

Potentiometric and Spectrophotometric Flow Injection Determination of Variamine Blue

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Abstract

Simple, rapid, and sensitive potentiometric and spectrophotometric methods were developed for flow injection determination of variamine blue (VB) dye. Novel variamine blue carbon paste electrodes (VB-CPEs) were constructed and characterized for flow injection potentiometric determination of VB. The fabricated electrodes work satisfactorily in the concentration range from 10^{-6} to 10^{-2} M and sampling through output 60 sample h^{-1} . The proposed spectrophotometric method was based oxidation on oxidation of VB with potassium persulfate, forming a deep violet blue colored quinonodimine species with an absorption maximum at 550 nm. FIA parameters such as reagent concentration, flow rate, sample volume and length of reaction coil were optimized to achieve the highest sensitivity, and sample output, with the advantage of accuracy and automation feasibility. Calibration graphs were linear in the concentration range from 4.6 to 80.0 μg VB and sampling through output 40 sample h^{-1} .

Key word: Flow injection analysis; Variamine blue; Potentiometry; Carbon paste sensor; Spectrophotometry.

1. Introduction

Variamine Blue (VB 4-Amino 4'-methoxydiphenylamine) indicator was first suggested by Erdey [1, 2]. VB was recommended as a redox indicator for potentiometric and visual titrations with Fe (III) [3, 4], bromamine-B [5] or bromate [6]. Simple, rapid and sensitive spectrophotometric methods utilizing VB as chromogenic reagent were also suggested for determination of arsenic [7], vanadium [8] or selenium [9]. In general, the utility of VB as an analytical reagent has been well reviewed by Bishop [10].

The yield of VB from an initial commercial manufactured sample was found to be about 75%; however, relatively little information on the analysis of such dyestuffs has been published; the book of Lastovskii and Vainshtein [11] is still a very useful manual. Electrochemical techniques are of choice since they possess the advantages of simplicity, accuracy and low cost without separation or pretreatment procedures. Although ion-selective electrodes (ISEs) were applied for dye analysis [12-16], only a PVC potentiometric sensor was used for batch determination of VB [17]. PVC membrane electrodes still have certain inherent limitations such as mechanically complicated and difficulty of and incorporation in flow injection analysis (FIA). To overcome the aforementioned PVC limitations, carbon paste electrodes (CPEs) have been developed and introduced as an alternative, possessing the advantages of long operational lifetime, short response time, and ease of fabrication and regeneration process [18-20].

Flow injection analysis (FIA) becomes a wide spread methodology characterized by its versatility, ease of automation, high sampling frequency and minimum sample treatment prior to injection into the system [21]. FIA is viewed as a well efficient mean for improving the performance characteristics of ISEs in comparable to the batch measurements as the permanent liquid stream has a conditioning effect on the sensor, leading to a better sensitivity and stability without major errors due to displacement of electrodes between measurements [22-25]. CPEs were more suitable for use in flow injection systems due their fast response time and mechanical strength.

The present work describes simple, direct, sensitive and precise spectrophotometric and potentiometric methods for the VB determination. Combination of FIA for both methods was also characterized for improving of sensitivity and sampling through output.

2. Experimental

2.1. Reagents

All reagents were of the analytical grade and bidistilled water was used throughout the experiments. Variamine Blue (10^{-2} M) stock solution was prepared by dissolving the appropriate weight of the VB. HCl ($C_{13}H_{14}N_2O.HCl$, BDH, UK assayed to be 77.5% by elemental analysis) in water. Hydrogen peroxide solution was prepared by dilution of 30% H_2O_2 (Merck); other oxidant solutions were prepared by dissolving the appropriate amounts of potassium bromate ($KBrO_3$, BDH), potassium iodate (KIO_3 , BDH), potassium periodate (KIO_4 , Analar) or potassium persulphate ($K_2S_2O_8$, Analar) in bidistilled water.

Sodium tetraphenylborate (NaTPB) solution (ca. 10^{-2} M) was prepared by dissolving a weighed amount of the substance in water and standardization against standard 10^{-2} M thallium (I) nitrate solution [26]. Potassium tetrakis (4-chlorophenyl) borate (KTCBPB, Fluka), reineckate ammonium salt (RAS, Fluka), phosphotungstic acid (PTA, BDH), or phosphomolybdic acid (PMA, Fluka) were used for precipitation of different VB ion pairs. Electrode plasticizer namely; *o*-Nitrophenyloctylether (*o*-NPOE), tricresylphosphate (TCP), dibutylphthalate (DBP), dioctylphthalate (DOP) and dioctylsebacate (DOS) were purchased from Sigma, BDH and AVOCADO, respectively. Graphite powder (synthetic 1–2 μm , Aldrich) was applied in electrode fabrication.

2.4. Apparatus

Potentiometric measurements were carried out using 692-pH meter (Metrohm, Herisau, Switzerland) with Ag/AgCl double-junction reference electrode and combined pH glass electrode. A V-570 double beam spectrophotometer (Jasco) with 10 mm light-path cells was used for absorbance measurements.

FIA manifold was composed of a four channel peristaltic pump (Ismatec, Zurich, Switzerland, MCP) and a sample injection valve (ECOM, Ventil C, Czech Republic) with exchangeable sample loops (5-500 μL).

Continuous flow cell [27] used in the potentiometric measurements provided a low dead volume, fast response, good wash characteristics, ease of construction, and compatibility with different electrodes. The cell was simply manufactured from Perspex cube with two cylindrical holes for fixation of electrodes, and internal tube within for connecting the two electrodes and carrier stream. The change of electrode potential

was monitored using 46-Range Digital Multimeter (Radioshack, China) with PC interface.

For spectrophotometric measurements, two line flow system with homemade flow cell (10 mm quartz cell filled with Perspex having an input and output tubes with total volume 300 μL) was used to detect the change in the absorbance of the effluents from the reaction coil at 550 nm [28].

2.5. General Procedures

2.5.1. Sensor construction

Modified CPEs were fabricated by mixing either 1.0mg of VB-TPB ion pair or 10.0 of KTCPB with 100 mg graphite powder and 40 μL *o*-NPOE. The paste components were mixed in an agate mortar and the result paste was used to fill the electrode body [19, 20]. The fabricated electrode were conditioned in 10^{-3} M VB solution for 24 h. Soaked CPEs were prepared without incorporation of modifier and soaked in freshly prepared VB-TPB ion pair suspensions for 24 h. Regeneration of the electrode surface was obtained by screwing the piston while holding the electrode surface against a flat solid support, polishing with a wet filter paper [19, 20].

2.5.2. Potentiometric measurements

Under batch conditions, CPEs were calibrated by transferring 25 mL aliquots of 10^{-7} - 10^{-2} M VB solutions into a 50 mL double jacket thermostated glass cell at 25°C. CPE and Ag/AgCl double junction reference electrode were immersed in the measuring solution. The potential readings were recorded and plotted against dye concentration in logarithmic scale ($-\log [\text{VB}]$) [29]. For FIA measurements, 200 μL of freshly prepared VB solutions covering the range from 10^{-6} to 10^{-2} M were injected in the flowing stream (45 mL min^{-1}) and the corresponding peak heights were recorded and used to draw the calibration graphs.

2.5.3. Spectrophotometric measurements

For batch measurements, aliquots containing different concentrations of VB were transferred into 10 mL volumetric flask followed by 2mL of acetate buffer (pH 4.0) and 2 mL of $\text{K}_2\text{S}_2\text{O}_8$ (10^{-2} M). The volume was completed to the mark with water and the absorbance of the formed blue violet species was measured at 550 nm against blank solution. Calibration graphs were constructed by plotting the absorbance versus the VB concentration. In FIA mode, 50 μL of VB solutions with different concentrations were injected into the acetate buffer carrier stream (pH 4.0 and flow rate 6.6 mL min^{-1}) which was then mixed with the persulphate stream (0.5 mol L^{-1} with a flow rate 6.6 mL min^{-1}) in the reaction coil. The change in absorbance of the effluents from the reaction coil was detected at 550 nm and the peak heights were proportional to the VB concentrations and used for construction of the calibration curve, five replicate injections per sample were made in all instances.

3. Results and Discussion

3.1. Potentiometric method

3.1.1. Optimization of the electrode matrix composition

VB is a tertiary amine dye that can form water insoluble ion-pair complexes with the oppositely charged anions such as TPB, RAS, PTA or PMA. The resultant IPs can be used as ion exchangers for VB potentiometric sensors [17]. Due to limitation accompanying PVC electrodes, the present work applied CPE for FIA potentiometric determination of VB. Both unmodified (plain) and modified electrodes (either with the VB-IPs, or the ion pairing agents) were prepared and tested for nature and content of modifier, plasticizer and response time.

CPEs modified in bulk with different VB-IPs as electroactive

components were prepared and conditioned in 10^{-3} M VB solution for 24 h. Preliminary experiments declared that electrodes that contain no electroactive material and plasticized with *o*-NPOE showed no response towards the VB, while those modified with VB-IPs gave Nernstian responses depending on the nature of the VB-IP used. Incorporation of VB-TPB showed the best electrode performance (slope 59.4 ± 2.3 mV decade $^{-1}$) compared with other VB-IPs modified electrodes. Furthermore, the influence of the VB-TPB content in the electrode matrix was tested; addition of 1mg gave the best performance.

Incorporation of a suitable ion pairing agent in the electrode matrix followed by soaking the electrode in the dye solution led to the formation of ion pair at the electrode surface which subsequently extracted by the plasticizer into the electrode bulk [30-31]. Electrode matrices containing different ion pairing agents (NaTPB, KTCPB, RAS, PTA and PMA) were prepared and presoaked in 10^{-2} M VB solution for 24 h. The obtained results indicated the priority of KTCPB incorporation indicated by the highest slope value (51.7 ± 1.1 mV decade $^{-1}$) compared to other ion pairing agents. The content of KTCPB within the electrode matrices was varied from 5 to 50 mg, and incorporation of 10 mg of KTCPB was selected.

In addition to the aforementioned methods for sensor fabrication, simple and reliable procedures could be applied by soaking the plain electrodes (fabricated without any modification) in aqueous suspension of the lipophilic VB-IPs solutions. The electrode mediator (plasticizer) extracts VB-IPs from their aqueous suspension, and becomes gradually saturated with this IP [32, 33]. Calibration graphs of electrodes soaked in different VB ion pair suspensions showed that soaking in the VB-TPB had the best sensitivity indicated by the highest slope (59.2 ± 0.7 mV decade $^{-1}$) when compared with other IPs. This behavior may be attributed to the low solubilities of different IPs in the electrode matrix [17].

Plasticizers play an important role in the behavior of ISEs since they improve the solubility of the sensing material and lower the overall electrode bulk resistance due to their polarity characteristics [32-37]. The effect of membrane plasticizer on the electrode performance has been studied. Electrode plasticized with *o*-NPOE was compared with those plasticized with TCP, DOS, DOP or DBP. Application of *o*-NPOE showed the highest sensitivity indicated by the highest slope values, which may be related to its high dielectric constant ($\epsilon=24.0$, 17.6, 3.88, 5.2, and 4.7 for the tested plasticizers in the same order).

When ISEs are used to monitor titration based on IP formation, the magnitude of both potential break and sharpness at the inflexion point of the titration curves are predetermined by the solubility of the corresponding IP in membrane plasticizer [26, 32, 33, 36]. The influence of the membrane plasticizer on the titration performance was investigated by performing the titration using electrodes plasticized with the aforementioned plasticizer. Electrodes plasticized with *o*-NPOE gave the highest total potential change ($\Delta E=170$ mV), which can be explained by higher extractability of the VB-TPB ion pairs into the membrane plasticizer and the relative higher dielectric constant of *o*-NPOE.

3.1.2. Sensor performance

The potentiometric response characteristics of different VB sensors fabricated under different methods (modification with VB-TPB ion pair, modification with KTCPB, or soaking in VB-TPB ion pair) were evaluated according to IUPAC recommendation. Data obtained (Table 1) indicated that the developed sensors can be successfully applied for the potentiometric determination of VB in the concentration range

from 10^{-6} to 10^{-2} M with Nernstian cationic slopes depend on the method of fabrication. Electrodes modified with VB-TPB ion-pair showed relatively higher slope (62.2 ± 1.4 mV decade $^{-1}$) compared with those modified with KTCBP or soaked electrodes. The limit of detection varies with the electrode type as it reached 6.3×10^{-7} M with the VB-TPB modified electrode, and 10^{-5} M for other electrodes.

Table 1: Analytical performances of various Variamine Blue sensors

Sensors	Modified		<i>In situ</i>	Soaked
	Batch	FIA		
Concentration range (M)	10^{-6} - 10^{-2}	10^{-6} - 10^{-2}	10^{-5} - 10^{-2}	10^{-5} - 10^{-2}
Slope (mV decade $^{-1}$)	62.2 ± 1.4	69.0 ± 2.8	51.7 ± 1.1	59.3 ± 0.7
r	0.9993	0.9975	0.9996	0.9999
LOD (M)	6.3×10^{-7}	1.0×10^{-6}	7.0×10^{-6}	7.6×10^{-6}
Response time (s)	2		4	3
Lifetime (Day)	60	25	45	30

For analytical applications, the response time of a new fabricated sensor was of critical importance. According to IUPAC recommendation, the average response time is defined as the time required for the electrode to reach a stable potential (within ± 1 mV of the final equilibrium value) after sudden 10-fold increase in analyte concentration. The response time was found to be 2s for concentration of more than 10^{-4} M and 4s for lower concentrations.

The lifetime of different VB sensor was tested by performing day-to-day calibration. Sensors showed useful lifetime of 21–28 days during which the Nernstian slopes did not change significantly (± 2 mV decade $^{-1}$), while the detection limit was shifted from 10^{-6} to 10^{-5} mol $^{-1}$ VB at the end of this period.

The selectivity of the prepared sensor was tested towards different interfering species using Matched Potential Method (MPM) and the fabricated electrodes showed high selectivity towards VB (Table 2).

Table 2: Selectivity coefficients for VB-CPE under batch and FIA conditions.

Interferent	$-\log K_{A,B}$	
	Batch*	FIA**
Na $^{+}$	3.70	3.85
K $^{+}$	2.95	3.25
Li $^{+}$	3.40	3.55
NH $_4^{+}$	2.60	2.90
Ca $^{2+}$	3.61	3.30
Mg $^{2+}$	3.36	3.41
Starch	3.00	
Maltose	2.70	
Sucrose	2.00	
Citrate	2.29	
Caffeine	3.18	
Glycine	2.86	

*Performed with MPM.

**Performed with SSM.

FIA is viewed as a well efficient mean for improving the performance characteristics of ISEs as the action of the flowing stream continuously cleans the electrode surface and the transient nature of the signal may help to overcome the effect of interfering ions. Under FIA conditions, the selectivity

coefficients were calculated according to the separate solution method (SSM), based on potential values corresponding to the peak heights for the same concentrations of VB and interferents.

The proposed electrode was successfully employed as indicator electrode for potentiometric titration of VB with NaTPB in the concentration range 6.0 to 20.0 mg VB. Data obtained (not shown) indicated satisfactory agreement between the VB contents in different samples determined by the proposed sensor and elemental analysis method as there is no official methods for VB.

3.1.3. Electrode response under FIA conditions

Incorporation of ISEs in flow injection systems has the advantages of automation with high sampling frequency [25]. In FIA combined with ISEs, systems performance and analytical throughput is controlled by the performance of the specific electrode, which mainly depends on the sensitivity and the response time of the electrode used. Incorporation of VB-PVC electrode in the flow system was unsatisfactory due to damage of the sensing membrane during electrode holding in the cell and the slow response time of the PVC electrodes (about 10s) which produces broad peaks with long tail. Contrary, incorporation of CPE in the FIA system was much easier due to the solid nature of the electrode and absence of the internal reference solution.

Under the optimized FIA conditions [27] and when 200 μ L of VB solutions at various concentrations were injected in the flowing stream (40 mL min $^{-1}$). The fabricated electrode showed sharp peaks with peak heights related to VB concentration (Fig. 1). Calibration graphs were linear in the concentration range from 10^{-6} to 10^{-2} M with Nernstian slopes of 69.0 ± 2.8 mV decade $^{-1}$ and sampling output of 60 sample h $^{-1}$. Reproducibility was evaluated from repeated 10 injections of 200 μ L of 10^{-3} M VB solution and the average peak heights were found to be 343.0 ± 2.5 mV.

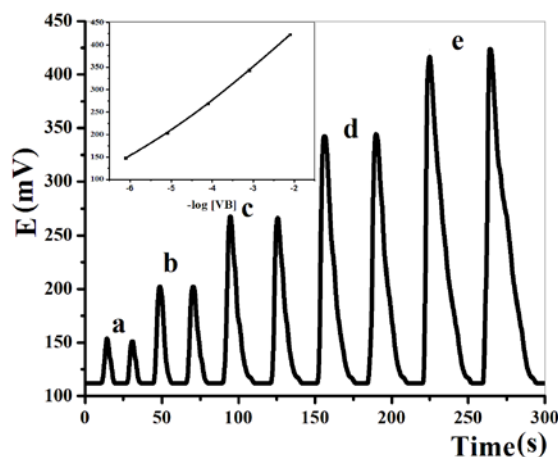
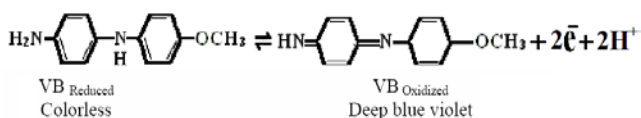


Fig. 1: FIA potentiometric determination of VB using VB-CPE: a) 1×10^{-6} , b) 1×10^{-5} , c) 1×10^{-4} , d) 1×10^{-3} , and e) 1×10^{-2} M; conditions; injected volume 200 μ L VB, at flow rate 45 mL min $^{-1}$.

3.2. Spectrophotometric method

3.2.1. Batch measurements

VB is a water soluble dye that has a pale gray color with very low molar absorptivity; upon oxidation, VB turns to a blue violet meriquinone form with absorption maximum at 550 nm. This oxidation was reported to take place through the transfer of two electrons to give rise to N-(4-methoxyphenyl)-quinonedimine (VB $_{ox}$) [3].



For the development of a new indicator reaction for practical applications in FIA measurements, attention should be paid to the reaction time to be short as possible to increase the sampling output and simplify the flow system. Oxidation of VB was performed using different oxidizing agents such as persulphate, periodate, bromate, iodate or hydrogen peroxide. In case of H_2O_2 , bromate or iodate, the oxidation was very slow, and applications of such oxidants were not suitable for FIA measurements (Fig. 2). On the other hand, KIO_4 and $\text{K}_2\text{S}_2\text{O}_8$ spontaneously react with VB to produce colored species which can be easily applied in FIA. The high difference in the molar absorptivity between both oxidized and reduced forms (about 6000 fold) greatly improves the sensitivity of the method.

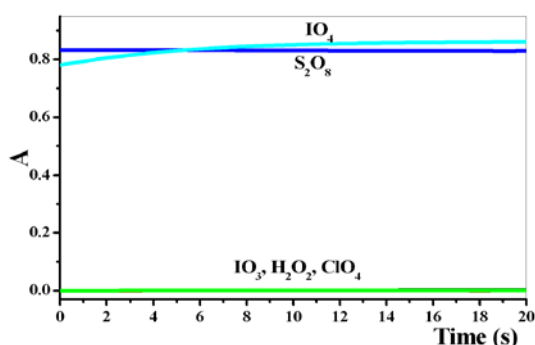


Fig. 2: Oxidation of VB with different oxidizing agents

3.2.2. FIA variables

FIA conditions such as reagent concentration, pH, flow rate, sample volume and the length of reaction coil were optimized in order to achieve the highest sensitivity. With injection of 80 μg VB in the flow system, the concentration of $\text{K}_2\text{S}_2\text{O}_8$ was changed from 10^{-3} to 10^{-1} M; 0.5 M was selected as it gave the highest sensitivity (Fig. 3 a). Acetate buffer with different pH values (3.6-5.6) were applied as a carrier stream for VB and pH 4.0 was the best (Fig. 2 b). Higher pH values, VB was precipitated as base and the absorbance greatly decreased.

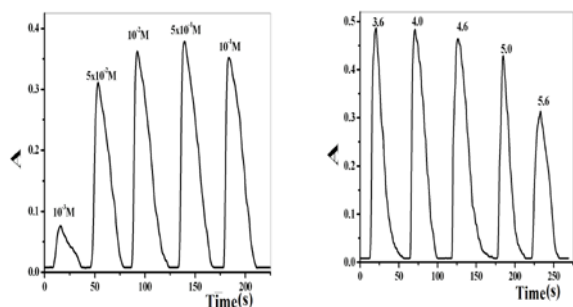


Fig. 3: Effect of the flow injection variables on the catalytic spectrophotometric determination of VB; a) effect of pH, and b) effect of oxidant concentration; conditions; 80 μg VB, at flow rate 10 mL min^{-1} .

The dependency of the peak height and residence time (time to recover the base line) on the flow rate was studied by applying different flow rates (1.5–22.2 mL min^{-1}). The flow rates of 6.6 mL min^{-1} were selected; slower flow rate gave broad peaks with

long tail while the faster one depressed the peak height (Fig. 3). An increase in the injection volume from 5 to 200 μL improved the peak height, though the sampling frequency decreased, injection of 50 μL was chosen as a compromise between the sensitivity and the sampling frequency. The length of the reaction coil was changed from 5 to 50 cm; for the sake of high sensitivity and sampling frequency, a 10 cm reaction coil was employed. Under the optimized conditions, the sampling through output 40 sample h^{-1} .

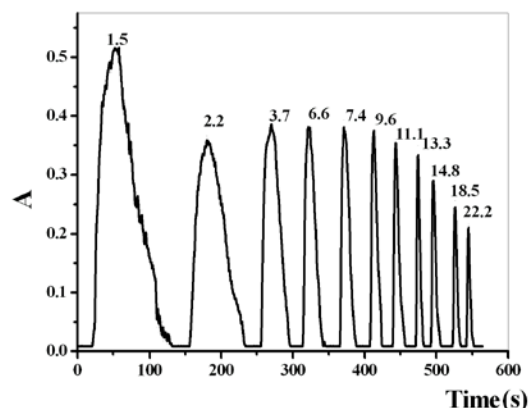


Fig. 3: Effect of the flow rate on the peak height and width of VB; conditions; 65 μg VB, at pH 4 and 0.5 mol L^{-1} $\text{K}_2\text{S}_2\text{O}_8$.

Typical FIA responses for the determination of VB are shown in Figure 4, the peaks were very sharp for all samples and the peak height was dependant on VB injected. Calibration graph was linear in the concentration range from 4.6 to 80 μg VB (Table 3). Reproducibility was evaluated from repeated 8 injections of 65 μg of VB solution; the average peak heights were 0.3928 ± 0.003 corresponding to recoveries $100.0 \pm 0.8 \%$.

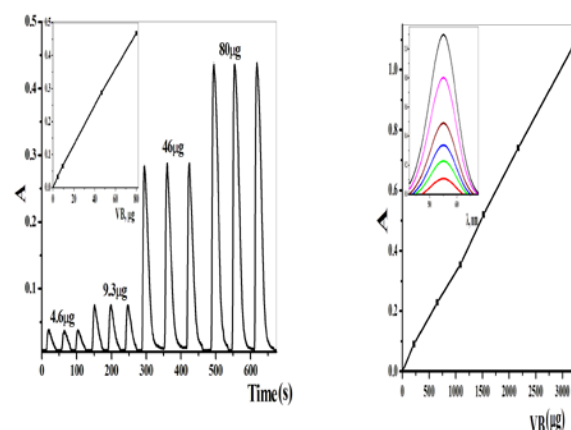


Fig. 5: Calibration curves for VB under optimized FIA and Batch conditions.

Contrary, under the optimized batch conditions (2mL of acetate buffer pH 4.0, 2 mL of $\text{K}_2\text{S}_2\text{O}_8$ 10^{-2} mol L^{-1}), the linear concentration range was from 217 to 3255 μg VB. The sensitivity was improved (about 17 times) under FIA with minimizing the exposure to the toxic organic solvents

Table 3: Characteristic parameters for FIA and batch spectrophotometric determination of VB

Item	Batch	FIA
λ_{\max} , nm		550
Beer's law limits ($\mu\text{g VB}$)	217 - 3255	4.6-80.0
Molar absorptivity ($\text{L mol}^{-1}\text{cm}^{-1}$)	1.31×10^3	
Detection limit ($\mu\text{g VB}$)	100	2.7
Reaction time (min)	Spontaneous	40 S hr^{-1}
Color stability (min)	90	
Regression equation*		
Slope (b)	3.4×10^{-4}	5.8×10^{-3}
Intercept (a)	6.4×10^{-4}	7.0×10^{-3}
S.D. of slope (S_b)	3.5×10^{-6}	1.1×10^{-4}
S.D. of intercept (S_a)	5.8×10^{-3}	4.9×10^{-3}
Correlation coefficient	0.99973	0.99939

* $A = a + bC$; where A is the absorbance and C is the VB concentration (μg)

4. CONCLUSION

This paper demonstrated simple potentiometric and spectrophotometric methods for VB determination under either the batch or FIA techniques. The potentiometric method was based on the fabrication of novel VB-CPE electrodes utilizing different preparation methods. The proposed electrodes showed Nernstian slopes in the concentration range from 10^{-6} to 10^{-2} M with fast response time (2 s) and long operational lifetime. CPEs were more suitable for use in flow injection systems due their fast response time and mechanical strength compared with PVC electrodes. The fabricated electrodes were successfully applied for the potentiometric determination of VB under FIA conditions with high sampling output (60 samples h^{-1}).

For spectrophotometric method, VB was oxidized with potassium persulfate forming a deep violet blue colored species with an absorption maximum at 550 nm. Under optimized FIA conditions, calibration graphs were linear in the concentration range from 4.6 to 80.0 μgVB and sampling through output 40 sample h^{-1} with high reproducibility.

These results may be the base for further research in routine analysis of dye in different industrial application stages, waste water and commercial dye products. The proposed potentiometric and spectrophotometric methods were efficient for determination of dyes specially that having low molar absorptivity.

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