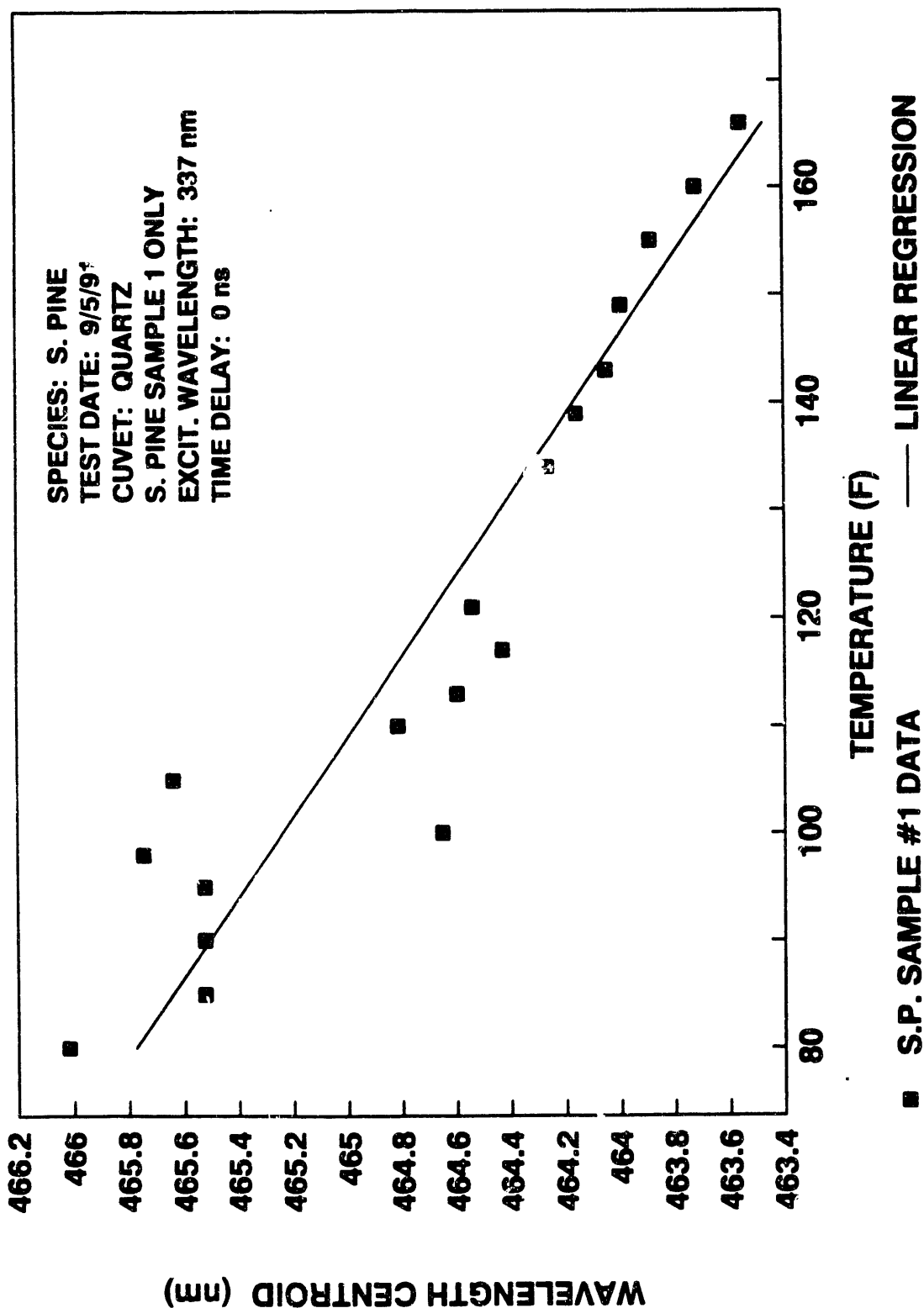
5.0 CONCLUSIONS/RECOMMENDATIONS

5.1 CONCLUSIONS

The laboratory characterization tests were undertaken to determine the source of the scatter observed in the Phase I feasibility tests and to provide the background data required for the design of a field prototype. As discussed in Section 6.8, instrumental artifacts were ruled out as a factor in the data. Nevertheless, it was found that the total fluorescence intensity is not a monotonically decreasing function of Kappa number and, therefore, not suitable as a control signal. The problem seems to be associated with the presence of an interfering species that disrupts the general downward trend of the curve.

Several of the techniques commonly used in fluorescence spectroscopy for dealing with interferants were investigated to determine if they could be used to provide a suitable control signal. These tests showed that:

- Both time and phase-resolved techniques provide discrimination against the interference, as shown in Figures 4-3 and 4-6. However, in both cases the sensitivity of the response function decreases at higher Kappa numbers. The ratio approach displayed in Figure 4-4 does improve resolution at high Kappa and results in species independence (at least for the two wood species tested). However, since these approaches are among the most complex and costly, we shall not pursue them as a first choice.

- Excitation of the fluorescence with wavelengths longer than the 337 nm nitrogen laser line results in total fluorescence vs Kappa number plots that are less monotonic than those for 337 nm excitation. This indicates that the longer wavelengths excite the fluorescence of the compound(s) not related to lignin concentration more strongly than the 337 nm excitation.

- Linear combination of the total fluorescence generated by excitation of the fluorescence with two different wavelengths (e.g., 337 nm and 442 nm) yields a response function that decreases monotonically with Kappa number (see Figure 4-8). This function could be used as a control function, although the sensitivity at high Kappa numbers is less than the sensitivity at low Kappa numbers.

- Two methods based on the Kappa number induced shift of the fluorescence spectral distribution were shown to give response functions very promising for control use. These are the "two wavelength band ratio method" shown in Figure 4-9, and the "wavelength centroid function" shown in Figure 4-10. Although both functions appear to show a dependence on wood species, they have several significant advantages over the other methods identified. Specifically:
  - instrumentally they do not require a fast gateable detector, or high-speed response detector as required by the time- and phase-resolved approaches.
  - they require excitation by only one wavelength rather than two as in the dual excitation wavelength approach.
  - they show no loss of sensitivity at higher Kappa numbers.
  - the control function 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.
  - the sensitivity of the centroid function to temperature of the pulp is only 0.07 Kappa/°F.

5.2 RECOMMENDATIONS & FUTURE WORK

The objective of the characterization tests discussed in this report was to generate the background information necessary for the design of a field testable prototype.

The information in this report was presented orally at the November 11, 1991 DOE/Industry Advanced Sensors Technical Conference.

Industry representatives recommended that the following additions to the scope of the project be carried out prior to the design of the field prototype.

- Develop laboratory test data on a wider variety of wood species.

- Investigate more fully the effect of various concentrations of black liquor on the results.

- Examine the "in-pipe" sensor applications as well as the wash-roller applications.

- Obtain pulp samples covering a greater range of Kappa numbers (3 through 100), including bleached pulps.

The characterization tests reported here have identified the wavelength centroid measurement as the preferred approach for incorporation into the field prototype. Although the wavelength centroid approach has been shown to provide a good measure of Kappa number under the conditions of our laboratory tests, the range of conditions included in the tests was limited. The four additions to the workscope enumerated above are intended to determine if the approach is applicable as the range of experimental conditions is expanded in various "dimensions".

We propose to design and conduct additional laboratory characterization studies aimed at addressing the four recommended additions. The tests will be designed to determine the range of applicability of the wavelength centroid approach.

After completion of the additional laboratory tests the remaining Phase II work will consist of the following:

- Design a prototype sensor using the "wavelength centroid function" as the primary measurement technique. The prototype will be designed using electronics and post-processing capabilities similar to those used in the laboratory tests. The prototype will include the capability of employing time-

resolution and variable wavelength excitation. Although the
results to date indicate that variable excitation and time
resolution are not needed in the instrument, the variable
excitation and time-resolved capability can be carried along
with little additional effort and would make the prototype
sensor more versatile. Once field testing is complete, some
of the capabilities of the prototype could be dropped to make
a more cost-effective production unit for the application.
The prototype will include temperature and pH measurements on-
line.

- Fabricate and debug the prototype sensor in the laboratory.

- Field test the prototype sensor at the final stage of a
  typical vacuum washer of one or more operating pulp mills.

- Conduct laboratory testing as required to support the
  prototype design and investigate questions raised during the
  field tests.

One of the reviewers of the draft version of this report
recommended laboratory testing to demonstrate the capability to
provide precision necessary for control over several narrow ranges of
kappa, e.g., 13-22, 22-40, and 80-100. While we agree that this
information is crucial to the final success of the product, we feel
that the most cost effective way to get this information is through
prototype tests at an operating mill. The test plan for the prototype
sensor will therefore address this issue.

6.0 APPARATUS

6.1 SYSTEM OVERVIEW

Figure 6-1 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 (less than 1 mm) spot on the sample.
- 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 sample is loaded into a standard cuvet (10 mm x 10 mm x 45 mm) that 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".

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 (microchanel 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 PC/AT compatible 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.

6.2 SYSTEM TIMING

As discussed above, the laser, detector gating, and readout are all synchronized. Figure 6-2 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.

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.

6.3 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 set-up 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 set-up 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 set-up 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.

6.4 ELECTRONICS

Figure 6-3 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 Hz).

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.

6.5 OPTICS

Figure 6-4 shows the layout of the optical system. The specimens (samples) are contained within standard 10 mm cuvets which mount on a precision X,Y,Z translation stage. During a standard 100 pulse data run, the laser is pulsed at a rate of 2 pulses/sec and the stepper motors provide 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 strikes the pulp at a previously unexposed point. This provides two important functions. First, it assures that the resultant data is independent of bleaching effects. Second, it distributes the exposure over an extended area to minimize the effect of localized variations in the pulp properties.

Both acrylic and quartz cuvets were employed to hold pulp specimens during fluorescence tests. The quartz cuvets were more uniform and had much less background fluorescence than the acrylic cuvets. Acrylic cuvets were used extensively during early testing for convenience in testing large numbers of samples. Since the acrylic

cuvets did introduce some aliasing and data scatter (see Section 6.9), the most critical tests were repeated using only quartz cuvets.

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$2x8 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.

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 6-4 are attached firmly to an optical breadboard.

6.6   REFLECTION TESTS

Not shown in Figures 6-1 or 6-4 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.

6.7   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 cuvets.

6.8   SYSTEM PERFORMANCE

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

- The apparatus exhibits repeatability on the order of ±5%.

- 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 that the measurements taken by exposing the front surface of the sample cuvet matched those from back surface exposure within about 5%.

- The fluorescence properties of the pulp samples remained stable over a five-month period of refrigerated storage.

- 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 cuvets used to hold the samples was negligible, being less than 0.3% of the fluorescence from the pulp samples.

- The greatest source of uncertainty in the results presented here is due to questions about the true Kappa number of the pulp samples (see Section 7.2).

6.9   FLUORESCENCE OF EMPTY CUVETS

Figure 6-5 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 6-7 (note that both the empty cuvets and the pulp filled cuvets 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 6-5 is typical of the majority of all cuvets used. Many hundreds of acrylic cuvets were used in the course of the test program and approximately 30 empty cuvets were tested at random during the course of the program. Until August of 1991, all empty cuvets tested displayed fluorescence spectra nearly identical to that shown in Figure 6-5. In August 1991, during the pH test series, tests on six empty acrylic cuvets from a cuvet carton of 50 were tested. The results of these tests are presented in Figure 6-6. As can be seen, three of the cuvets produced spectra nearly identical to that shown on Figure 6-5, while the others displayed significantly different spectra (significantly higher in intensity and shape). The pH testing had already been completed on acrylic filled cuvets and was not repeated. The peak intensity from the "worst" empty cuvet in Figure 6-6 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 cuvets.
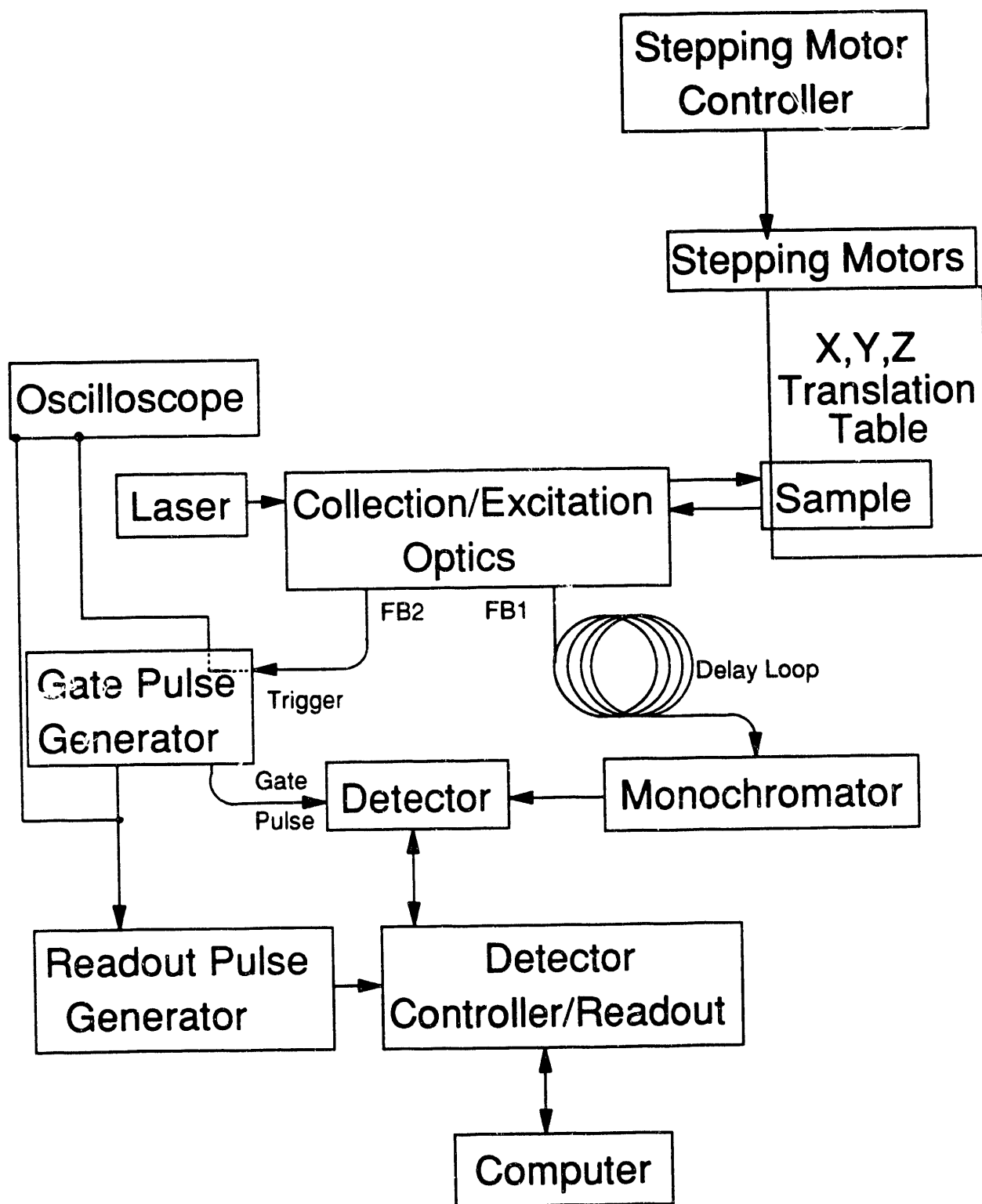
Figure 6-1. Block Diagram of Fluorescence Spectroscopy System

Laser Pulse

Fluorescence Pulse

Gate Pulse

Variable Pulse Width (10-2000 nS)

Variable Pulse Start
20 to 1700 nS After Trigger

Arrival of Fluorescence
at Detector

Detector Readout Trigger
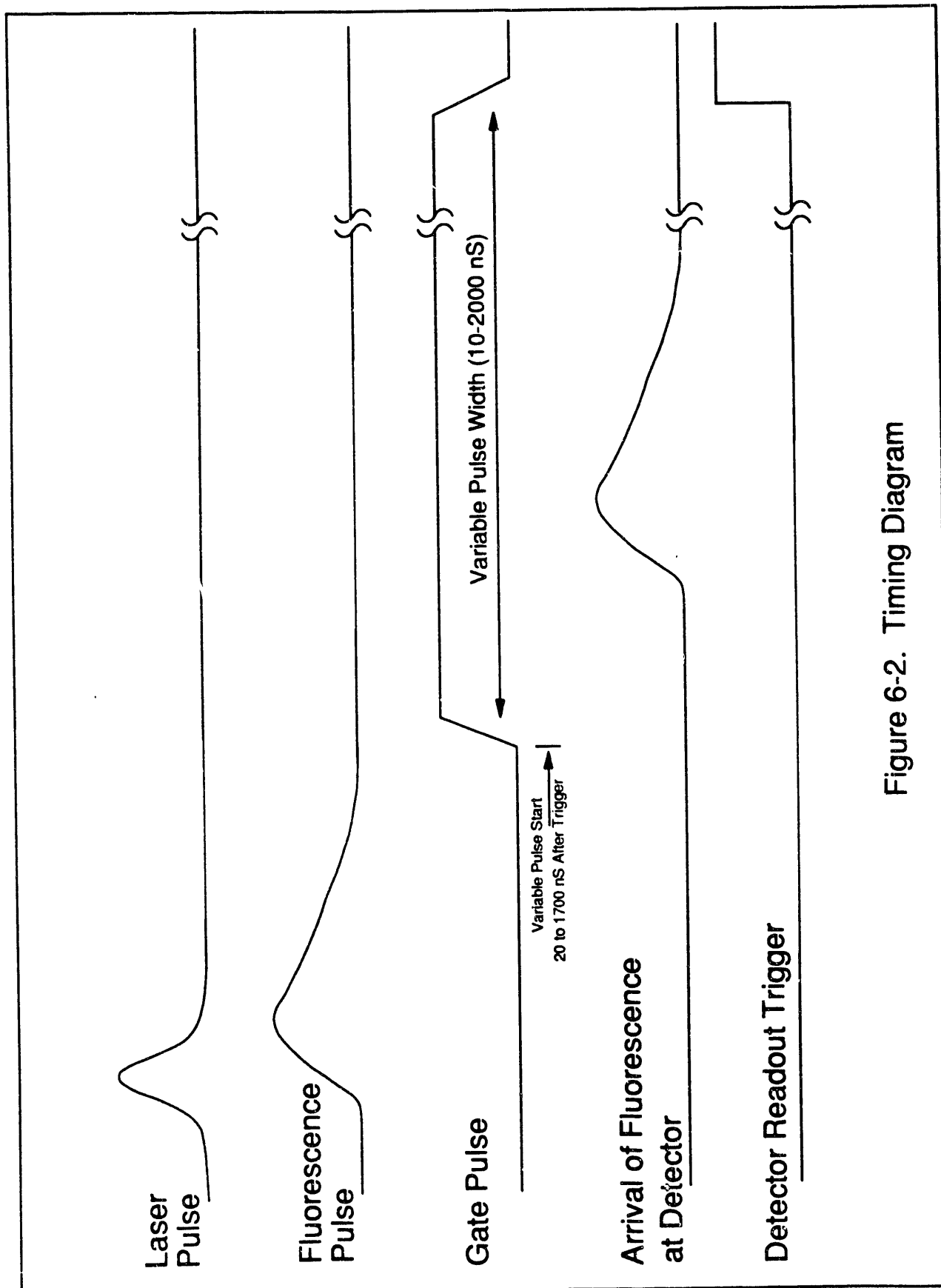
Figure 6-2. Timing Diagram
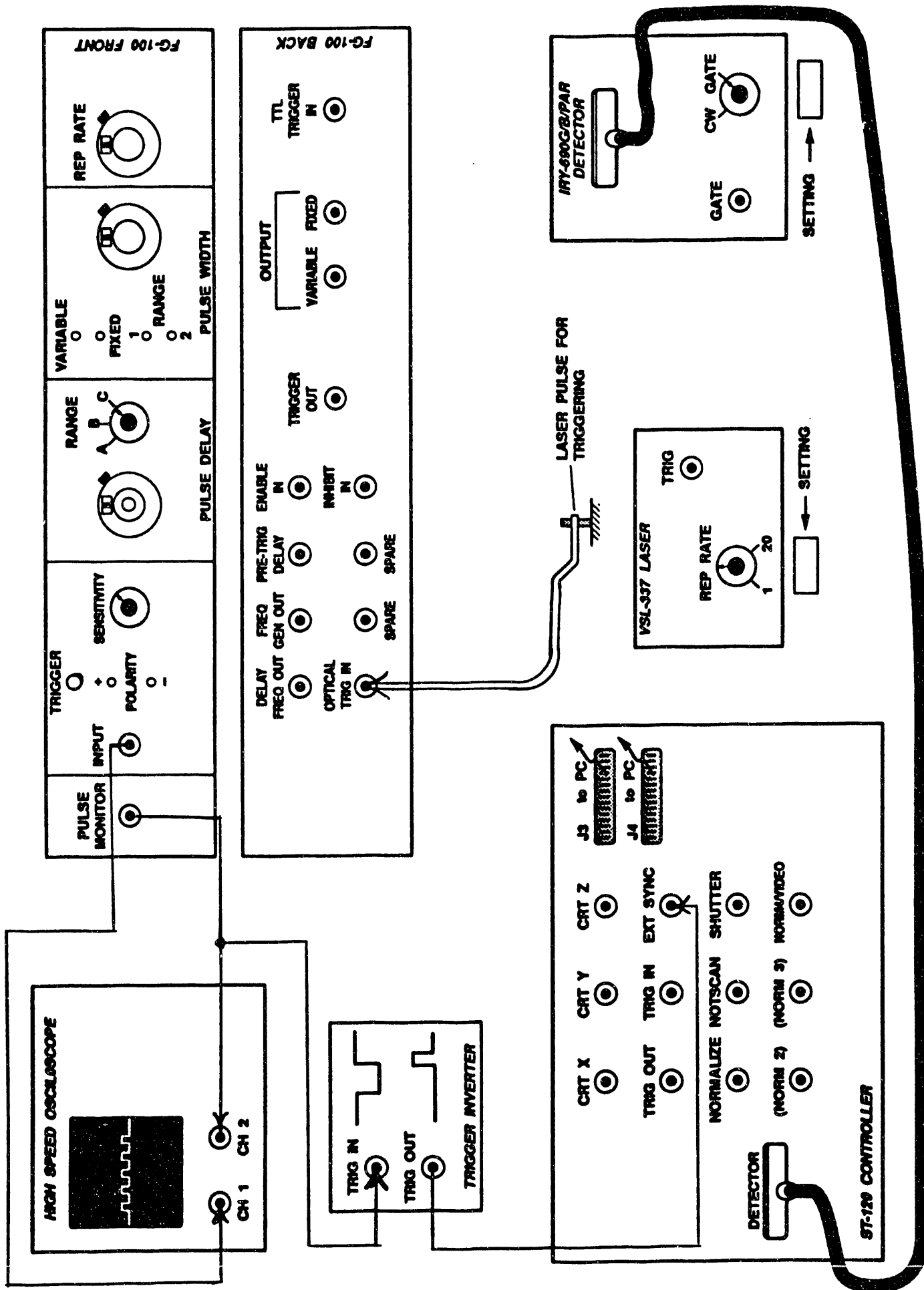
Figure 6-3   Interconnection of Electronics
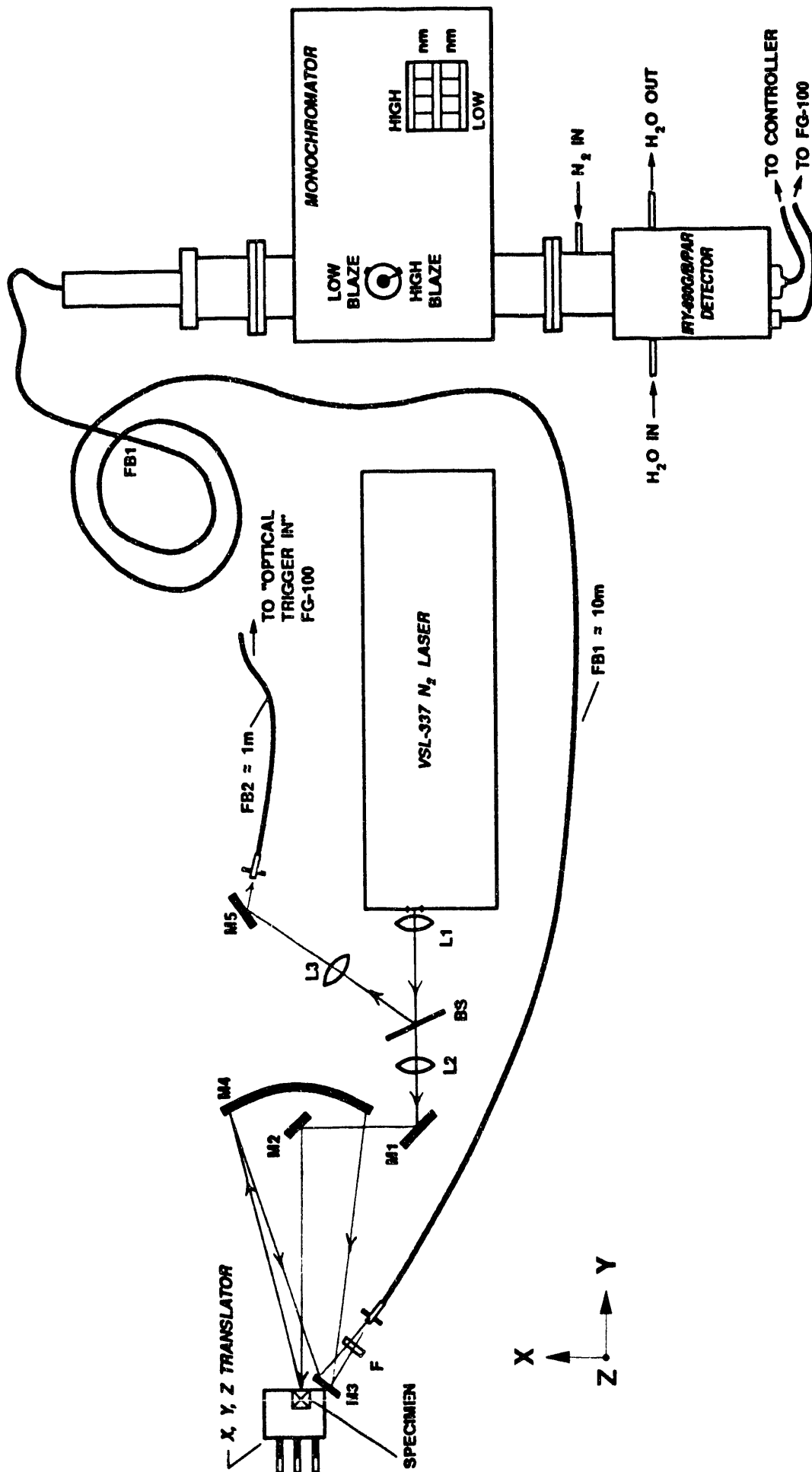
Figure 6-4   Optical System Layout

6-13

FIGURE 6-5
TYPICAL FLUORESCENCE FROM QUARTZ AND ACRYLIC CUVETS

EMPTY CUVETS
TEST DATE: 9/4/91
CUVETS: QUARTZ AND
        FISHER ACRYLIC

EXCIT. WAVELENGTH: 337 nm
TIME DELAY: 0 ns

ACRYLIC CUVET

QUARTZ CUVET

FLUORESCENCE INTENSITY
(Thousands)

DIODE NUMBER
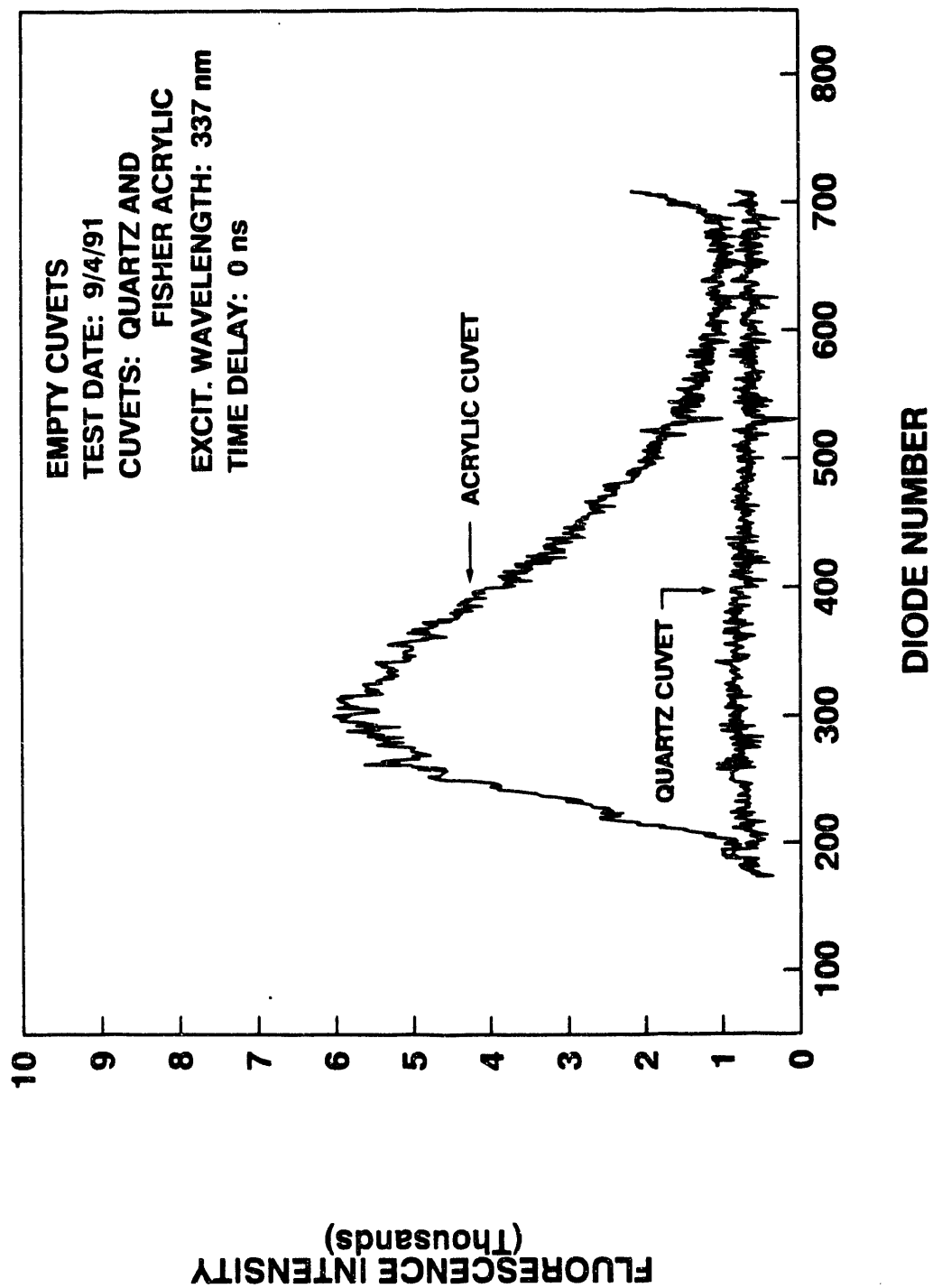
FIGURE 6-6

FLUORESCENCE OF SIX DIFFERENT EMPTY ACRYLIC CUVETS

EMPTY CUVETS
TEST DATE: 9/4/91
CUVETS: FISHER ACRYLIC
EXCIT. WAVELENGTH: 337 nm
TIME DELAY: 0 ns
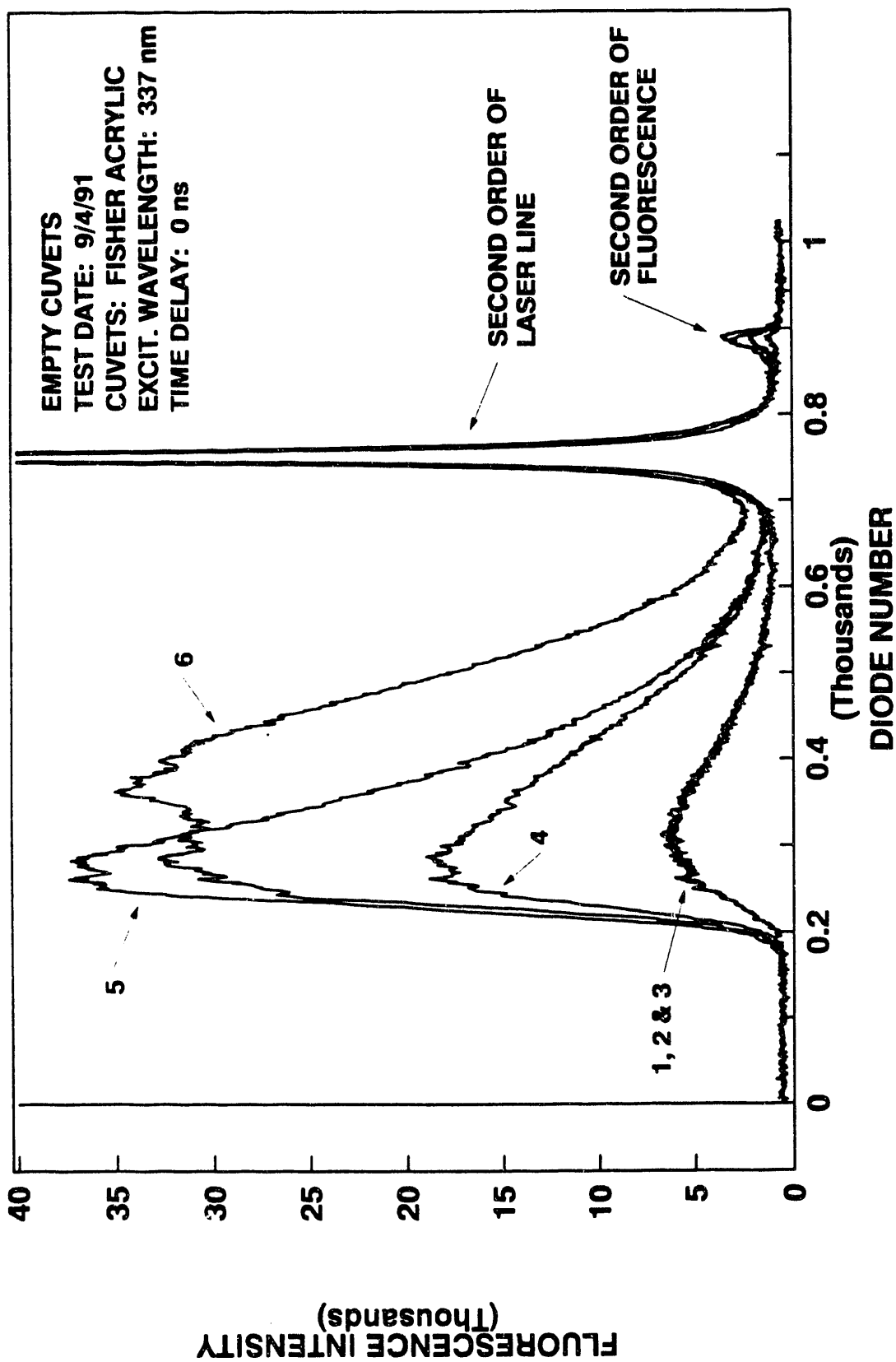
FIGURE 6-7   FLUORESCENCE OF S. PINE SAMPLE #1
IN ACRYLIC CUVET

SPECIES: S. PINE
(SAMPLE #1)
TEST DATE: 9/4/91
CUVET: FISHER ACRYLIC
EXCIT. WAVELENGTH: 337 nm
TIME DELAY: 0 ns

SECOND ORDER OF
337 nm LASER

FLUORESCENCE INTENSITY
(Thousands)

150
140
130
120
110
100
90
80
70
60
50
40
30
20
10
0

0   0.2   0.4   0.6   0.8   1

(Thousands)
DIODE NUMBER
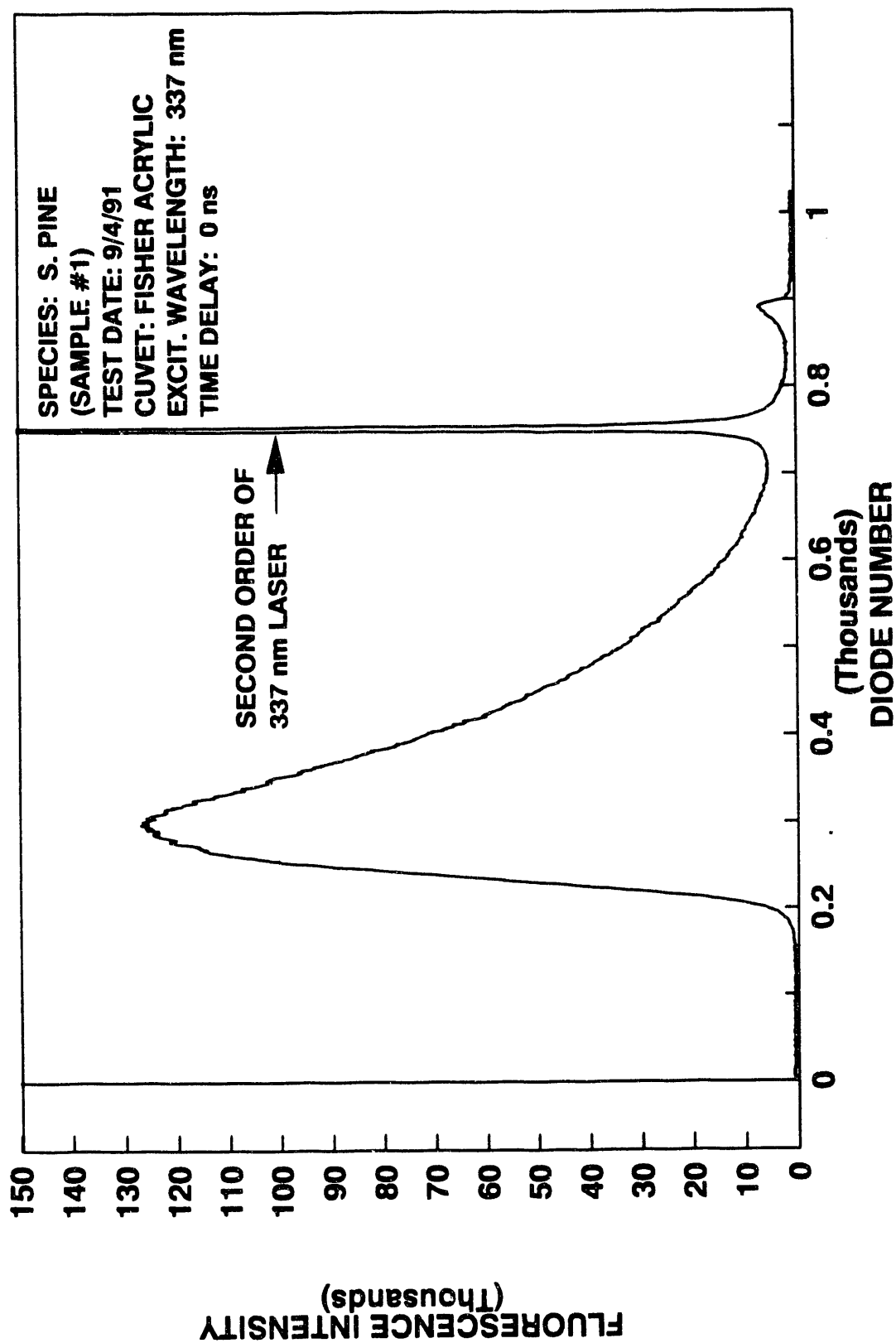
7.0 PREPARATION AND TESTING OF PULP SAMPLES

7.1 PULP PROCUREMENT

A homogeneous set of wood chips from two wood species (southern pine and northern pine) were procured and digested to varying degrees in laboratory digesters at Miami University in Oxford, Ohio. Eight cooks of each species were prepared with the objective of obtaining pulp samples with Kappa numbers ranging from 15 through 50. All cooks of each species were made with identical chemical charge but with varying time and temperature to achieve the different Kappa numbers.

After digesting, the samples were washed, screened, and refrigerated. In the case of the southern pine samples, all of the pulp was washed and screened. In the case of the northern pine samples, approximately a third of the pulp was kept in the condition as it exited the digester, a third was washed, and a third was washed and screened. Samples of the black liquor exiting the digester were also obtained and kept for future use.

The southern pine samples were digested in September 1990 while the northern pine samples were digested in June 1991.

7.2 KAPPA NUMBER TESTING ON SAMPLES

At the time each species was digested, 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

7-1

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. This led to the conclusion that the procedures used by the two labs were not compatible and that one, or both, of the lab results were in error. At the time of the writing of this report, both labs have been asked to collaborate to determine the cause of the discrepancy and are conducting further tests.

The northern pine pulp samples were tested in quadruplicate for Kappa number by Miami University at the time that the pulp was digested. No independent Kappa number tests were conducted. The results of the Kappa number testing on southern pine pulp are:

SOUTHERN PINE AVERAGE KAPPA NUMBER

	LAB	MIAMI	MIAMI	IPST
	DATE	09/90	05/91	04/91
SAMPLE NUMBER	# OF TRIALS:	3	3	2
1		13.9	14.0	15.6
2		19.6	18.1	21.2
3		24.3	21.7	25.6
4		28.8	26.9	31.9
5		35.1	34.8	43.1
6		39.6	37.3	49.5
7		46.2	44.4	51.0
8		51.6	46.4	58.5

The plot of this average data is presented in Figure 7-1 and the individual trial data is presented in Figures 7-2 and 7-3.

At the time of this writing, Miami University and IPST are attempting to resolve the differences in the Kappa number test results.

The results of the Kappa number testing on northern pine pulp are:

NORTHERN PINE AVERAGE KAPPA NUMBER

	LAB	MIAMI
	DATE	06/91
SAMPLE NUMBER	# OF TRIALS	4
1		15.1
2		21.8
3		24.7
4		27.7
5		33.8
6		42.9
7		47.1
8		51.0

A plot of the data from the four individual trials, whose average is shown above, is presented in Figure 7-4.

7.3 KLASON LIGNIN TESTS

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 being 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.

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

	LAB	IPST	IPST	IPST
	DATE	04/91	04/91	04/91
	# OF TRIALS	1	1	2
	TYPE	KLASON	EQUIV.KLASON	KAPPA
SAMPLE NUMBER	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

A plot of this data is presented in Figure 7-5. 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.

7.4 PULP pH TESTING

The pH of lignin has been demonstrated to affect the absorbance spectra of ultraviolet light [18]. Since fluorescence is a direct result of the absorption of ultraviolet light, all pulp samples were tested in accordance with TAPPI 252 om-90, for pH at 25°C. the results of that testing are:

SPECIES	SAMPLE	pH
S PINE	1	9.12
S PINE	2	9.04
S PINE	3	9.05
S PINE	4	8.94
S PINE	5	8.28
S PINE	6	8.71
S PINE	7	8.91
S PINE	8	8.91
N PINE	1	7.95
N PINE	2	7.72
N PINE	3	7.93
N PINE	4	8.34
N PINE	5	8.32
N PINE	6	8.16
N PINE	7	7.87
N PINE	8	7.85

A plot of this data is shown in Figure 7-6.

7.5 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 PINE	8	1	1.54
N PINE	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 range of wavelengths of interest (250 nm - 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 one 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.

FIGURE 7-1 COMPARISON OF MIAMI UNIVERSITY AND IPST MEASUREMENTS OF KAPPA NUMBER ON SOUTHERN PINE SAMPLES

SPECIES: S. PINE
TEST DATES: 9/90, 4/91, 5/91
MIAMI 9/90: AVG. OF 3 SPECIMENS
MIAMI 5/91: AVG. OF 3 SPECIMENS
IPST 4/91: AVG. OF 2 SPECIMENS

■ MIAMI 9/90   + MIAMI 5/91   ◇ IPST 4/91
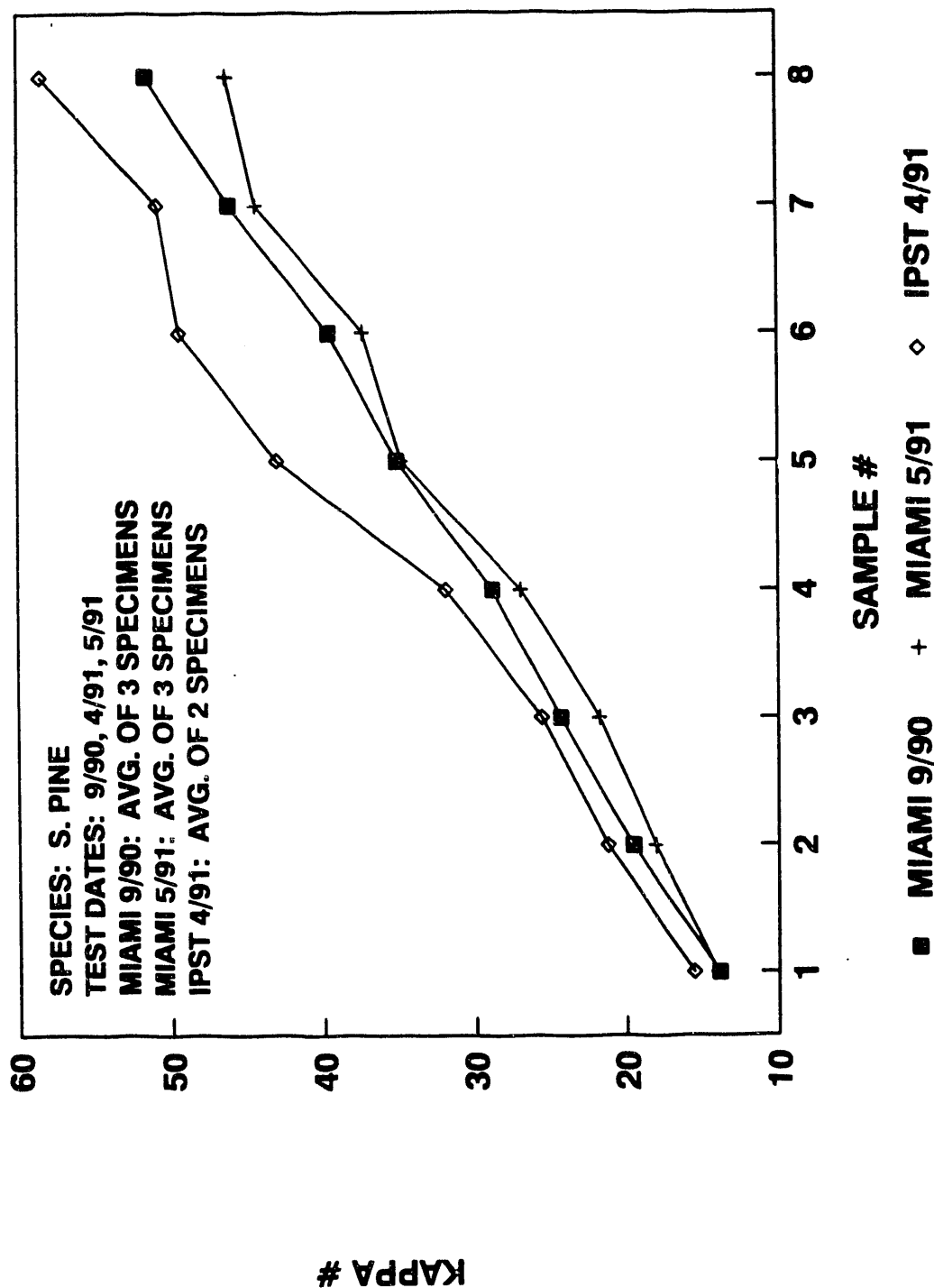
FIGURE 7-2   RESULTS OF INDIVIDUAL S. PINE
               KAPPA TESTS AT IPST

SPECIES: S. PINE
IPST TEST RESULTS, 4/91

KAPPA #

SAMPLE #

■ 4/91-TRIAL 1   +   4/91-TRIAL 2
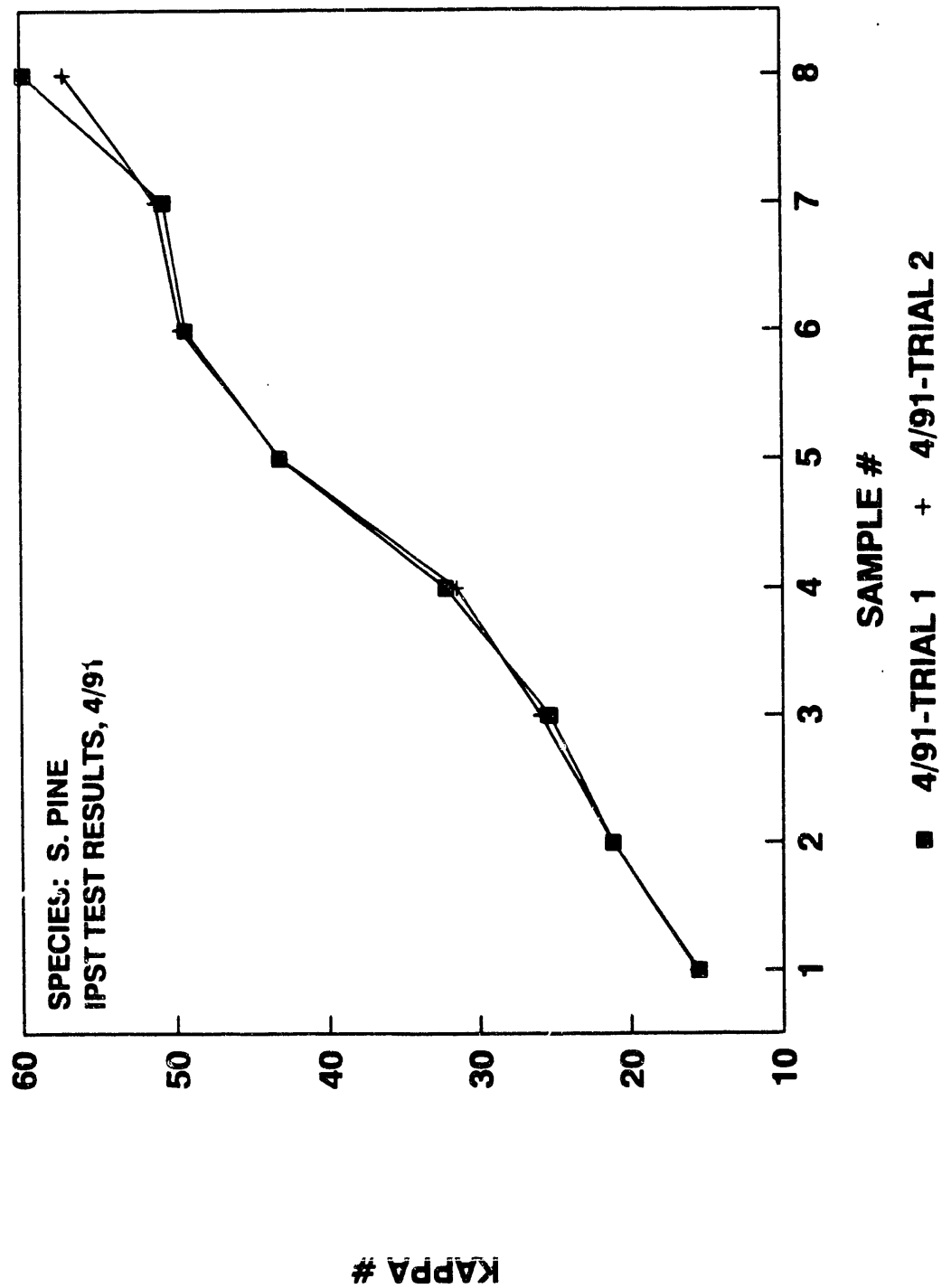
FIGURE 7-3   RESULTS OF INDIVIDUAL S. PINE KAPPA TESTS AT MIAMI UNIVERSITY

SPECIES: S. PINE
MIAMI TEST RESULTS 9/90 & 5/91

KAPPA #

SAMPLE #

■ 9/90-1   + 9/90-2   ◇ 9/90-3   △ 5/91-1   × 5/91-2   ▽ 5/91-3
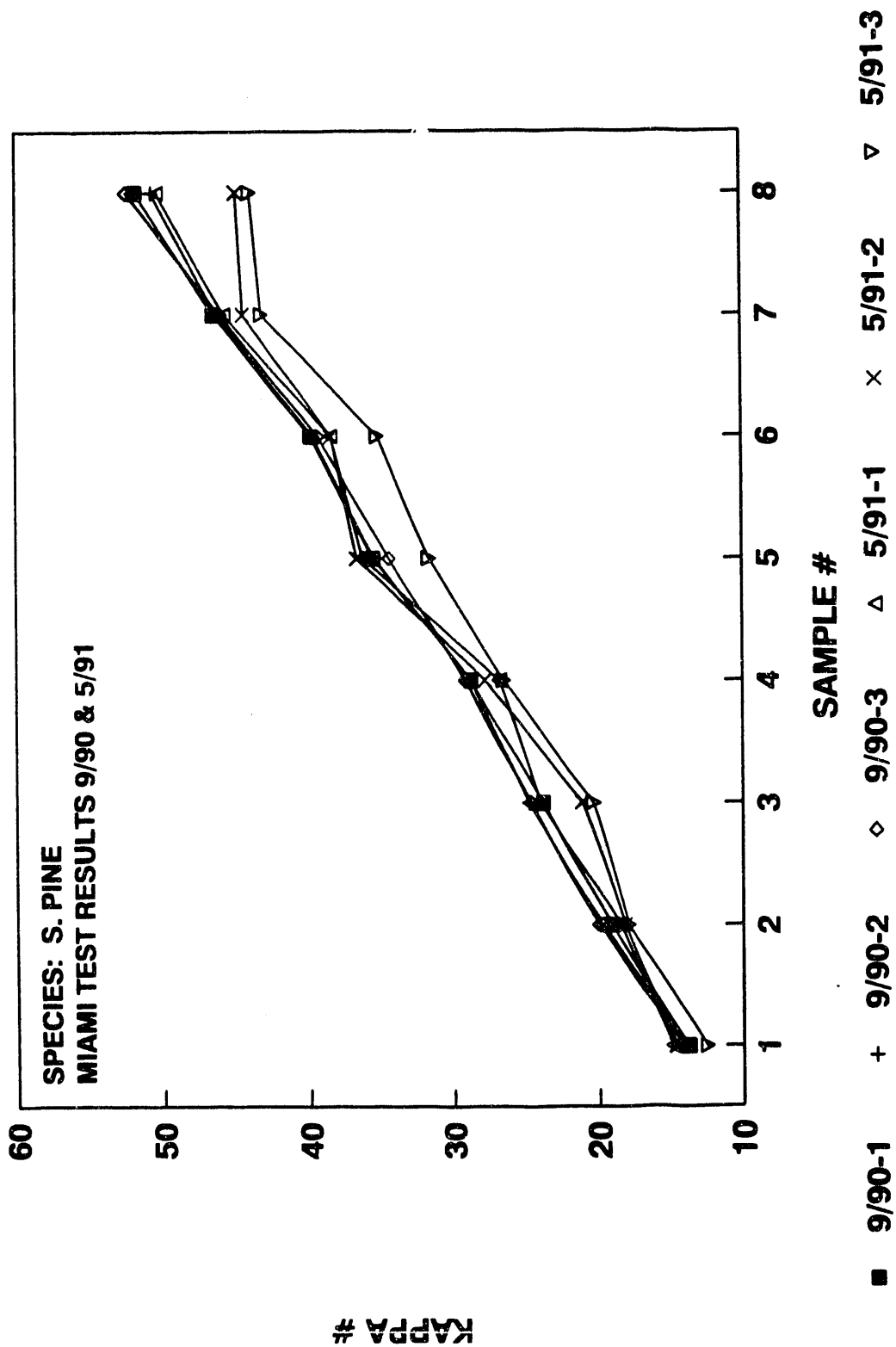
FIGURE 7-4   RESULTS OF INDIVIDUAL N. PINE KAPPA
TESTS AT MIAMI UNIVERSITY

SPECIES: N. PINE
MIAMI TEST RESULTS

KAPPA NUMBER

SAMPLE NUMBER

■ TRIAL 1   +   TRIAL 2   ◇   TRIAL 3   △   TRIAL 4
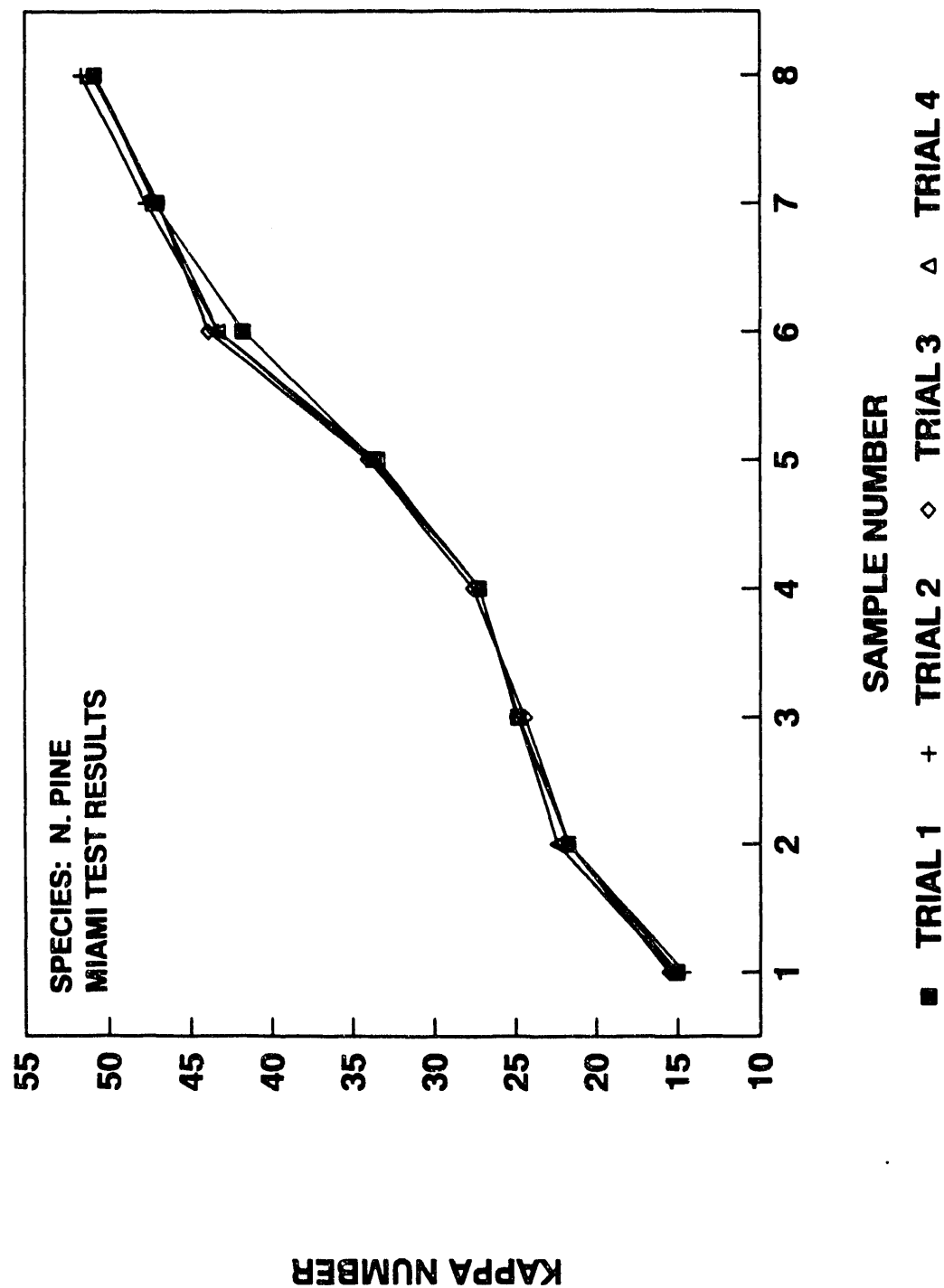
FIGURE 7-5   COMPARISON OF KLASSON LIGNIN MEASUREMENTS TO KAPPA NUMBER MEASUREMENTS OF LIGNIN

SPECIES: S. PINE
IPST TEST RESULTS

IPST KLASSON LIGNIN   IPST KAPPA*0.15

IPST KAPPA NUMBER

% LIGNIN
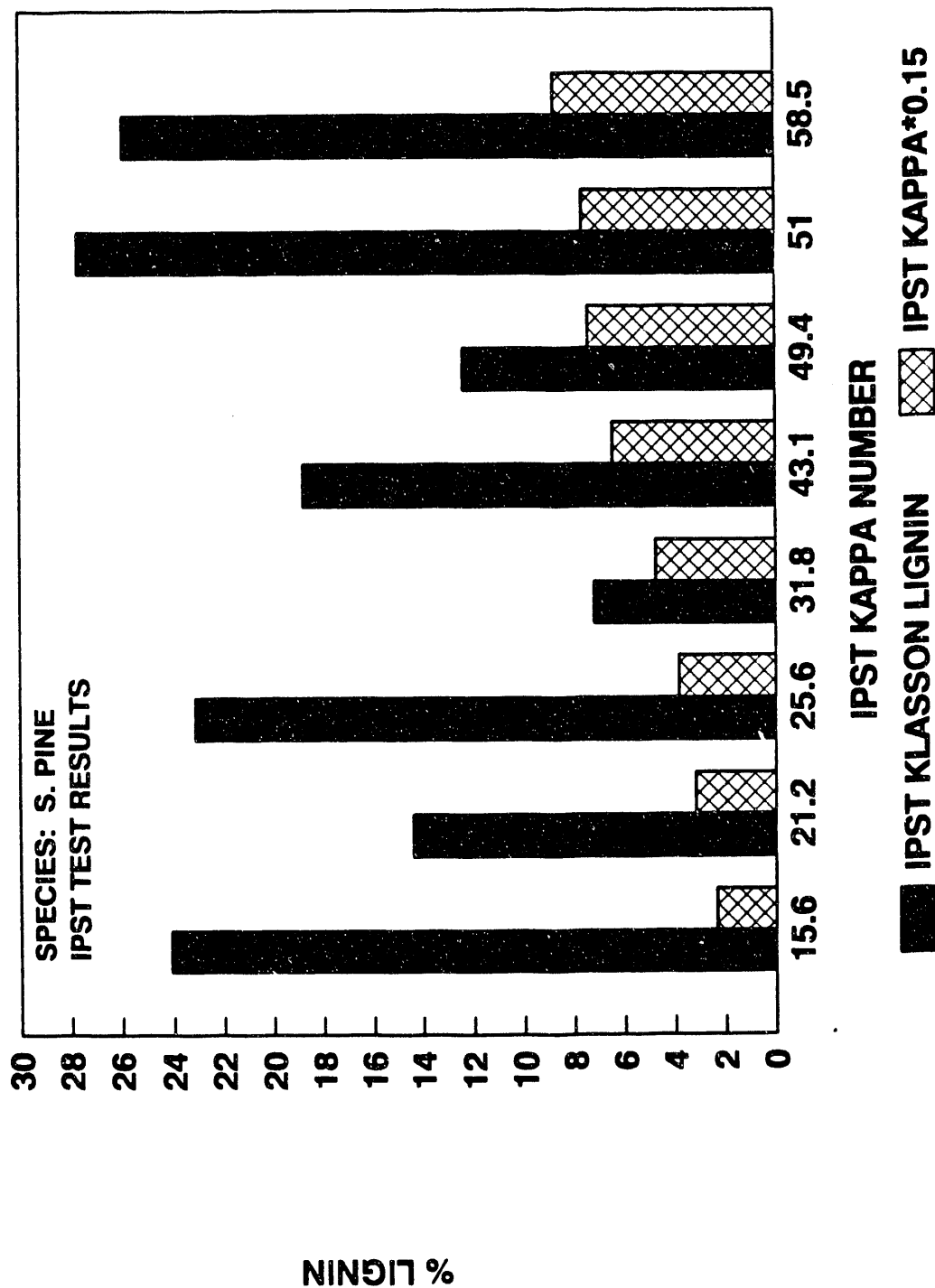
FIGURE 7-6   pH OF PULP SAMPLES PER TAPPI T252

SPECIES: S. PINE & N. PINE
TEST TEMP: 25°C

SAMPLE NUMBER
■ S PINE   + N PINE
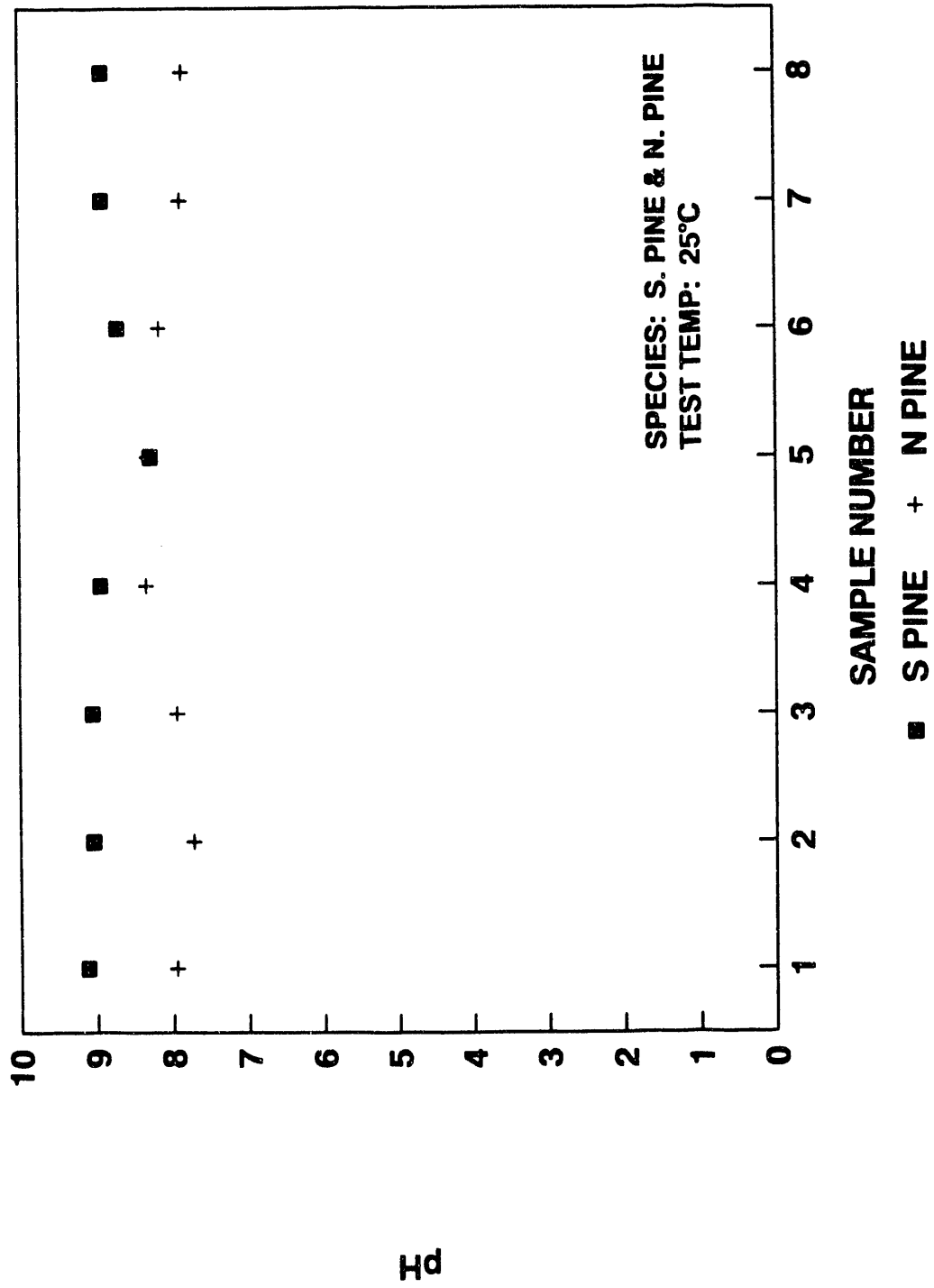
8.0 ANALYSIS

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 range, $\Delta\lambda$. Figure 8-1 shows typical
1024 element spectra. 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 of the form shown in Figure 8-1. Using a discharge lamp
with a series of narrow spectral lines of known wavelength the system
was calibrated so that the data could be presented as shown in Figure
8-2, in terms of the wavelength spectrum rather than diode number.
The shape of the spectra shown in Figures 8-1 and 8-2 are distorted by
the response of the optics and the sensitivity of the detector to
wavelength. The optical transmission of some major optical and
electronics components is shown in Figure 8-3.

Most of the results presented in Section 4.0 are given in terms
of the total fluorescence intensity rather than the spectral
distribution. The total fluorescence intensity, F_T, can be calculated
from the raw data using the formula

$$F_T = \sum_{n=1}^{1024} F_n \qquad (8-1)$$

A C language program with Fortran calls was written to facilitate
the reduction/manipulation of the raw data. This analysis program
allows the user to designate which stored files are to be analyzed and
to select four ranges over which to sum the values of F_n. Once these
are specified the computation is performed and the results of the
analysis are stored in a LOTUS 1-2-3 compatible file. Table 8-1 shows
the first few rows of an analysis file.

Table 8-1. Format of Analysis File Output

FILE TIMERES.WK1   ON DISK 103191-02
TIME RESOLVED FLUORESCENCE ON S. PINE AND N. PINE
EXCITATION = 337 NM
ALL PULP SAMPLES IN QUARTZ CUVETS

FILE NAME	MONTH	DAY	HOUR	MINUTE	SPECIES	SURFACE	SAMPLE	DELAY	CENTROID OF DIODES 173-708	PEAK INTENSITY BETWEEN DIODES 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
AF1A00	10	31	14	38	SP	F	1	00	370.6	543263	20922	1.1E+08	11090198	395460
AF1B00	10	31	14	40	SP	F	3	00	373.7	353379	11505	72881067	7215069	287984
AF1C00	10	31	14	41	SP	F	3	00	379.6	266846	7745	57503628	5504259	273201

The six-character file name was encoded so that the analysis program could interpret the experimental conditions. The code is given below:

- Character 1: specifies the excitation wavelength.
  A = 337 nm, B = 442 nm, C = 488 nm

- Character 2: is either F or B indicating exposure of the front or back surface of the cuvet. Since the excitation light is completely absorbed very near the surface, the front and back of the cuvets represent two independent samples which provides a convenient way to determine the sample to sample repeatability and therefore gage the representativeness of the measurement procedure.

- Character 3: is 1 or 2 for a regular spectral fluorescence test, 3 for a bleaching test, and 4 for a reflection test. In the regular fluorescence tests, the sample is raster scanned so that the 90 laser pulses constituting the total exposure are spread over an extended area with no overlap. This assures that the results are independent of bleaching effects. The 1 or 2 in the third file name digit merely indicates two different scanned areas.

- Character 4: designates the pulp sample. A thru H correspond to southern pine samples 1 thru 8, respectively; while I thru P indicate northern pine samples 1 thru 8.

- Characters 5&6: indicate the gate delay time in nsec.

Note that special tests, e.g. tests on pH samples, use a slightly different code.

The last six columns shown in Table 8-1 are derived from calculations made during the analysis.

The column titled Centroid of Diodes gives the results of the calculation.

$$C \equiv \frac{\sum_{n=173}^{708} \lambda_n F_n}{\sum_{n=173}^{708} F_n} \qquad (8-2)$$

where F_n is the measured response for the nth diode and λ_n is the wavelength corresponding to the nth diode.

The limits of the summation (integration) can be selected in the analysis program prior to the calculation. The limits shown in Equation 8-2 were chosen to include the total range over which significant fluorescence occurs. Above and below these limits the readings are dominated by electronic noise and scattered light.

The second calculation column indicates the highest single diode reading found between the specified limits.

The third calculation column gives the results of the calculation

$$A_1 = \sum_{n=25}^{140} F_n \qquad (8-3)$$

The range (25 to 140) includes only unintensified diodes and the resultant A_1 is due strictly to "dark-current" electronic noise. This information is used to correct the fluorescence data for electronic noise. In fact, the data acquisition program provides first order correction for noise by automatically subtracting a stored noise spectrum from the measured data before storing the result to the data file. The purpose of the additional correction supplied by the Equation 8-3 calculation is to correct for any slow drift of the dark-noise that might occur during an extended testing period.

The average noise per diode, d, is calculated from the measured A_1 and used in the calculation of the last three data columns shown in Table 8-1. The formula used is

$$A_i = \sum_{n=a}^{b} \left(F_n - d\right) \tag{8-4}$$

where i = 2, 3, or 4, and a & b are summation limits that are specified prior to the analysis.

In Section 4, the results reported as total fluorescence intensity are the results of integration over the range from diode 173 to 708 which, as mentioned above, is the range over which all significant fluorescence occurs. The results of summation over this range are the same as the summation over the entire range (1 to 1024) indicated in Equation 8-1 except for the additional noise included in the Equation 8-1 calculation.

FIGURE 8-1

TYPICAL RAW DATA PLOT:
COUNTS VS. DIODE NUMBER

SPECIES: S. PINE
TEST DATE: 10/31/91
CUVETS: QUARTZ
EXCIT. WAVELENGTH: 337 nm
TIME DELAY: 0 ns

SAMPLE 1

SAMPLE 2

SAMPLE 6

DIODE NUMBER

FLUORESCENCE INTENSITY
(Thousands)
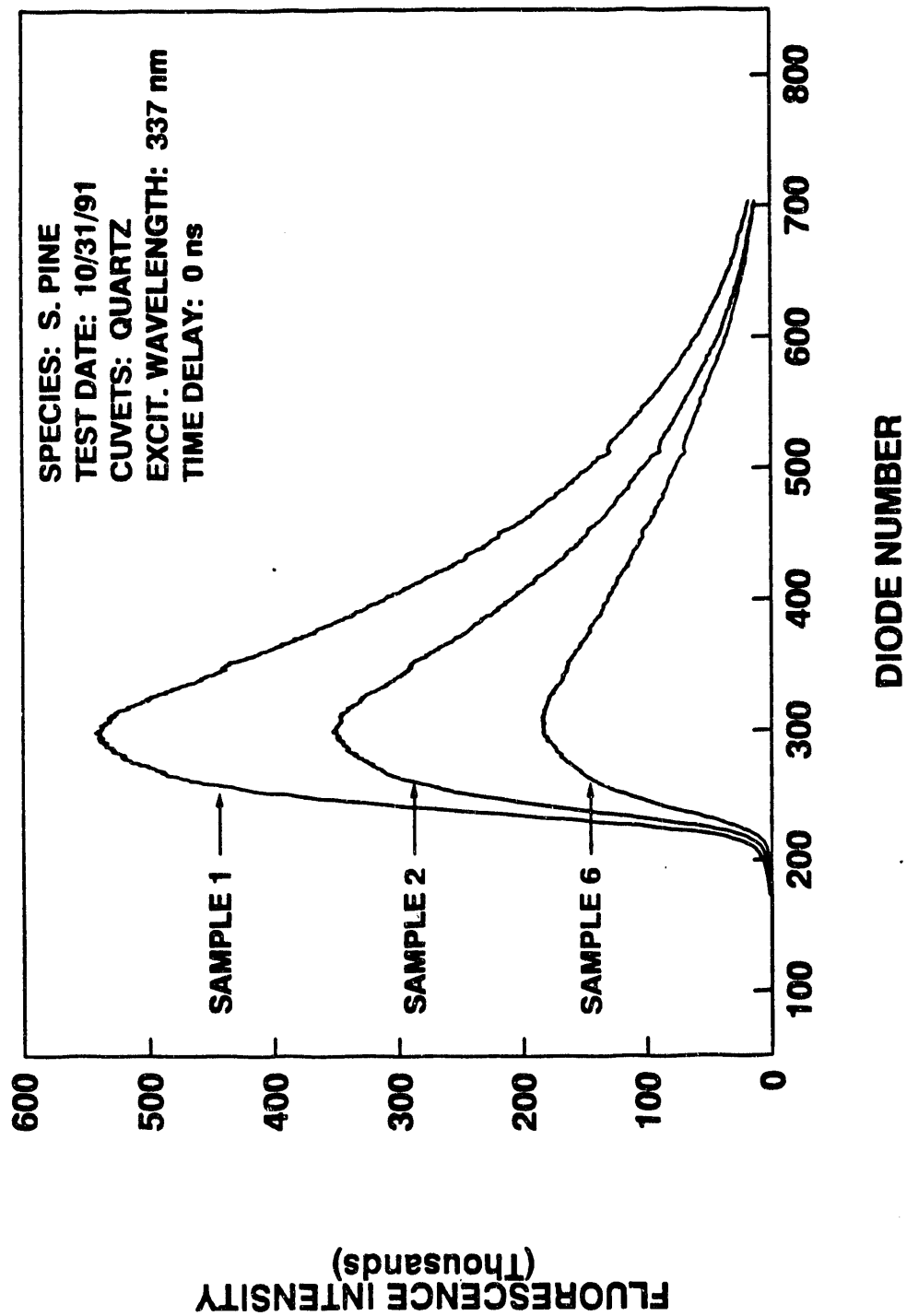
FIGURE 8-2

RAW DATA PLOT WITH CALIBRATED WAVELENGTH SCALE

SPECIES: S. PINE
TEST DATE: 10/31/91
CUVETS: QUARTZ
EXCIT. WAVELENGTH: 337 nm
TIME DELAY: 0 ns

SAMPLE 1
SAMPLE 2
SAMPLE 6

FLUORESCENCE INTENSITY (Thousands)

WAVELENGTH (nm)
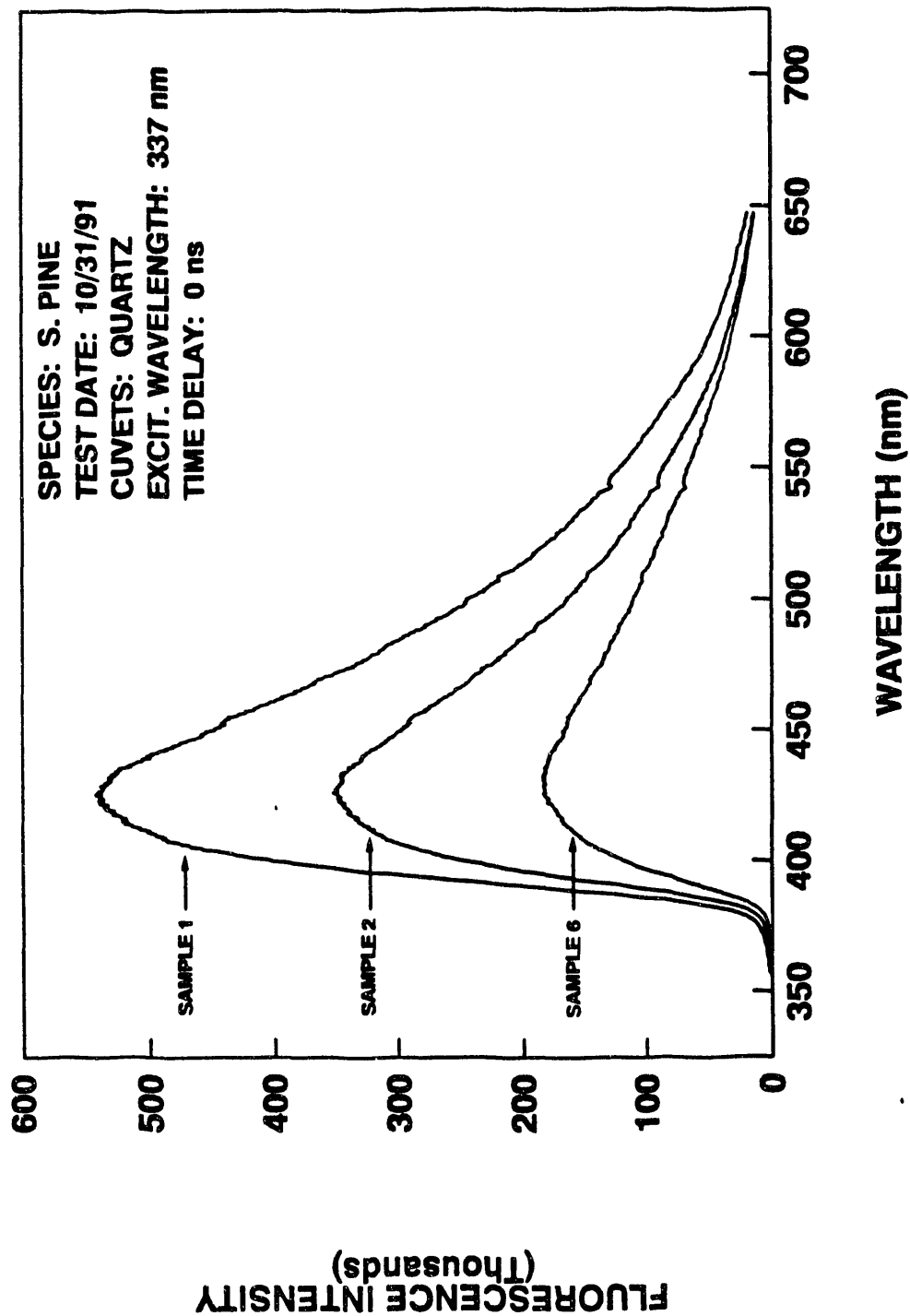
FIGURE 8-3

SENSITIVITY / TRANSMISSION CURVE OF LAB SETUP - DETECTOR, GRATING & FILTER

NORMAL SENSITIVITY OR TRANSMISSION

WAVELENGTH (nm)

■ DETECTOR SENSITIVITY   + 500 nm BLAZE GRATING   ◇ 380 nm LP FILTER TRANSMISSION   △ ALL THREE
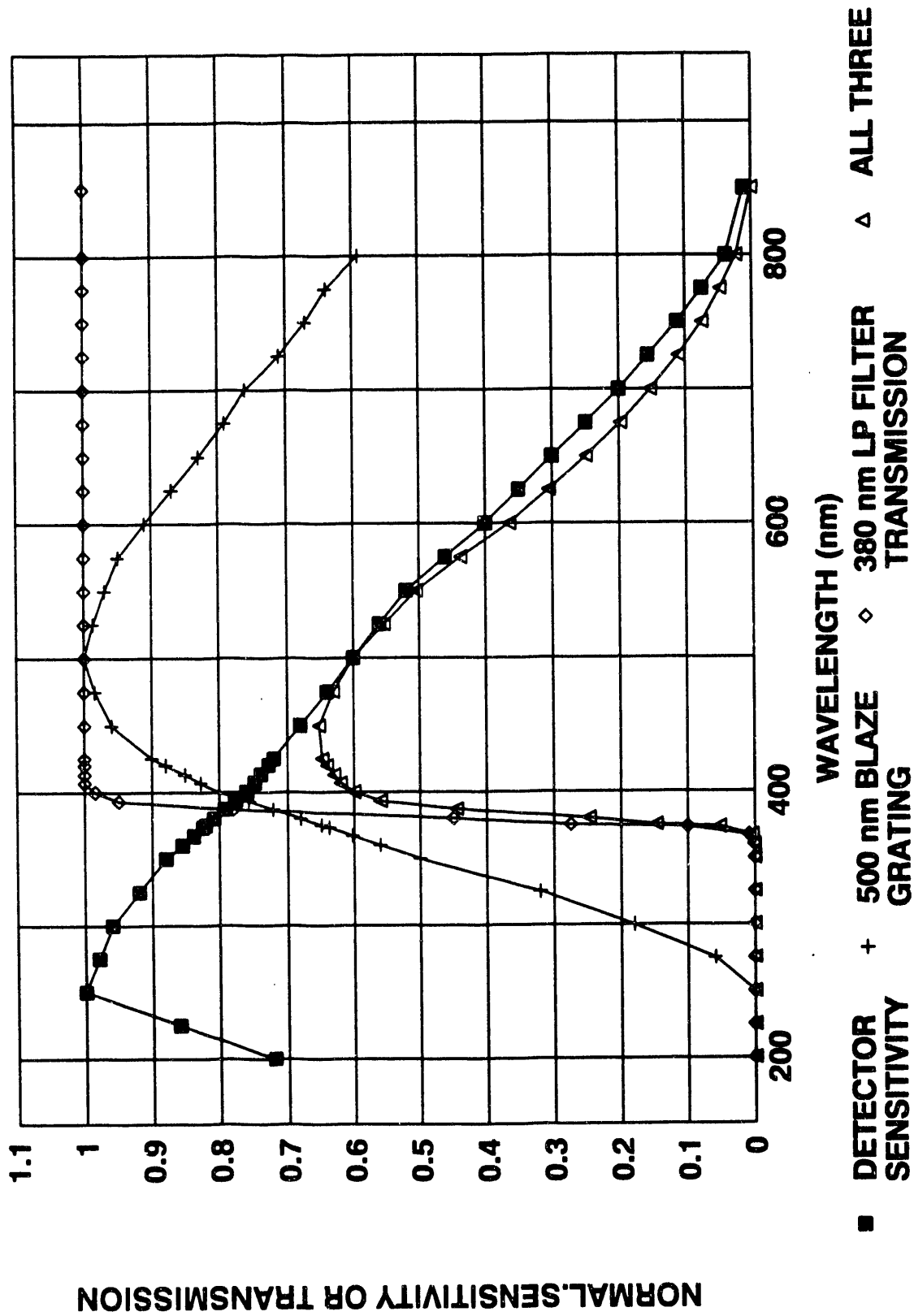
9.0 SUPPLEMENTAL TESTING

9.1 EFFECT OF SPECIMEN PREPARATION ON FLUORESCENCE INTENSITY

The wood pulp specimens were all held in standard laboratory cuvets during the fluorescence testing. In the preliminary tests, plastic (acrylic) cuvets were used but for the final tests, reported here, quartz cuvets were used to eliminate the effect of cuvet fluorescence.

The wood pulp samples were inhomogeneous and wet. 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 cuvets were "filled" with very loose packing and four others with the most dense packing possible. 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 both the front and back surfaces. This resulted in 10 samples of the loose-packed and 8 samples of the dense-packed. Table 9-1 summarizes the results of this test.

Table 9-1   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 cuvets, although perhaps not to the maximum possible density.

9.2 APPARATUS STABILITY

The data presented in Section 4.0, with the exception of the phase-resolved and temperature effect results, was all taken during a series of tests on 10/31/91 thru 11/1/91. Table 9-2 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 reflection (see Section 9.6). 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 9-1A and 9-1B. It can be seen that the readings all are repeatable within ±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.

In May 1991, a series of tests were conducted on eight southern pine samples in acrylic cuvets 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 executed 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 cuvets as well as the back face of the cuvets, 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 9-3 and the results are plotted in Figures 9-1C, 9-1D, and 9-1E. Figure 9-1C contains the results of all six trials (three on the front face and three on the back face).

Figure 9-1D contains the results of the three front face trials only. The maximum difference between any two trials is 10.8 % (±5.2%) and occurs for sample number 2 (KAPPA = 21). For all other samples the error is less than ±3%.

Figure 9-1E contains the results of the three back face trials only. The maximum difference between any two trials is 7.3% (±3.65%) and occurs for sample number 7 (KAPPA = 51). For all other samples the error is less than ±3%.

9.3 BLEACHING

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 9-2 shows the results of an experiment where a fixed spot on the pulp sample received 10^4 laser pulses. The spectra in Figure 9-2 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 9-2 data suggests that the initial bleaching rate may be as high as 0.1%/pulse.

9.4   TEMPERATURE EFFECT TESTS

The effect of pulp temperature on fluorescence intensity was determined using the standard set-up and procedure, i.e., exposing the sample to multiple pulses while scanning the sample so that each subsequent pulse hits 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 an aluminum block that is approximately a 4 cm cube. This cube 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 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 somewhat noisy and unreliable due to condensation on the cuvet face.

9.5   pH TESTS

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, a series of tests were made with pH buffered pulp samples.

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 cuvets 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). The results of litmus paper testing of the buffered specimens are presented in Table 9-4.

Figures 9-3 and 9-4 show the fluorescence intensity as a function of Kappa number for the northern and southern pine samples, respectively. In both species the overall fluorescence intensity increases with increasing pH. Figures 9-5 and 9-6 show the effect of pH on the wavelength centroid. 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 pine.

The 48 acrylic cuvets (2 species x 8 samples x 3 pH's) used in the tests were all taken from the same carton. As discussed in Section 6.9, some significant differences in cuvet fluorescence were discovered after the pH tests were completed. Therefore, only the trends shown in Figure 9-3 through 9-6 can be relied upon (i.e., shift toward higher intensity and longer wavelength with increasing pH).

9.6   REFLECTION TESTS

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 9-7 for 40 MHz modulation and in Figure 9-8 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 4-5 and 4-6, 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 6-4. 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 9-9 through 9-12. 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 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.

9.7 DERIVATIVE SPECTROSCOPY

A technique, commonly employed in UV spectroscopy to separate the absorption effects due to species with overlapping spectral lines, is to take the first and sometimes higher order derivatives of the measured spectrum.

Figure 9-13 shows the fluorescence spectra and the first three derivatives for southern pine samples #1 through #6. Although the derivatives do show that there are repeatable features in the

structure, none of the features appear to offer a way to separate the closely spaced samples 4, 5 and 6.

TABLE 9-2 ANALYSIS FILE FROM 10/31/91 TEST OF 337 nm EXCITATION

FILE TIMERES.WK1   ON DISK 103191-02
TIME RESOLVED FLUORESCENCE ON S. PINE AND N. PINE
EXCITATION - 337 NM
ALL PULP SAMPLSE IN QUARTZ CUVETS

FILE NAME	MONTH	DAY	HOUR	MINUTE	SPECIES	SURFACE	SAMPLE	DELAY	SUFFIX	CENTROID OF DIODES 173-708	PEAK INTENSITY BETWEEN 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
AF1A00	10	31	14	38	SP	F	1	00		370.6	543263	20922	1.1E+08	11090198	395460
AF1B00	10	31	14	40	SP	F	2	00		373.7	353379	11505	72881067	7215069	287984
AF1C00	10	31	14	41	SP	F	3	00		379.6	266846	7748	57503628	5504359	273201
AF1D00	10	31	14	42	SP	F	4	00		386.5	270520	8279	61844368	5602096	325298
AF1E00	10	31	14	43	SP	F	5	00		390.3	265368	8636	61628545	5483022	372380
AF1F00	10	31	14	44	SP	F	6	00		393.2	183996	4628	44105776	3828327	285569
AF1G00	10	31	14	46	SP	F	7	00		395	166320	3108	40152830	3438784	276579
AF1H00	10	31	14	47	SP	F	8	00		398.4	159214	3243	39861918	3316134	282375
AB1A00	10	31	14	59	SP	B	1	00		370.1	533598	20431	1.1E+08	10832518	387290
AB1B00	10	31	15	0	SP	B	2	00		374.6	343415	10079	71796857	7056447	294562
AB1C00	10	31	15	1	SP	B	3	00		379.9	251312	6970	54275334	5182744	263528
AB1D00	10	31	15	3	SP	B	4	00		387	260656	8175	59554946	5387090	319380
AB1E00	10	31	15	4	SP	B	5	00		390.4	260604	8141	60793396	5400099	371093
AB1F00	10	31	15	5	SP	B	6	00		393.1	174027	3492	41593733	3608935	270151
AB1G00	10	31	15	6	SP	B	7	00		395.9	168405	3713	40774474	3478950	288812
AB1H00	10	31	15	7	SP	B	8	00		398.5	156223	3145	38946924	3239757	276183
AF1A06	10	31	15	55	SP	F	1	06		369.5	73995	-2638	15275814	1511750	34624
AF1B06	10	31	15	56	SP	F	2	06		371.8	40701	-3733	8524582	828089	18903
AF1C06	10	31	15	57	SP	F	3	06		375.1	32078	-4841	6868947	657925	15880
AF1D06	10	31	15	58	SP	F	4	06		380.1	28731	-4707	6426870	587212	15976
AF1E06	10	31	15	59	SP	F	5	06		382.3	26283	-5332	5957408	540359	15364
AF1F06	10	31	16	0	SP	F	6	06		382.5	17036	-5220	3904177	350992	9816
AF1G06	10	31	16	1	SP	F	7	06		382	14653	-6200	3348782	305064	8401
AF1H06	10	31	16	2	SP	F	8	06		385.1	13227	-5871	3077718	272319	7690
AB1A06	10	31	15	27	SP	B	1	06		369	72368	-2776	14952999	1483405	33184
AB1B06	10	31	15	28	SP	B	2	06		372.2	43763	-4325	9218638	892962	22160
AB1C06	10	31	15	29	SP	B	3	06		374.8	29992	-5240	6437097	617224	15231
AB1D06	10	31	15	31	SP	B	4	06		380.5	27149	-7596	6132194	560543	15129
AB1E06	10	31	15	32	SP	B	5	06		382.4	27455	-4498	6225143	563599	17265
AB1F06	10	31	15	42	SP	B	6	06		381.7	14896	-5450	3355327	305766	8797
AB1G06	10	31	15	43	SP	B	7	06		383	10644	-3855	2409872	214978	6218
AB1H06	10	31	15	44	SP	B	8	06		384.5	13807	-5476	3250253	286379	8438
AF1A12A	10	31	16	41	SP	F	1	12	A	385	13335	-7775	3009316	274748	6184
AF1B12A	10	31	16	42	SP	F	2	12	A	387	7925	-6799	1800104	161990	1827
AF1C12A	10	31	16	43	SP	F	3	12	A	389.7	5628	-6841	1262870	110111	1058
AF1D12A	10	31	16	44	SP	F	4	12	A	394.7	4795	-7939	1150976	94051	1147
AF1E12	10	31	16	45	SP	F	5	12		397	4601	-7672	1103519	90089	1292
AF1F12	10	31	16	46	SP	F	6	12		396	2989	-7357	701647	56948	-440
AF1G12	10	31	16	47	SP	F	7	12		396.6	2376	-7546	575042	46028	-1176
AF1H12	10	31	16	48	SP	F	8	12		395.7	2365	-7718	557536	44661	-699
AB1A12	10	31	17	0	SP	B	1	12		384.7	13157	-6573	2937534	271671	4752
AB1B12	10	31	17	1	SP	B	2	12		386.5	7586	-6459	1713778	153975	2484
AB1C12	10	31	17	2	SP	B	3	12		389.1	5000	-7617	1170263	101891	235
AB1D12	10	31	17	4	SP	B	4	12		396.4	4833	-6299	1175430	95183	922
AB1E12	10	31	17	5	SP	B	5	12		398.8	4390	-6593	1102035	88112	905
AB1F12	10	31	17	6	SP	B	6	12		394.9	2835	-7034	665780	54336	-719
AB1G12	10	31	17	7	SP	B	7	12		397.6	2542	-6471	594205	47138	-668
AB1H12	10	31	17	8	SP	B	8	12		390.7	2728	-6329	660604	53508	-839

TABLE 9-2 ANALYSIS FILE FROM 10/31/91 TEST OF 337 nm EXCITATION (CONT)

FILE NAME	MONTH	DAY	HOUR	MINUTE	SPECIES	SURFACE	SAMPLE	DELAY	SUFFIX	CENTROID OF DIODES 173-708	PEAK INTENSITY BETWEEN 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	F	1	00		369.3	719902	28919	1.4E+08	14763113	471372
AF1J00	10	31	14	49	NP	F	2	00		375.3	502742	19039	1.1E+08	10310074	415642
AF1K00	10	31	14	51	NP	F	3	00		376.4	531620	20061	1.1E+08	10917733	464229
AF1L00	10	31	14	52	NP	F	4	00		378.6	461525	17189	97622810	9538776	435967
AF1M00	10	31	14	53	NP	F	5	00		383.2	334777	10857	73590103	6886078	371253
AF1N00	10	31	14	54	NP	F	6	00		387	354172	13035	80020035	7317619	437370
AF1O00	10	31	14	55	NP	F	7	00		388	333298	11885	75869801	6894515	427914
AF1P00	10	31	14	56	NP	F	8	00		390.4	317833	10922	73775737	6602568	438481
AB1I00	10	31	15	8	NP	B	1	00		369.1	684227	26871	1.4E+08	14004796	440709
AB1J00	10	31	15	9	NP	B	2	00		374.3	460429	16884	95474782	9445445	361008
AB1K00	10	31	15	10	NP	B	3	00		376.7	472847	17935	99425455	9741677	421896
AB1L00	10	31	15	11	NP	B	4	00		379.7	396973	13876	85089721	8151079	390208
AB1M00	10	31	15	12	NP	B	5	00		383.8	297812	9572	65892885	6147013	342114
AB1N00	10	31	15	13	NP	B	6	00		387.1	301577	10017	68332949	6243072	378980
AB1O00	10	31	15	14	NP	B	7	00		388.6	299055	10445	68570017	6196664	396336
AB1P00	10	31	15	15	NP	B	8	00		390.9	281860	9201	65957638	5865696	398279
AF1I06	10	31	16	4	NP	F	1	06		370	91070	-1509	18801778	1866854	41008
AF1J06	10	31	16	5	NP	F	2	06		373.9	55983	-3311	11880742	1135571	27346
AF1K06	10	31	16	6	NP	F	3	06		375	58452	-3397	12637662	1201914	30314
AF1L06	10	31	16	7	NP	F	4	06		376.3	47715	-4440	10366632	982171	25325
AF1M06	10	31	16	8	NP	F	5	06		378.4	33415	-5183	7403269	685717	17888
AF1N06	10	31	16	9	NP	F	6	06		380.7	33695	-4668	7559277	690424	21099
AF1O06	10	31	16	10	NP	F	7	06		381.6	30063	-5562	6779634	616058	18730
AF1P06A	10	31	16	18	NP	F	8	06	A	382.8	26510	-5473	6079329	548488	16664
AB1I06	10	31	15	46	NP	B	1	06		369.4	94922	-1723	19502135	1942889	41762
AB1J06	10	31	15	47	NP	B	2	06		373.1	61020	-3126	13003840	1246264	29422
AB1K06	10	31	15	48	NP	B	3	06		375.1	57915	-3275	12491152	1189284	30511
AB1L06	10	31	15	49	NP	B	4	06		376.7	45118	-4222	9864945	930028	24296
AB1M06	10	31	15	50	NP	B	5	06		378.8	32736	-4407	7284902	675574	17204
AB1N06	10	31	15	51	NP	B	6	06		381.6	30365	-4932	6849725	622226	17754
AB1O06	10	31	15	52	NP	B	7	06		381.7	29420	-4262	6643471	603658	16494
AB1P06	10	31	15	53	NP	B	8	06		383.4	27458	-4401	6240522	561880	17277
AF1I12	10	31	16	49	NP	F	1	12		384.7	16471	-6032	3658731	335023	7255
AF1J12	10	31	16	50	NP	F	2	12		390.1	9253	-6362	2209836	190155	4336
AF1K12	10	31	16	51	NP	F	3	12		391.1	10101	-6542	2373117	199980	4570
AF1L12	10	31	16	54	NP	F	4	12		393.1	7805	-6854	1862947	156274	3390
AF1M12	10	31	16	55	NP	F	5	12		394.8	5439	6634	1314661	108784	1512
AF1N12	10	31	16	56	NP	F	6	12		398.6	5107	-6807	1291107	103250	2291
AF1O12	10	31	16	58	NP	F	7	12		397.8	4916	-6627	1198309	97334	1479
AF1P12	10	31	16	59	NP	F	8	12		399.1	4484	-7018	1112016	88211	1518
AB1I12	10	31	17	9	NP	B	1	12		384.7	17015	-6038	3768469	347070	7438
AB1J12	10	31	17	10	NP	B	2	12		389	9627	-6148	2294613	197094	3675
AB1K12	10	31	17	11	NP	B	3	12		391.5	10012	-6744	2352064	202373	4913
AB1L12	10	31	17	12	NP	B	4	12		392.8	7641	-6402	1840467	154482	3258
AB1M12	10	31	17	13	NP	B	5	12		394.6	5296	-6710	1293203	106907	1320
AB1N12	10	31	17	14	NP	B	6	12		397.7	5084	-6234	1243682	99054	1371
AB1O12	10	31	17	15	NP	B	7	12		398.3	4830	-6390	1213271	97038	1792
AB1P12	10	31	17	16	NP	B	8	12		400.1	4508	-6654	1107496	86143	1306

TABLE 9-3 SEQUENCE OF TESTING ON 5/29/9

TRIAL	SAMPLE	CUVET FACE	....TIME... (HR)	(MIN)
1	2	F	9	25
1	5	F	9	29
1	1	F	9	33
1	8	F	9	35
1	4	F	9	37
1	3	F	9	39
1	7	F	9	40
1	6	F	9	42
3	2	B	9	44
3	5	B	9	47
3	1	B	9	48
3	8	B	9	49
3	4	B	9	51
3	3	B	9	52
3	7	B	9	54
3	6	B	9	55
2	2	F	14	19
2	5	F	14	21
2	1	F	14	23
2	8	F	14	24
2	4	F	14	25
2	3	F	14	27
2	7	F	14	28
2	6	F	14	29

TABLE 9-3 SEQUENCE OF TESTING ON 5/29/9 (CONT)

TRIAL	SAMPLE	CUVET FACE	....TIME... (HR)	(MIN)
1	2	B	14	31
1	5	B	14	33
1	1	B	14	35
1	8	B	14	36
1	4	B	14	37
1	3	B	14	38
1	7	B	14	40
1	6	B	14	41
3	2	F	15	59
3	5	F	16	2
3	1	F	16	4
3	8	F	16	5
3	4	F	16	6
3	3	F	16	7
3	7	F	16	9
3	6	F	16	10
2	2	B	16	12
2	5	B	16	15
2	1	B	16	16
2	8	B	16	17
2	4	B	16	18
2	3	B	16	20
2	7	B	16	21
2	6	B	16	22

FIGURE 9-4 RESULTS OF LITMUS PAPER TESTS OF BUFFERED PULP SAMPLES

FILE"LITMUS.WK1" PROJ 4040 (LIGNIN IN PULP)
DATE OF TESTING: 8/21/91 (14:15 - 15:15)
BY M MALITO & K NEVITT
PAPER USED FOR TESTS WAS FROM "MICRO ESSENTIAL LAB, INC"
 H2O : pHydron 5.6 - 6.8
 pH 7 : pHydron 6.8 - 8.4
 pH 10: pHydron 9.2 - 10.6

PRIOR TO TESTING, A BROAD RANGE pH PAPER WAS USED TO VERIFY
 THAT THE ABOVE NOTED PAPER RANGES WERE APPROPRIATE.
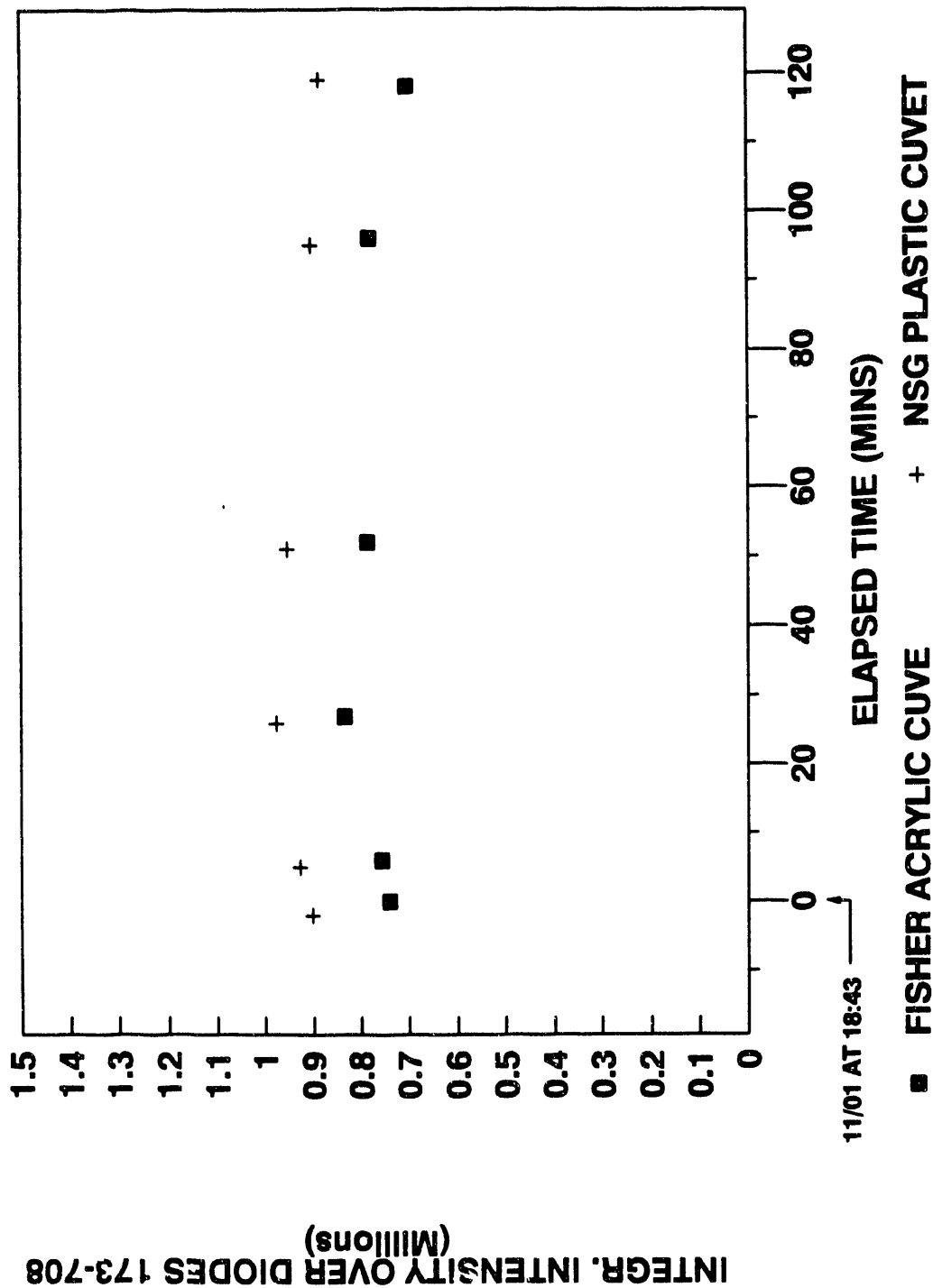
```
S   S   B                    S   S   B
P   A   U                    P   A   U
E   M   F                    E   M   F
C   P   F                    C   P   F
I   L   E                    I   L   E
E   E   R                    E   E   R
S                            S
```

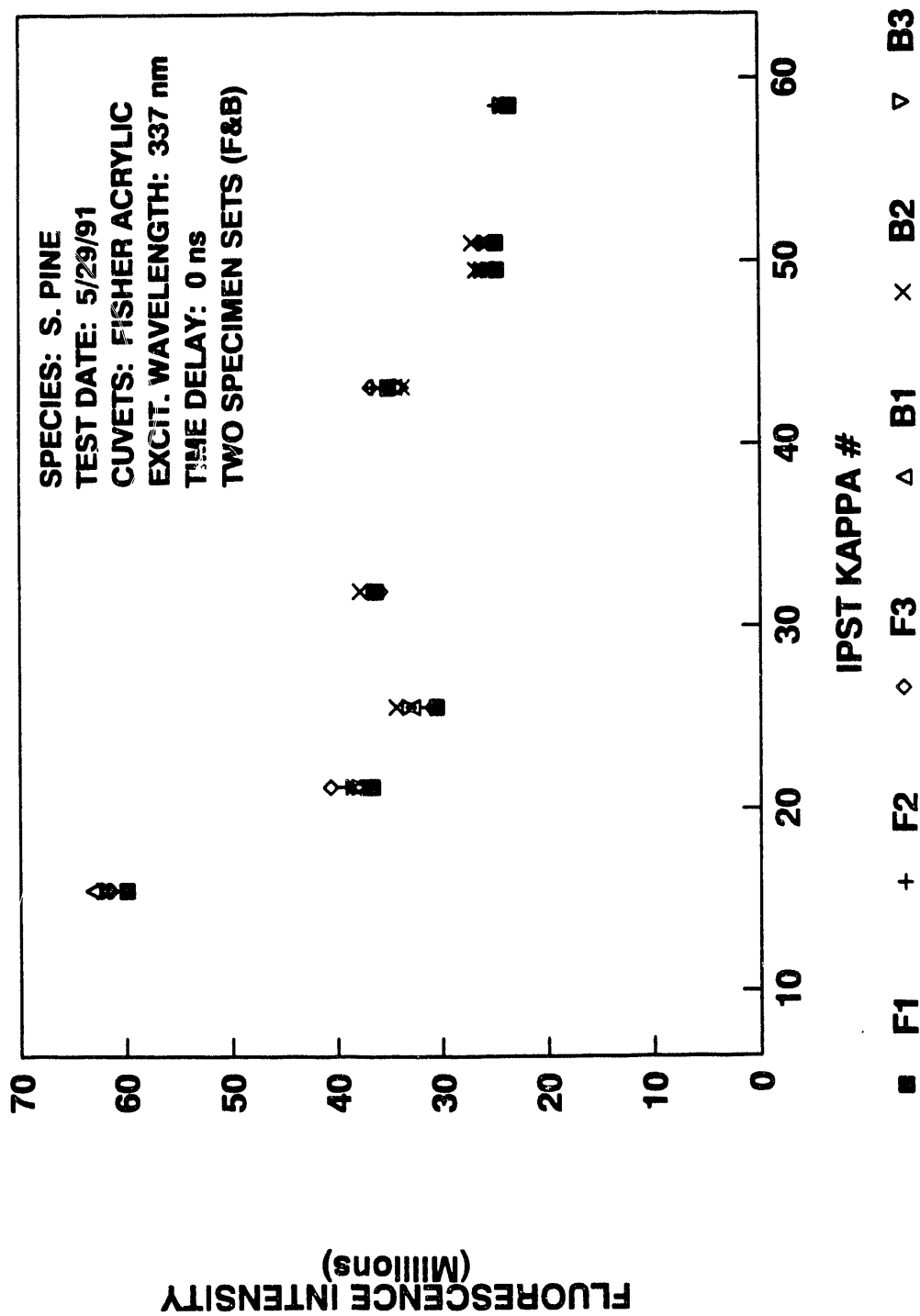| BOTTLE LABEL		pH MEASURED	BOTTLE LABEL		pH MEASURED
SP	1 H20	6.2	NP	1 H20	6.2
	2	6.2		2	6.1
	3	6.2		3	6.2
	4	6.2		4	6.3
	5	6.1		5	6.2
	6	6.1		6	6.2
	7	6.2		7	6.2
	8	6.2		8	6.2
SP	1 pH 7	7.0	NP	1 pH 7	7.0
	2	7.0		2	7.0
	3	7.0		3	7.1
	4	7.0		4	7.1
	5	7.0		5	7.0
	6	7.0		6	7.1
	7	7.0		7	7.1
	8	7.1		8	7.1
SP	1 pH 10	10.0	NP	1 pH 10	10.1
	2	10.0		2	10.1
	3	10.0		3	10.0
	4	10.0		4	10.0
	5	10.0		5	10.1
	6	10.0		6	10.1
	7	10.0		7	10.1
	8	10.0		8	10.1

FIGURE 9-1A   FLUORESCENCE OF STANDARDS DURING
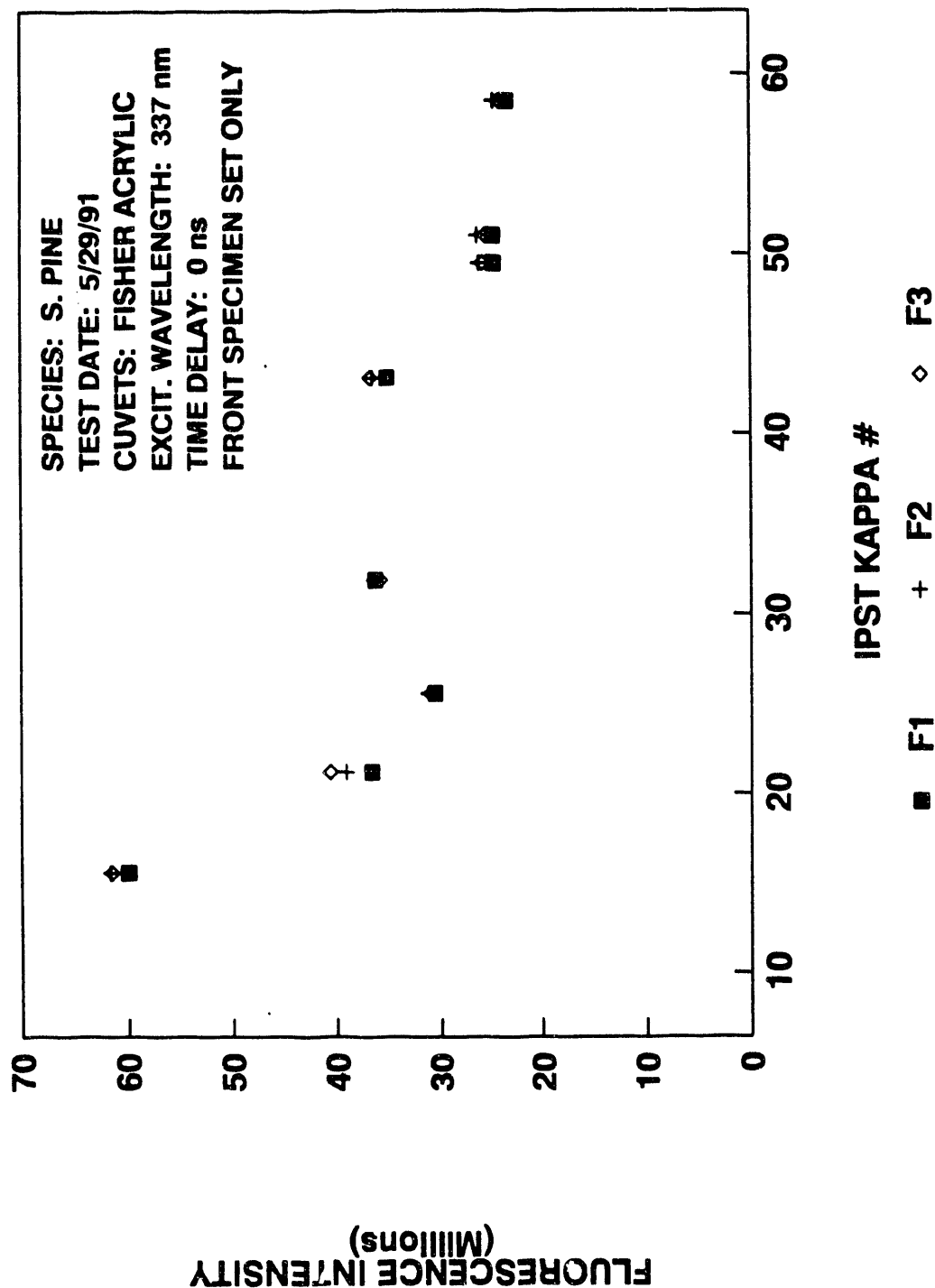TEST PROGRAM ON 10/31/91 & 11/01/91
337 nm EXCITATION

9-13
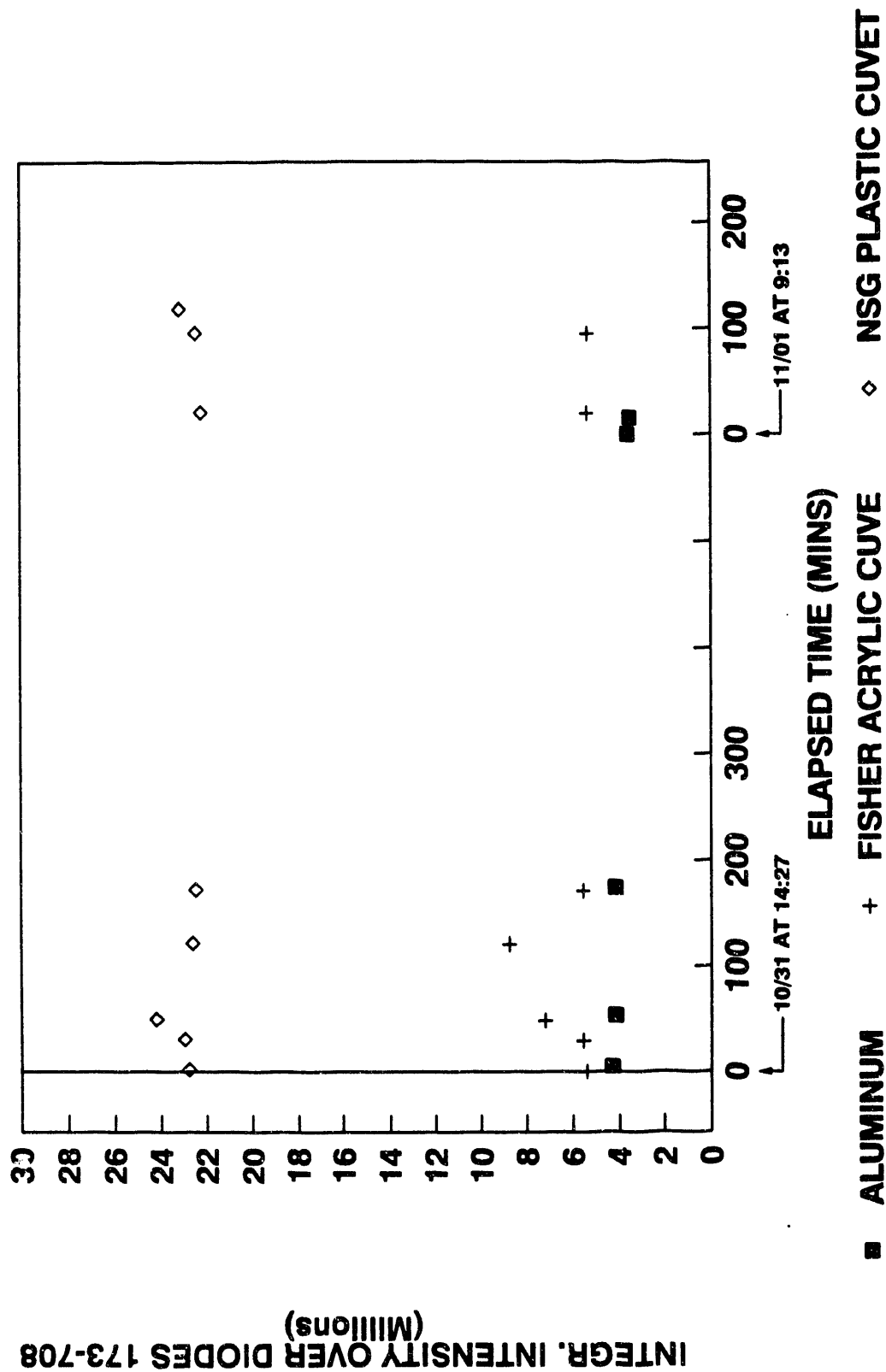
FIGURE 9-1B

FLUORESCENCE OF STANDARDS DURING
TEST PROGRAM ON 11/01/91
EXCITATION AT 442 nm

■ FISHER ACRYLIC CUVET   + NSG PLASTIC CUVET

ELAPSED TIME (MINS)

11/01 AT 18:43

INTEGR. INTENSITY OVER DIODES 173-708
(Millions)

FIGURE 9-1C REPEATABILITY OF S. PINE FLUORESCENCE
TWO SPECIMEN SETS (FRONT AND BACK)
3 TRIALS EACH

SPECIES: S. PINE
TEST DATE: 5/29/91
CUVETS: FISHER ACRYLIC
EXCIT. WAVELENGTH: 337 nm
TIME DELAY: 0 ns
TWO SPECIMEN SETS (F&B)

FLUORESCENCE INTENSITY
(Millions)

IPST KAPPA #

■ F1   + F2   ◇ F3   △ B1   × B2   ▽ B3

FIGURE 9-1D   REPEATABILITY OF S. PINE FLUORESCENCE
FRONT SPECIMEN SET, 3 TRIALS EACH

SPECIES: S. PINE
TEST DATE: 5/29/91
CUVETS: FISHER ACRYLIC
EXCIT. WAVELENGTH: 337 nm
TIME DELAY: 0 ns
FRONT SPECIMEN SET ONLY

■ F1   + F2   ◇ F3

IPST KAPPA #

FLUORESCENCE INTENSITY (Millions)

FIGURE 9-1E   REPEATABILITY OF S. PINE FLUORESCENCE
BACK SPECIMEN SET, 3 TRIALS EACH

SPECIES: S. PINE
TEST DATE: 5/29/91
CUVETS: FISHER ACRYLIC
EXCIT. WAVELENGTH: 337 nm
TIME DELAY: 0 ns
BACK SURFACE SPECIMEN SET ONLY

IPST KAPPA #

△ B1   × B2   ▽ B3
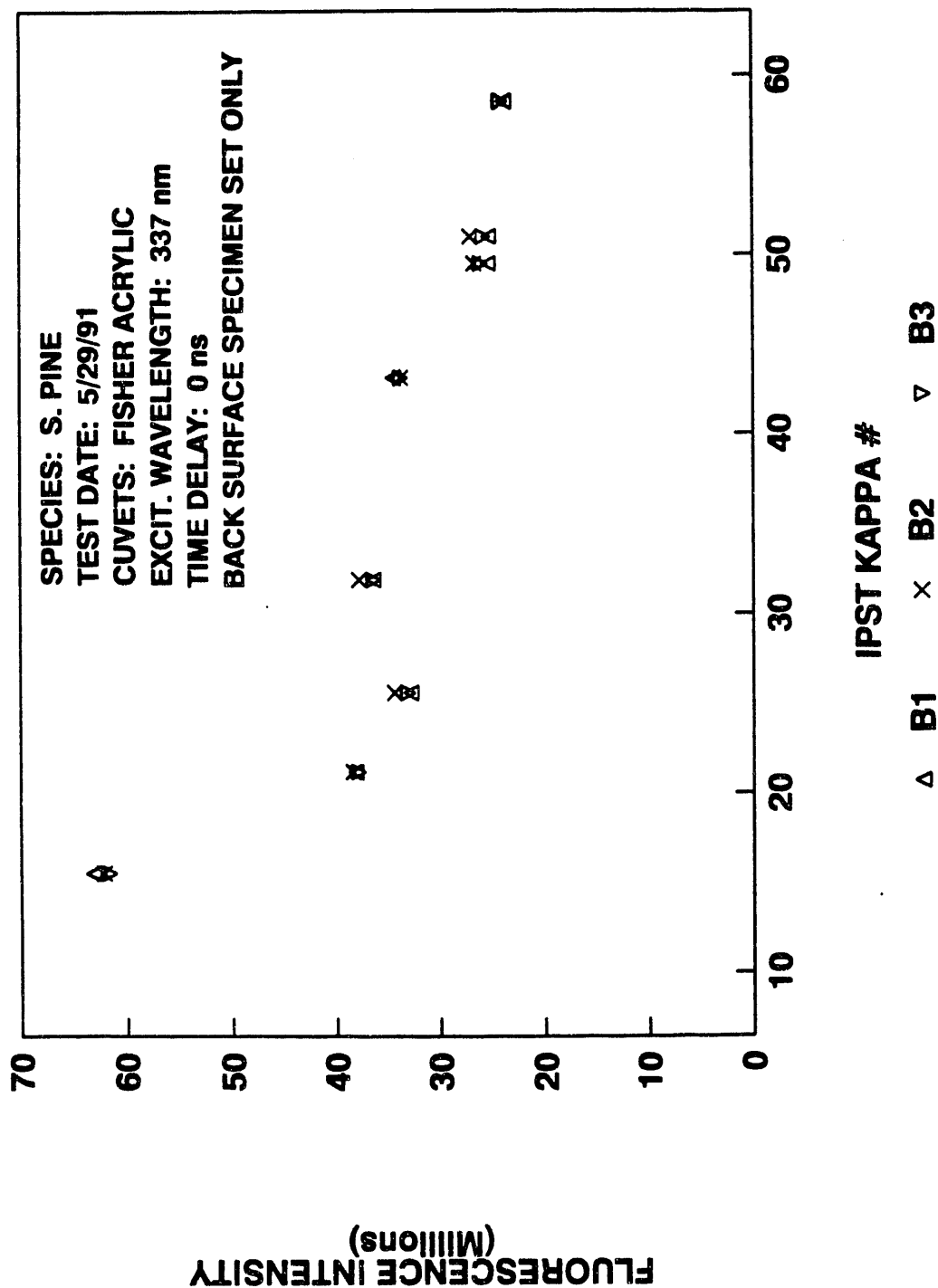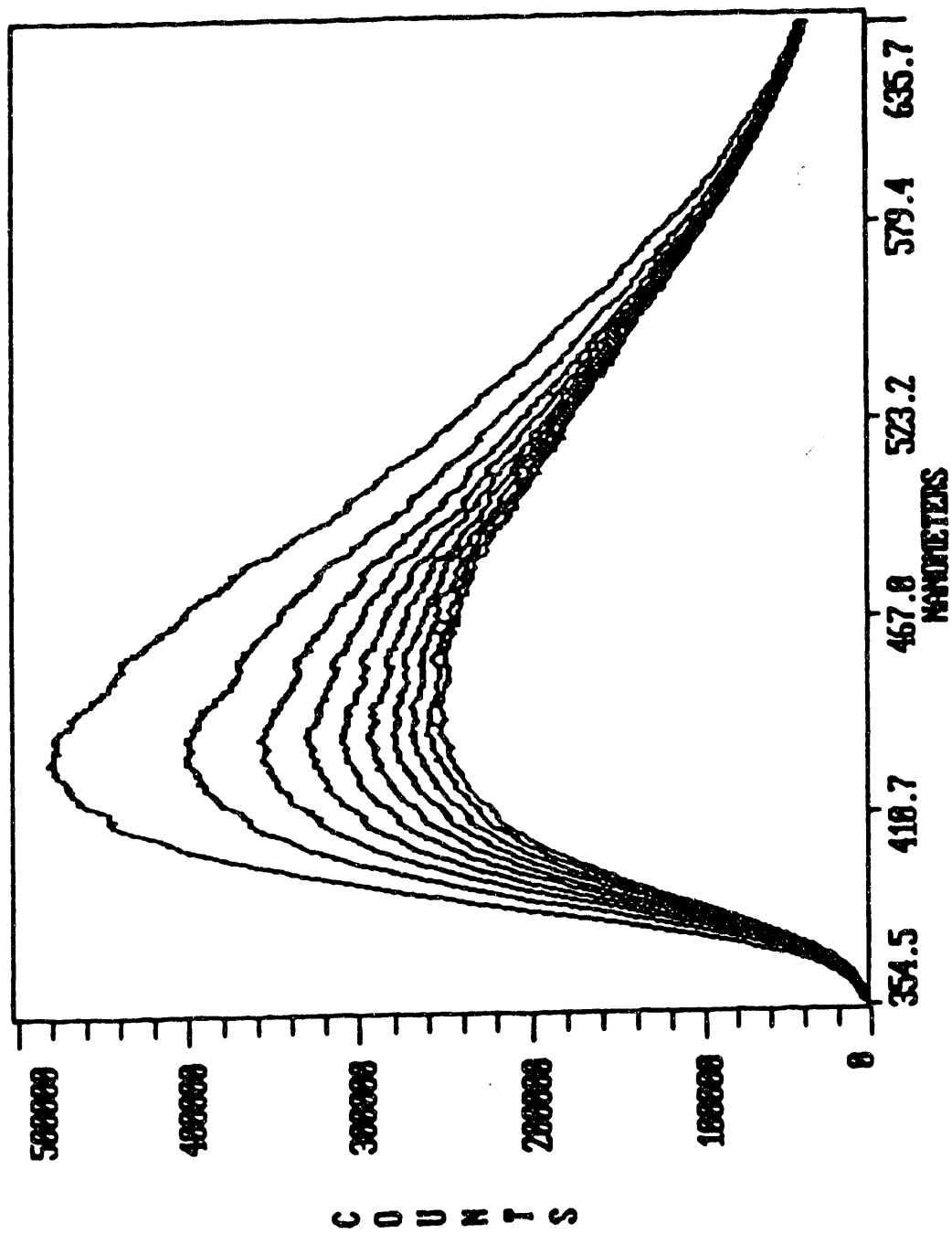
Figure 9-2. Bleaching Effect During 10,000 Pulse Exposure

FIGURE 9-3 EFFECT OF pH ON FLUORESCENCE INTENSITY OF NORTHERN PINE SAMPLES

SPECIES: N. PINE
TEST DATE: 8/22/91
CUVETS: FISHER ACRYLIC
EXCIT. WAVELENGTH: 337 nm
TIME DELAY: 0 ns

INTEGRATED FLUORESCENCE INTENSITY
(Millions)

MIAMI KAPPA #

■ pH H2O   + pH 7   ◇ pH 10
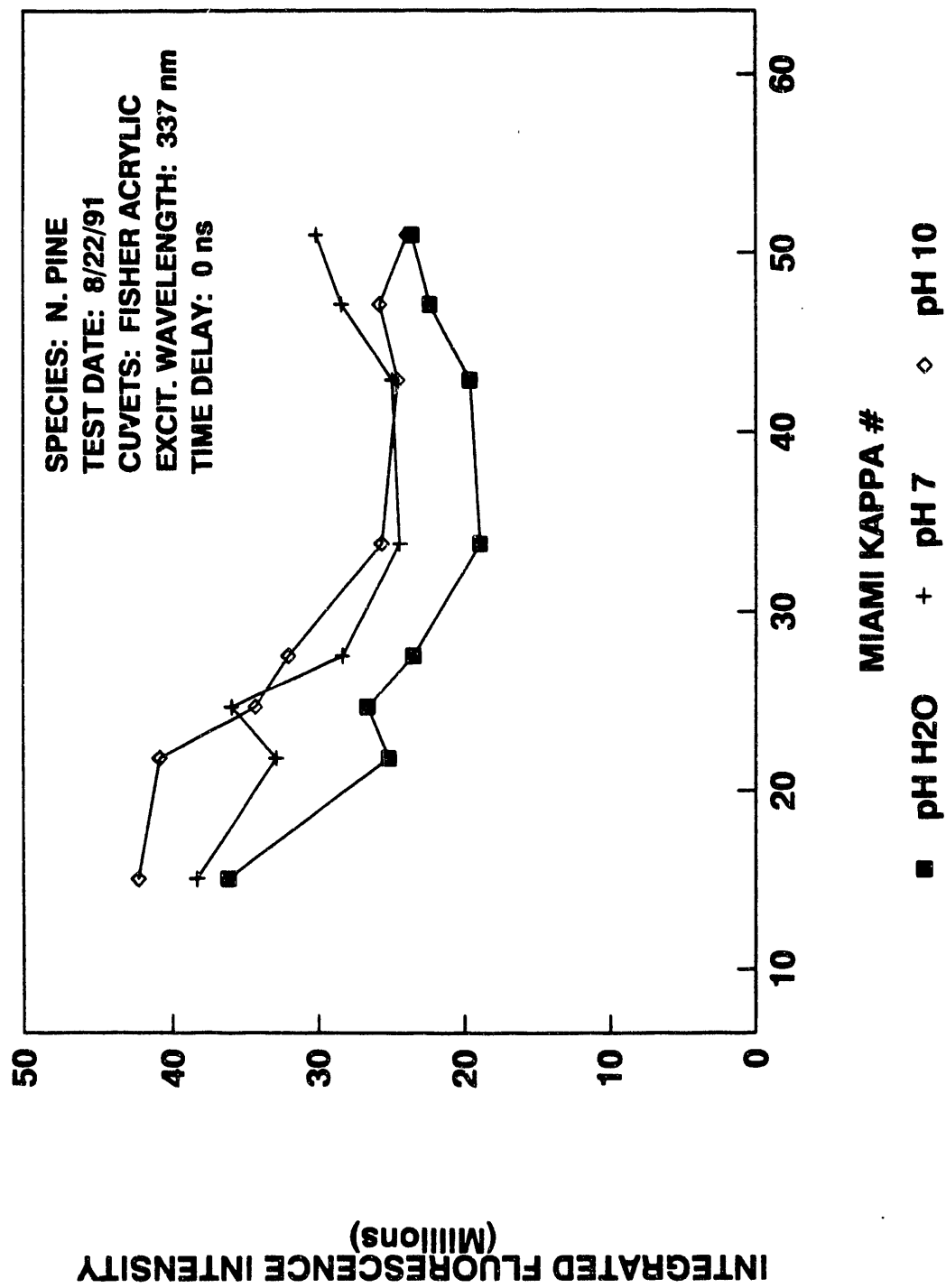
FIGURE 9-4   EFFECT OF pH ON FLUORESCENCE INTENSITY OF SOUTHERN PINE SAMPLES

SPECIES: S. PINE
TEST DATE: 8/22/91
CUVETS: FISHER ACRYLIC
EXCIT. WAVELENGTH: 337 nm
TIME DELAY: 0 ns

■ pH H2O   + pH 7   ◇ pH 10

MIAMI KAPPA #

INTEGRATED FLUORESCENCE INTENSITY (Millions)
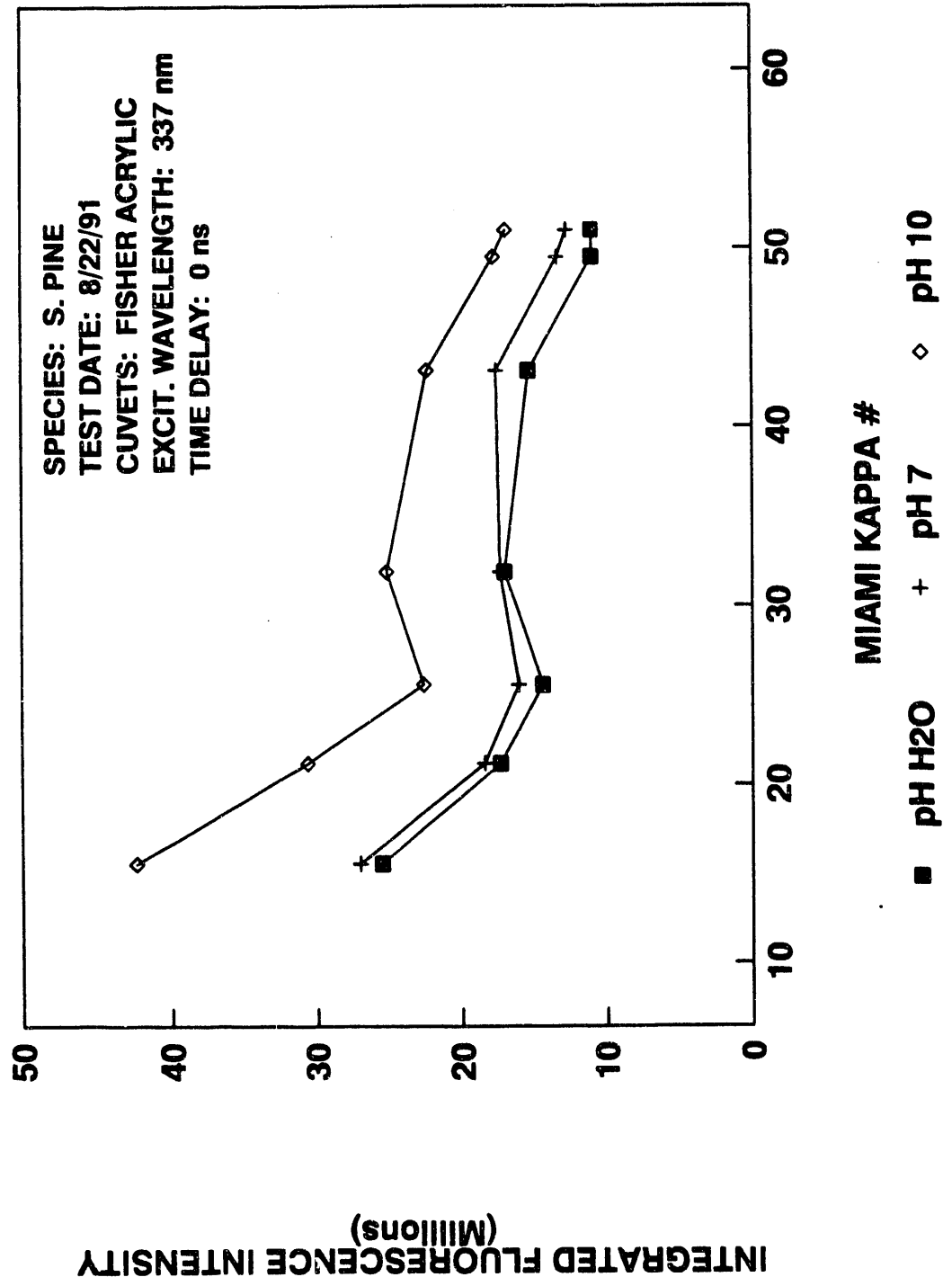
FIGURE 9-5　EFFECT OF pH ON WAVELEGTH CENTROID OF NORTHERN PINE SAMPLES

SPECIES: N. PINE
TEST DATE: 8/22/91
CUVETS: ACRYLIC
EXCIT. WAVELENGTH: 337 nm
TIME DELAY: 0 ns

MIAMI KAPPA #

■ pH H2O　+ pH 7　◇ pH 10

WAVELENGTH CENTROID - nm

9-6
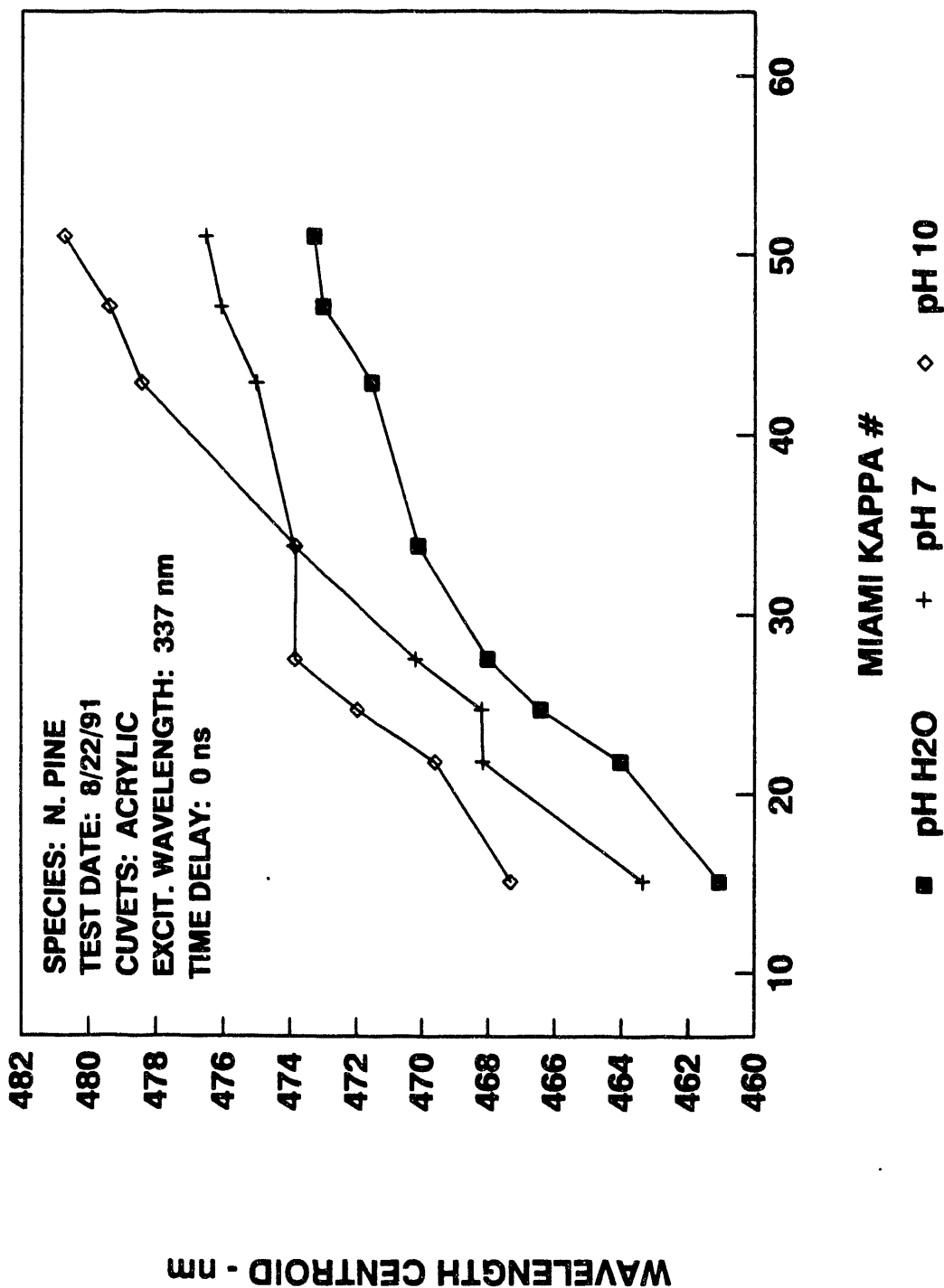
FIGURE 9-6   EFFECT OF pH ON WAVELENGTH CENTROID OF SOUTHERN PINE SAMPLES

SPECIES: S. PINE
TEST DATE: 8/22/91
CUVETS: ACRYLIC
EXCIT. WAVELENGTH: 337 nm
TIME DELAY: 0 ns

WAVELENGTH CENTROID - nm

IPST KAPPA #

■ pH H2O   + pH 7   ◇ pH 10
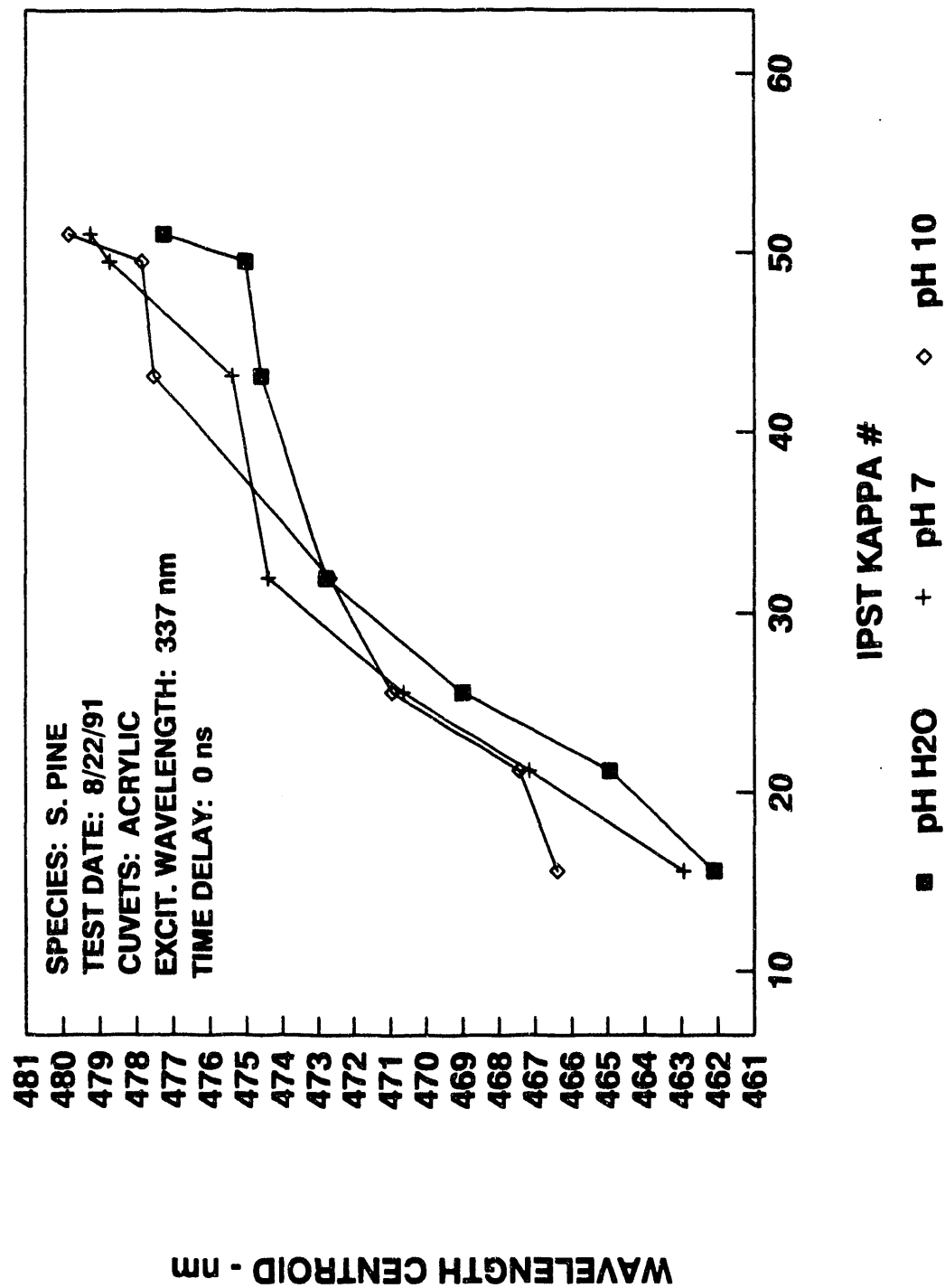
S. PINE, PHASE RESOLV. AT 40 MHz
REFL. INTENS. AT 442 nm "PH40442"
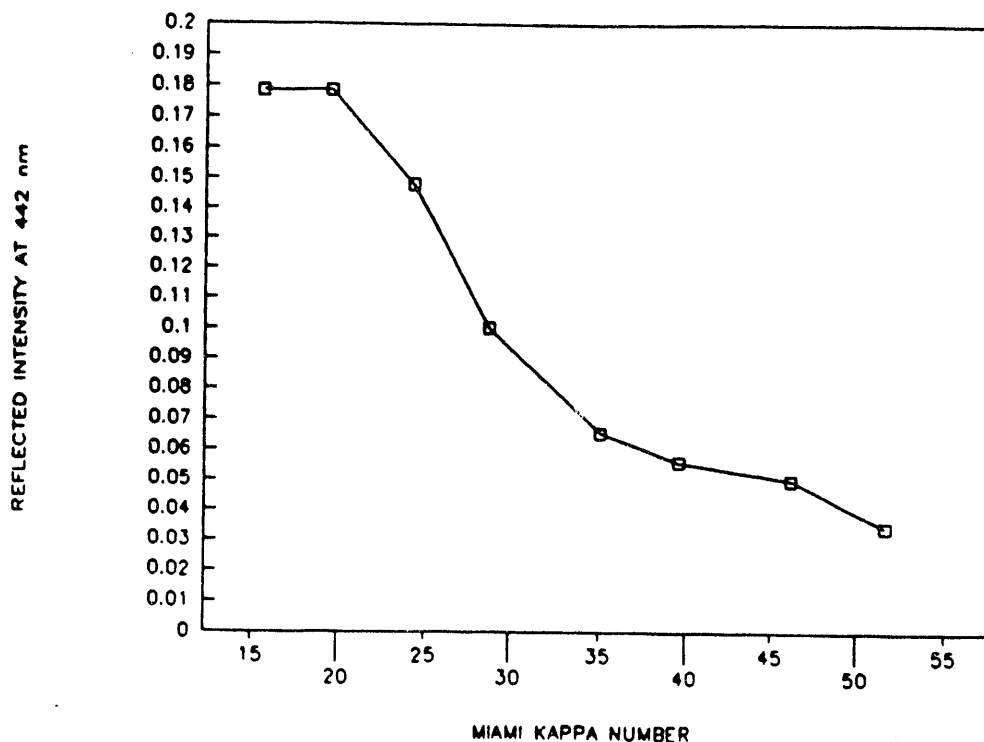
Figure 9-7   Intensity of 442 nm Reflected Light as a Function of Kappa
Number for 40 MHz Modulation

S. PINE, PHASE RESOLV. AT 60 MHz
REFL. INTENS. AT 442 nm "PH60442"
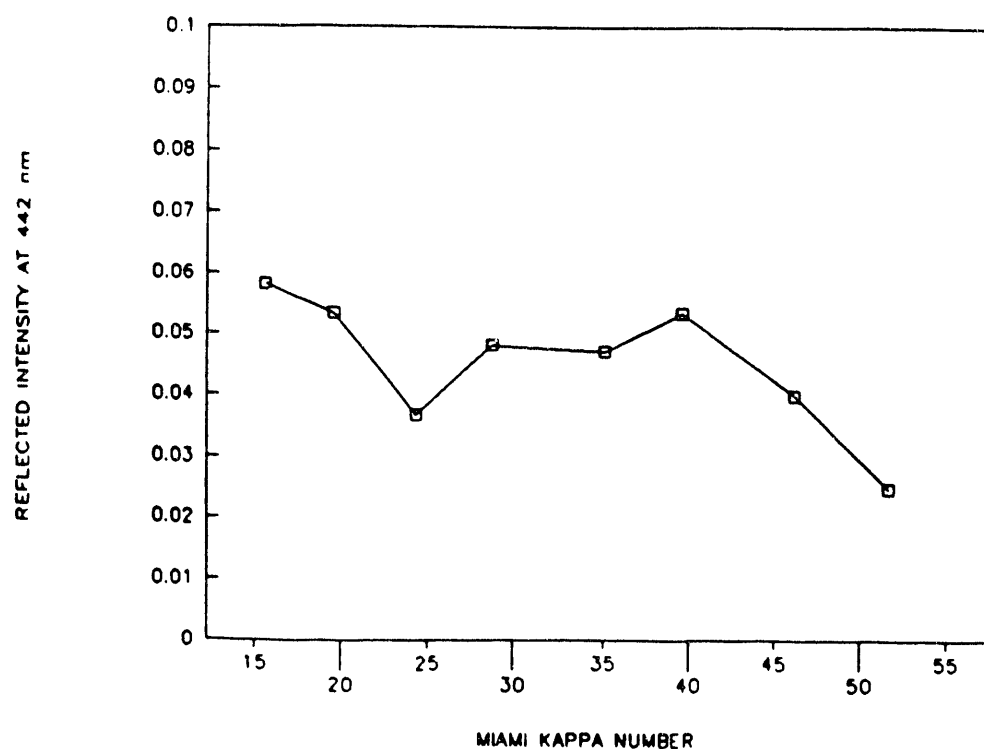
Figure 9-8   Intensity of 442 nm Reflected Light as a Function of Kappa
Number for 60 MHz Modulation

S PINE TESTS 11/1/91
633 nm   "SPFB633"
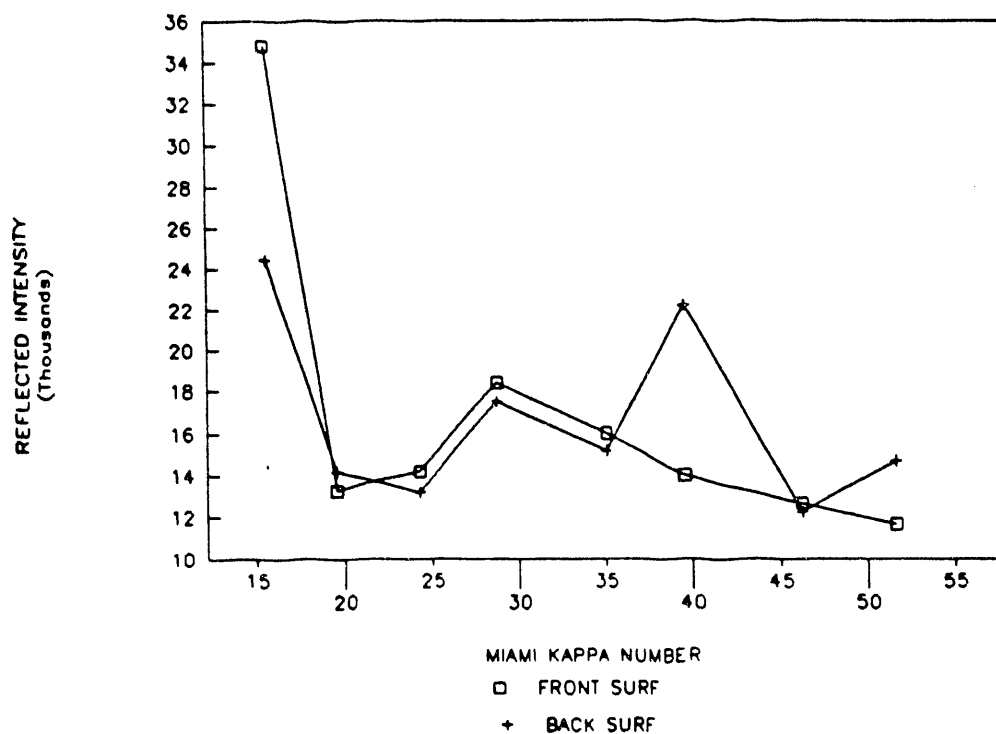
Figure 9-9   Intensity of 633 nm Reflection vs Kappa Number for Southern Pine Samples

S PINE TESTS 11/1/91
543 nm   "SPFB543"
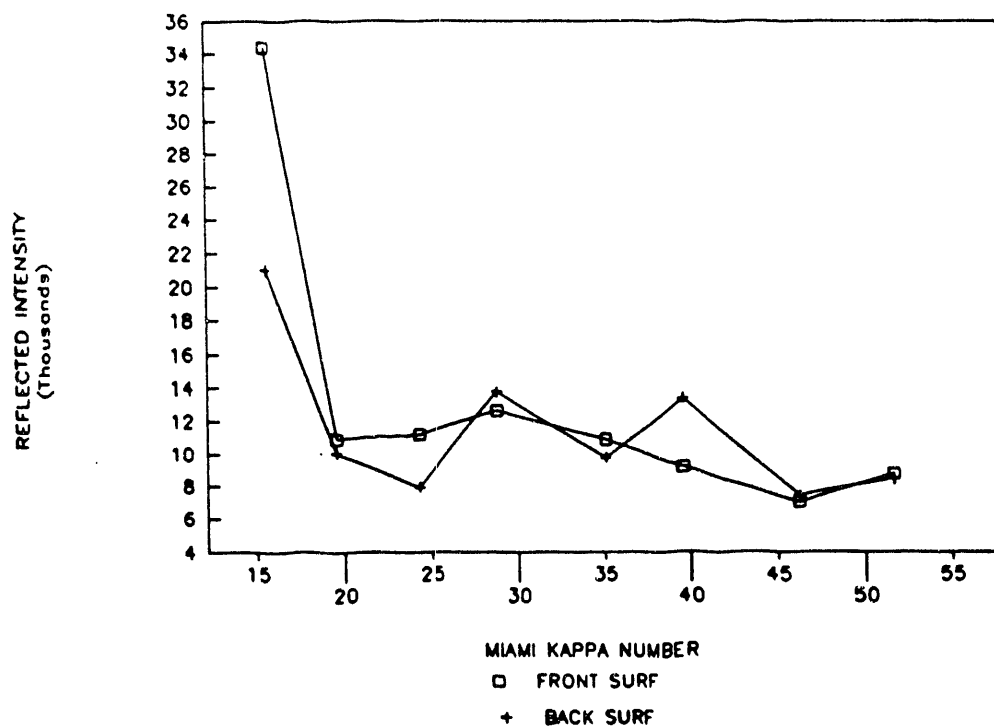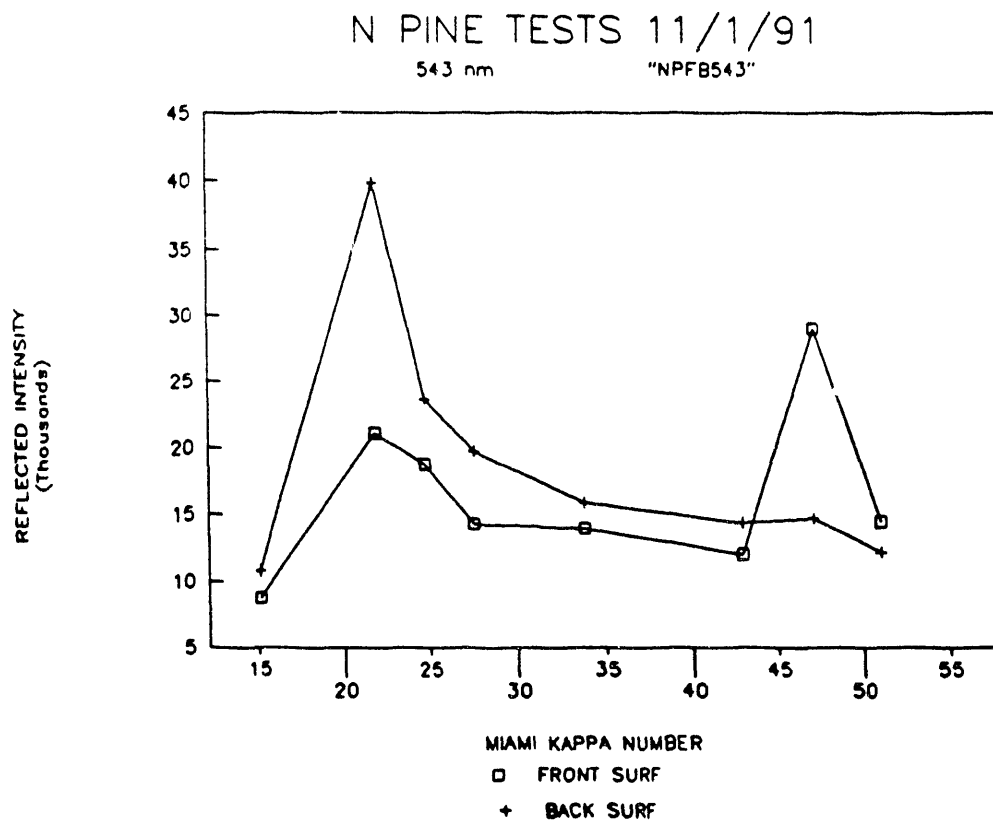
Figure 9-10   Intensity of 543 nm Reflection vs Kappa Number for Southern Pine Samples

N PINE TESTS 11/1/91

633 nm   "NPFB633"

REFLECTED INTENSITY
(Thousands)

MIAMI KAPPA NUMBER

□   FRONT SURF

+   BACK SURF
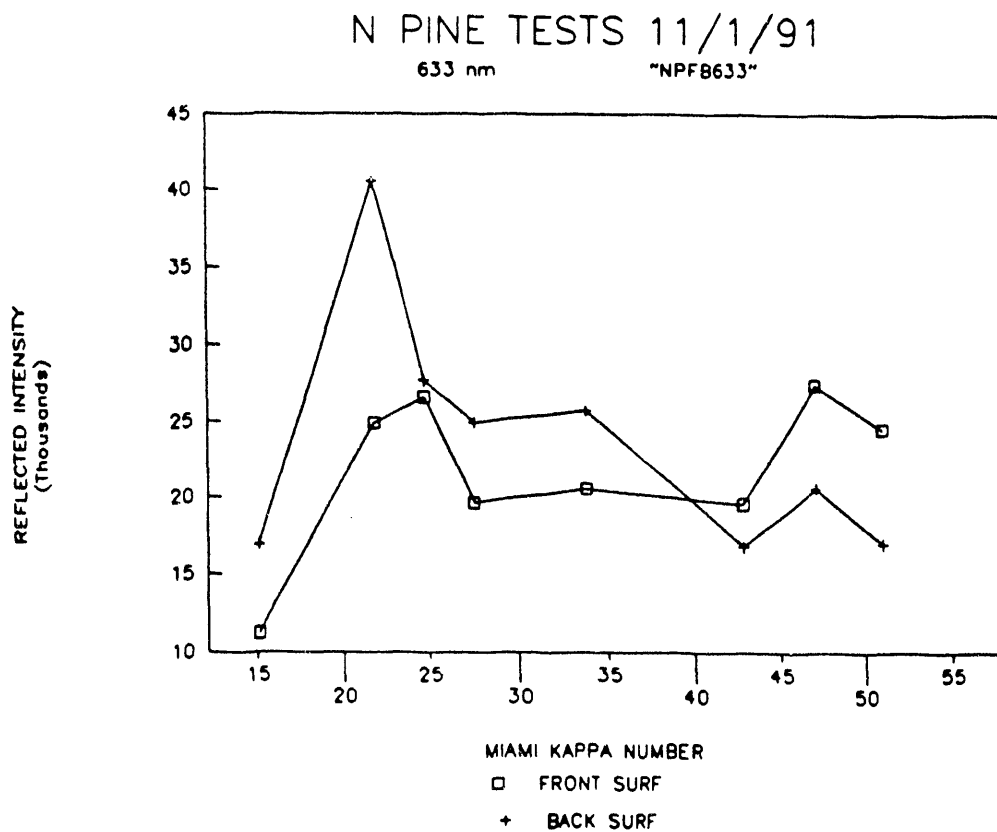
Figure 9-11   Intensity of 633 nm Reflection vs Kappa Number for
Northern Pine Samples

N PINE TESTS 11/1/91

543 nm   "NPFB543"

REFLECTED INTENSITY
(Thousands)

MIAMI KAPPA NUMBER

□   FRONT SURF

+   BACK SURF

Figure 9-12   Intensity of 543 nm Reflection vs Kappa Number for
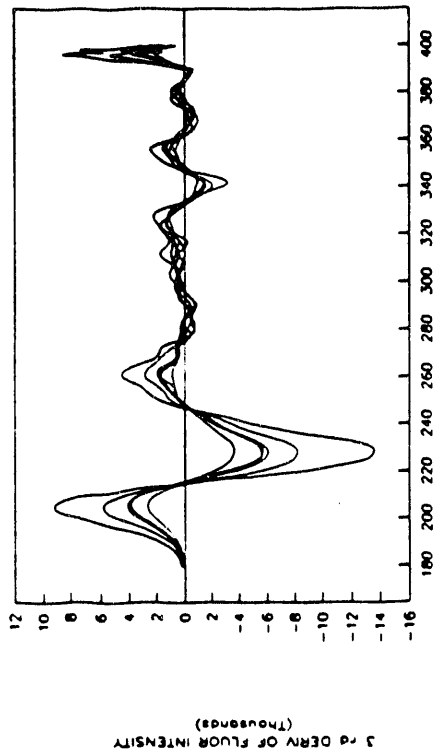Northern Pine Samples
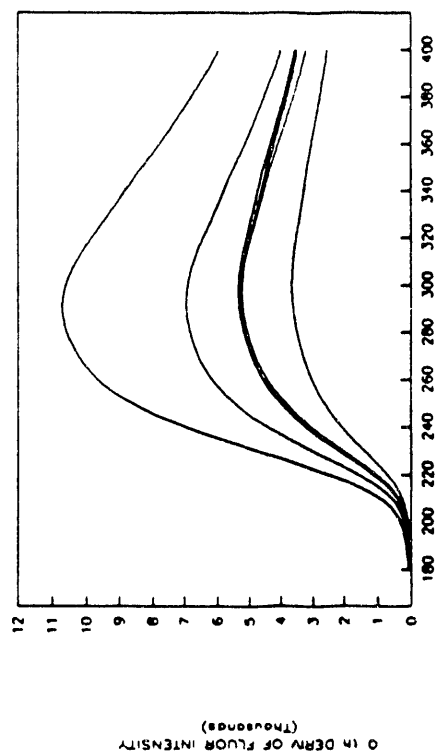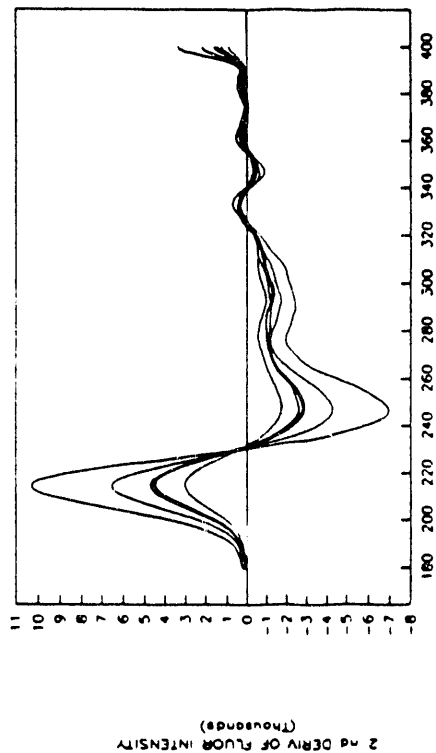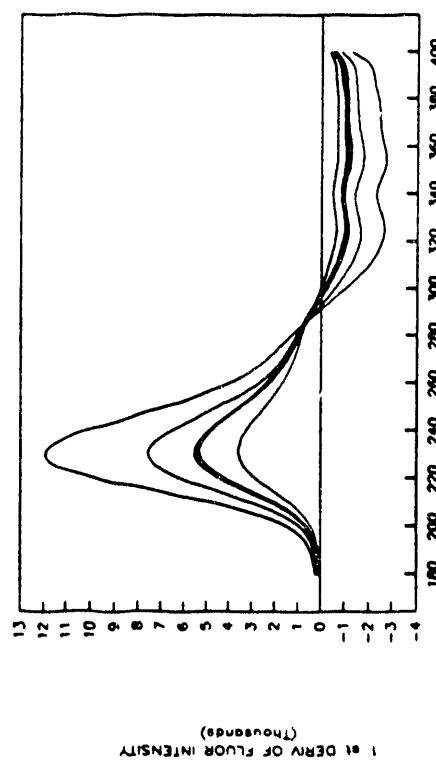
Figure 9-13 Fluorescence Emission Spectrum and Its First Three Derivatives for Southern Pine Samples #1 thru #6

10.0 REFERENCES

1. Smook, G. A., _Handbook for Pulp & Paper Technologists_, Joint Textbook Committee of the Paper Industry of the United States and Canada, 1982.

2. TAPPI Procedure T236 hm-85, "Kappa Number of Pulp".

3. "Advanced Sensor Development Program for the Pulp and Paper Industry," Annual Report No. 1, DOE/PR/06010-T13 (DE83017094), U.S. Department of Energy, Dec. 13, 1982.

4. "Advanced Sensor Development Program for the Pulp and Paper Industry," Annual Report No. 2, DOE/PR/06010-T33 (DE84008548), U.S. Department of Energy.

5. Horvath, J. J., Semerjian, H. G., "Laser Excited Fluorescence Studies of Black Liquor", Proceedings of the SPIE, Vol. 665, June 1986, pp. 258-264.

6. "Research and Development in Sensor Technology," DOE/NBM-7012450 (DE87012450), U.S. Department of Energy, April 1987.

7. "Report of the Critical Review Panel on the Advanced Sensor Program for the Paper Industry," prepared for the U.S. Department of Energy, July 1988.

8. Tikka, P.O., and Virkola, N. E., "A New Kraft Pulping Analyzer for Monitoring Organic and Inorganic Substances," TAPPI Journal, June 1966, pp. 66-71.

9. Williams, D.J., "The Application of Ultra-Violate Absorption Characteristic of Lignin to the Control of Pulp Uniformity," Appita, Vol. 22, o .2, September 1968, pp. 45-52.

10. Carpart, R., Obese-Jecty K., LeCardinal, G., and Gelus, M., "Contribution to the On-Line Kraft Pulping Control," PRP 4 Proceedings, Ghent, 1980.

11. "Kubulnieks, E., Lundqvist, S., and Pettersson, T., "The STFI OPTI-Kappa Analyzer, Applications and Accuracy", TAPPI Journal, November 1987, pp. 38-42.

12. "Kappa Number Analyzer," Preliminary Data Sheet D218.66e-a, The Bonnier Technology Group, Decatur, Ga., 1988.

13. Kleinert, T.N., and Joyce, C.S., "Short Wavelength Ultraviolet Absorption of Various Lignins and Related Substances," Part I, Pulp and Paper Magazine, Can. 58, No. 5, April 1957, pp. 154-158.

14. Joyce, C.S. and Kleinert, T.N., Ibid., Part II, Pulp and Paper Magazine, Can. 58, No. 6, May 1957, pp. 131-148.

15. Kleinert, T.N. and Joyce, C.S. Ibid., Part III, Pulp and Paper Magazine, Can. 58, No. 7, June 1957, pp. 215-219.

16. Kleinert, T.N. and Joyce, C.S., Ibid., Part IV, Pulp and Paper
    Magazine, Can. 58, Oct. 1957, pp. 147-152.

17. Hartler, N. and Norrstrom, H., Light Absorbing Properties of Pulp
    and Pulp Components", TAPPI, Vol. 52, No. 9, September, 1969.

18. Norrstrom, H., and Teder, A., "Absorption Bands in Electronic
    Spectra of Lignins, Part 2 Band Intensities for Alkali Lignins
    from Spruce," Svensk Paperstidning, 15 June 1971.

19. Sjostrom, E., and Haglund, P., "Spectrophotometric Determination
    of the Dissolution of Lignin During Sulfite Cooking, "TAPPI, Vol.
    47, No. 5, May 1964.

20. Berben, S.A., Rademacher, J.P., Sell, L.O., and Easty, D.B.,
    "Estimation of Lignin in Wood Pulp by Diffuse Reflectance
    Fourier-Transform Infrared Spectrometry," TAPPI Journal, November
    1987, pp. 129-133.

21. Bublitz, W.J., "Fluorescence of Pulping Liquors: A Tool for
    Digester Control"?

22. Baumgartner, D.J., Feldman, M.H., and Gibbons, C.L., "A Procedure
    for Trancing Kraft Mill Effluent from an Ocean by Constituent
    Fluorescence," Water Research, Pergamom Press, Vol. 5, 1971, pp.
    533-544.

23. Bublitz, W.J. and Wade, D.C., "Applying Waste Liquor Fluorescence
    to Control Pulp Quality," Svensk Papperstidning, No. 18, 1979.

24. Wilander, A., Kvarnas, H. and Lindell, T., "A Modified
    Fluorometric Method for Measurement of Lignin Sulfonates and Its
    In-Situ Application in Natural Waters," Water Research, Vol. 8,
    1974, pp. 1037-1045.

25. Demas, J.N., "Excited State Lifetime Measurements," Academic
    Press, New York, 1983.

END

DATE
FILMED
4/20/93