

## **ABSTRACT**

SHI, JINGLING. Measurement of Vat Dye Concentrations for Real-Time Dyebath Monitoring. (Under the direction of Dr. Warren J. Jasper).

Dyebath monitoring systems have been developed to improve color yields and optimize the dyeing process by reducing the consumption of energy, water, and time. These systems are based on predicating the concentration of dyes in dyebath using spectrophotometric measurements. The accurate determination of the concentration of vat dyes, however, is difficult since vat dyes are not water soluble and their absorbance spectra change in the reduced or leuco form. In the present study a new approach was developed to measure the concentrations of vat dyes in their reduced form after preconditioning the dyes prior to measuring their absorbances. Three vat dyes, C.I. Vat Blue 6, C.I. Vat Red 10 and C.I. Vat Violet 1 along with two reducing methods based on - sodium hydrosulfite/NaOH and sodium borohydride/sodium metabisulfite/NaOH were studied and compared. In all cases, excellent calibration models were obtained that could predict dye concentrations, on average, to a precision of 0.01 g/L over a range of 0 to 2 g/L. Two dye mixtures were also investigated which showed similar results. Measurements of the vat dyes in their unreduced form gave the most accurate concentration predictions. Statistically, the two reducing methods provided similar leuco reduction potentials in the range of -820 to -890 mV, and their dye prediction performance was found to be statistically comparable.

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Measurement of Vat Dye Concentrations for Real-Time Dyebath Monitoring

by  
Jingling Shi

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APPROVED BY:

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Dr. Peter J. Hauser

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Dr. Renzo Shamey

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Dr. Warren J. Jasper  
Chair of Advisory Committee

## **DEDICATION**

This work is dedicated to my family for their support and encouragement.

## **BIOGRAPHY**

Jingling Shi was born on April 1<sup>st</sup>, 1991 in Quanzhou, Fujian Province of China, a well-known city for the production of various textile apparel and sports brands. She is the daughter of Deyi Shi and Guiyang Wu. She graduated from Donghua University, Shanghai, in 2013 and obtained her Bachelor's degree in Textile Engineering and Textile Design. She was admitted to the "3+X" program at North Carolina State University in August 2012 to pursue a Master's degree in Textile Engineering.

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## CHAPTER 1 INTRODUCTION

Vat dyes play an important role in today's dyeing industry due to their excellent wash and light fastness properties which makes vat dyes an ideal choice for dyeing yarns to be used in manufacturing colored woven goods like uniforms, shirts, handkerchiefs, and towels. Vat dyes diffuse into cotton fibers only after they are converted into soluble compounds by reduction, and need to be re-oxidized back so as to be trapped within the fiber. This unique characteristic makes achieving level dyeing and target shades more difficult in vat dyeing.

It is critical to provide favorable conditions in textile dyeing in order to reach the desired target shades. This involves dyebath analysis in which the most important parameter, dye concentrations in solution, must be identified and measured as precisely, accurately and quickly as possible. The most common method is to spectrophotometrically determine the concentration using Beer's Law. However, the analysis of colorants which are in pigment form, during at least part of the dyeing process, such as vat dyes, poses particular problems because particles not only absorb but also scatter light. Flow injection analysis (FIA) has been demonstrated to be a very effective analytical technique for the determination of indigo dye concentration by converting the dyes into their soluble form while eliminating the possibility of oxygen contamination within the closed system. This has allowed for reliable indigo dyebath monitoring in real-time<sup>[1]</sup>.

The objective of this research is to evaluate the capability of measuring vat dye concentrations

using an advanced real-time dyebath monitoring system. Such a system was developed using the FIA technique in conjunction with spectral measurements capable of real-time measurements of dye concentrations during the dyeing process. Both the original water-insoluble form and the reduced soluble leuco form were investigated at four different concentrations. Two suitable reduction systems, sodium hydrosulfite/NaOH and sodium borohydride/sodium metabisulfite/NaOH, were selected for use in reducing vat dyes. Their reduction potentials and corresponding leuco reduction potentials of the reduced vat dye solutions were also assessed.

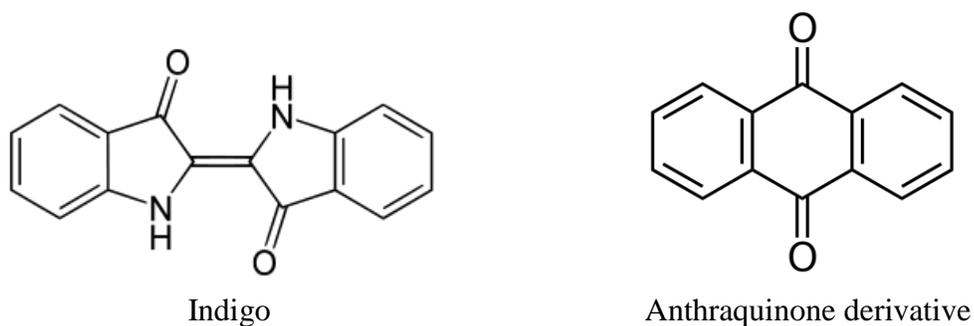
## CHAPTER 2 LITERATURE REVIEW

### 2.1 Vat Dyes

Vat dyes are amongst the oldest colorants used in textiles, dating back over 2000 years. Since vat dyes are water insoluble, they cannot be applied directly onto textile fibers and fabrics. Dyeing with vat dyes is based on the principle of converting the vat dye from its water-insoluble form into a water-soluble form (leuco dye) by means of reduction, which allows the dye to penetrate into the fiber where it is then reconverted by oxidation into the original insoluble form <sup>[2]</sup>. Vat dyes are used predominantly for dyeing cellulosic fibers in relatively dull shades, although in ancient times vat dyes were also used to dye wool. Vat dyes have excellent all around fastness properties, which include wash, light, and chlorine fastness, which is uncommon in other dye classes. On the other hand, vat dyes tend to have poor rubbing fastness, but this can be mitigated with particular treatments of the dyed fabric.

#### 2.1.1 Classification and Composition of Vat Dyes

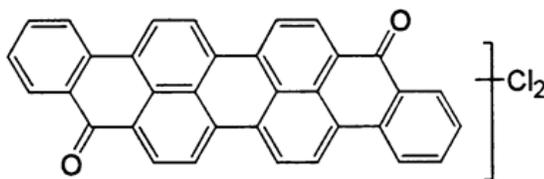
All vat dyes contain a quinonoid system based on carbonyl groups, separated by a conjugated system of double bonds. Indigo was one of the earliest vat dyes, and many vat dyes are derivatives of indigo. The majority of vat dyes used in dyeing applications today are mainly derivatives of anthraquinone and of higher condensed aromatic ring systems with a closed system of conjugated double bonds <sup>[2]</sup>. The chemical structures of Vat Blue 1 (indigo), and anthraquinone dyes, are shown in Figure 2.1.



**Figure 2.1 Indigo and Anthraquinone Derivative**

The chemical structure of the dye affects the properties of its leuco form in the dyeing process, as well as the properties of the resultant dyeing.

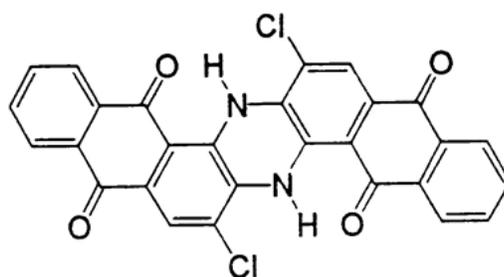
The isodibenzanthrone dyes, also known as isoviolanthrones, include some deep violet colors, such as C.I. Vat Violet 1 (Figure 2.2), a brilliant blue purple, which has a high color strength and good fastness to bleaching, but lower fastness to rubbing, hot pressing and water spotting.



**Figure 2.2. C.I. Vat Violet 1**

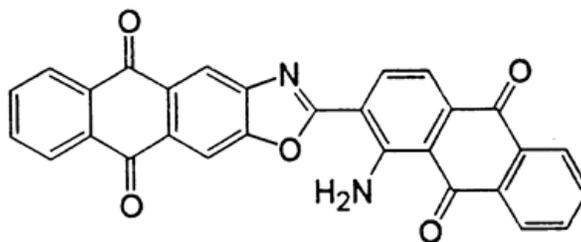
The indanthrones are blue dyes, forming one of the most important classes of vat dyes, such as C.I. Vat Blue 4, 6 and 14. During the dyeing process it is important to avoid over-reduction

and over-oxidation so as not to damage the chromophore. On the other hand, indanthrones continue to be widely used because of their pleasing colors, excellent fastness and reasonable price. Figure 2.3 shows the structure of C.I. Vat Blue 6, which is used in large quantities for the production of bright blues of outstanding light fastness and very good general fastness including bleach fastness.



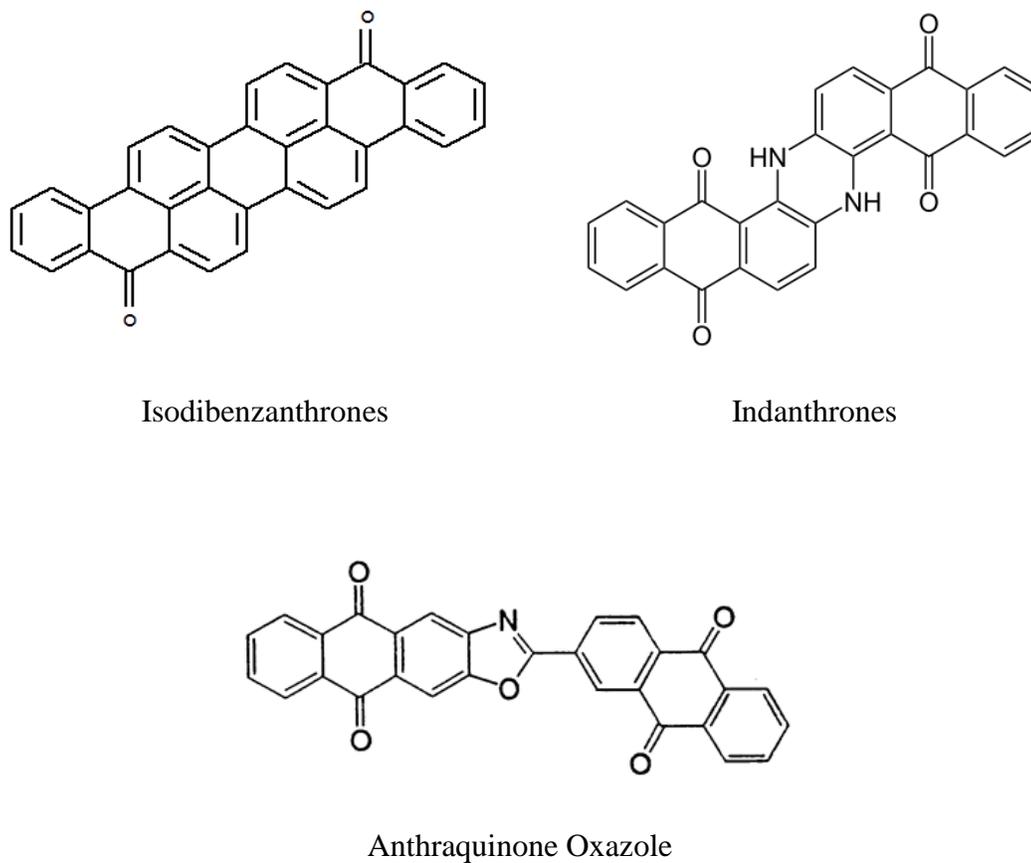
**Figure 2.3. C.I. Vat Blue 6**

The anthraquinone oxazole types represent another class of vat dyes. The main representative of this type is C.I. Vat Red 10 (Figure 2.4), which is a strong brilliant red that possesses good leveling properties during dyeing and has good fastness <sup>[2]</sup>.



**Figure 2.4. C.I. Vat Red 10**

Figure 2.5 illustrates the structural elements of the three most important vat dyes described above.



**Figure 2.5. Isodibenzanthrones, Indanthrones and Anthraquinone Oxazole**

Based on leuco compound substantivity and the required dyeing conditions, vat dyes are also classified into three groups or classes:

- IN or CI dyes (Hot dyeing. e.g. Vat Violet 1 and Vat Blue 6). IN or CI dyes require a high

amount of sodium hydroxide at relatively high temperatures (around 60°C) during the dyeing process. No salt is added to the dyebath because of the high substantivity of the leuco dyes for cotton. Since CI dyes have poor levelling properties, more levelling agent is required.

- IW or CII dyes (Warm dyeing, e.g. Vat Red 10). CII dyes require a medium amount of sodium hydroxide and medium temperature at which 50°C is the temperature of maximum affinity. Some addition of salt is required to aid exhaustion during dyeing since the leuco dyes have moderate substantivity for cotton. Some levelling agent is needed for better levelling when CII dyes are applied.

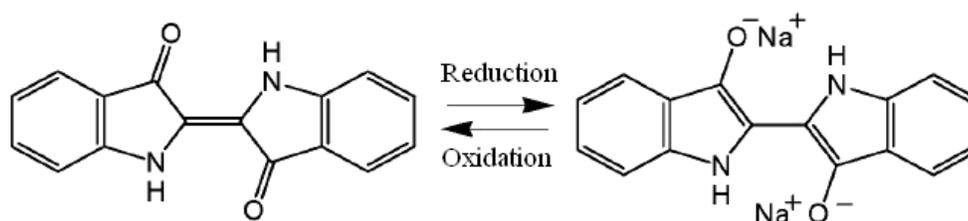
- IK or CIII dyes (Cold dyeing). For CIII dyes, only low amounts of sodium hydroxide and low temperatures are necessary, and the temperature of maximum affinity is as low as 20°C. These dyes have low substantivity for cotton and need high amount of salt for good dyebath exhaustion<sup>[3]</sup>. Moreover, these dyes have good levelling properties and thus no levelling agent is required.

Therefore, the amounts of the various chemicals required for different amounts of dye and liquor ratios should be determined accurately.

### **2.1.2 Dyeing Process and Principles**

Before the actual dyeing operation, the water-insoluble dye must be converted into the water-soluble substantive form in the presence of a strong reducing agent and caustic soda. This is

achieved by ‘vatting’ or ‘reduction’ (Figure 2.6). On completion of vatting, the stock vat is dosed into the dye vessel and combined with the cellulosic fabric where the diffusion of the leuco vat dye occurs.



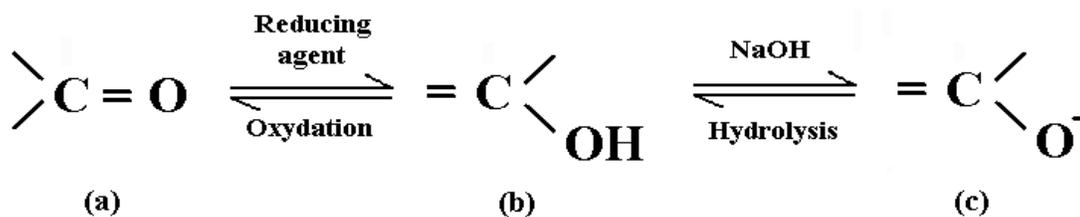
**Figure 2.6. Reduction and Oxidation**

On completion of dyeing, the material has first to be freed from surplus dye liquor and its pH reduced to a suitable level for oxidizing. This is done by suctioning off, squeezing, dropping the bath and/or rinsing. The ideal is to do rinsing thoroughly at low temperature at a rinsing bath pH value of 7. The next operation after rinsing is oxidation with the purpose of converting the water-soluble leuco form back into the insoluble pigment form. This can be achieved by using a mild oxidizing agent, such as 2-4 ml/l hydrogen peroxide or 2-4 g/l sodium perborate at 30-60°C for 15-30 minutes, or simply air <sup>[4]</sup>. After oxidizing, soaping is required to remove any dye that has not diffused into the fiber, and during which the isolated molecules of vat pigments are re-orientated and associate into a different, more crystalline form, which stabilizes the final shade and improves fastness properties. After soaping, the fabric is again given hot and cold rinses, and if necessary acidified with acetic acid.

## 2.2 Reduction

Reduction is a process of converting insoluble vat pigment into soluble leuco-vat anions, also known as ‘vatting’. When vat dyes are reduced, they do not generally produce the same color as unreduced vat dyes.

Experiments suggest that the actual chemical reaction proceeds as a two-electron transfer <sup>[5]</sup>, illustrated in Figure 2.7. The rate of reaction is determined by a combination of the reducing agent with the oxygen atom in the keto group (a) of the dye. This group is then rapidly split off by the action of the hydroxyl ions, leaving the two bonding electrons with the keto oxygen (b). Finally there is an electron shift to stabilize the dye in the leuco form (c).



**Figure 2.7. Reduction Mechanism**

### 2.2.1 Reducing Agents

It is necessary to have a sufficient level of reducing agent to reduce all vat dyes to their water-soluble form quickly and economically. Sodium hydrosulfite, known as hydro but more correctly known as sodium dithionite, which has the chemical formula  $\text{Na}_2\text{S}_2\text{O}_4$ , is the commonly used reducing agent in the industrial reduction of vat dyes. It is used with all vat

dyes at temperatures ranging up from 30 °C <sup>[6]</sup>. The advantage with sodium hydrosulfite is that it causes swift reduction of vat dyes and it enables very short fixing times in various dyeing methods and produces levelness in continuous dyeing <sup>[7]</sup>.

However, the disadvantage of sodium hydrosulfite is that it is unstable, it is very easily oxidized by atmospheric oxygen and the stability of its alkaline solutions reduces with the increase of temperature even in the absence of oxygen <sup>[8]</sup>. It is now being criticized for the formation of environmentally unfriendly oxidation byproducts such as sulfite ( $\text{SO}_3^{2-}$ ), sulphate ( $\text{SO}_4^{2-}$ ), thiosulphate ions ( $\text{S}_2\text{O}_3^{2-}$ ) and toxic sulphur <sup>[9]</sup>. To eliminate or minimize the production of inorganic waste from chemical reducing agents, many attempts have been made to create alternatives for the sodium hydrosulfite that cause less pollution.

Ferrous sulphate, as well as its combination with sodium hydrosulfite ( $\text{FeSO}_4 + \text{Na}_2\text{S}_2\text{O}_4$ ), has been employed as a reducing agent for effective vat dyeing on cotton fabric <sup>[10]</sup>. Some encouraging results have been observed with the combination of ferrous sulphate and sodium hydrosulfite. A 99.17% color strength, similar to that obtained for sodium hydrosulfite, has been observed with uniform dyeing throughout the dyeing process. The average effluent load from the vat dyebath using ferrous sulphate has been found to be less than that of sodium hydrosulfite. Nevertheless, ferrous sulphate reduction does not seem to have yielded significant results in improving the eco-efficiency of the vatting process. Electrochemical reduction is an attractive alternative to vatting techniques employing chemical reducing agents. However, the most challenging engineering task is to achieve dyestuff reduction rates which are high enough

to make electrochemical reduction industrially feasible <sup>[11]</sup>. Physical techniques, for example using ultrasound, magnetic fields or UV have been shown to be effective only when used to accelerate methods using classical reduction process. However, although these methods offer some environmental benefits, there is still no satisfactory alternative reducing agent available today.

Sodium borohydride, also known as sodium tetrahydroborate, with the chemical formula  $\text{NaBH}_4$ , is a versatile reducing agent, typically used in the laboratory for converting ketones and aldehydes to alcohols. Sodium borohydride has been evaluated in vat dyeing on its own, however, it has been found to slowly react with vat dyes for practical usage <sup>[12]</sup>. In a recent patent <sup>[13]</sup> a method for vat dyeing in the presence of sodium borohydride and sodium bisulfite has been introduced. Reduction is achieved by producing sodium hydrosulfite in situ from the reaction of sodium borohydride and sodium bisulfite.



This reduction system has been demonstrated to be more efficient than the conventional hydrosulfite alone and it has been claimed to give a dyestuff saving of around 15% in the application of indigo on cotton warps <sup>[13]</sup>. Furthermore, hydrosulfite produced in this way is found to be virtually free of by-products that result from its decomposition during storage <sup>[14]</sup>. Preferably, sodium borohydride is added in the form of an aqueous solution containing 12% active sodium borohydride and about 40% sodium hydroxide that stabilizes the solution.

Bisulfite is also preferably added as an aqueous solution. It has been stated that combining water and sodium metabisulfite,  $\text{Na}_2\text{S}_2\text{O}_5$ , generates bisulfite, which gives a hint that the alternative generation of sodium hydrosulfite in situ can be achieved by mixing sodium borohydride and sodium metabisulfite <sup>[15]</sup>. It has been found that a mixture of sodium borohydride solution (12%) and the sodium metabisulfite in the ratio of 1:3.8 is suitable for application of vat dyes under alkaline conditions. Furthermore, one unit of sodium borohydride has been stated to be equally efficient as four units of sodium hydrosulfite.

### **2.2.2 Vatting with Sodium Hydrosulfite**

The traditional method of preparing the leuco form of a vat dye involves using the reducing agent sodium hydrosulfite and sodium hydroxide. Sodium hydrosulfite has a good negative reduction potential which allows it to effectively reduce all vat dyes. This compound is not stable in a neutral or acidic solution but is stable in strongly alkaline solutions in the absence of air. Thus, sodium hydroxide (caustic soda) is used as a solubilizing agent suitable for dyeing. Vat dyes can be vatted in the stock vat in the dye bath <sup>[4]</sup>. Soft or demineralized water is required for both vatting and dyeing.

#### **Vatting in the Stock Vat**

Stock vatting procedures are categorized into three types – A, B and C, as shown in Table 2.1. After the dye has been thoroughly dispersed, it is vatted by adding caustic soda, and then slowly stirring in the hydrosulfite. On the completion of vatting, the stock vat is strained into the dye bath.

Industrially, C.I. Vat Red 10 is vatted by stock vating procedure A that requires a medium amount of hydrosulfite and caustic soda at a medium temperature of 50 °C. Stock vating procedure C is appropriate for vating C.I. Vat Blue 6 and C.I. Vat Violet 1, as high amounts of hydrosulfite and caustic soda are needed at relatively high temperature of 60°C.

**Table 2.1. Stock Vating Procedures** <sup>[4]</sup>

	<b>Units</b>	<b>A</b>	<b>B</b>	<b>C</b>
Vat dyes	kg	1	1	1
Water	liter	50	50	100
Caustic soda (30%)	liter	2	3	6
Hydrosulfite conc.	kg	0.75	1	2
Temperature	°C	50	60	60
Vating time	minute	10-15	10-15	10-15

### 2.2.3 Oxidation-Reduction Potential (ORP)

One way to quantify the oxidizing or reducing capability of a solution is to use the oxidation-reduction potential or redox potential, which is a measure of the activity or strength of oxidizing and reducing agents in relation to their concentrations. It is widely used as the basis for automated chemical control equipment because an ORP sensor can deliver an accurate feedback signal to achieve control and adjustment. A reducing agent or leuco dye solution has a negative potential whereas a positive redox potential indicates an oxidizing agent. The more negative the potential is the more likely it will be reduced and vice versa.

It is critical that the reducing agent has a sufficiently negative oxidation-reduction potential to effectively reduce vat dyes. Normally, the leuco reduction potential of all vat dyes, measured with a calomel electrode under standard conditions, lies between -650 mV and -1000 mV, thus it is important that the reducing agents have a similar or even more negative reduction potential<sup>[9]</sup>. Sodium borohydride increases the negative potential of the dyebath when used as an additive. It gives a reduction potential comparable with or even higher (more negative) than that obtained with sodium hydrosulfite<sup>[16]</sup>. Nevertheless, the frequently postulated relationship between the leuco potential and the dyeing properties is still disputed.

### **2.3 Dyebath Monitoring Systems**

Textile dyeing is a process during which it is very important to provide favorable conditions to achieve the desired effects. In the past, it was not unusual for a dyer to make several modifications (adds) to the dyebath formula until the desired target shade was reached. Reworks result in the waste of labor, time and energy, as well as unnecessary increases in total costs. As in most dyeing techniques, dyebath analysis involves several important chemical variables including the reducing agent concentration, dye concentration and pH, as well as mechanical variables that have chemical feed rates, yarn feed rates, dip and oxidation timing and temperature. Because so many of these parameters are intimately related, it is difficult to separate and control individual factors.

In dyebath analysis, the quantification of the dye concentrations in solution by spectroscopic

measurements has helped improve the scientific understanding of the dyeing process and plays a key role in process optimization <sup>[17, 18]</sup>. The available methods by which dye bath measurements are used to monitor processes could be categorized as follows <sup>[19]</sup>.

- On-line (dynamic) versus off-line (static) measurement
- Direct dye liquor measurement versus dye liquor sampling techniques
- Closed-loop control versus open-loop control
- Laboratory scale versus bulk scale
- Reflectance versus transmission measurement
- Continuous dyeing versus batch (exhaust) dyeing

### **2.3.1 Measurement Challenges**

It can be difficult to accurately determine the dye concentration due to deviations from the Beer-Lambert law <sup>[20, 21]</sup>. Generally speaking, two types of methods have been developed to overcome these difficulties.

The first method attempts to bring the dyebath sample to standard conditions before the measurement. This typically includes control of temperature, pH and dye concentration. Flow Injection Analysis (FIA) and Sequential Injection Analysis (SIA) are examples of systems conditioning a dyebath stream before measurement. This method allows one to monitor dyeings with direct, basic, acid, disperse and reactive dyes <sup>[22, 23]</sup>. Even with dyebath

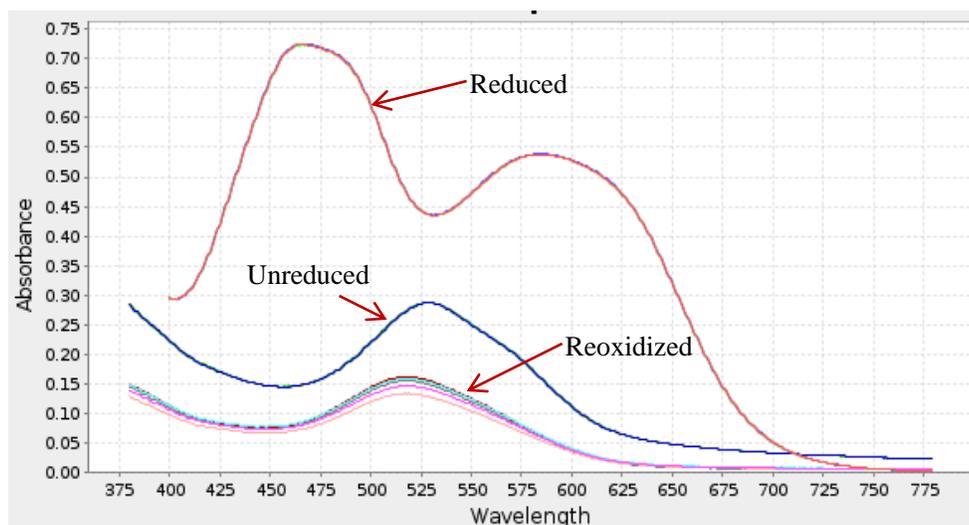
conditioning, lot to lot variations in the extinction coefficient can cause difficulties in concentration prediction <sup>[21]</sup>.

The second method intends to directly measure the concentration in the dyebath. Therefore, the effects of temperature, pH and dye concentration on the extinction coefficient of the dye have to be modeled and taken into consideration in the conversion from absorbance to concentration values <sup>[19]</sup>. Commercial systems have generally focused on direct dyebath measurements, providing dyeing process analysis with on-line bath monitoring <sup>[18, 24]</sup> or a dyeing machine with an automatic in-line dip depletion control <sup>[25]</sup>.

Problems arise in the spectral analysis of colorants which are not water soluble during the dyeing process, such as disperse dyes, sulphur dyes and vat dyes. This is because such dye particles tend to aggregate and scatter rather than absorb light. Thus the relationship between the incident and transmitted light becomes much more complex <sup>[19]</sup>. As illustrated in Figure 2.8, unlike the reduced vat dye that has a consistent spectra, the varying absorbance curves of the re-oxidized form introduces potential sources of error in the identification of the compound. This is attributed to the insolubility of the reoxidized dye, dye aggregation causing light scattering and varying particle sizes. One possible approach to solve this problem is to convert the particles into their soluble form by adjustment of pH in the case of sulfur and vat dyes <sup>[26]</sup> and by solubilization in acetone/water mixtures in the case of disperse dyes <sup>[27]</sup>.

In a study of indigo dyeing processes, the dye concentration has been monitored by three

methods including direct spectrophotometric measurement, titrimetric measurement and flow injection analysis (FIA). The possibility of determining reduced indigo concentration by spectrophotometry as well as ferricyanide titration has been confirmed whereas the accuracy is highly dependent on the oxygen contamination of the sample. On the other hand, FIA was very effective in measuring the indigo concentration without risking exposure of the reduced dye to atmospheric oxygen. It provided a means for tracking indigo concentration with reasonable response times during the dyeing operation and obtaining reproducible and reliable results [26].



**Figure 2.8. Absorbance Spectra Comparison of C.I. Vat Red 10 in Unreduced, Reduced and Re-oxidized Forms**

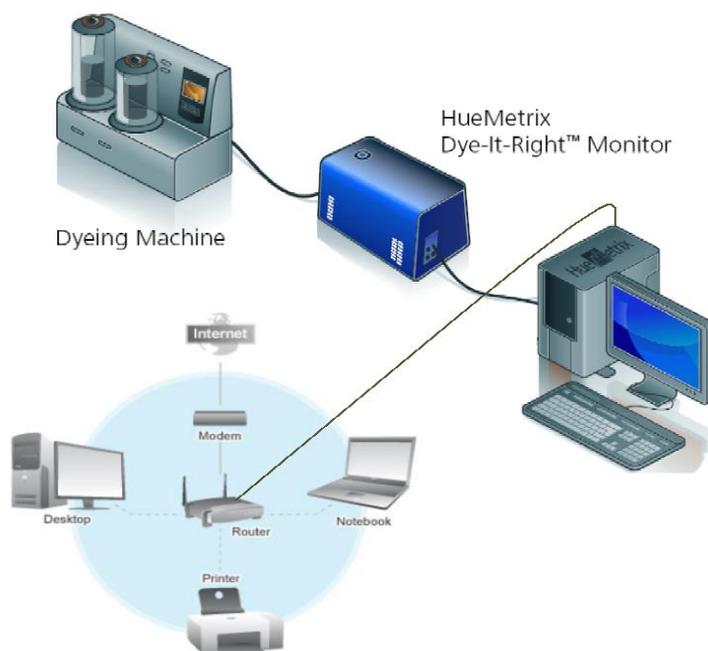
### 2.3.2 Future Developments

Variation in shade has always been a serious problem in commercial dye-houses. Many attempts have been made in creating and improving dyebath monitoring systems, and practical

experience has shown their capability in providing useful information to troubleshoot and optimize the dyeing processes. The first step in finding root causes in any dyeing process is to measure quantities of interest such as exhaustion, dye strength, temperature, and pH to better understand their relationship on the final shade.

## 2.4 HueMetrix Dye-It-Right™ Monitoring System

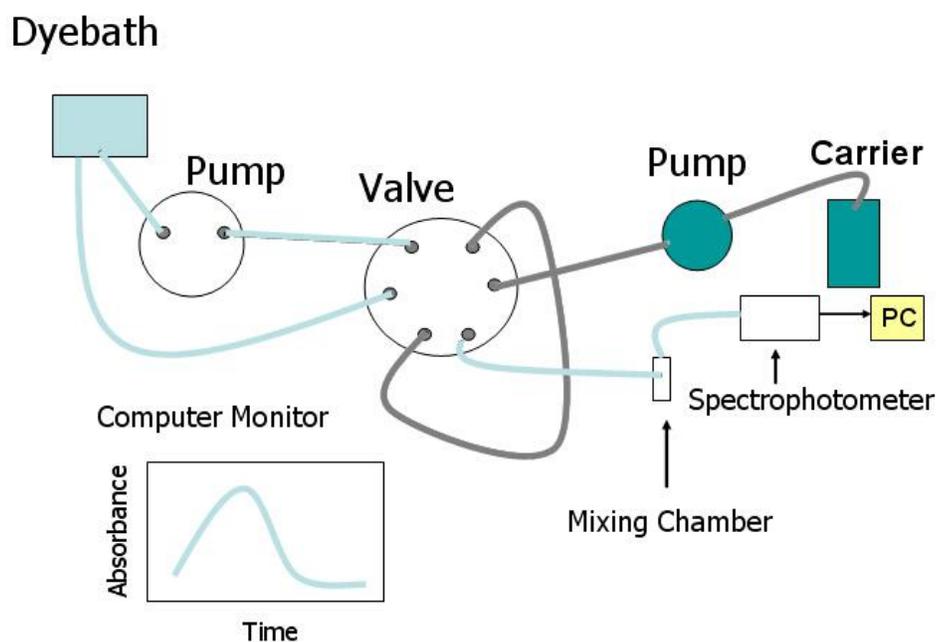
The basic hardware configuration of the HueMetrix Dye-It-Right™ monitoring system is shown in Figure 2.9. The HueMetrix monitor is connected to a Mathis FJL dyeing machine and monitors dyebath concentration as well as pH, conductivity and temperature. All the data acquired on the monitor is stored in a web accessible database for subsequent analysis.



**Figure 2.9. Typical HueMetrix Dye-It-Right™ Monitor Setup** <sup>[28]</sup>

The Dye-It-Right™ instrument conditions and processes dyebath samples and establishes communication with the computer for analysis and display. The mechanism of determination of dye concentrations in real-time, illustrated in Figure 2.10, is as follows:

First, approximately 100  $\mu\text{L}$  of dye is injected into a sample loop. Then a syringe-pump pumps the carrier fluid along with the dye slug into a mixing chamber where a controlled dilution takes place. While in the mixing chamber, absorbance measurements are taken of the dye while it is being diluted by the carrier stream. From these spectral absorbance measurements, the dye concentration is determined.



**Figure 2.10. Mechanism of HueMetrix Dye-It-Right™ Monitor** <sup>[28]</sup>

The system determines the dye concentration or concentrations of individual components of mixtures according to the Beer-Lambert law <sup>[29]</sup>, shown in Equation 2, and spectral additivity of an individual dye spectrum.

$$A(\lambda) = \varepsilon(\lambda) \cdot \ell \cdot c \quad (2)$$

where A is the absorbance (AU),  $\lambda$  is the wavelength (nm) ,  $\ell$  is the pathlength of the solution that the light passes through (cm), c is the dye concentration (g/L), and  $\varepsilon$  is molar absorptivity or molar absorption coefficient particular to a specific dye. When the measurement system is stable, the term  $\varepsilon(\lambda) \cdot \ell$  is constant and the concentration is proportional to the absorbance.

## CHAPTER 3 EXPERIMENTAL

### 3.1 Materials

#### 3.1.1 Vat Dyes

The three vat dyes used in this study are summarized in Table 3.1 along with their commercial name, C.I. name, C.I. Constitution Number, chemical class and shade. Rojo Novasol 2B MD is manufactured by Huntsman, Azul Indanthren CLF is made by DyeStar and Violeta Benzathren 2R ESP is made by CHT. Commercial vat dyes also contain amounts of a dispersion agent along with other unspecified auxiliaries. The characteristics and chemical structures of three vat dyes are described in Section 2.1.1.

**Table 3.1. Vat Dyes**

<b>Commercial Name</b>	<b>C.I. Name</b>	<b>C.I. Constitution Number</b>	<b>Chemical Class</b>	<b>Shade</b>
Azul Indanthren CLF	C.I. Vat Blue 6	69825	Anthraquinone	Brilliant blue
Rojo Novasol 2B MD	C.I. Vat Red 10	67000	Anthraquinone	Blue-ray red
Violeta Benzathren 2R ESP	C.I. Violet 1	60010	Anthraquinone	Bright bluish violet

#### 3.1.2 Chemicals

Two reduction systems were employed to reduce the three vat dyes in this study, i.e. sodium hydrosulfite/NaOH and sodium borohydride/sodium metabisulfite/NaOH. Table 3.2 gives

pertinent information for the reducing agents and other chemicals. All chemicals used were of laboratory grade.

**Table 3.2. Chemicals**

<b>Chemical Name</b>	<b>Chemical Formula</b>	<b>Description</b>
Sodium Hydrosulfite	$\text{Na}_2\text{S}_2\text{O}_4$	Anhydrous powder
Sodium Borohydride	$\text{NaBH}_4$	12% aqueous solution
Sodium Hydroxide	$\text{NaOH}$	50% aqueous solution
Sodium Metabisulfite	$\text{Na}_2\text{S}_2\text{O}_5$	Anhydrous powder

### 3.2 Equipment

A commercial HueMetrix Dye-It-Right™ Monitor was used to measure the dye concentrations of single solutions and two dye mixtures. The absorbance and concentration data set were recorded by the software in an SQL database for subsequent analysis.

To make direct measurements of the reduction potentials of the reduced vat dye solutions and reduction systems, a Thermo Scientific Orion 5-Star pH/RmV Meter (Oxidation-Reduction Potential technique) designed for electrochemistry measurement was employed, along with a Thermo Scientific Orion ORP electrode that combines a platinum redox sensing electrode and a silver/silver chloride reference electrode in one body. Orion ORP calibration standard was also used to ensure accurate ORP measurements.

### **3.3 Carrier Fluids Preparation**

One of the advantages of using flow injection analysis or FIA over direct measurements is that the carrier fluid can be used to condition the dye prior to dilution. Distilled water was used as the carrier fluid for the unreduced dye, while four different carrier fluids consisting of reducing agents were used to either dilute the dye or keep the dye in the reduced form while performing FIA.

#### **Carrier Fluid R**

Carrier fluid R is based on the sodium hydrosulfite reduction system, suitable for the blue (Azul Indanthren CLF) and red (Rojo Novasol 2B MD) vat dyes that are reduced by sodium hydrosulfite. To a 1 L volumetric flask half full of distilled water, 10 g of sodium hydroxide (10 g/L) was added and mixed. To this solution, 10 g sodium hydrosulfite (10 g/L) was added and mixed. This reducing solution was then brought to volume, capped and shaken thoroughly.

#### **Carrier Fluid R<sup>+</sup>**

Similar to fluid R, carrier fluid R<sup>+</sup> is specifically formulated for the violet vat dye (Violeta Benzathren 2R ESP), by increasing by 50% the concentration of sodium hydrosulfite and sodium hydroxide to 15 g/L.

#### **Carrier Fluid BH**

The preparation of carrier fluid BH was as follows: 3 g of sodium borohydride (for a final concentration of 3 g/L) was dissolved with 30 ml of distilled water and 11.4 g of sodium

metabisulfite (for a final concentration of 11.4 g/L) was dissolved in 114 ml of distilled water; these were then mixed together and diluted to 500 ml with distilled water. To this solution 11.6 g of sodium hydroxide was added and dissolved (for a final concentration of 11.6 g/L); the solution was transferred into a 1 L volumetric flask, brought to volume, capped and shaken thoroughly. Carrier Fluid BH was used for the blue and red dyes that were reduced by sodium borohydride.

### **Carrier Fluid BH<sup>+</sup>**

Carrier fluid BH<sup>+</sup> was made with a similar formulation as the carrier fluid BH but with a 50% increase in concentration (4.5 g/L of sodium borohydride, 17.1 g/L of sodium metabisulfite and 17.4 g/L of sodium hydroxide). It is formulated specifically for the violet dye that is reduced by sodium borohydride.

## **3.4 Preparation of Vat Dyes**

Three vat dyes, Violeta Benzathren 2R ESP, Rojo Novasol 2B MD, and Azul Indanthren CLF, were prepared respectively in the unreduced water-insoluble form, hydro-reduced water-soluble leuco form and boro-reduced water-soluble leuco form by the following methods. All solution preparations were conducted at room temperature.

### **3.4.1 Unreduced Solution Make Up**

Unreduced vat dye solutions at four different concentrations, i.e. 0.25 g/L, 0.5 g/L, 1.0 g/L and

2.0 g/L, were prepared.

- 1) To a beaker 2 g of vat dye powder was accurately added followed by distilled water and mixed until vat dye was thoroughly dispersed. The solution was transferred into a 1 L volumetric flask, made up to the mark with distilled water, capped, and mixed. This was used as a 2 g/L unreduced stock solution.
- 2) Various amounts of the 2 g/L unreduced stock solution, i.e. 100, 50 and 25 mL were pipetted respectively into three separate 200 mL volumetric flasks. Solutions were made up to the mark with distilled water, capped and shaken to produce 1, 0.5 and 0.25 g/L unreduced solutions respectively.

#### **3.4.2 Sodium Hydrosulfite Reduction Treatment**

For the reduction of blue and red vat dyes, 10 g of sodium hydrosulfite and 10 g of sodium hydroxide were weighed and dissolved in distilled water in a 1 L volumetric flask. Powdered vat dye (2 g) was dissolved in distilled water and slowly added into the solution, made up to 1 L with distilled water, capped and shaken thoroughly. The solution was left for 15 minutes of vatting. In a different flask, 2 g of powdered violet dye was reduced by 15 g of sodium hydrosulfite and 15 g of sodium hydroxide, where the solution was made up to 1 L with distilled water. These solutions constituted the 2 g/L hydro-reduced stock solutions.

Various amounts of the 2 g/L hydro-reduced stock solution, i.e. 100, 50 and 25 mL, were

pipetted respectively in three individual 200 mL volumetric flasks. These were brought to the mark with the carrier fluid R (for diluting hydro-reduced blue and red dye solutions) or carrier fluid R<sup>+</sup> (for diluting hydro-reduced violet solutions) making 1, 0.5 and 0.25 g/L of hydro-reduced solutions respectively.

### **3.4.3 Sodium Borohydride Reduction Treatment**

In reducing the blue and red vat dyes, 3 g of sodium borohydride was dissolved with 30 mL distilled water and 11.4 g of sodium metabisulfite was dissolved in 114 mL distilled water and mixed and then diluted to 500 mL with distilled water. After 2 minutes, 11.6 g of sodium hydroxide was added and the mixture stirred until the effervescence had ceased. The solution was transferred into a 1 L volumetric flask, followed by dissolving 2 g of powdered vat dye with distilled water and adding slowly into the solution, which was then brought to 1 L with distilled water, capped and shaken thoroughly. The solution was left for 15 minutes to allow for complete vatting. Two grams of powdered violet vat dye were reduced using a solution that had 50% increase in concentrations described above. The 2 g/L boro-reduced stock solutions were thus obtained.

Various amounts of the 2 g/L boro-reduced stock solution, i.e. 100 mL, 50 mL and 25 mL, were pipetted respectively in three individual 200 mL volumetric flasks. These were brought to the mark with carrier fluid BH (for diluting boro-reduced blue and red dye solutions) or carrier fluid BH<sup>+</sup> (for diluting boro-reduced violet dye solutions). They constituted the 1 g/L, 0.5 g/L and 0.25 g/L of boro-reduced solutions.

### 3.5 Dye Mixture Preparation

Blue and red dye solutions were combined for the unreduced, hydro-reduced and boro-reduced forms. The mixtures consisted of 0.2 g of blue dye, 0.2 g of red dye and 200 mL of either distilled water, carrier fluid R or carrier fluid BH, respectively. The mixture was capped and shaken thoroughly. The solutions were left for 30 minutes before measurements were taken.

### 3.6 ORP Measurement

Before each measurement, the ORP electrodes were thoroughly rinsed and calibrated in a known standard. Since the room temperature of the lab was maintained between 21-23°C, the standard  $E_H$  mV values were set between 421 and 423 RmV <sup>[30]</sup>.

Oxidation-reduction potentials of the four carrier fluids (R, R<sup>+</sup>, BH, BH<sup>+</sup>) and the six leuco dye solutions (hydro-reduced/boro-reduced of Azul Indanthren CLF, Rojo Novasol 2B MD and Violeta Benzathren 2R ESP at 2.0 g/L) were measured respectively over a 60 minute period, and the mV potentials were recorded at 10 minute intervals once the readings stabilized. To prevent the premature oxidation of the leuco dyes when exposed to the air, small-bore beaker flasks (50 mL) were used which were completely filled with the samples in which the electrode was placed for measurement. The electrodes were thoroughly rinsed with distilled water between measurements to avoid contamination.

### **3.7 HueMetrix Dye-It-Right™ Monitor Measurement**

The instrument was turned on and allowed to warm up for approximately 10 minutes before use. The information about three vat dyes was created and entered prior to carrying out any operation.

#### **3.7.1 Test Spectrum**

It is critical that the instrument is clean of all contaminants, and so the following protocol was used. The system was flushed with distilled water several times first, and then the raw photon count was examined. The maximum photon count should be around 25000 at around 570 nm, as shown in Figure 4.1. In the absorbance mode, the readings for DI water should read +/- 0.0005 absorbance units from about 400 to 780 nm. Four types of carrier fluid (R, R<sup>+</sup>, BH, BH<sup>+</sup>) were flushed and tested. Since the photon counts dramatically dropped to zero at wavelengths below 400 nm, the wavelength range of interest was modified to be between 400 and 780 nm.

#### **3.7.2 Calibration**

Calibration is the process by which the instrument learns the spectral characteristics of a specific dye. Before monitoring dye concentrations, the instrument had to be calibrated for the three vat dyes. Calibration solutions were made (Section 3.4) for each individual vat dye in three different forms with four different concentrations, as summarized in Table 3.3. The instrument was calibrated with these solutions, with at least three repeats each.

**Table 3.3. Calibration Information**

<b>Form</b>	<b>Setting</b>	<b>Dyes</b>	<b>Concentrations (g/L)</b>	<b>Carrier fluids</b>
Unreduced	Default setting	Azul Indanthren CLF Rojo Novasol 2B MD Violeta Benzathren 2R ESP	0.250, 0.500 1.000, 2.000	Distilled water
Hydro-reduced	Vat dye setting	Azul Indanthren CLF Rojo Novasol 2B MD	0.250, 0.500 1.000, 2.000	R
		Violeta Benzathren 2R ESP	0.000, 0.250 0.500, 1.000	R <sup>+</sup>
Boro-reduced	Vat dye setting	Azul Indanthren CLF Rojo Novasol 2B MD	0.250, 0.500 1.000, 2.000	BH
		Violeta Benzathren 2R ESP	0.000, 0.250 0.500, 1.000	BH <sup>+</sup>

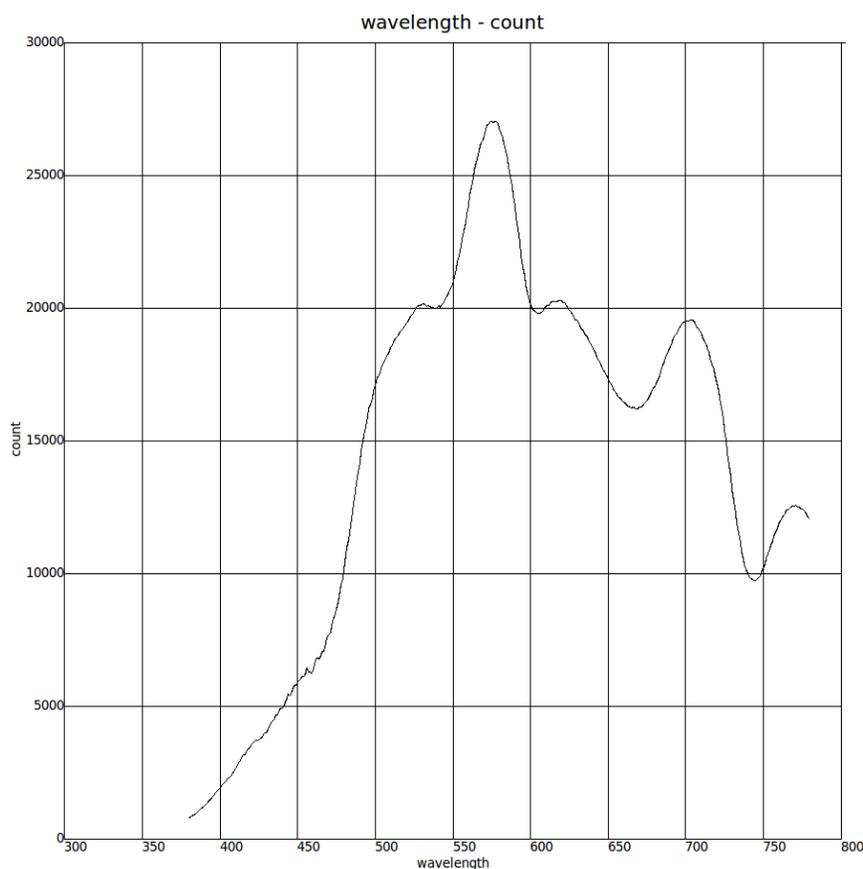
### 3.7.3 Dye Check

The concentrations of three vat dyes in the unreduced, hydro-reduced and boro-reduced forms were measured individually, as well as in a mixture of Azul Indanthren CLF and Rojo Novasol 2B MD. The solution injecting operation followed the same procedures as in the calibration. Each concentration was measured at least three times repeatedly. The predicted absorbance curves were plotted by the software and the measured concentration values were reported numerically with the expected concentration. Statistical information consisting of average measured concentration, standard deviation and CV % (coefficient of variation) were also provided for analysis.

## CHAPTER 4 RESULTS AND DISCUSSION

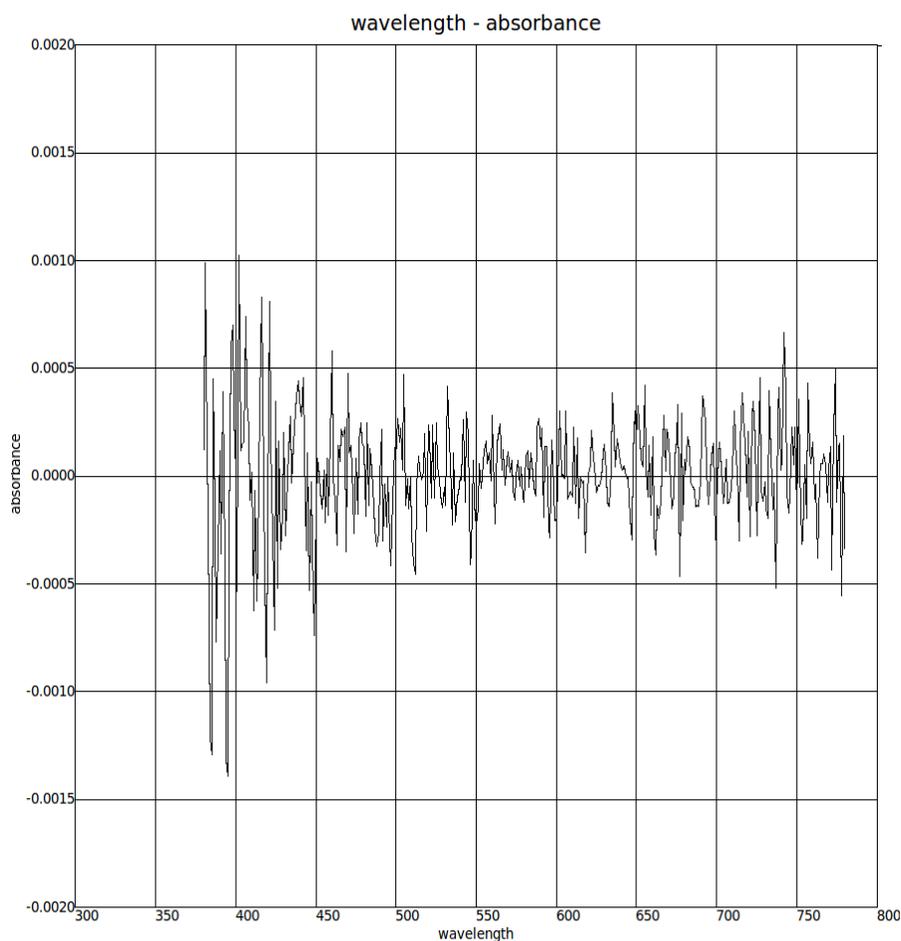
### 4.1 The Effects of Carrier Fluids on Test Spectrum

As stated in section 3.6.1, confirming that the instrument is working properly is the very first step prior to the calibration or checking dyes. This is done by flushing carrier fluid through the system to inspect the system's cleanliness and operability and to get ready for the calibration or monitoring of dyes. The raw spectrum of a tungsten light source transmitted through distilled water is shown in Figure 4.1.



**Figure 4.1. Raw Spectrum of Distilled Water**

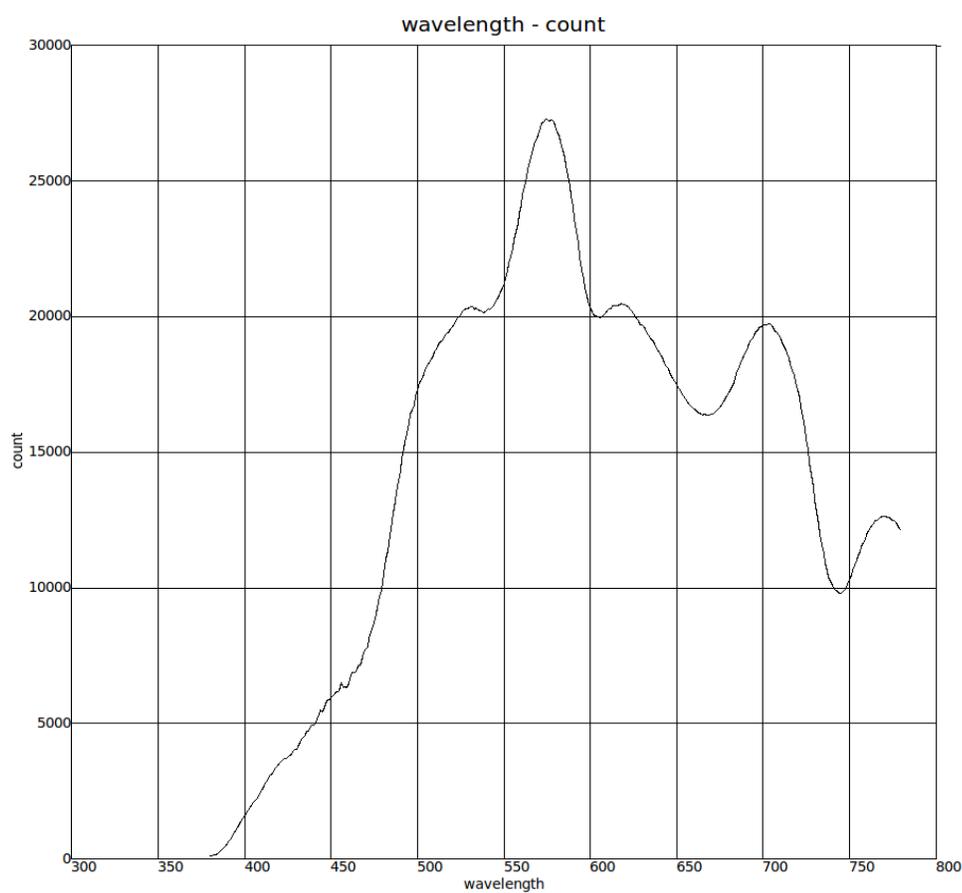
The max peak or photon count is between 25000 and 30000 at a wavelength of around 570 nm. The absorbance spectrum of distilled water is shown in Figure 4.2. When the instrument is clean and running properly, the absorbance values should be in the range of +/- 0.0005 AU.



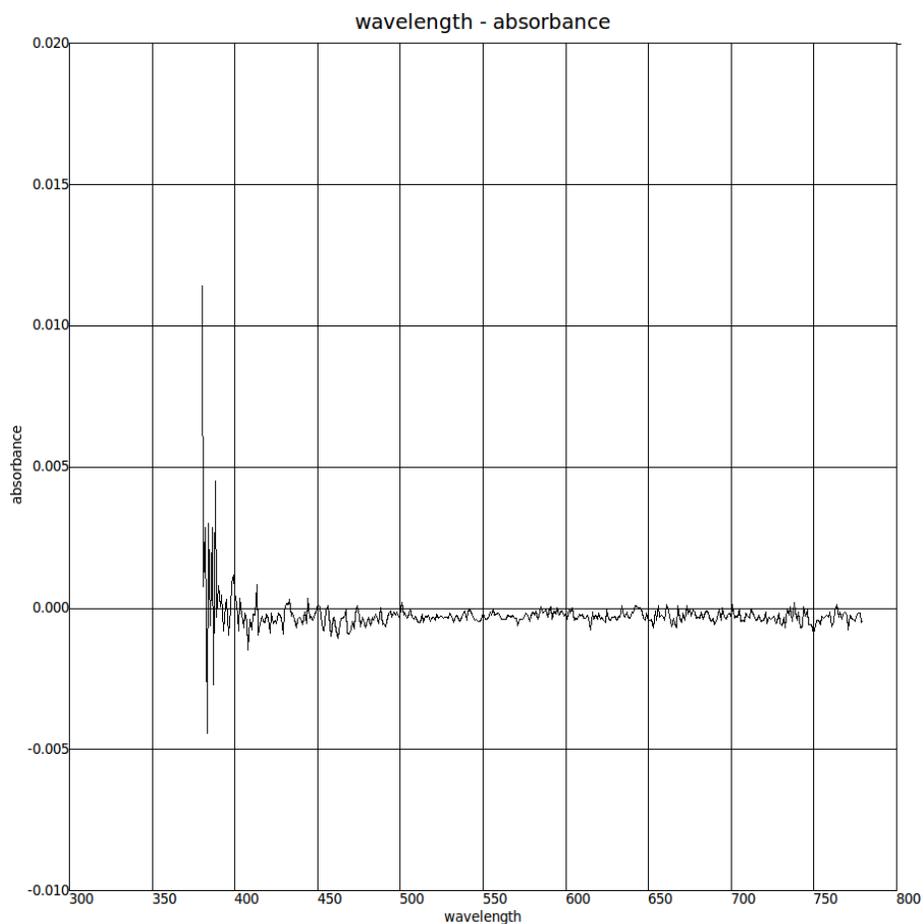
**Figure 4.2. Absorbance vs. Wavelength of Distilled Water**

The absorbance spectra are very similar for the four carrier fluids (R, R<sup>+</sup>, BH and BH<sup>+</sup>) but have noticeable differences when compared to distilled water, especially between 380 and 400 nm. As shown in Figure 4.3, the raw counts are dramatically reduced and even drop down to

zero at the lowest wavelength. As a result, the absorbance values in Figure 4.4 experience a significant increase or decrease in the range of 380 to 400 nm due to the fact that the carrier fluid absorbs light in that wavelength range. To solve this problem, the effective range for the dye analysis was changed to be between 400 and 780 nm.



**Figure 4.3. Raw Spectrum of Carrier Fluid R, R<sup>+</sup>, BH, BH<sup>+</sup>**



**Figure 4.4. Absorbance vs. Wavelength of Carrier Fluid R, R<sup>+</sup>, BH, BH<sup>+</sup>**

#### **4.2 Reduction Potential of Carrier Fluid**

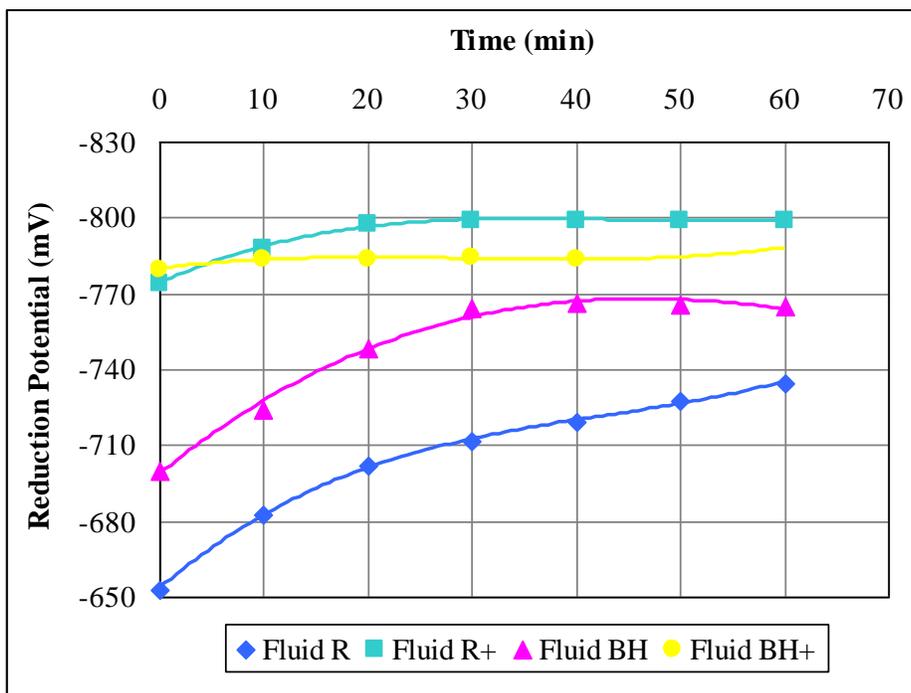
To obtain consistent measurements, the dye must be kept in the reduced form. The carrier fluid plays an important role in keeping the injected leuco dyes in reduction. Reduction potentials measured by the ORP meter help to quantify the reductive strength of the carrier fluids. Figure 4.5 was plotted on the basis of Table 4.1. Graphically the reduction potentials of fluid R and BH experience a distinct rise during the first 30 minutes, ranging from 9 to 13% and then level

off. Therefore, measurements were taken after 30 minutes or during equilibrium. It is interesting that the ORP reading for fluid BH is approximately 30 mV higher (more negative) than fluid R, which might suggest that the sodium borohydride reduction system has better reductive strength than the sodium hydrosulfite reduction system.

With a 50% increase in fluid concentrations, both fluid R<sup>+</sup> and BH<sup>+</sup> exhibit a slight increase in reduction potential values, as well as a rather steady reduction potential trend over time. Nevertheless, further addition of borohydride and hydrosulfite resulted in only a small increase in the reduction potential. In other words, the first 10 g/L borohydride gave a potential of -764.9 mV, and a 50% increase produced only about a 2.4% increase in the reduction potential. The first 10g/L hydrosulfite gave a potential of -734.8 mV, and a 50% increase in its concentration only produced about a 4.1% increase in the reduction potential.

**Table 4.1. Reduction Potentials of Carrier Fluid R, R<sup>+</sup>, BH, BH<sup>+</sup>**

<b>Time (min)</b>	<b>Reduction Potential (mV)</b>			
	<b>Fluid R</b>	<b>Fluid R<sup>+</sup></b>	<b>Fluid BH</b>	<b>Fluid BH<sup>+</sup></b>
<b>0</b>	-653.1	-774.1	-699.7	-779.8
<b>10</b>	-682.4	-788.1	-724.4	-783.6
<b>20</b>	-701.7	-797.2	-748.2	-783.8
<b>30</b>	-711.6	-798.9	-764	-784.1
<b>40</b>	-719.5	-799.1	-766	-783.4
<b>50</b>	-727.4	-799.1	-765.4	--
<b>60</b>	-734.8	-798.9	-764.9	--



**Figure 4.5. Reduction Potentials vs. Time  
(Carrier Fluid R, R<sup>+</sup>, BH, BH<sup>+</sup>)**

### 4.3 Leuco Reduction Potential of Vat Dye and its Stability

As stated in section 2.3.2, the leuco reduction potential of vat dyes lies between -650 mV and -1000 mV. Moreover, the stability of reduced dyes is critical in all experiments and can be assessed by the leuco reduction potential change over a period of time.

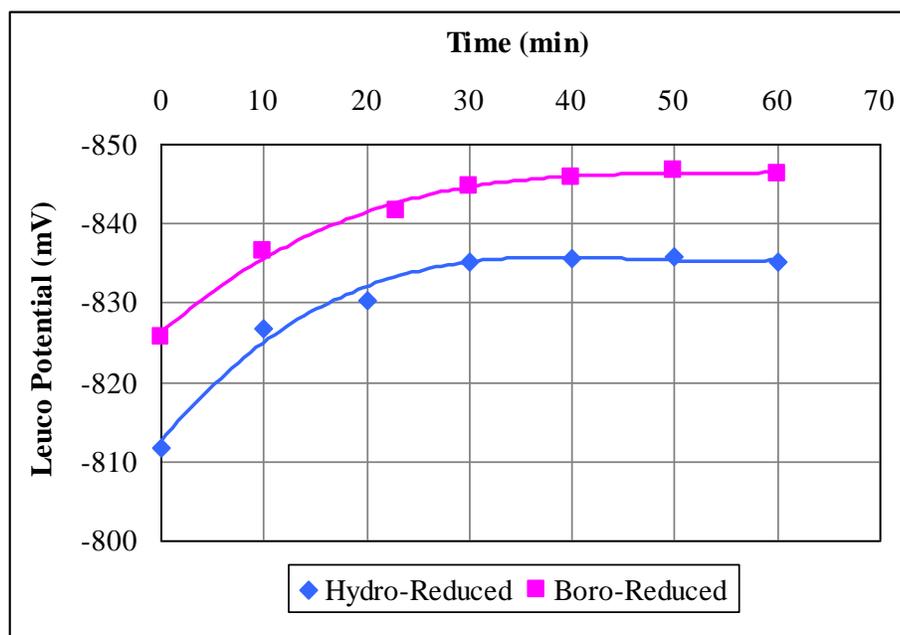
#### 4.3.1 Azul Indanthren CLF

Table 4.2 and Figure 4.6 show a comparison of the leuco reduction potentials of Azul Indanthren CLF when reduced with hydro and borohydride. The steady state values differ by

less than 2%. The graph shows that both the hydro and borohydride reduction methods are stable in the absence of air and give similar results.

**Table 4.2. Leuco Reduction Potentials of 2.0 g/L of Azul Indanthren CLF**

Time (min)	Leuco Reduction Potential (mV)	
	Hydro-Reduced	Boro-Reduced
0	-811.8	-825.7
10	-826.7	-836.4
20	-830.4	--
23	--	-841.6
30	-835.2	-844.7
40	-835.7	-845.9
50	-835.8	-846.6
60	-835.1	-846.2



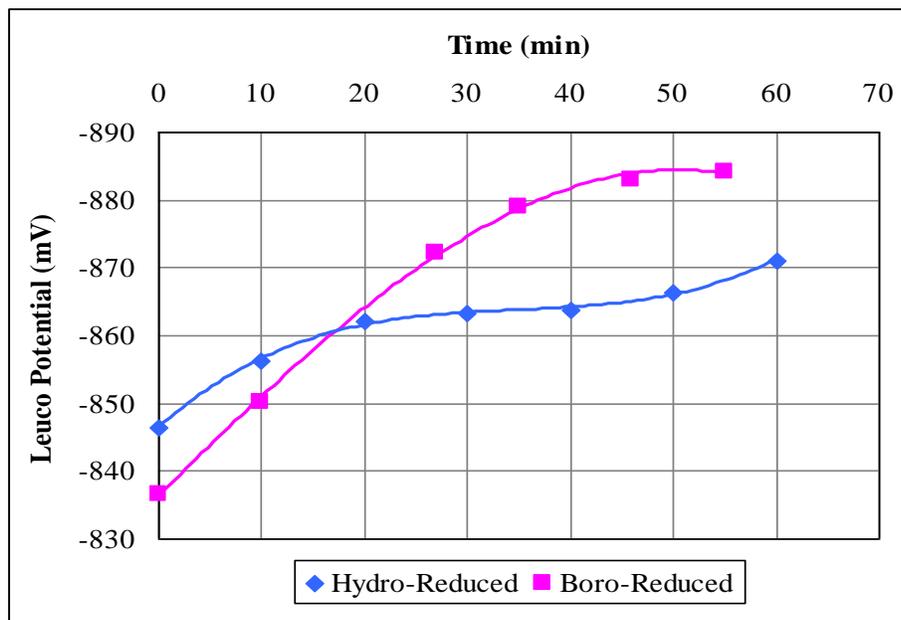
**Figure 4.6. Leuco Reduction Potentials vs. Time (Azul Indanthren CLF at 2.0 g/L)**

### 4.3.2 Rojo Novasol 2B MD

Table 4.3 and Figure 4.7 show a comparison of the leuco reduction potentials of the Red Novasol 2B MD when reduced with hydro and borohydride. The steady state values differ by less than 2% and the steady state values are in the range of -865 to -885 mV. The graph shows that both the hydro and borohydride reduction methods are stable in the absence of air and give similar results.

**Table 4.3. Leuco Reduction Potentials of 2.0 g/L of Rojo Novasol 2B MD**

<b>Leuco Reduction Potential (mV)</b>			
<b>Time (min)</b>	<b>Hydro-Reduced</b>	<b>Boro-Reduced</b>	<b>Time (min)</b>
0	-846.4	-836.5	0
10	-856.2	-850.2	10
20	-862.0	-872.2	27
30	-863.3	-879.0	35
40	-863.7	-882.9	46
50	-866.4	-884.2	55
60	-871.0	--	--



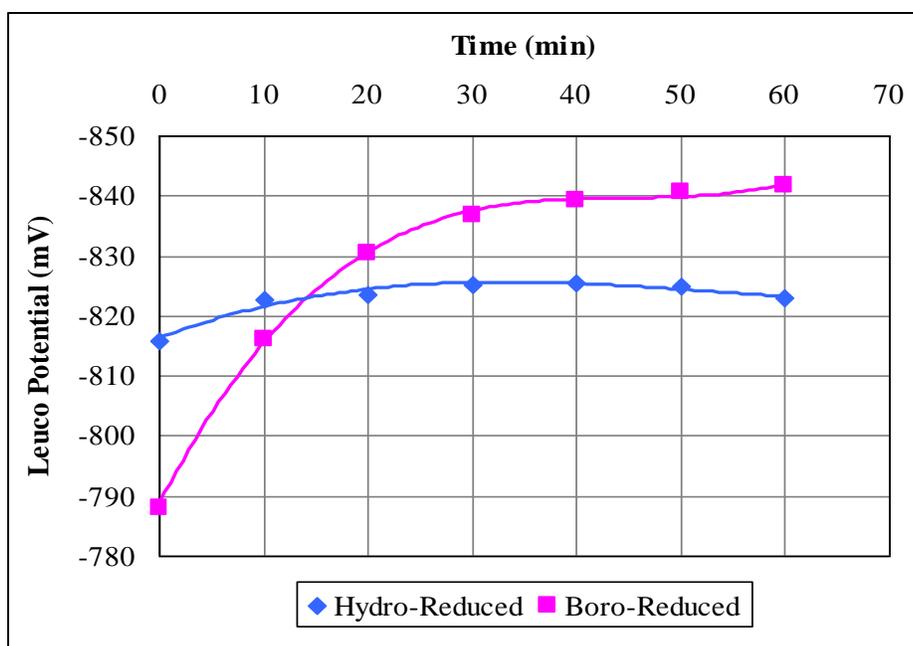
**Figure 4.7. Leuco Reduction Potentials vs. Time  
(Rojo Novasol 2B MD at 2.0 g/L)**

### 4.3.3 Violeta Benzathren 2R ESP

Table 4.4 and Figure 4.8 show a comparison of the leuco reduction potentials of the Violet Benzathren 2R ESP when reduced with hydro and borohydride. The steady state values differ by less than 2.5% and the steady state values are in the range of -822 to -840 mV. The graph shows that both the hydro and borohydride reduction methods are stable in the absence of air and give similar results. The data seems to suggest that it takes about 30 minutes for the Violet to be fully reduced and reach a steady state ORP value when reduced with the borohydride.

**Table 4.4. Leuco Reduction Potentials of 2.0 g/L of Violeta Benzathren 2R ESP**

Time/min	Leuco Reduction Potential (mV)	
	Hydro-Reduced	Boro-Reduced
0	-815.8	-788.1
10	-822.7	-816.1
20	-823.5	-830.3
30	-825.3	-836.9
40	-825.5	-839.2
50	-824.8	-840.6
60	-822.9	-841.6



**Figure 4.8. Leuco Reduction Potentials vs. Time (Violeta Benzathren 2R ESP at 2.0 g/L)**

#### 4.4 Calibration Results

Three vat dyes were calibrated individually in the unreduced, hydro-reduced and boro-reduced forms. The calibration model constructed for the vat dyes is based on the Beer-Lambert Law given in Equation 2. Some additional calibration information is included in Appendices, including the calibration summary of the predicted concentration against the actual concentration and calibration spectra.

##### 4.4.1 Calibration Results - Azul Indanthren CLF

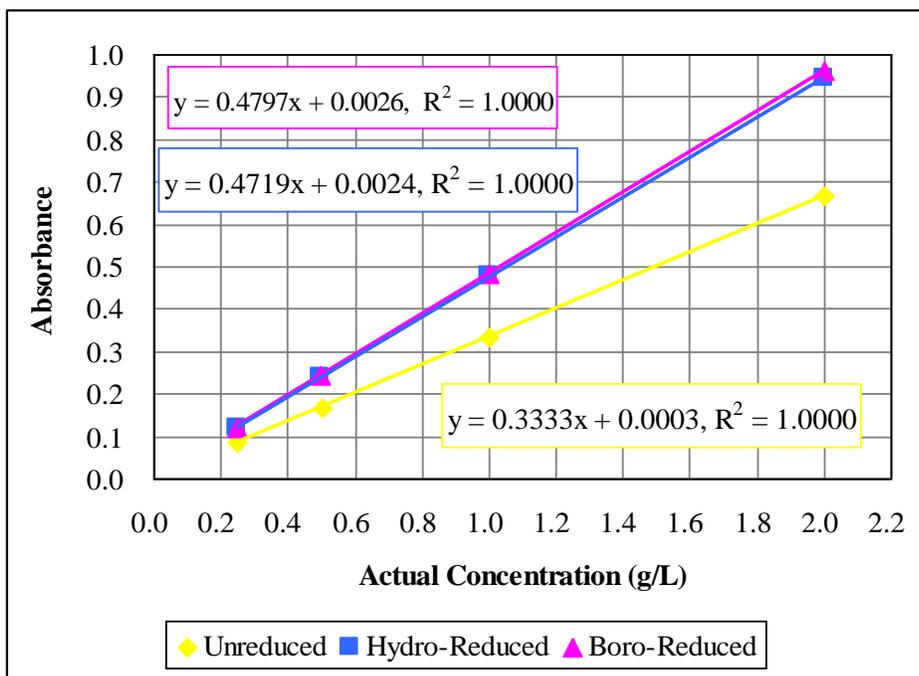
The calibration results of unreduced state shown in Figure 4.9 were plotted at 380 nm, the wavelength of maximum absorbance. In the reduced state, the absorbance spectrum shifted to a  $\lambda_{\text{max}}$  value of approximately 466 nm, followed by a color change from bright blue to black green.

In Figure 4.9, three calibration models were developed for the blue dye. Correlation coefficients ( $R^2$ ) for the models are 1.0000, suggesting good linearity of absorbance against actual concentration for three blue dye forms. A perfect model would have a y-intercept of 0. In this case, y-intercepts vary from 0.0003 to 0.0026 AU, which are quite close to 0. There is a noticeable difference in the slopes between the reduced and the unreduced dye. The larger the slope, the more sensitive the relationship between absorbance and concentration. For all the cases studied, the reduced dyes had a larger slope than the unreduced dye suggesting a way to approximate the reductive strength of the dyebath. Generally the absorbance curves of boro-reduced blue were slightly above those of the hydro-reduced blue. It is possible that the 1.2%

difference in leuco reduction potential could contribute to the small difference in the reduction of blue dye.

**Table 4.5. Absorbance of Azul Indanthren CLF**

<b>Dye</b>		<b>Azul Indanthren CLF</b>		
		<b><math>\lambda</math> (nm)</b>	380	467
<b>Actual Concentration (g/L)</b>		<b>Absorbance at <math>\lambda</math></b>		
		<b>Unreduced</b>	<b>Hydro-Reduced</b>	<b>Boro-Reduced</b>
0.2502	0.2500	0.0853	0.1182	0.1217
		0.0847	0.1175	0.1215
		0.0854	0.1174	0.1216
		0.0820		
0.5005	0.5000	0.1653	0.2392	0.2426
		0.1667	0.2383	0.2417
		0.1665	0.2388	0.2420
1.0010	1.0000	0.3340	0.4769	0.4836
		0.3329	0.4798	0.4838
		0.3343	0.4778	0.4835
			0.4779	
2.0020	2.0000	0.6679	0.9450	0.9614
		0.6657	0.9472	0.9621
		0.6666	0.9495	



**Figure 4.9. Absorbance vs. Actual Concentration of Azul Indanthren CLF**

#### 4.4.2 Calibration Results – Rojo Novasol 2B MD

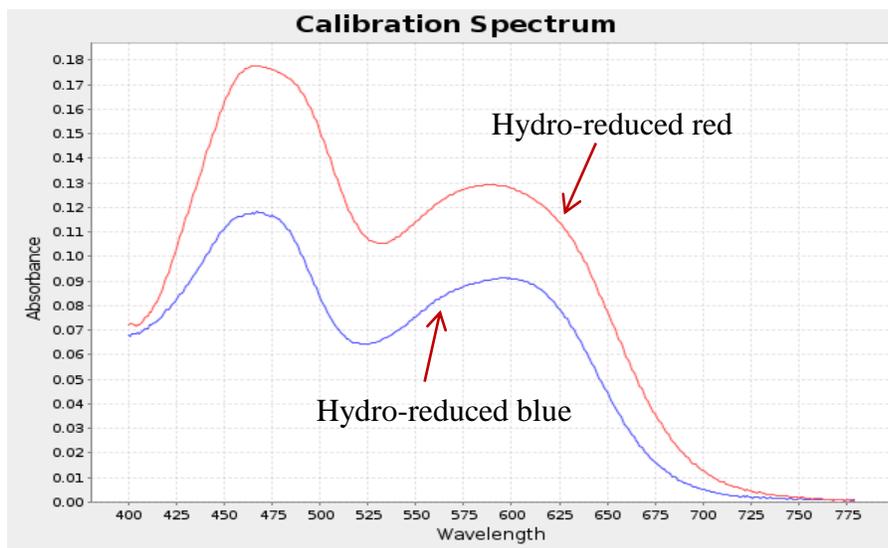
As shown in Table 4.6, the red dye has a  $\lambda_{\max}$  of 529 nm in the unreduced form, and 466 nm in reduced form which is coincidentally the same as that of the reduced blue. Of greater interest is the absorbance spectrum of the reduced blue and the reduced red dyes which appear to be almost identical, as shown in Figure 4.10. The original red color of the dye was changed to black green due to reduction. The similar absorbance spectra might cause the difficulties in dye mixture prediction since the system determines the dye concentrations of mixtures based on the Beer-Lambert Law, as well as spectral additivity of an individual dye spectrum.

In Figure 4.11, three calibration models were constructed for the red dye. The correlation

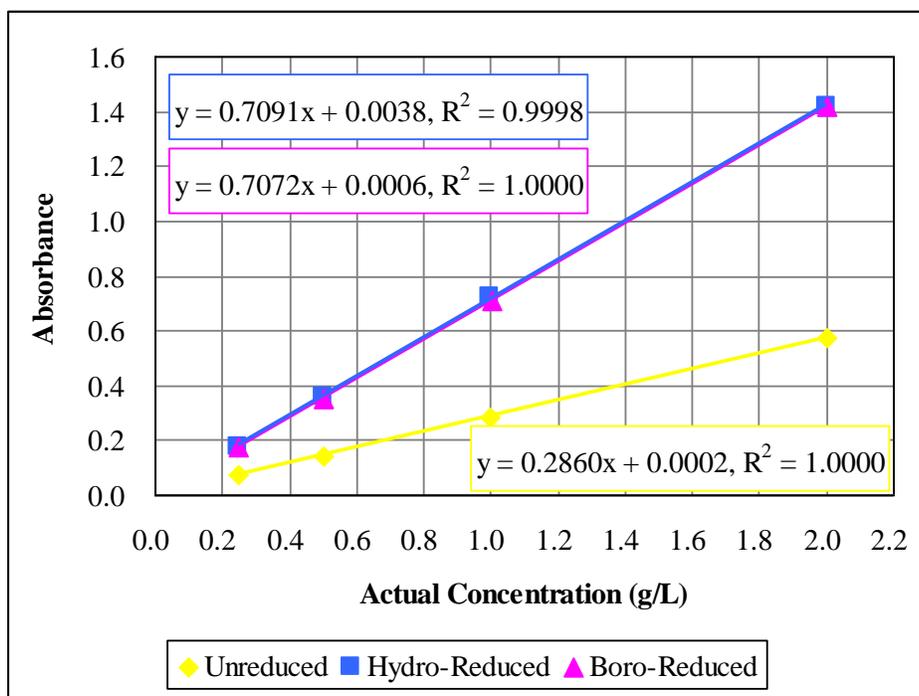
coefficients of 0.9998, 1.0000 and 1.0000, show excellent agreement with Beer's Law. The y-intercepts of 0.0038, 0.0006 and 0.0002 are also quite close to 0. The slopes of the hydro-reduced and boro-reduced calibration curves are also almost the same, which correlates with the ORP measurements which differed by less than 1.5%. This can be attributed to the characteristics of C.I. Vat Red 10, which only requires a medium amount of reducing agent for vatting, and excess amounts of reducing solution would not further reduce the red dye.

**Table 4.6. Absorbance of Rojo Novasol 2B MD**

Dye		Rojo Novasol 2B MD		
		$\lambda$ (nm)	529	466
Actual Concentration (g/L)		Absorbance at $\lambda$		
		Unreduced	Hydro-Reduced	Boro-Reduced
0.2501	0.2502	0.0711	0.1778	0.1761
		0.0712	0.1772	0.1772
		0.0711	0.1784	0.1771
0.5002	0.5004	0.1436	0.3557	0.3541
		0.1438	0.3554	0.3560
		0.1432	0.3563	0.3549
				0.3546
1.0004	1.0008	0.2868	0.7233	0.7112
		0.2871	0.7246	0.7109
		0.2868	0.7231	0.7127
			0.7241	
2.0008	2.0016	0.5721	1.4187	1.4148
		0.5720	1.4175	1.4163
		0.5717	1.4185	



**Figure 4.10. Calibration Spectrum Comparison between Hydro-Reduced Red and Hydro-Reduced Blue at 0.25 g/L**



**Figure 4.11. Absorbance vs. Actual Concentration of Rojo Novasol 2B MD**

#### 4.4.3 Calibration Results – Violeta Benzathren 2R ESP

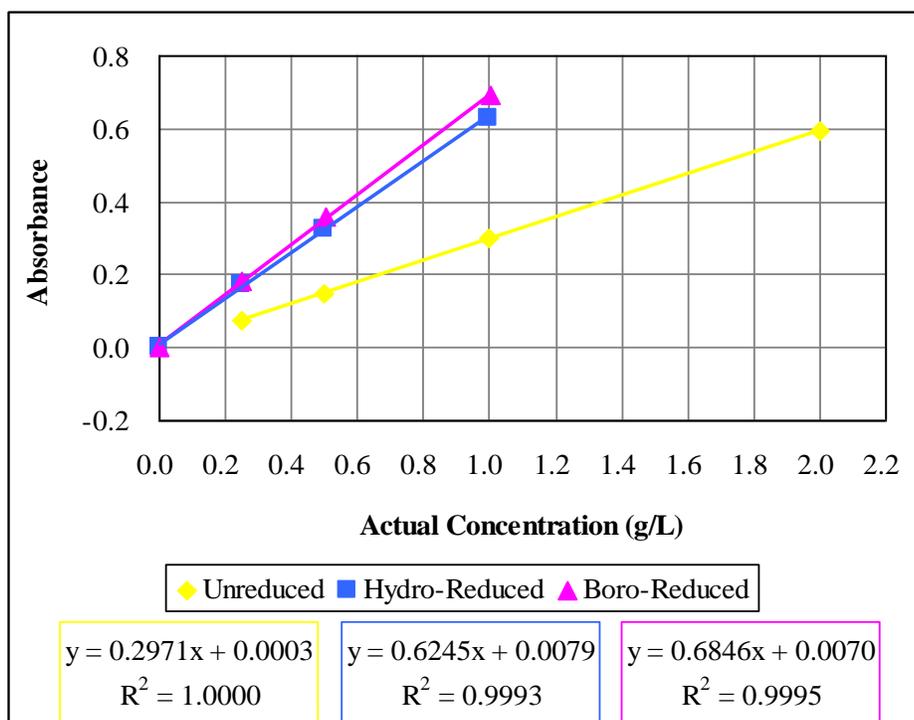
As shown in Table 4.7, the  $\lambda_{\max}$  of the unreduced violet dye shifted from 534 nm to 654 nm in the reduced form, resulting in a color change from bluish violet to deep blue. As plotted in Figure 4.12, the calibration models showed a strong linear relationship between the dye concentration and the measured absorbance, with nearly zero y-intercept values. Nevertheless, the slopes of the reduced violet had a noticeable difference of 0.0601, which suggests that the violet dye was slightly more reduced by the borohydride reduction system.

**Table 4.7. Absorbance of Violeta Benzathren 2R ESP**

Dye		Violeta Benzathren 2R ESP		
$\lambda$ (nm)		534	654	654
Actual Concentration (g/L)		Absorbance at $\lambda$		
		Unreduced	Hydro-Reduced	Boro-Reduced
0.0000			0.0000	-0.0001
			-0.0001	-0.0002
			0.0002	0.0001
0.2500	0.2510	0.0739	0.1713	0.1846
		0.0749	0.1684	0.1846
		0.0750	0.1680	0.1845
				0.1844
0.5000	0.5021	0.1489	0.3252	0.3564
		0.1486	0.3277	0.3600
		0.1486	0.3251	0.3591
				0.3603
1.0000	1.0042	0.2984	0.6281	0.6902
		0.2991	0.6275	0.6895
		0.2991	0.6248	0.6933
				0.6911
2.0000	---	0.5940		
		0.5953		

Table 4.7. Continued

2.0000	--	0.5952		
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**Figure 4.12. Absorbance vs. Actual Concentration of Violeta Benzathren 2R ESP**

#### 4.5 Dye Prediction

A series of statistical analysis based on the dye prediction errors were conducted to evaluate the accuracy of the system, as well as the effect of the two reduction systems. Dye prediction errors were calculated by Equation 3, and accordingly the mean error and the standard

deviation of the dye prediction error were also computed for each of vat dyes in the unreduced, hydro-reduced and boro-reduced forms.

$$\text{Dye Prediction Error} = \text{Actual Concentration} - \text{Measured Concentration, (g/L)} \quad (3)$$

Ideally, the mean error and the standard deviation should be close to zero, indicating that the measured concentrations are exactly consistent with the actual concentrations. For most dyes and practical applications, an error of within 0.01 g/L is acceptable and visually difficult to discern. In addition, the statistical t-test was used to determine if the three sets of error (unreduced, hydro-reduced and boro-reduced) were significantly different from each other.

#### **4.5.1 Azul Indanthren CLF**

##### **4.5.1.1 Results of Dye Prediction - Azul Indanthren CLF**

The measured concentrations, tabulated to three significant figures, are given in Table 4.8. In the Actual Concentration column, the leftmost column represents the unreduced blue dye solutions that were made up to 0.2502, 0.5005, 1.0010 and 2.0020 g/L, while the rightmost column represents both of the hydro-reduced and boro-reduced blue dye concentrations that were 0.2500, 0.5000, 1.000 and 2.000 g/L.

##### **4.5.1.2 Statistical Analysis - Azul Indanthren CLF**

Table 4.9 shows the statistical results of dye prediction error. The unreduced blue dye has the lowest mean error with the lowest standard deviation. The hydro-reduced blue has a medium

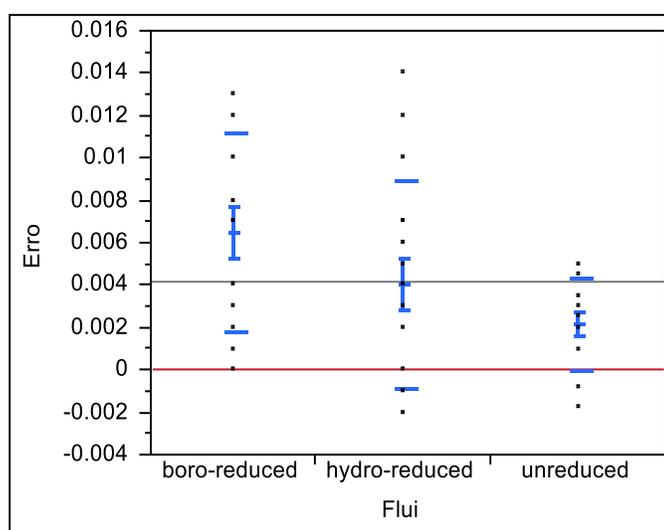
mean error with the highest standard deviation, whereas the mean error of the boro-reduced blue is approximately three times greater than that of the unreduced blue, and its standard deviation is two times larger, similar to results for the hydro-reduced solution. As shown in Figure 4.13, the unreduced blue has errors within 0.004, indicating that the predicted concentrations are in agreement with the actual concentrations, while almost all of the error of the boro-reduced and the hydro-reduced blue are on the high side, and a small number of them are outside the acceptable error range of 0.01.

**Table 4.8. Dye Prediction of Azul Indanthren CLF**

Actual Concentration (g/L)		Predicted Concentration (g/L)		
		Unreduced	Hydro-Reduced	Boro-Reduced
0.2502	0.2500	0.251	0.251	0.248
		0.252	0.252	0.247
		0.251	0.250	0.249
		0.251	0.247	0.250
0.5005	0.5000	0.498	0.502	0.496
		0.496	0.498	0.498
		0.496	0.497	0.497
		0.496	0.496	
		0.497		
1.0010	1.0000	0.998	0.993	0.987
		0.999	0.995	0.988
		0.998	0.994	0.988
			1.001	0.992
2.0020	2.0000	1.997	1.990	1.993
		2.001	1.988	1.993
		2.000	1.986	1.990
		1.999	1.996	1.987

**Table 4.9. Dye Prediction Error of Azul Indanthren CLF**

<b>Azul Indanthren CLF</b>	<b>Mean Error</b>	<b>Standard Deviation</b>
Unreduced	0.002144	0.002189
Hydro-Reduced	0.004000	0.004885
Boro-Reduced	0.006467	0.004658

**Figure 4.13. Mean Errors and Std. Deviations of Azul Indanthren CLF**

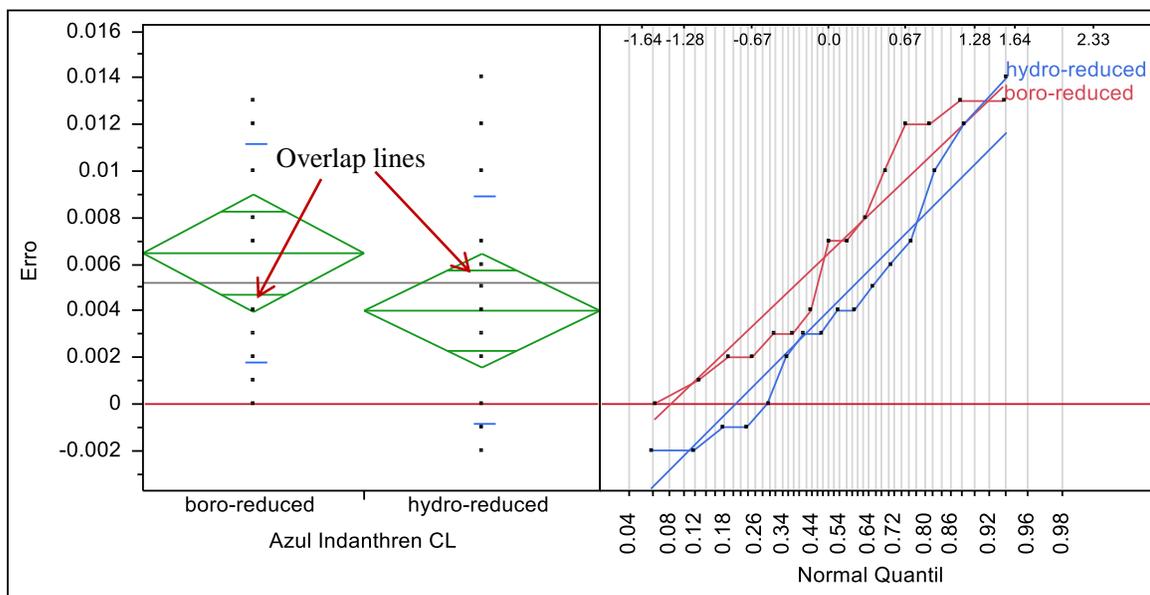
To further investigate whether there is a significant difference between the mean errors of hydro-reduced (group 1) and boro-reduced (group 2) blue dye values, a two sample t-test was conducted to compare these two independent groups. The hypothesis being tested is:

$$H_0: \mu_1 = \mu_2 \text{ versus } H_a: \mu_1 \neq \mu_2$$

Two assumptions of the two sample t-test were evaluated:

1) The sample means are normally distributed for each population. In Figure 4.14, the data

points for each group follow the reference line for that group. Therefore, sample errors are normally distributed for each population.



**Figure 4.14. One way Analysis of Dye Prediction Error – Azul Indanthren CLF**

2) The variance for group 1 equals the variance for group 2. The normal quantile plot can also be used to validate whether or not the variances for the two groups are equal. The slopes of the reference lines are proportional to the group standard deviation. As shown in Figure 4.14, the slopes are approximately parallel, so the group variances are approximately equal. To make a more reliable determination, a Levene Test was used. The p-value is given to be 0.7600, much greater than  $\alpha=0.05$ , thus we fail to reject the hypothesis. The variance for group 1 is statistically equal to the variance for group 2.

Assuming equal variances, a t-test was performed. Graphically, the means can be compared using the diamonds in Figure 4.14. The overlap lines intersect with the other triangle, implying the means are not significantly different. Additionally, looking into the results of the two sample t-test, a p-value of 0.1615 is greater than  $\alpha=0.05$ , thus we fail to reject the null hypothesis. There is not a significant difference between the mean errors of the hydro-reduced and boro-reduced blue dye predictions. Therefore, the two reduction systems based on sodium hydrosulfite and sodium borohydride appear to provide a comparable dye prediction performance and acceptable precision.

## **4.5.2 Rojo Novasol 2B MD**

### **4.5.2.1 Results of Dye Prediction - Rojo Novasol 2B MD**

In Table 4.10, the leftmost column of Actual Concentration represents unreduced and hydro-reduced red dye solutions that were made up to 0.2501, 0.5002, 1.0004 and 2.0008 g/L, while the rightmost column represents boro-reduced red solutions that were 0.2500, 0.5000, 1.0000 and 2.0000 g/L. As actual concentration increases, the error becomes more obvious, especially at 2.0000 g/L of reduced form. It appears to coincide with the formation of a vat skin on the surface of the reduced solution in contact with atmospheric oxygen. The human operation is therefore required to be highly accurate and careful, in particular, pipetting solutions to beaker, mixing gently and immediately injecting them to the system without any air bubbles, so as to avoid or minimize the reoxidation.

**Table 4.10. Dye Prediction of Rojo Novasol 2B MD**

Actual Concentration (g/L)		Predicted Concentration (g/L)		
		Unreduced	Hydro-Reduced	Boro-Reduced
0.2501	0.2500	0.250	0.247	0.250
		0.250	0.254	0.252
		0.250	0.249	0.254
			0.250	0.248
				0.248
				0.247
0.5002	0.5000	0.500	0.501	0.496
		0.500	0.502	0.499
		0.499	0.502	0.499
			0.503	0.500
				0.503
				0.502
1.0004	1.0000	0.999	0.990	0.986
		0.996	0.984	0.992
		0.996	0.993	1.002
		0.995	0.982	1.005
				1.005
				0.994
2.0008	2.0000	1.984	1.977	1.982
		1.983	1.965	1.986
		1.981		1.981
		1.979		2.005
				2.011
				2.014
				2.012

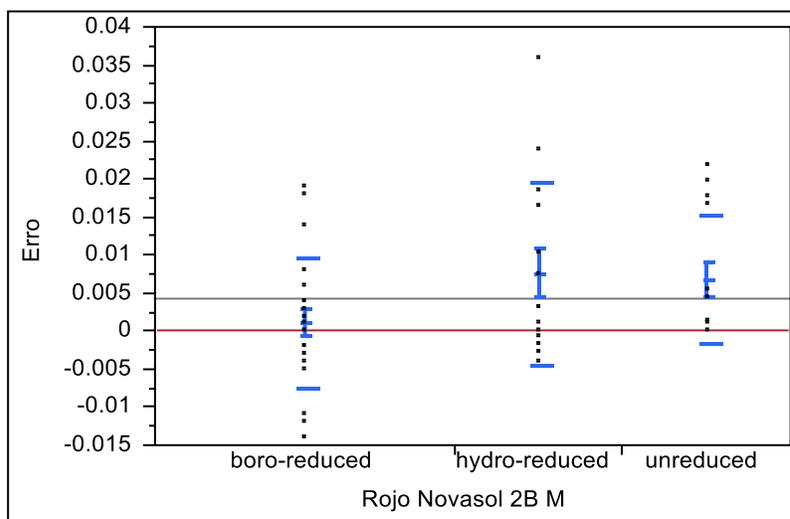
#### 4.5.2.2 Statistical Analysis - Rojo Novasol 2B MD

Table 4.11 and Figure 4.15 show the comparison of mean errors and standard deviations. For the three methods tested, the boro-reduced red dye has the smallest mean error and standard deviation, indicating the best dye prediction performance. Unreduced red dye data has a similar

standard deviation but a higher mean error. Hydro-reduced red dye data appears to have the highest mean error and standard deviation.

**Table 4.11. Dye Prediction Error of Rojo Novasol 2B MD**

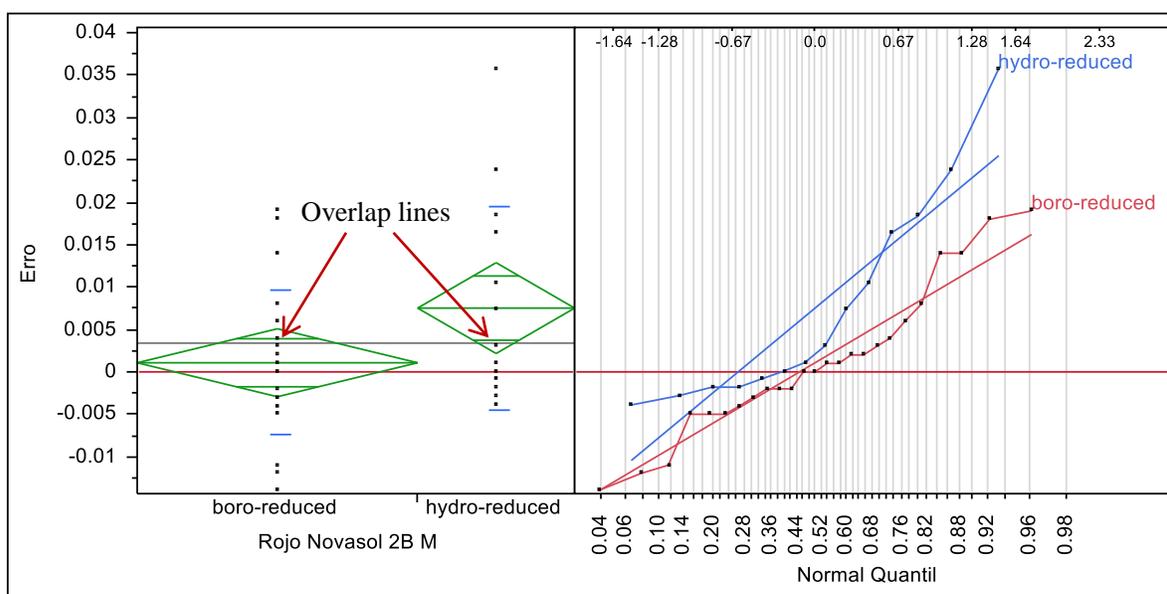
Rojo Novasol 2B MD	Mean Error	Standard Deviation
Unreduced	0.006693	0.008369
Hydro-Reduced	0.007529	0.011981
Boro-Reduced	0.001080	0.008553



**Figure 4.15. Mean Errors and Std. Deviations of Rojo Novasol 2B MD**

Same statistical two-sample mean t-test was used in the case of red dye prediction. As shown in Normal Quantile plot in Figure 4.16, the data points for each group follow the reference line for that group. Hence, sample mean are normally distributed for each population. The slopes of two reference lines intersect, which means the group variances are unequal. Consequently

assuming unequal variances, a t-test was conducted. Graphically, the overlap lines of the diamonds intersect with the other triangle, so the mean errors are not significantly different. Furthermore, the p-value is 0.0905, slightly greater than  $\alpha=0.05$ , thus we fail to reject the null hypothesis, and assume that statistically, the mean errors are the same.



**Figure 4.16. Oneway Analysis of Dye Prediction Error – Rojo Novasol 2B MD**

### 4.5.3 Violeta Benzathren 2R ESP

#### 4.5.3.1 Results of Dye Prediction – Violeta Benzathren 2R ESP

In Table 4.12, the leftmost column under Actual Concentration represents the unreduced and hydro-reduced violet dye solutions which were 0.2500, 0.5000, 1.0000 and 2.0000 g/L, and the rightmost column represents the actual concentrations of the boro-reduced violet solutions which were 0.2510, 0.5021, 1.0042 g/L.

**Table 4.12. Dye Prediction of Violeta Benzathren 2R ESP**

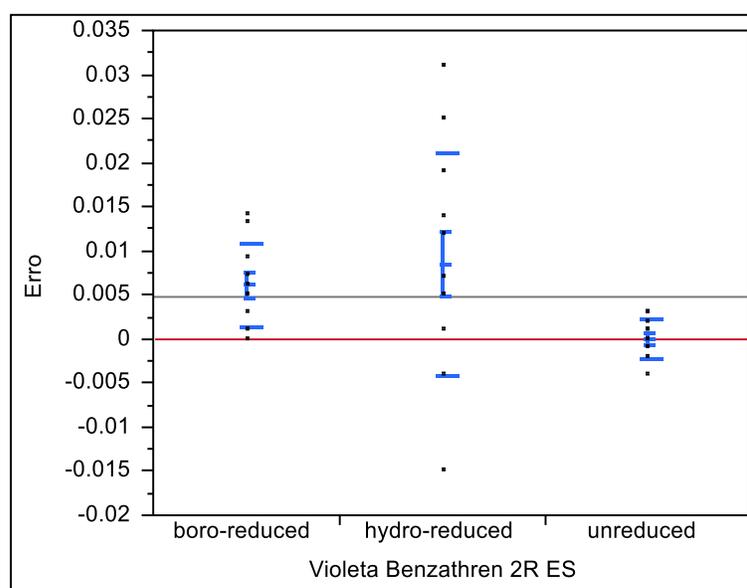
Actual Concentration (g/L)		Predicted Concentration (g/L)		
		Unreduced	Hydro-Reduced	Boro-Reduced
0.2500	0.2510	0.252	0.254	0.248
		0.251	0.245	0.250
		0.250	0.249	0.250
			0.245	0.251
0.5000	0.5021	0.501	0.486	0.497
		0.502	0.488	0.495
		0.499	0.475	0.496
			0.499	
1.0000	1.0042	0.998	0.969	0.995
		0.997	0.981	0.997
		1.004	1.015	0.991
			0.993	0.990
2.0000	--	1.999	--	--
		1.997		
		2.001		

#### 4.5.3.2 Statistical Analysis - Violeta Benzathren 2R ESP

From Table 4.13 and Figure 4.17, it appears that the mean error and standard deviation of the unreduced violet dye give the best predictions. Hydro-reduced violet has the highest mean error and standard deviation. This may partly be due to the fact that Violeta Benzathren is difficult to reduce and maintain in its leuco form. On the other hand, the boro-reduced violet has a medium mean error and small standard deviation, resulting in a good dye prediction measurement.

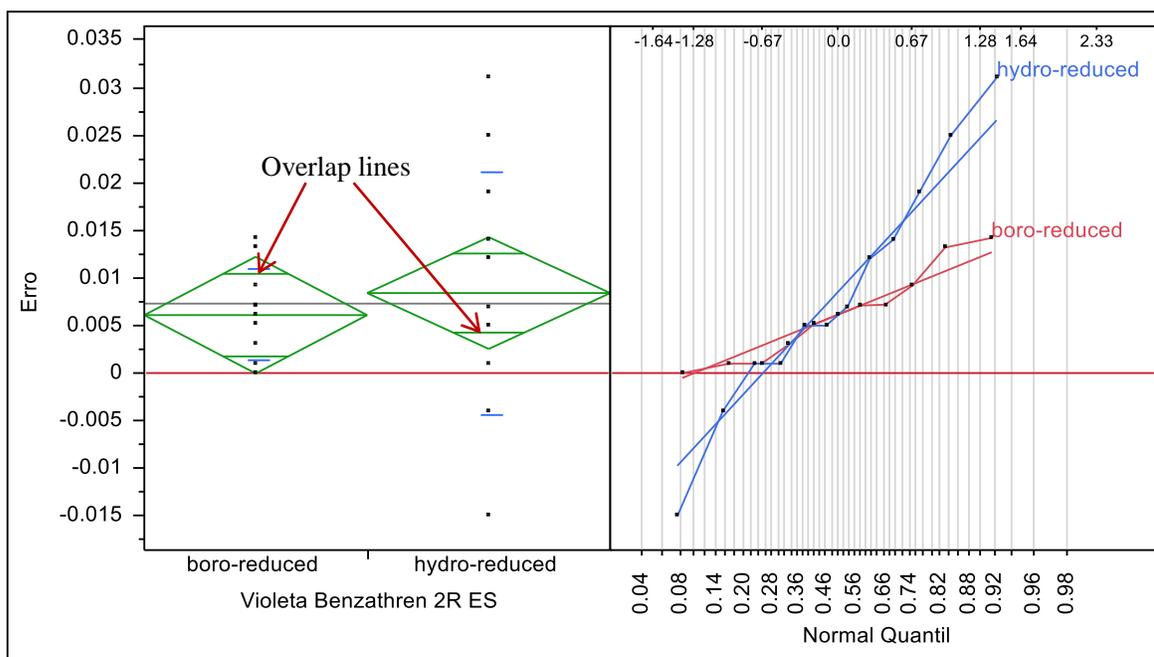
**Table 4.13. Dye Prediction Error of Violeta Benzathren 2R ESP**

<b>Violeta Benzathren 2R ESP</b>	<b>Mean Error</b>	<b>Standard Deviation</b>
Unreduced	-0.0000833	0.002151
Hydro-Reduced	0.00842	0.012717
Boro-Reduced	0.00610	0.004772

**Figure 4.17. Mean Errors and Std. Deviations of Violeta Benzathren 2R ESP**

Same statistical two-sample mean t-test was conducted in the case of violet dye prediction. As shown in Normal Quantile plot in Figure 4.18, the data points for each group follow the reference line for that group. Hence, sample mean are normally distributed for each population. The slopes of two reference lines intersect, which means the group variances are unequal. Therefore, assuming unequal variances, a t-test was conducted. Graphically, the overlap lines of the diamonds significantly intersect with the other triangle, so the mean errors are not

significantly different. Furthermore, the p-value is 0.5660 which is much greater than  $\alpha=0.05$ , thus we fail to reject the null hypothesis, and assume that the mean errors are statistically the same.



**Figure 4.18. Oneway Analysis of Dye Prediction Error – Violeta Benzathren 2R ESP**

#### 4.6 Dye Prediction of Dye Mixture Solutions

The measured concentrations for the mixture of blue and red dyes are tabulated in Tables 4.14, 4.15 and 4.16. The statistical results of the dye prediction errors of either blue or red in its mixture solution in unreduced, hydro-reduced and boro-reduced forms are also given in Table 4.17. The overall prediction performance is not better than the single dye prediction

performances, in particular, the boro-reduced and hydro-reduced dye mixture solutions result in some predictions being above 0.01 g/L with their mean errors being higher than those for the single dye case, as expected in Figure 4.10. In other word, similar absorbance spectra of vat dyes in the mixture tend to result in higher prediction error. Nevertheless, prediction errors are mostly within 0.01 g/L, indicating a feasibility of accurately measuring and predicting dye mixture concentrations.

**Table 4.14. Dye Prediction of Unreduced Dye Mixture Solution**

	<b>Azul Indanthren CLF</b>	<b>Rojo Novasol 2B MD</b>
<b>Actual Concentration (g/L)</b>	1.0010	1.0004
<b>Predicted Concentration (g/L)</b>	0.992	1.000
	0.990	0.998
	0.989	0.996

**Table 4.15. Dye Prediction of Boro-Reduced Dye Mixture Solution**

	<b>Azul Indanthren CLF</b>	<b>Rojo Novasol 2B MD</b>
<b>Actual Concentration (g/L)</b>	1.0020	1.0040
<b>Predicted Concentration (g/L)</b>	0.974	1.005
	0.981	1.007
	0.985	1.009
	0.988	1.008

**Table 4.16. Dye Prediction of Hydro-Reduced Dye Mixture Solution**

	<b>Azul Indanthren CLF</b>	<b>Rojo Novasol 2B MD</b>
<b>Actual Concentration (g/L)</b>	0.9980	1.0240
<b>Predicted Concentration (g/L)</b>	0.975	1.022
	0.990	1.021
	1.000	1.019
	0.985	0.996
	0.996	0.994

**Table 4.17. Dye Prediction Error of Dye Mixture Solutions**

<b>Mean Error</b>	<b>Unreduced</b>	<b>Boro-Reduced</b>	<b>Hydro-Reduced</b>
<b>Blue</b>	0.0107	0.0173	0.0088
<b>Red</b>	0.0024	-0.004	0.0136

## CHAPTER 5 CONCLUSIONS

The ability to accurately predict the concentration of vat dyes in both the reduced and unreduced forms was investigated. Based on the data, it is possible to use absorbance measurements to accurately predict the dye concentrations in unreduced mixtures of vat dyes to better than 0.01 g/L over a 0 to 2 g/L range, as such dispersions appear to follow the Beer-Lambert Law. However, in the presence of reducing agents such as sodium hydrosulfite or sodium borohydride, it is not possible to use a single calibration curve for the unreduced dye to predict the concentration of the dyes in the reduced form. For this reason, a new technique was developed which preconditions the dye into the reduced form before measurements. However, it was found that dyes with very different absorbance spectra in the unreduced form had almost identical absorbance spectra in the reduced form. By taking readings over the visible range from 400 to 780 nm, it was possible to resolve the dye concentrations of these dyes also to within 0.01 g/L. Such levels of accuracy are deemed necessary, as below 0.01 g/L it is difficult to discern visual color differences in the dyed fabric.

A comparison for two reducing methods was investigated. The reduced dye solutions, based on both the sodium hydrosulfite/NaOH and sodium borohydride/sodium metabisulfite reduction systems have been measured to have relatively steady leuco potentials which lie between -820 to -890 mV and which achieve steady state after about 30 minutes. Accordingly, the calibration models that were constructed for the reduced dyes showed a good linearity of absorbance to actual concentration. The dye prediction performance in all reduced cases

studied, including single dye solutions and dye mixture solutions, were within the acceptable levels with the average errors to within 0.01 g/L. Statistically, there was not a significant difference in the mean errors, and therefore both of reduction systems appeared to provide a comparable dye prediction performance.

It has been observed that as the actual concentration increased, especially at or above 2 g/L, the model tended to under-predict the actual dye concentrations, probably due to dye aggregation or re-oxidation of the leuco dyes. This may be circumvented by using stronger reducing agents to ensure that the dyes are fully reduced.

## CHAPTER 6 FUTURE WORK

The following areas are recommended for future work:

- (1) Previous experiments demonstrated the feasibility of determining the vat dye concentration for vat dyeing in the presence of sodium borohydride and sodium metabisulfite. However, just one set of concentration of this reduction system has been investigated. Thus, the reduction system of varying reducing levels should be produced and used for assessing reduction performance as well as vat dye concentration prediction performance.
- (2) The two vat dyes, Rojo Novasol 2B MD and Azul Indanthren CLF, used in preparing dye mixture solutions, have highly similar absorbance spectra, which resulted in higher prediction error than in the single dye case. Therefore, vat dyes of different absorbance spectra should be further employed in the dye mixture prediction and compared with single dye prediction performance.
- (3) Current experiments of the determination of dye concentration were done manually using HueMetrix Dye-It-Right™ system, which requires the injection of dye solution via syringe from the luer-lock syringe port of the instrument. Further experiment should be focused on the vat dyeing during which a dyebath sample is circulating in the circulation loop taken from the dyebath. The results should be then presented in real-time dye monitoring data for investigating the measurement of vat dye concentrations.

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**APPENDIX**

### Appendix A: Calibration Summary of Azul Indanthren CLF

**Table A.1. Calibration Summary of Azul Indanthren CLF**

<b>Dye</b>	<b>Azul Indanthren CLF</b>		
<b>Setting</b>	Default setting	Vat dye setting	Vat dye setting
<b>Fluid</b>	DI Water	R	BH
<b>Actual Concentration (g/L)</b>	<b>Predicted Concentration (g/L)</b>		
	<b>Unreduced</b>	<b>Hydro-Reduced</b>	<b>Boro-Reduced</b>
0.250	0.2504	0.2500	0.2496
	0.2497	0.2496	0.2502
	0.2512	0.2504	0.2502
	0.2495		
0.500	0.5002	0.5011	0.5014
	0.5006	0.4986	0.4994
	0.5007	0.5003	0.4993
1.000	1.0022	0.9951	1.0002
	1.0024	1.0048	1.0008
	1.0014	0.9986	1.0005
		1.0006	
2.000	2.0001	1.9904	2.0002
	2.0016	1.9943	2.0040
	2.0000	2.0068	

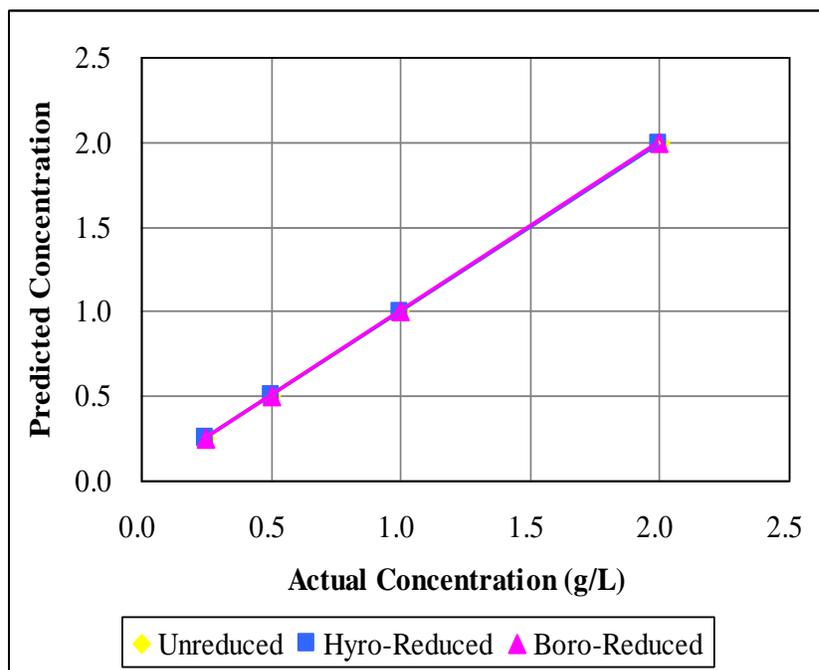


Figure A.1. Calibration Analysis of Azul Indanthren CLF

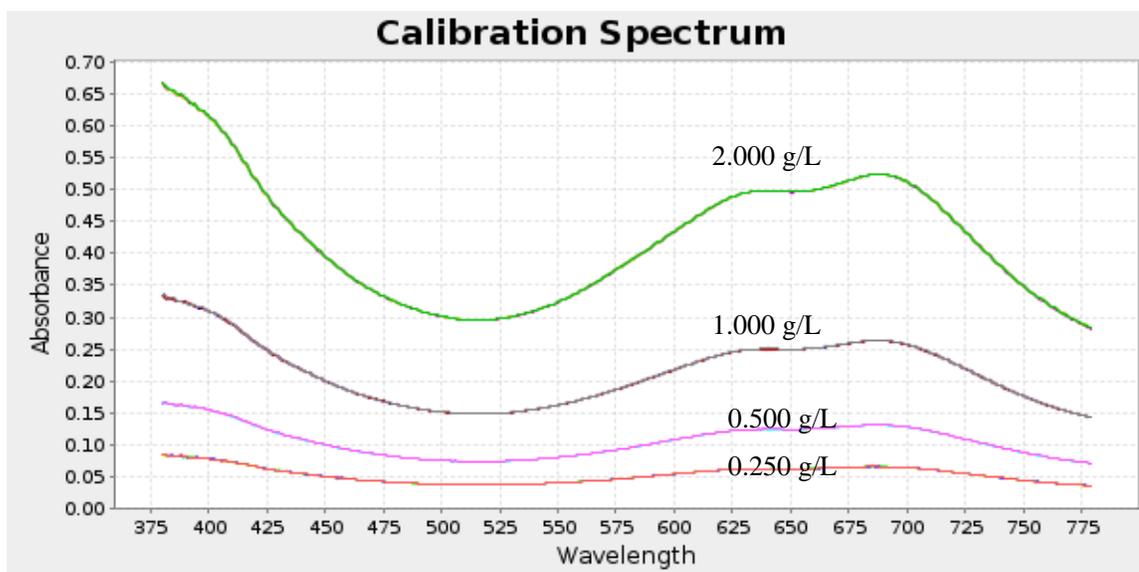
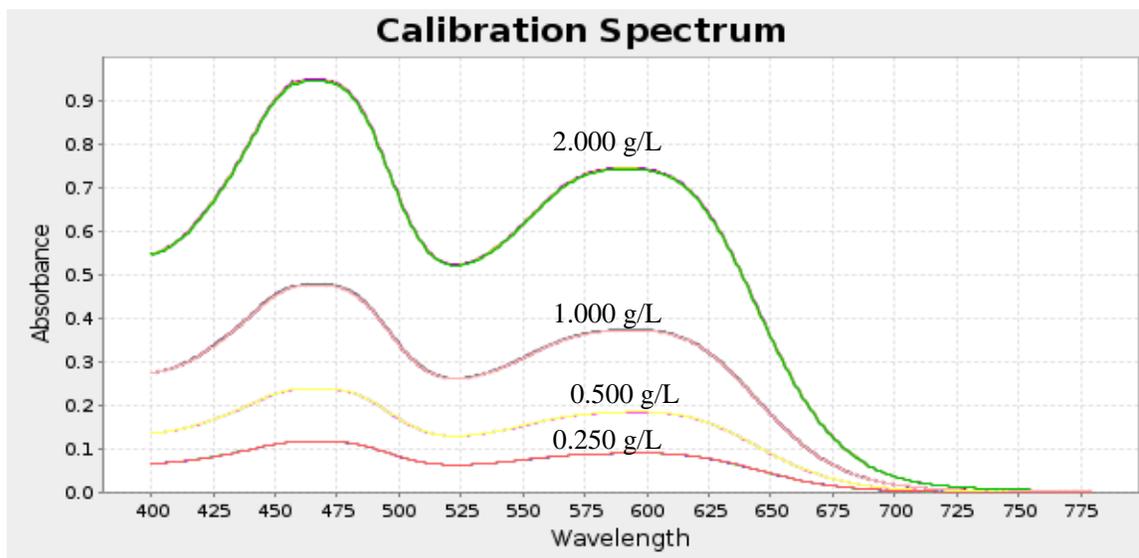
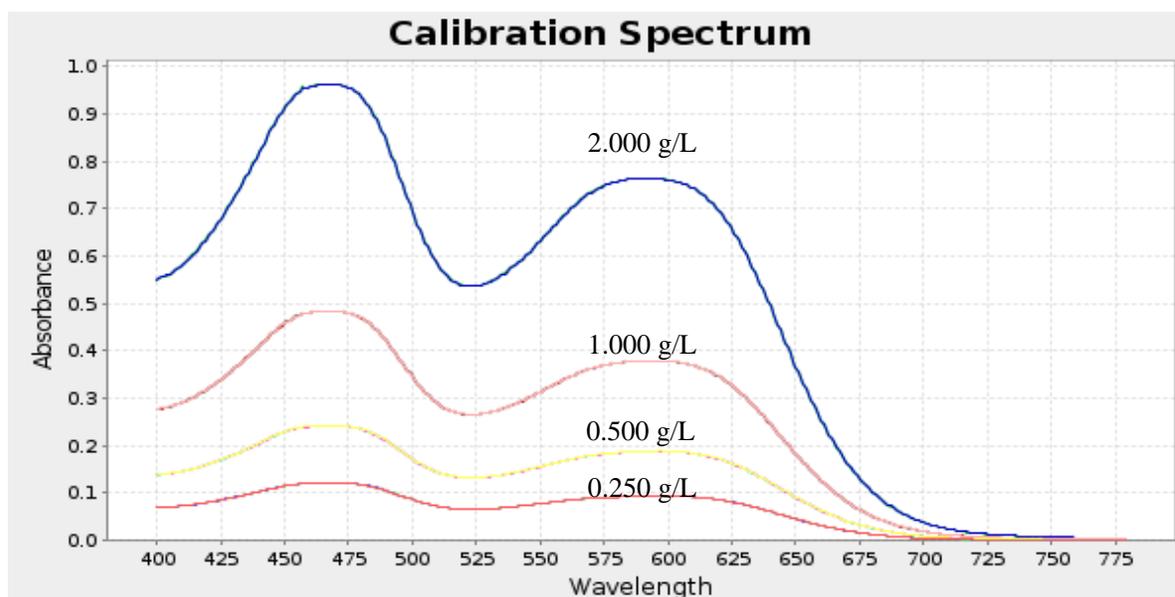


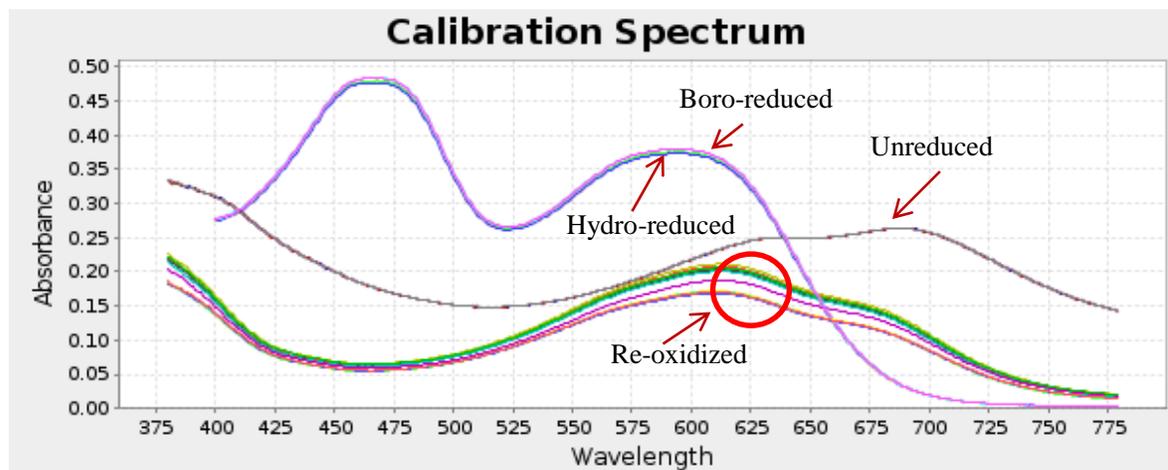
Figure A.2. Absorbance vs. Wavelength (Unreduced Azul Indanthren CLF)



**Figure A.3. Absorbance vs. Wavelength (Hydro-Reduced Azul Indanthren CLF)**



**Figure A.4. Absorbance vs. Wavelength (Boro-Reduced Azul Indanthren CLF)**

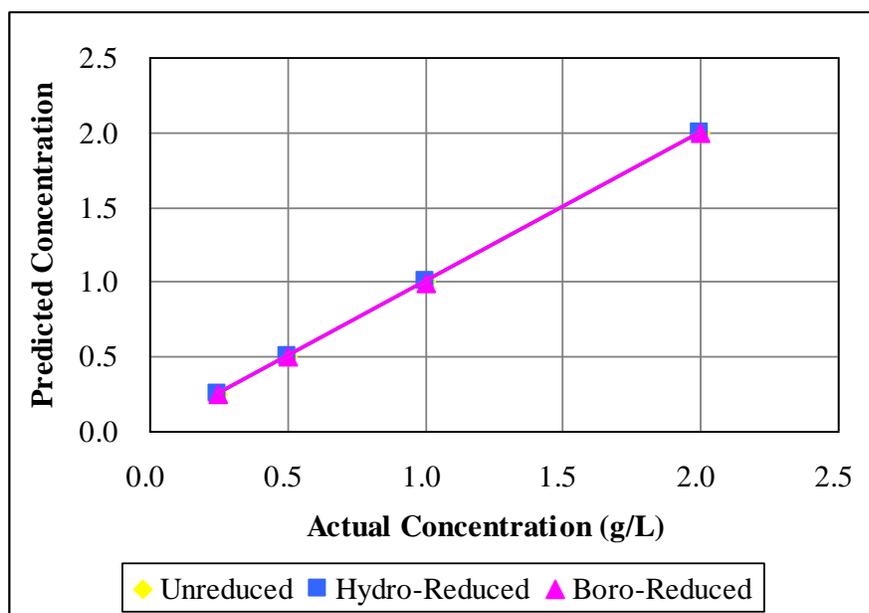


**Figure A.5. Comparison of Calibration Spectra between Boro-Reduced, Hydro-Reduced, Unreduced and Re-oxidized Azul Indanthren CLF at 1.0 g/L**

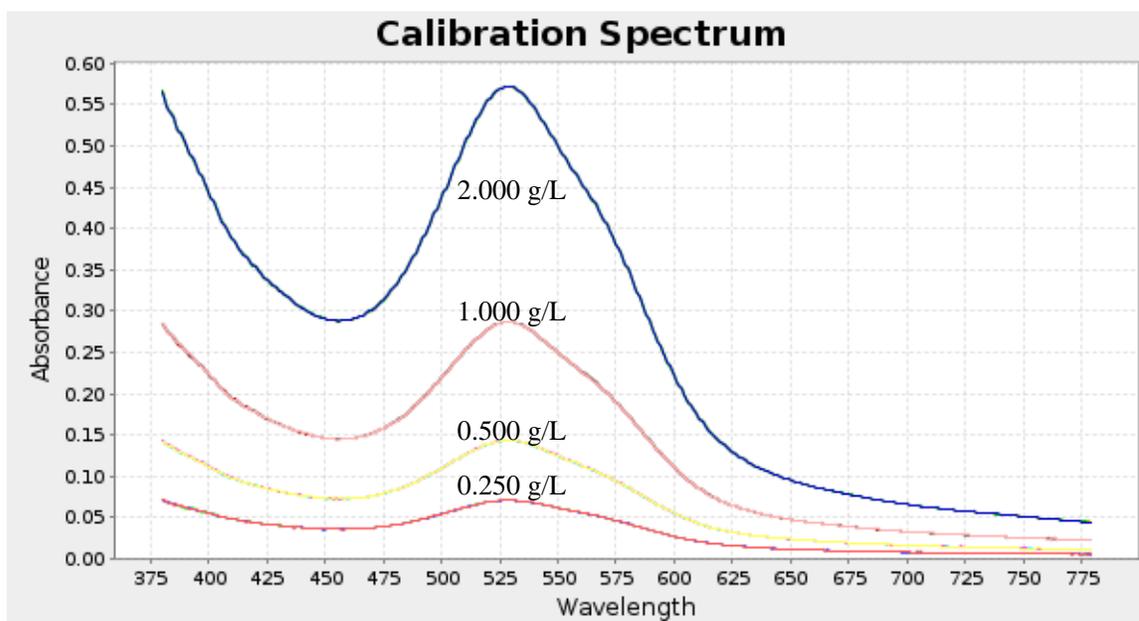
## Appendix B: Calibration Summary of Rojo Novasol 2B MD

**Table B.1. Calibration Summary of Rojo Novasol 2B MD**

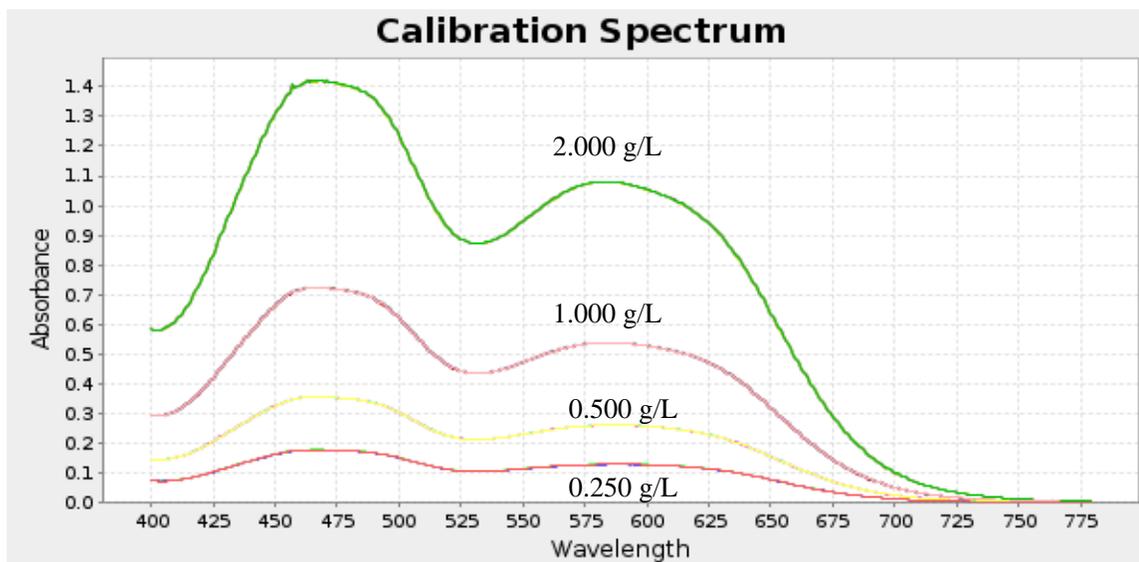
<b>Dye</b>	<b>Rojo Novasol 2B MD</b>		
<b>Setting</b>	Default setting	Vat dye setting	Vat dye setting
<b>Fluid</b>	DI Water	R	BH
<b>Actual Concentration (g/L)</b>	<b>Predicted Concentration (g/L)</b>		
	<b>Unreduced</b>	<b>Hydro-Reduced</b>	<b>Boro-Reduced</b>
0.250	0.2510	0.2500	0.2491
	0.2496	0.2490	0.2503
	0.2497	0.2514	0.2512
0.500	0.4995	0.4993	0.4990
	0.5023	0.4995	0.5023
	0.4987	0.5017	0.5008
			0.4995
1.000	1.0010	1.0017	0.9984
	0.9990	1.0031	1.0001
	0.9998	1.0003	1.0053
		1.0021	
2.000	1.9974	2.0013	1.9981
	1.9998	1.9979	2.0008
	2.0004	1.9991	



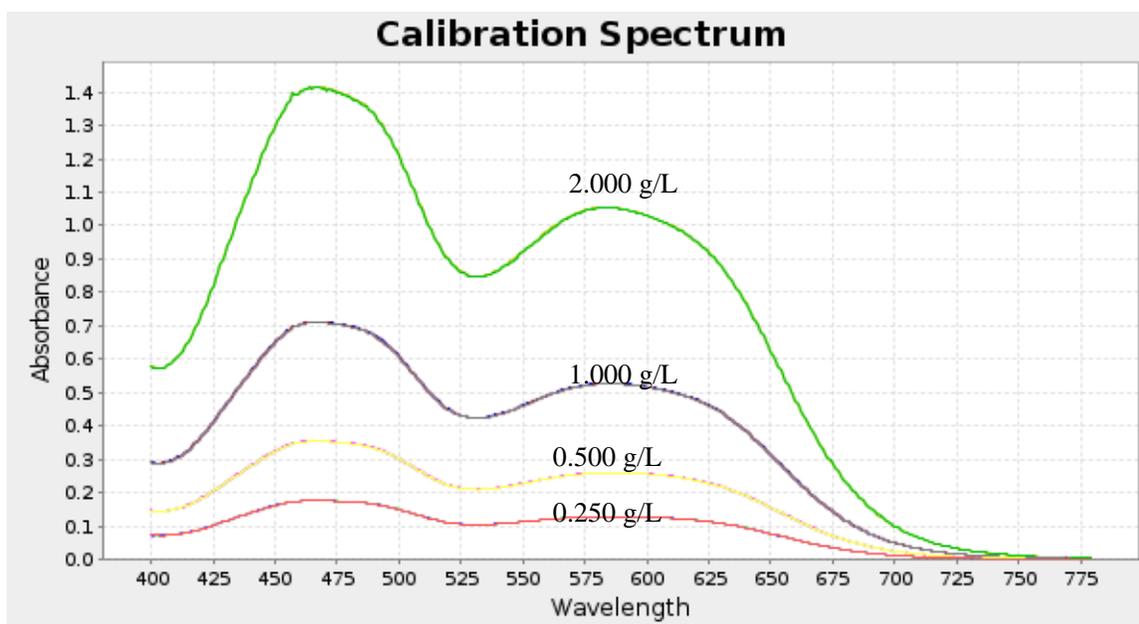
**Figure B.1. Calibration Analysis of Rojo Novasol 2B MD**



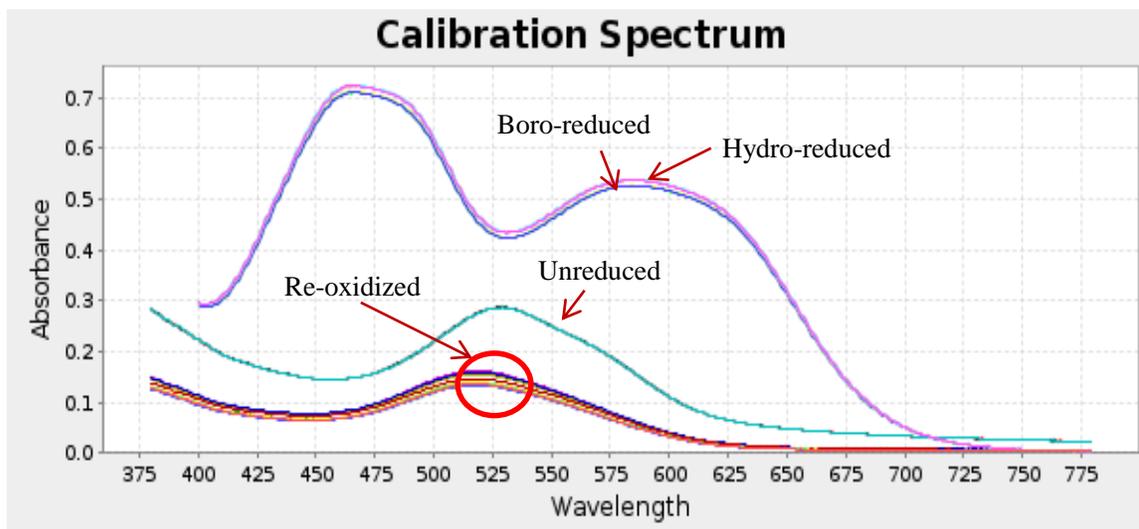
**Figure B.2. Absorbance vs. Wavelength (Unreduced Rojo Novasol 2B MD)**



**Figure B.3. Absorbance vs. Wavelength (Hydro-Reduced Rojo Novasol 2B MD)**



**Figure B.4. Absorbance vs. Wavelength (Boro-Reduced Rojo Novasol 2B MD)**



**Figure B.5. Comparison of Calibration Spectra between Hydro-Reduced, Boro-Reduced, Unreduced and Re-oxidized Rojo Novasol 2B MD at 1.0 g/L**

### Appendix C: Calibration Summary of Violeta Benzathren 2R ESP

**Table C.1. Calibration Summary of Violeta Benzathren 2R ESP**

<b>Dye</b>	<b>Violeta Benzathren 2R ESP</b>		
<b>Setting</b>	Default setting	Vat dye setting	Vat dye setting
<b>Fluid</b>	DI Water	R <sup>+</sup>	BH <sup>+</sup>
<b>Actual Concentration (g/L)</b>	<b>Predicted Concentration (g/L)</b>		
	<b>Unreduced</b>	<b>Hydro-Reduced</b>	<b>Boro-Reduced</b>
0.000		-0.0025	-0.0015
		-0.0024	-0.0015
		-0.0025	-0.0014
0.250	0.2478	0.2576	0.2532
	0.2544	0.2529	0.2533
	0.2480	0.2516	0.2523
			0.2522
0.500	0.5017	0.4951	0.4953
	0.4988	0.5021	0.5041
	0.4994	0.4954	0.5022
			0.5028
1.000	1.0023	0.9995	0.9986
	0.9996	0.9981	0.9987
	1.0003	0.9885	1.0085
			1.0014
2.000	2.0085		
	1.9992		
	1.9933		

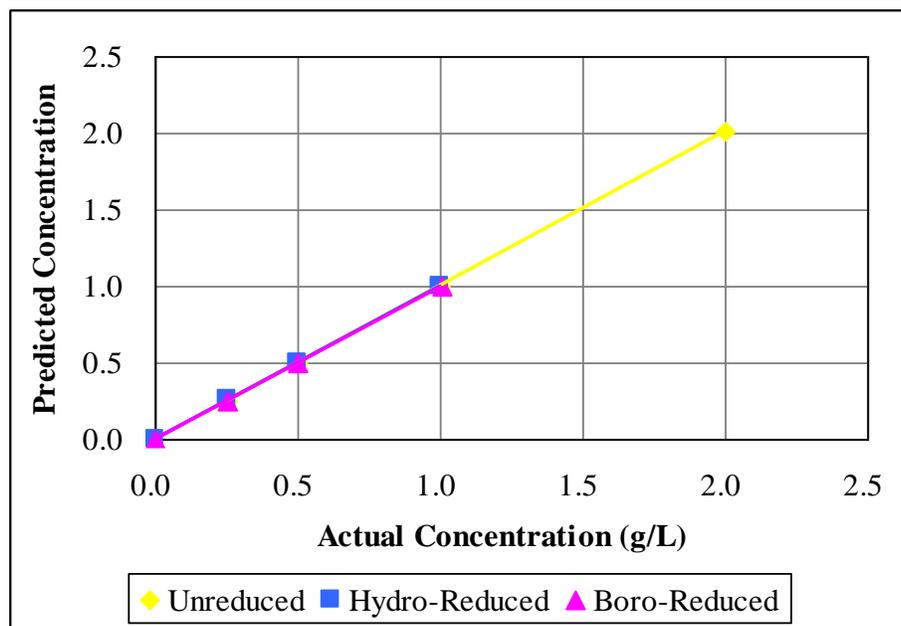


Figure C.1. Calibration Analysis of Violeta Benzathren 2R ESP

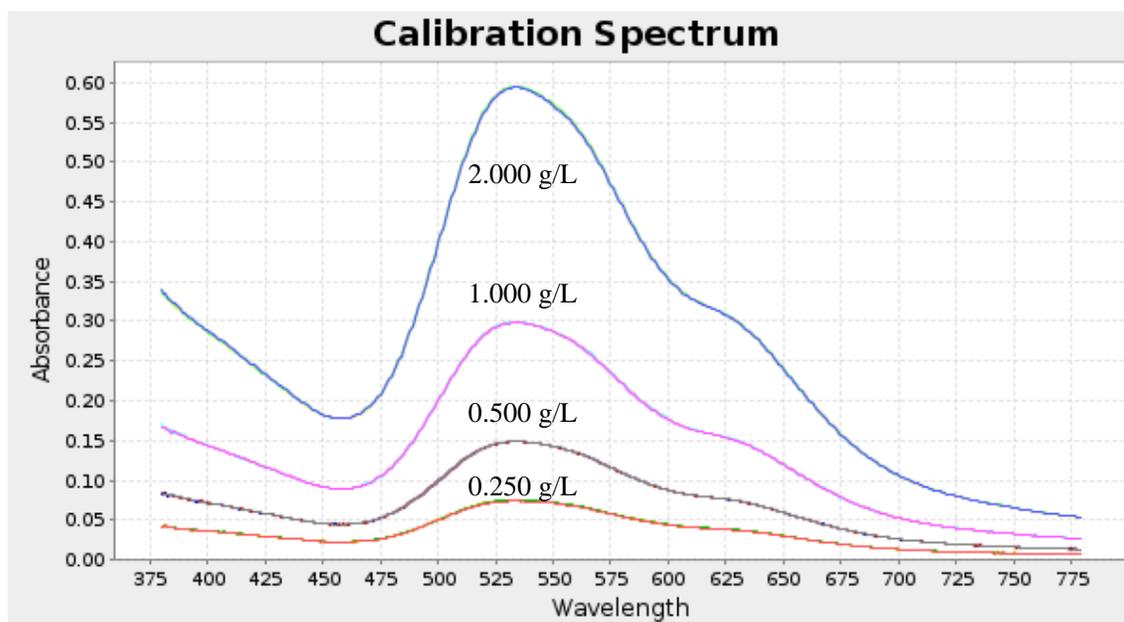


Figure C.2. Absorbance vs. Wavelength (Unreduced Violeta Benzathren 2R ESP)

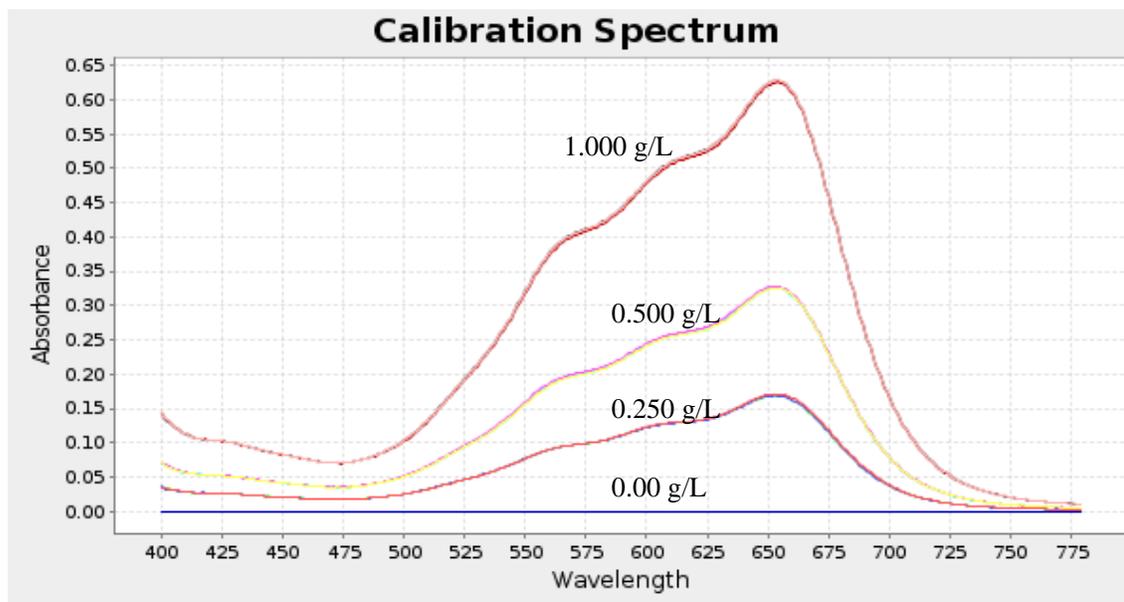


Figure C.3. Absorbance vs. Wavelength (Hydro-Reduced Violeta Benzathren 2R ESP)

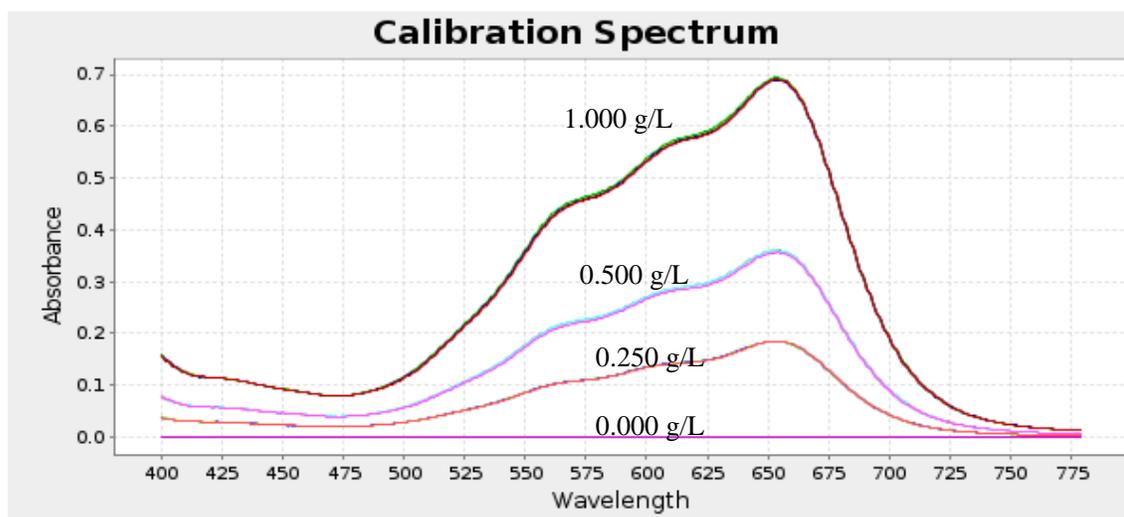
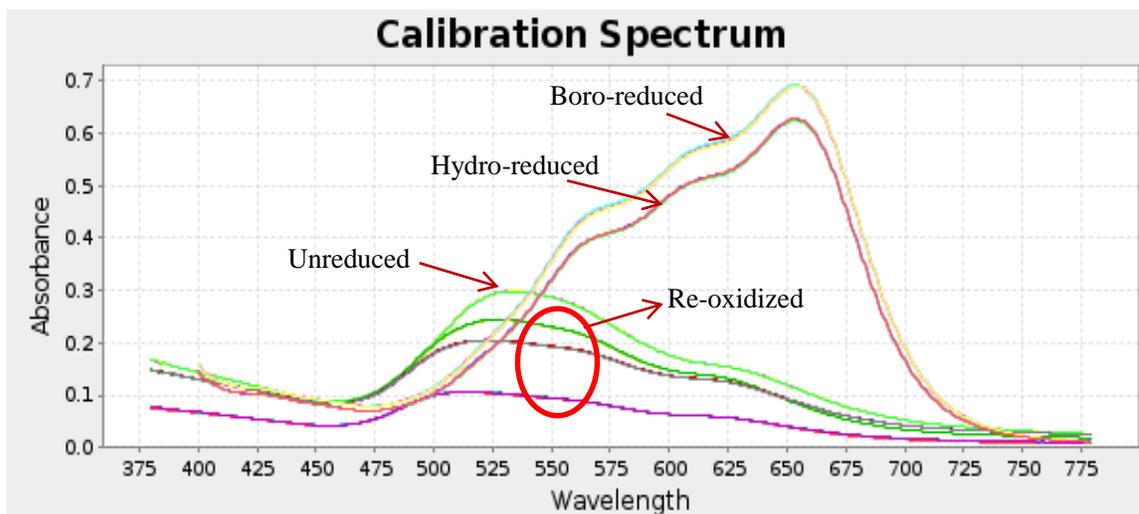


Figure C.4. Absorbance vs. Wavelength (Boro-Reduced Violeta Benzathren 2R ESP)



**Figure C.5. Comparison of Calibration Spectra between Boro-Reduced, Hydro-Reduced, Unreduced and Re-oxidized Violeta Benzathren 2R at 1.0 g/L**