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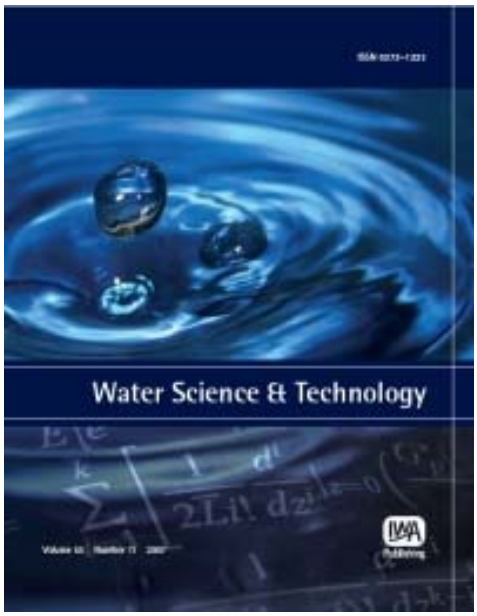

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A simple and accurate analytical method for determination of three commercial dyes in different water systems using partial least squares regression

Yahya S. Al-Degs, Amjad H. El-Sheikh, Ayman A. Issa, Mohammad A. Al-Ghouti and Mahmoud Sunjuk

ABSTRACT

A simple analytical procedure is proposed for simultaneous determination of three common dyes (Basic Blue 9, Brilliant Blue E-4BA, and Reactive Blue 2) in natural waters without prior separation of the solutes. A popular chemometric method, partial least squares regression PLS-1, was effectively applied for spectral resolution of a highly overlapping system. At the best modeling conditions, mean recoveries and relative standard deviations (RSD) for dyes quantification by PLS-1 were found to be 102.1 (4.4), 95.7 (8.4), and 98.9 (6.2) for Basic Blue, Brilliant Blue, and Reactive Blue, respectively. The estimated limits of detection (LOD) were estimated using net-analyte signal concept and were 0.11, 0.52, 0.49 mg L^{-1} for Basic Blue, Brilliant Blue, and Reactive Blue, respectively. The quantitative determination of dyes spiked in real water samples was carried out successfully by PLS-1 with satisfactory recoveries for dyes (90–106%).

Key words | cationic and anionic dyes, chemometry, PLS-1 calibration, spectral overlap

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INTRODUCTION

Organic dyes can be categorized into three types according to their chemical structure: cationic, nonionic, and anionic (Ramakrishna & Viraraghavan 1997). Synthetic organic dyes are heavily used in many industries including food, pharmaceutical, cosmetics, textile, and leather industries (Ramakrishna & Viraraghavan 1997). The effluents of the earlier industries are highly colored and disposal of these wastes into natural waters would cause damage to the environment (Ramakrishna & Viraraghavan 1997; Lambert *et al.* 1997; Al-Degs & Sweileh 2012). Direct, acid and reactive dyes are typical examples of anionic dyes (Lambert *et al.* 1997; Mottaleb & Littlejohn 2001). It is difficult to remove dyes from effluents as they are stable to light, heat and oxidizing agents and also are biologically stable (Lambert *et al.* 1997). Some classes of dyes are harmful to aquatic life even at lower concentrations (Ramakrishna & Viraraghavan 1997; Lambert *et al.* 1997). It is pointed out that less than 1.0 mg L^{-1} of dye content causes obvious water coloration (Ramakrishna & Viraraghavan 1997; Al-Degs & Sweileh 2012).

Dye levels in dye house effluents would be within the range 10–25 mg L^{-1} (O'Neill *et al.* 1999). After mixing with external water streams, further dilution for dyes occurs. A concentration of 1.0 μg/dm^3 is reported for cationic dyes in wastewater (Şahin *et al.* 2006). In response to concerns regarding the health risks associated with the use of reactive dyes, an increasing number of analytical methods have been developed in recent years for their determination. Several reports described the applications of new analytical procedures for the detection and determination of dyes in various matrices such water, wastewater, fish tissue, and animal feed (Hansa *et al.* 1999; Mottaleb & Littlejohn 2001). The spectrophotometric determination of a mixture of dyes is a hard analytical task due to the spectral overlapping between dyes (Peralta-Zamora *et al.* 1998) and this problem becomes more complicated for real matrices. Accordingly, the classical univariate calibration is impractical, because of the contribution of one species to the absorption signals of other species, and vice versa. In recent years, method development for resolution of highly overlapped spectra has increased exceptionally due to the availability of powerful instrumentation and robust numerical methods. For example, derivative spectrophotometry

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(Berzas Nevado *et al.* 1995), H-point standard addition method (Reig & Falcó 1988), chemometric methods including multilinear regression (MLR), principal-components regression (PCR), and partial least squares regression (PLS-1 or PLS-2) (Haaland & Thomas 1988; Geladi 2003; Hemmateenejad *et al.* 2005; Al-Degs *et al.* 2008) have been employed to overcome the problems of interference due to spectral overlapping or even the presence of unexpected chemical interferences. A limited number of studies has been reported on the application of multivariate calibration for determination of mixture of dyes in water and wastewater (Peralta-Zamora *et al.* 1998; López-de-Alba *et al.* 2001; Şahin *et al.* 2006; Al-Degs *et al.* 2008). While the use of spectrophotometric techniques is preferred because of their low operational cost, their application to real samples is limited due to their modest sensitivity (López-de-Alba *et al.* 2002).

In this work, the simultaneous determination of Basic Blue, Brilliant Blue, and Reactive Blue dyes in water is demonstrated using multivariate calibration. The selected dyes have strong spectral overlapping which retard their direct quantification by simple spectroscopy. The quantification of dyes is investigated by employing PLS-1 calibration along with the spectral data of dyes. The figures of merit including selectivity, sensitivity, limit of detection (LOD) and analytical sensitivity for PLS-1 method are estimated. The final aim of this study is to quantify the earlier ternary dye system in different water systems with aid of PLS-1 method and hence avoiding expensive chromatographic procedures.

THEORETICAL BACKGROUNDS

PLS-1 method

The following notations were adopted in this work, boldface capital letters for matrices, e.g. **A** and **C**, boldface small characters for vectors, e.g. **b** and small characters for scalars. The Beer's law model for m calibration standards containing l chemical components with spectra of n digitized absorbances can be presented in matrix notation as (Haaland & Thomas 1988):

$$\mathbf{A} = \mathbf{CK} + \mathbf{E} \tag{1}$$

where **A** is the $m \times n$ absorption matrix of calibration spectra, **C** is the $m \times l$ concentration matrix of components (dyes in this study) concentrations, **K** is the $l \times n$ matrix of absorptivity constants for dyes estimated at all wavelengths. **E** is the $m \times n$ matrix of spectral errors that do not fit by the model. The elements of **K** matrix could be determined by measuring spectra of individual components; however, this does not takes into account the interactions (or overlapping) between components. In literature, there are many multivariate calibration methods that are applied to model Equation (1) and correlate **A** with **C** with minimum residual error in **E**. These calibration methods, MLR, principal component regression, and PLSs regression are the most employed methods in multivariate calibration (Haaland & Thomas 1988; Brereton 2004). In PLS-1, the calibration sensitivity vector **b** is estimated as: $\mathbf{b} = \mathbf{W}(\mathbf{PTW})^{-1}\mathbf{q}$, where **W**, **P**, and **q** were estimated using PLS-1 algorithm using the optimum number of latent variables. In a separate step, prediction of dyes in unknown samples (i.e. not included in the calibration stage) is carried out as: $\mathbf{c}_{un} = \mathbf{A}_{un}\mathbf{b}$. The earlier steps are repeated for each solute/dye. In fact, the prediction of the three dyes could be carried out in one step, however, using PLS-2 calibration method (Brereton 2004). Multivariate calculation by PLS-1 was carried using MVC1 program which is available on the Internet and performs under Matlab environment (Matlab®, version 6) (Olivieri *et al.* 2004). Before running MVC1, the spectral data for calibration, validation and real water samples were saved in special format that is compatible with MVC1. MVC1 contains many first-order multivariate calibration methods and has the ability to display 3D plot beside other graphical presentations related to calibration tools (Olivieri *et al.* 2004).

Figures of merits for the analytical method

The selectivity, sensitivity and LOD are estimated to evaluate the proposed analytical method. Selectivity is expressed as (Lorber 1986):

$$\mathrm{SEL}k = ||\mathbf{s}_k^*||/||\mathbf{s}_k|| \tag{2}$$

where $\mathbf{s}_k^*$ is the projection of $\mathbf{s}_k$ (the vector of the spectral sensitivities of pure solute k) onto the so-called net analyte signal space (Lorber 1986). The symbol || || stands for the Euclidian norm of the vector. Sensitivity for analyte k can be calculated using the following equation (Lorber 1986; Olivieri *et al.* 2004):

$$\mathrm{SEN}_k = ||\mathbf{s}_k^*|| \tag{3}$$

Another important figure of merit is LOD, which is found as (Espinosa-Mansilla *et al.* 2004):

$$\mathrm{LOD}_k = 3||\boldsymbol{\varepsilon}||/|\mathbf{s}_k^*|| \quad (4)$$

where $\boldsymbol{\varepsilon}$ is a measure of the instrumental noise. MVC1 contains a special sub-routine based on net analyte signal concept for estimation of figures of merit for the analytical method (Olivieri *et al.* 2004).

MATERIALS AND METHODS

Instrumentation and software

The absorbance measurements were obtained using a double beam Unicam spectrophotometer (Cary 50 UV-Vis spectrophotometer). The UV-Vis spectra were recorded over the wavelength range of 400–800 nm and digitized absorbance was sampled at 1.0 nm intervals and then transferred to a Pentium(IV) personal computer for subsequent analysis. The data treatment was carried out using MATLAB (version 6). pH measurements were made with a WTW-Inolab (Germany) pH-meter using a companied glass electrode.

Reagents

Doubly distilled water and high purity reagents were used for all preparations of the standard and sample solutions. The selected dyes which have a wide application in many industries-were: Basic Blue 9, Brilliant Blue E-4BA, and Reactive Blue 2. Dye materials of analytical grade (>99.9%) were purchased from Aldrich Company. The chemical structures of dyes are illustrated in Figure 1.

The employed dyes were heavily used in clothes dyeing. Standard stock solutions of 100 mg L^{-1} of dyes were prepared individually by dissolving 0.100 (±0.001 g) in doubly distilled water in a 1,000 cm^3 volumetric flask. Dilute solutions were prepared by the appropriate dilution of the stock solution in doubly distilled water.

Optimization of dyes solution pH

Due to the significant effect of pH on dyes absorption, the optimum pH (the one that would ensure high sensitivity and selectivity for analysis) should be selected beforehand. To achieve that purpose, both selectivity SEL and sensitivity SEN for each dye were calculated for each tested pH. The net-analyte signal concept, originally developed by

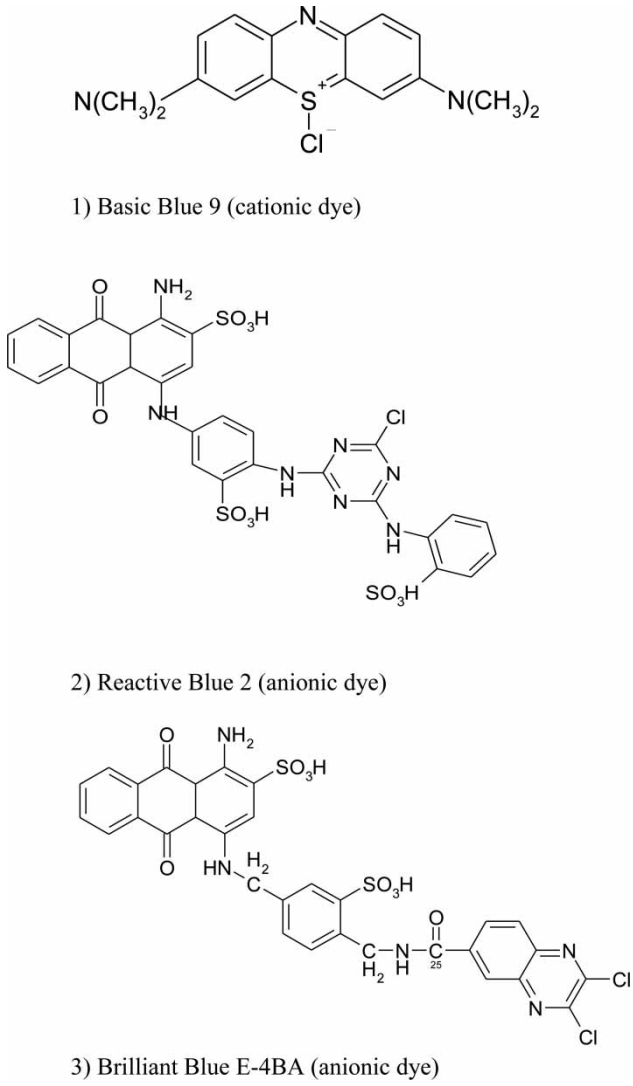

Figure 1 | Structural formulae of the studied dyes.

Lorber (Lorber 1986) was applied to find SEL and SEN (Equations (2) & (3)). The adjustment of pH of dye solutions was carried out using 0.5 M HNO_3 or 0.5 M NaOH. The ionic strength of dye solutions was adjusted by adding NaCl.

Development and validation of PLS-1 method

Due to the high spectral overlap (98% overlap) between dyes, large number of calibration samples were necessary to build PLS-1 model. Typical one-compound calibration experiments (univariate calibration) were carried out to establish the concentration ranges for the determination in mixtures. Solutions of absorbance values

higher than 1.0 were diluted. Twenty-eight ternary synthetic mixtures (maintained at pH 6.0 and ionic strength of 0.10 M NaCl) of dyes were carefully prepared. From these solutions, 20 solutions were selected as the calibration set and the rest of solutions were kept for validation. The calibration and prediction sets were presented as 3D plot so as to view the homogeneity between them (Figure 2).

To reduce the collinearity in the absorption matrix **A**, the design for calibration set was based on four-level fractional factorial designs according to Brereton's procedure (Brereton 1997). The prediction set was selected randomly. For best calibration results, the spectral region within the range (400–800 nm) was selected. The number of experimental points per spectrum is 401 where each spectrum is subdivided into 1.0 nm intervals. Within this spectral region, maximum spectral information was available. Accordingly, the dimension of calibration absorption matrix (**A**) is 20×401, while the dimension for calibration concentration vector (c) is 20×1. The concentration range of dyes in the prediction samples should be within the space of calibration samples which is clear in the 3D plot (Figure 2).

Determination of dyes in real water systems

Natural water samples including sea, river, and treated wastewater were collected from different locations. Samples of water (1,000 mL) were obtained directly from source and stored in polyethylene bottles at 10 °C. Prior to spiking with dyes, the samples were filtered through a cellulose membrane filter (Millipore) of 0.45 μm pore size to remove any suspended matter. Furthermore, the pH of water samples was adjusted to 6.0 using diluted acid. The spectra of water samples were recorded over the region 400–800 nm and the obtained data were digitized and analyzed by the proposed PLS-1 method to determine level of dyes.

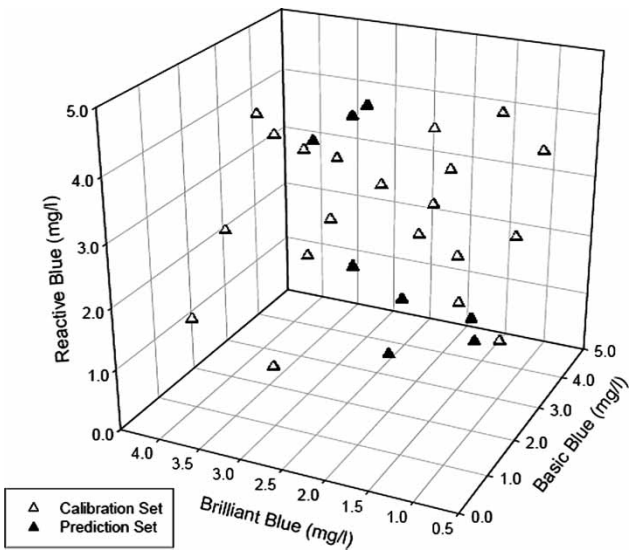

Figure 2 | A 3D plot showing the composition of the three dyes used in PLS-1 calibration and validation.

RESULTS AND DISCUSSION

Determination of dye mixture in water or wastewater can be carried out using high performance liquid chromatography (HPLC), gas chromatography/mass spectrometry (GC-MS), liquid chromatography/mass spectrometry (LC-MS), and capillary electrophoresis (CE) (Şahin *et al.* 2006). However, chromatographic determination of dyes in the mixture is a lengthy procedure and also previous clean-up and preconcentration steps are essential in some instances. Multivariate calibration methods (particularly PCR and PLS-1) have been applied to highly overlapped spectra or chromatograms (Abbaspour & Najafi 2003; Hemmateenejad *et al.* 2006). The advantages of applying multivariate calibration methods were to minimize or eliminate sample preparation and also to avoid a preliminary separation step in complex matrices (Hemmateenejad *et al.* 2007). The application of multivariate calibration for different types of dyes quantification has been reported in literature (Al-Degs *et al.* 2008; Al-Degs & Sweileh 2012).

Extent of spectral overlap between dyes and the importance of chemometry

Figure 3 shows the visible absorption spectra of the three dyes used in this study.

As can be seen, an important degree of spectral overlap occurs between studied dyes. The degree of spectral overlap was estimated as outlined in the literature (Goicoechea & Olivieri 1998). The spectral overlap between Brilliant Blue and Reactive Blue was 92%. However, a lower overlap was noted for Basic Blue with the other two dyes (70–85%). Due to the significant spectral overlapping (85–92%), the conventional calibration procedures would have a limited application for quantitative determination. Therefore, the simultaneous determination of these dyes requires the application of PLS-1 method to overcome

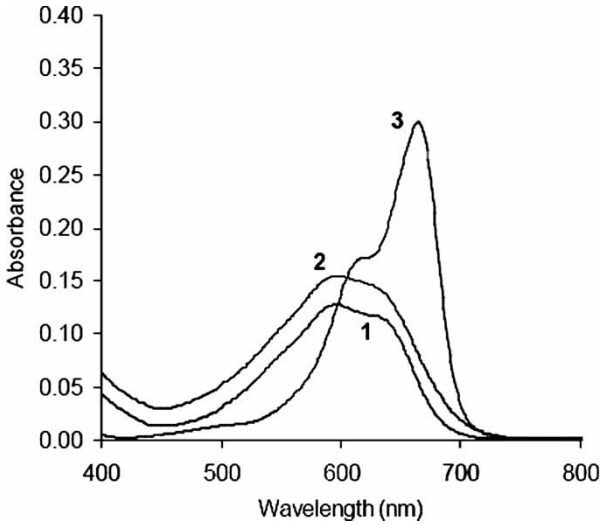

Figure 3 | Absorption spectra of dye. Brilliant Blue 18 mg L^{-1} (1), Reactive Blue 14 mg L^{-1} (2), Basic Blue 1.0 mg L^{-1}. pH 6.0 and 0.10 M NaCl.

such a high spectral overlap. The linear working concentration range of each dye was determined separately. These concentration ranges were useful in building both calibration and prediction sets. The linear concentration range of each dye was determined by regressing absorbance at the corresponding λ_{max} against concentration at pH 6. LOD was taken as 3σ/slope where σ is the standard deviation of ten measurements of the blank. Three straight lines were noted for dyes calibration with $r^2 = 0.9995$, 0.9993, and 0.9997 for Basic Blue, Brilliant Blue and Reactive Blue, respectively. Linearity was observed between 1.0 and 30.0 mg L^{-1} for both Brilliant Blue ($\lambda_{max} = 605$ nm) and Reactive Blue ($\lambda_{max} = 615$ nm) and from 0.15 to 8.0 mg L^{-1} for Basic Blue ($\lambda_{max} = 671$ nm). The LOD values were 0.048, 0.35, and 0.31 mg L^{-1} for Basic Blue, Brilliant Blue and Reactive Blue, respectively. The molar absorptivities (in $cm^{-1} M^{-1}$) for dyes were 6.1×104, 7.7×103, and 7.0×103 for Basic Blue, Brilliant Blue and Reactive Blue, respectively. Compared with the rest of dyes, Basic Blue has a high molar absorptivity value which will improve its analytic selectivity and sensitivity as will be shown later. The selected concentration ranges of dyes used in multi-component samples were selected in a way to avoid excessive absorbance of the mixtures (López-de-Alba *et al*. 2006).

Optimization of experimental conditions affecting dyes absorption

Many experimental conditions may affect the absorption characteristics of dyes, among these pH, temperature and ionic strength of solution are the most important. The influence of pH on dyes absorption intensity was studied over a wide pH range (2–12) at constant solution ionic strength (0.1 M NaCl) and temperature 26 °C. The initial spectral studies indicated that the spectra of Reactive Blue and Brilliant Blue did not alter over the investigated pH range (2–12). However, large spectral changes were observed for Basic Blue especially in basic media (pH > 7.5). Accordingly, the pH value (or pH range) at which the maximum SEN and SEL for all dyes are achieved should be determined. As mentioned before, both SEN and SEL values (at each pH) were obtained using NAS concept and the results are all given in Table 1.

As indicated from Table 1, Basic Blue has a high SEL and SEN values compared with the rest of dyes at pH ≤ 8. Above pH 8, a considerable decrease in the sensitivity is observed and this could be attributed to the changes the dye structure due to reaction with hydroxyl ions. Slight changes were observed in the values of SEL and SEN for Brilliant Blue and Reactive Blue dyes over the entire pH range. The high SEL and SEN values observed for Basic Blue could be attributed to the high molar absorptivity for this dye which is 7–10-fold higher than the rest of dyes. Accordingly, the optimum pH range for dyes analysis is 2–8 and pH 6 was selected from this range.

Table 1 | The values of SEL and SEN obtained for dyes at different pH values

pH	Basic Blue		Brilliant Blue		Reactive Blue	
	SEL	SEN	SEL	SEN	SEL	SEN
2	0.822	0.0871	0.423	0.0221	0.482	0.0326
4	0.825	0.0873	0.444	0.0206	0.472	0.0325
6	0.872	0.0882	0.432	0.0223	0.489	0.0321
8	0.725	0.0752	0.452	0.0226	0.478	0.0330
10	0.720	0.0251	0.456	0.0252	0.486	0.0328
12	0.625	0.0110	0.462	0.0245	0.478	0.0326

Calibration by PLS-1 and selection of the optimum number of latent variables (*h*)

Determination the optimum number of latent variables (*h*) to be used in PLS-1 method is essential to achieve high prediction. This allows modeling of the system with the optimum amount of information and avoiding overfitting (Brereton 2004). To avoid overfitting, leave-one-out cross validation procedure was adopted (Brereton 2004). Simply, for *m* calibration set (20 solutions in our case), the PLS-1 was performed on $m-1$ calibration solutions, and use this calibration to predict the concentration in the sample left out. This process was repeated 20 times until each sample has been left out once (Brereton 2004). The selection of spectral region for numerical analysis was carried out by applying a moving window strategy to the calibration set itself as outlined in the literature (Hemmateenejad *et al.* 2007). The predicted concentration for each sample is then compared with the true concentration value. PRESS (prediction error sum of squares), which measures the difference between predicted concentration and the true one, is then estimated for all calibration samples in the set (Brereton 2004). The effectiveness of PLS-1 for dyes prediction in the validation set was determined by calculating relative error of prediction (REP), root mean squares difference (RMSD), standard error of calibration or prediction SEC(P), and square of the correlation coefficient (r^2). Statistical parameters for PLS-1 method and the figures of merit for dyes determination are presented in Table 2.

As can be seen in Table 2, the obtained latent variables were higher than 3 for Brilliant Blue and Reactive Blue, indicating that the variability sources number in the presently studied system exceeds the number of studied analytes (three analytes). Figure 4 depicts the PRESS–Latent variable plot obtained from cross validation technique.

Figure 4 indicates that PRESS values estimated for dyes were significantly reduced by increasing number of latent variables needed for modeling spectral data. It is interesting to notice that similar spectral regions were used in PLS-1 for both Brilliant Blue and Reactive Blue, however, for Basic Blue the spectral regions was extended from 510 to 720 nm. High prediction power was noted for PLS-1 for all dyes in the calibration samples as indicated from r^2 and REP% values. Usually, the multivariate selectivity values ranges between zero (complete overlap between analyte and other interferences) and unity (no or small overlap between analyte and other analytes or interferences) (Boqué *et al.* 2000). The lower selectivities obtained for

Table 2 | Statistical parameters and the figures of merit for PLS-1 method

Calibration parameter	Basic Blue	Brilliant Blue	Reactive Blue
Spectral region (nm)	510–720	440–680	430–705
Number of factors (*h*)	3	4	4
PRESS ($mg^2\ L^{-2}$)	2.15	5.53	7.02
RMSD ($mg\ L^{-1}$)[a]	0.36	0.53	0.58
REP%[b]	1.1	2.9	4.0
SEC[c]	0.15	0.24	0.13
r^{2}[d]	0.9986	0.9865	0.9803
SEN	0.09	0.02	0.03
SEL	0.87	0.43	0.49
LOD[e] ($mg\ L^{-1}$)	0.11	0.52	0.49

[a]RMSD was estimated as (Abbaspour & Najafi 2003): $\text{RMSD} = 1/\sqrt{n}\sum_{i=1}^{n}(C_{i,\text{pred}} - C_{i,\text{act}})^2$, where *n* is the number of samples in the prediction set (eight samples in this study).

[b]REP% was estimated as (Hemmateenejad *et al.* 2006):

$$\text{REP\%} = 100 \times \left(\sum_{i=1}^{n}(C_{i,\text{pred}} - C_{i,\text{act}})^2 \Big/ \sum_{i=1}^{n}(C_{i,\text{act}})^2\right)^{1/2}.$$

[c]SEC or SEP values were calculated as (López-de-Alba *et al.* 2006):

$$\text{SEC(P)} = \sqrt{\sum_{i=1}^{n}(C_{i,\text{pred}} - C_{i,\text{act}})^2/1 - n}.$$

[d]r^2 was estimated as (Abbaspour & Najafi 2003):

$$r^2 = 1 - \left(\sum_{i=1}^{n}(C_{i,\text{pred}} - C_{i,\text{act}})^2 \Big/ \sum_{i=1}^{n}(C_{i,\text{act}} - \overline{C})^2\right).$$

[e]LOD was estimated using $\|\varepsilon\| = 0.007$ absorbance units (see Equation (4) above).

Brilliant Blue (0.43) and Reactive Blue (0.49) compare to Basic Blue (0.87) were is expected due to the high spectral overlap between Brilliant Blue and Reactive Blue as shown in Figure 3. On the other hand, the high sensitivity value (0.09) observed for Basic Blue is expected due to the high molar absorptivity of this dye compared with the rest of dyes. The multivariate LODs as estimated from NAS concept were 0.11, 0.52 and 0.49 for Basic Blue, Brilliant Blue,

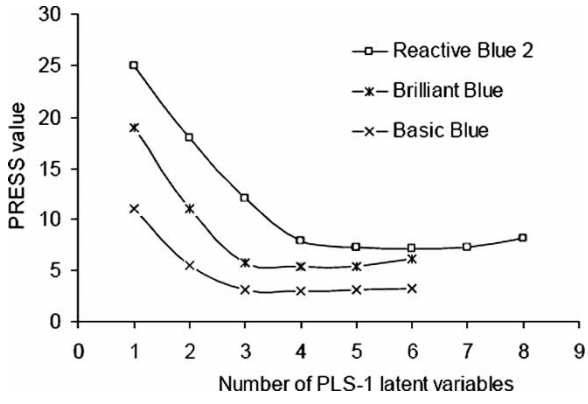

Figure 4 | Plot of PRESS against PLS-1 latent variables.

Table 3 | Statistical parameters for external validation of PLS-1 method for dyes

No.	Added (mg L^{-1}) Basic Blue	Brilliant Blue	Reactive Blue	PLS-1 prediction (mg L^{-1}) Basic Blue	Brilliant Blue	Reactive Blue
1	3.5	3.0	1.5	3.4	2.8	1.4
2	3.5	1.5	1.0	3.5	l.6	0.9
3	2.0	1.0	1.5	2.1	1.1	1.5
4	1.0	1.5	2.5	0.9	1.4	2.5
5	2.0	2.0	1.0	2.1	1.7	0.9
6	3.5	3.0	4.0	3.4	2.8	4.1
7	4.0	3.0	4.0	4.2	2.7	3.9
8	3.5	3.5	3.5	3.4	3.3	3.5
	Statistical analysis					
	Average recovery ± R (In = 8)			102.1 (4.4)	95.7 (8.4)	98.9 (6.2)
	SEP			0.14	0.22	0.14
	REP%			1.6	3.1	5.1

and Reactive Blue, respectively. The optimized PLS-1 calibration method was further validated by finding dye contents in the validation set. The mean recovery percentages, RSD, SEP, and REP% obtained for prediction or validation set are presented in Table 3.

The results were satisfactory indicating the successful application of the proposed method for simultaneous determination of the three dyes in water. Relatively speaking, the PLS-1 method was more effective in internal validation compared with external validation as indicated from the values of REP% for both sets. Comparison between SEC and SEP values allows identification of an overfitting or underfitting in the model, with more or less latent variables than necessarily required (López-de-Alba *et al.* 2001). For each dye, the magnitude of SEC and SEP were fairly similar which confirmed the perfect selection of the number of latent variables in both cases.

Determination of dye mixtures spiked in different real water samples using PLS-1 method

The next step was to test how well the proposed PLS-1 method will do when applied to dye determination present in real water systems, considering the fact that the calibration set was designed using standards where other interferences were not accounted for. As stated earlier, the main aim of this study was to develop an analytical method with a minimal sample preparation and find a simple analytical method to replace the current analytical methods (Hansa *et al.* 1999). Nine ternary mixtures with variable concentrations of dyes were spiked in different natural water samples. The concentration levels of added dyes were selected to be determined by PLS-1 method. The percentages recoveries and RSD values obtained by PLS-1 are summarized in Table 4.

The obtained recoveries were satisfactory in all samples analyzed where the values of RSD were less than 10%. The prediction power of PLS-1 can be considered acceptable taking into account the complexity of the sample being analyzed. The good agreement between the PLS-1 results and the spiked values is an indication of the effectiveness of the proposed method for simultaneous determination of Basic Blue, Brilliant Blue, and Reactive Blue in real samples. In fact, other interferences that are present in natural water samples which where not considered in the calibration model, e.g. Cl^-, SO_4^{2-}, NO_3^-, OM, etc., did not strongly interfere with dye analysis. In fact, the spectral regions that selected for dye analysis was within the visible region which probably means that the absorption of natural organic matters is not high in that region.

CONCLUSIONS

The results indicated that PLS-1 method is a rapid, easy and of low cost method for simultaneous determination of three commercial dyes (two anionic dyes and one cationic) in different water systems. The proposed method could be used for the screening of dyes in water (e.g. in situ analyses) or as a quantification method in cases where the

Table 4 | Determination of dyes in different water systems by PLS-1 method

Water body	No.	Mixture	Added[d]	Found[d]	Recovery (RSD)[e]
River water[a]	1	Basic Blue	4.5	4.4	96.4 (2.1)
		Brilliant Blue	1.0	0.9	94.0 (1.5)
		Reactive Blue	4.0	4.1	99.9 (5.4)
	2	Basic Blue	1.0	1.1	94.7 (0.8)
		Brilliant Blue	4.0	4.0	100.4 (3.6)
		Reactive Blue	1.5	1.5	101.2 (5.2)
	3	Basic Blue	1.0	0.9	94.8 (1.4)
		Brilliant Blue	4.5	4.3	94.8 (2.6)
		Reactive Blue	4.5	4.4	95.8 (3.9)
Sea water[b]	4	Basic Blue	4.5	4.3	96.1 (7.6)
		Brilliant Blue	1.0	1.0	99.0 (9.6)
		Reactive Blue	4.0	4.1	97.7 (5.5)
	5	Basic Blue	1.0	1.0	106.0 (8.4)
		Brilliant Blue	4.0	4.0	100.8 (5.2)
		Reactive Blue	1.5	1.6	106.4 (3.9)
	6	Basic Blue	1.0	0.9	101.4 (8.5)
		Brilliant Blue	4.5	4.3	95.6 (5.9)
		Reactive Blue	4.5	4.4	97.3 (6.2)
Textile treated wastewater[c]	7	Basic Blue	4.5	4.6	103.4 (9.8)
		Brilliant Blue	1.0	0.9	90.0 (5.0)
		Reactive Blue	4.0	3.9	98.3 (8.4)
	8	Basic Blue	1.0	0.9	90.3 (4.6)
		Brilliant Blue	4.0	3.8	94.2 (9.5)
		Reactive Blue	1.5	1.4	91.1 (10.0)
	9	Basic Blue	1.0	1.1	91.3 (5.4)
		Brilliant Blue	4.5	4.6	103.2 (9.9)
		Reactive Blue	4.5	4.5	101.2 (9.6)

[a]The employed river water contains : $[Cl^-] = 0.12$ M, total hardness (as $CaCO_3$) = 680 mg L^{-1}, and alkalinity (as $CaCO_3$) = 75 mg L^{-1}.
[b]The employed sea water contains: $[Cl^-] = 0.45$ M, total hardness (as $CaCO_3$) = 850 mg L^{-1}, alkalinity (as $CaCO_3$) = 220 mg L^{-1}.
[c]The employed textile treated wastewater contains: total hardness (as $CaCO_3$) = 550 mg L^{-1}. $[SO_4^{2-}] = 110$ mg L^{-1}, $[NO_3^-] = 45$ mg L^{-1}, BOD = 13 mg L^{-1}, COD = 20 mg L^{-1}.
[d]Expressed in mg L^{-1}.
[e]Relative standard deviation ($n = 3$).

chromatographic ones cannot be implemented owing to cost limitations, or lack of analytical instrumentation. Quantitative determination of dyes in real water samples was carried out successfully by the proposed method with recoveries ranging between 90 and 106% with RSD values <10%.

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