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Voltammetric Determination of Boron using Cobalt Phthalocyanine Modified Carbon Paste Electrode

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An alternative mercury-free voltammetric method based on the complexation of boron with alizarin red S (ARS) for the determination of boron using cobalt phthalocyanine modified carbon paste electrode (CoPcMCPE) was described. The parameters affecting peak current such as supporting electrolyte, pH, concentration of ARS and accumulation potential in the method using CoPcMCPE were determined as ammonium acetate-ammonia mixture, pH = 7.5, $1x10^{-5}$ mol L^{-1} and -800 mV, respectively. The detection and quantitation limits of the method based on the standard deviation calculated from all points of the calibration equation for accumulation time of 0 and 30 s were calculated as 0.064 and 0.213 mg L^{-1}, and 9.9 and 32.9 µg L^{-1}, respectively. The method was applied to the determination of boron in water samples with boron content. The accuracy and repeatability of the method were checked by applying the standard addition method for 30 s accumulation time, and by comparing the results obtained from Azomethine H method. The results obtained from two methods were compared by using student's t-test and no statistical difference was found between the results for 95% confidence level. The recoveries were calculated in the range of 99-104% and the relative standard deviations were below 10%.

Keywords: Adsorptive stripping voltammetry, alizarin red S, boron, cobalt phthalocyanine, modified carbon paste electrode.

1. INTRODUCTION

Boron and its compounds have been widely used in agricultural and industrial fields such as nuclear energy, metallurgy, electronic, pharmacy and glass manufacturing. Moreover, it is useful element for plants and animals while the excess boron is accepted as toxic for plants and humans [1].

Provisional guideline value for boron in drinking water is given as 0.5 mg L^{-1} [2,3]. Therefore, the determination of boron in industrial and environmental samples is most important.

Several spectrometric and electrometric analytical methods have been developed for the determination of boron in various samples. Among the spectrometric techniques, spectrophotometry [4-6], spectrofluorimetry [7] atomic absorption spectrometry [8] inductively coupled plasma-atomic emission spectrometry [9,10], inductively coupled plasma-mass spectrometry [11-15], and X-ray fluorescence spectrometry [16] have been used. On the other hand, electrochemical voltammetric methods have been also used for the determination of boron. Since it is electrochemically inactive it has been determined indirectly in all of the electrochemical voltammetric methods. The existing voltammetric methods are summarized in Table.1. A cathodic stripping polarographic method based on the peak current decrease of As(V) in the presence of mannitol, copper and selenium in sulphuric acid medium developed for the determination of boron in mg/L level [17]. A differential puls polarographic method using tetraborate-copper complex formation has been reported for trace determination of tetraborate indirectly in waste and drinking water samples [18]. On the other hand, Beryllon (III) [19-22], Azomethine H [23] and Alizarin Red S (ARS) [24] have been used as complexing agents for voltammetric determination of boron at hanging mercury drop electrode (HMDE). Among those, more sensitive Beryllon (III) method has time consuming steps such as boiling for 15 min and waiting for ca. 15 h [20] or only waiting for 25 h [21] due to slow complex formation between boron and Beryllon (III) in room temperature. A mercury drop electrode has been used in all of the aferomentioned electrochemical methods. However, new alternative electrode materials are highly desired because of the toxicity of mercury. Recently, a differential pulse voltammetric method using glassy carbon electrode and based on boron-tiron complexation for indirect determination of boron has been reported [25]. The method was applied for determination of boron in reverse osmosis water samples. The limit of detection of the method for boron was reported as 0.11 mg L^{-1} and 0.08 mg L^{-1} for the reverse osmosis samples and sea water samples, respectively. However, these values are not enough for trace determination of boron in various samples using a mercury-free voltammetric method. Therefore, alternative and sensitive mercury-free voltammetric methods for determination of boron have been still needed.

In the present study it was proposed that an alternative mercury-free voltammetric method which was based on the complexation of boron with Alizarin Red S for the determination of boron at phthalocyanine modified carbon paste electrode (CoPMCPE). Although CoPMCPEs have been used for determination of organic compounds such as phenols and dithiocarbamate fungucides, there is no study attempting to assess electrochemical determination of boron by using a chemically modified carbon paste electrode. The chemical and instrumental parameters affecting the peak current such as supporting electrolyte, pH, concentration of ARS, accumulation potential and accumulation time have been investigated by using the new alternative method.

Table 1. Some voltammetric methods used for determination of boron.

Technique	Medium and electrode	Sample	Interference information	LOD	Ref.
DPCSV	0.8 mg/L As (V), 0.1 M mannitol, 22.5 mg/L Cu(II) and 60 µg/L Se(IV) in 0.1 M sulphuric acid medium, HMDE.	Water	n.r.	2.7 mg L^{-1} t_{dep}= 90 s	17
DPP	Cu(II) in 0.5 M KNO_3, DME.	Waste and drinking water	Pb(II), Cd(II) and Zn(II) did not interfere	34.5 µg L^{-1}	18
DPAdCSV	$1x10^{-5}$ M Beryllon III, in 0.06 M NO_3^- -0.04 M SO_4^{2-}, pH=4.5, 24h complexation time, HMDE.	Iron and steel	1mg/L of Al(III), As(III), Bi(III), Ca(II), Cd(II), Co(II), Mn(II), Ni(II), Pb(II), Sb(III), Si(IV), Zn(II), Zr(IV), chloride, or phosphate, 0.5mg/L Cu(II), or 0.1mg/LV(V) did not interfere.	0.2 µg B/L t_{dep}= 60 s	21
SWV	$1x10^{-3}$ M Azomethine H, 1M AcH-0.5 M NH_4Ac, pH=4.4, HMDE.	Natural water	n.r.	45 µg L^{-1}	23
DPASV	$1x10^{-6}$ M Alizarin red S, in NH_4Ac- phosphate buffer,pH=7, HMDE.	Water and seawater	As(III), Ca(II), Cd(II), Co(II), Cr(III), Cu(II), Mg(II), Ni(II) and Se(IV) did not interfere. The interference of Al(III), Fe(III), Zn(II) and Pb(II) eliminated by adding EDTA. Sb(III) is serious interfere.	15 µg L^{-1} without accumulation	24
DPV	$5x10^{-3}$ M Tiron, GCE.	Reverse osmosis water	Interference from Cu(II), Pb(II), Cd(II) and Zn(II) have been reported as negligible.	110 µg L^{-1}	25
DPAdSV	$1x10^{-5}$ M Alizarin red S, in NH_4Ac-ammonia mixture, pH=7.5, CoPcMCPE	Water	1000 µg/L of As(III) and Ca(II), 50 µg/L of Al(III), Cu(II), Fe(III), Mg(II), Ni(II), Pb(II), and Zn(II) did not interfere.	64 µg L^{-1} for t_{dep}= 0 s 9.9 µg L^{-1} for t_{dep}= 30 s	The proposed method

DPCSV:Differential pulse cathodic stripping voltammetry, DPP: Differential pulse polarography, DPAdCSV: Differential pulse adsorptive cathodic stripping voltammetry SWV:Square wave voltammetry, DPASV: Differential pulse anodic stripping voltammetry, DPV: Differential pulse voltammetry.

2.MATERIALS AND METHODS

2.1.Reagents

Cobalt phthalocyanine was purchased from Alfa Aesar. Graphite powder and mineral oil (Nujol) were purchased from Sigma. ARS (Alizarin Red S, Fluka) and boron (Boric acid, Merck) stock solutions were prepared by dissolving appropriate amounts of these chemicals in deionized water. The other chemicals used throughout the study were of analytical grade. All of the aqueous solutions were prepared with ultrapure deionized water supplied by ELGA PURELAB Option-Q model water purification system.

2.2.Apparatus

Voltammetric measurements were performed with an electrochemical system comprising Radiometer Pol 150 Polarographic Analyzer and the MDE 150 polarographic stand. The system was controlled with Trace Master 5 software. A conventional three-electrode cell assembly consisting of an unmodified carbon paste electrode (CPE) or a cobalt phthalocyanine modified carbon paste electrode (CoPcMCPE) as working electrodes, an Ag/AgCl (sat.KCl) reference electrode and a platinium wire counter electrode was used. A WTW Inolab pH-meter with combined glass electrode was used to measure the pH of the solutions. The pH-meter was calibrated by using the standard buffer solutions prior to measurement of the pHs. Micropipettes (10-100 μL, 100-1000 μL and 1-5 mL, Proline, Biohit) equipped with appropriate disposable tips were used to add the solutions.

2.3.Preparation of unmodified and modified carbon paste electrodes

Unmodified carbon paste electrode was prepared by thoroughly mixing nujol and graphite powder in a ratio of 28:72 (w/w) in a mortar with pestle. CoPcCPE was prepared by hand-mixing % 70 of graphite powder with 2% of cobalt phthalocyanine taking 28% (w/w) of nujol in a mortar with pestle. The bodies of the unmodified and modified CPE were a glass tube (ca. 3 mm i.d.) filled with the carbon paste. Copper wire was used for establishing the electrical contact. The electrode surface was polished on a smooth paper sheet and then rinsed with ethanol and distilled water, respectively. To obtain a good analytical signal, electrode was placed in supporting electrolyte and conditioned at 1 V for 120 s, then the potential was scanned cyclically from -1.0 V to 1.0V at 100 mV/s until the baseline became stable. After each run, it was transferred into the supporting electrolyte and electrolyzed at -1 V under stirring for 60 s to clean its surface. The next new electrode surfaces were activated as previously described for all subsequent measurements.

2.4.Procedure

The general procedure in the experiments was as follows: 1 ml of $1x10^{-4}$ mol L^{-1} of ARS, 1 ml of 1 mol L^{-1} ammonium acetate-ammonia mixture (pH 7.5) and the required amount of boron (or water

sample) were pipetted into a 10 ml of volumetric flask and completed to 10 ml with deionized water. Nitrogen gas was purged for 5 min. after the solution was transferred to the voltammetric cell. Then, accumulation on CoPcMCPE was performed at -800 mV by stirring the solution at 400 rpm for 30 s (this step was omitted in the case of unmodified CPE). After that, stripping was initiated toward anodic direction by using DP modulation in quiescent solutions after 20 s of rest time. The other instrumental parameters were step duration of 0.1 s, step amplitude of 2 mV, pulse duration of 0.02 s and pulse amplitude of 25 mV. All the measurements were performed at room temperature.

3.RESULTS AND DISCUSSION

3.1.Voltammetric Peak Characteristics of the Boron-ARS Complex at CoPcMCPE

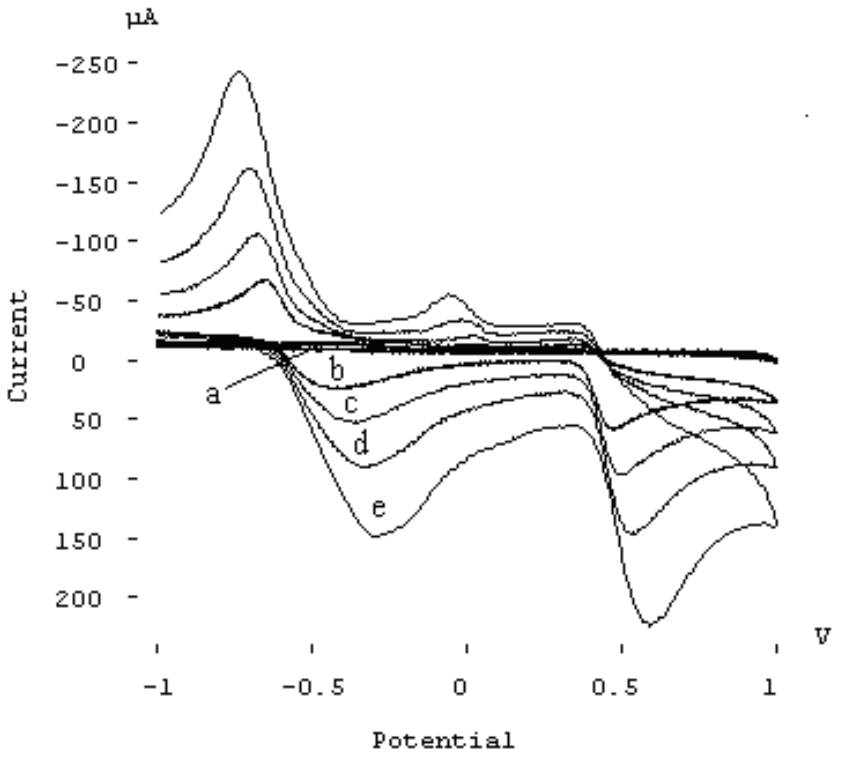

Figure 1. Cyclic voltammograms of ARS ($1x10^{-3}$ mol L^{-1}) at CPcMCPE for various scan rates in solution containing 0.1 mol L^{-1} ammonium acetate-ammonia mixture (pH 7.5). (a) 100 mV/s (b)200 mV/s (c)500 mV/s, (d)1000 mV/s and (e)2000 mV/s.

It is well-known that phthalocyanine has an electrocatalytic effect in electrode reaction of organic compounds. For this reason phthalocyanine modified carbon paste electrode was chosen to investigate the electrochemical behaviour of ARS. Fig.1 shows cyclic voltammograms of $1x10^{-3}$ mol L^{-1} ARS for various scan rates in 0.1 mol L^{-1} ammonium acetate-ammonia mixture (pH 7.5). In this medium, ARS has two anodic peak at ca. -400 mV and ca. 600 mV, respectively. The peak at ca. 600

mV is irreversible while the peak at ca. -400 mV is quasireversible. The anodic peak current of ARS at ca. -400 V was plotted versus potential scan rate. The peak current linearly changed with potential scan rate (I_p=0.068υ+16.10, r=0.995) indicating that is an adsorption process. Cyclic voltammograms for various scan rates (200, 500, 1000 ,2000 mV/s) in the solution containing $1x10^{-3}$ mol L^{-1} of ARS, $5x10^{-3}$ mol L^{-1} of boron and 0.1 mol L^{-1} of ammonium acetate-ammonia mixture at pH 7.5 were also recorded (not shown). The same linearity between peak current and potential scan rate was observed (I_p=0.0674υ+13.165, r=0.995) supporting the adsorption process.

The differential pulse voltammograms of ARS and boron-ARS complex at CoPcMCPE are shown in Fig. 2. A peak is present at –600 mV in a solution of $1x10^{-5}$ mol L^{-1} of ARS at pH 7.5 when the potential is scanning towards anodic direction. After the addition of boron to the solution a new peak at –464 mV appears. This new peak proportionally increases with increasing concentration of boron while the peak at –600 mV significantly decreases. This indicates that the boron-ARS complex presents the same behaviour at CoPcMCPE with hanging mercury electrode [24], and boron can be determined using a mercury-free carbon based electrode.

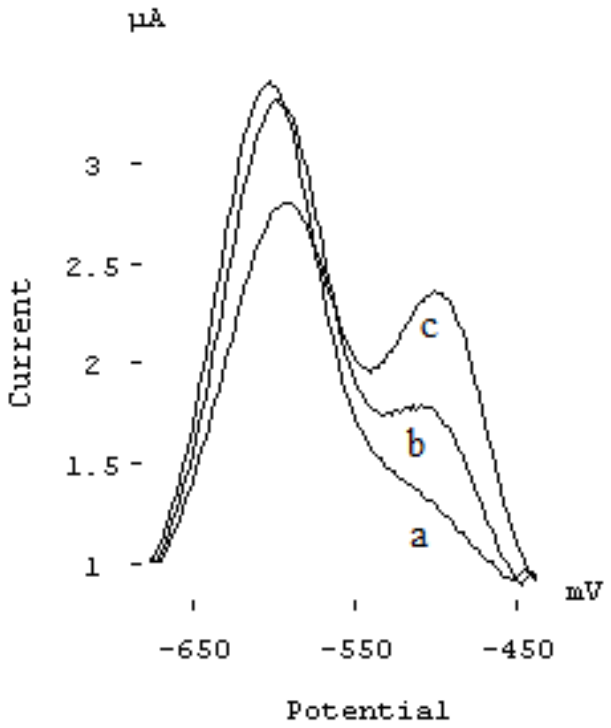

Figure 2. Differential pulse voltammograms for ARS and B-ARS complex at CoPcMCPE in solution containing 0.1 mol L^{-1} ammonium acetate-ammonia mixture (pH 7.5) without accumulation. Other conditions; pulse amplitude:25 mV, scan rate 20 mV/s. (a) $1x10^{-5}$ mol L^{-1} of ARS, (b) a+ $3x10^{-4}$ mol L^{-1} (3.2 mg L^{-1}) of B, (c) a+ $1x10^{-3}$ mol L^{-1} (10.8 mg L^{-1}) of B.

3.2. Effect of pH and Supporting Electrolyte

The effect of pH on the peak current of ARS in the B-ARS complex was studied over the range of 7.0-8.5 pHs (Fig. 3). The results showed that the peak current rapidly increases from pH 7.0 to 7.5

and then, sharply decreases by increasing of pH. A negative shift in the peak potential of the boron-ARS complex was observed with increase in pH. No significant signal related to the oxidation of ARS in the complex was obtained below pH 7.0. The optimum pH was selected as 7.5 to carry out subsequent experiments. Additionally, phosphate buffer, acetic acid-phosphoric acid mixture and ammonium acetate-ammonia mixture were tested as supporting electrolyte at pH 7.5. Among those, 0.1 mol L^{-1} ammonium acetate-ammonia mixture (pH=7.5) gave the maximum peak current and the best resolution. The peak belongs to boron-ARS complex disappeared in solution containing phosphate while the peak of free ARS decreases. This situation can be attributed that the $H_2PO_4^-$ and HPO_4^{2-} species preferably adsorbed the electrode surface than that of boron-ARS complex.

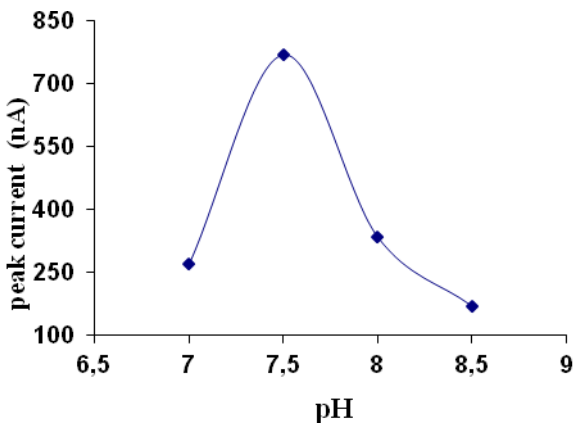

Figure 3. The effect of pH on the peak current. Conditions: $5x10^{-4}$ mol L^{-1} (5.4 mg L^{-1}) of B, $1x10^{-5}$ mol L^{-1} of ARS, other conditions are as in Fig.2.

3.3. Effect of ARS Concentration

The effect of the ARS concentration on the peak current of ARS in the boron–ARS complex was examined over the concentration range of $1.0x10^{-6}$ to $1.0x10^{-4}$ mol L^{-1} in the presence of $5x10^{-4}$ mol L^{-1} boron and supporting electrolyte at pH 7.5 (Fig.4.). The results showed that peak height of boron–ARS complex increases with the ligand concentration but the resolution was getting bad. For this reason, $1x10^{-5}$ mol L^{-1} of ARS was selected. It can be thought that the ligand concentration should be higher than that of boron in the solution. However, this situation can be valid in the case of adsorptive stripping determination of an electroactive metal ion in the ML complex, adsorbed to the electrode surface. It should be noted here that boron is not electroactive and it is determined indirectly by monitoring the oxidation of ARS in the boron-ARS complex. As a result, the concentration of ARS can be higher than concentration of boron in the solution. Thus, the solution characteristic of the method is different from the conventional methods in terms of boron/ARS ratio. The same situation was also observed and discussed in our previous study [24].

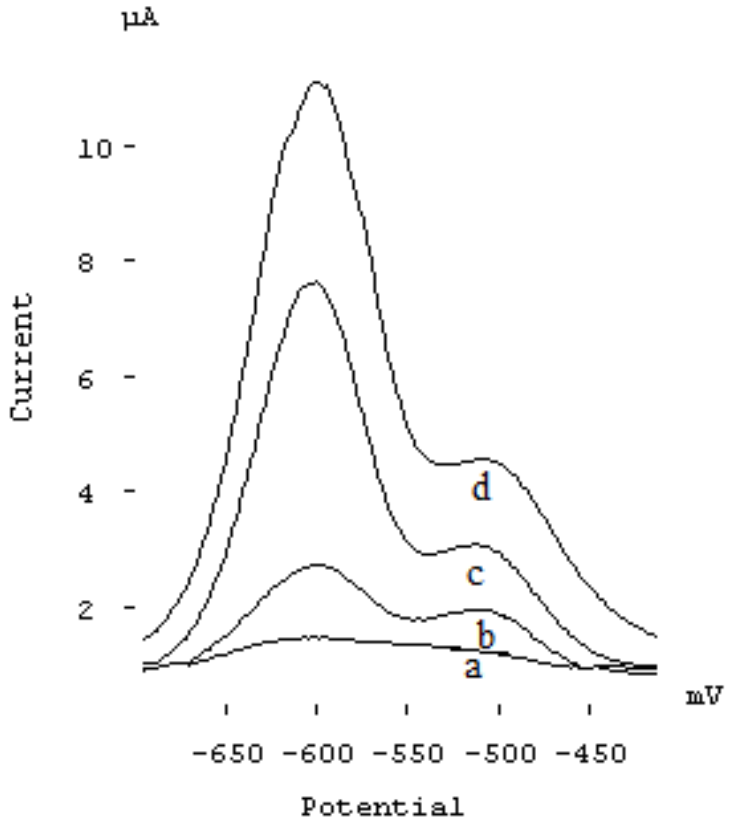

Figure 4.DP voltammograms obtained for various concentration of ARS in the presence of $5.x10^{-4}$ mol L^{-1} (5.4 mg L^{-1}) of B. (a) 10^{-6} mol L^{-1}, (b) $1x10^{-5}$ mol L^{-1}, (c) $5x10^{-5}$ mol L^{-1}, (d) $1x10^{-4}$ mol L^{-1}. Other conditions are as in Fig.2.

3.4. Effect of Accumulation Potential and Accumulation Time

The effect of accumulation potential on the peak current was studied for accumulation time of 5 s at different potential values such as -1000, -900, -800 and -700 mV but the scan was initiated from –700 mV in each experiment. The peak current maximum was observed at -800 mV and thereafter, this potential was preferred.

The variation of peak current as a function of accumulation time at unmodified CPE and CPcMCPE is shown in Fig.5. As follows Fig.5.A, at unmodified CPE, the current increases with accumulation time and reach a maximum at 5 s and then, almost remain constant This behaviour attributed that the complex and the free ligand were adsorbed competitively on the electrode surface. This kind of behaviour was also observed for the complex at hanging mercury electrode [24]. Yet, peak current increases with accumulation time as expected from conventional adsorptive stripping phenomenon at CoPcMCPE and saturated at accumulation time of 90 s (Fig.5.B). This behaviour shows that sensitivity can be improved for determination of boron using CoPcMCPE.

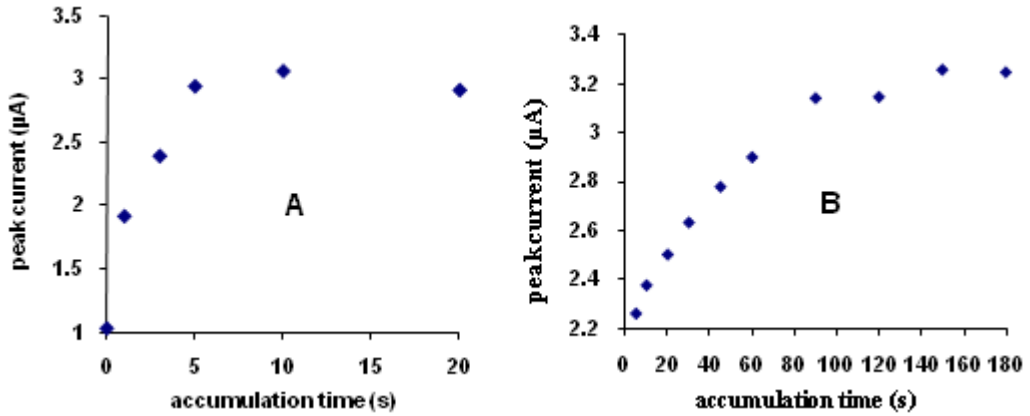

Figure 5. The effect of accumulation time on peak current. (A) at unmodified CPE, (B) at CoPcMCPE. Conditions: $5x10^{-4}$ mol L^{-1} (5.4 mg L^{-1}) of B, $1x10^{-5}$ mol L^{-1} of ARS, other conditions are as in Fig.2.

3.5. Validation and Application of The Method

Under the optimized conditions, calibration curves for accumulation times of 0 and 30 were constructed for determination of boron. It was noted that the calibration equation and the linear range varied according to accumulation time used. The calibration equations, coefficient of correlation and the linear range obtained for accumulation time of 0 and 30 were found as I_p=376.64C_B+ 2982.1, r=0.998, 0.213-1.00 mg L^{-1} and I_p=11.0C_B+ 1737.5, r=0.994, 32.9-70.0 µg L^{-1}, respectively. The detection and quantitation limits of the method based on the standart deviation calculated from all points of the calibration equation were calculated for accumulation time of 0 and 30s, as 0.064 and 0.213 mg L^{-1} and 9.9 and 32.9 µg L^{-1}, respectively.

The interferences of various ions such as Al(III), As(III), Ca(II), Cu(II), Fe(III), Mg(II), Ni(II), Pb(II), Sb(III) and Zn(II) were examined in the presence of 50 µg L^{-1} of boron. Among those, 1000 µg L^{-1} of As(III) and Ca(II), 50 µg L^{-1} of Al(III), Cu(II), Fe(III), Mg(II), Ni(II), Pb(II), and Zn(II) did not interfere. The interference from all the metal ions except Sb(III) was eliminated by the addition of small amount of EDTA. The interference that could not be removed by using EDTA from Sb(III) was observed.

The proposed method was applied to the determination of boron in tap water samples. Fig.6 shows the standard addition voltammograms obtained for accumulation time of 30 s.The boron concentration in the water samples and the recoveries obtained from the boron spiked water samples are shown in Table 2. The required dilution was made for all of the samples. The recoveries were calculated in the range of 99-104% and the relative standard deviations were below 10%. Azomethine-H method was used for checking the accuracy of the proposed method. The results obtained are listed in Table 2. Statistical evaluation of the results using Student's t test (for %95 confidence level) show that there is a good agreement between the mean concentrations obtained by the two methods.

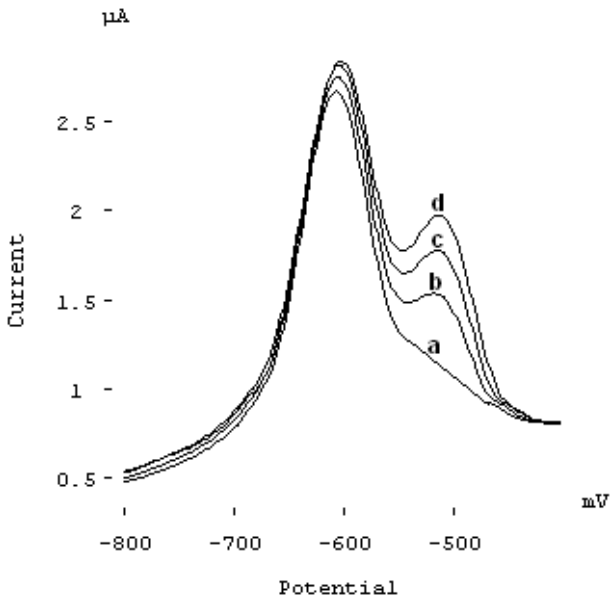

Figure 6. Standard addition voltammograms obtained for determination of boron in water sample at CoPcMCPE. (a)blank ($1x10^{-5}$ mol L^{-1} ARS + 0.1 mol L^{-1} ammonium acetate-ammonia mixture, pH=7.5), (b)a+water sample, (c) b+20 µg L^{-1} boron, (d)b+40 µg L^{-1} boron. Conditions:E_{acc}=-800 mV, t_{acc}=30 s.

Table 2. The results and the statistical evaluations obtained from the proposed method and Azomethine-H method for the determination of boron in water samples.

Water samples	Added (µg L^{-1})[a]	Found (µg L^{-1})[a]	Found by Azomethine-H method (µg L^{-1})[a]	calculated F value[b]	calculated t value[c]	RSD (%)	Recovery (%)
A[d]	-	875±14	845±20	2.01	2.09	1.60	-
	800	1663±20	-		-	1.20	99
B[d]	800	795±67	857±17	14.96	1.54	8.43	99
C[d]	800	828±77	874±33	5.33	0.95	9.30	104

[a]Average of three independent determinations. [b] Critical value for $F_{3,3}$ at the 95 % level is 19. [c] Critical t-value for 4 degrees of freedom at the 95 % level is 2.78. [d]Samples was diluted 1:40 with deionized water for the proposed method.

4. CONCLUSIONS

An alternative mercury-free voltammetric method based on the complexation of boron with Alizarin Red S for the determination of boron using cobalt phthalocyanine modified carbon paste electrode (CoPMCPE) was described. CoPMCPEs were used for the voltammetric determination of boron for the first time. An accumulation time of 30 s results in a detection limit of 9.9 µg L^{-1}which has ca. 10 fold enhancement than the present mercury-free method reported by Fujimoro et all. The

detection limit of the method is also lower than that reported for mercury electrodes [17,18, 23, 24], excluding Beryllon (III) method. However, the method is simple and rapid than Beryllon (III) method due to not require time consuming steps such as boiling and waiting. As a result, it was demonstrated that the optimized method is suitable for detecting low levels of boron as good as the other reported voltammetric methods in water samples. Serious interference from Sb(III) is the main drawback of the method. Therefore, the method is recommended for determination of boron in samples not including Sb(III).

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