ABSTRACT

CHEN, KANGQIN. Analysis of Reactive Dye Mixtures — Characterization of Products from Bis-Dichlorotriazine Dye Synthesis. (Under the direction of Dr. Harold S. Freeman and Dr. C. Brent Smith).

Products from the synthesis of bis-dichlorotriazine (DCT) reactive dyes having cysteamine or cysteine as a linking group have been characterized. Commercial DCT dyes **29** and **34** were converted to intermediates **30**, **36**, **38** and **39** at various pH levels and the effect of pH on the number, distribution, and types of products was assessed using reversed phase HPLC.

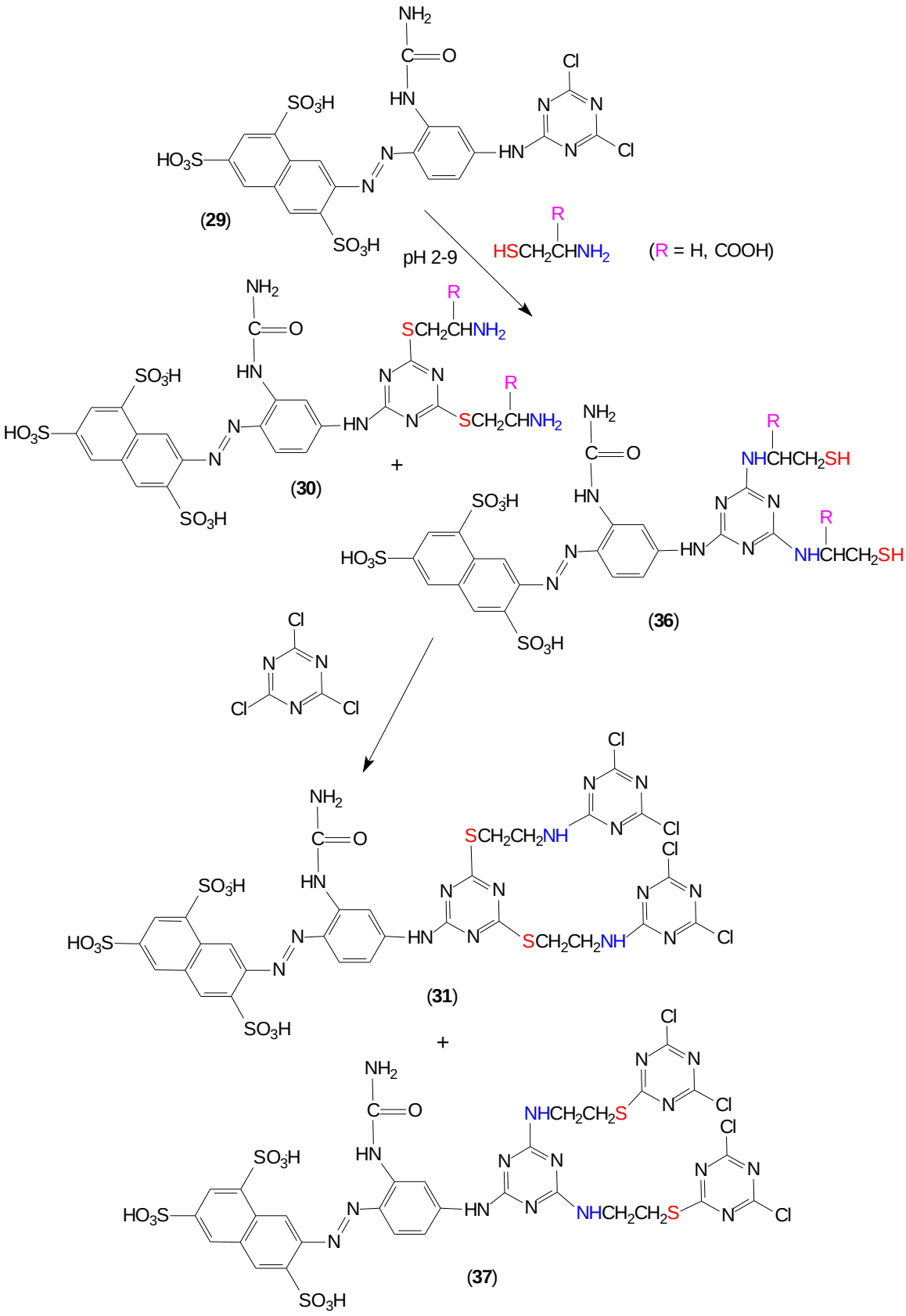
HPLC methods for separating the products obtained from step one of the synthesis were developed. Following an examination of many isocratic and gradient methods, it was determined that the optimum procedures involved gradient methods.

Results from HPLC studies employing the optimized methods indicated that type **30** and **38** structures were obtained when cysteamine (R=H) was used as the linking group at pH ≤ 4. When pH > 4 was used, cysteamine underwent reaction mainly at the $–NH_2$ end, giving type **36** and **39** structures. On the other hand, the reaction between cysteine (R=COOH) and the starting DCT dyes was much less sensitive to pH, as the reaction occurred mainly at the –SH group, presumably for steric reasons.

The developed HPLC methods were used to analyze bis-DCT dyes (**30**, **36**, **38**-**39**) obtained in step two of the synthesis. In this aspect of the study, dyes

obtained using cysteamine as the linking group were synthesized and analyzed. The results indicated that bis-DCT dye isomers could be readily separated and that the distribution of isomers as a function of pH could be determined. The methods employed also permitted a comparison of bis-DCT dyes synthesized in our laboratory with those produced by a contract industrial plant in Poland.

Part two of this study involved assessing the effects of pH used in dye synthesis on the dyeing properties and fastness properties of the target bis-DCT dyes. This aspect of the study involved developing an optimized dyeing procedure for applying the dyes to cotton fabric. Comparisons with commercial dyes were made and it was found that the new bis-DCT dyes gave deeper shades on cotton using less salt and dye than the commercial DCT dyes. It was also determined that the use of pH 4 for dye synthesis led to the best dye uptake and fastness properties.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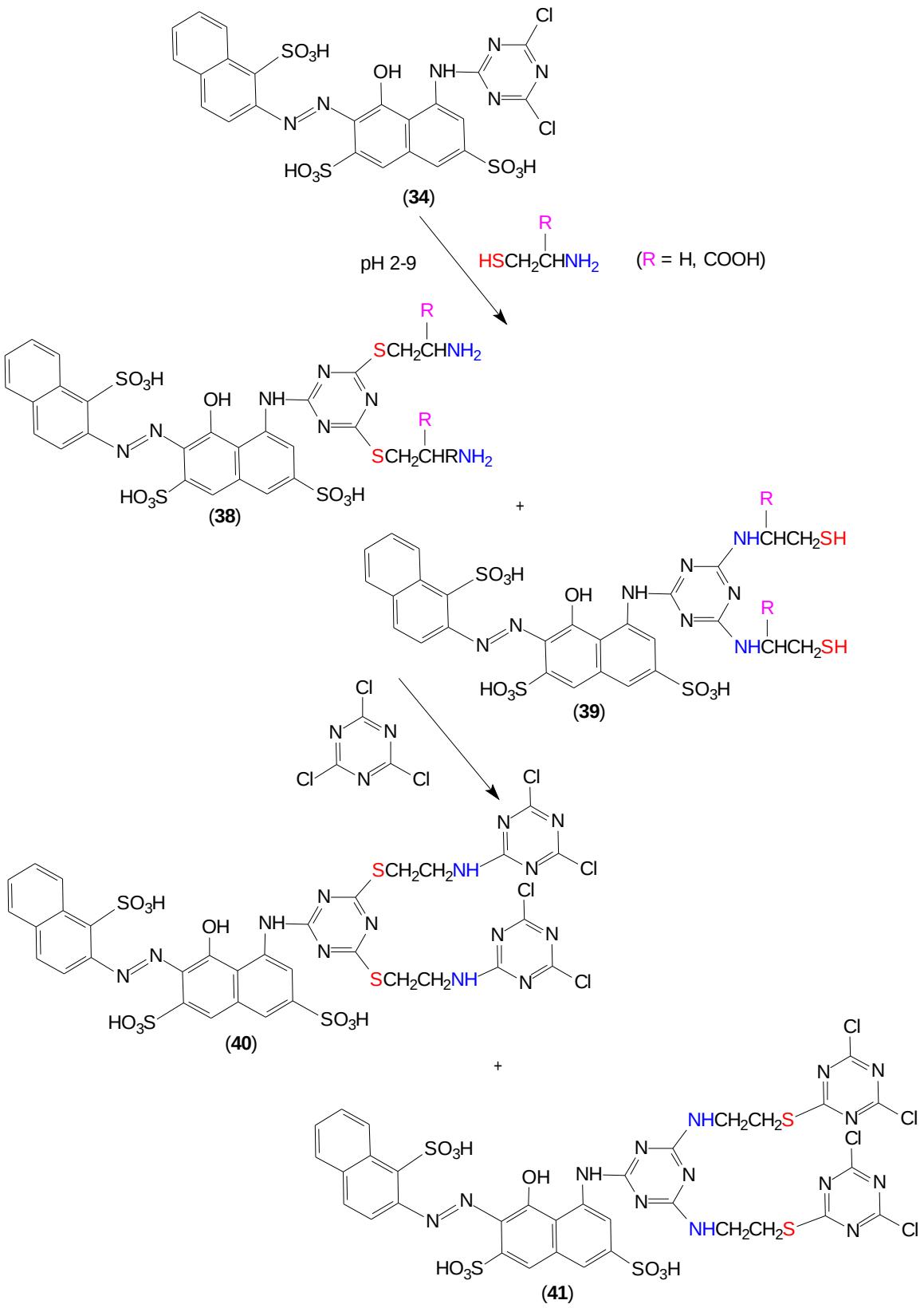
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ANALYSIS OF REACTIVE DYE MIXTURES

— CHARACTERIZATION OF PRODUCTS FROM BIS-DICHLOROTRIAZINE DYE SYNTHESIS

by

KANGQIN CHEN

A thesis submitted to the Graduate Faculty of
North Carolina State University
in partial fulfillment of the
requirements for the Degree of
Master of Science

Textile Chemistry

Raleigh

2006

Approved By:

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Dr. Harold S. Freeman	**Dr. C. Brent Smith**
Chair of Advisory Committee	**Co-chair of Advisory Committee**

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Dr. Kenneth W. Hanck

DEDICATION

I would like to dedicate this work to my father Dequan Chen, who passed away in 2005. Even in the last few days in his life, he never stopped thinking about my future and encouraging me to continue my graduate studies. Dad, I will always remember you and miss you!

BIOGRAPHY

Kangqin Chen was born in Rudong, Jiangsu, China on April 23, 1977 as the first and only child of Xiumei Wu and Dequan Chen. In 1994, Kangqin graduated from Rudong High School. She then attended Nanjing University and received a bachelor's degree in chemistry in 1998. After graduation, she became a lecturer at Nanjing Architecture and Civil Engineering Institute, now named Nanjing University of Technology, and worked there for 3 years. In 1999, she married Tong Wu. In fall of 2001, she came to the USA to accompany her husband, and entered the College of Textiles at North Carolina State University in 2004 fall. She is a candidate for the Master of Science degree in Textile Chemistry.

ACKNOWLEDGMENTS

I would like to thank Dr. Harold S. Freeman, my committee chair, for his support and constant guidance in my research efforts. He were always willingly to clarify many key points, and I greatly appreciate his taking the time to mentor me. To my co-chair advisor Dr. C. Brent Smith, thank you for your willingly answering all my questions. And to Dr. Kenth W. Hanck, thank you for being gently agree to be my committee member.

I also thank Dr. Keith Beck for sharing his expertise in HPLC, Dr. Malgorzata Szymczyk for conducting the synthesis of intermediates and dyes used in my experiments, and Cindy T. Salley and Dr. Ahmed El-Shafei for their help with HPLC experiments. Thanks are extended to Mrs. Birgit Andersen, Mrs. Judy D. Elson and Mr. Jeffrey D. Krauss for their kindness and help during my studies. This study was supported through a gift from Procter and Gamble. The author wishes to thank the company for its support.

Special thanks go to my husband, Tong Wu, who faithfully supported me, gave me help and kept me from being overly stressed during this process. To my mom, Xiumei Wu, I am more grateful than you will ever know for everything that you have done, especially for your strong support when dad passed away. To my parents in law, Fenghua Dai and Xueshun Wu, thank you for your support, encouragement and push over the years.

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I. INTRODUCTION

1. HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

1.1 Chromatography

Chromatography encompasses a versatile group of methods that permit the separation of closely related components in complex mixtures. It is a physical method in which the components to be separated are selectively distributed between two immiscible phases: a mobile phase is flowing through a stationary phase [1].

Column chromatography was originally used in 1906 by the Russian botanist Mikhail Tswett to conduct the separation of various plant pigments, notably chlorophylls and xanthophylls and reported. A glass column packed with finely divided $CaCO_3$ was used to separate the components of a petroleum extract of dried leaves [2]. Although it was not recognized until Kuhn and Lederer's work involving the separation of carotene into its α- and β- isomers was reported, it is generally accepted that Tswett first demonstrated the principles and the potential of chromatography and named this method [2, 3].

The initial discoveries led to the development of partition chromatography in 1941, paper chromatography in 1944, thin-layer chromatography in 1951, and gas-liquid chromatography. These methods and ion-exchange and gradient elution chromatography are described in a review paper published by Straw [2].

The two major components of chromatography are the mobile phase and a stationary phase. The mobile phase is the solvent moving through the column, which is either a liquid or a gas. The stationary phase stays in place inside the

column. Most commonly this is a viscous liquid coated on the inside of a capillary tube or the surface of solid particles packed into the column. The solid particles themselves can be the stationary phase too [2-5].

Chromatography is divided into categories according to the mechanism associated with the interaction between the stationary phase and the solute (sample). There are five major types of chromatography.

Type 1: Adsorption chromatography. This type uses a relatively polar material with a high surface area as a stationary phase that adsorbs solutes on the surface of solid particles, and a mobile phase comprising a relatively non-polar liquid or gas that passes through the stationary phase to separate the different solutes. The stronger the adsorption of the solute, or the higher the polarity of the solute, the longer it takes to complete the chromatography. This is also known as normal phase chromatography, and includes thin-layer chromatography (TLC) and classic column chromatography [4, 5].

Type 2: Reversed-phase chromatography. This type involves a non-polar material, which forms a thin layer on the surface of a solid support like silica, and a relatively polar (water to tetrahydrofuran) liquid or gaseous mobile phase. The solute equilibrates between the stationary phase and the mobile phase, which allows for separation of components in the sample. The subtypes are derived from the mobile phase used: Liquid chromatography (LC), gas chromatography (GC) and supercritical fluid chromatography (SFC) [4, 5].

Type 3: Ion-exchange chromatography (IEC). IEC is often used to analyze samples that contain ionic groups, such as amino acids, ionic metabolites and

organic ions. The stationary phase in IEC contains anions (e.g. —SO_3^-) or cations (e.g. —$N(CH_3)_3^+$) that are covalently attached to a solid phase, which is typically a resin. A liquid mobile phase is used, and sample ions of the opposite charge are interact with the stationary phase by electrostatic bonding. A special type of IEC is ion chromatography, which is used to separate strong acids and bases, but the equipment is different [4, 5].

Type 4: Molecular exclusion chromatography. This types also known as size-exclusion chromatography, gel permeation chromatography (with organic solvents), or gel filtration chromatography (with aqueous solutions), is separation based on molecular size and can be used to analyze polymers as well as small molecules. The mobile phase carries the sample through the stationary phase, which is actually a porous gel. The largest molecules elute first, since they are too big to enter the pores, and the smallest molecules are eluted last. This is the best method to choose when the molecular mass differences are at least 10% for the sample mixture [4, 5].

Type 5: Affinity chromatography. This is one of the most selective types of chromatography. Highly specific biochemical interactions are account for the observed separation. Separation is achieved when the stationary phase contains molecular groups that can only adsorb specific types of molecules. This method has been used to isolate compounds such as proteins and lipids from complex mixtures [4, 5].

1.2 Liquid Chromatography

Liquid chromatography is very important because most compounds are not volatile enough for gas chromatography [5]. The diagram in Figure 1.1 illustrates the case in which solute A has greater affinity for the stationary phase than solute B. In this example, analyte and eluent are applied to the top of an open, gravity-fed column containing the stationary phase, providing the basis for modern chromatography. Solute diffusion and the finite rate of mass transfer between the mobile and stationary phase often leads to band broadening, which makes the separation difficult. Minimization of band broadening is achieved by a column, in which the stationary phase is supported by a porous nylon net beneath which is very little dead space (Figure 1.2). An adjustable flow adaptor that presses tightly against the top of the stationary phase prevents sample and solvent from mixing above the column. Inlet and outlet tubing have a 1-mm diameter to minimize mixing of liquids within the tubing. All of these features decrease band broadening and increase resolution.

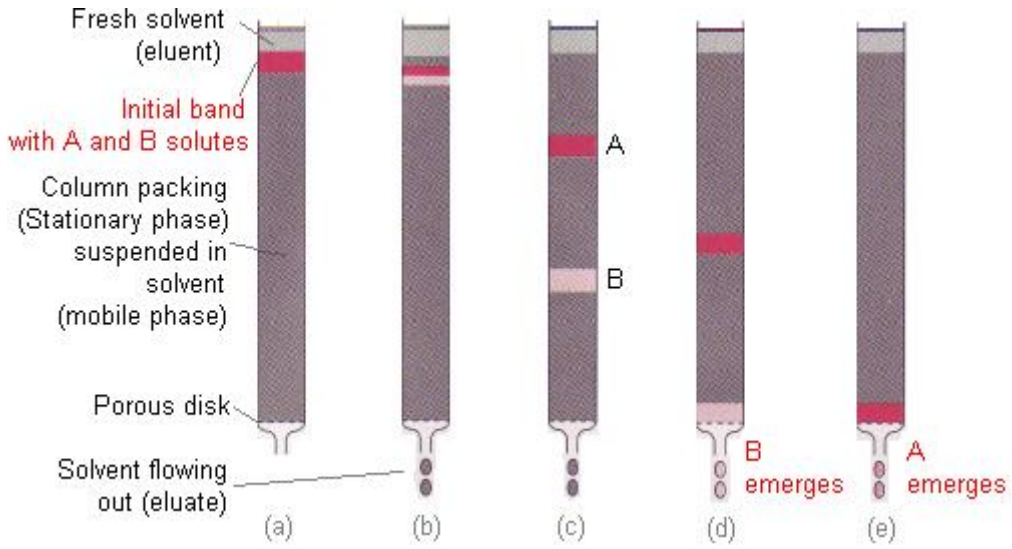


Figure 1.1. Schematic representation of column chromatography.

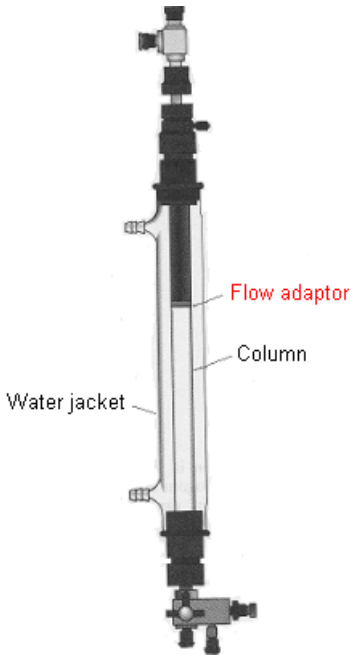


Figure 1.2. Glass chromatography column with a flow adaptor at the top.

1.2.1 The Stationary Phase

The three most common adsorbents are silica gel ($SiO_2 \cdot xH_2O$), alumina ($Al_2O_3 \cdot xH_2O$) and cellulose. Silica is weakly acidic and interacts most strongly with basic solutes. Alumina is typically sold in acidic (pH 4), neutral (pH 7), or basic (pH 10) forms. Neutral alumina is used for most non-aqueous separations. Basic alumina has cation-exchage properties in aqueous solution, and acidic alumina is an anion exchanger. Cellulose is the adsorbent for compounds that are too polar to be eluted from silica gel or alumina. Other stationary phases are activated charcoal, Florisil, and magnesia [5].

1.2.2 Solvents

Solvents compete with the solute for adsorption sites on the stationary phase. The relative abilities of different solvents to elute a given solute from the

column are practically independent of the solute itself. The eluent strength is a measure of the solvent adsorption energy. The more polar the solvent, the greater its eluting power. In general, the greater an eluent's strength, the more rapidly the solutes will be eluted from the column. A gradient of increasing eluent strength is very useful for many separations. First, a solvent of low eluent strength solvent elutes weakly retained solutes. Then a second solvent is mixed with the first to increase eluent strength and elute more strongly adsorbed solutes. A small amount of polar solvent will increase the eluent strength of a non-polar solvent dramatically [5].

1.3 High Performance Liquid Chromatography

High Performance Liquid Chromatography (HPLC) is a powerful separation method [3, 4]. It is one of the most popular techniques used by scientists to separate mixtures into their individual components. HPLC utilizes high pressure to force a solvent (mobile phase) through a column. The basic components of an HPLC system include mobile phase reservoirs, pump, sample injector, column, detector, and data recorder [3].

1.3.1 Mobile phase reservoirs

One or more glass or stainless steel reservoirs are used in a modern HPLC apparatus. The reservoirs are often equipped with a means of removing dissolved gases and a means of filtering dust and particulate matter. The dissolved gases interfere by forming bubbles in the column and detector system. Bubbles cause band broadening in the column and interfere with the

performance of detector. The dust and particulate mater will damage the pumping or injection system or clog the column. But it is not necessary to make the filters and degasser integral parts of the HPLC system. A common way of treating solvents before introducing them to the reservoirs is to filter them through a milipore filter under vacuum [3, 5].

Modern HPLC equipment is often equipped with devices that introduce solvents from two or more reservoirs into a mixing chamber at various rates [3, 5]. This makes both isocratic and gradient elution possible. An isocratic elution is a separation that employs a single solvent (or homogeneous solvent mixture) of constant composition. It does not always discriminate adequately between several components of a mixture, or provide sufficiently rapid elution of all components. Frequently, a gradient elution can greatly enhance separation efficiency. Here, two or three solvent systems that differ significantly in polarity are employed. After elution begins, the ratio of the solvents is varied in a programmed way, sometimes continuously and sometimes in a series of steps.

1.3.2 Pumping System

The requirements for an HPLC pumping system are severe. They include: (1) the generation of pressures of up to 6000psi, (2) pulse-free output, (3) flow rates ranging from 0.1 to 10 mL/min, (4) flow control and flow reproducibility of 0.5% relative or better, and (5) corrosion-resistant components (seals of stainless steel or Teflon). Three types of pumps are encountered: reciprocating pumps, syringe or displacement-type pumps, and pneumatic or constant pressure pumps.

Reciprocating pumps are currently used in about 90% of commercially available HPLC systems [3, 4].

Many commercial instruments are equipped with computer-controlled devices for measuring flow rate, by determining the pressure drop across a restrictor located at the outlet of the pumping system. Any difference in signal from a preset value is then used to correct the speed of the pump motor. Most instruments also have a means for varying the composition of the solvent continuously or step-wisely [3-5].

1.3.3 Sample Injection System

Sample feed is one of the critical aspects of HPLC. If the injection is not carried out carefully, even the best column will produce a poor separation. Theoretically, an infinitely small volume of sample mixture should be placed in the center of the column head, carefully enough to avoid having air entering at the same time. There are various possibilities for sample injection: (a) with syringe and septum injector, (b) with a loop valve, and (c) with an automated injection system (autosampler) [4].

The earliest and simplest means of sample introduction was syringe injection through a self-sealing elastomeric septum, which yields the lowest possible band broadening. Unfortunately, this method is not suitable for HPLC because it is limited to pressures below 100bar, and the reproducibility of syringe injections is often <2-3% [3, 4].

The most widely used method of sample introduction in liquid chromatography involves sampling loops. The loop is filled with sample solution

and the internal channeled rotor seal is then engaged bring the loop within the eluent flux.

An autosampler also uses a six-port loop valve. The mechanism associated with the autosampler is same as that for loop injection except it can inject many samples into the loop one by one automatically by programming [4].

1.3.4 Columns

Columns are ordinarily made of smooth-bore stainless steel tubing, also some heavy-walled glass tubing is encountered which is only used for pressures less than 600 psi. Columns mainly range from 10 to 30cm in length, 4 to 10mm in inside diameter, and the most common particle size packings is 5 or 10 μm [3]. Recently, high-speed, high-performance columns, which have inside diameters of 1 to 4.6mm, 3 or 5 μm particles, and lengths as short as 3 to 7.5 cm, have been produced [3]. Typically the analytical columns have porous particle packings. This type packing consists of porous microparticles having diameters of 3 to 10 μm. For a given size particle, the particle size distribution should be as narrow as possible. The reason is that the smallest particles determine column permeability and the largest particles determine the plate number. Small particles produce high flow resistance and large particles are responsible for the degree of band broadening [3, 4].

Often a hydrophobic stationary phase is bonded to a solid, which is often silica. Silica carries OH groups (silanol groups) on its surface and may be chemically modified to give stationary phases with specific properties. The silanol group can be esterified with an alcohol, ROH. For steric reasons, the reaction is

confined to the silica surface and does not involve the solid body interior, so that the bonded residues project from the silica, like tails or “brushes”. Esterfied silica is easy to hydrolyze, so it cannot be used with a mobile phase containing water or alcohol. The silanol group reacts with thionyl chloride ($SOCl_2$) and produces S–Cl groups that combine with amines to give Si-N bonds. These groups have better hydrolytic stability than ester linkages. The most stable derivations of silica are formed by generating Si-O-Si-C bonds. Octadecylsilicane (C^{18} silica gel) is the most widely used of these chemically modified products. It is extremely non-polar and is the preferred choice for use in reversed-phase chromatography. Polymer structures rather than brushes can also be produced by chemical modification of silica [4].

1.3.5 Detectors

The detector should be able to recognize when a component of the solute is eluted from the column. It has to be able to monitor the change in mobile phase composition in some way, convert this change into an electric signal and then convey the signal to the recorder or display where it is shown as a deviation from the base line [4]. The ideal detector is sensitive to low concentrations of every analyte, provides a linear response which means the signal is proportional to analyte concentration, does not broaden the eluted peaks which requires the cell volume should be small, and insensitive to changes in temperature and solvent composition [3-5].

Liquid chromatographic detectors are of two basic types. Bulk property detectors respond to a mobile phase bulk property, such as refractive index,

dielectric constant, or density, which is modulated by the presence of solutes [3]. Solute property detectors respond to some property of solutes, such as UV absorbance, fluorescence, or diffusion current, that is not possessed by the mobile phase [3]. The most common detector for HPLC is the UV detector. UV detectors are sensitive to compounds that absorb UV or visible light, have a wide linear range, are relatively unaffected by temperature fluctuations, and are suitable for gradient elution with non-absorbing solvents [4]. The simplest UV absorption detectors are filter photometers with a mercury lamp as the source. It allows for one or two wavelengths to be used in the analysis by changing filters. The most powerful UV detectors are photodiode array (PDA) detectors. They have monochromators that allow the full range of wavelengths to be recorded. This kind of detector can be useful for sample components that absorb light at different wavelengths [3]. The refractive index detector has the significant advantage of responding to almost every solute, but has a lower detection limit (1000 times less than UV) and is not good for gradient elution because the baseline changes as the solvent changes [3, 5]. Inductivity coupled atomic emission, mass spectrometry, and Fourier transform infrared spectroscopy have also served as detectors in HPLC studies [5].

1.4 Ion Pair Chromatography (IPC)

Ion pair chromatography (also called ion-interaction chromatography) is a form of reverse-phase partition chromatography that is used for the separation and determination of ionic species [3, 5]. IPC represents an alternative to ion-exchange chromatography (IEC). IEC uses columns packed with anion-

exchange or cation-exchange resins for analysis of ionic species [3]. Many problems can be solved using either method. For the separation of small inorganic and organic ions, IEC is preferred unless selectivity is a problem. But IEC is not as good for separating mixtures of bases, acids, and certain neutral products, while IPC is capable of dealing with all of these compounds [4]. Reversed phase chromatography, allows for separation of charged species that would not otherwise be amenable to analysis. The mobile phase in ion-pair chromatography consists of an aqueous buffer in an organic solvent (preferably methanol or acetonitrile) and an ionic compound containing a counter ion of opposite charge to the analyte [3].

The advantages of ion-pair chromatography for separating ionic samples include the use of reversed-phase systems, suitability for mixtures of acids, bases and neutral products, and amphoteric molecules that have one cationic and one anionic group, the preferred choice when the analytes have very similar pKa values. In the latter case, selectivity can be influenced by the choice of the counter ion and the many available ion-pair reagents [4, 5].

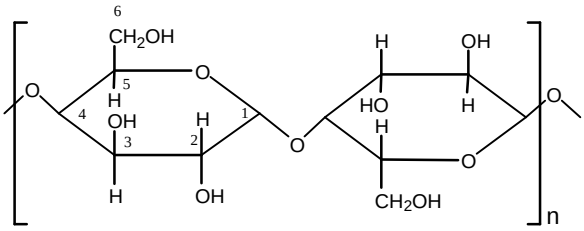
2. CELLULOSIC FIBERS

Cellulose is the most abundant naturally occurring organic polymer. The term “cellulosic fibers” is frequently used, but the type is significantly dominated by cotton, the purest form of cellulose found in nature. Cotton is the seed hair of plants of the genus *Gossypium*. Other cellulosic fibers are viscose rayon, linen, cupraammonium rayon, and jute, which can be dyed with dyes used on cotton [7-9]. Cellulosic fibers can be divided into three types. Type 1 comprises fibers

having average fiber lengths of 25 to 60 mm. Type 2 comprises coarser species with fiber lengths of 13 to 33 mm and type 3 species of still shorter fiber lengths (9 to 25 mm) [8, 9].

2.1 Cellulose Chemical Structure

The molecular structure of cellulose has always been of great interest to scientists and over time several structures have been proposed. The linear polymer, β-D-glucopyronose with 1,4-glycosidic bonds (**1**), is the widely accepted structure for cellulose. Consequently it may be considered as a polyhydric alcohol. Each glucopyranose ring in the cellulose chain contains three hydroxyl groups, a primary hydroxyl group in the 6- position and secondary hydroxyl groups in the 2- and 3- positions.



(**1**)

Cellulose forms a ribbon-like structure, which is capable of bending and twisting due to the oxygen bridges that connect the glucose rings. Six hydroxyl groups protrude from each cellobiose repeat unit in the chain. These groups aid the stability of the molecule by forming intermolecular (O-6-H and O-3 of another chain) and intramolecular (O-3-H and O-5', O-2-H and O-6') hydrogen bonds [10, 11]. The hydrogen bonds in the chains help connect the neighboring chains together in the structure. Intermolecular hydrogen bonds formed between the O-6

proton and the O-3 are to stabilize the structure of Cellulose I [10]. The degree of polymerization (DP) for cellulose depends on the source. The DP can be as low as 100 for regenerated cellulose powders and as high as 14,000 for natural cellulose fibers such as cotton [8, 10].

Naturally occurring cellulosic materials have been evaluated with respect to their fine structure and morphology. The degree of crystallinity of the cellulose substrate depends on the origin and the pretreatment of the sample [10]. It has been determined that the degree of order for cotton fibers is 2:1 crystalline regions to amorphous regions [12]. In the cellulose structure the highly oriented molecules spiral around one another in the fiber. The spiral angle for cellulose depends on the source. Cotton has a spiral angle of 20°- 30°. Flax, jute and hemp have a smaller spiral angle of 6°, which provide these fibers with higher strength [12].

2.2 Cellulose in the Presence of Alkali

The acidity of hydroxyl groups in cellulose decreases in the order:

6-OH > 2-OH >3-OH

A polyhydric alcohol such as cellulose is more acidic than a simple alcohol and, in fact is comparable with water as shown by the dissociation constants (K):

Water: $K= 2.09x10^{-14}$

Methanol: $K= 8.1x10^{-15}$

Manitol: $K= 7.5x10^{-14}$

Cellulose: $K= 1.84x10^{-14}$

The dissociation constant for cellulose refers to the ionization of the hydroxyl group in the 6- position of the glucopyranose ring. The hydroxyl groups in positions 2- and 3- of the ring are less acidic. Therefore, cellulose is ionized under alkaline conditions and can behave as a nucleophile towards compounds containing electron-deficient carbon atoms (e.g. reactive dyes) [13-15].

When cellulose (Cell—OH) is treated with alkali (OH^-), a cellulosate anion ($Cell—O^-$) is formed. The ionization equation for this reaction is:

$$Cell—OH + OH^- \longleftrightarrow Cell—O^- + H_2O$$

The cellulosate anion is capable of reacting with suitable dyes by nucleophilic substitution or addition reactions to form covalent bonds [15, 16].

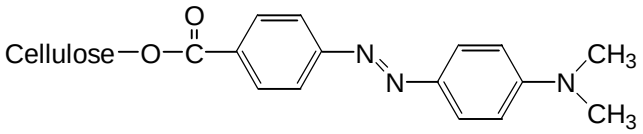
Esterification of cellulose is possible with most inorganic and organic acids by methods similarly used with simple alcohols. By the esterification of the cellulose molecules acetates can be formed. Cellulose acetates are important textile fibers and are used in the formation of industrial products, such as sheeting and molded plastics. Acetylation is usually achieved through the addition of acetic anhydride and an added acid catalyst [9]. The reaction can be written as: $Cell{-}OH + (CH_3CO)_2 \xrightarrow{H^\oplus} Cell{-}O{-}COCH_3 + CH_3COOH$

3. REACTIVE DYES

Fiber reactive dyes are colored organic compounds that have suitable groups capable of forming covalent bonds between reactive groups of the dye molecule and nucleophilic groups on the polymer chains within the fiber. In principle, a reactive dye should contain a leaving group (X) which can undergo nucleophilic displacement by a hydroxyl group of cellulose in the presence of

aqueous alkali (Dye—X + Cell—O^- ⟶ Dye—O— Cell + X^-), or an activated C═C bond which is able to add to a hydroxyl group of cellulose (–CH═CH_2 + Cell—OH ⟶ –CH_2—CH_2—O—Cell) [2, 17].

The first covalent dye-cellulose bond was achieved in 1895 by Cross and Bevan. Cellulose was treated with strong caustic soda solution. The resultant "soda cellulose" was benzoylated, nitrated, reduced, diazotized and coupled with amines or phenols to form azo dyes that were linked to cellulose through an ester bond (e.g. **2**). Yellow and red colors with excellent washfastness were obtained. However, the required reaction conditions were much too harsh for the cellulose fibers, causing severe degradation. The early attempts were mainly of academic interest [9,18,19].



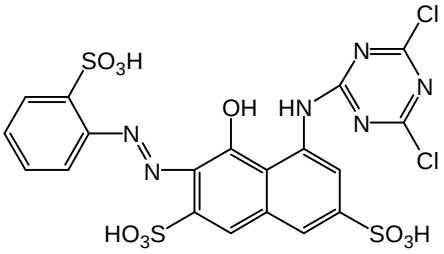
(**2**)

The first commercial reactive dyes for cellulose were developed by Rattee and Stephen and marketed by ICI in 1956 under the trade name Procion M [21]. This development was more than 60 years after the work of Cross and Bevan. The major factor contributing to this long delay in reactive dye commercialization was the widely held belief that cellulose was a relatively inert substrate requiring drastic and probably anhydrous condition to bring it into reaction with acylating agents [22]. Therefore, in early studies dyestuff chemists were led astray in thinking that they needed to convert cellulose to the more reactive soda cellulose to make fiber reactivity possible [22]. No one expected that any reactive group

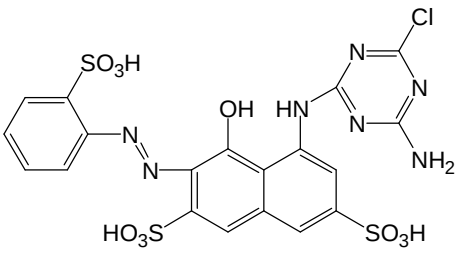
would prefer to react with a hydroxyl group of cellulose when cotton was placed in an aqueous dyebath containing numerous competitive hydroxyl groups from water [23].

The Procion M dyes contained dichlorotriazine reactive groups that were capable of reacting with Cell—OH at low temperatures (20-40°C) [22]. There have been many advances in reactive dyes since the first commercialization of the Procion dyes. When the Procion dyes were patented, it was discovered that Ciba was already producing a monochlorotriazine (MCT) “reactive dye” and sold as direct dyes without knowing that the dye was forming a covalent bond with cellulose. Ciba began marketing the MCT dyes as Cibacron dyes which were suitable for hot-dyeing and printing at the same time of ICI’s introduction of Procion H dyes in 1957 [9, 22].

Procion Brilliant Red M-2B (**3**) and Cibacron Brilliant Red B (**4**) are two of the early members of the reactive dye family [22]. These dyes were introduced for brilliant shades and the ability to be applied to a cellulosic fabric using a variety of different applications. They are more stable to light and wet treatment than direct dyes, and have a more simplistic application than vat dyes [20, 24].



(**3**)



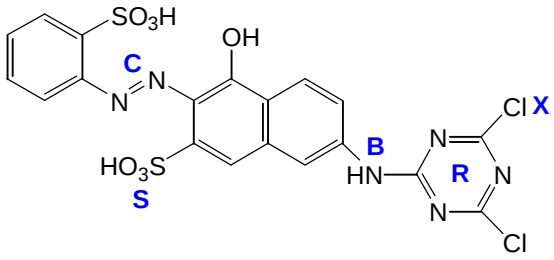
(**4**)

In the years that followed, a large number of reactive dyes with varieties of reactive groups were developed. A summary of the history of commercial reactive dyes is shown in Table 1.1 [18, 25].

Table 1.1. Introduction of commercial reactive dyes.

Year	Commercial name	Company
1956	Procion M	ICI
1957	Procion H	ICI
1957	Cibacron	Ciba
1958	Remazol	Hoechst
1958	Levafix	Bayer
1959	Reactone	Geigy
1959	Drimarene	Sandoz
1961	Levafix E	Bayer
1963	Elisiane	Francolor
1964	Primazin P	BASF
1964	Solidazol	Cassella
1964	Procilan	ICI
1966	Levafix P	Bayer
1966	Lanasol	Ciba
1968	Reactofil	Geigy
1970	Procion HE	ICI
1970	Verofix	Bayer
1970	Drimalan	Sandoz
1977	Procion T	ICI
1979	Procion H-EG	ICI
1984	Kayacelon	Nippon Kayaku
1987	Procilene	ICI
1988	Cibacron C	Ciba

The structure of a reactive dye (**5**) consists of a solubilizing group (S), a chromogen (C), a bridging group (B), and a reactive group (R) containing a leaving group (X). The solubilizing groups make the dye soluble which is very important for cellulose dyeing, and most of time they are $–SO_3Na$ groups. The chromogen provides the color. The bridge insulates the conjugated system from the reactive group to preserve the color of the original dye. The reactive group is capable of reacting with nucleophilic groups ($-NH_2$, -SH, and –OH) in textile fibers by addition or substitution reactions so that the leaving groups will be replaced by the neucleophilic groups of the fibers [17, 18].



(**5**)

3.1. Reactive Groups

Reactive dyes are classified by the groups that facilitate covalent bonding to the fiber. The important reactive groups, including monofunctional and bifunctional reactive systems, are listed in Table 1.2 [8,13].

3.1.1 Monofunctional Reactive Systems

These systems can react only once with the nucleophilic groups in the fiber. They include triazine, vinylsulfone, pyrimidine and quinoxaline systems.

Table 1.2. Important reactive dye systems.

Reactive Group	Commercial Name
Monofunctional	
Dichlorotriazine	Procion MX
Monochlorotriazine	Procion H
Monofluorotriazine	Cibacron F
Trichloropyrimidine	Drimarene X
Difluorochloropyrimidine	Drimarene K
Dichloroquinoxaline	Levafix E
Sulphatoethylsulfone	Remazol
Sulphatoethylsulfonamide	Remazol D
Bifunctional	
Bis(monochlorotriazine)	Procion HE
Bis(mononicotinotriazine)	Kayacelon React
Monochlorotriazine-sulphatoethylsulfone	Sumifix Supra
Monofluorotriazine-sulphatoethylsulfone	Cibacron C

A. Triazine System

The first commercial reactive dyes were derivatives of cyanuric chloride. Cyanuric chloride is a very important synthetic compound because of the stepwise reactivity of its chlorine atoms. The first chlorine atom can be replaced by a nucleophile at 0-5°C, the second at 35-40°C, the third at 80-85°C. Commonly, the first chlorine atom is conveniently substituted by a chromogen to form a reactive dye, and then one or two of the remaining chlorine atoms is replaced by the cellulosate anions (Cell-O^-) [13, 18].

The reaction of cyanuric chloride with a chromogen containing an amino group produces a dichlorotriazinyl (DCT) dye (**6**). DCT dyes are highly reactive and are very sensitive to hydrolysis. A monochlorotriazinyl (MCT) (**7**) dye will be formed by replacing one of the chlorine atoms in the DCT with a non-labile species such as an amine or alkoxide [18]. The MCT dyes are less reactive than the DCT dyes and require higher temperatures and more alkali for reaction with cellulose. Reactivity of the MCT dye structures can be increased by replacing the chlorine atom with a fluorine atom or through reaction with tertiary amines (Figure 1.3) [9, 13, 18].

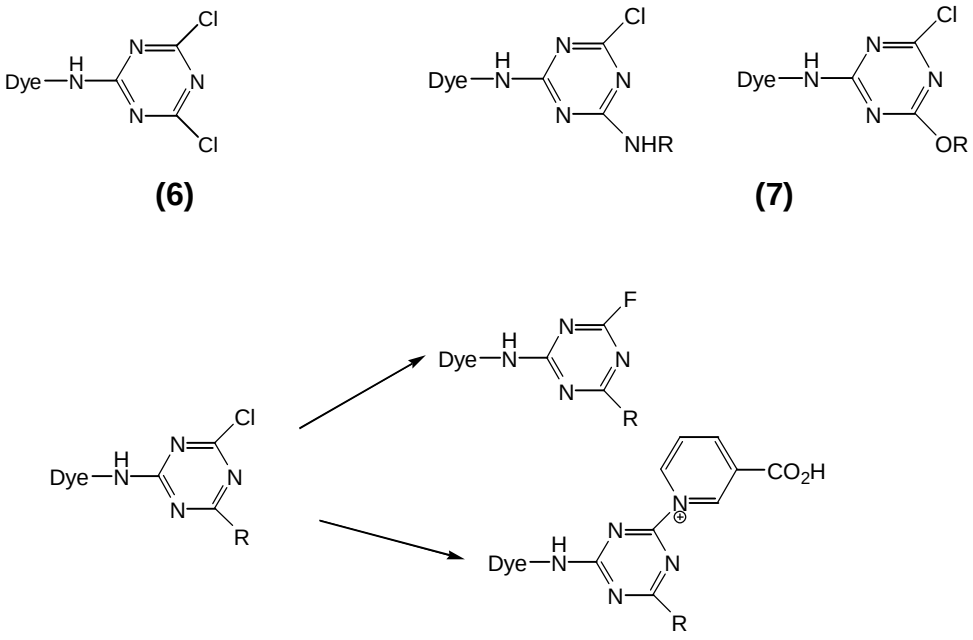


Figure 1.3. Conversion of an MCT reactive dye to fluoro and ammonium counterparts.

B. Vinyl Sulfone System

The Hoechst Remazol “vinyl sulfone” reactive dyes are the sulfonate esters of hydroxyethyl sulfonyl dyes that react with mild alkali to generate the

vinyl sulfone group that will react with cellulosate to form an ether linkage (Figure 1.4). Due to their relatively low substantivity, these dyes are suitable for printing. However, they also dye cellulose from a dyebath at 50 -60°C [13, 18].

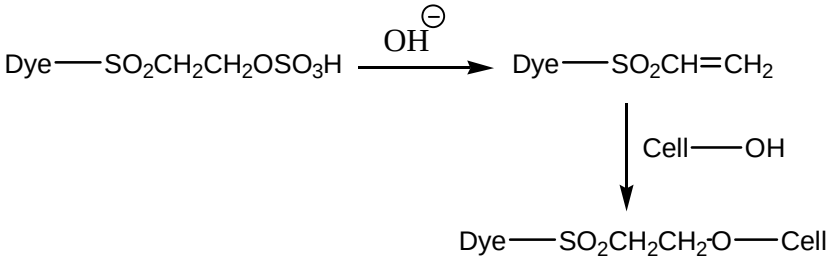


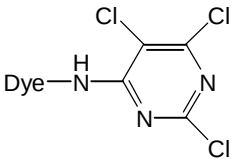
Figure 1.4. Reaction of Remazol dyes with cellulose.

C. Pyrimidine System

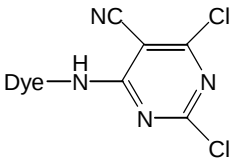
Due to the structural similarities between the 1,3,5-triazinyl and 1,3-diazinyl systems, pyrimidine ring has also been involed in reactive dye production. Drimarene (Sandoz) and reactone (Geigy) are two good examples of this type of dye (**8**). These dyes have reactivity similar to MCT dyes and their reactivity can be increased by the presence of an electron-withdrawing group at 5- position illustrated as in 5-cyano 2,4-dichloropyrimidine (**9**) [13, 18].

D. Quinoxaline reactive system

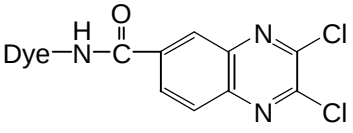
The Bayer Levafix E dyes (**10**) illustrate the quinoxaline system. They have comparable reactivity to the DCT dyes [18].



(**8**)



(**9**)



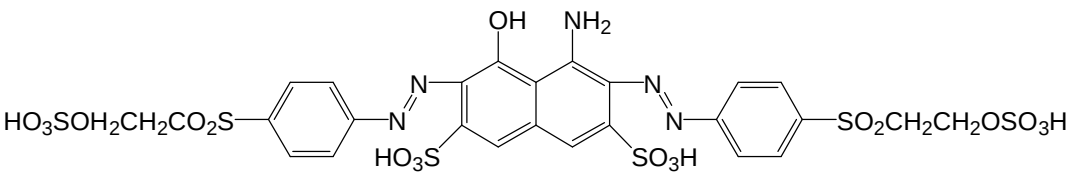
(**10**)

3.1.2 Bifunctional Reactive Systems

An inadequate degree of fixation has been regarded one of the problems of dyeing. Introducing two or more reactive systems into a dye molecular was viewed as a logical was to enhance the percent of reaction between dye and fiber [23, 26]. Bifunctional reactive dyes contain two separate reactive centers capable of reacting with hydroxyl groups in the cellulose chain. Analytical techniques, such as electron microscopy, surface area determination, and swelling in cadoxen solvent, have been used to provide evidence for the formation of crosslinks between adjacent cellulose chains in cotton dyed with bi- and poly- functional reactive dyes [27]. Bifunctional reactive dyes can be divided into two classes: homobifunctional dyes containing two of the same reactive groups and heterobifunctional dyes with two different reactive groups in the reactive dye structure.

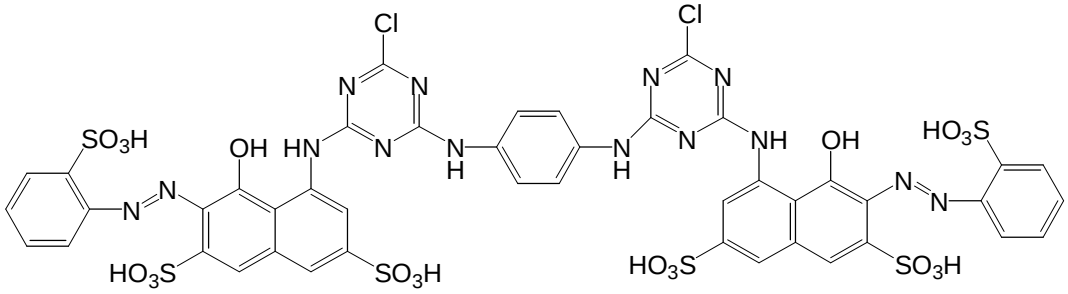
3.1.2.1 Homobifunctional Reactive Dyes

The earliest commercial dye based on a homobifunctional reactive system is Remazol Black B (**11**) (C.I. Reactive Black 5). The bis-vinylsulfone reactive system gives excellent fixation efficiency under alkaline conditions, and after fixation the unfixed dye is easily washed off. This dye has poor alkaline fastness and the four solubilizing groups cause low substantivity in the parent dye [23, 26].



(**11**)

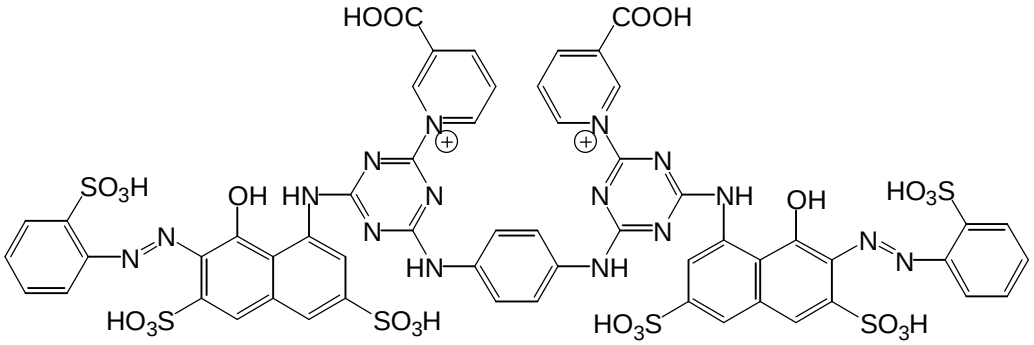
C.I. Reactive Red 120 (**12**) is an example of a reactive dye that contains two monochlorotriazine groups [23]. These bifunctional dyes are approximately twice the size of analogous monofunctional types. Their substantivity is much higher than the bis-vinylsulfone dyes. This allows them to give excellent exhaustion under batch dyeing conditions, leading to fixation values of about 70-80% using less salt. Wash-off properties are poorer because of their high substantivity, and some do not have good fastness properties in acidic media [8, 23].



(**12**)

An aminochlortriazine dye will react with a tertiary amine that has a sterically accessible nitrogen atom to produce a quaternary ammonium derivative. The positive charge increases the polarization of the C-N bond that links the ammonium group to the triazine ring, improving the reactivity of the dye. A full range of bis-mononicotinotriazine dyes was introduced following the observation that alkali was not required for fixation to the fiber. An example of this dye type is C.I. Reactive Red 221 (Kayacelon React Red CN-3B) (**13**). Exhaust dyeing employs a neutral dyebath at a temperature above the boil. These dyes are suitable for the one-bath dyeing of polyester/cotton blends. Operating the

temperature in the region of 130°C minimizes the diffusion problems expected with such a large molecule [8, 26].



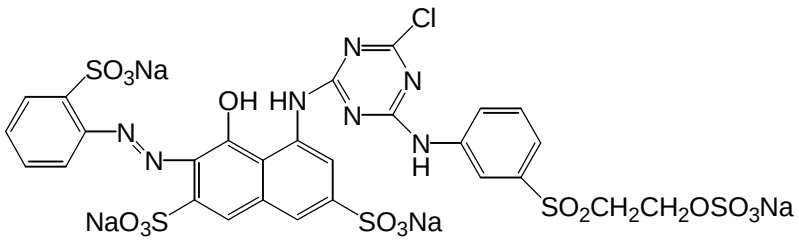
(**13**)

3.1.1.2 Heterobifunctional Reactive Dyes

The deficiencies of homobifuntional reactive dyes caused reactive dye research to move away from simple homobifunctional to heterobifunctional dyes in the late 1970s. Heterobifunctional reactive dyes contain careful selected reactive groups and the right chromophore. In the 1980s the heterobifunctional reactive dyes became widely used in the reactive dye market place. These dyes offer several advantages over traditional mono functional and homobifunctional reactive dyes. They are less sensitive to temperature and many similar dyes can be mixed together to get a variety of shades. Also the low sensitivity to dyeing parameters (temperatures, salt levels) leads to a lack of correlation between fixation yield and final color depth. The combination of different reactive groups also provides good fastness over a wide pH range. There are two classes of commercially significant heterobifunctional dyes [23, 26].

A. Monochlorotriazine/sulphatoethylsulfone dyes

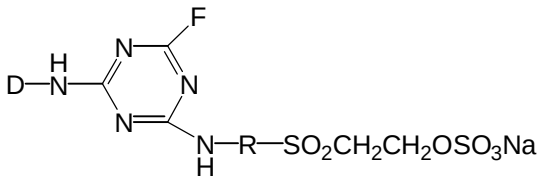
A monochlorotriazinyl group with the more reactive 2- sulphato ethylsulfone group is the most common combination. The first products of this type were the Sumifix Supra dyes marketed by Sumitomo in the 1980s [26]. With this system it is possible to obtain a wide variety of shades. By combining monochlorotriazine and sulphatoethylsulfone groups in one dye molecule, it was expected that a higher fixation values would be obtained [14, 23, 28]. Both reactive groups can contribute to the fixation process but the relatively higher reactivity of the vinylsulfone group ensures that most of the fixation occurs through this functional group [26,29, 30]. Low dyeing temperatures favor the reaction between the vinylsulfone group and fiber and at higher temperatures fixation via chlorotriazine group is preferred [8]. Due to the electrophilic property of the cyanuric chloride group, a wide range of chromophores can be selected. Fibers dyed with these dyes have excellent storage stability because a chemical bond between a vinyl sulfone and cellulosic fibers is very stable to acid hydrolysis. Although these dyes give high exhaustion and fixation levels, they also have good wash off properties [23, 26]. An example is C.I. Reactive Red 194 (Sumifix Supra Brilliant Red 2BF) (**14**) [8].



(**14**)

B. Monofluorotriazine/sulphatoethylsulfone dyes

Ciba-Geigy introduced Cibacron C dyes that contain a new aliphatic vinylsulfone system and a monoflurotriazine bridging group in early 1988. A generic structure (**15**) has been cited. This dye type is characterized by medium to low affinity, good build-up, easy wash-off and high fixation. Their outstanding bath stability and high fixation make them especially suitable for pad-batch dyeing. The reactivity of the fluorotriazine group and vinylsulfone group matches more closely than that of chlorotrizine and vinylsulfone groups [8, 31]. Both groups contribute to effective fixation under virtually the same conditions. The triazine-fiber bonds are stable to an alkaline medium while the vinylsulfone-fiber bonds are stable to an acidic medium [8, 23]. The cost of these dyes is relatively high but cost-effectiveness is enhanced by their very high fixation and easy wash-off. Also this is possibly the best approach so far towards environmentally acceptable reactive dyes [8].



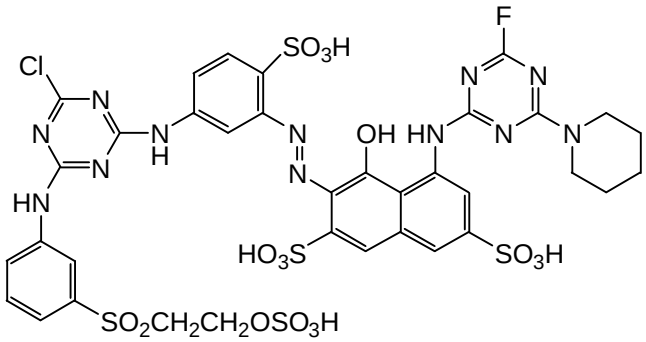
D= dye chromophore R= aliphatic group

(**15**)

3.1.3 Polyfunctional Reactive Systems

Theoretically, it should be possible to get even greater fixation efficiency by introducing additional reactive groups into the dye molecule. In practice, this approach can be counterproductive due to the detrimental effect that the additional reactive groups can have on important physical properties such as

migration, especially at heavy depths, and poor build-up. Reactive groups increase the molecular weight of a dye but do not improve color strength if the trifunctional dyes only possess one chromogen unit. So the latter type structure which links two similar, economic, reactive dye units together via a reactive chlorotriazinyl bridge, and thus contains two chromogen units and three reactive groups was produced. In this regard, the structure of trifunctional reactive dyes having a monochlorotriazine, monofluorotriazine and vinylsulfone combinations (**16**) were disclosed by Bayer. They are claimed to give high reactivity and excellent fixation yields, and are insensitive to minor variations in fixation temperature, even when dyeing at long liquor ratios [31].



(**16**)

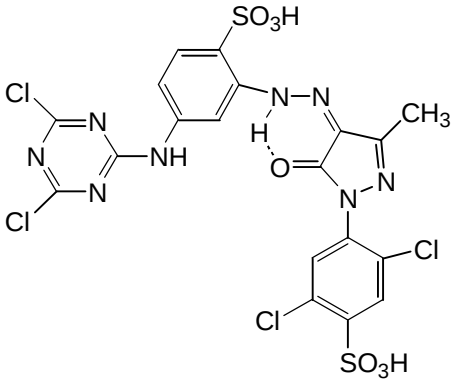
3.2 Chromogens

The chromogen is the colored portion of a reactive dye. Proper selection of the chromogen for commercial reactive dyes is essential to achieving the desired shade. The size of the chromogen often determines the substantivity and the diffusion properties of a reactive dye [19, 22]. Reactive dye chromogens include monoazo, disazo, metallized monoazo, metallized disazo, formazan, anthraquinone, triphenodioxazine, and phthalocyanine systems [18].

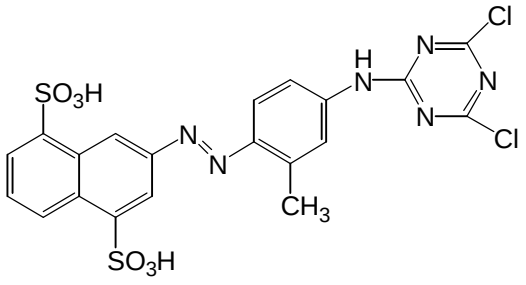
3.2.1 Azo Reactive Dyes

Azo dyes are compounds containing azo groups (—N═N—) that are linked to sp^2-hybridized carbon atoms. According to the number of azo groups, the dyes are named as mono-, dis-, tris, (etc.) azo dyes. Most azo groups are bound to benzene or naphthalene rings. Sometimes they are also attached to aromatic heterocycles or enolizable aliphatic groups. Azo coupling, the reaction of an aromatic or heteroaromatic diazo compound with a so-called coupling component, is the most significant method for synthesizing azo dyes [32]. By varying couplers, diazo components and reactive systems, many different dyes can be obtained. Almost 80% of all reactive dyes contain an azo group [7, 32].

Yellow dyes are usually of the simple monoazo type. Greenish yellow reactive dyes such as C.I. Reactive Yellow 1 (**17**) are usually monoazo dyes utilizing heterocyclic couplers, while middle to reddish yellow reactive dyes, e.g. C.I. Reactive Yellow 4 (**18**), usually have monoazo structures with aniline or naphthylamine couplers [7, 32].



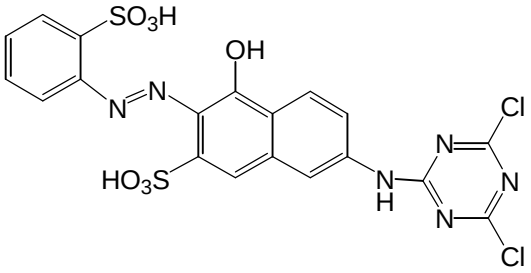
(**17**)



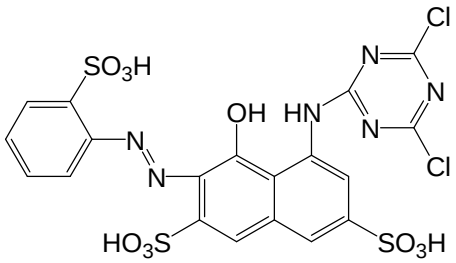
(**18**)

The most generally used coupling components are the aminonaphthols, which can be used to produce hues from orange to black. J-acid is often used in

the production of orange dyes, an example of which is C.I. Reactive Orange 1 (**19**). Using H-acid in place of J-acid will give a bright bluish-red dye, such as C.I. Reactive Red 12 (**20**) [7, 33].

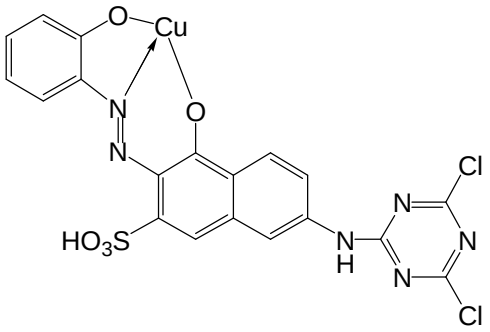


(**19**)

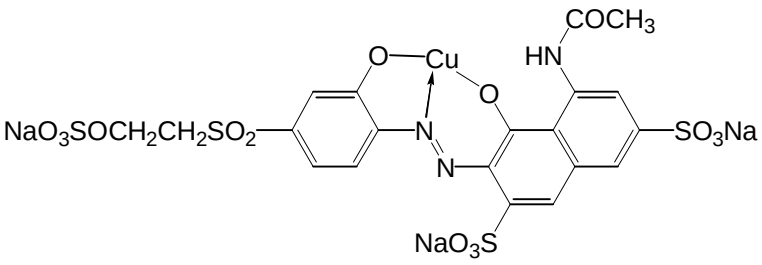


(**20**)

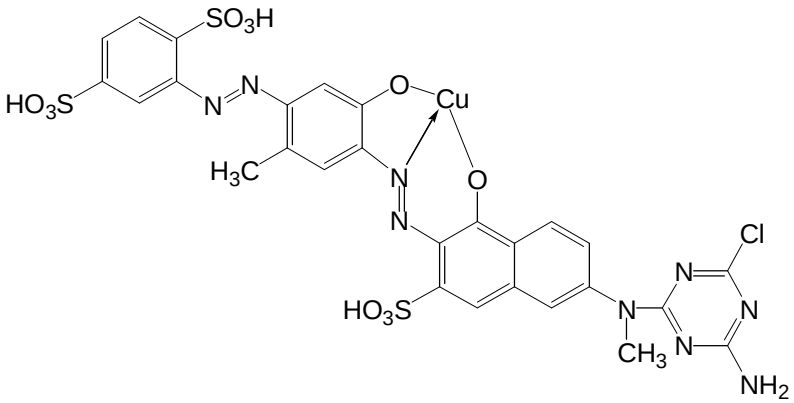
For more bathochromic monoazo or disazo dyes, formation of the metal complex is necessary. Rubine, violet and blue dyes can be obtained by using copper complexes which are planar and more substantive. Examples are rubine dye C.I. Reactive Red 6 (**21**), violet dye C.I. Reactive Violet 5 (**22**), navy blue dye C.I. Reactive Blue 40 (**23**) [7, 33].



(**21**)

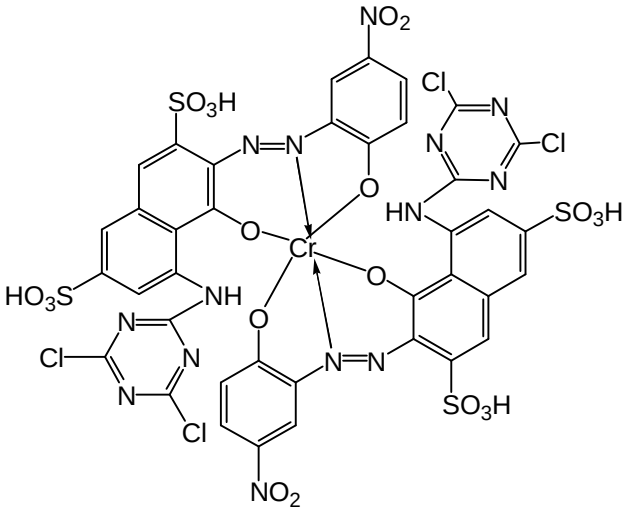


(**22**)



(**23**)

Cobalt and chromium complexes are used to produce gray and black dyes. These dyes are large molecules because the octahedral spatial arrangement of the bonds of chromium and cobalt chelates requires that one metal atom combines with two chromogen molecules. A good example is C.I. Reactive Black 4 (**24**). This results in nonplanar structures and low substantivity on cotton and led to restrict them mainly to printing applications [7].

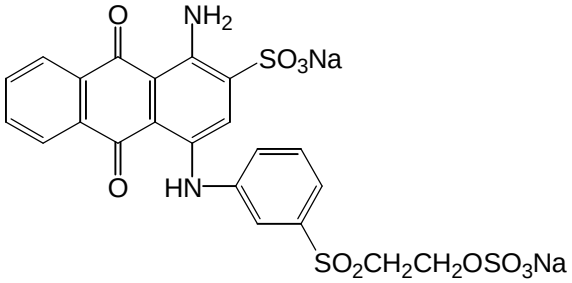


(24)

3.2.2 Anthraquinone Reactive Dyes

Anthraquinone reactive dyes are second only to azo dyes in overall importance. The most commonly used dyes have bluish violet to bluish green

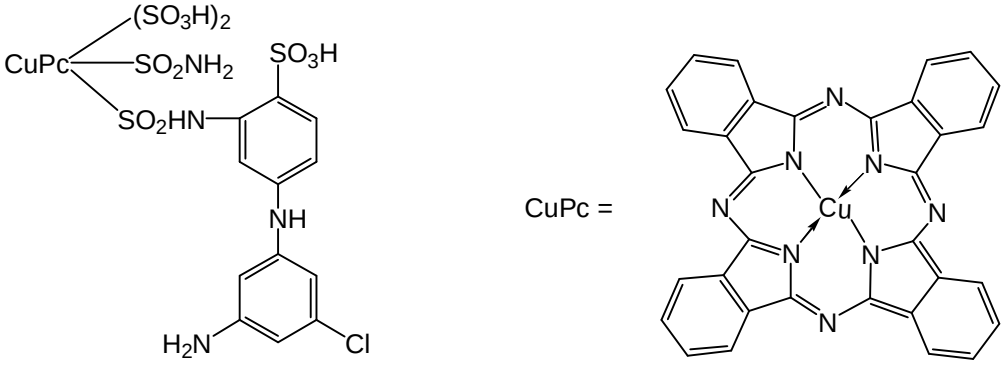
colors with the bright reddish to mid-blues. C.I. Reactive Blue 19 (**25**) is a typical anthraquinone reactive dye [7, 18].



(**25**)

3.2.3 Phthalocyanine Reactive Dyes

Solubilized phthalocyanine reactive dyes are used for bright turquoise hues that cannot be produced by using either azo or anthraquinone dyes. The phthalocyanine structure usually contains copper or nickel as the central metal ion. Copper phthalocyanine is most commonly used and is solubilized by incorporating sulfonic acid groups by sulfonation or chlorosulfonation. C.I. Reactive Blue 7 (**26**) is an example of this type of dyes [7, 18, 33].

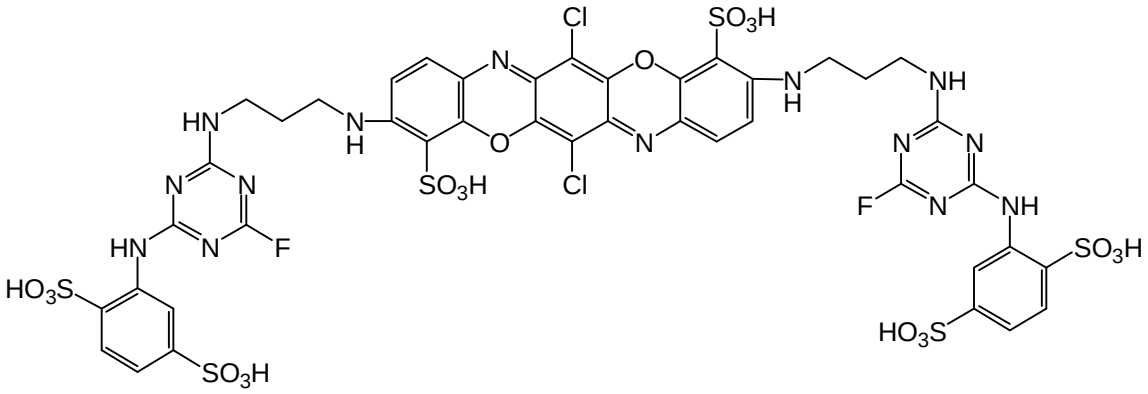


(**26**)

3.2.4 Triphenodioxazine Reactive Dyes

Triphenodioxazine dyes can be used to produce deep, bright blue shades on cotton. Because the triphenodioxazine dyes offer bright hues, and are

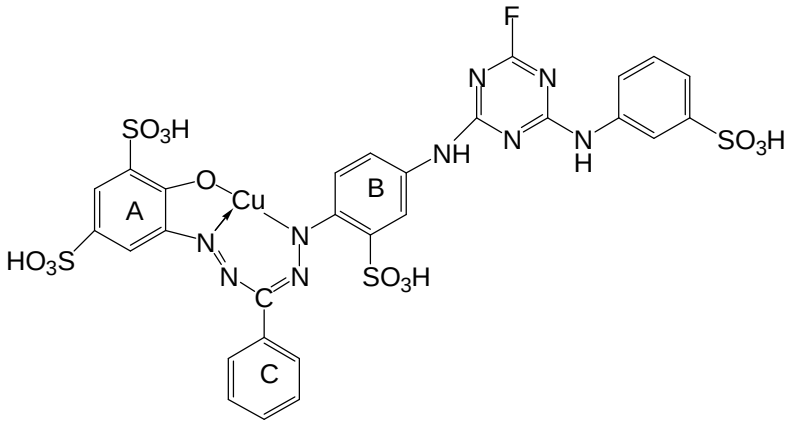
tinctorically stronger than anthraquinone dyes, they have recently gained approximately 10% of the blue reactive dye market, which is mainly at the expense of anthraquinones. C.I. Reactive Blue 204 (**27**) developed by Ciba-Geigy is an example of this dye type [7].



(**27**)

3.2.5 Formazan Reactive Dyes

Copper complexes of formazan dyes are capable of producing bluish red to blue shades. These dyes also provide an alternative to the anthraquinone blues. Research activity in the formazan reactive dye area has increased, since these dyes exhibit high color strength and have good solubility and reactivity. An example of a formazan reactive dye is (**28**) [7, 18].



(28)

3.3 Bridging Groups

A bridging group is the group that links the reactive system to the chromogen. While these groups are necessary for synthetic reasons, they also influence the reactivity, degree of fixation, stability of the dye-fiber bond, and dyeing characteristics such as substantivity and migration. The typical bridging group is an imino (-NH-) group. Ether or mercapto groups have been examined but generally the bonds do not have acceptable stability. They are also less easy to form than imino bridging groups. Carboxamide and sulfonamide groups are stable and have been used as bridging groups to a limited extent [19, 32].

3.4 Solubilizing Groups

Good solubility in water is another important characteristic for a good reactive dye. Solubilizing groups also promote substantivity, migration and wash off. The dominant solubilizing group in reactive dyes is the $–SO_3Na$ group [19, 32].

3.5 Reactive Dye-fiber Fixation

Rreactive dyes can be applied by any conventional batchwise dyeing method for cellulose, including circulating-liquor machines for loose stock, yarn or woven fabrics and jets, winches or jigs for piece dyeing. There are three principle steps of all reactive dyeing: exhaustion, fixation or reaction and washing-off [7, 8, 17, 34].

Exhaustion: In conventional processes the required amount of dye is added to the dyebath at ambient temperature and circulated with the goods. The

temperature is raised to the preferred dyeing temperature and the required amount of salt is added in portions, to exhaust the dye under neutral conditions.

Fixation: The required amount of alkali is added to the bath with efficient circulation and fixation occurs. This step is the most important and complicated among all three steps. It will be discussed in more detail later.

Washing Off: The washing-off process is often long but cannot be avoided. All of the hydrolyzed and unfixed dye has to be removed to avoid compromising wet fastness. The difficulty of this process is determined by the substantivity of the unfixed dye. The more substantive the unfixed dye, the more difficult the wash off process.

During the fixation stage, hydroxide ions enter the fiber pore structure and ionize cellulose hydroxyl groups. This produces the two possibilities for a nucleophilic reaction with the dye: one in the fiber with the cellulosate moiety, one in the dyebath with hydroxide ions. When the dye reacts with hydroxide ions in the dyebath, it produces the unreactive hydrolyzed dye that will be held to the fiber by substantivity. Dye inside the fiber reacts with cellulose to give a dye-fiber bond. The reaction level between reactive dyes and fibers vary with the reactive systems of the dye. Often only 50-75% fixation occurs [34].

3.5.1 Nucleophilic Substitution

Nucleophilic substitution occurs when a leaving group in the reactive system is displaced as a result of an attack by the cellulosate anion (Cell—O^-). The reaction of a monochlorotriazine reactive dye with cellulosate is typical example of this process. The mechanism is shown in Figure 1.5. The

commercially useful nucleophilic substitution-type reactive dyes for cellulose are shown in Table 1.3 [13].

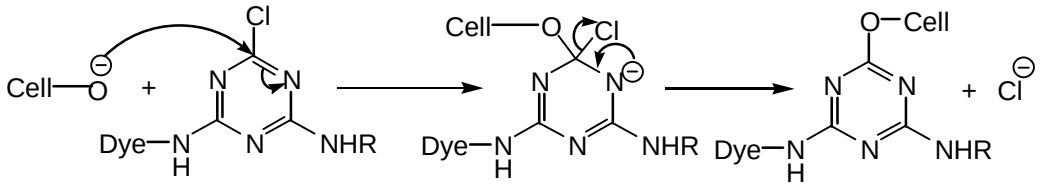


Figure 1.5. Mechanism of reaction of a monochlorotriazine dye with the cellulosate ion.

3.5.2 Nucleophilic Addition

This mechanism is associated with reactive dyes capable of undergoing an addition reaction. Such dyes have a positively polarized, unsaturated carbon-carbon double bond in the reactive group that can be attacked by nucleophilic cellulosate anions. Most of reactive systems used in these dyes contain a vinylsulfone group or one of its derivatives. The vinylsulfone reactive group itself is usually not present in commercial dyes. It is more convenient to use a more stable precursor such as the β-sulphatoethylsulfone group. These dyes react with cellulose under alkaline conditions involving two stages [13]:

(1) $Dye—SO_2CH_2CH_2OSO_3Na + NaOH \rightarrow Dye—SO_2CH{=}CH_2 + Na_2SO_4 + H_2O$

(2) $Dye—SO_2CH{=}CH_2 + Cell—OH \rightarrow Dye—SO_2CH_2— CH_2—O—Cell$

Like the nucleophilic substitution type reactive dyes, the side reaction with the hydroxyl ions in the dyebath also occurs during the dyeing process. This type of dyes is more important for wool dyeing, but there is also a selected range of them available for the coloration of the cellulose. Examples of reactive systems for cotton are given in Table 1.4 [13].

Table 1.3. Substitution-type reactive dyes for cellulose.

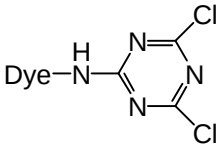
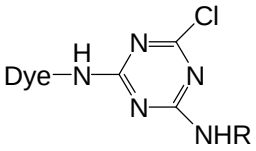
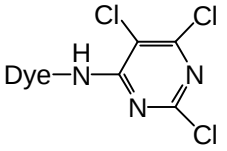
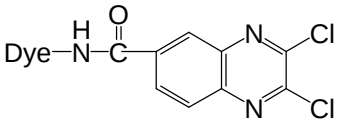
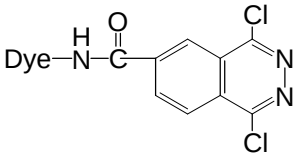
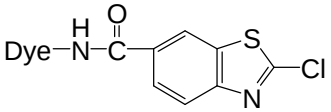
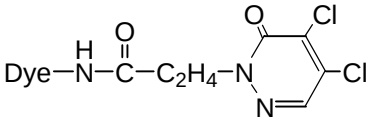
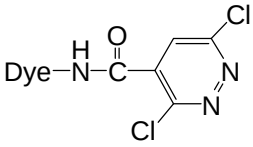
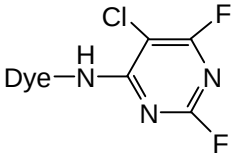
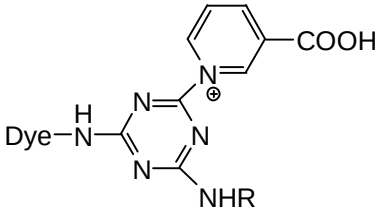
Reactive Group	Chemical Structure
Dichlorotriazine	
Monochlorotriazine	
Trichloropyrimidine	
2,3-Dichloroquinoxaline-6-carbonyl	
Dichlorophthalazine	
Chlorobenzothiazole	
Dichloropyridazone	
Dichloropyridazine	
Difluorochloropyrimidine	
Mononicotinotriazine dyes	

Table 1.4. Addition-type reactive dyes for cellulose.

Reactive Group	**Chemical Structure**
Sulfatoethylsulfone	Dye—$SO_2CH_2CH_2OSO_3Na$
β-Alkylamine salt	Dye—$SO_2CH_2CH_2NH(Alkyl)_2(NaSO_4)^-$
Sulphatopropylamide	Dye—$NHCOCH_2CH_2OSO_3Na$
Chloropropylamide	Dye—$NHCOCH_2CH_2Cl$
β-Sulfophenylacroylamino	Dye—$NHCOCH_2CH_2SO_2Ph$
β- Sulphatoethyl sulfonamide	Dye—$SO_2NHCH_2CH_2OSO_3Na$

3.6 Fixation of Bifunctional Reactive Dyes

Probability of fixation of bifunctional reactive dyes is much higher than conventional monfunctional reactive dyes [34]. For a bifunctional reactive dye, both reactive groups, R1 and R2, react with the cellulosate ion at a rate corresponding to their reactivity. The more reactive group determines the course of the reaction (Figure 1.6). If a bifunctional reactive dye is bound to the fiber by one reactive group, the second reactive group can form a second linkage with the fiber or, if this is impossible due to steric reasons, it can be hydrolyzed. So the bifunctional dyes can be bound to the fiber in three ways: by a linkage via R1, via R2, or via R1 and R2, while the monoreactive dyes only have one way to bind to the fiber.

Table 1.5 demonstrates why a typical bifunctional reactive dye gives higher percent fixation than conventional monofunctional reactive dyes. In the pad-batch method, monofunctional reactive dyes achieve at best an average of

75% fixation. The remaining 25% of the dye is hydrolyzed and finds its way into the effluent. In the case of a bifunctional reactive dye, one reactive group (R1) could react exactly like the monoreactive dye: 75%with the fiber, and 25% with the water. However, the partially hydrolyzed but still reactive dye can react further by the second reactive group (R2). Therefore, about 94% (75% + 25% x 75%) of the amount of dye is linked to the fiber and only 6% is wasted once 75% of the partially hydrolyzed dye reacts with the fiber. The same principle can apply in exhaust dyeing. The degree of fixation in exhaust dyeing is lower because the dye does not fully exhaust onto the fiber. When a bifunctional reactive dye exhausts 85%, a fixation of 80% can be obtained. For the same degree of exhaustion, the fixation of a monofunctional dye is on average only to 60-65% and much more dye has to be removed during the wash off process [35].

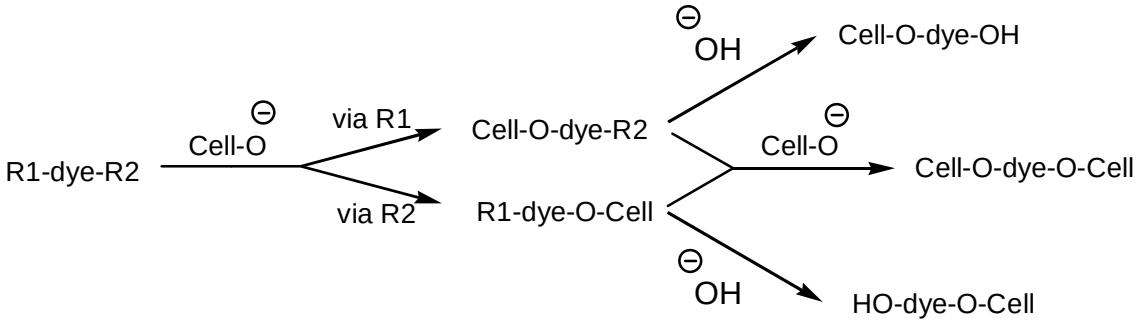
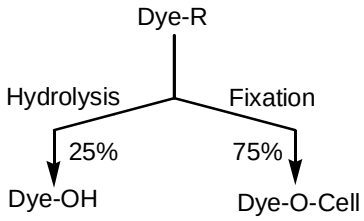
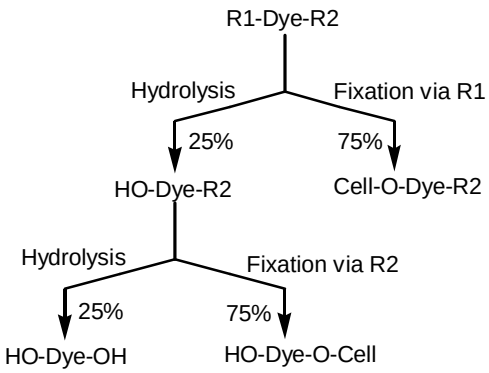


Figure 1.6. Fixation of a bifunctional reactive dye to cellulose in the presence of alkali.

4. DYE APPLICATION

When the reactive dyes are applied to cotton and viscose in loose fiber, yarn, and piece forms, batch-wise, semi-continuous, and continuous processes are used [7].

Table 1.5. Fixation properties of Cibacron C and conventional monoreactive dyes.

Monoreactive dye	Cibacron C
	
Hydrolyzed dye: 25%	6%
Fixed dye: 75%	94%

4.1 Batch-wise Dyeing

The principle for the batch-wise dyeing process is to exhaust as much of the dye as possible onto the fiber under neutral or weakly acidic conditions before the fixation step. The initial dyebath contains a dye dissolved completely in water, a solubilizing agent such as urea, and an exhausting agent — an electrolyte such as common salt or Glauber's salt. Under these conditions, the dye does not react or reacts very slowly with cellulose and water so that leveling can occur prior to fixation. The pH of the dyebath is then increased by the addition of alkali to make the reaction between the dye and the cellulose take place [36]. The particular type of reactive dye being used governs the choice of alkali and temperature. The last step is the washing off process, which removes unfixed dye, alkali and electrolyte to produce the desired shade and fastness properties [34].

Batch-wise dyeing may be done on a jig machine for woven cotton or a winch and jet machine for knitted or lightweight woven fabrics. This type dyeing split into four different categories: Traditional or Conventional, One Step or All-In, Constant Temperature, and High Temperature [8, 34].

4.1.1 The Traditional or Conventional Method

This method was introduced in section 3.2. In this dyeing method, the temperature is raised to exhaust dye with electrolyte prior to alkali addition. If the rate of salt addition and temperature rise are not controlled well, unleveled dyeings may occur [34, 36].

4.1.2 One Step or All-In Method

This method is the simplest and quickest method available because the dye, salt and alkali are added to the dyebath together prior to heating to the dyeing temperature, so that no additions need to be made during the dyeing process. This method has drawbacks when compared to the conventional method. Maintaining the starting temperature is critical for repeatability, and controlling the rate of heating is essential for levelness since exhaustion and irreversible fixation are occurring simultaneously from the beginning. In addition, there is a possibility of lower color yield due to hydrolysis [34].

4.1.3 The Constant Temperature Dyeing Method

In this method, the temperature is fixed throughout the dyeing process. Dye is added at the beginning of the cycle. Electrolyte may be added at the beginning or in portions and then alkali is added after a proper time interval to fix

the dye. The problem of improper temperature control on the rate of temperature rising is completely eliminated [34].

4.1.4 The High Temperature Dyeing Method

The principle use of this method is for dyeing fabrics from high twist yarns, tightly woven goods, or for viscose rayon fabrics. This method starts dyeing at a higher temperature than that of fixation in the presence of salt, and drops the temperature to the fixation temperature before the addition of alkali. Elevating the temperature can improve the leveling of the dye on fabric [34, 36].

4.2 Semi-Continuous or Pad-Batch Dyeing Processes

The lower limit of the liquor ratio achievable in a batchwise dyeing process is about 5:1, or in specially designed ULLR (Ultra-low liquor ratio) equipment, possibly 3:1. Padding methods extend this further to the range 1:1 to 0.5:1. Thus, semi-continuous or continuous dyeing processes can significantly improve the exhaustion and fixation characteristics of short- liquor exhaust dyeing [8].

The semi-continuous method represents the minimum possible investment for dyeing large yardages of woven, knit, tubular or flat cellulosic fabrics with cold dyeing, highly reactive dyes [34]. In this method, the fabric is padded with a solution containing dyes and base, and then wound onto a roll. A feeding device is used to mix dye solution with the base solution just before adding them to the padding bath to avoid the hydrolysis of the reactive dyes before impregnate on the fabric. Since the volume of the padding bath is made as small as possible to avoid tailing, and the fabric is padded at a rate of at least 60 yd/min and the dye-

base mixture is added continuously. The padded rolls are covered with plastic sheets to prevent evaporation of water and the reaction of alkali with the carbon dioxide in the air, and left at room temperature (or a temperature controlled area for good lot to lot reproducibility) for 2-24 h depend on the dye reactivity and pH. To avoid preferential drainage, the rolls are rotated once in a while [8, 17, 34]. For the high-reactivity dye, the dwell time or the batch time may as short as 2-4 h. But due to some demands for specific hues, fastness or cost advantages, low-reactivity dyes at high pH which need dwell time as long as 16-24 h may be applied [8]. The unfixed dye is then washed off by rinsing with cold and warm water and soap at the boil. The wash off can be done on conventional available equipment such as a continuous wash-range or equipment used in exhaust dyeing [17, 34].

4.3 Continuous Dyeing Processes

In this method the dwell time after impregnation (padding) is reduced to a few seconds or minutes because the rate of reaction is increased by heating the padded fabrics [15]. Continuous dyeing offers economic advantages when long runs are required in a limited range of colors. Excellent reproducibility is possible with saving in handling and labor costs [8]. This method is carried out either by a one-bath or two-bath process. In the one-bath process, alkali is incorporated in the aqueous padding bath containing dye whereas in the two-bath process, the alkali is padded from the second bath. The fixation step is generally done by dry heat (thermo-fixation), or by moist heat (steam fixation), and is followed by the washing off step [36].

4.3.1 The Conventional Dyeing Process (Pad-Dry-Pad-Steam)

This method is used for 100% cotton. The dye is applied at the first pad bath and then the fabric is dried. No solubility problem of the dye will occur in this method because of the minimal amount of salt in the pad bath and the low substantively dyes do not have an opportunity to undergo migration. Some salt and antimigrant may be necessary in the first pad bath to prevent the dye solution moving from the wet parts to dry parts on the impregnated fabric during the drying step and achieve uniformly colored fabrics. After drying, the goods are passed through a second pad bath containing salt and alkali, and bleeding into the pad bath should be minimal. The goods are then steamed, washed off and scoured as they move down the dye range [17, 34]. The wet fastness of the goods from this method is not as good as from batchwise dyeing because not all unfixed dye can be washed off due to the short exposure to the wash liquors. This method is well adapted for polyester/cotton blend dyeing with reactive/disperse dye combinations because the conventional full continuous dye ranges always have a thermosol oven (for developing the disperse dye) before the second padder. The presence of the neutral reactive dyes does not interfere with the application of the disperse dyes from the first padder [34, 37].

4.3.2 Pad-Steam Dyeing Process

Dye, alkali and salt are added to the pad bath. Dye hydrolysis should not be a problem if the pad is small and dye and alkali are continuously fed into the pad from separate feed tanks. However, the salt concentration may cause dye solubility problems but the substitution of Na_2SO_4 for NaCl can help [34]. This

process was developed so that the intermediate drying step of the conventional method could be eliminated. The main application of this system is for towels and pile fabrics, such as corduroy, where the cost and difficulty of drying dyed goods is prohibitive. Dyes of high reactivity are preferred but the color yield is often very low [34, 37].

4.3.3 Wet-On-Wet Method (Pad-Pad-Steam)

This may be the first practical dyeing method devised for reactive dyes. The fabric is padded in a neutral dye solution and then in a dilute solution of alkali in saturated brine before steaming to achieve dye-fiber fixation. This wet-on-wet sequence can lead to serious problems of dye bleeding into the alkali bath even at maximum salt concentration [8]. This method finds its greatest use in terry cloth even the process is not efficient [34].

4.3.4 Pad-Dry-Cure Method

This method is an interesting one. Some reactive dyes are padded onto cotton in the presence of $NaHCO_3$ and urea. Urea can help dissolve the reactive dyes by disrupting aggregation. Under the conditions of thermofixation and in the presence of water, bicarbonate is converted to carbonate which provides alkali for the fixation step. Urea's extremely hydrotropic nature also helps bring sufficient water into the thermosol oven to permit the formation of alkali and the fixation of the dye. However, the drawback of this process is that undesirable smoke generation and yellowing of cellulose can occur [17, 34].

5. PROPOSED PROJECT

As part of a project aimed at developing new hair dyes, a group at Leeds University synthesized some interesting derivatives of commercial dichlorotriazine (DCT) reactive dyes that were later determined to have affinity for cotton [38, 39]. These new dyes were prepared by reacting commercial DCT dyes with either cysteamine or cysteine, according to the chemistry illustrated in Figures 1.7-1.8 for yellow dyes. As indicated in the two figures, the reaction with cysteamine or cysteine is followed by a reaction with either cyanuric chloride to give Types 1 and 2 bis-DCT dyes or a second molecule of the starting DCT dye to give Types 3 and 4 MCT dyes. In the same way, red DCT dye (**34**) and blue DCT dye (**35**) were converted to the corresponding Types 1-4 structures. Procter and Gamble, who assigned the name "Teegafix" to the new dyes, sponsored this work.

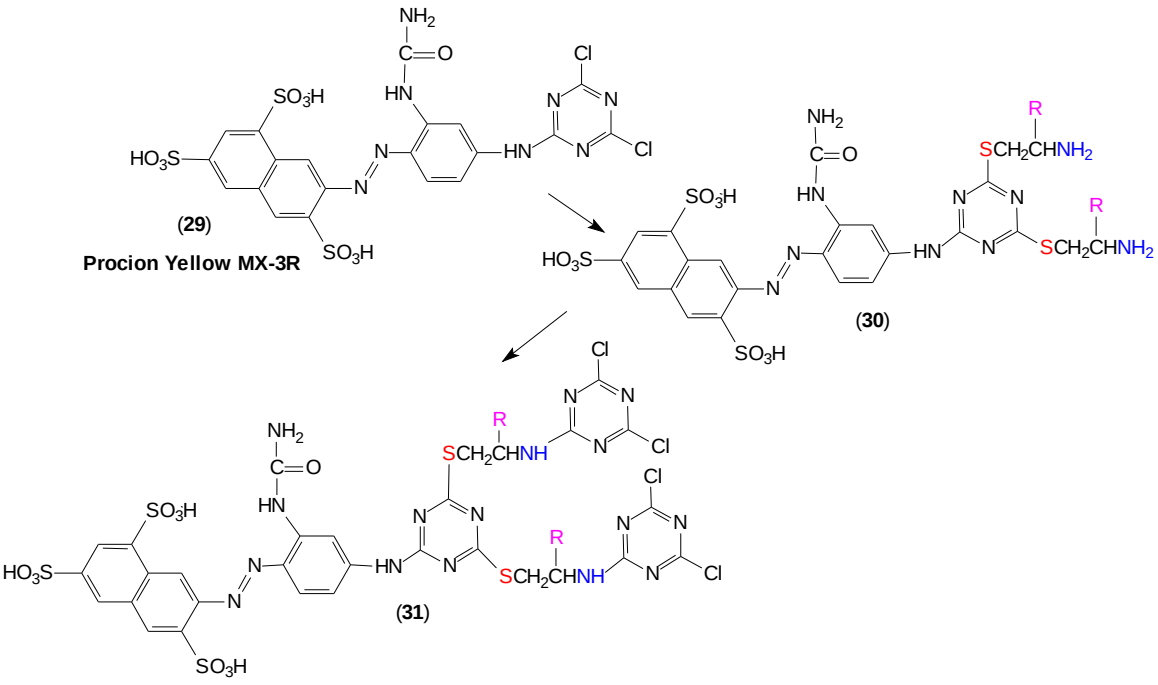


Figure 1.7. Synthesis of types 1 (R = CO_2H) and 2 (R = H) Teegafix yellow dyes.

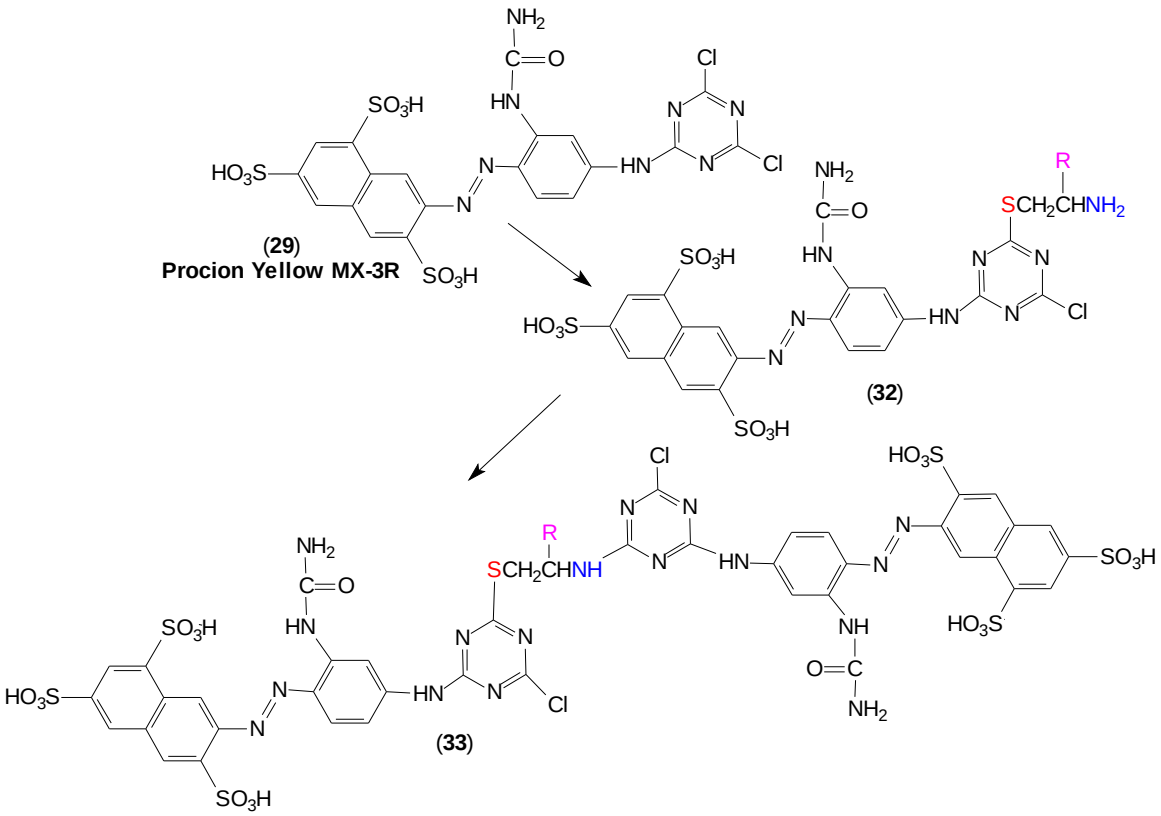
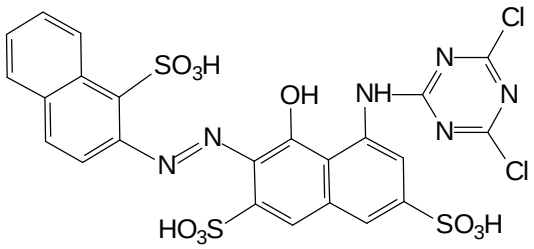
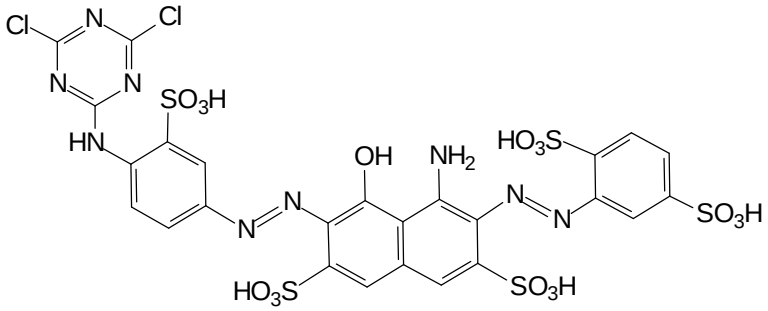


Figure 1.8. Synthesis of types 3 (R = CO_2H) and 4 (R = H) Teegafix yellow dyes.



(**34**)



(**35**)

The Teegafix technology was donated to N.C. State University in 2003, in anticipation that studies leading to commercialization would be undertaken. The N.C. State group conducted studies leading to optimization of synthetic and dyeing processes and to selection of the most promising Teegafix dye type. In the initial study, the properties of the four structural types were assessed using equilibrium exhaustion and laboratory scale dyeing experiments. Equilibrium exhaustion experiments were conducted at two temperatures and four salt levels. Types 2 and 4 dyes had greater affinity for cotton than the corresponding commercial dyes. These two dye types were further examined in laboratory dyeing experiments. It was found that Type 2 dyes had the best affinity for cotton, giving higher K/S values at lower salt and alkali levels in laboratory scale dyeings [40]. Results from molecular modeling studies accounted for these results, in that it was shown that Type 2 dyes had the more linear structures. In addition, the larger bis-DCT structures, versus the commercial DCT dye structures, led to higher affinities and fixation levels.

In a second study, it was found that Type 2 Teegafix dyes could be applied to cotton fabric using a commercial scale dyeing machine and that significantly less dye was required to give the same shade depths obtained when the commercial yellow and blue dyes were employed [41]. More of the Teegafix red dye was required, however, to give the same shade depth obtained using the commercial red, for reasons that were not clear at that time. Physical testing was also conducted on the dyed fabric samples, including crockfastness, wet color transfer, and lightfastness. There were no significant decreases in the fastness

properties of the Teegafix dyes when compared to the commercially available dyes.

The goal of the present study is to develop a method for characterizing the structures produced when cysteamine and cysteine react with commercial DCT dyes at various pH levels. It is anticipated that the results will provide optimum conditions for dye synthesis, an explanation for the inferior properties of the Teegafix red dye versus the commercial red, and a correlation between dye fastness properties and conditions of synthesis. A key aspect of this work, involves isolation of the intermediate products leading to Type 2 dyes.

In part 1 of this study, the synthesis of the new compounds will be carried out according to the routes shown in Figure 1.9-1.10. Intermediates **30, 36** and **38**-**39** (**a**-**b**) will be generated at pH 2 and 9. Under these conditions, reaction should occur selectively at the –SH group (pH 2) or $–NH_2$ group (pH 9). Following the synthesis of intermediates, the products will be analyzed for purity and molecular composition using HPLC.

In part 2 of this study, the synthesis of the new compounds will be repeated. In this case, intermediates **30a**/**36a** and **38a**/**39a** will be generated at pH 3-6. These products will then be converted to final dyes **31**/**37** and **40**/**41**. Following their synthesis, all products will be analyzed for purity and molecular composition. The commercial dyes and final dyes will be applied to cotton fabric and the fastness properties of the dyed fabrics will be assessed.

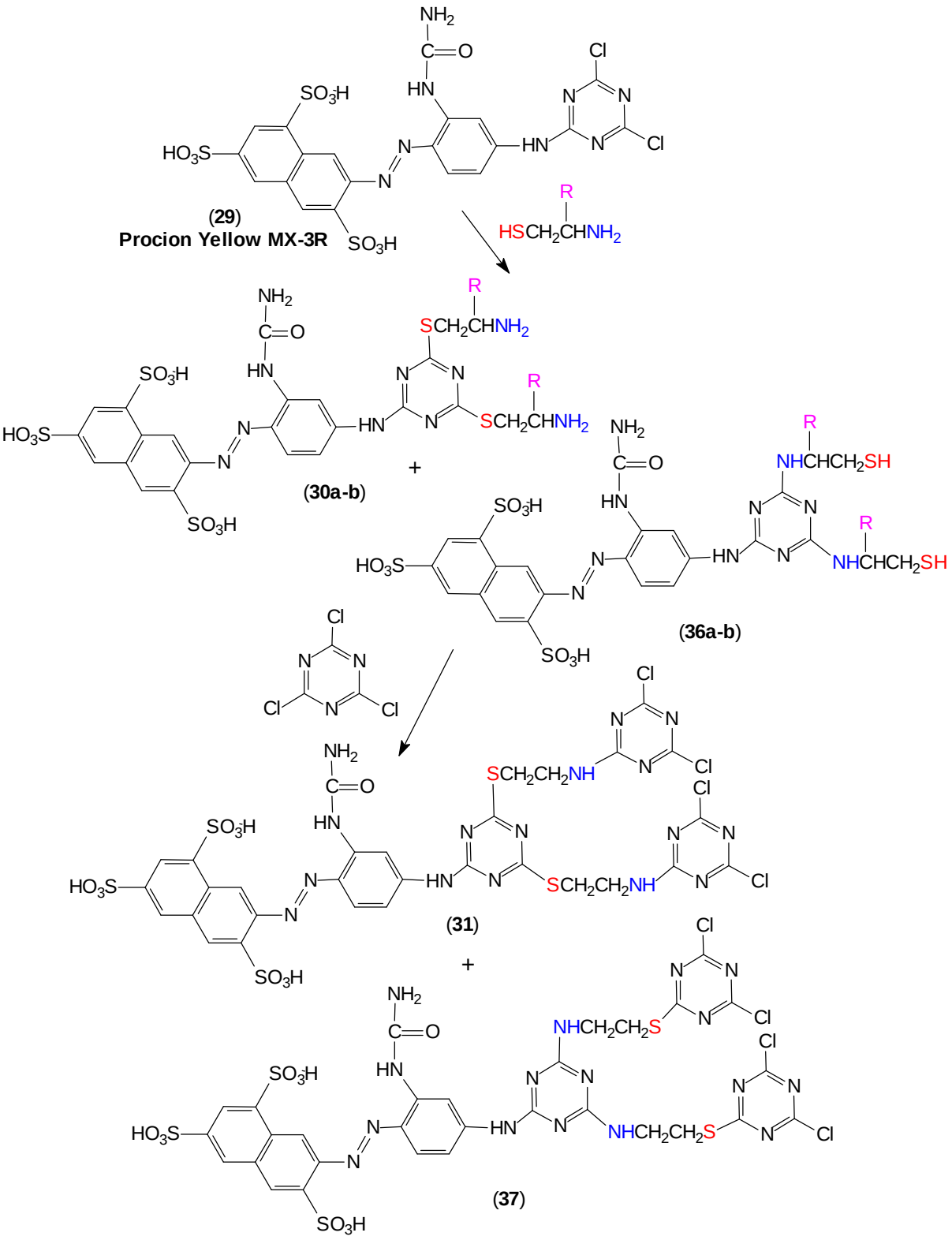


Figure 1.9. Potential Teegafix yellow dye structures from varying the pH of synthesis (R = H, CO_2H).

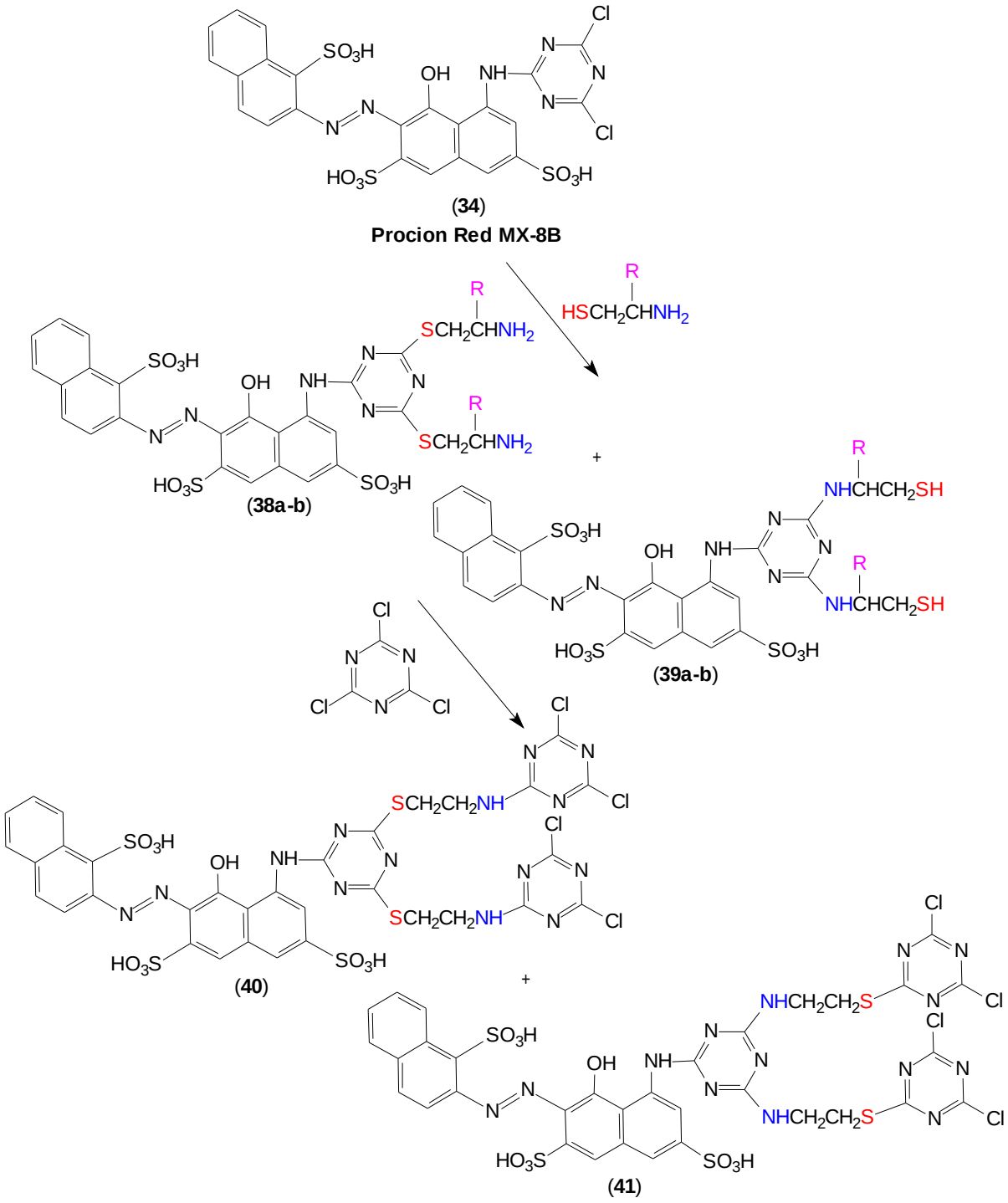


Figure 1.10. Potential Teegafix red dye structures from varying the pH of synthesis (R = H, CO_2H).

II. EXPERIMENTAL METHODS AND PROCEDURES

1. HIGH PERFORMANCE LIQUID CHROMATOGRAPHY (HPLC)

1.1 General Information

The water used in HPLC experiments was 18M ohm water obtained from a US Filter Purelab Plus system. The column utilized in this study was a Waters Nova-Pak C^{18} analytical column. Its inner diameter = 3.9 mm, length = 150mm, and particle size = 4 μm.

HPLC grade acetonitrile (AN) was obtained from Sigma-Aldrich Inc. Tetrabutylammonium bromide (TBAB) from Eastman Kodak Company was used as an ion pairing agent (IPA). A.C.S. grade monobasic ammonium phosphate ($NH_4H_2PO_4$) obtained from Fisher Chemical was used as a buffer.

The commercial dyes (Procion MX-8B, Procion Yellow MX-3R) were obtained from DyStar. The homobifunctional reactive dyes and intermediates were synthesized by Dr. Malgorzata Szymczyk at North Carolina State University and provided for these studies. All dyes were purified of salt and other non-dye impurities by Dr. Szymczyk.

1.2 HPLC Systems

Two HPLC systems were utilized in this study. The first system used was an Alliance system, but the majority of the experiments were performed on a Waters HPLC system.

1.2.1 Alliance HPLC System

The Alliance chromatographic system was operated through a Dell Optiplex GX270 workstation. The Waters Alliance 2695 Separations Module system consisted of a four-bottle solvent reservoir, solvent management system, Performance Plus inline degasser, and an autosampler. Analyte detection was performed using a Waters 2487 Dual Absorbance Detector. Samples were introduced to the column via automatic injection through a 250 µl syringe into a 100 µl sample loop, where 10 µl of sample was injected into the column. Data collection, storage, and peak analysis were performed by Empower Pro software.

1.2.2 Waters HPLC System

The Waters HPLC system consisted of a Waters In-Line Degasser (AF), a Waters IEEE8 Pump Control Module, a Waters Associates Chromatography pump as pump A, a Waters 510 HPLC pump as pump B, a Waters 486 Tunable Absorbance Detector, and a Waters 717 plus autosampler. Samples were introduced to the column via automatic injection through a 250 µl syringe into a 200 µl sample loop, where 10 µl of sample was injected into the column. Data collection, storage, and peak analysis were performed using Empower Pro software. This system is operated using an IBM Netvista workstation.

1.3 UV-Visible Spectroscopy

For UV-Visible analysis, all dyes and intermediates were dissolved in deionized (DI) water. A Cary 3E UV-Visible spectrophotometer (Varian, Inc.) was used with Cary WinUV software operated in Scan mode. All sample solutions

were placed in disposable polystyrene curvettes (Fisher Scientific) with a 10mm light path. The absorption maximum wavelength (λ_{max}) of each dye was obtained and used to select the wavelength of analysis in HPLC studies.

1.4 HPLC Mobile Phase Preparation

The mobile phases were prepared in two 1000 mL volumetric flasks for phase A (organic phase) and phase B (mixed phase). TBAB (8.06g, 0.025 mol) was added to the 1000 mL volumetric flask, dissolved in 1000mL HPLC grade acetonitrile (AN) and shaking to produce mobile phase A. $NH_4H_2PO_4$ (4.03g, 0.035 mol) was added to a second 1000mL volumetric flask and dissolved in 300 mL 18M ohm water, diluted incrementally with 300mL mobile phase A, and to 1000 mL using 18M ohm water to produce mobile phase B. The two phases were filtered using 0.22µm, 47mm MAGNA Nylon filters (Fisher Chemical) and placed in the solvent reservoirs of the HPLC system. The phase A was placed in reservoir A, and the phase B was placed in reservoir B.

1.5 Column Wash

The HPLC column underwent a 30 min 18M ohm water wash at 1mL/min before the mobile phase was introduced. When all analytical runs were finished or at the end of a day, the column was subjected to another 30 min 18M ohm water wash at the same flow rate to ensure that the buffer salts were completely removed from the column. That wash was followed by a 15 min rinse at 1mL/min with either 100% AN or 52/48 AN/H_2O. Prior to the washing process, the 18M

ohm water was filtered through a 0.45µm, 47mm mixed cellulose ester filter and AN was filtered using a 0.22µm, 47mm MAGNA Nylon filter (Osmonics Inc.).

1.6 Sample Solution Preparation

All of the sample solutions were prepared by placing 30 mg of sample powder in a 100 mL volumetric flask and dissolved in 100mL18M ohm water. Each solution was filtered using 0.2µm, 17mm PVDF syringe filters obtained from Alltech Associates Inc.

1.7 HPLC Analysis

The first HPLC experiment on each sample employed gradient system 1 (Table 2.1). This mobile phase gradient takes advantage of the previous work of Smith and Thakore with some adjustments [42]. The flow rate was reduced from 1.5 mL/min to 1.0 mL/min, and the gradient was shortened from 5.0 min to 1.5 min and from 7.0 min to 3.5 min.

Table 2.1. Properties of gradient system 1 used for HPLC studies.

Time (min)	Flow (mL/min)	% Phase A*	% Phase B**
0	1.00	30.0	70.0
1.50	1.00	50.0	50.0
3.50	1.00	30.0	70.0

*Phase A: 100% AN + 0.025 M TBAB

**Phase B: 30% Phase A/70% H_2O + 0.05 M $NH_4H_2PO_4$

Since products from the synthesis have more components than the commercial dyes, further adjustments were made to the gradient elution system

to optimize the separation of components in these samples. After gradient elution system optimization achieved, the samples were analyzed on the Alliance HPLC system to confirm that separations were similar to those obtained using the Waters HPLC system. All HPLC experiments were repeated at least twice to confirm reproducibility. % Area differences recorded in the tables have errors of ± 0.01.

2. DYE APPLICATION

2.1 General Information

A 100% plain weave cotton fabric weighing approximately 5.5 oz/yd^2 (156 g/m^2) was used for the dyeing experiments. The fabric was cut into 9 in x 11 in rectangles that weighed 10.00 ± 0.01g. The chemicals used during the dyeing experiments were ACS grade NaCl (salt) and Na_2CO_3 from Fisher Scientific. Stock solutions of 250g/L NaCl and 250 g/L of Na_2CO_3 were used in the dyeing experiments. Apolloscour SDRS (Apollo Chemical Corporation) was used as a surfactant to remove unfixed dyes during the washing off procedure following the dyeing step.

2.2 Dyeing Procedures

These experiments were conducted using an Ahiba Texomat laboratory dyeing machine with a 40:1 bath ratio. The initial dyebaths were set up for 1.0% (owf) dyeing. The appropriate amount of dye was dissolved in 300 mL water and the dye solution was added to each dyeing chamber. Additional water was added to give a final bath ratio of 40:1, once the salt solution added later had been

introduced. The tubes were then placed in the Ahiba Texomat machine at a temperature of 30°C. A 4mL aliquot of the original dyebath was removed and placed in a sealed container for subsequent analysis. Ten-gram cotton samples were wet out with water and then passed through a padder to remove excess water. The fabric samples were then mounted on Ahiba sample holders and placed in the baths to agitate.

The temperature was increased to 90°C at the maximum rate of rise and held for 5 min. The baths were then cooled to 60°C at the maximum rate of cooling and held for 10 min. Salt solution (25%, 64mL) was added to the baths in two equal doses spaced 1 min apart. Dye exhaustion was continued for 15 min and 4mL dyebath was removed and placed in a sealed container for subsequent analysis. Na_2CO_3 (16mL, 25%) was added in 2mL, 2mL, 4mL and 8mL portions over a 15 min time period and dyeing was continued for 30 min. The fabric was removed from the hot baths and 5 mL dyebath was removed and placed in a sealed container for subsequent analysis.

2.3 Washing Off Procedure

At the end of the dyeing process the fabric samples were washed by stirring them in water at room temperature successively for 2 min and 3 min. Excess water was removed by blotting on paper towels and fabrics were scoured at 90°C using 0.25 g/L Apolloscour SDRS. After 5 min the fabrics were rinsed in cool water, and excess water was removed by centrifuging. The fabric samples were then dried in a Yamato Mechanical Convectional Oven DKN810 at 65°C for 15 min.

2.4 Determination of Dye Exhaustion

The standard Beer-Lambert Law was used to determine the dye concentration of the final dyebath. A buffer solution (pH=7) containing KH_2PO_4 and NaOH was used to dilute the dyebath (prior to and after dyeing) to neutralize the solution (pH=7) for the UV-Visible analysis. The absorbance of each solution was measured on a Cary 3E UV-Visible Spectrophotometer. Since the concentrations of the initial dyebaths (c^i) were known, the measured absorbencies of the diluted dyebaths along with the Beer-Lambert Law was used to determine the concentration of dye remaining after dyeing (c^s).

The conservation of mass was used to calculate dye exhaustion. This indicates that the total amount of dye used in the dyeing process equals the amount of dye left in the dyebath and the amount of exhausted dye (E).

$c^i m^i = E + c^s m^s$

Where m^i represents the mass of the initial solution, m^s is the mass of the solution after dyeing, $m^i \neq m^s$.

The percent exhaustion (% E) was calculated for each of the dyeing experiments, using the following formula.

$\% E = [E/ (c^i m^i)] \times 100\%$

2.5 Colorimetric Data Collection

To obtain colorimetric data, the dyed fabric samples were dried and pressed with an iron set on medium high (162°C). The samples were then analyzed using a Datacolor International Spectraflash SF600X equipped with SLI-Form® N/G software (GretagMacbeth, Greensboro, USA). The

spectrophotometer set up was as follows: specular included, illuminant D65, 10° standard observer. Measurements were made on 4-ply fabric and each sample was measured four times and the data averaged. The L*, a*, b*, K/S value, and the wavelength at which the maximum K/S value was observed were recorded for each sample.

2.6 Physical Testing

Several physical tests were performed on the fabric samples:

Color Fastness to Light - AATCC Test Method 16-2004

Color Fastness to Water - AATCC Test Method 107-2002

Color Fastness to Crocking - AATCC Test Method 8-2004

Color Fastness to Laundering - AATCC Test Method 61-2003

2.6.1 Color Fastness to Light

Colorfastness to light was determined according to AATCC Test Method 16-2004 [43]. The dyed fabric samples were exposed to a Xenon light for 20 and 40h time intervals, using an Atlas 3SUN Hi35 High Irradiance Xenon weatherometer. Change in color was quantitatively determined by measuring the color difference between the unexposed sample and a test specimen using a Datacolor Spectraflash SF600X instrument equipped with SLI-Form® software that can also rate the color change on the Gray Scale grade according to AATCC Evaluation Procedure 7 [43]. The settings of the spectrophotometer and the testing method were same as colorimetric data collection. Ratings were assigned to each sample with a potential range of 1 (poor) – 5 (excellent).

2.6.2 Colorfastness to Water (Wet Color Transfer)

Colorfastness to water was evaluated using AATCC Test Method 107-2002 [43]. The fabric samples were attacked to a multi fiber test fabric (Test Fabrics, Inc.) and wet out thoroughly with the wet weight about 2.5-3.0 times the dry weight. The test specimens were placed in the perspiration tester with the pressure of 10 lb. The loaded specimen unit was held in an oven for a period of 18 h at 38°C. The specimen was removed and hung for drying at room temperature. The color change was quantitatively determined by measuring the color difference between the original sample and a test specimen on a Datacolor Spectraflash SF600X equipped with SLI-Form® software that can also rate the color change on the Gray Scale grade according to AATCC Evaluation Procedure 7 [43]. The settings of the spectrophotometer and the testing method were same as colorimetric data collection. Ratings were assigned to each sample with a potential range of 1 (poor) – 5 (excellent). The multifiber fabric samples were evaluated for staining using the AATCC Gray Scale for Evaluating Staining according to the AATCC Evaluation Procedure 2. A rating of 1 (poor) – 5 (excellent) was assigned to each of the six fiber strips in the fabric.

2.6.3 Colorfastness to Crocking (Rubbing)

Colorfastness to wet and dry crocking was evaluated using the AATCC Test Method 8-2004 [43]. Ratings for the amount of color transferred from the dyed sample to the white test square were assigned by using the AATCC Gray Scale for Staining according to the AATCC Evaluation Procedure 2 [43]. While evaluating, each test square was backed with three layers of original white cotton

fabric used for dyeing. A rating of 1 (poor) – 5 (excellent) was given to each fabric sample.

2.6.4 Colorfastness to Laundering

Colorfastness to laundering was evaluated using AATCC test method 61-2003, test No. 2A [43]. The test conditions are shown below:

Temperature: 49°C

Bath volume: 150 ml

% Detergent of total volume: 0.15%

Number of steel balls: 50

Time: 45 min

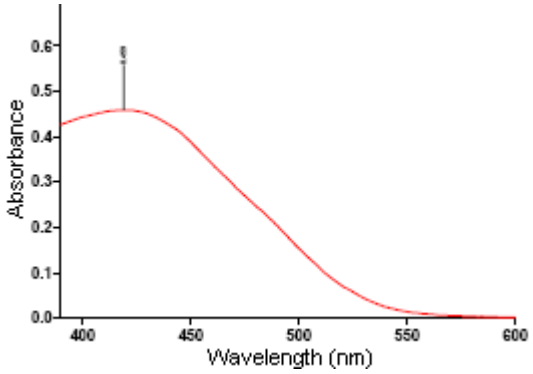
The dyed fabric samples employed were 2.0x6.0 in cotton samples and 2.0x2.0 in multifiber test fabrics (Test Fabrics, Inc.) were attached to each fabric sample to assess staining. The color change was quantitatively determined by measuring the color difference between the original sample and a test specimen using a Datacolor Spectraflash SF600X equipped with SLI-Form® software that can also rate the color change on the Gray Scale grade according to AATCC Evaluation Procedure 7 [43]. The settings of the spectrophotometer and the testing method were same as colorimetric data collection. Ratings were assigned to each sample with a potential range of 1 (poor) – 5 (excellent). The staining on the multifiber fabric samples was evaluated using the AATCC Gray Scale for Evaluating Staining according to the AATCC Evaluation Procedure 2. A rating of 1 (poor) – 5 (excellent) was assigned to each of the six fiber strips in the fabric.

III. RESULTS AND DISCUSSION

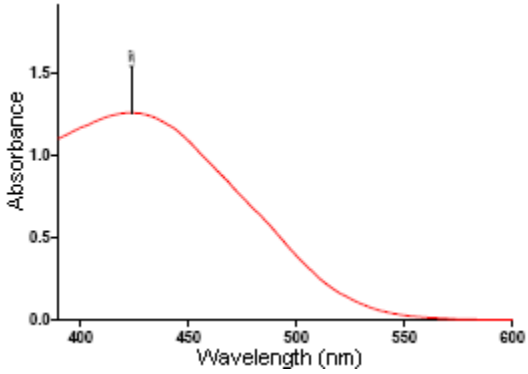
1. HPLC METHOD DEVELOPMENT

1.1 Visible Spectra for Dye Intermediates

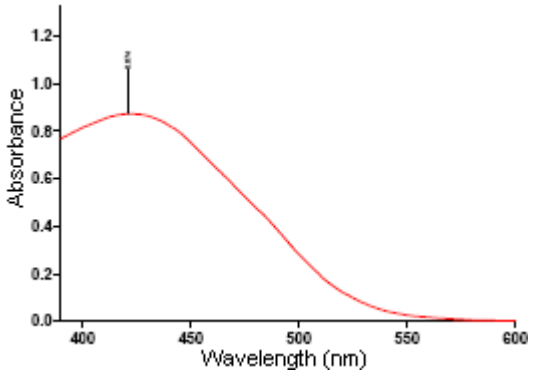
The UV-Visible spectra of intermediates **30**, **36** and **38**-**39** and the 2 commercial dyes (**29**, **34**) are shown in Figures 3.1-3.2 and the corresponding λ_{max} values are listed in Table 3.1.



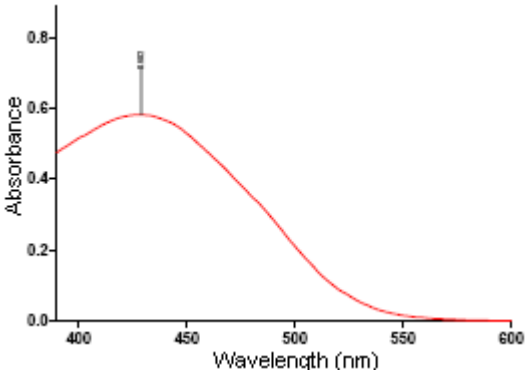
30a (pH=2, R=H)



30b (pH=2, R=COOH)

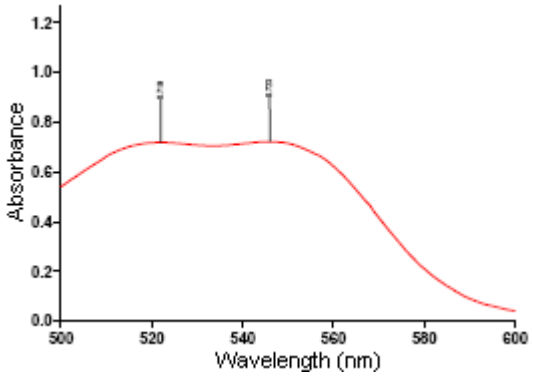


36a (pH=9, R=H)

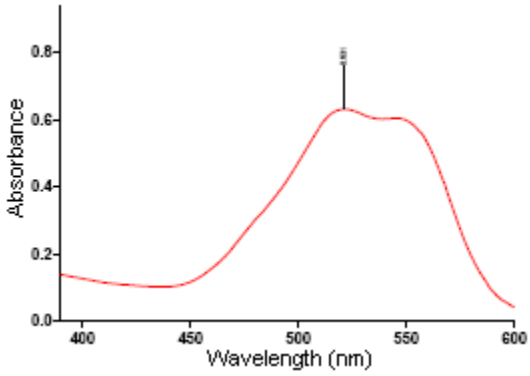


36b (pH=9, R=COOH)

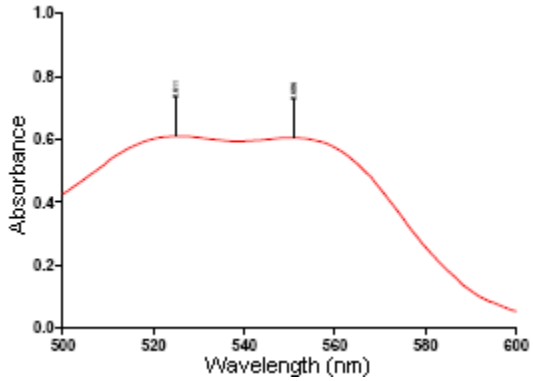
Figure 3.1. Visible absorption spectra for yellow dye intermediates (**30a**-**b**, **36a**-**b**) synthesized at pH 2 and pH 9.



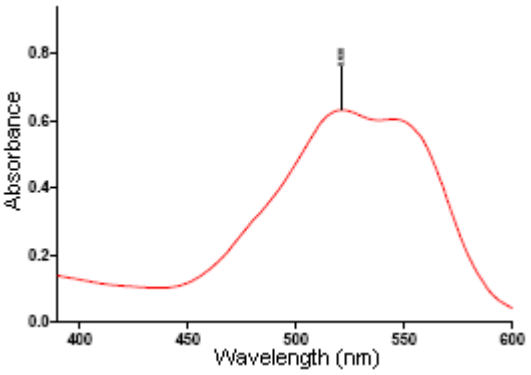
38a (pH=2, R=H)



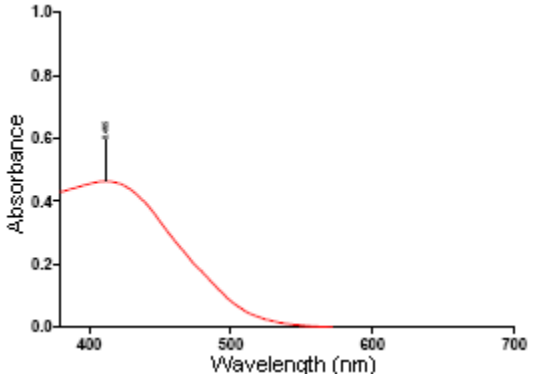
38b (pH=2, R=COOH)



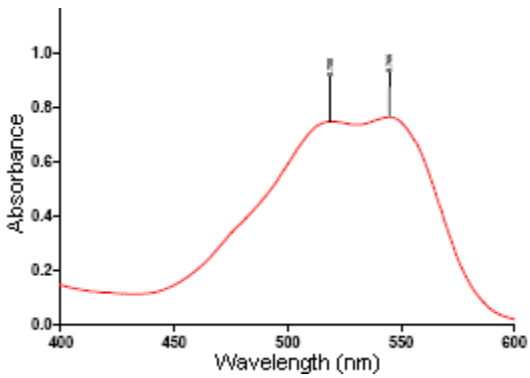
39a (pH=9, R=H)



39b (pH=9, R=COOH)



Yellow Dye **29**



Red Dye **34**

Figure 3.2. Visible absorption spectra for red dye intermediates (**38a**-**b**, **39a**-**b**) synthesized at pH 2 and pH 9 and commercial dyes.

Table 3.1. Data for the intermediates and commercial dyes.

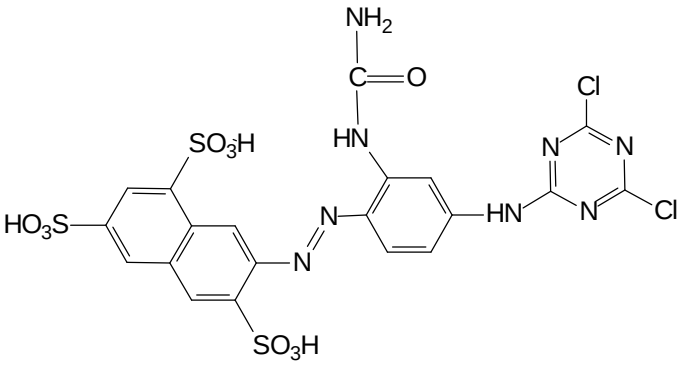
Color	Compound	R	pH*	λ_{max} (nm)
Yellow	**30a**	H	2	419
	30b	COOH	2	424
	36a	H	9	421
	36b	COOH	9	429
Red	**38a**	H	2	546
	38b	COOH	2	521
	39a	H	9	525
	39b	COOH	9	521
Commercial Yellow Dye (**29**)				412
Commercial Red Dye (**34**)				544

*pH: pH used for the synthesis

Based on Table 3.1, the use of cysteine gave slightly higher λ_{max} values than cysteamine in the case of yellow dye intermediates. Similarly, slightly higher λ_{max} values were obtained when pH 9 was used for yellow dye synthesis. The red dye gave mixed results. Cysteamine gave slightly higher λ_{max} values. No correlation with pH of synthesis was observed. All yellow intermediates exhibited a bathochromic shift from the λ_{max} of the commercial yellow dye. But for the red intermediates, there was mostly a hypsochromic shift. All of the red dyes had two peaks, the main one appearing near 522nm except for **38a**, which has λ_{max} near that of the parent dye. The peak at longer wavelength corresponds to the hydrazone form of the dye.

1.2 HPLC Results

Results from using gradient system 1 (Table 2.1) are shown in Figures 3.3-3.12, Tables 3.2-3.11.



(**29**)

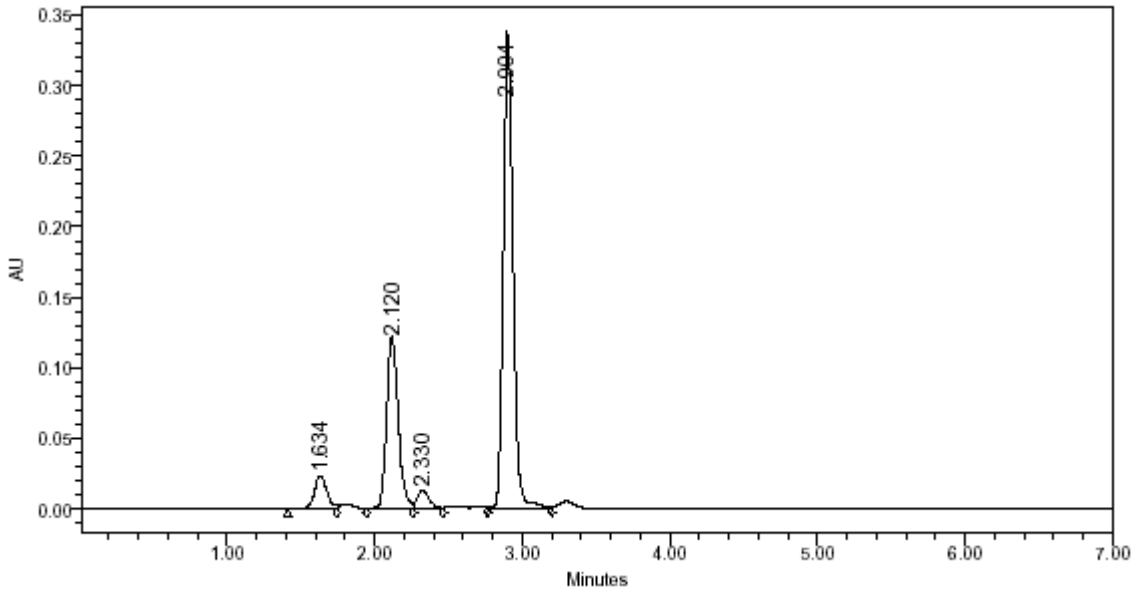
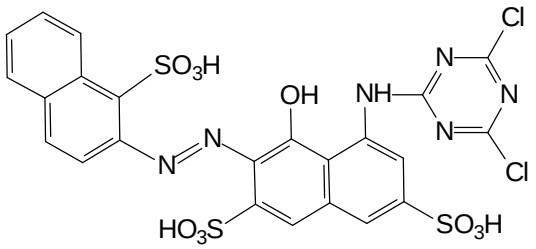


Figure 3.3. Chromatogram of commercial dye (**29**) using gradient system 1.

Table 3.2. Major peaks in the chromatogram of dye (**29**) using gradient system 1*.

Peak	Retention Time (min)	Area	% Area	Height
1	2.12	656491	27.3	120805
2	2.90	1552759	64.5	332221

* Gradient system 1 see Table 2.1, page 55



(**34**)

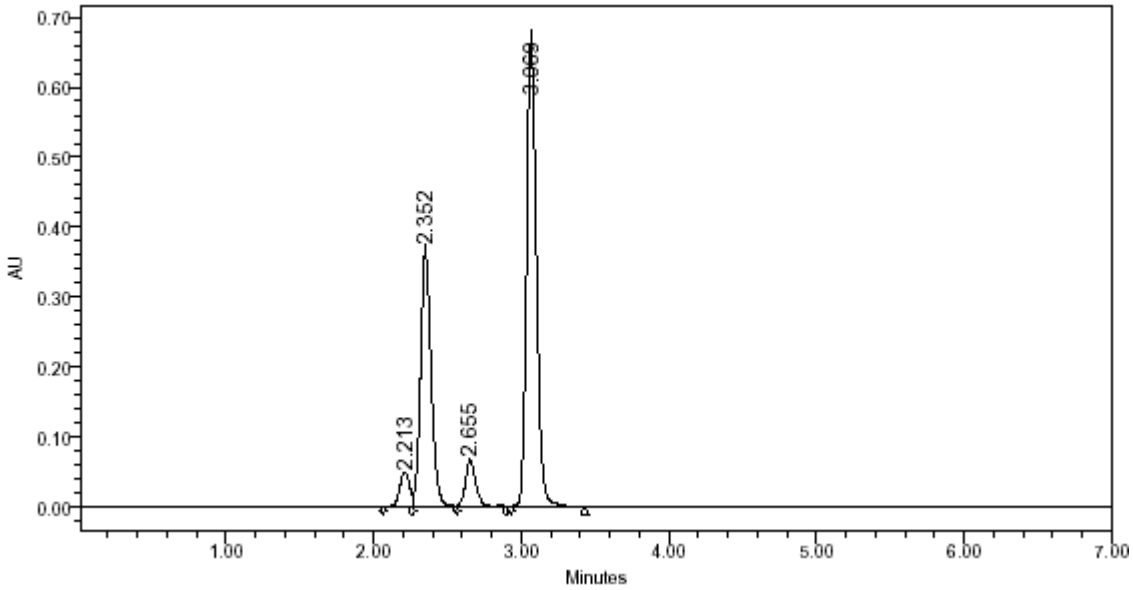
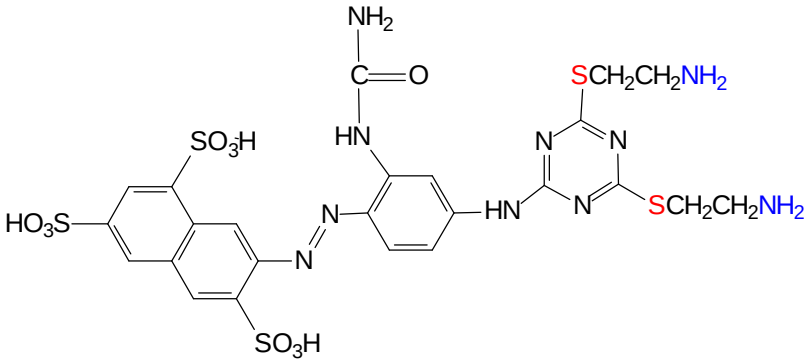


Figure 3.4. Chromatogram of commercial dye (**34**) using gradient system 1.

Table 3.3. Major peaks in the chromatogram of dye (**34**) using gradient system 1*.

Peak	Retention Time (min)	Area	% Area	Height
1	2.35	1821544	33.6	369445
2	3.07	3060684	56.4	666262

* Gradient system 1 see Table 2.1, page 55



(**30a**)

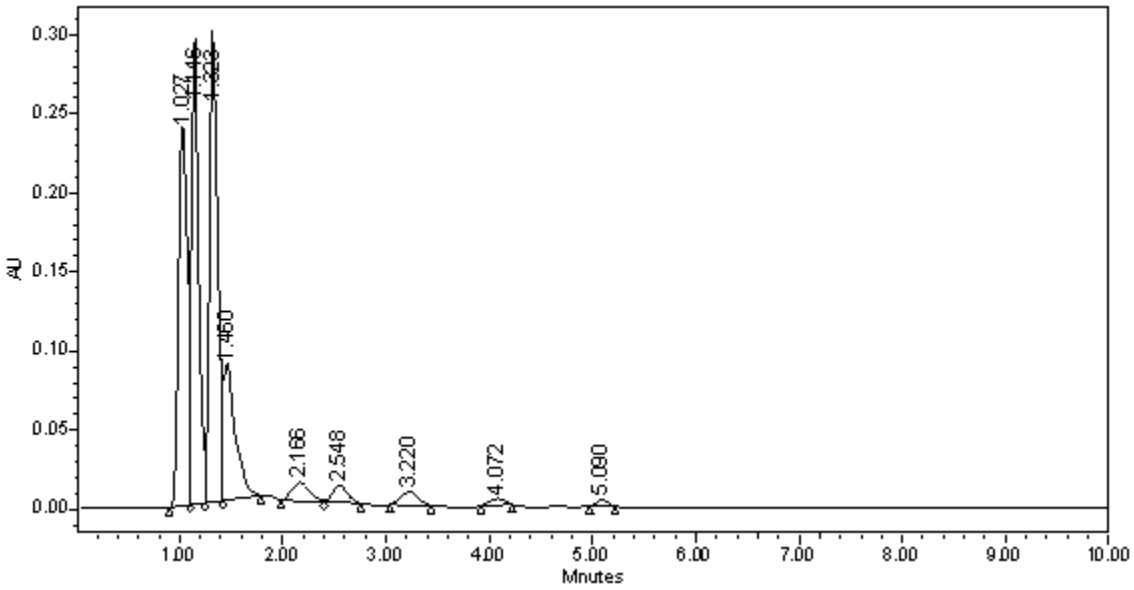
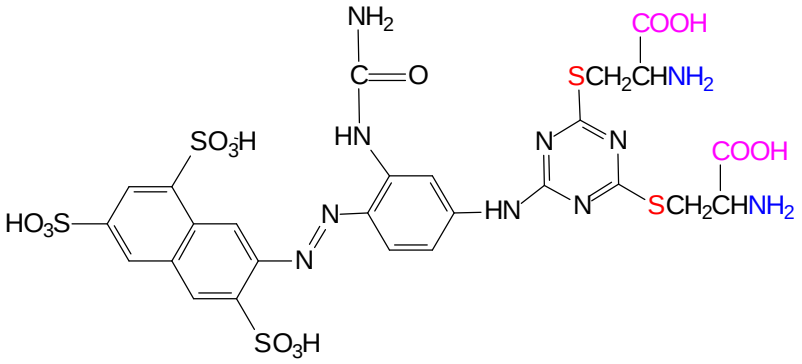


Figure 3.5. Chromatogram of dye intermediate **30a** using gradient system 1.

Table 3.4. Major peaks in the chromatogram of **30a** using gradient system 1*.

Peak	Retention Time (min)	Area	% Area	Height
1	1.03	1449937	25.9	243255
2	1.15	1401688	25.0	288416
3	1.32	1649991	29.4	296441

* Gradient system 1 see Table 2.1, page 55



(**30b**)

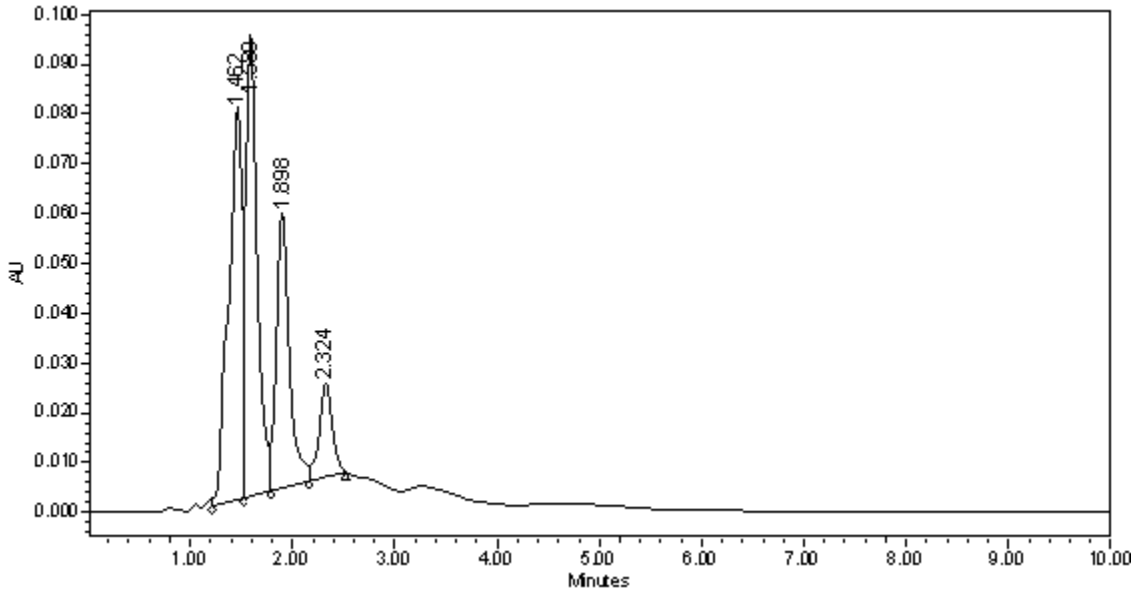
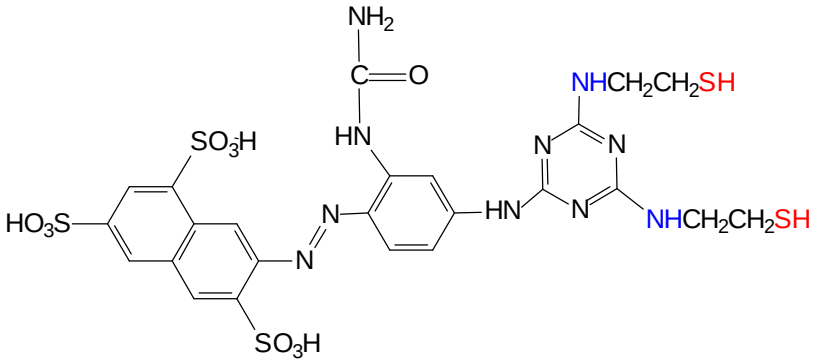


Figure 3.6. Chromatogram of dye intermediate **30b** using gradient system 1.

Table 3.5. Major peaks in the chromatogram of **30b** using gradient system 1*.

Peak	Retention Time (min)	Area	% Area	Height
1	1.462	700565	33.21	78627
2	1.589	754281	35.76	92681
3	1.898	487776	23.12	55239
4	2.324	166798	7.91	18821

* Gradient system 1 see Table 2.1, page 55



(**36a**)

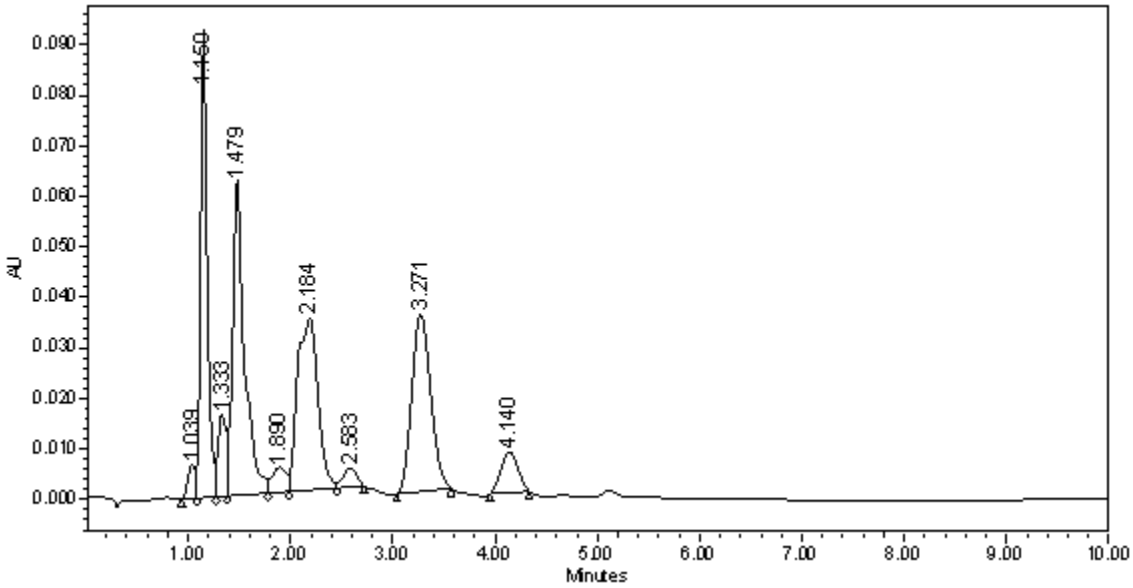
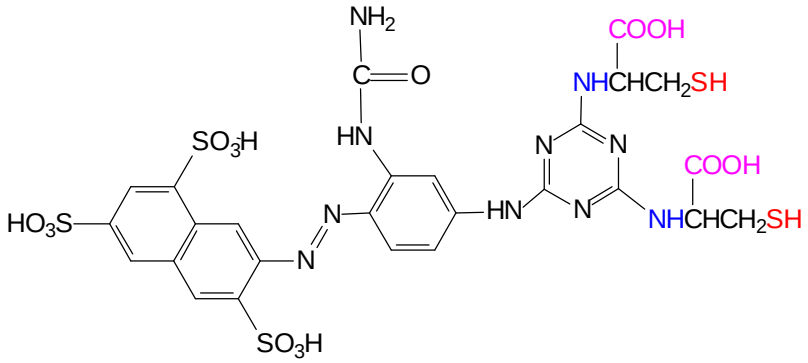


Figure 3.7. Chromatogram of dye intermediate **36a** using gradient system 1.

Table 3.6. Major peaks in the chromatogram of **36a** using gradient system 1*.

Peak	Retention Time (min)	Area	% Area	Height
1	1.15	415151	19.4	89885
2	1.48	504040	23.5	62050
3	2.18	472666	22.0	34027
4	3.27	451358	21.1	35177

* Gradient system 1 see Table 2.1, page 55



(**36b**)

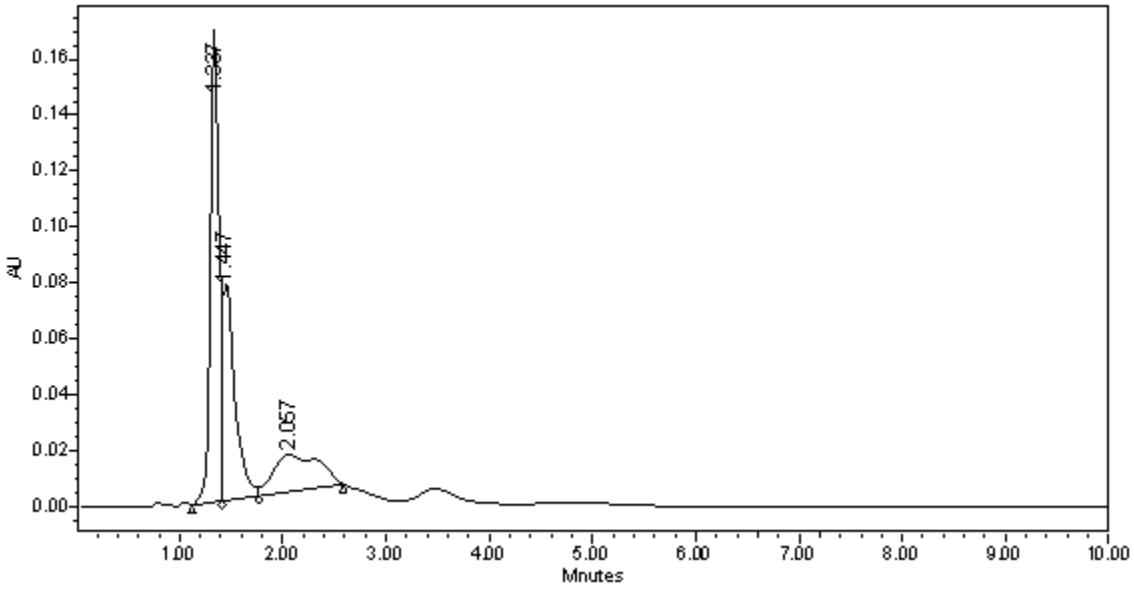
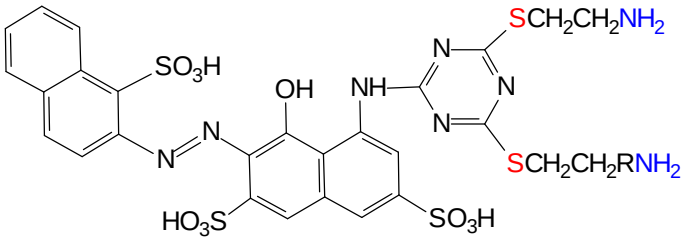


Figure 3.8. Chromatogram of dye intermediate **36b** using gradient system 1.

Table 3.7. Major peaks in the chromatogram of **36b** using gradient system 1.

Peak	Retention Time (min)	Area	% Area	Height
1 +2	1.34 + 1.45	1007374 +622358	49.5 + 30.6	167653

* Gradient system 1 see Table 2.1, page 55



(**38a**)

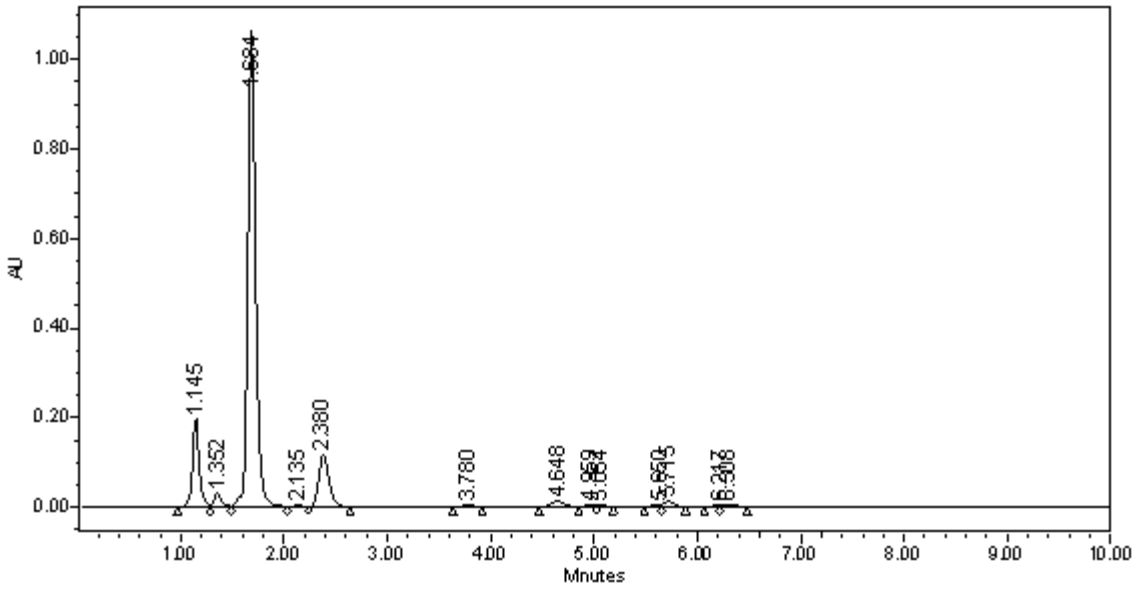
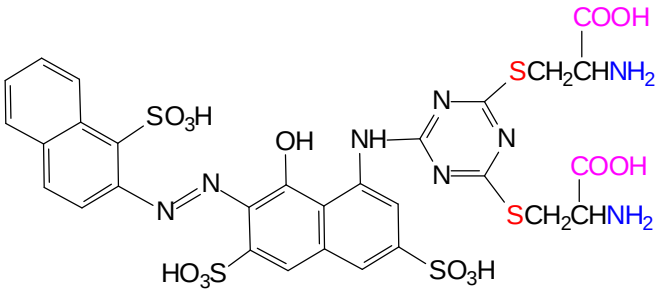


Figure 3.9. Chromatogram of dye intermediate **38a** using gradient system 1.

Table 3.8. Major peaks in the chromatogram of **38a** using gradient system 1*.

Peak	Retention Time (min)	Area	% Area	Height
1	1.15	906801	11.6	193859
2	1.68	5542507	70.9	1043310
3	2.38	807441	10.3	116438

* Gradient system 1 see Table 2.1, page 55



(**38b**)

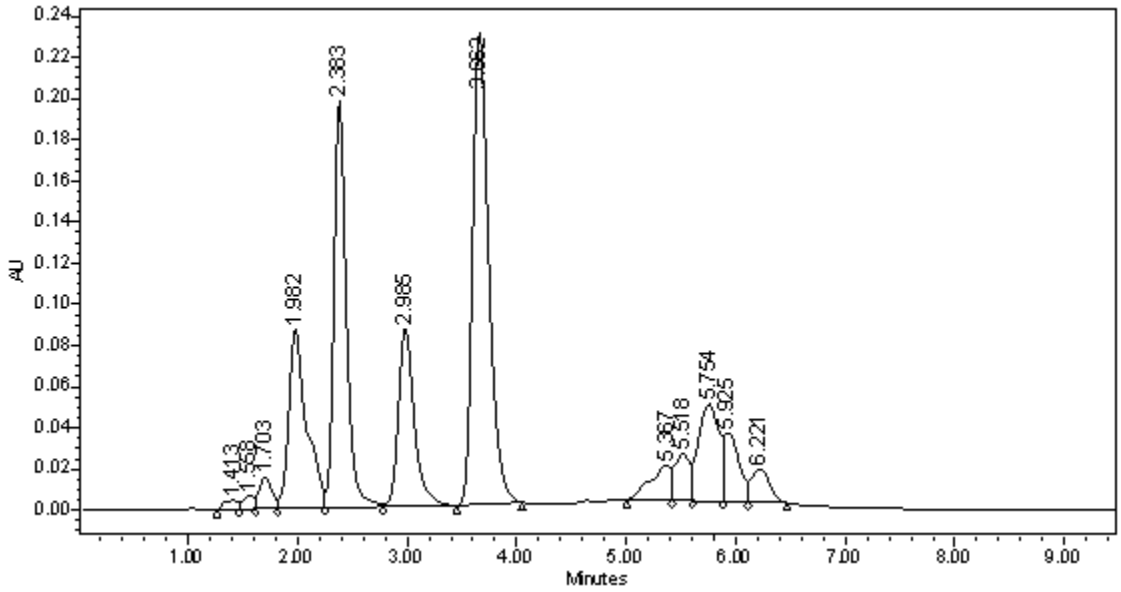
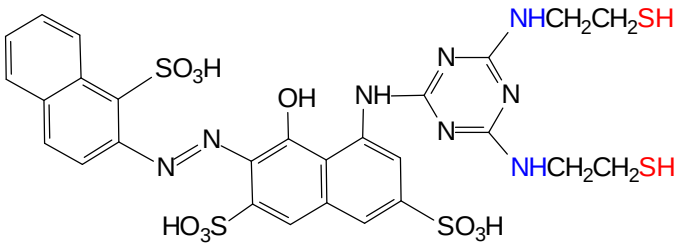


Figure 3.10. Chromatogram of dye intermediate **38b** using gradient system 1.

Table 3.9. Major peaks in the chromatogram of **38b** using gradient system 1*.

Peak	Retention Time (min)	Area	% Area	Height
1	1.98	978341	13.0	86864
2	2.38	1551995	20.6	197374
3	2.99	873329	11.6	86489
4	3.66	2338845	31.1	229611

* Gradient system 1 see Table 2.1, page 55



(**39a**)

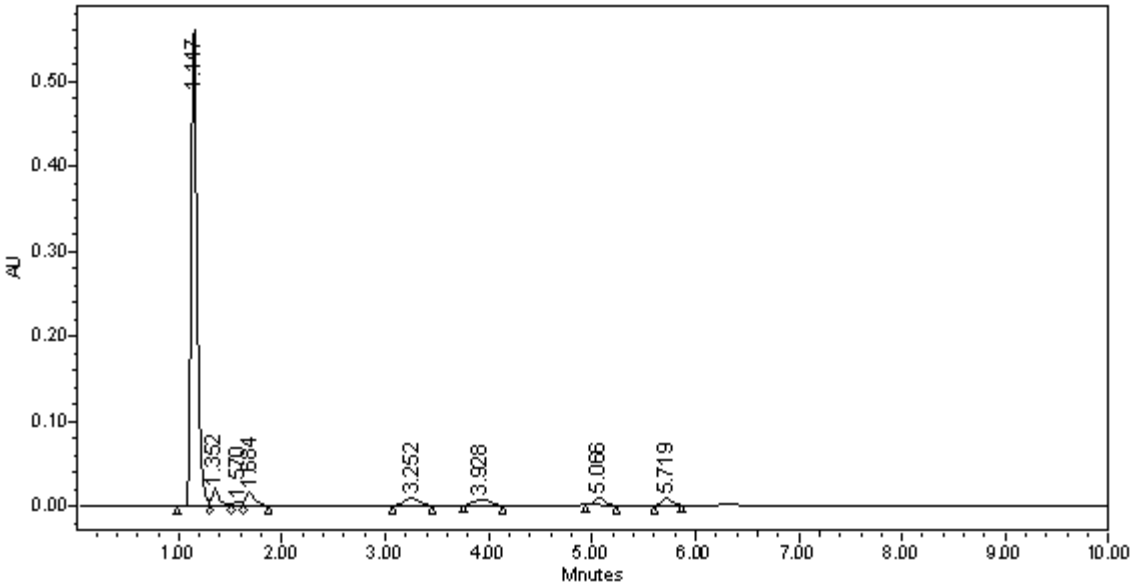
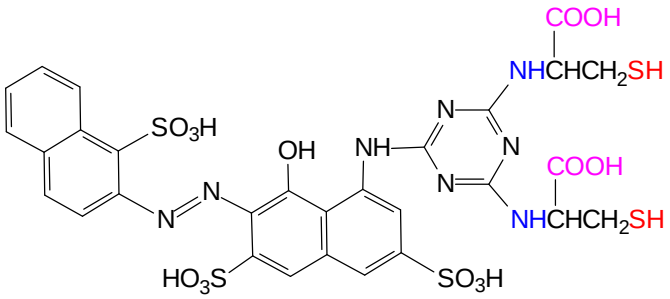


Figure 3.11. Chromatogram of dye intermediate **39a** using gradient system 1.

Table 3.10. Major peaks in the chromatogram of **39a** using gradient system 1*.

Peak	Retention Time (min)	Area	% Area	Height
1	1.15	2265576	81.1	545236

* Gradient system 1 see Table 2.1, page 55



(**39b**)

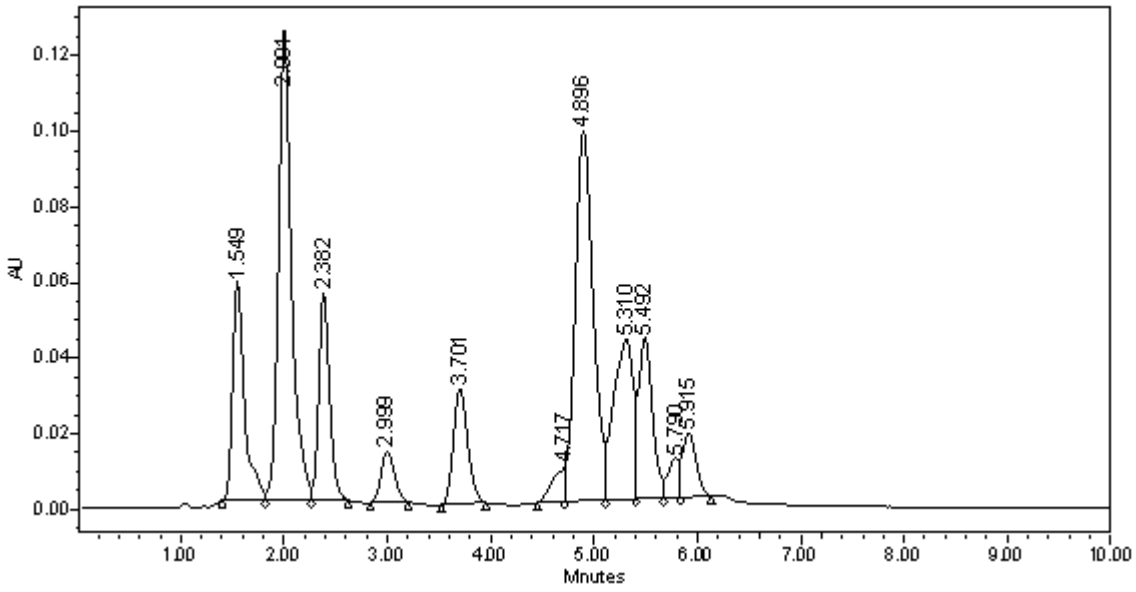


Figure 3.12. Chromatogram of dye intermediate **39b** using gradient system 1.

Table 3.11. Major peaks in the chromatogram of **39b** using gradient system 1*.

Peak	Retention Time	Area	% Area	Height
1	1.55	457896	9.53	57460
2	2.00	1089968	22.7	123748
3	2.38	393344	8.18	54549
4	4.90	1190759	24.8	98072

* Gradient system 1 see Table 2.1, page 55

Among these 8 samples, **38a** and **39a** gave good separations using gradient system 1. The other samples required adjustments to the initial gradient system. For example, for intermediate **30a**, when using gradient system 1, the chromatogram shown in Figure 3.5 was obtained. To improve the separation, a reduction in the percentage of mobile phase A was considered since solvent A was the good solvent for the sample while solvent B is a poorer solvent. This led to gradient system 2 (Table 3.12) and to the chromatogram shown in Figure 3.13, where it could be seen that the peaks were still overlapping. Next, isocratic elution system 1 (Table 3.13) was used, the results of which are shown in Figure 3.14. In this case the peaks separated well, but some components did not elute from the column, as indicated by the small peak at 14.8 min. After further modifications, the optimized gradient system for intermediate **30a** was decided to be gradient system 3 (Table 3.14). Results using this system are shown in Figure 3.15 and Table 3.15.

Table 3.12. Properties of gradient system 2 used for HPLC studies.

Flow (mL/min)	% Phase A*	%Phase B**	Time (min)	
			Gradient 2	Gradient 1
1.00	30.0	70.0	0	0
1.00	50.0	50.0	3.00	1.50
1.00	30.0	70.0	5.00	3.50

*Phase A: 100% AN + 0.025 M TBAB

**Phase B: 30% A/70% H_2O + 0.05 M $NH_4H_2PO_4$

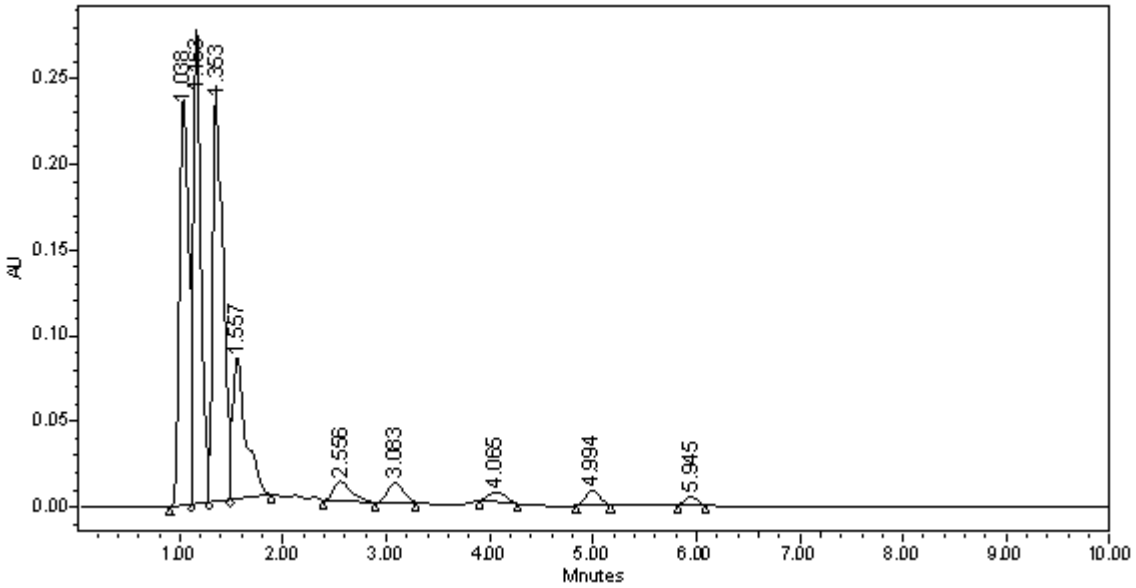


Figure 3.13. Chromatogram of dye intermediate **30a** using gradient system 2.

Table 3.13. Properties of isocratic elution system 1 used in HPLC studies.

Solvent	%	Contents
A	10	100% AN + 0.025 M TBAB
B	90	30% Phase A/70% H_2O + 0.05 M $NH_4H_2PO_4$

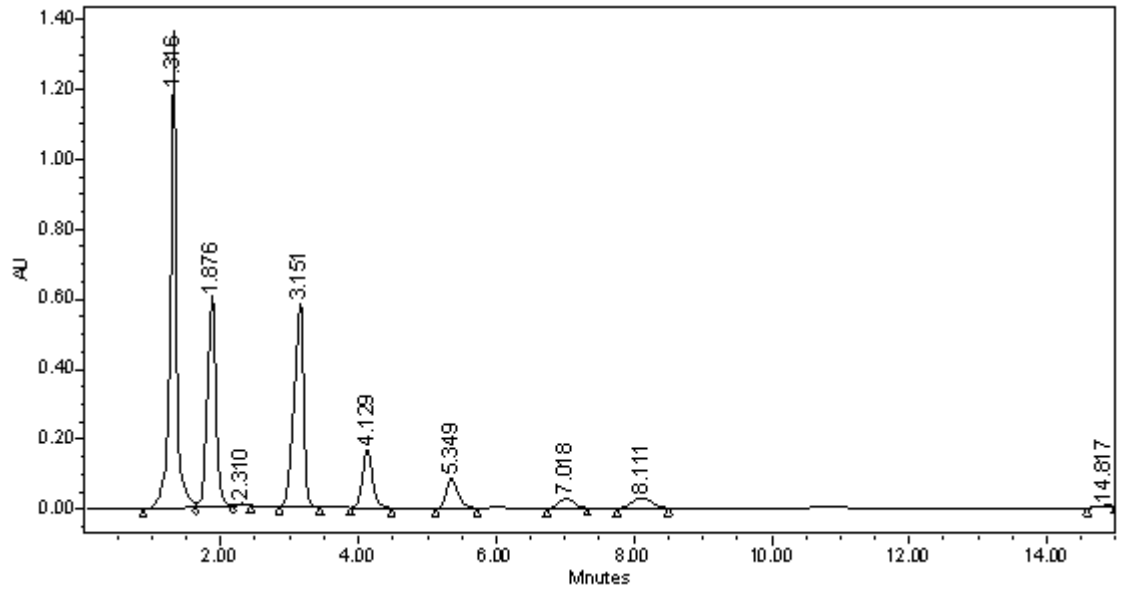


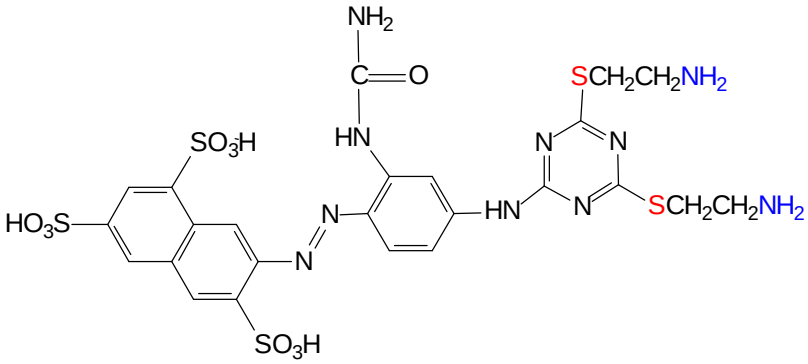
Figure 3.14. Chromatogram of dye intermediate **30a** using isocratic system 1.

Table 3.14. Properties of gradient system 3 used in HPLC studies.

Time (min)	Flow (mL/min)	% Phase A*	% Phase B**
0	1.00	10.0	90.0
2.00	1.00	10.0	90.0
2.20	1.00	30.0	70.0
4.20	1.00	30.0	70.0
4.50	1.00	50.0	50.0
6.00	1.00	50.0	50.0
6.20	1.00	5.0	95.0
9.00	1.00	5.0	95.0
9.20	1.00	10.0	90.0

*Phase A: 100% AN + 0.025 M TBAB

**Phase B: 30% Phase A/70% H_2O + 0.05 M $NH_4H_2PO_4$



(**30a**)

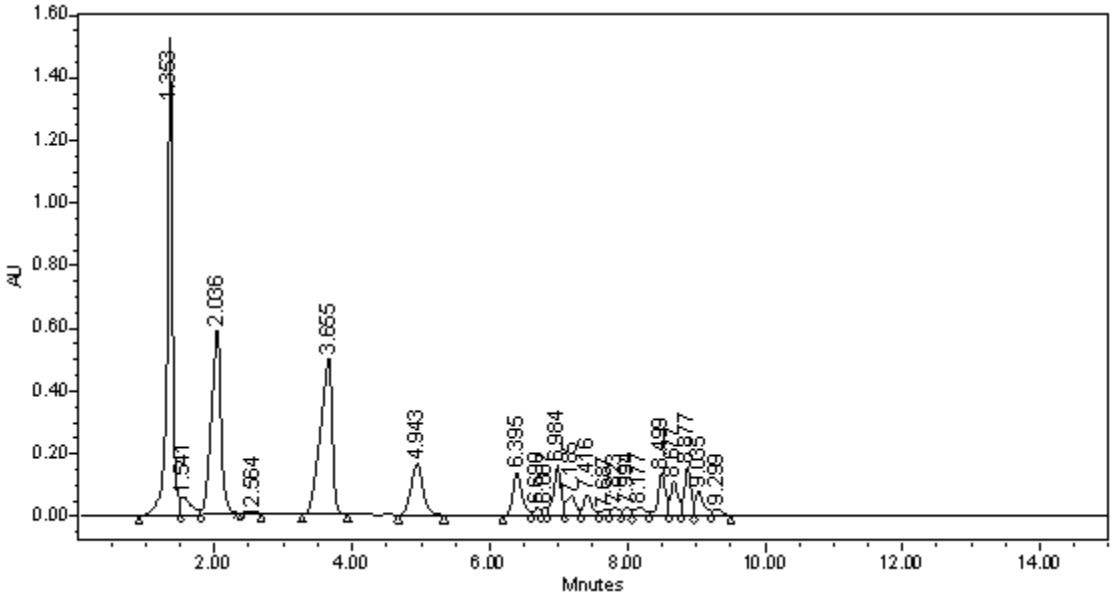
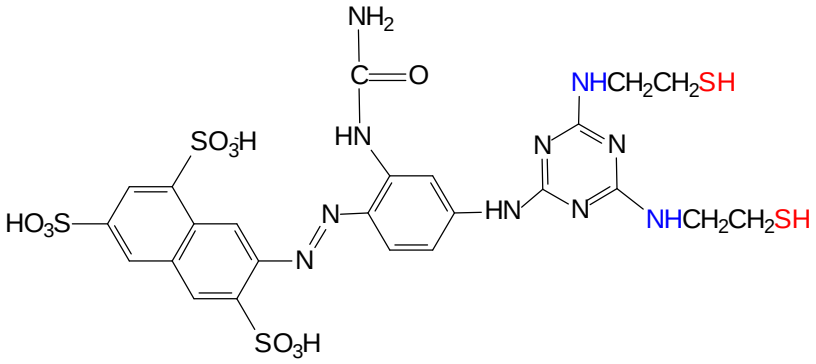


Figure 3.15. Chromatogram of dye intermediate **30a** using gradient system 3.

Table 3.15. Major peaks in the chromatogram of **30a** using gradient system 3.

Peak	Retention Time (min)	Area	% Area	Height
1	1.35	8055542	26.4	1470866
2	2.04	5732598	18.8	586840
3	3.66	5954924	19.5	503458

Gradient system 3 worked well for intermediate **30a**, with all of the main peaks coming out within 6 min and clearly separated. Components eluting after 6 min were regarded as impurities. With these results in mind, intermediates **30a-b**, **36a-b**, **38a-b**, **39a-b** were analyzed using the same solvent systems. The results from using gradient system 3 for intermediate **36a** are shown in Figure 3.16 and Table 3.16.



(**36a**)

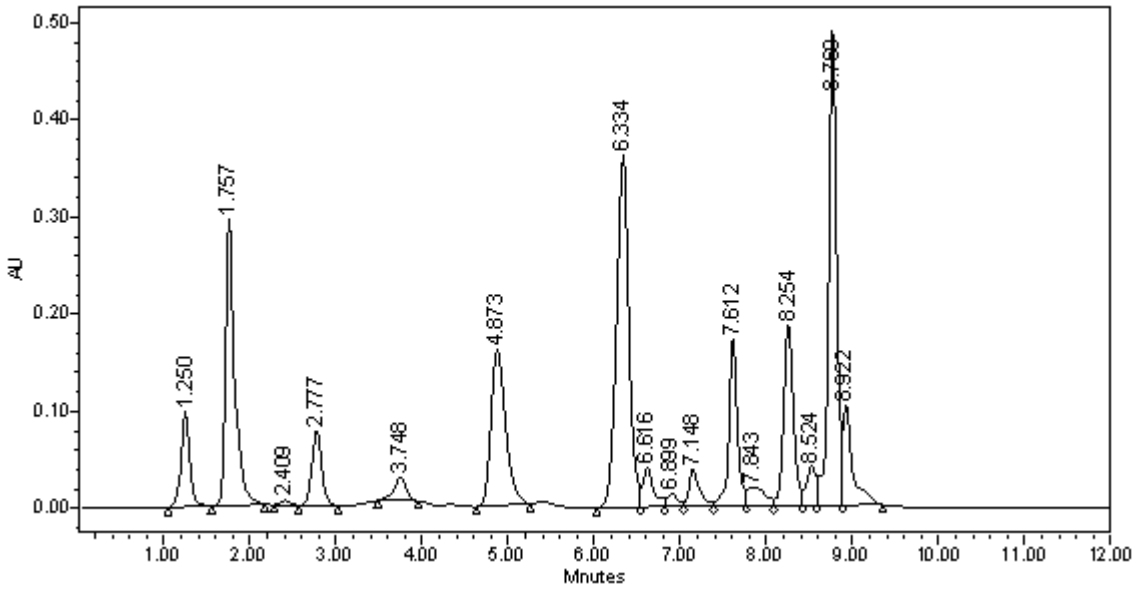


Figure 3.16. Chromatogram of dye intermediate **36a** using gradient system 3.

Table 3.16. Major peaks in the chromatogram of **36a** using gradient system 3.

Peak	Retention Time (min)	Area	% Area	Height
1	1.76	2170868	12.6	297507
2	6.33	3610761	20.9	361849
3	8.77	3219224	18.7	484354

Comparing the chromatograms of intermediates **30a** (Figure 3.15) and **36a** (Figure 3.16), it was clear that few common retention times existed, which meant that synthesizing these intermediates at pH 2 and pH 9 did not produce the same compounds though the starting compounds were the same.

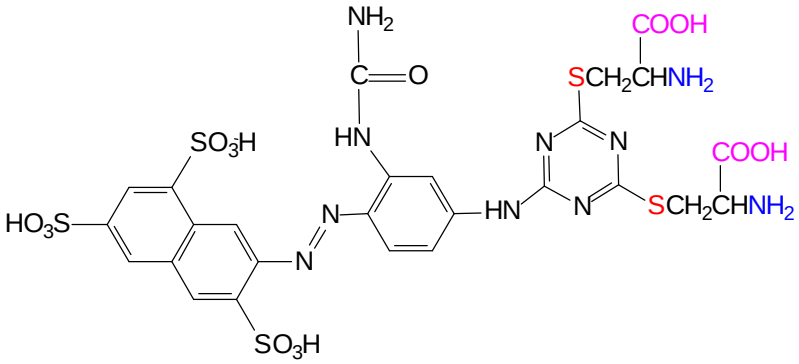
All of the other compounds were analyzed using their optimized gradient system. For intermediates **30b** and **36b**, gradient system 4 (Table 3.17) gave the best results, and for intermediates **38b** and **39b**, gradient system 5 (Table 3.20) gave optimum separation.

Table 3.17. Properties of gradient system 4 used in HPLC studies.

Time (min)	Flow (mL/min)	% Phase A*	% Phase B**
0	1.00	15.0	85.0
6.5	1.00	15.0	85.0
7.0	1.00	50.0	50.0
8.5	1.00	50.0	50.0
9.0	1.00	15.0	85.0

*Phase A: 100% AN + 0.025 M TBAB

**Phase B: 30% Phase A/70% H_2O + 0.05 M $NH_4H_2PO_4$



(**30b**)

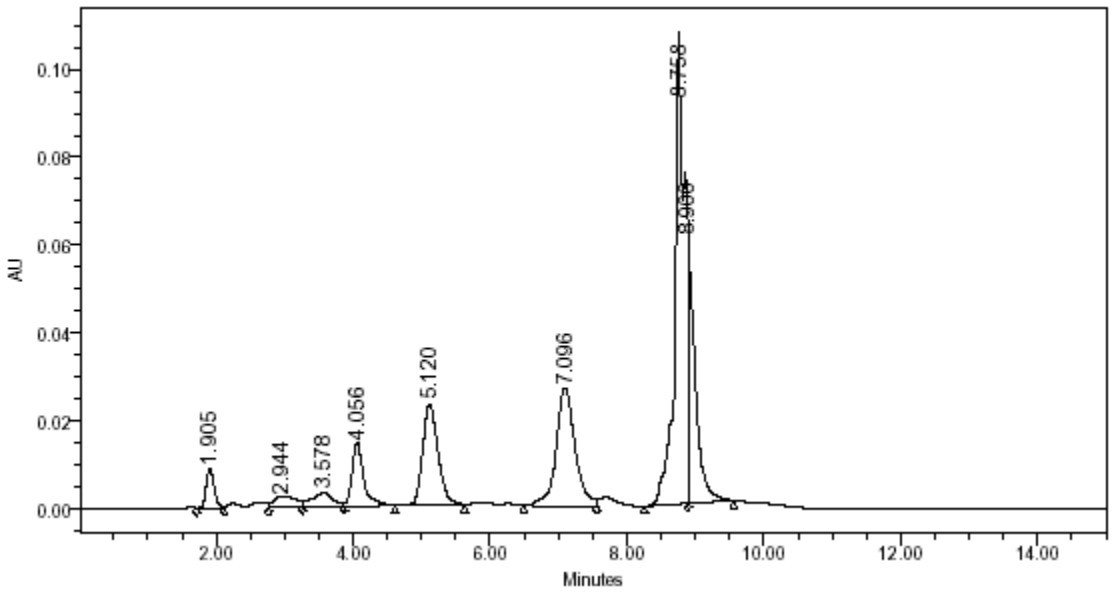
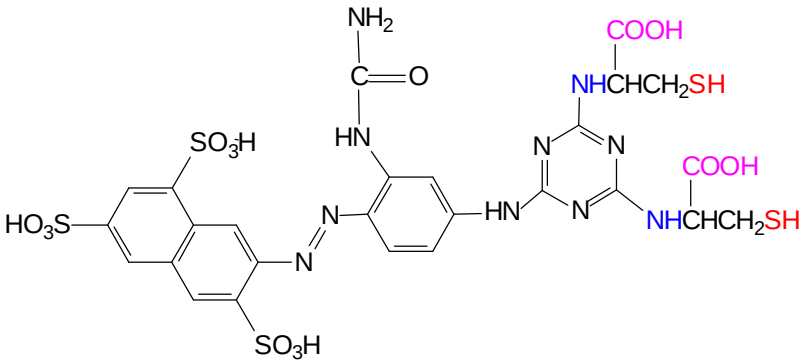


Figure 3.17. Chromatogram of dye intermediate **30b** using gradient system 4.

Table 3.18. Major peaks in chromatogram of **30b** using gradient system 4.

Peak	Retention Time (min)	Area	% Area	Height
1	5.12	350831	12.8	22897
2	7.10	509344	18.6	26842
3 +4	8.76 + 8.90	1096771 + 417929	40.1 +15.3	107219



(**36b**)

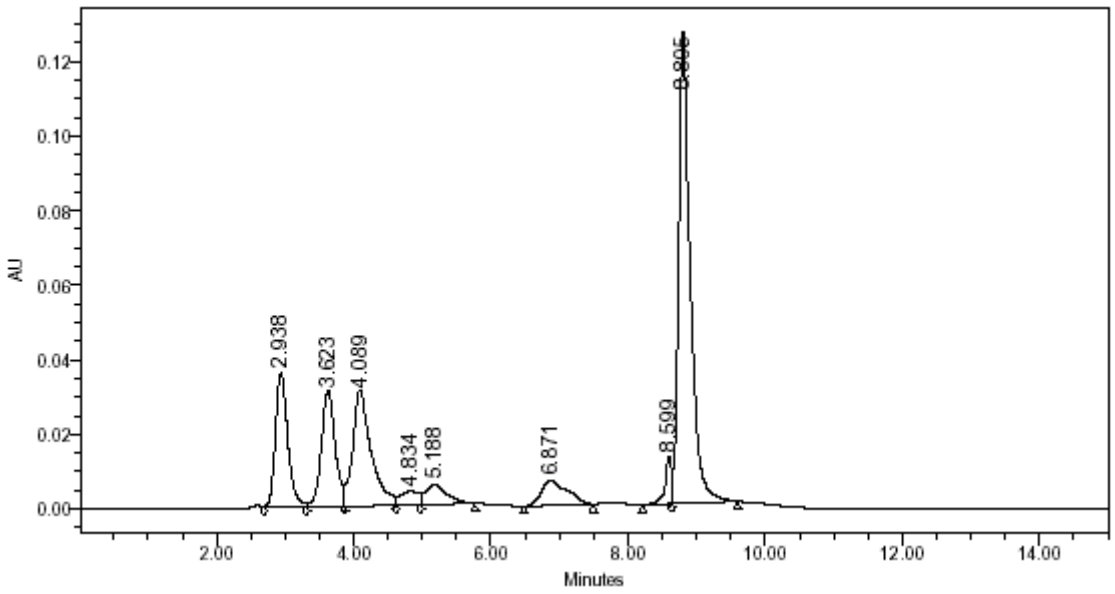


Figure 3.18. Chromatogram of dye intermediate **36b** using gradient system 4.

Table 3.19. Major peaks in chromatogram of **36b** using gradient system 4.

Peak	Retention Time (min)	Area	% Area	Height
1	2.94	452112	13.4	36113
2	3.62	429212	12.7	30971
3	4.09	569151	16.9	31030
4	8.81	1483474	43.9	126675

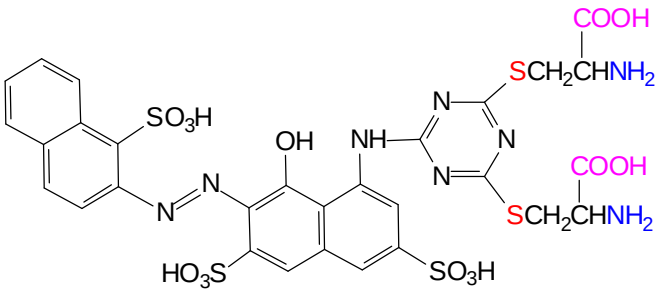
Comparing the chromatograms of intermediates **30b** (Figure 3.17) and **36b** (Figure 3.18), it is clear that both intermediates gave a major peak near a retention time of 8.80 min, which differs from **30a** and **36a**. In this case, the R group is COOH rather than H. It is likely that steric effects of the COOH group promotes reaction at the –SH end of the cysteine molecule at pH 2 and pH 9.

Table 3.20. Properties of gradient system 5 used in HPLC studies.

Time (min)	Flow (mL/min)	% Phase A*	% Phase B**
0	1.00	30.0	70.0
4.00	1.00	30.0	70.0
5.00	1.00	50.0	50.0
7.00	1.00	30.0	70.0

*Phase A: 100% AN + 0.025 M TBAB

**Phase B: 30% Phase A/70% H_2O + 0.05 M $NH_4H_2PO_4$



(38b)

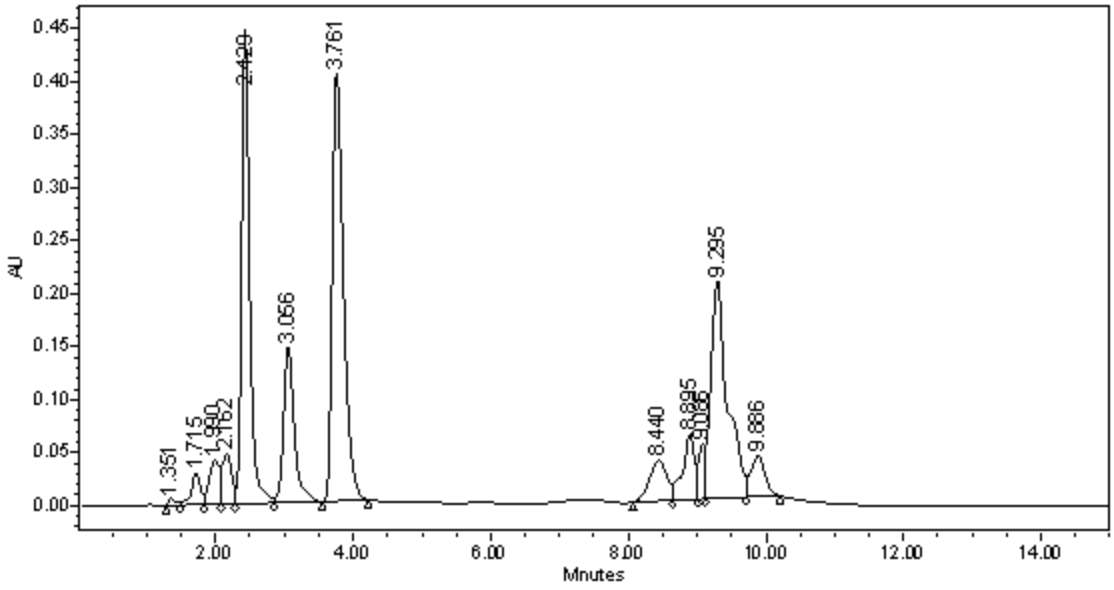
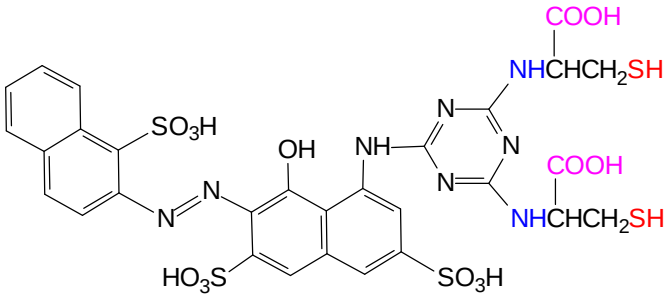


Figure 3.19. Chromatogram of dye intermediate **38b** using gradient system 5.

Table 3.21. Major peaks in the chromatogram of **38b** using gradient system 5.

Peak	Retention Time (min)	Area	% Area	Height
1	2.43	3641930	21.8	447750
2	3.76	4548903	27.2	404535
3	9.30	3473047	20.7	205720



(39b)

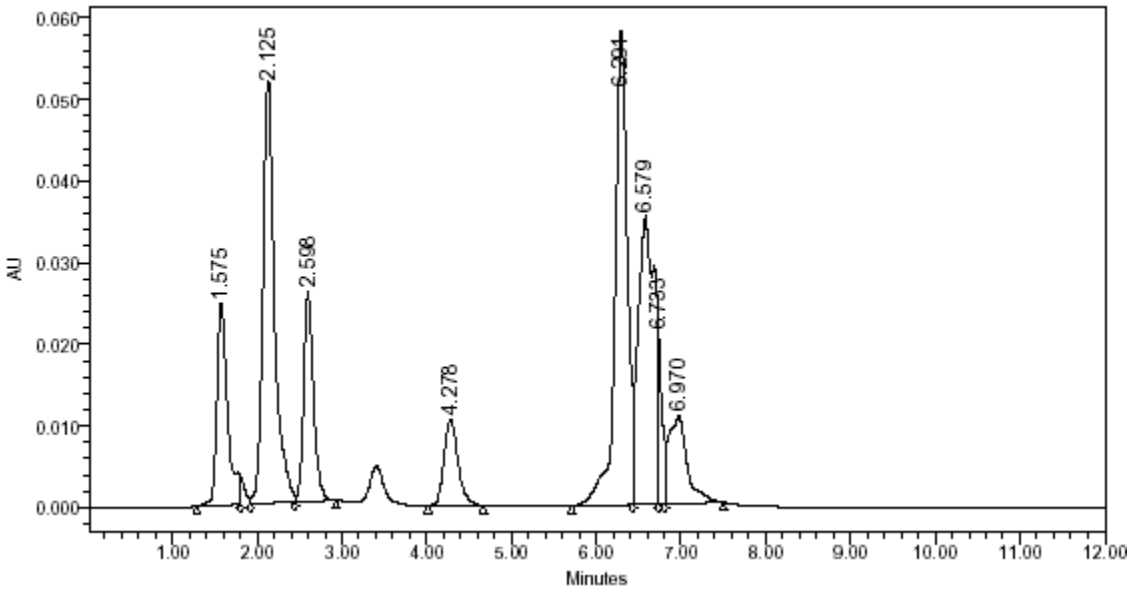


Figure 3.20. Chromatogram of dye intermediate **39b** using gradient system 5.

Table 3.22. Major peaks in the chromatogram of **39b** using gradient system 5.

Peak	Retention Time (min)	Area	% Area	Height
1	1.58	215081	9.26	24752
2	2.13	494507	21.3	51908
3	2.60	205439	8.85	25692
4	6.29	583919	25.2	58424
5	6.58	482881	20.8	35200

Comparing the chromatograms of intermediates **38b** (Figure 3.19) and **39b** (Figure 3.20), it could be seen that intermediate **38b** did not have a significant peak before 2.40 min, while intermediate **39b** had a big component eluting at 2.13 min, but no peaks after 7 min, on the other hand, 20% of intermediate **38b** eluted after 7 min. Both intermediates had major, well separated peaks appearing before 5 min.

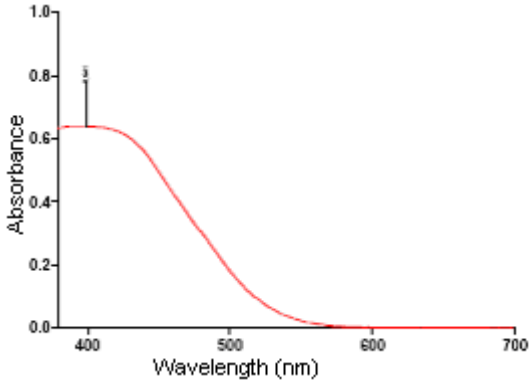
Intermediates **38a** and **39a** also gave well separated peaks using gradient system 1, as shown by the results in Figures 3.9 and 3.11, Tables 3.8 and 3.10. Comparing the two chromatograms, it was very clear that intermediate **39a** gave a predominant peak at 1.15 min while intermediate **38a** gave a dominant peak at 1.68 min. Intermediate **38a** also had a component (10%) eluting at 1.15 min that corresponded to the major component in intermediate **39a**.

Overall, the results of HPLC analysis indicated that while the types of products from cysteine were more similar, the complexity of the chromatograms was greater. It was possible that the –COOH group also serves as a nucleophile in the reaction of the cysteine and the parent DCT dyes.

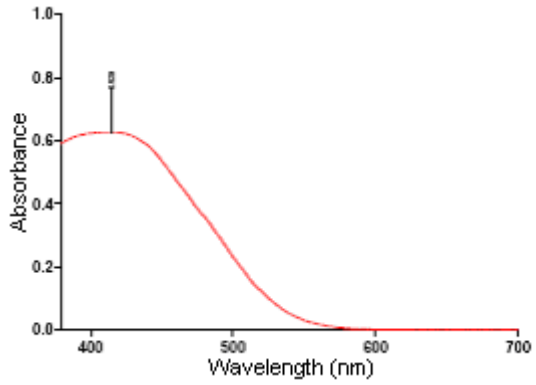
2. ANALYSIS OF DCT DYES AND THEIR INTERMEDIATES

2.1 Visible Absorption Spectra

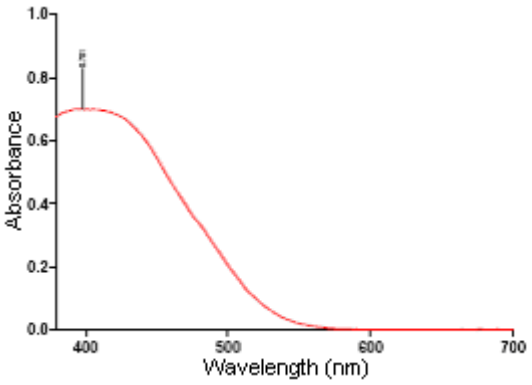
The spectra of the intermediate dyes are shown in Figures 3.21-3.22, and λ_{max} and ε_{max} are recorded in Table 3.23. The spectra of dyes made from these intermediates are shown in Figures 3.23-3.24, and their λ_{max} and ε_{max} values are recorded in Table 3.24.



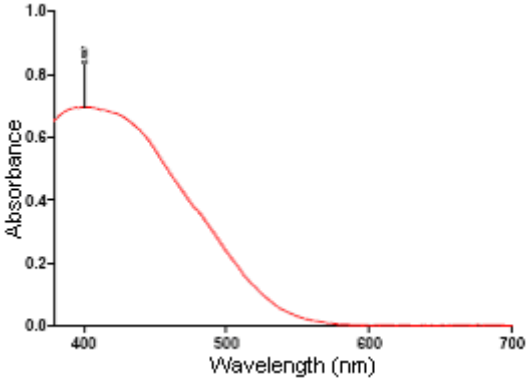
Yellow Intermediate (pH 3)



Yellow Intermediate (pH 4)



Yellow Intermediate (pH 5)



Yellow Intermediate (pH 6)

Figure 3.21. Visible absorption spectra for yellow dye intermediates (**30a**/**36a**) synthesized using cysteamine at pH 3-6.

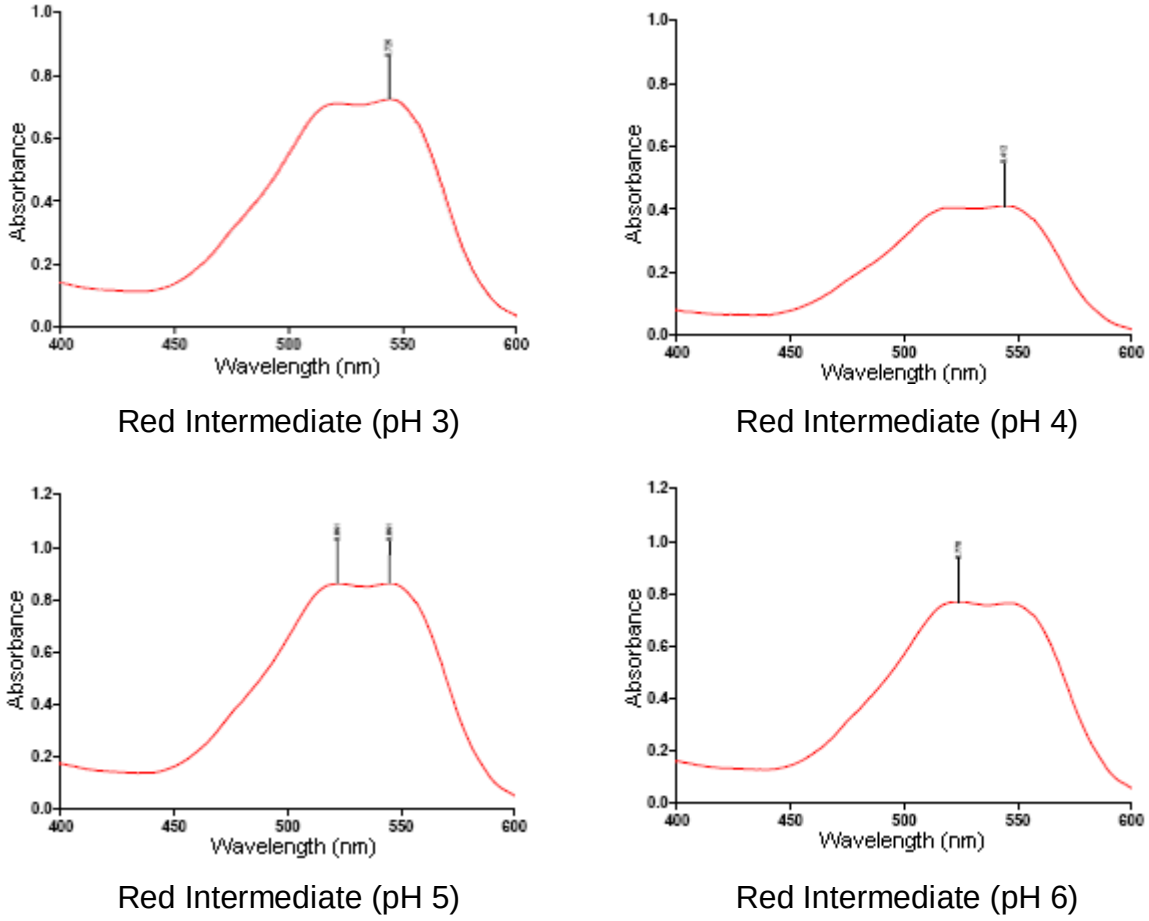
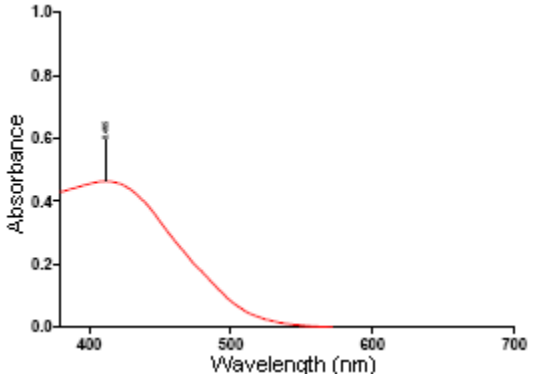


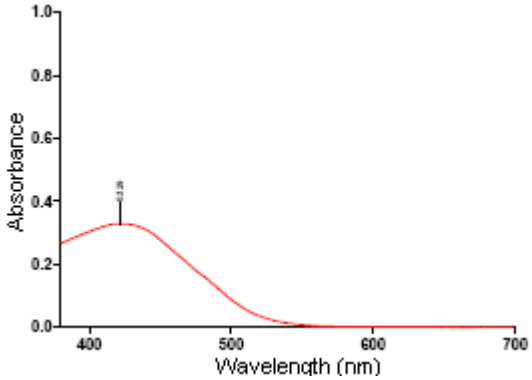
Figure 3.22. Visible absorption spectra for red dye intermediates (**38a**/**39a**) synthesized using cysteamine at pH 3-6.

Table 3.23. The λ_{max} and ε_{max} values for dye intermediates prepared at pH 3-6.

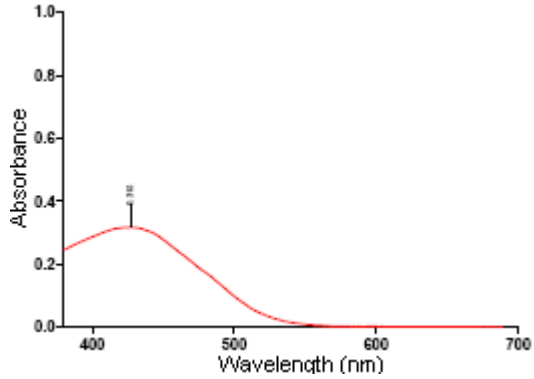
Dye Intermediates	pH Used for Synthesis	λ_{max} (nm)	ε_{max} ($x10^4$ $L \cdot mol^{-1} \cdot cm^{-1}$)
Yellow (**30a**/**36a**)	3	399	0.8
	4	415	0.5
	5	398	0.6
	6	401	0.8
Red (**38a**/**39a**)	3	544	1.9
	4	544	2.8
	5	545	1.5
	6	524	2.1



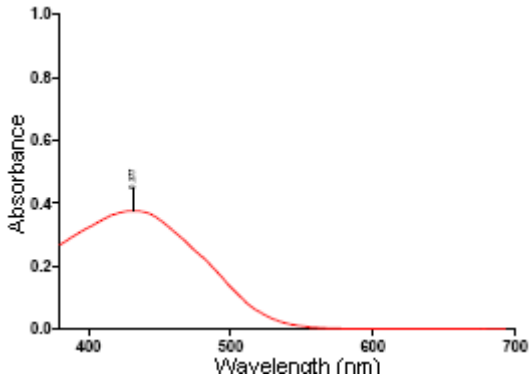
Dye **29** (Commercial)



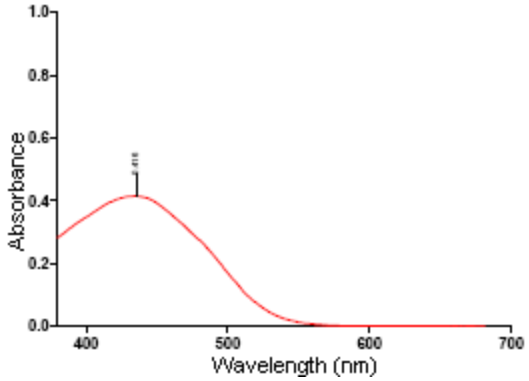
Yellow Dye from **30a**/**36a** (pH 3)



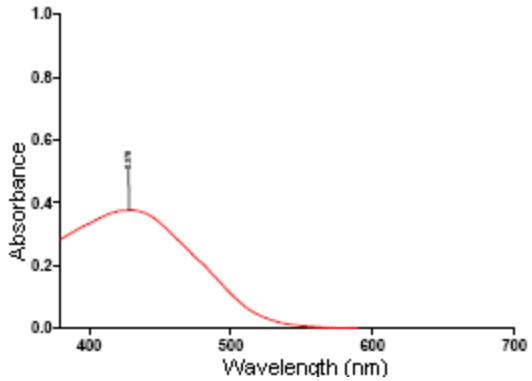
Yellow Dye from **30a**/**36a** (pH 4)



Yellow Dye from **30a**/**36a** (pH 5)

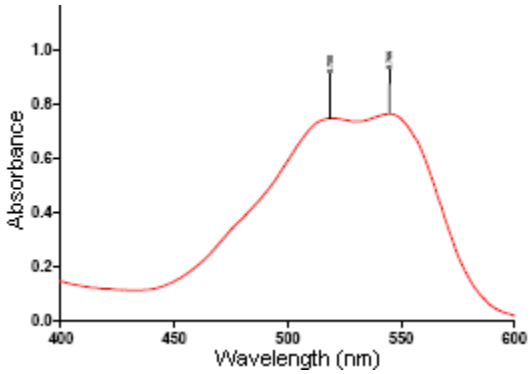


Yellow Dye from **30a**/**36a** (pH 6)

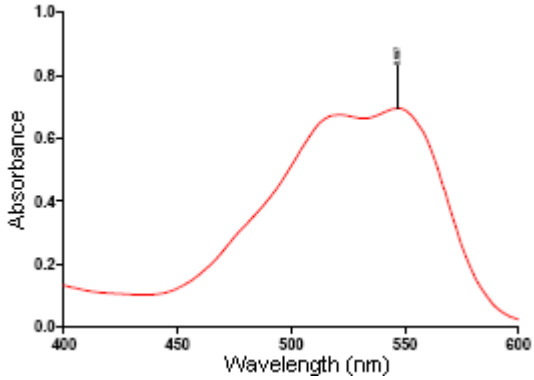


Yellow Dye from **30a**/**36a** (Factory Sample)

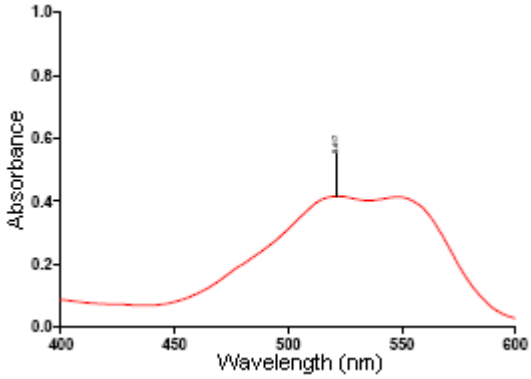
Figure 3.23. Visible absorption spectra for the commercial yellow dye (**29**) and the modified dyes (**31**/**37**) synthesized using cysteamine at pH 3-6.



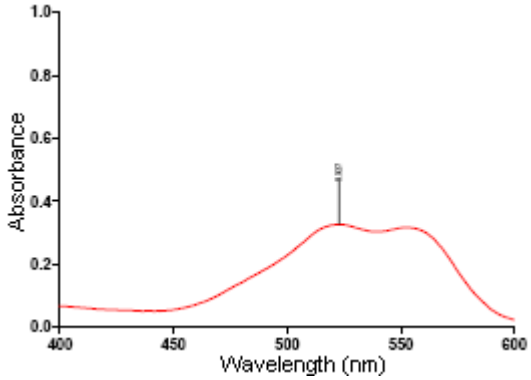
Dye **34** (Commercial)



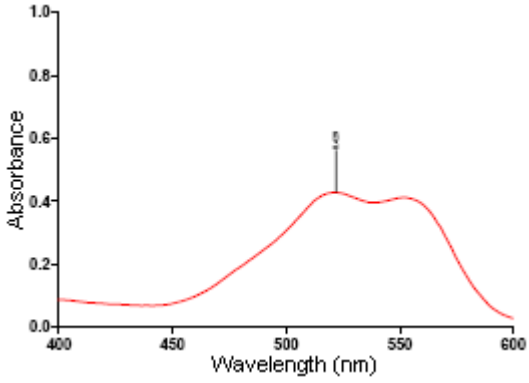
Red Dye from **38a**/**39a** (pH 3)



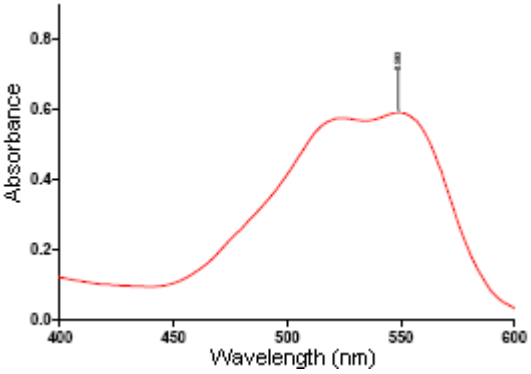
Red Dye from **38a**/**39a** (pH 4)



Red Dye from **38a**/**39a** (pH 5)



Red Dye from **38a**/**39a** (pH 6)



Red Dye from **38a**/**39a** (Factory Sample)

Figure 3.24. Visible absorption spectra for the commercial red dye (**34**) and the modified dyes (**40**/**41**) synthesized using cysteamine at pH 3-6.

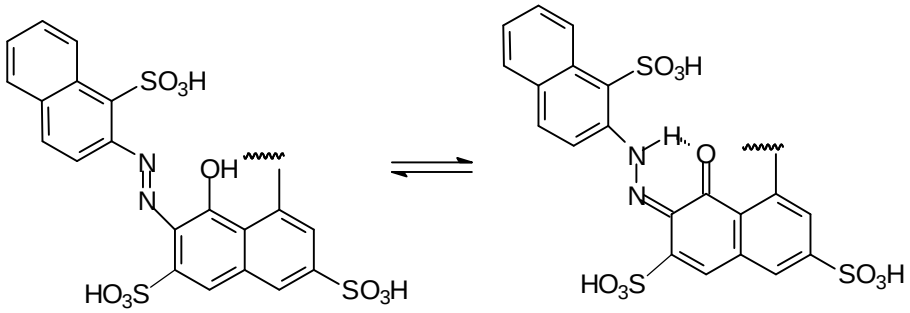
Table 3.24. The λ_{max} and ε_{max} values for DCT based dyes evaluated in this study.

Dye	λ_{max} (nm)	ε_{max} ($x10^4$ $L \cdot mol^{-1} \cdot cm^{-1}$)
Dye **29** (Commercial)	412	1.2
Yellow Dye **31**/**37** (pH 3)	422	1.8
Yellow Dye **31**/**37** (pH 4)	427	1.6
Yellow Dye **31**/**37** (pH 5)	431	2.1
Yellow Dye **31**/**37** (pH 6)	435	2.1
Yellow Dye **31**/**37** (Factory Sample)	428	1.9
Dye **34** (Commercial)	545	2.5
Red Dye **40**/**41** (pH 3)	547	3.6
Red Dye **40**/**41** (pH 4)	521	3.4
Red Dye **40**/**41** (pH 5)	523	2.8
Red Dye **40**/**41** (pH 6)	522	3.1
Red Dye **40**/**41** (Factory Sample)	549	3.1

The λ_{max} values for the yellow intermediates (Figure 3.21) are higher than the commercial yellow dye (412 nm) except for the one synthesized from cysteamine at pH=4 (415 nm). This suggests that pH 4 gave optimum reaction at the –SH group and that substitution of –Cl by –S– had a beneficial effect on color depth. Interestingly, the more acidic pH levels gave higher ε_{max} values for the red dyes, but the λ_{max} did not correlate with pH of synthesis

The final yellow dyes were more bathochromic than the commercial yellow dye and the corresponding intermediates. However the final red dyes did not exhibit a significant chromic shift in λ_{max}. All of the red dyes had two peaks, one

was near 522nm and the other was near 545nm. This corresponds to azo/hydrazone tautomerism (**42**/**43**) for the red dyes.



(**42**)
Azo form

(**43**)
Hydrazone form

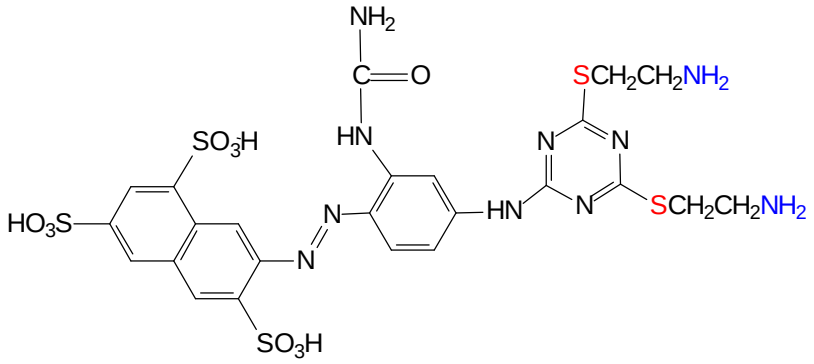
2.2 HPLC Analysis of Dye Intermediates from Cysteamine

All of the yellow and red intermediates synthesized from cysteamine at pH 3-6 were dissolved in 18M ohm water and analyzed using isocratic elution system 2 (Table 3.25). These analyses were conducted on the Waters HPLC system, the results of which are shown in Figures 3.25-3.32.

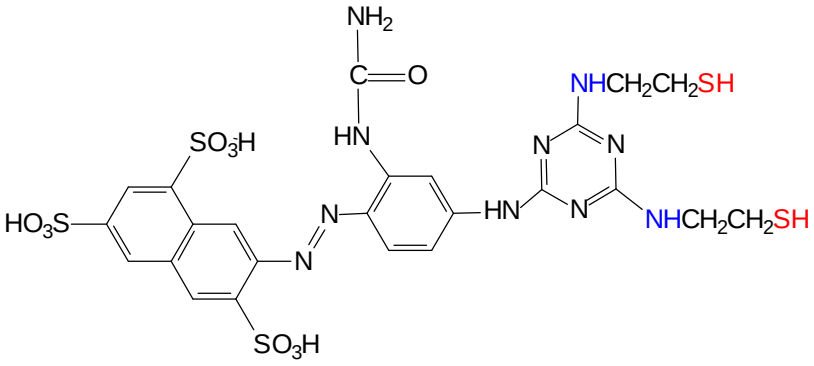
All 4 yellow and 4 red intermediates were synthesized by adding a solution of commercial dye to a solution of cysteamine chloride at pH 3, 4, 5 and 6. A summary of results is provided in Tables 3.26-3.27.

Table 3. 25. Properties of isocratic elution system 2 used in HPLC studies.

Solvent	%	Contents
A	30	100% AN + 0.025 M TBAB
B	70	30% Phase A/70% H_2O + 0.05 M $NH_4H_2PO_4$



(**30a**)



(**36a**)

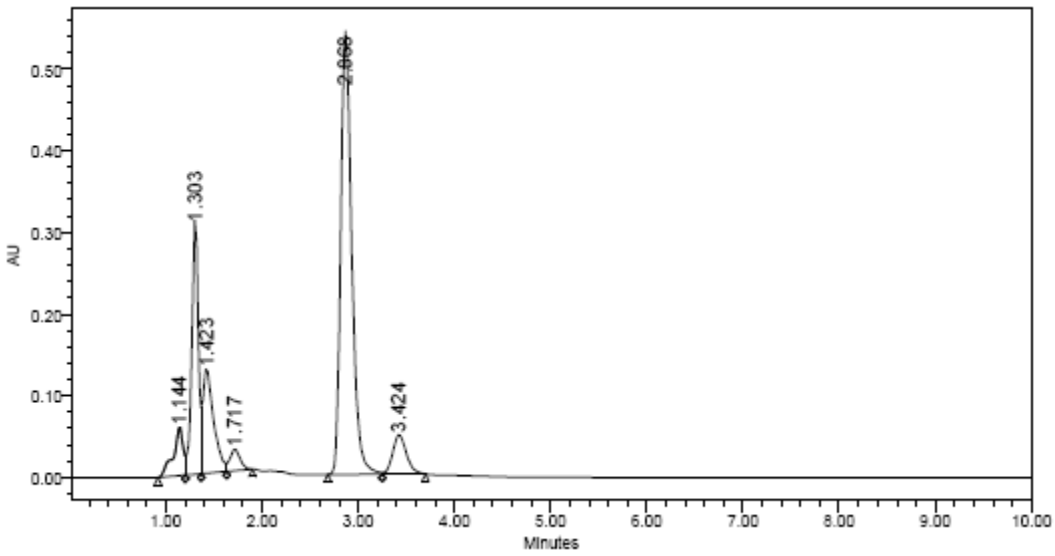


Figure 3.25. Chromatogram of **30a**/**36a** (pH 3) using isocratic elution system 2.

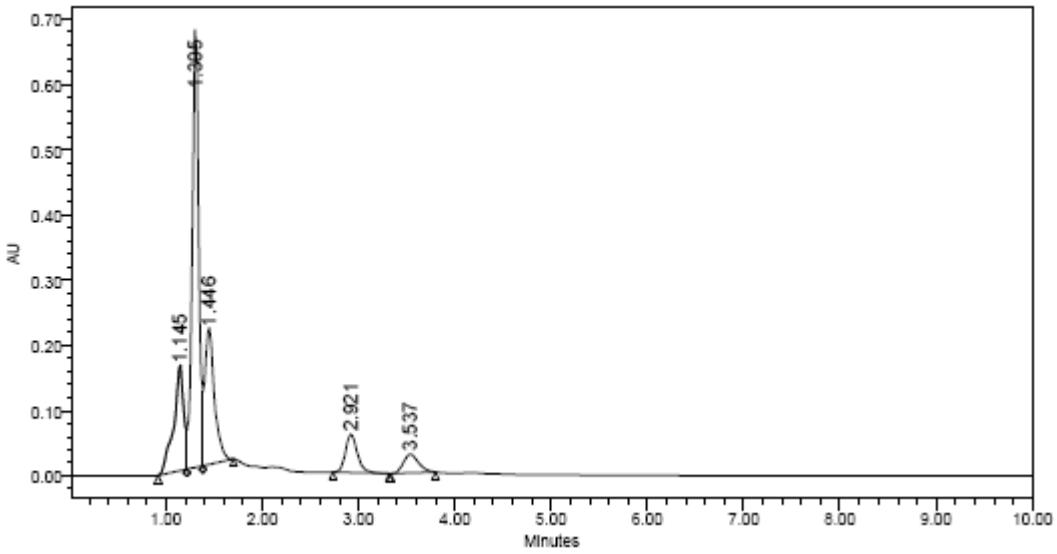


Figure 3.26. Chromatogram of **30a/36a** (pH 4) using isocratic elution system 2.

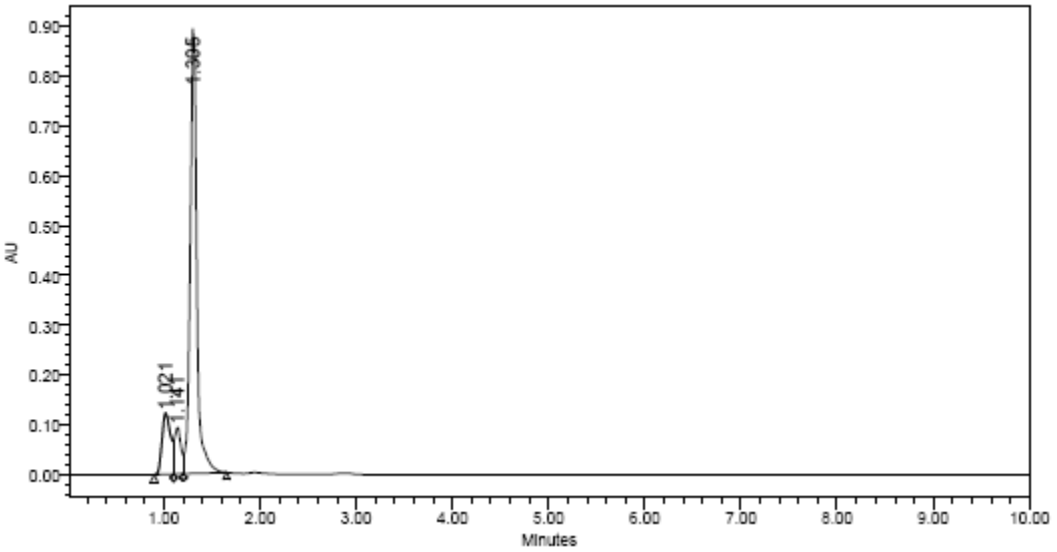


Figure 3.27. Chromatogram of **30a/36a** (pH 5) using isocratic elution system 2.

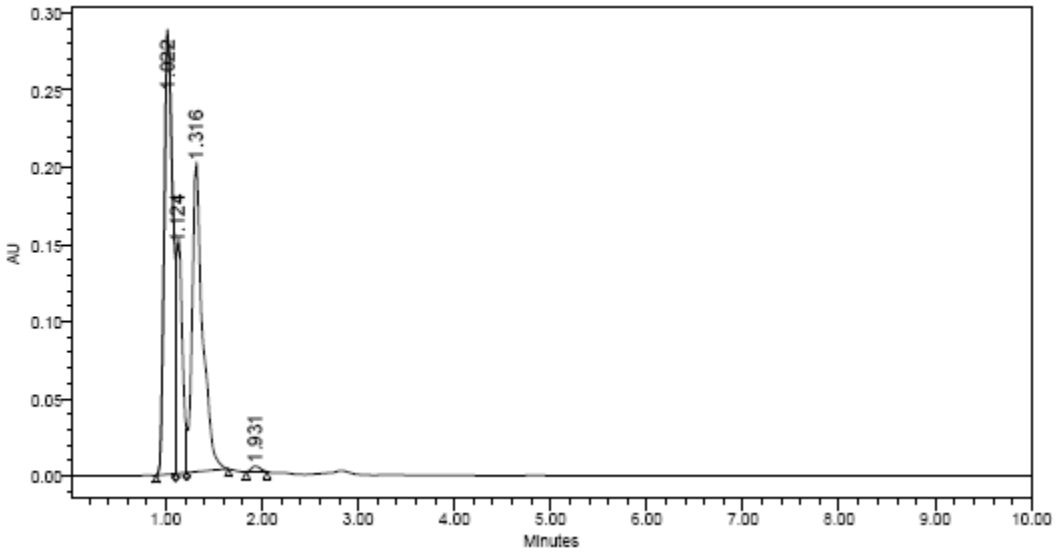
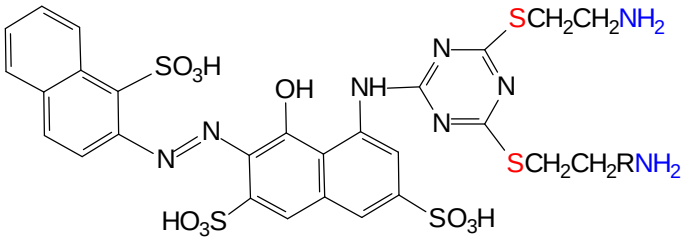


Figure 3.28. Chromatogram of **30a**/**36a** (pH 6) using isocratic elution system 2.

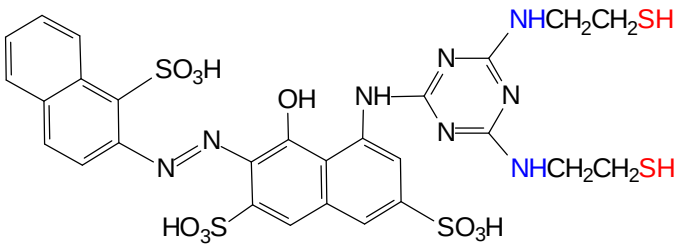
Table 3.26 provided a summary of results from HPLC analysis of products from synthesizing yellow dye intermediates at pH 3-6. From pH 3 to pH 4, peak 5 decreased significantly and peaks 2, 3 and 4 increased significantly. Increasing the pH from 4 to 5, caused peaks 2 and 4 to decrease or disappear, peaks 1 and 3 to appear or increase. Peak 3 was produced at all pH levels, while peak 5 was observed only at pH 3.

Table 3.26. Summary of the results from HPLC analysis of yellow dye intermediates.

Peak	Retention Time (min) / %Area			
	pH 3	pH 4	pH 5	pH 6
1			1.02/14.0	1.02/43.9
2		1.15/17.8	1.14/7.84	1.12/17.7
3	1.30/18.4	1.31/47.8	1.31/78.2	1.32/37.8
4	1.42/12.9	1.45/22.0		
5	2.87/55.0			



(**38a**)



(**39a**)

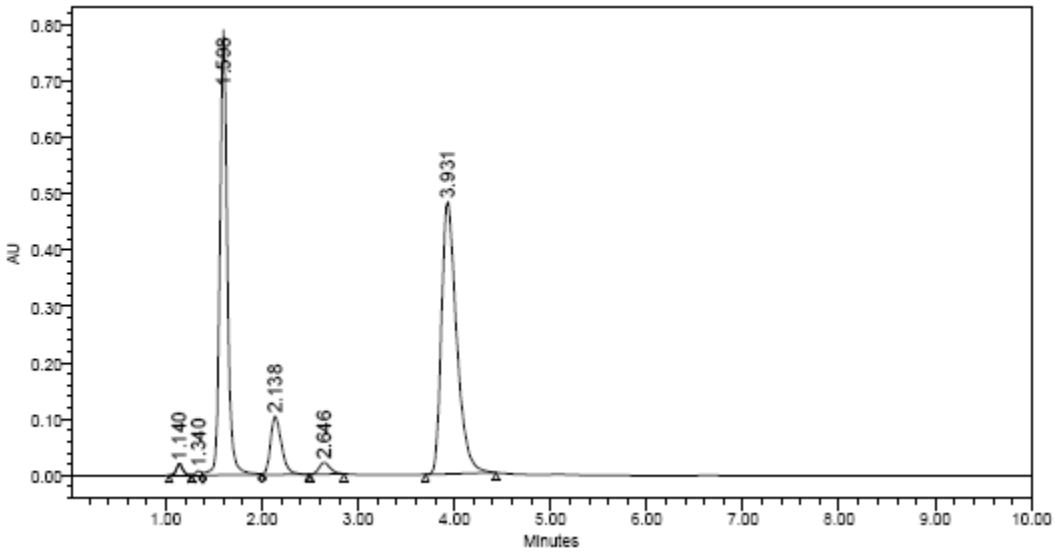


Figure 3.29. Chromatogram of **38a**/**39a** (pH 3) using isocratic elution system 2.

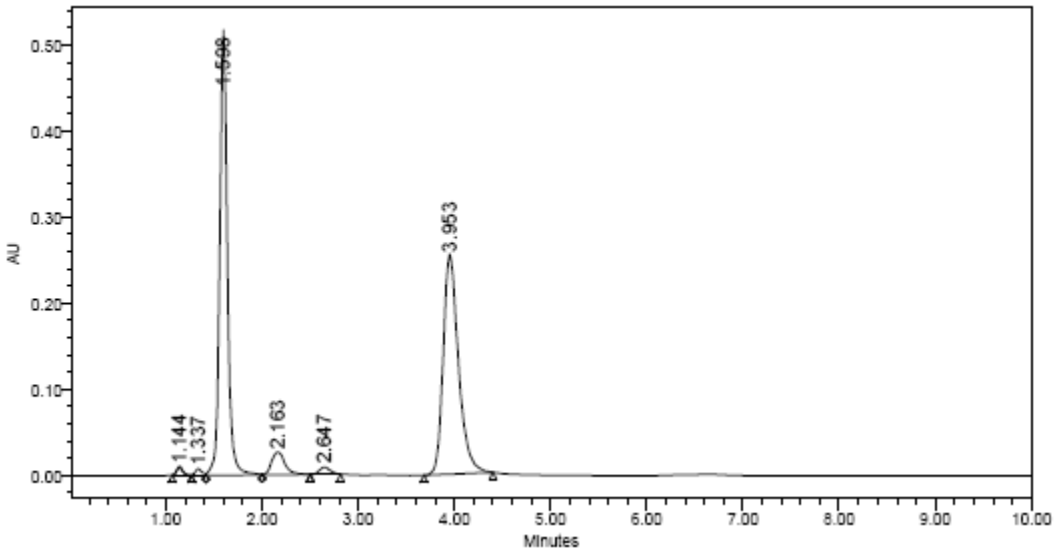


Figure 3.30. Chromatogram of **38a/39a** (pH 4) using isocratic elution system 2.

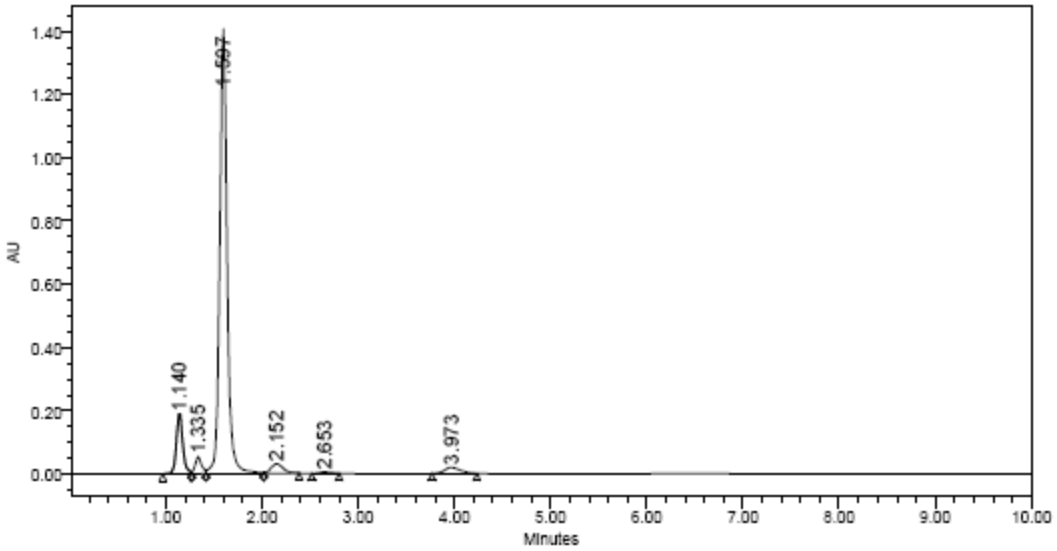


Figure 3.31. Chromatogram of **38a/39a** (pH 5) using isocratic elution system 2.

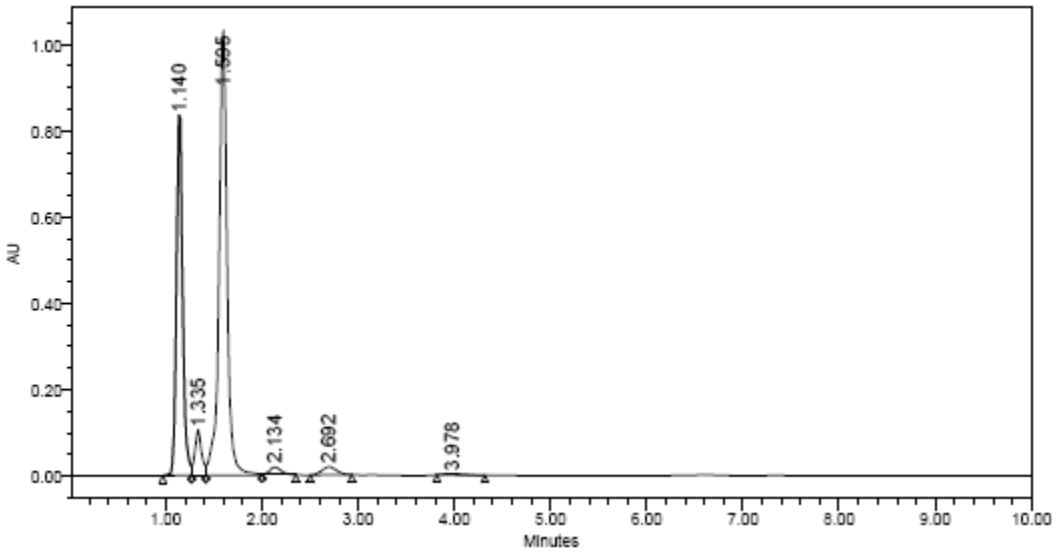


Figure 3.32. Chromatogram of **38a**/**39a** (pH 6) using isocratic elution system 2.

Table 3.27 provides a summary of results from HPLC analysis of products from synthesizing red dye intermediates at pH 3-6. Increasing the reaction pH from 3 to 4 caused little changes on peak 3, with a slight increase in peak 2; changing from pH 4 to pH 5, peak 3 disappeared, peak 2 became dominant and peak 1 appeared. When the pH was increased from 5 to 6, peak 2 decreased and peak 1 increased significantly.

Table 3.27 Summary of the results from HPLC analysis of red dye intermediates.

Peak	Retention Time (min) / %Area			
	pH=3	pH=4	pH=5	pH=6
1			1.14/ 9.64	1.14/35.0
2	1.60/40.0	1.60/47.2	1.60/ 82.2	1.60/56.6
3	3.93/ 49.6	3.95/ 46.3		

2.3 Characterization of Dye Intermediates from Cysteamine

HPLC was used to aid the characterization of all 4 yellow and 4 red intermediates synthesized at different pH levels. Figures 3.33-3.34 show the expected course of the reactions as a function of pH. At the lower level of the pH range, it was anticipated that the $–NH_2$ group of cysteamine would be protonated and that the reaction with dye **29** and **34** would take place at the –SH group, giving the protonated form of dye **30a** and **38a**. Treatment with $NaHCO_3$ would then give dye **30a** and **38a** themselves. At the upper level of the pH range, reaction at $–NH_2$ would be favored, giving dye **36a** and **39a**. Accordingly, solutions of yellow and red dye intermediates produced at pH 3-4 were neutralized with $NaHCO_3$ solution and HPLC analysis repeated. Figures 3.35-3.38 and Figures 3.41-3.44 provided comparisons of the composition of dye intermediates synthesized at pH 3-4 before and after neutralization. Also shown were chromatograms from synthesis conducted at pH 5-6 (Figure 3.39-3.40 and Figures 3.45-3.46).

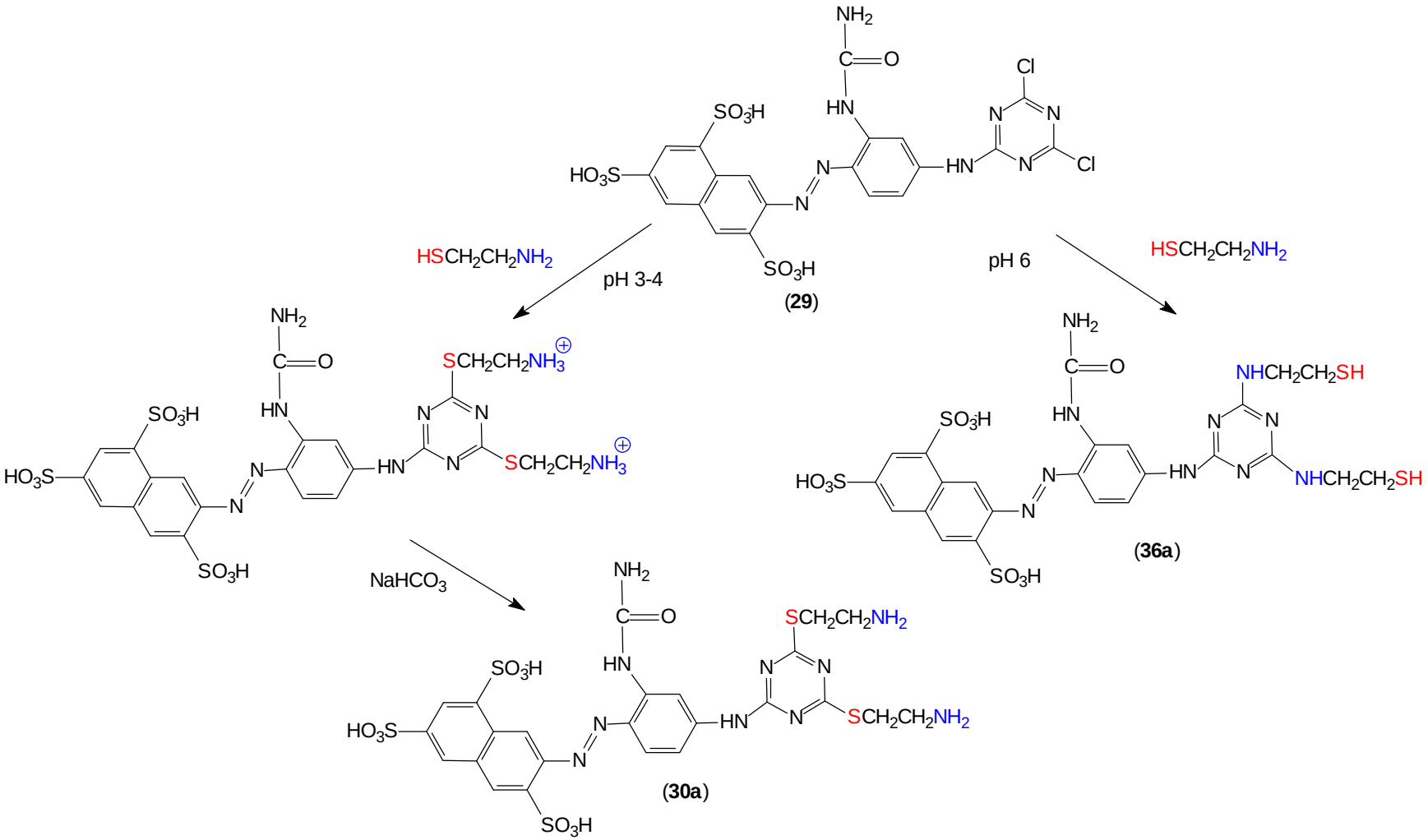


Figure 3.33. Synthesis of yellow dye intermediates from cysteamine at different pH levels.

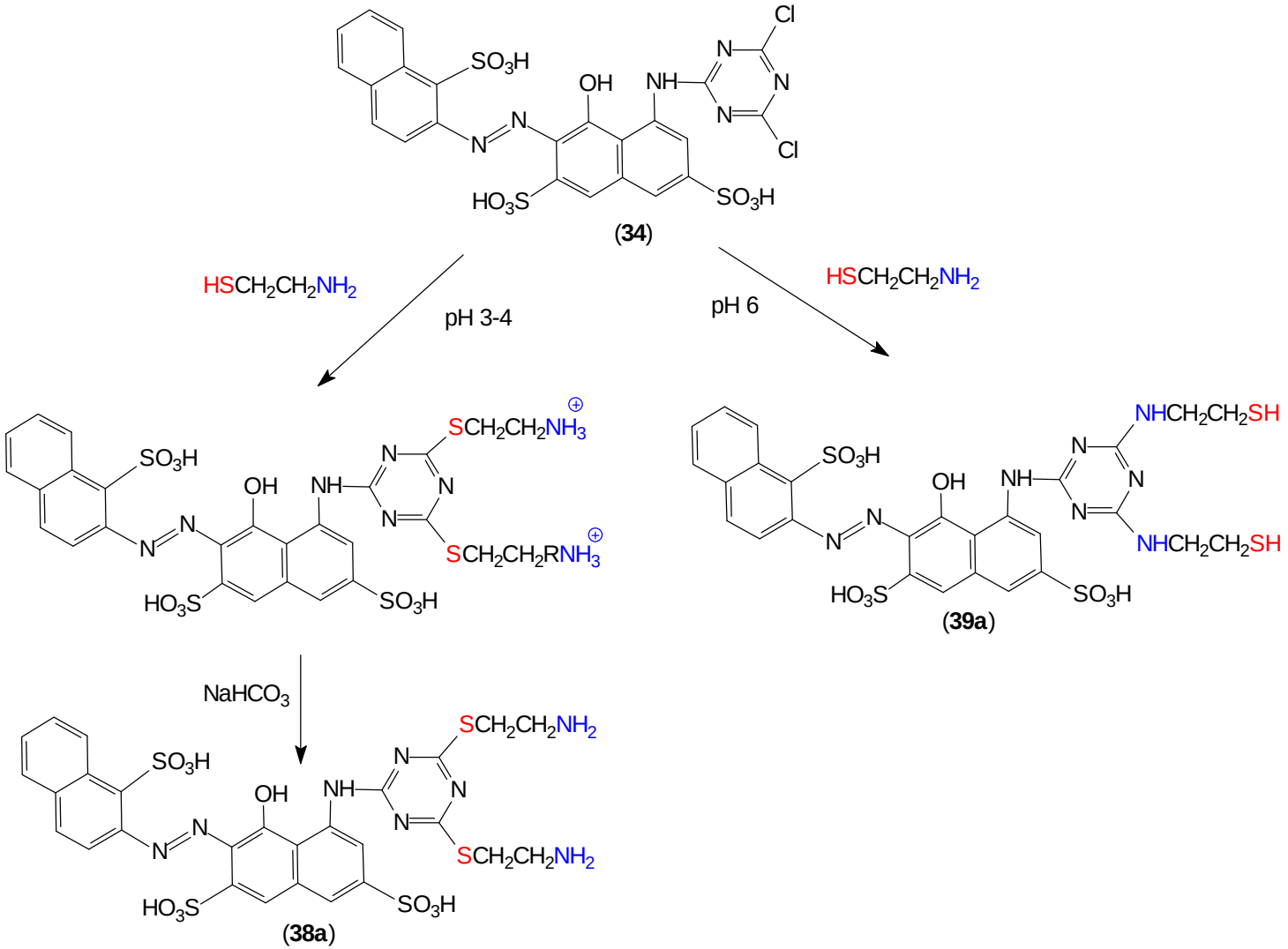
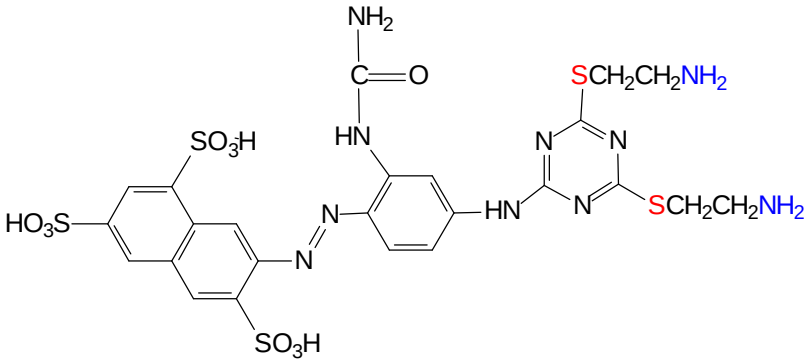
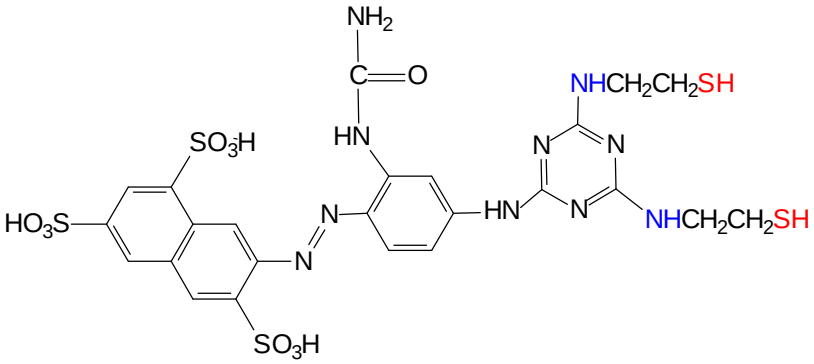


Figure 3.34. Synthesis of red dye intermediates from cysteamine at different pH levels.



(**30a**)



(**36a**)

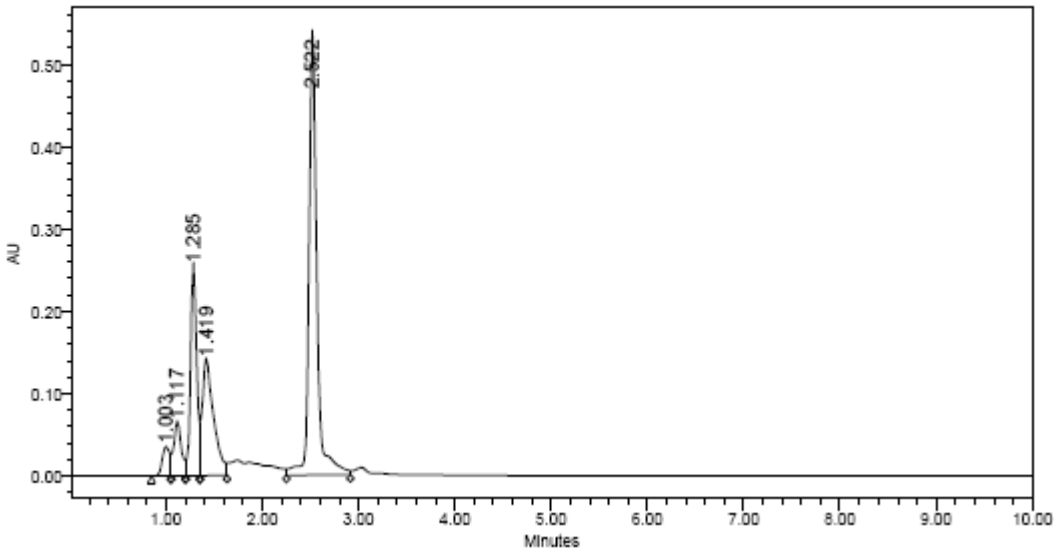


Figure 3.35. Chromatogram of **30a**/**36a** (pH 3) before neutralization using gradient system 1.

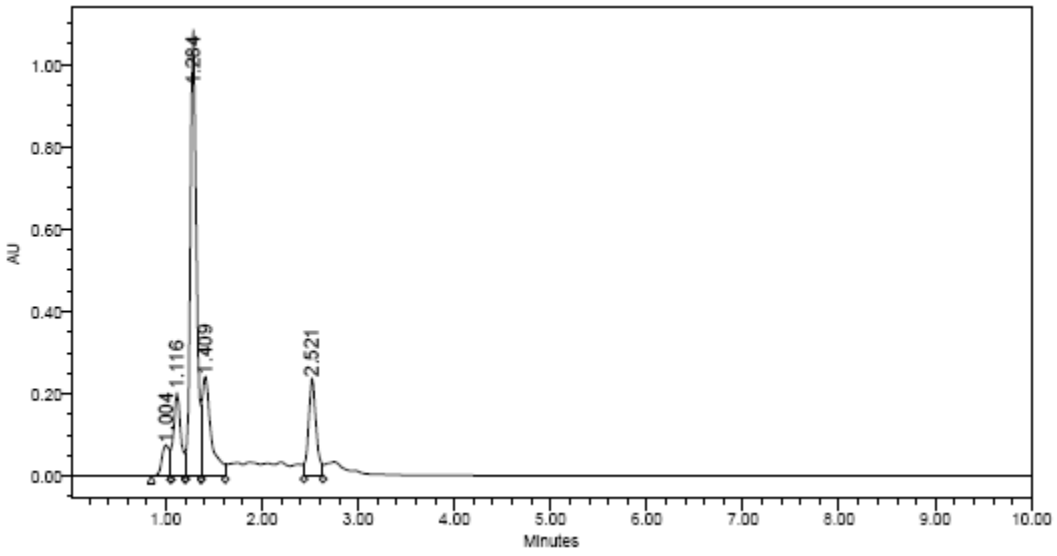


Figure 3.36. Chromatogram of **30a**/**36a** (pH 3) after neutralization using gradient system 1.

Table 3.28. Comparison of peaks in chromatograms of the pH 3 yellow dye intermediates before and after neutralization.

Peak	Before Neutralization		After Neutralization	
	Retention Time (min)	% Area	Retention Time (min)	% Area
1	1.28	18.5	1.28	51.7
2	2.52	52.6	2.52	14.5

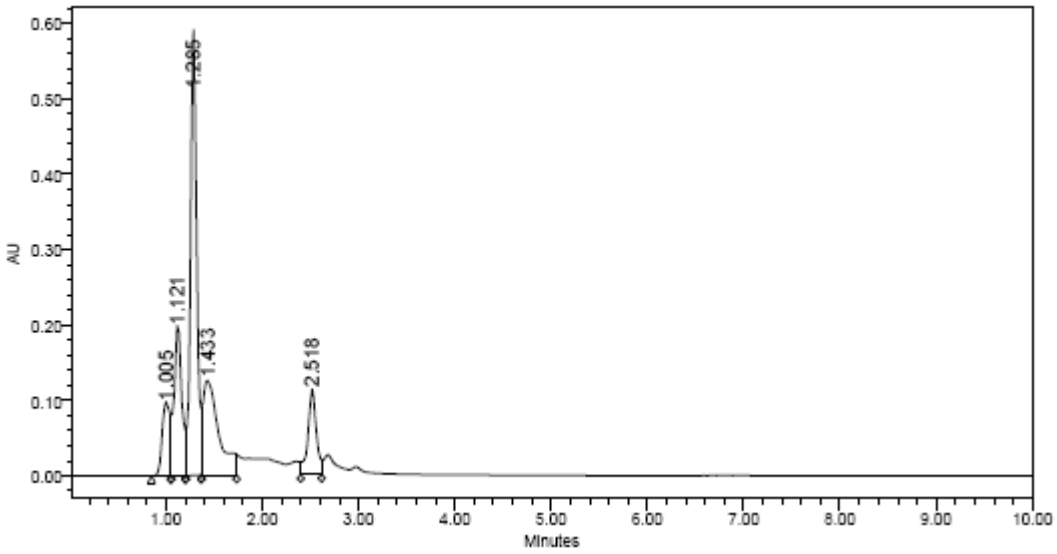


Figure 3.37. Chromatogram of **30a**/**36a** (pH 4) before neutralization using gradient system 1.

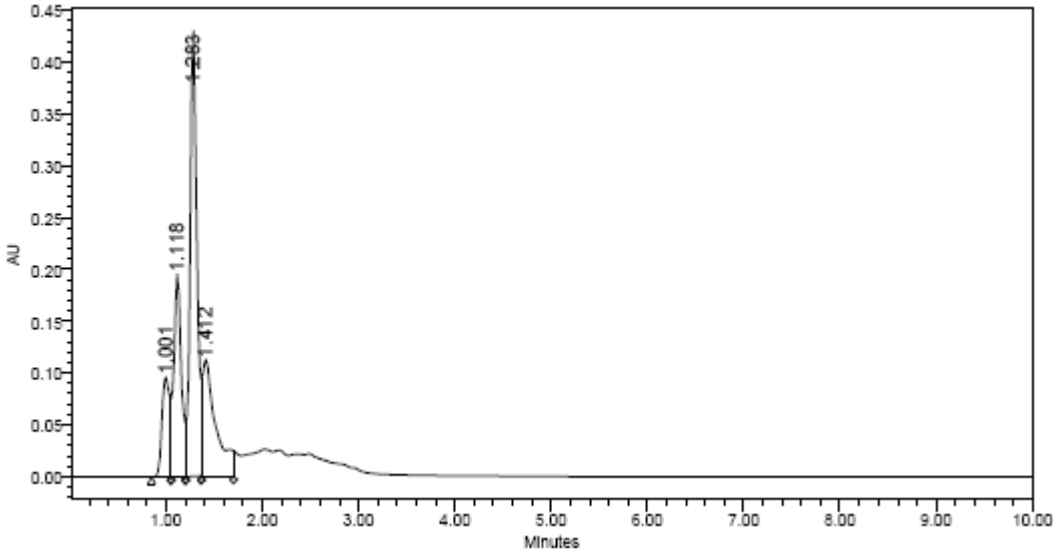


Figure 3.38. Chromatogram of **30a**/**36a** (pH 4) after neutralization using gradient system 1.

Table 3.29. Comparison of peaks in chromatograms of the pH 4 yellow dye intermediates before and after neutralization.

Peak	Before Neutralization		After Neutralization	
	Retention Time (min)	% Area	Retention Time (min)	% Area
1	1.12	17.4	1.12	22.2
2	1.28	40.6	1.28	43.7
3	2.52	10.7		

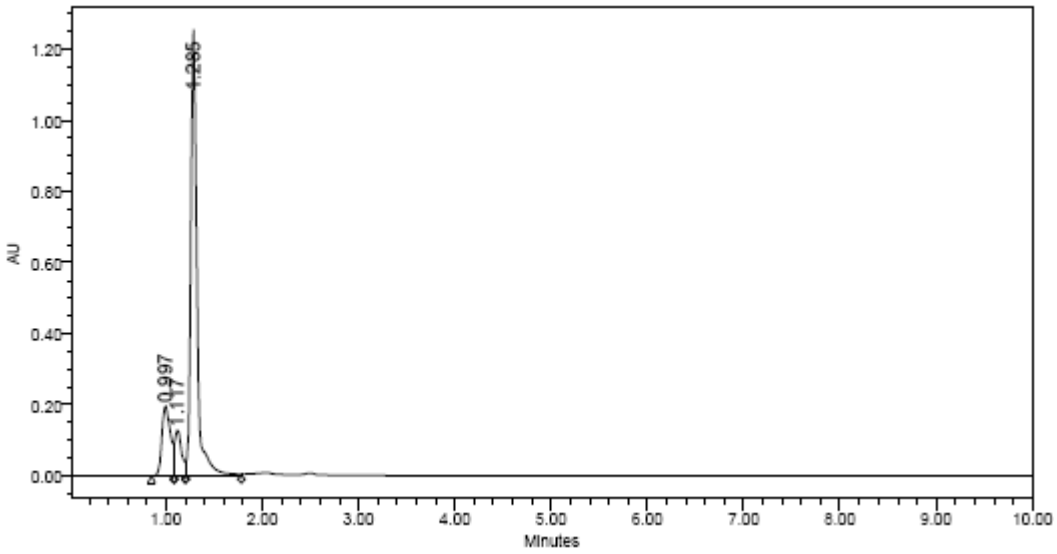


Figure 3.39. Chromatogram of **30a**/**36a** (pH 5) using gradient system 1.

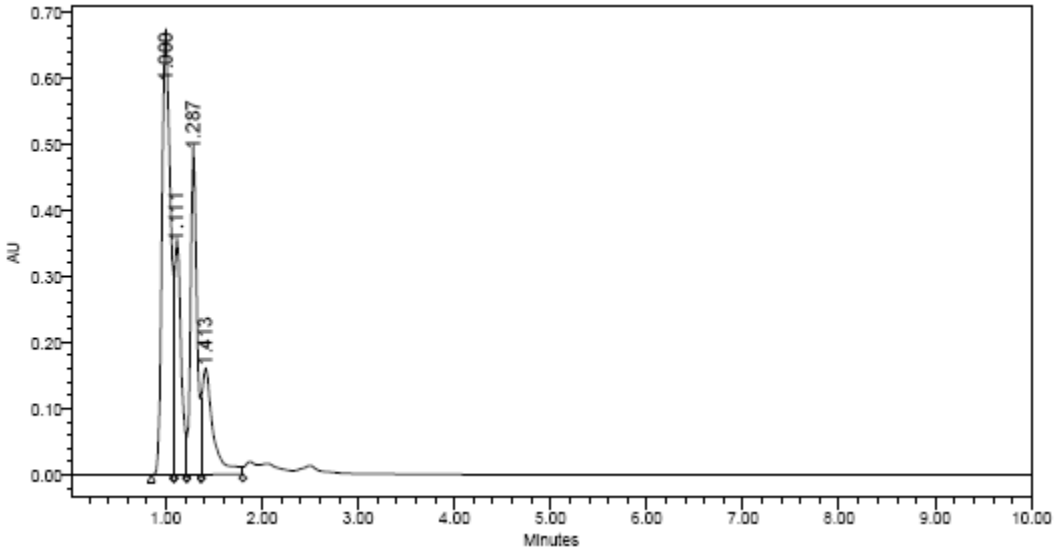


Figure 3.40. Chromatogram of **30a**/**36a** (pH 6) using gradient system 1.

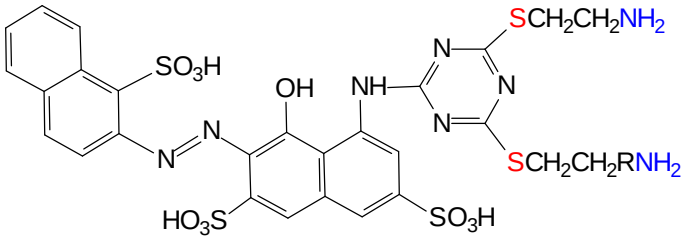
Table 3.30. Summary of the results from HPLC analysis of yellow dye intermediates.

Peak	Retention Time (min) / %Area			
	pH 3 (neutralized)	pH 4 (neutralized)	pH 5	pH 6
1			1.00/16.9	1.00/44.5
2		1.12/22.2	1.12/8.4	1.11/18.3
3	1.28/51.7	1.28/43.7	1.28/74.7	1.29/23.4
4	2.52/14.5			

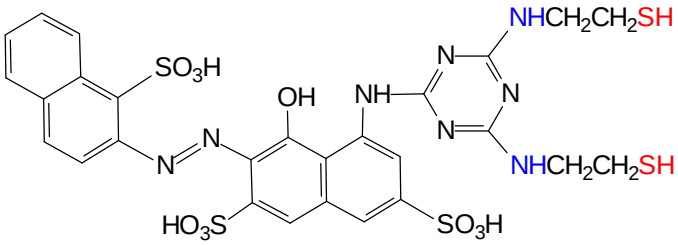
Neutralization of solutions of yellow dye intermediates synthesized at pH 3-4 led to a reduction in the intensity of the peak at 2.52 min and an increase in intensity of the peak at 1.28 min. However, the peak at 1.00 min was not affected by neutralization. This peak increased in intensity as the pH level of synthesis increased. These results suggested that the peaks at 1.28 min and 2.52 min

arose from products formed by reaction at the –SH group of cysteamine (**30a**) and the peak at 1.00 min represented the product from reaction at the $–NH_2$ group of the cysteamine (**36a**). The peak at 2.52 min would be the protonated ($-NH_3^+$) form of **30a**.

The red dye intermediates underwent the same type changes as the yellow dye intermediates following neutralization. The intermediates produced at pH 3-4 did not contain the component eluting at 1.13 min but contained a major peak eluting at 2.83 min. The reverse was true for the intermediate obtained at pH 6, as it contained the major peak at 1.13 min but lacked the peak at 2.83 min. In this case, the peak at 2.83 min decreased following the neutralization and corresponded to the protonated form of dye intermediate **38a**, while the peak at 1.60 min increased and was free amine form **38a** itself. Similarly, the peak at 1.13 min corresponded to dye intermediate **39a**.



(**38a**)



(**39a**)

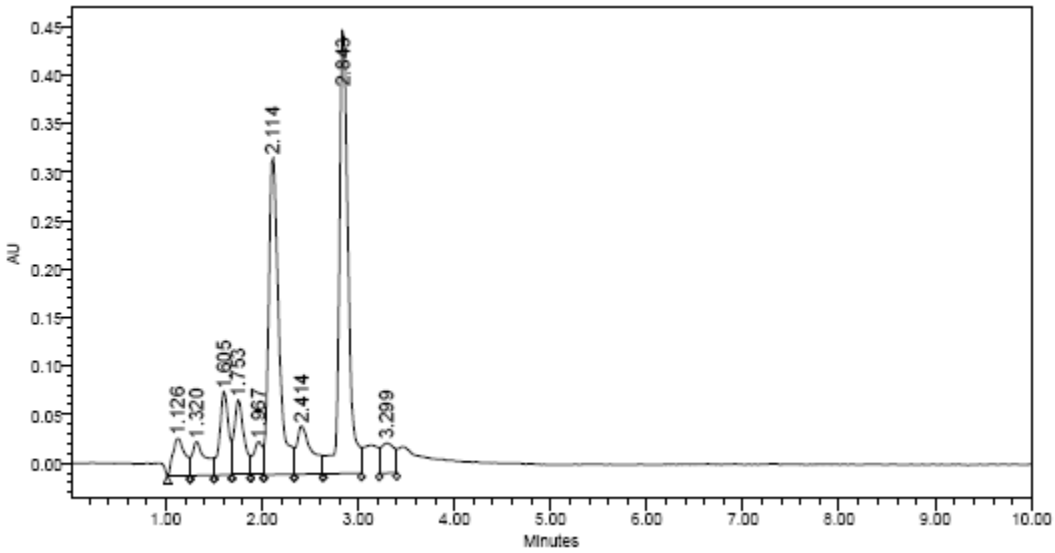


Figure 3.41. Chromatogram of **38a**/**39a** (pH 3) before neutralization using gradient system 1.

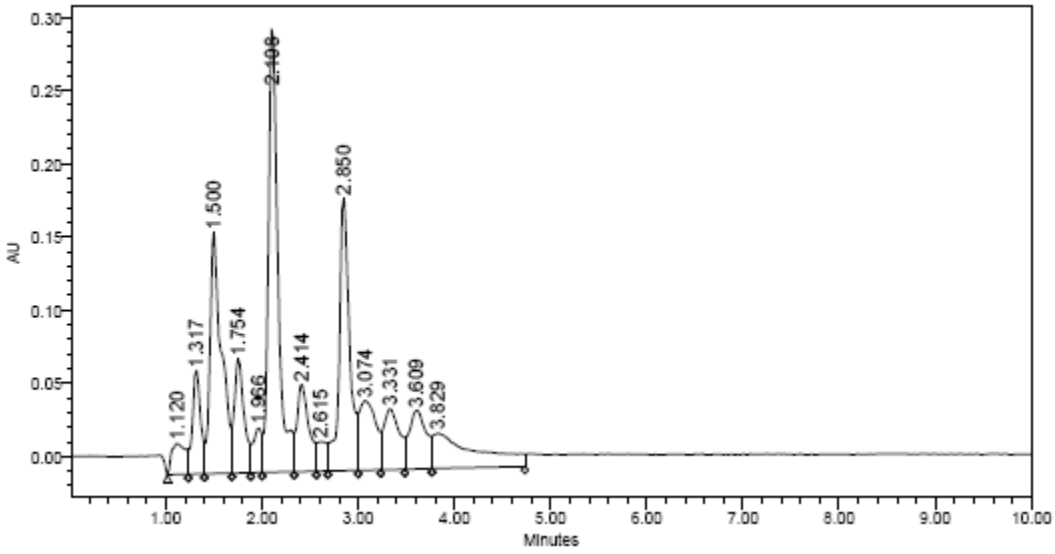


Figure 3.42. Chromatogram of **38a**/**39a** (pH 3) after neutralization using gradient system 1.

Table 3.31. Comparison of peaks in chromatograms of the pH 3 red dye intermediates before and after neutralization.

Peak	Before Neutralization		After Neutralization	
	Retention Time (min)	% Area	Retention Time (min)	% Area
1	1.60	6.7	1.50	15.0
2	2.11	29.1	2.11	23.1
3	2.84	36.2	2.85	15.2

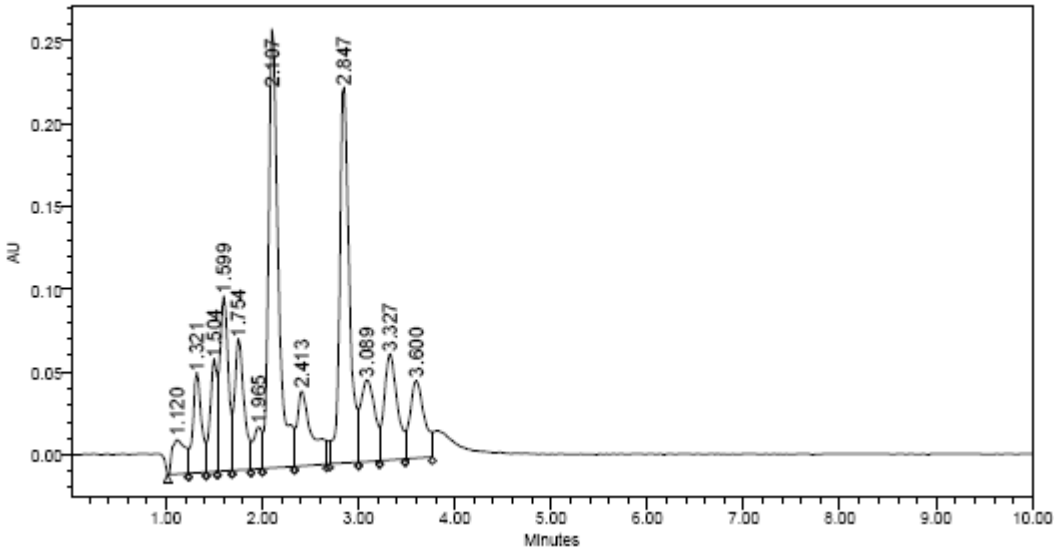


Figure 3.43. Chromatogram of **38a**/**39a** (pH 4) before neutralization using gradient system 1.

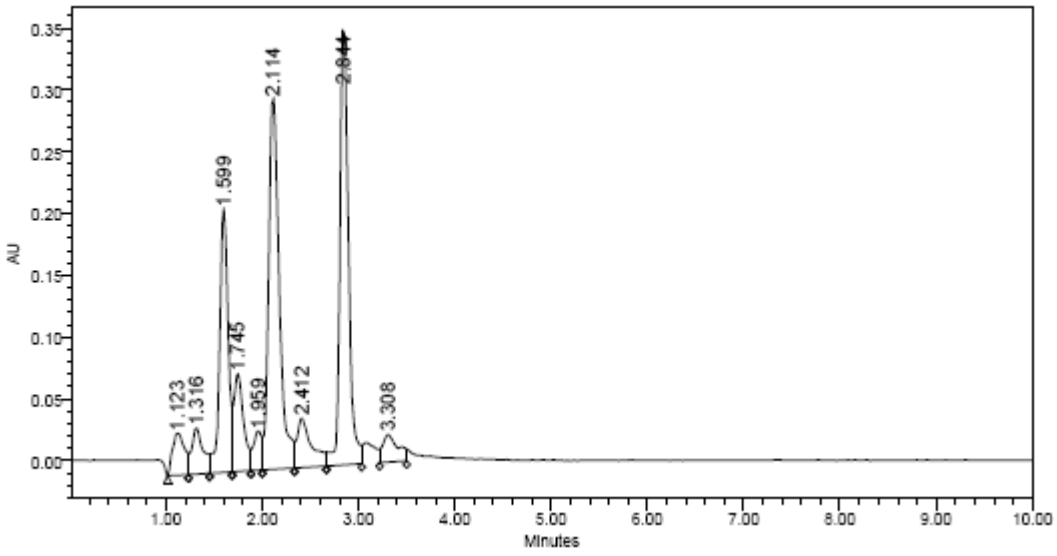


Figure 3.44. Chromatogram of **38a**/**39a** (pH 4) after neutralization using gradient system 1.

Table 3.32. Comparison of peaks in chromatograms of the pH 4 red dye intermediates before and after neutralization.

Peak	Before Neutralization		After Neutralization	
	Retention Time (min)	% Area	Retention Time (min)	% Area
1	1.60	8.5	1.60	16.5
2	2.10	24.1	2.11	29.5
3	2.85	20.4	2.84	28.1

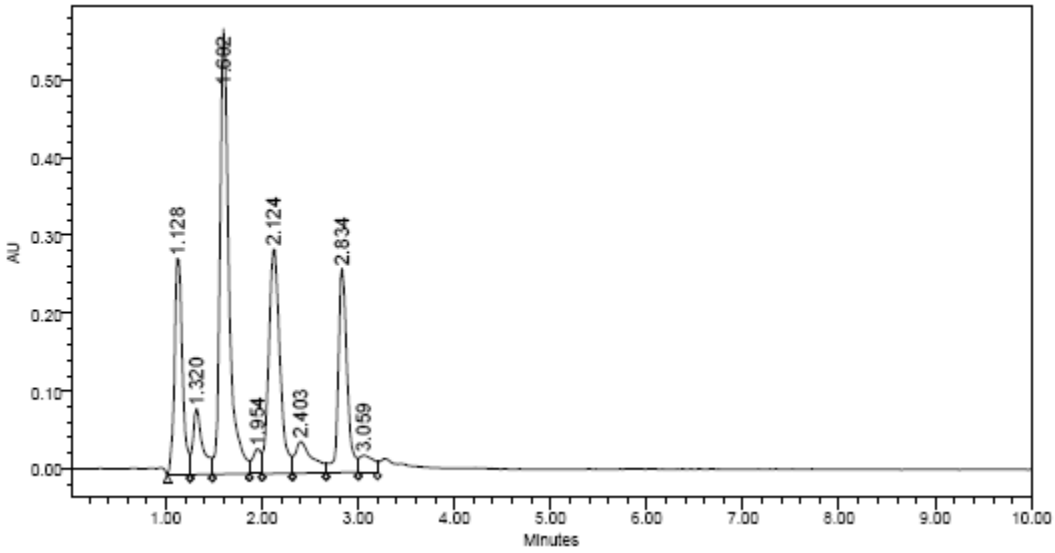


Figure 3.45. Chromatogram of **38a**/**39a** (pH 5) using gradient system 1.

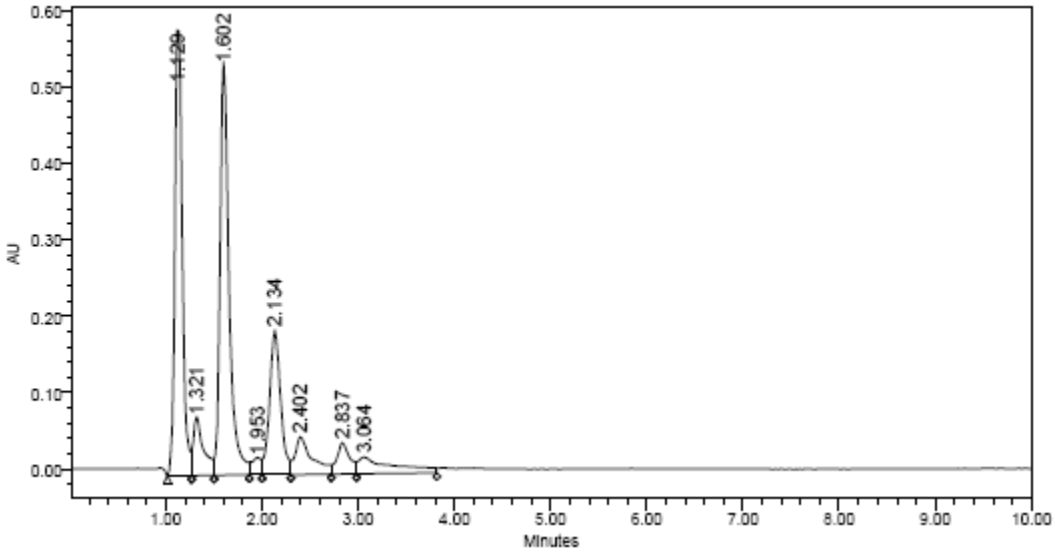


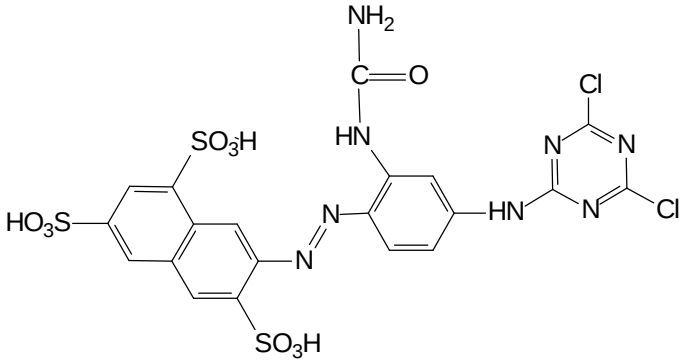
Figure 3.46. Chromatogram of **38a**/**39a** (pH 6) using gradient system 1.

Table 3.33. Summary of the results from HPLC analysis of red dye intermediates.

Peak	Retention Time (min) / %Area			
	pH 3 (neutralized)	pH 4 (neutralized)	pH 5	pH 6
1			1.13/14.7	1.13/30.2
2	1.50/15.0	1.60/16.5	1.60/34.5	1.60/33.8
3	2.11/23.1	2.11/29.5	2.12/21.4	2.13/14.4
4	2.85/15.2	2.84/28.1	2.83/15.5	

2.4 HPLC Analysis of Dyes 31, 37 and 40-41

The new dyes (**31**/**37** and **40**/**41**) were analyzed using gradient system 1 (Table 2.1) using the Waters HPLC System, the results of which are shown in Figures 3.48-3.52 and Figures 3.54-3.58. Results from the corresponding parent dyes (**29**) and (**34**) are included (Figures 3.47 and 3.53) for comparison. Tables 3.34-3.35 provide a summary of these results.



(**29**)

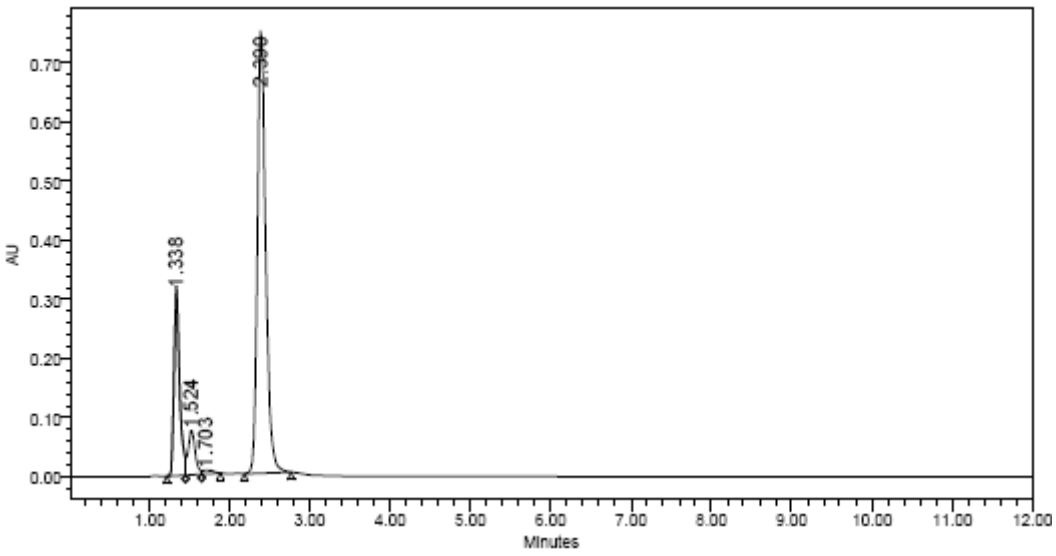
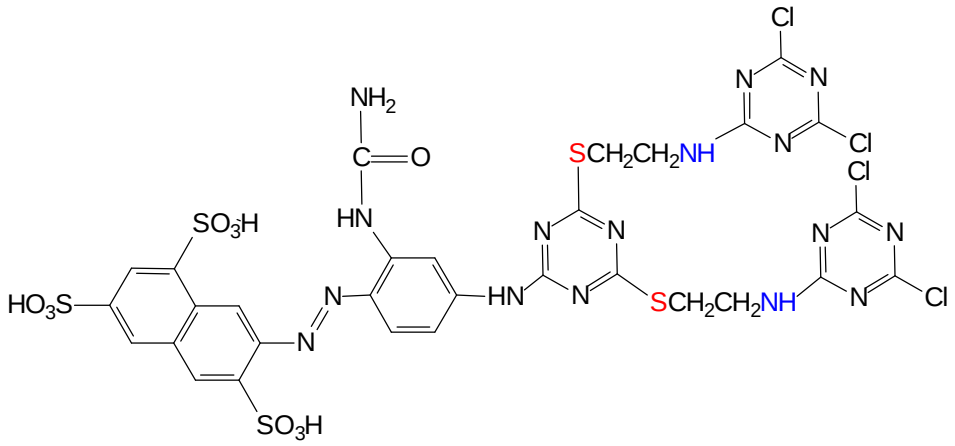
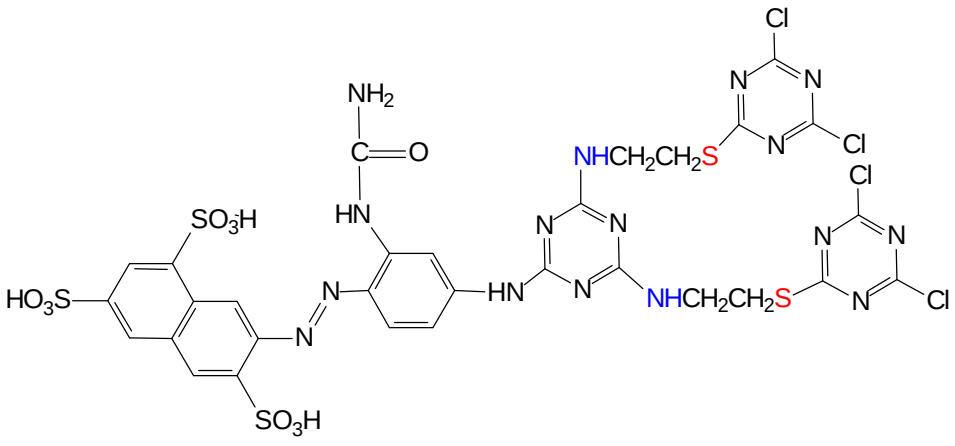


Figure 3.47. Chromatogram of dye **29** using gradient system 1.



(**31**)



(**37**)

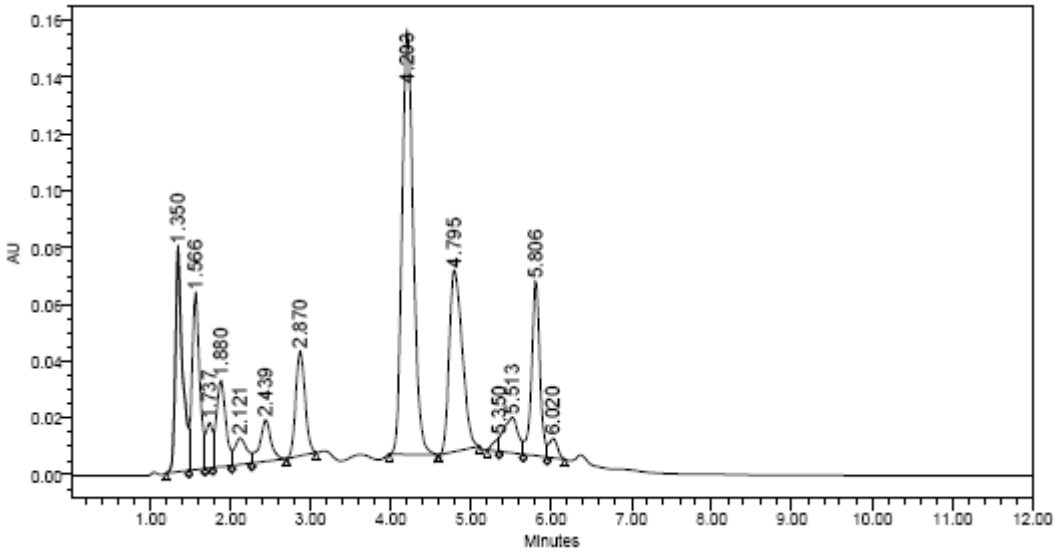


Figure 3.48. Chromatogram of dye **31**/**37** (pH 3) using gradient system 1.

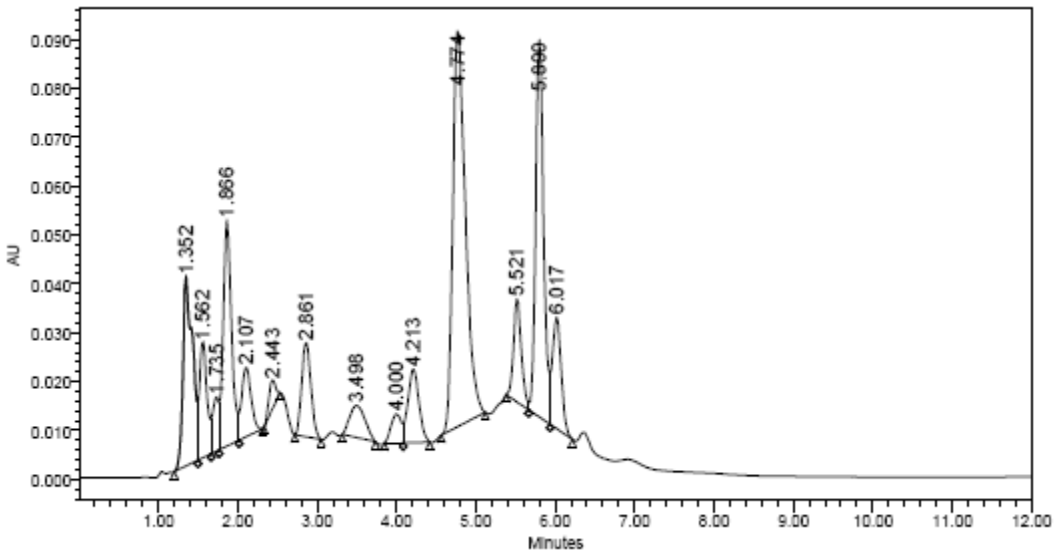


Figure 3.49. Chromatogram of dye **31**/**37** (pH 4) using gradient system 1.

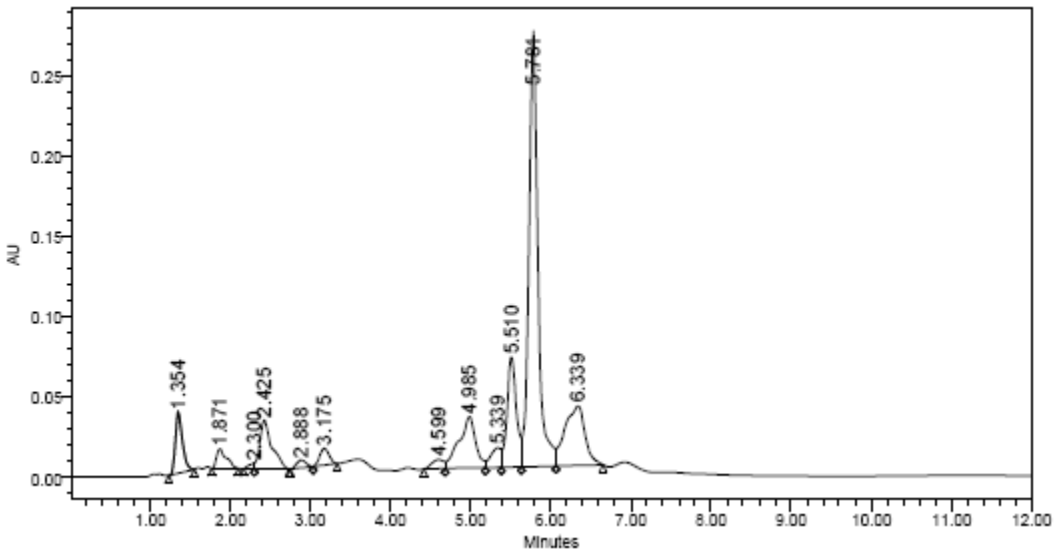


Figure 3.50. Chromatogram of dye **31**/**37** (pH 5) using gradient system 1.

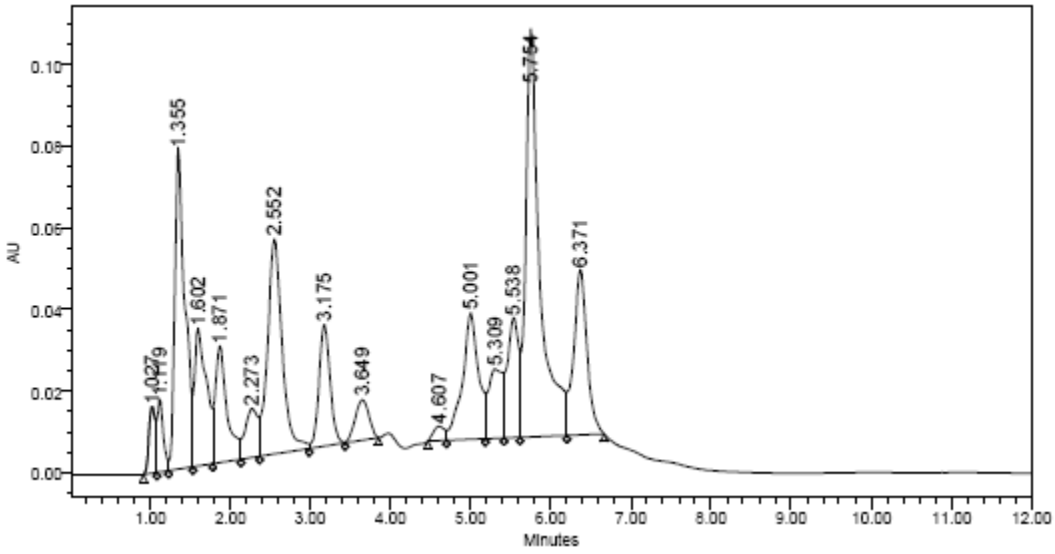


Figure 3.51. Chromatogram of dye **31**/**37** (pH 6) using gradient system 1.

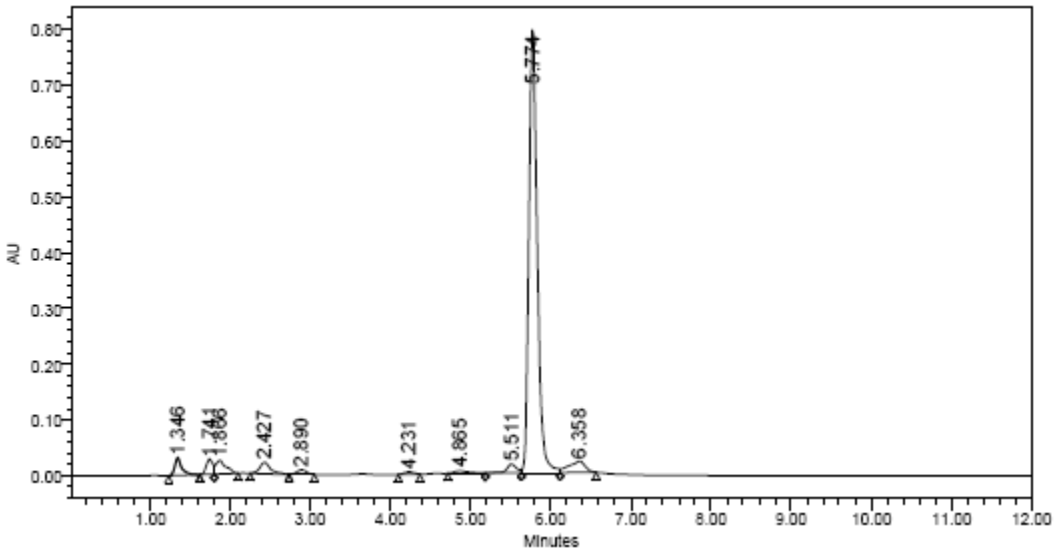
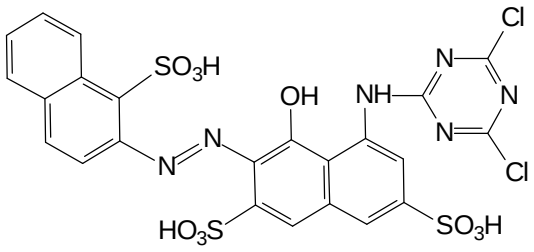


Figure 3.52. Chromatogram of dye **31**/**37** (factory sample) using gradient system 1.

Table 3.34. Summary of major peaks in the chromatograms of yellow DCT dyes employed in this study.

Peak	Retention Time (min) / % Area					
	Dye **29**	New Yellow Dyes (**31**/**37**)				
		pH 3	pH 4	pH 5	pH 6	Factory
1	1.34/ 20.4	1.35/ 10.4	1.35/ 10.1	1.35/4.9	1.35/ 12.9	
2			1.87/ 10.6			
3	2.39/ 72.7					
4					2.55/ 12.4	
5		4.20/ 31.5				
6		4.79/ 15.6	4.77/ 27.7			
7		5.80/ 9.6	5.80/ 16.5	5.78/ 44.8	5.75/ 23.0	5.77/ 81.2

Several points were evident from Table 3.34: 1) the dye synthesized at pH 5 was most similar to that made by the Polish factory; 2) each of the yellow dyes made in this study contained the component eluting at 5.80 min; 3) each dye also contained a component eluting at 1.35 min, which was also found in the parent yellow dye and probably is the hydrolyzed commercial dye; 4) the dyes prepared at pH 3-4 contained components eluting at 4.20-4.80 min that were missing from the samples synthesized at higher pH levels, including the factory prepared dye; 5) increasing the pH level generally increased the proportion of the component eluting at 5.8 min; and 6) all of the reactive form of the parent yellow dye (**29**) was fully consumed. These results suggested that the components eluting at 4.20-4.80 min corresponded to a reaction at the –SH group of cysteamine, while the one eluting at 5.80 min corresponded to a reaction at the $–NH_2$ group.



(**34**)

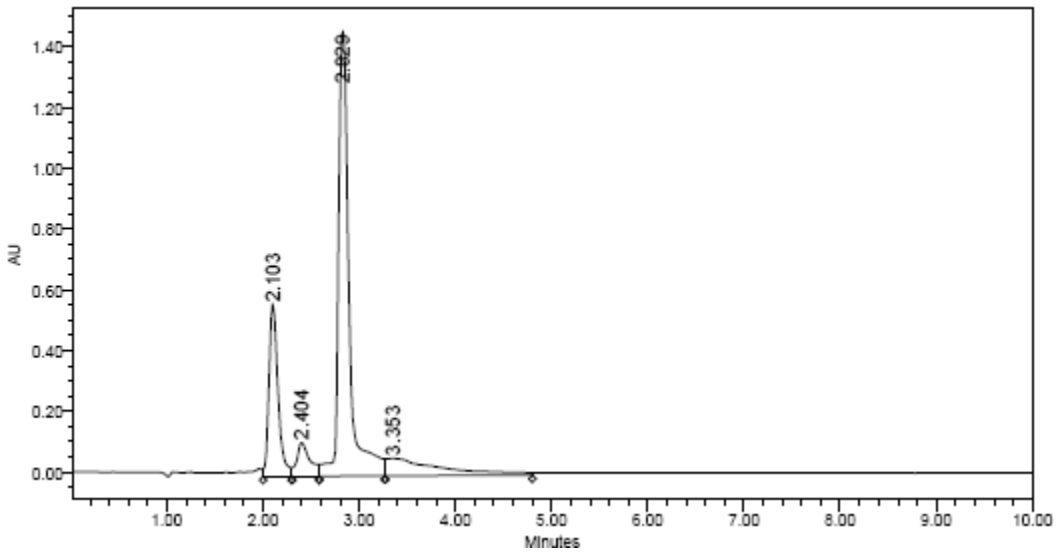
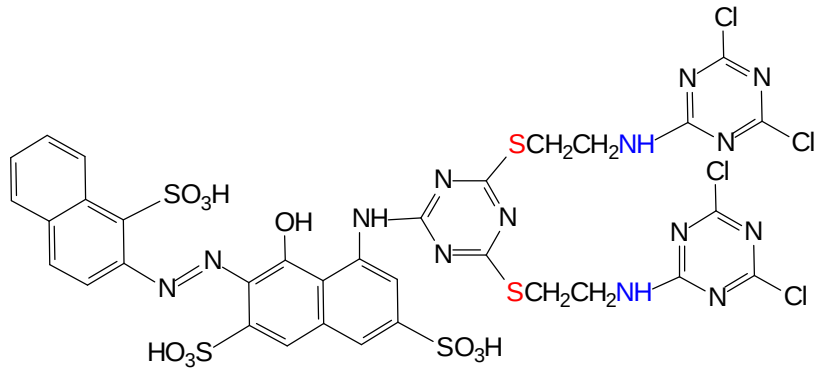
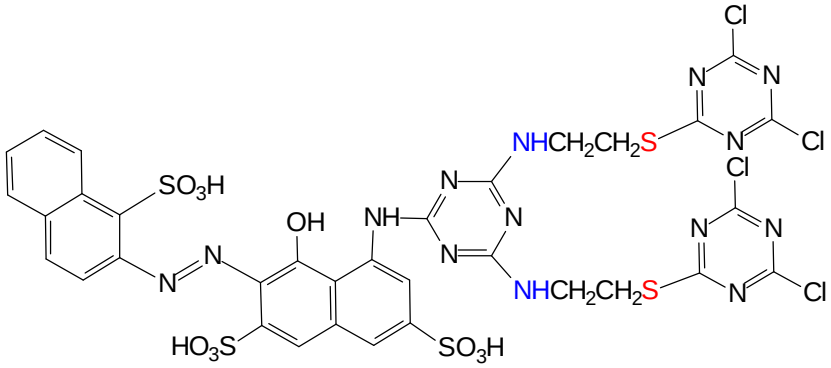


Figure 3.53. Chromatogram of dye **34** using gradient system 1.



(**40**)



(**41**)

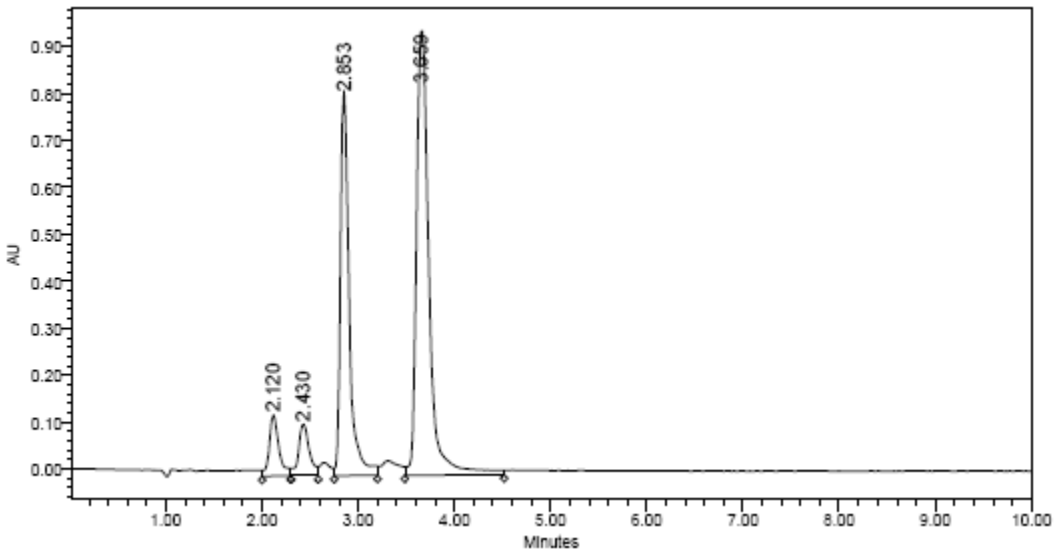


Figure 3.54. Chromatogram of dye **40**/**41** (pH 3) using gradient system 1.

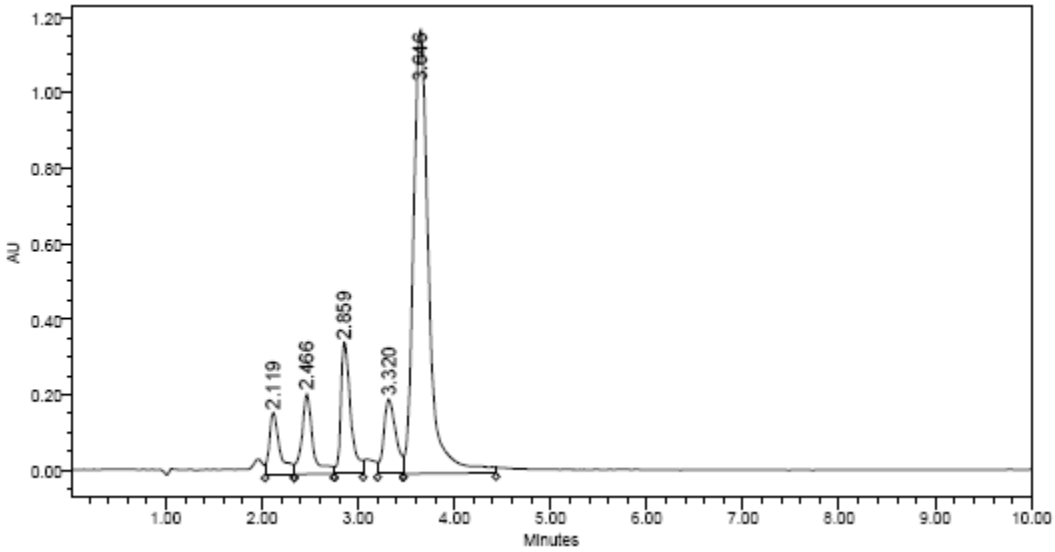


Figure 3.55. Chromatogram of dye **40**/**41** (pH 4) using gradient system 1.

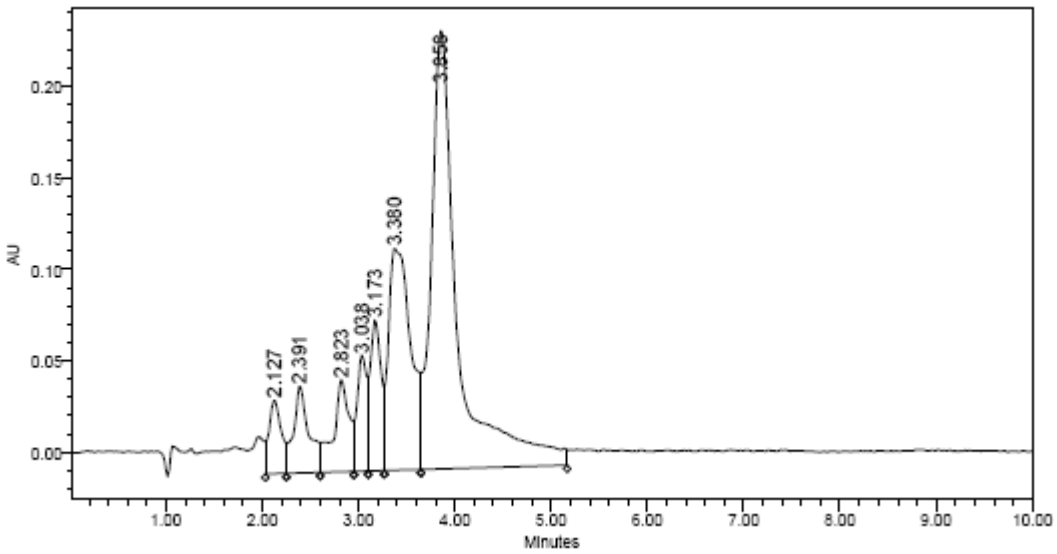


Figure 3.56. Chromatogram of dye **40**/**41** (pH 5) using gradient system 1.

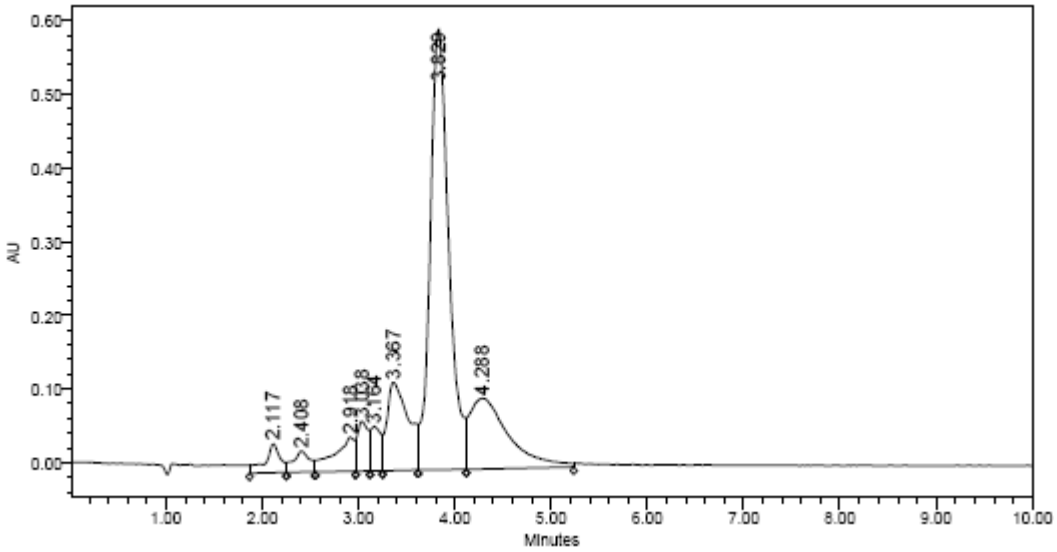


Figure 3.57. Chromatogram of dye **40**/**41** (pH 6) using gradient system 1.

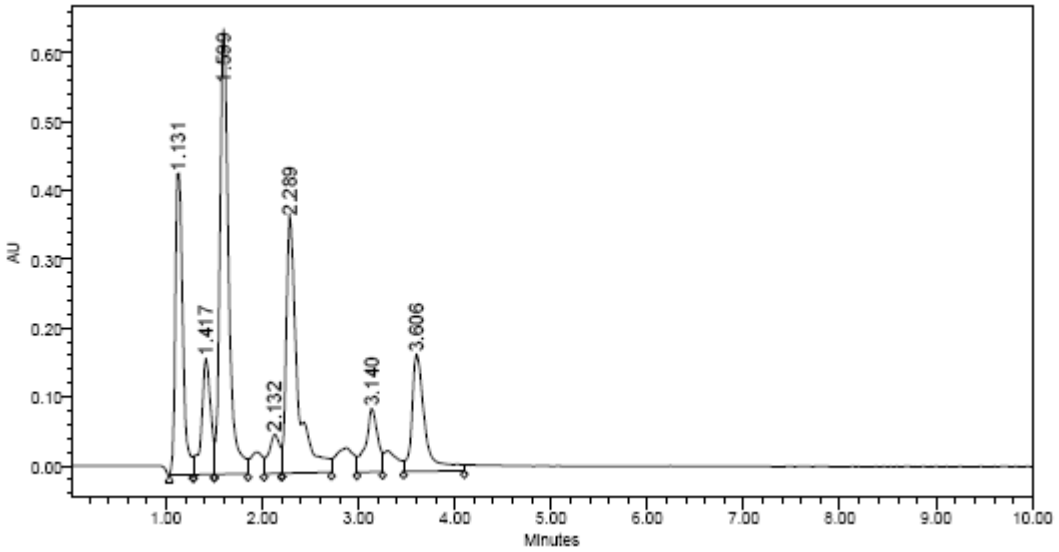


Figure 3.58. Chromatogram of dye **40**/**41** (factory sample) using gradient system 1.

Table 3.35. Summary of major peaks in the chromatograms of red DCT dyes employed in this study.

Peak	Retention Time (min) / % Area					
	Dye **30**	New Red Dye (**40**/**41**)				
		pH 3	pH 4	pH 5	pH 6	Factory
1						1.13/17.7
2						1.60/30.6
3	2.10/20.2					2.29/22.6
4	2.83/61.7	2.85/33.6	2.86/12.2			
5				3.38/21.5	3.37/12.2	
6		3.66/55.0	3.65/64.6			3.61/11.9
7				3.86/50.4	3.83/53.6	

Several points were evident from Table 3.35: 1) the dyes synthesized at pH 3-4 contained a component eluting at 2.85 min, which was also found in the parent red dye and probably was unconverted commercial dye; 2) the dyes

prepared at pH 3-4 contained components eluting at 3.65 min that were missing from the samples synthesized at higher pH levels, which was also found in the dye made by the Polish factory; 3) the dyes prepared at pH 5-6 contained components eluting at 3.38 min and 3.85 min that were missing from the samples synthesized at lower pH level; and 4) The dye made by the Polish factory contained peaks eluting at 1.13-1.60 min that were not found in other dyes, including the parent red dye. These results suggested that the components eluting at 3.65 min corresponded to a reaction at the –SH group of, while the one eluting at 3.85 min corresponded to a reaction at the $–NH_2$.

2.5 Dyeing Studies

To determine the optimum salt concentration to be used in the dyeing studies, fabric samples 1-4 were dyed with commercial red dye (**34**) at salt concentrations of 40, 60, 80 100g/L, respectively, and sample 5 was dyed with bis-DCT red dye (**40**/**41**) made by the Polish factory at a salt concentration of 40g/L. The results of these experiments are shown in Figure 3.59 and Table 3.36.

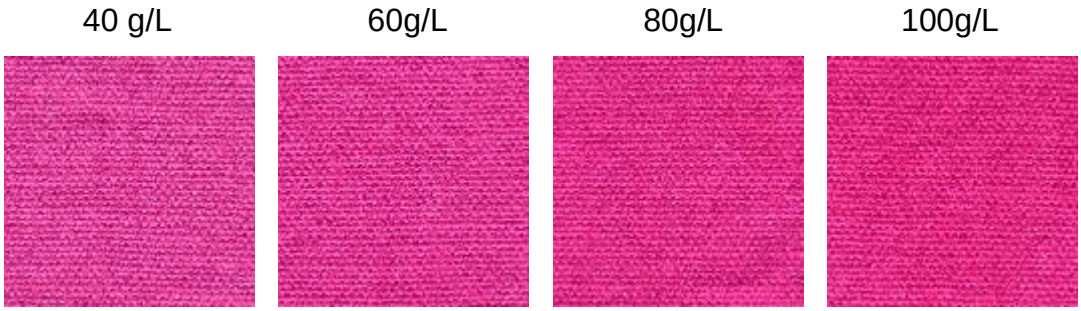


Figure 3.59. Fabrics dyed with commercial red dye at different salt levels.

Table 3.36. Results from dyeing trials using two types of DCT red dyes.

Dye Name	Sample No.	Salt Conc. (g/L)	% E	Dye in Fabric (mg/g)	K/S
Red Dye **34** (Commercial)	1	40	28.1	2.81	3.52
	2	60	30.9	3.09	4.09
	3	80	37.3	3.73	5.34
	4	100	48.9	4.89	6.57
New Red Dye **40**/**41** (Factory)	5	40	68.3	6.83	5.85

From the dyeing trials, it was evident that 40 g/L salt was not enough to get a deep color with the commercial red dye (K/S is only 3.52), but it was sufficient for the new bis-DCT red dye (K/S=5.85). As a basis for comparing results, the 40g/L salt level was used for all subsequent dyeings.

In order to check the reproducibility of the color shade depth on the fabric after dyeing, each dyeing was conducted twice using the same dyeing procedure. The results are shown in Figures 3.60-3.61 and Table 3.37. The results indicated that the repeatability of the dyeings was quite good. As expected, increasing dye uptake, increased K/S and the color shade depth.

Figure 3.60. Fabrics dyed with commercial and new dyes.

Table 3.37. Percent exhaustion and K/S values from duplicate dyeing studies.

Dye Name	Sample No.	% E	OWG(mg/g)	K/S
Yellow Dye **29** (Commercial)	1	33.0	3.3	2.96
	2	32.9	3.3	2.82
New Yellow Dye (pH 3)	1	58.3	6.0	5.67
	2	58.3	6.0	5.90
New Yellow Dye (pH 4)	1	61.4	6.1	6.28
	2	61.6	6.2	6.68
New Yellow Dye (pH 5)	1	63.9	6.4	7.29
	2	64.0	6.4	7.61
New Yellow Dye (pH 6)	1	65.7	6.6	6.82
	2	65.5	6.6	6.52
New Yellow Dye (Factory)	1	60.3	6.0	6.44
	2	60.2	6.0	6.20
Red Dye **34** (Commercial)	1	30.3	3.0	3.42
	2	27.0	2.7	2.40
New Red Dye (pH 3)	1	47.6	4.8	6.39
	2	48.7	4.9	6.83
New Red Dye (pH 4)	1	57.3	5.7	9.51
	2	57.3	5.7	9.48
New Red Dye (pH 5)	1	62.2	6.2	8.09
	2	62.8	6.3	8.30
New Red Dye (pH 6)	1	66.3	6.6	7.29
	2	67.1	6.7	7.53
New Red Dye (Factory)	1	67.5	6.8	5.71
	2	67.7	6.8	5.76

2.6 Colorimetric Data

All of the dyed fabrics were evaluated using a Datacolor Spectraflash SF600X instrument equipped with SLI-Form® software. The port size used was 9mm and averaged 4 reads for each sample. The L*, a*, b*, maximum K/S value, and the wavelength at which the maximum K/S value was observed are recorded in Tables 3.38-3.39.

Table 3.38. Colorimetric data for fabrics dyed with the two types of DCT dyes.

Dye Name	Sample No.	L*	a*	b*	K/S	λ (nm)
Red Dye **34** (Commercial)	1	55.6	50.1	-11.4	3.52	550
	2	54.2	51.9	-11.2	4.09	550
	3	51.4	54.2	-10.4	5.34	550
	4	49.3	55.7	-9.5	6.57	550
New Red Dye (Factory)	5	49.0	52.0	-13.0	5.85	560

The results in Table 3.38 indicate that for the fabrics dyed with commercial red dye, increasing the salt concentration used for dyeing led to a decrease in L* value, which means the lightness of the shade decreased; a slight increase in a* indicates an increase in redness, and a less negative b* value indicates a decrease in blueness [44]. When the same salt concentration was used for dyeing fabrics with commercial dye and the new dye, the fabric dyed with the new dye had a lower L* value, a higher a* value and more negative b* value.

Table 3.39. Colorimetric data for fabrics from duplicate dyeing studies.

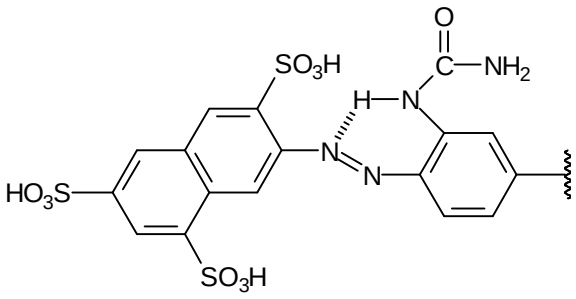
Dye Name	Sample No.	L*	a*	b*	K/S	λ (nm)
Yellow Dye **29** (Commercial)	1	82.2	14.1	61.4	2.96	430
	2	82.0	14.3	59.9	2.82	430
New Yellow Dye (pH 3)	1	77.5	20.9	70.5	5.67	430
	2	76.5	21.7	70.1	5.90	430
New Yellow Dye (pH 4)	1	76.9	22.2	72.2	6.28	430
	2	75.7	23.2	71.7	6.68	430
New Yellow Dye (pH 5)	1	75.6	24.9	74.2	7.29	430
	2	75.2	25.7	74.4	7.61	430
New Yellow Dye (pH 6)	1	75.0	25.7	72.2	6.82	440
	2	74.2	27.1	73.2	6.52	440
New Yellow Dye (Factory)	1	77.2	23.1	73.3	6.44	430
	2	78.0	22.5	73.6	6.20	430
Red Dye **34** (Commercial)	1	55.9	49.8	-11.4	3.42	550
	2	60.0	46.7	-11.9	2.40	550
New Red Dye (pH 3)	1	49.0	54.5	-11.3	6.39	560
	2	48.4	55.3	-10.7	6.83	560
New Red Dye (pH 4)	1	44.9	56.6	-9.5	9.51	560
	2	45.1	56.9	-9.4	9.48	560
New Red Dye (pH 5)	1	46.0	55.1	-11.8	8.09	560
	2	45.8	55.2	-11.5	8.30	560
New Red Dye (pH 6)	1	47.5	54.8	-12.3	7.29	560
	2	47.3	55.2	-11.9	7.53	560
New Red Dye (Factory)	1	49.2	51.4	-13.5	5.71	560
	2	49.1	51.8	-13.0	5.76	560

The results in Table 3.39 indicates that all fabrics dyed with yellow dyes have L*>74, which means the fabric shade is relatively light, a*>0 indicates an attribute of redness, and b*>0 indicates an attribute of yellowness [44]. Thus, the color of the shade is relatively light and simultaneously has red and yellow character, which produces an overall orange color. All fabrics dyed with red dyes have 44<L*<60, which means the color is medium light, and possesses red and blue character. Thus, the color of the shade is medium light bluish-red. Comparing the dyed yellow fabrics, the one dyed with commercial yellow dye gives highest L* value and possesses least level of redness. Among the red dyed fabrics, the one dyed with the commercial red dye also gives the lightest shade.

2.7 Fastness Properties

2.7.1 Color Fastness to Light

The lightfastness test was conducted for 20 and 40h, the results of which are listed in Table 3.40. The yellow dyes exhibited better lighfastness than the red dyes, as the gray scale ratings for fabrics exposed for 20h were 4.5-5 for yellow fabrics but 3-3.5 for red samples. This is because of greater protection of the azo bond due to the intramolecular H-bonding (**44**) in the yellow dyes. After 40h exposures, the ratings were 3.5-4 for yellow fabrics and 2-3 for red fabrics. It was also evident that the lightfastness of commercial DCT dyes and modified bis-DCT dyes were not significantly different.



(**44**)

Table 3.40. Results from lightfastness testing.

Dye Name	Light Fastness			
	Exposure=20 hr		Exposure=40 hr	
	DE_{CMC}	Gray Scale Rating	DE_{CMC}	Gray Scale Rating
Yellow Dye **29** (Commercial)	0.56	4.5	1.86	3.5
New Yellow Dye (pH 3)	0.88	4.5	2.28	3.5
New Yellow Dye (pH 4)	0.82	4.5	2.37	3.5
New Yellow Dye (pH 5)	0.77	4.5	1.56	4
New Yellow Dye (pH 6)	1.02	4.5	2.13	3.5
New Yellow Dye (Factory)	0.23	5	1.83	4
Red Dye **34** (Commercial)	1.80	3.5	2.55	3
New Red Dye (pH 3)	1.49	3.5	2.57	3
New Red Dye (pH 4)	1.44	3.5	3.86	2
New Red Dye (pH 5)	1.63	3.5	2.97	2.5
New Red Dye (pH 6)	1.81	3.5	2.75	2.5
New Red Dye (Factory)	2.41	3	4.47	2

2.7.2 Color Fastness to Water (Wet Color Transfer)

The results are listed in Table 3.41. For this test, all of the multi fiber fabrics attached to red samples exhibited more color transfer than the ones

attached to yellow samples. Almost all of the yellow samples gave gray scale ratings of 4.5 or 5, except that the nylon and wool bands on the multi fiber fabric attached to the sample dyed with the modified yellow dye synthesized at pH 6 had a rating of 4. For the red fabrics, the color of the samples changed noticeably, especially the one dyed with the factory made dye, which gave a gray scale rating of 3.5. For the red dyed fabrics, acetate experienced the least staining, acrylic was second, then polyester. Cotton, nylon and wool were stained more. The commercial dye gave better results than the modified dyes.

Table 3.41. Results from wet color transfer testing.

Dye Name	Wet Color Transfer							
	Color Change		Staining					
	DE_{CMC}	G. S.	Ace.	Cott.	Nyl.	Poly	Acr.	Wool
Yellow Dye **29** (Commercial)	0.43	4.5	5	5	5	5	5	4.5
New Yellow Dye (pH 3)	0.73	4.5	5	5	4.5	5	5	4.5
New Yellow Dye (pH 4)	0.41	4.5	5	4.5	4.5	5	5	4.5
New Yellow Dye (pH 5)	0.83	4.5	5	5	4.5	5	5	4.5
New Yellow Dye (pH 6)	0.45	4.5	5	4.5	4	5	5	4
New Yellow Dye (Factory)	1.35	4	5	5	5	5	5	5
Red Dye **34** (Commercial)	0.51	4.5	5	4	4.5	4.5	5	3.5
New Red Dye (pH 3)	0.74	4	5	3.5	4	4.5	4.5	3
New Red Dye (pH 4)	0.58	4.5	5	2.5	3.5	4.5	4.5	3
New Red Dye (pH 5)	0.46	4.5	4.5	2.5	2.5	4	4.5	2.5
New Red Dye (pH 6)	0.80	4	4.5	3	3	4.5	4.5	3
New Red Dye (Factory)	1.48	3.5	4.5	2	2	3.5	4	3

2.7.3 Color Fastness to Crocking (Rubbing)

The crockfastness test was carried out on dry and wet samples and the results are listed in Table 3.42. The dry crockfastness was very good for all samples, with very slight staining on the test squares from the yellow fabrics. Wet crockfastness was not good. In this case, there was little difference between red and yellow samples or between modified and commercial dyes.

Table 3.42. Results from crockfastness testing.

Dye Name	Crocking Fastness	
	Dry	Wet
Yellow Dye **29** (Commercial)	4.5	4.5
New Yellow Dye (pH 3)	4.5	4
New Yellow Dye (pH 4)	4.5	4
New Yellow Dye (pH 5)	4.5	4
New Yellow Dye (pH 6)	5	3.5
New Yellow Dye (Factory)	5	4.5
Red Dye **34** (Commercial)	5	4.5
New Red Dye (pH 3)	5	3.5
New Red Dye (pH 4)	5	4
New Red Dye (pH 5)	5	3.5
New Red Dye (pH 6)	5	4
New Red Dye (Factory)	5	4.5

2.7.4 Color Fastness to Laundering (Washfastness)

The washfastness results are listed in Table 3.43. It could be seen that the washfastness for all of the samples was very good. This was the case for color change and staining on the multi fiber fabrics attached to them. All had a rating of 4-5 on the gray scale.

Table 3.43. Results from washfastness testing.

Dye Name	Wash Fastness							
	Color Change		Staining					
	DE_{CMC}	G. S.	Ace.	Cott.	Nyl.	Poly	Acr.	Wo.
Yellow Dye **29** (Commercial)	0.50	4.5	5	4.5	5	5	5	4.5
New Yellow Dye (pH 3)	1.01	4.5	5	4.5	4.5	5	5	5
New Yellow Dye (pH 4)	1.16	4	5	4	4.5	5	5	4.5
New Yellow Dye (pH 5)	0.92	4.5	5	4.5	5	5	5	4.5
New Yellow Dye (pH 6)	0.36	5	5	5	5	5	5	4.5
New Yellow Dye (Factory)	0.31	4.5	5	5	5	5	5	5
Red Dye **34** (Commercial)	0.44	4.5	5	4.5	4.5	5	5	4.5
New Red Dye (pH 3)	0.38	4.5	5	4.5	4.5	5	5	4.5
New Red Dye (pH 4)	0.68	4.5	5	4.5	4.5	5	5	4.5
New Red Dye (pH 5)	0.65	4.5	4.5	4.5	4.5	4.5	5	4.5
New Red Dye (pH 6)	0.42	4.5	4.5	4.5	4.5	4.5	5	4.5
New Red Dye (Factory)	0.51	4.5	4.5	4	4.5	4.5	5	4.5

IV. CONCLUSIONS

HPLC methods for analyzing products produced from reactions between commercial DCT reactive dyes and cysteamine or cysteine have been developed. Gradient methods produce better separations than isocratic methods.

The chromatograms obtained indicate that the pH of the reaction medium greatly impacts the types of products produced when cysteamine was used but not when cysteine was used. In the case of cysteine, the presence of a –COOH alpha to the $–NH_2$ group promotes a reaction at the less sterically hindered –SH group. It is also evident from HPLC that the use of cysteine leads to a more complex mixture of components in the reaction product.

In a second set of HPLC experiments, the nature of the reaction between cysteamine and DCT reactive dyes was elucidated. It is now clear that the lower the reaction pH, the higher the proportion of product obtained from a reaction at the –SH group, as would be anticipated. In this case, the reaction at –SH occured at pH 2-4 but at the $–NH_2$ moiety at pH 6.

The HPLC methods could also be used to analyze bis-DCT reactive dyes synthesized from a two-step process involving a reaction between commercial DCT dyes and cysteamine followed by reaction with cyanuric chloride. In this case, the effects of pH used in the first step of dye synthesis on the distribution and types of components in the final bis-DCT dye were assessed. This aspect of the research permitted a comparison of the laboratory synthesized dyes with those synthesized in an industrial plant. Specifically, the manner in which the dye intermediates were combined was established.

The effects of pH used in dye synthesis on the dyeing and fastness properties was assessed. It was evident that pH did not adversely affect dye uptake or reproducibility but in some cases an adverse effect on color fastness to crocking and laundering occurred. In all cases, however, the fastness properties of the bis-DCT dyes were good. Yellow dyes had better lightfastness and wet color transfer properties than red dyes, the former of which could be attributed to intramolecular H-bonding between the azo bond and the –NH– group of the ureido moiety.

The results of this study suggested that pH 4 is the optimum level for dye synthesis, in that it gives the desired reaction at the –SH group and dyes with the best overall fastness properties.

V. RECOMMENDATIONS FOR FUTURE WORK

This study focused on the separation of the products from the conversion of commercial DCT reactive dyes to bis-DCT dyes having cysteamine as the linking group. HPLC was used in the separations and was instrumental in characterizing the reaction between cysteamine and DCT dyes. The logical next step would involve the use of mass spectrometry and NMR spectroscopy to support conclusions made from HPLC experiments. The proposed experiments would benefit from access to a semi-preparative column to collect the individual LC peaks to obtain sufficient amounts of pure components for instrumental analysis. ^{13}C-NMR would detect C-N vs. C-S bond formation at the triazine rings. Similarly, electrospray mass spectrometry would confirm that the products believed to arise from regioselectivity as a function of pH are indeed isomeric structures. Also, reaction components believed to arise from partial or complete hydrolysis would be confirmed.

Arrangements had been made for FT-Raman spectroscopy to be conducted on the yellow dye intermediates obtained from the reaction of cysteamine with the parent dye. Raman is known to be more effective for detecting –SH groups than FT-IR. These results would facilitate publication of the present work.

VI. REFERENCES

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