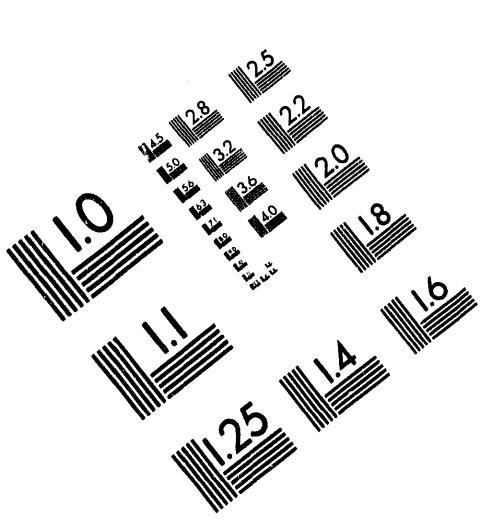

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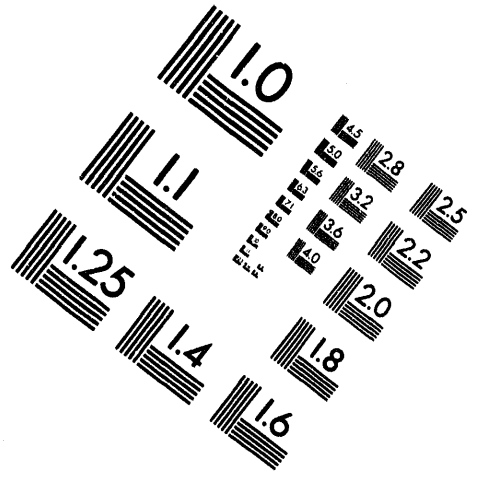

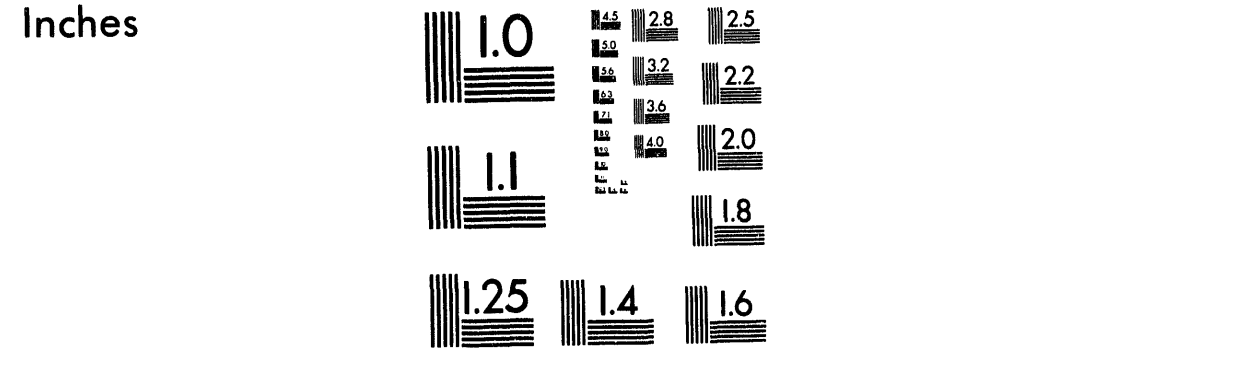

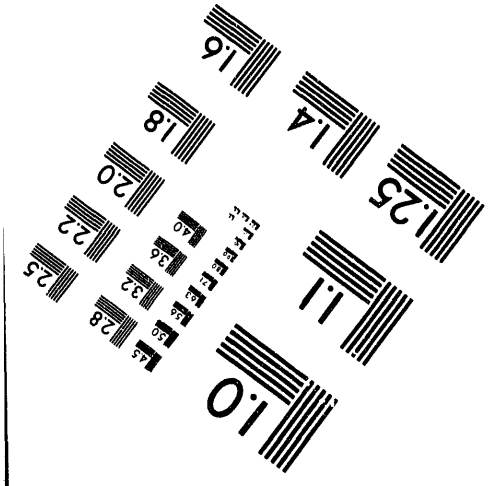

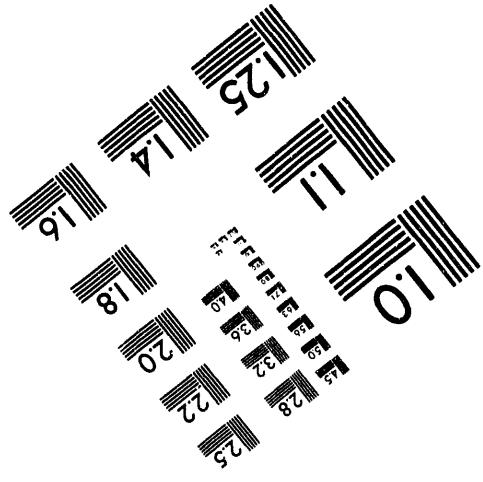

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CONTINUOUS ON-LINE MEASUREMENT OF LIGNIN CONCENTRATION IN WOOD PULP

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ABSTRACT

We are working toward the development of an instrument for the continuous, on-line measurement of the lignin concentration in wood pulp. The instrument is based on laser induced fluorescence of the wood pulp and is to be used as a primary sensor for both feedback control of the pulping and feedforward control of bleaching. We report here the results of a series of laboratory tests that characterized the fluorescence properties of wood pulp and demonstrated a correlation between various fluorescence functions and the Kappa number of the pulps as determined by TAPPI Procedure T236.

INTRODUCTION

Bublitz [1] demonstrated that fluorescence intensity is directly proportional to lignin concentration in diluted liquor samples withdrawn from digesters during both acid sulfite and kraft cooks. Horvath and Semerjian [2] examined the fluorescence spectra of black liquor solutions excited by various laser wavelengths from 290 to 403 nm and concluded that the technique could be a strong candidate for in-situ monitoring of the pulping process. To avoid the problems associated with sampling and diluting liquor samples, Berthold & Malito [3] looked at the fluorescence from undiluted pulp samples. They found that the fluorescence intensity was inversely proportional to the Kappa number of the pulp as measured using Tappi procedure T-236. This preliminary feasibility study led to the Department of Energy sponsored program discussed in this report.

The objective of the program is the commercialization of a laser-induced-fluorescence (LIF) based sensor for the on-line measurement of lignin concentration in wood pulp. The target sensor will provide a continuous, real-time signal for use both for feedback control of the pulping and for feed forward control of bleaching. The target sensor will provide direct, in-situ measurement with no sampling or dilution required.

The development program is divided into four stages:

- Laboratory characterization tests to define the fluorescence properties of washed pulp samples typical of those found at the final brownstock washing stage which is the target location for the initial prototype sensor.
- Extended tests to better define the range of applicability of the preferred approach identified in the initial characterization tests.
- Development and field testing of a prototype system to demonstrate the feasibility in actual application.
- Commercialization.

In this paper we report the results of the laboratory characteri-zation tests and discuss the scope of the extended tests which are now underway.

APPARATUS

Although the initial feasibility study [3] indicated an inverse correlation between fluorescence and Kappa number, there was a great deal of scatter in the results due to a combination of the following factors:

- instrumentation error (drift of optical alignment, drift of source excitation intensity and wavelength, etc.).
- local variations of Kappa number within the pulp samples (area sampled by the fluorescence probe not representative of the bulk sample).
- bleaching effects (the extent to which exposure to the excitation light caused irreversible chemical changes that effected the fluorescence efficiency) were unknown and the total exposure experienced during the tests was not controlled.
- temperature effects (neither the sensitivity of the fluorescence to temperature changes, nor the magnitude of temperature variations during the tests were known).
- errors in the measured values of Kappa number.
- fluorescence interference of non-lignins (the

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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.

The first step in our characterization tests was to develop an apparatus and procedures that minimized and quantified the errors due to the first five factors listed above.

Figure 1 is a block diagram showing the major components of the fluorescence spectroscopy system.

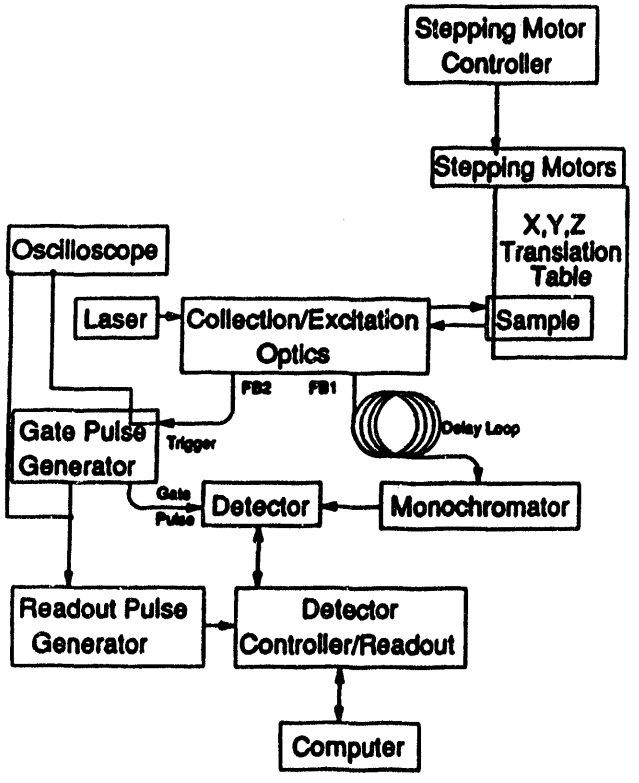

Figure 1. Block Diagram of Fluorescence Spectroscopy System

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

- focus the laser beam to a 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.

Two methods of pulp sample presentation have been used. In the first the pulp sample is loaded into a standard cuvet (10 mm x 10 mm x 45 mm). In the second, the pulp is loaded into an open jar so that the laser directly illuminates the pulp. Results obtained with the two methods are comparable but the open jar approach allows better control and wider variation of the pulp consistency.

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

The detector controller (Princeton Instruments Model ST120) provides periodic readout of the detector under software control through a 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.

The computer provides:

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

PULP SAMPLE SETS

Two controlled pulp sample sets were 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.

After digesting, the samples were washed, screened, and refrigerated. Both sample sets were prepared by the Paper Science and Engineering Department at Miami University in Oxford, Ohio. Miami University also made Kappa number measurements, in triplicate, on each of the samples at the time of the preparation.

RESULTS

Tests were run to determine the repeatability:

- among a set of 10 different specimens, all prepared from the same pulp sample.
- for a given specimen over the period of a six-hour test series.
- of the southern pine samples as measured before and after 5 months refrigerated storage.

In all cases the results were repeatable to within ±5%.

The relationship between total fluorescence (spectral fluorescence integrated over the entire emission spectral range) and Kappa number is shown in Figure 2 where it can be seen there are serious deviations from the expected inverse dependence. These deviations are repeatable (even over a 2-year period) and suggest the presence of "interfering" components in the pulp samples that preclude the straight-forward use of total fluorescence as a control signal.

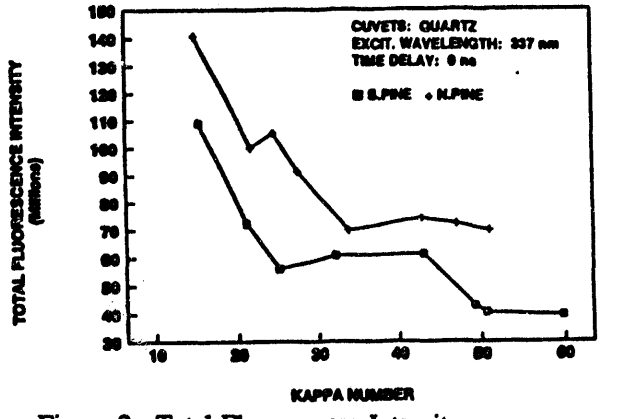

Figure 2. Total Fluorescence Intensity vs Kappa Number

A wide range of testing techniques and data reduction techniques were explored with the objective of identifying an approach that could give a suitable measure of Kappa number in the presence of the interfering components. Each of the methods we explored are discussed below:

Temporal behavior. Interference due to other fluorescing species can often be suppressed if the time constant for fluorescent decay is significantly different for the two species. We set the detector gating pulse to turn the detector on only after a time delay. The value of the delay was set anywhere from 6 to 30 nsec. The response measured after the time delay is predominantly from the species having the longer time constant. Figure 3 shows the results of normalizing the fluorescence measured at 12 nsec delay to that measured with no delay. As can be seen, the resultant function is mono-tonically decreasing and could be used as a control signal.

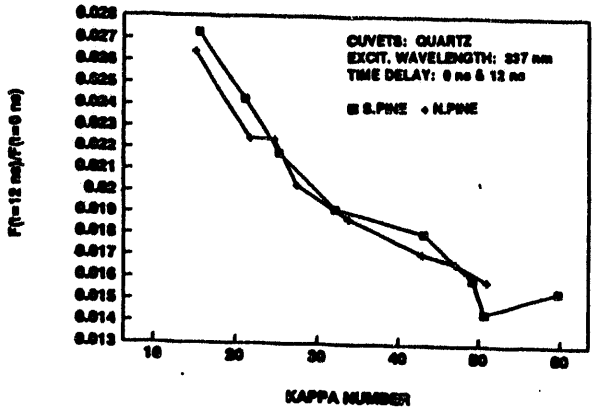

Figure 3. Ratio of 12 ns Delayed Fluorescence to 0 ns Delayed Fluorescence vs. Kappa Number

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 the tunable dye-laser as the source. Figure 4 plots a function that is a linear combination of the fluorescence measured at two different wavelengths. Again, the "deviations" are suppressed providing a potential control signal.

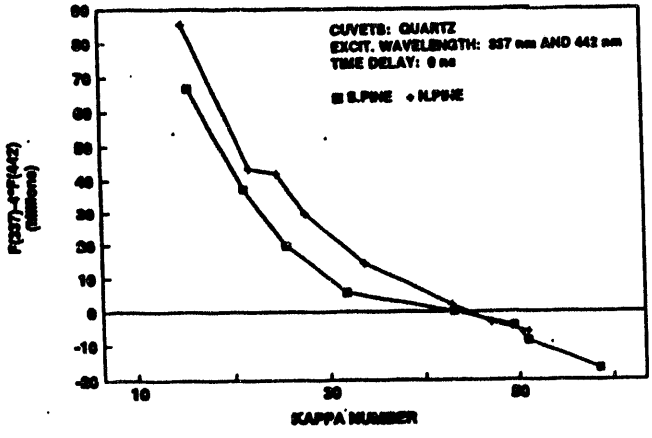

Figure 4. Dual Excitation-Wavelength Response Function vs Kappa Number

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. As an instrumentally convenient way of characterizing the shape of the spectral distribution, we have employed the wavelength centroid defined as

$$C \equiv \frac{\sum_{n=0}^{700} \lambda_n F_n}{\sum_{n=0}^{700} F_n} \qquad (1)$$

where λ_n is the wavelength at the nth element of the detector array

F_n is the fluorescence intensity at the nth element of the detector array and the summation is taken over the 700 elements of the array.

The wavelength centroid provides a good measure of the Kappa number as can be seen in Figure 5. The excellent repeatability between identical specimens can also be seen by comparison of the results from the front surface of the cuvet to those from the back. Since the laser radiation is absorbed very close to the surface, the front and back are essentially independent specimens.

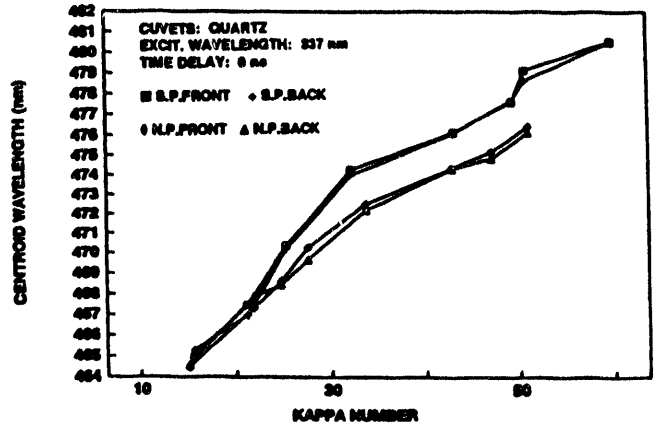

Figure 5. Wavelength Centroid vs. Kappa Number

EXTENDED TESTS

The initial prototype system is intended for use at the final stage of brownstock washing. The characterization tests summarized above showed that although a direct measurement of total fluorescence is not suitable, any of the three "compensation" methods can be used to determine the Kappa number for the two sample sets investigated. We are currently conducting

additional laboratory tests to determine how far beyond the initially tested conditions the approach can be applied. The tests are aimed at evaluating the extension to:

- other wood species
- both higher and lower values of Kappa number
- measurements at locations closer to the digester where the pulp is not as well washed
- in-pipe measurements where the pulp is in a slurry.

The extended tests will be limited to an evaluation in terms of the wavelength centroid method. This is because, of the three compensation techniques discussed above, the wavelength centroid approach is instrumentally preferred. It requires fewer, and less costly components to implement, and it provides the very important feature of being independent of the measured intensity. Variations of laser output with age, detector sensitivity variations, and efficiency of the optical system (dirty windows, etc.) are all automatically compensated to the degree that they are wavelength independent.

CONCLUSIONS

A laser-induced-fluorescence based system for the continuous on-line measurement of lignin concentration in wood pulp is feasible. Direct measurement of total fluorescence does not provide a useable control signal but several "compensation" approaches can provide suitable control functions.

The wavelength centroid which is a measure of the shape of the emission spectrum is instrumentally preferred and will be pursued in the development of a field prototype.

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ACKNOWLEDGEMENT

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