Project Title: Real Time Analysis And Control of Batch Dyeing Processes

Project Number: S95-4

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Goals:

The primary goal of this new project is to improve the consistency and control of batch dyeing processes. To achieve this goal, we will:

1. Update current literature review on control of dyeing in the area of dyeing machinery and processes, and identify the most promising theoretical process models. Extend the theory where possible , and express the theory in practically useful mathematical models, for conversion to usable software. Develop or use special numerical methods as required to improve computation accuracy and speed for dyeing process simulation and control. Continue evaluations of different types of hardware for a prototype control system for industry.

2. Introduce a modem, object-oriented standards approach to software development and software management. This facilitates rapid prototyping and subsequent technology transfer. Integrate the theoretical model computations with the dyeing control software, in continuous software and system development.

3. Develop useful theoretical and process models for application to specific types of dyeing machinery, as an extension of goal 1 above and, for the optimized models, develop, select, compile and publish practically useful parameter values.

4. Assess the absolute level of control possible, and develop optimum control procedures and strategies for dye mixtures in specific dyeing systems.

5. Develop Flow Injection Analysis (FIA) methods for the analysis of dyebaths containing disperse and vat dyes, e.g. using solvents for disperse dyes, and redox systems for vat dyes. Develop pH buffers for use with FIA of various other dye classes.

6. Develop FIA/HPLC methods for in-process analysis of both hydrolyzed dye and reactive dye in reactive dyeing processes

7. Extend current dosing studies to the acid dyeing of polyamide fibers, with emphasis on both the coverage of yarn streakiness, and on the achievement of maximum final dyebath exhaustions.

8. Extend research to the modeling and simulation of package dyeing.

Abstract:

This report describes recent progress in real-time monitoring, modeling , and controlling batch dyeing pmcesses. Several hardware and software improvements to the flow injection analysis monitoring system are described. Package dyeings of cotton with direct dyes and acetate with disperse dyes have been monitored by FIA. New data acquisition software has been written in a Unix' environment to allow both real-time monitoring and control from a personal computer. Significant progress has been made in assembling the combined FIA/HPLC system for monitoring reactive dye exhaustion and hydrolysis. Two different kinetic models for direct dyeing of cotton have been developed and evaluated as predictive tools for controlling dye exhaustion. Equilibrium parameters for acid dyes on nylon have been measured in preparation for controlling dye exhaustion by varying pH. Details for this progress are reported.

Relevance to NTC Goals:

1. This project will develop innovative and improved closed-loop dyeing processes based upon modern theory and modern control strategies and methods.
2. The strong contacts already developed with industrial companies through projects S92- 10 and S-94TT-1 will be maintained and enhanced, with particular attention to transfer of results to commerce. Education and training, both of graduate students and industry personnel, are already underway. This will be continued to ensure the future competitiveness of the industry.
3. There is a unique collaboration between textile chemists, mechanical engineers, and textile engineers at the heart of this project, which may serve as a model for the industry.

Technical Approach:

Key questions:
1. Can the consistency of batch-dyeing be improved by closed-loop control?
2. What are the best control and monitoring procedures and strategies?
3. Can these strategies be adapted for specific commercial dyeing machinery and processes?

The barriers:
1. The limitations of the best existing theoretical models of the physical chemistry of dyeing.
2. The multiplicity of parameters which can influence a dyeing process, and the difficulty of monitoring and evaluating them all.
3. The proprietary natures and complex compositions of commercial dye preparations.
4. The complexity of the mass transfer processes characteristic of specific batch dyeing machinery.

Current state of the art:

1. Our NTC work to date represents, to the best of our knowledge, the state of the art in closed-loop-adaptive, and fuzzy-logic-based control methods for dyeing processes, and in the application of both FIA and spectral transmittance measurements for dyebath monitoring.
2. In general, predeveloped and "pre-optimized" dyeing procedures arc used without closed-loop

feedback control. These are compromise procedures, for a family of dyes and a general class of fiber for example, and are not truly optimal.
3. Dyebath monitoring for dye exhaustion if monitored at all is generally based on relatively primitive methods which yield insufficient information.
4. Dosing of dyes and chemicals for process control is common, but closed-loop control of dosing appears not to be used. Dosing profiles are pre-set (See # 1 above).
5. At least one group in England has developed a computer model of the package dyeing process, which is stated to produce information on the instantaneous distribution of dye in the fibers, and in the yarns and packages. The mathematics involved has not been published to our knowledge, but it is most probably a simplified model.
6. Professor Rys's group at ETH has produced an impressive supercomputer simulation of the instantaneous distribution of dye in a random array of fibers during a dyeing process, based on simultaneous solution of the fluid flow, diffusion, and sorption equations. This is a very interesting development.

Industry Outreach:

We have collaborated actively with the ciba laboratories at Greensboro, NC and more recently also with Cotton Incorporated. Dupont Fibers also has an interest in some aspects of our work. Monsanto recently hired one of the graduate students working on the previous project S92-10. Two other graduate students accepted positions with companies specializing in control software and hardware. We expect this type of activity and interaction to increase, and we expect to continue as a source of highly trained personnel for our industry. We have an excellent group of graduate students who will complete their programs in the next few years, and can help us to train their successors before they leave us. These valuable contacts and interactions will increase as this research continues.

Current Progress:

In this section, the following six aspects of the project are covered: Software and System Development, FIA Methods for Reactive Dyes, FIA for Package Dyeing, Kinetic Modeling of Mixture Dyeing with Direct Cotton Dyes, Closed-Loop Control of the Acid Dyeing of Polyamides, and FIA Methods for Disperse Dyes.

1. Software and System Development:

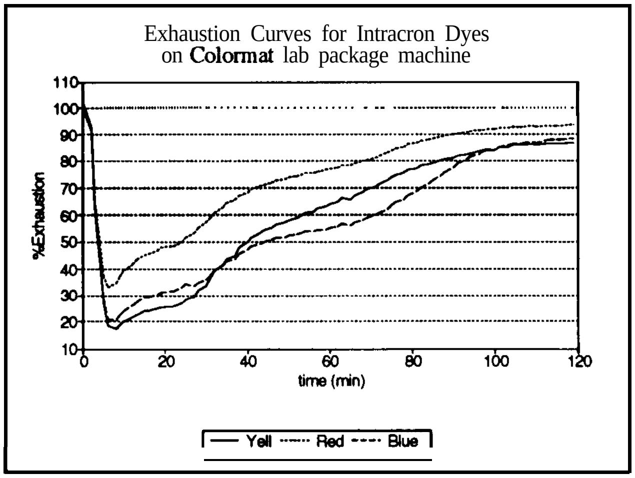
A new generation data acquisition and control system, centered around the Ocean Optics CCD spectrophotometer, has been developed to facilitate technology transfer, to conform to standards in software development, and to enhance our understanding of the batch dyeing process through better software tools.

Currently, the software consists of two major programs: XDye and SpeXtra. Both programs are Motif applications, and XDye currently runs on a variety of UNIX platforms. SpeXtra consists of a graphical user interface (GUI) to the spectrophotometer, and in the future, to FIA pumps. It is a real-time interactive program which collects and stores spectrophotometric data and performs filtering and digital signal processing. It currently runs on a **Pentium®** P-90 processor running Linux, the public domain version of UNIX@ for the PCs. **XDye** is a postprocessing program which takes data from the spectrophotometer and processes it using a UNIX based spreadsheet called **Xess®.** It is **network based and** displays, in real time, the concentrations of individual dyes in mixtures and also the dye exhaustions. **XDye** and **SpeXtra** need not run on the same computer nor at the same time. Further information can be found at our Internet@ site: **http://www.tx.ncsu.edu/html/research/wjj/rtda-batch-dye.html.**

2. FIA Methods for Reactive Dyes:

Several improvements to the FIA system have been made. A mixing chamber, constructed of PTFE and similar in design to the previous one, has been incorporated into the system. A PTFE chamber, which is inert to most solvents, is necessary in order to use solvent mixtures for dissolving and diluting the disperse dyes to be studied in this new project.

The original injection valve has been moved to a position between the mixing chamber and the spectrophotometer. A new sample injection valve which has a micro&chic actuator to allow the sample size to be determined by two different means has been installed. In addition to the conventional **fixed** loop with a given volume, a delay time can be set for the valve to rotate from one position to the other and back. Thus, the delay time and flow rate determine the volume of sample injected into the FIA system. With this option, changing sample size becomes a simple **software** selection which will allow various sample sizes to be used in the course of a dyeing, and further extend the useful dynamic concentration range of the **FIA** system.

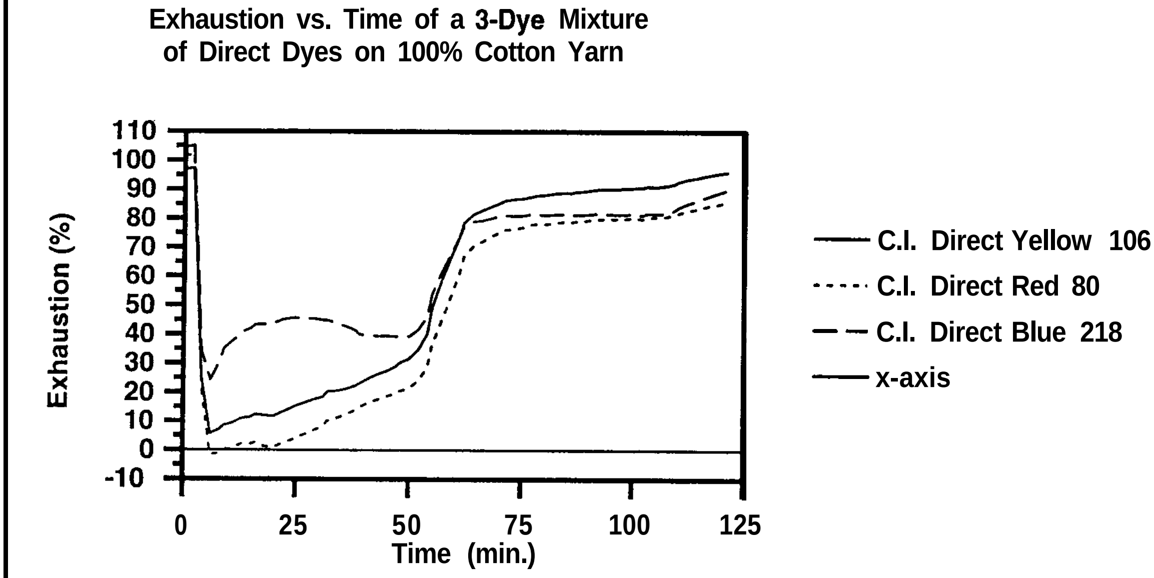


For new work on reactive dyeing, the original high-pressure valve will be **used** to inject part of the diluted and buffered **FIA** sample into an HPLC column. In conjunction with FIA, the fiber reactive dye sample will also be analyzed by reversed-phase, ion-pair chromatography to determine the extent of hydrolysis. By combining these **data** with the exhaustion percentages calculated in the FIA system, the percentage of dye fixed in the fiber may be determined. An HPLC method for separating the fiber reactive dye sample into starting material, mono-, and d&hydrolyzed components is currently being developed. These HPLC system components will be fully interfaced **with** the **FIA** hardware. The FIA data acquisition software is being modified to include the HPLC injection, and the software selection of injection volume for FIA.

An experiment with involving several dyeings with three-component mixtures is being designed. The resulting analyses will be used to optimize dyeing procedures for the chosen set of fiber reactive dyes. Exhaustion curves from FIA monitoring of a dyeing with Intracron” Yellow **VS-4GLS,** Red **VS-4BL,** and Blue **VS-4RL** (Crompton **&** Knowles) are shown in the above figure.

3. FIA of Package Dyeing:

As an initial step in extending our methods to commercial dyeing machinery, **the** FIA system has been used to monitor the exhaustion of tertiary mixtures of direct dyes on 100% cotton yarn in a laboratory package dyeing machine. An 80-g package of yarn was dyed in a Datacolor **Colormat®** yarn package dyeing machine, at a bath ratio of 9: 1. The direct dyes used were **Superlitefast®** Yellow EFC (C.I. Direct Yellow **106),** Sol-Aqua-Fast@ Red 2BL (C.I. Direct Red **80),** and **Superlitefast®** Blue **3GLST** (C.I. Direct Blue 218) from Crompton **&** Knowles. The exhaustion vs. time data from this dyeing are presented in the figure.



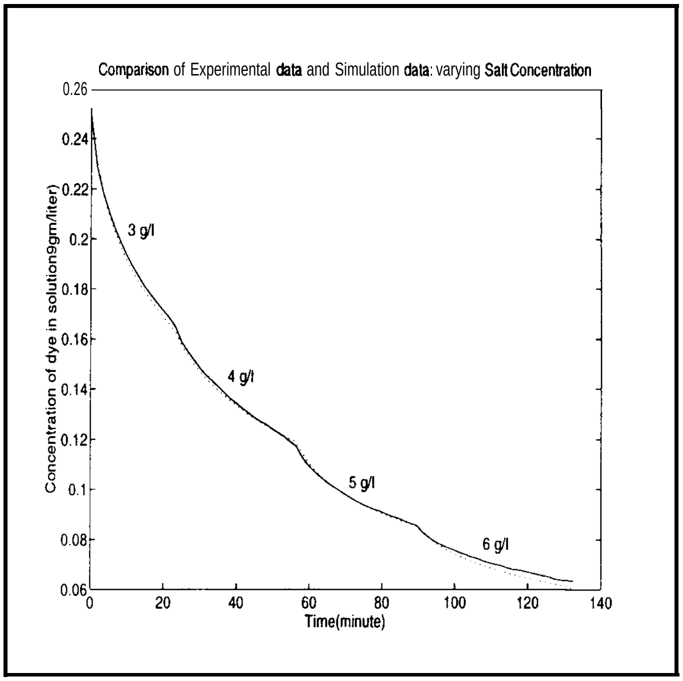
The Datacolor **Colormat®** dyeing machine has been modified so that the **dyebath** can be circulated out of the dyeing vessel via the sampling port, through the FIA apparatus, and back into the dyeing vessel through a port in the dye vessel lid. Filtered water was used as the carrier for the direct dyes. No buffer was needed as the carrier since the **pH** of the **dyebath** remains relatively neutral throughout the dyeing process.

Some problems had to be overcome in order to incorporate the **Colormat®** into the FIA monitoring loop. A pump had to be added upstream of the valve, mixing chamber, and spectrophotometer, to provide the pressure necessary to circulate the **dyebath** through the tubing. Also, the direct dyeing procedure calls for a dyeing temperature of 100°C. Since this temperature is too high for the circulation pump, the dye solution must be cooled. This cooling was effected by passing the dye solution through ice-cooled stainless steel tubing. These modifications, along with continuing optimization of the FIA system, have led to dependable, accurate, and repeatable monitoring of the exhaustion of individual direct dyes in tertiary mixtures on cotton yarn.

4. Kinetic Modeling of Mixture Dyeing with Direct Cotton Dyes:

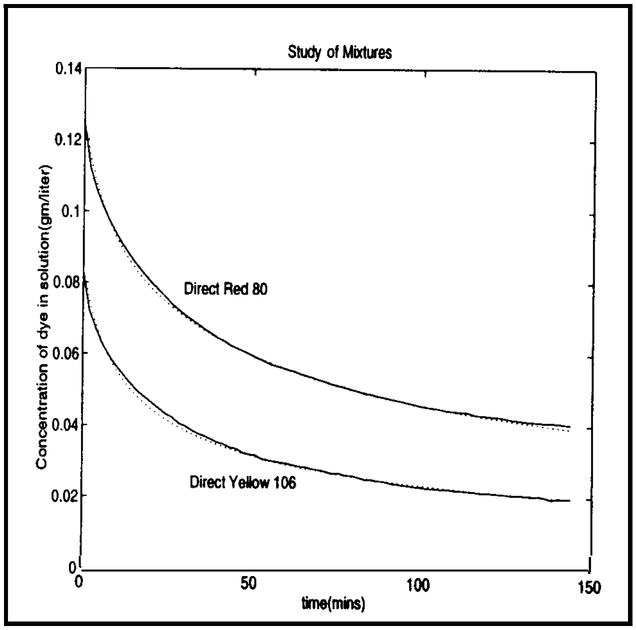
In an extension of earlier work on project S-92-10, kinetic models have been developed for the batch dyeing process, for use in the control of the dye uptake obtained from a mixture dyeing. Two different models, one based on the **Langmuir** kinetic model and one based on the mathematics of diffusion controlled sorption processes, were found to be suitable for predicting the dye transfer from the solution to the fabric for a direct dye on cotton cellulose dyeing system. These models were developed earlier for the case of a single dye in solution, for both constant and varying temperature conditions.

Recently this approach was extended, for both models, to incorporate salt effects on the behavior of a single dye, and also the kinetic interaction effects in mixture dyeing.In constant-temperature batch dyeing, when all the dye is added to the dyebath at the beginning of dyeing, the dye uptake is most rapid at the beginning and then slows down as the process continues. A limited, constant rate of dye transfer is preferred for an on-tone build-up of shade, and also for level dyeing of the fabric. This can be achieved at constant temperature by using salt dosing as a control parameter. Salt, in general, increases both the final exhaustion of the dye and the rate of dyeing, so by progressively adding suitable amounts of salt the dye transfer can be maintained at a uniform rate.



Methods have been developed for determining the parameter values for each model as a function of the amount of salt in the solution. These methods, used in conjunction with the kinetic models developed earlier, can predict the dyeing behavior of a single dye under varying salt conditions. The figure compares the actual dye transfer profile (shown with a solid line) with the predicted dye transfer profile using the diffusion model (shown with a dotted line). The amount of salt in the solution at different times during the dyeing is also shown in the figure. Additional work has also been done to extend the kinetic models to the prediction of the behavior of dyes used in mixtures. Several dyeings using sets of two dyes in varying mole ratios have been performed to determine the deviation in the behavior of dyes in mixtures, from their behavior when used alone. Results show that the uptake of a dye depends on the amount of the other dye present in the solution, rather than on the amount of the other dye present in the fiber.

Kinetic models developed for a single dye have been modified to consider the presence of two dyes in solution, and to incorporate the change in parameter values due to interactions. Some results obtained by modeling the parameter values of a dye for the diffusion model as a function of the amount of the second dye in the solution are shown in the figure. The amounts of C.I. Direct Red 80 and C. I. Direct Yellow 106 (Crompton **&** Knowles) in solution during the dyeing, measured from a mixture dyeing, is shown along with the predicted values using the modified diffusion model. Additional work needs to be done in modeling the interactions, and also in incorporating the temperature and salt effects on the dyes for the mixture case. **Our** previous work has shown that the behavior of three-dye mixtures can be predicted from appropriate interaction data for two-dye mixtures.



5. Closed-Loop Control of the Acid Dyeing of Polyamides:

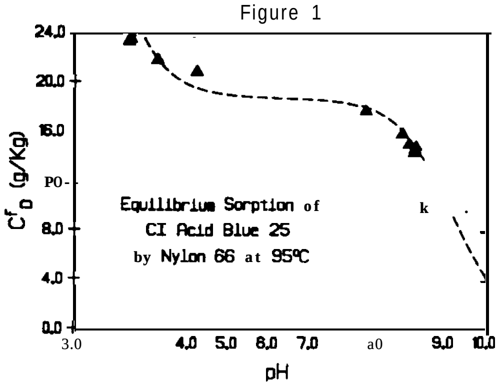
In this project, parallel work is underway on theoretical process models, on obtaining equilibrium dye sorption data, and on control hardware and software for polyamide dyeing. A set of piston pumps is being used to dose the dyes and the acid or alkali into the **dyebath.** The pumps have been calibrated, tested for their precision, and connected to the DARG computer for closed loop control of the addition of dyes and chemicals. Controlling the concentrations of the dyes and the concentrations of acid or alkali in the **dyebath** will help to control the uptake of the dyes by the substrate.

It appears to be possible in principle to use equilibrium dye sorption data for the closed-loop control of some key aspects of some practical dyeing processes. Experiments have been initiated to determine key equilibrium dye sorption data for the constant-temperature acid dyeing of polyamide fibers. The dimensionless equilibrium model, developed earlier **[1],** will be used to control some aspects of the uptake of acid dyes, individually and in mixtures, by nylon 66 fibers.

The parameters in the dimensionless model have been estimated from a set of **equilibrium** experiments conducted with this system. The dyeings were carried out with both single dyes and binary acid dye mixtures of C.I. Acid Blue 25 and C.I. Acid Yellow 49 (Crompton **&** Knowles). The equilibrium dyeings were carried out using about 4% owf of the commercial dyes at **pH** values ranging from 410. The dyeings were performed in a shaker bath at **95°C.** The **pH** of the **dyebaths** was set using appropriate volumes of ammonium hydroxide and acetic acid solutions. The amount of dye taken up by the substrate was measured by taking the difference between the concentration of dye in the initial **dyebath** solution and in the solution remaining after the dyeing had been **performed.**

It had been ascertained earlier that the **absorbances** of the dyes under study do not change with the **pH** of the solution. Therefore, the initial and final dye solutions could be compared with one another. The final **pH** values of the **dyebath** solutions were also measured.

Figure 1



The data for the equilibrium **pH**, as well as the dye concentrations in the solution and in the fiber, were fitted to the equilibrium model, and the parameters in the model were estimated. The figure shows one such tit for the equilibrium uptake of C.I. Acid Blue 25 by nylon 66 fibers.

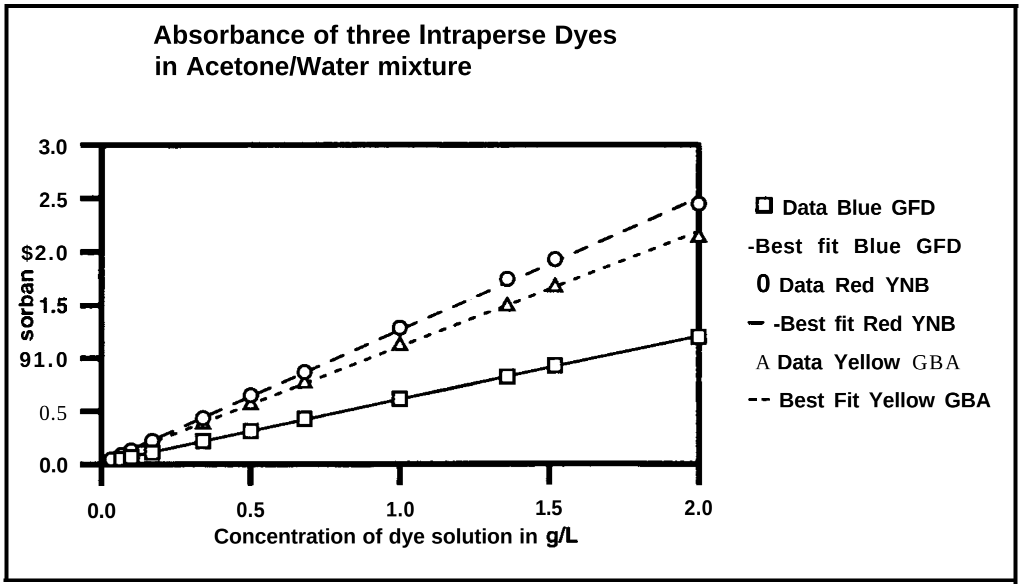
Since the commercial dyes also contain diluents, the parameters estimated by using the dimensionless model will be affected by the concentrations of these diluents. Commercial dyes have been purified using the method of Delmenico and Peters **[2]**. The equilibrium parameters based on these purified dyes are now being estimated by conducting equilibrium experiments using these dyes, to determine the effects of the diluents.

The equilibrium pammeters estimated above will be used to control certain aspects of the uptake of the dyes. This will be done by changing the concentrations of the dyes and the **pH** of the **dyebath** by dosing the dyes and acid or alkali into it. The concentrations of the dyes required in the **dyebath** can be calculated using the dimensionless model, given sufficient information about the polyamide fiber.

6. **FIA** Methods for Disperse Dyes

The disperse dyes selected for FIA method **dyebath** monitoring, **were Intraperse®** Yellow GBA extra (C.I. Disperse Yellow **3), Intraperse®** Blue **GFD** 150% (C.I. Disperse Blue **102),** and **Intraperse®** Red YNB extra (C.I. Disperse Red 17) (Crompton **&** Knowles), which dye acetate as well as polyester. Basol” WS (Miles Inc.)was used as a dispersing agent.

The initial focus was to find a suitable solvent/water mixture that would dissolve the disperse dye for determination by **FIA.** The mixture needed to contain an adequate amount of solvent to guarantee dissolution of the disperse dye as well as a reasonable amount of water to dissolve the dispersing agent.


Absorbance of three Intraperse Dyes in Acetone/Water mixture

Two different solvent/water mixtures were evaluated. The **first** contained acetone and water in varying amounts. The second contained acetone/M-pyml and water in varying amounts. Laser Light Scattering **(LLS)** experiments were run to determine which solvent mixture and what amount of solvent would provide the least scattering. Small particle **size** was related to low scattering intensities and characterized an acceptable solution of the disperse dyes. Thus a solvent mixture with low scattering intensity was sufficient for the FIA system. The mixture chosen was **acetone/water** 70 parts/30 parts. The acetone/water mixture was used in the FIA system to measure the spectra of single dye dispersions, in varying concentrations, to establish that Beer's Law applied to all measurements of the selected disperse dyes in the chosen solvent/water mixture. The **figure** shows typical data.

The disperse dye was pumped into the FIA system through the circulation pump. The solvent mixture was pumped into the FIA **system** through the Hamilton **Microlab®** M syringe pump. Both **were** injected through the injection valve into the mixing chamber. The solution and dilution of the disperse dye dispersion took place in the mixing chamber. The solvent/water/disperse dye solution was then run through the flow cell of the spectrophotometer and spectra were taken. Calibrations for the FIA system with sets of trichromatic mixtures of disperse dyes and the acetone/water mixture were run. The calibration showed that the predictions by the FIA system about the actual dye contents of a disperse dye dispersion of a tri-chromatic mixture of disperse dyes were acceptable. All disperse dyeings were done in the Datacolor **Colormat®** package dyeing machine, with acetate fabric at a liquor ratio of 15: 1.

References:

1). Arora, M.S., and McGregor, R., Dimensionless Groups for the Equilibrium Sorption of Polysulfonatcd Acid Dyes By Polyamides, Textile Research Journal, **65 (7),** 385-391 (1995).

2). Dehnenico, J.,and Peters, R.H., Application of the **Donnan** Equilibrium to the Distribution of Dye and Inorganic Ions between Wool and Solutions Part II: Dye Anions of Relatively Low Affinity, Textile Research Journal, **35 (1),** 14-32 (1965).