

Simple and rapid voltammetric determination of boron in water and steel samples using a pencil graphite electrode

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Received: 22.07.2015

Accepted/Published Online: 27.11.2015

Final Version: 17.05.2016

Abstract: This paper presents a simple, rapid, and accurate voltammetric method for determination of boron in water and steel samples using a disposable pencil graphite electrode. The oxidation of Tiron in the boron–Tiron complex in phosphate buffer at pH 7.5 was measured as a response. Type and concentration of supporting electrolyte, pH, ionic strength, Tiron concentration, scan rate, step amplitude, pulse amplitude, and pencil grade were investigated as the parameters affecting the peak current. The limit of detection (3s) was estimated as 84 $\mu\text{g/L}$. The relative standard deviation of the method was 4.6 for 1 mg B/L ($N = 7$). The recovery results varied between 90% and 103% for water samples and between 94% and 108% for steel samples. The results were compared with those obtained from the ICP-OES method and no statistically significant difference between the methods was found.

Key words: Pencil graphite electrode, boron, voltammetry, water, steel

1. Introduction

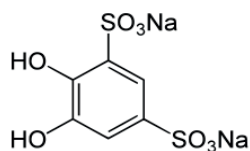
Boron compounds have been commonly used in various industrial fields such as metallurgy, glass manufacturing, nuclear energy, electronics, and pharmacy. Furthermore, boron is a supportive element for animals and plants even though it can be toxic for humans and plants in excess amounts [<http://www.atsdr.cdc.gov/mrls.html>]. The natural sources of boron in ground water are water–rock interactions in geothermal regions and seawater intrusion. Boron exists predominantly as boric acid (H_3BO_3) in water samples at pH lower than 7, while metaborate anion $\text{B}(\text{OH})_4^-$ is the main species at pH higher than 10. The boron content of irrigation water is most important because water containing more than 1.0 mg/L boron may cause severe damage to some sensitive plants such as lemon, blackberry, orange, apricot, wheat, and sunflower [<http://www.fao.org/docrep/003/T0234E/T0234E05.htm>]. The value recommended by the WHO¹ for boron in drinking water is 2.4 mg/L. On the other hand, boron is used in steelmaking in small quantities in order to increase the hardenability of the steel. Therefore, simple, cheap, rapid, and accurate determination of boron is important in water, environmental, and industrial samples.

Molecular spectrometric^{2–7} and atomic spectrometric methods^{8–17} have been reported for boron determination. Among these, UV-vis spectrophotometric^{2–4} and plasma source atomic spectrometric methods^{10–16} have been widely used. However, complicated procedures such as coloration steps, lack of applicability in colorful

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samples, various interferences, low sensitivity, and low precision are common disadvantages of spectrophotometric methods. On the other hand, high instrumental cost and being cumbersome are general difficulties of the atomic spectrometric methods. The spectroscopic methods used for determination of boron have been reviewed by Sah and Brown.¹⁸ Contrary to these methods, easy, cheap, sensitive, and portable voltammetric methods have been reported for boron determination in recent years. Actually, the direct voltammetric determination of boron is not possible for the reason that boron is electrochemically inactive. Thus, complex formation of boron with an electroactive ligand has been typically used for indirect voltammetric determination of boron. A cathodic stripping voltammetric method was developed monitoring the decrease in As(V) peak current in solutions containing sulfuric acid, copper, selenium, and mannitol. Boron was determined at mg/L level due to the formation of boron–mannitol complex.¹⁹ A differential pulse polarographic method based on formation of tetraborate–copper complex in solution containing 0.5 mg/L KNO₃ has been described for determination of tetraborate in drinking and wastewater samples.²⁰ The detection limit of this method for tetraborate was 124 μg/L. An adsorptive cathodic stripping voltammetric method using beryllon (III)–boron complex has been used for boron determination in plants and soil, food, plasma, and steel samples.^{21–24} However, this method requires heat and about a day for completing the complex formation. A square wave voltammetric method with a limit of detection of about 45 μg/L using azomethine H as complexing agent has been reported by Isbir.²⁵ Nevertheless, this method requires the solution to be left in the dark for 80 min for complex formation. The aforementioned methods are based on cathodic potential scanning for voltammetric determination of boron. In our previous studies, we reported two anodic stripping voltammetric methods at a hanging mercury drop electrode and a cobalt phthalocyanine modified carbon paste electrode (PCMCPE) using Alizarin Red S (ARS) as a ligand for boron determination in water samples.^{26,27} Recently, Fujimoro et al.²⁸ reported a differential pulse voltammetric method based on oxidation of Tiron (Scheme 1) in the boron–Tiron complex at a glassy carbon electrode (GCE). The method was applied to reverse osmosis and seawater samples for boron determination. The limit of detection for the method was reported to be 0.11 mg/L and 0.08 mg/L for reverse osmosis and seawater samples, respectively. The anodic peak of diols such as ARS and Tiron shifts to more positive potential because of complex formation with boric acid. This behavior enables boric acid to be determined in the samples. The existing voltammetric procedures mentioned above used mercury electrodes or carbon-based electrodes such as a PCMCPE and GCE. However, the toxicity of mercury-based electrodes is the greatest drawback in their practical application. On the other hand, time-consuming steps such as electrode preparation, surface renewing, and polishing are the common difficulties for the PCMCPE and GCE. However, a disposable pencil graphite electrode (PGE) can be used as an alternative electrode material. Properties such as low cost, commercial availability, good mechanical rigidity, and high electrochemical reactivity are the main superiorities of PGEs over the other carbon-based electrodes.^{29,30} For this reason, it can be used as disposable electrode material without any time-consuming processes such as electrode preparation, surface renewing, and polishing. To the best of our knowledge, there is no study on the determination of boron in any real samples using a disposable pencil graphite electrode.

The aim of the present work was to optimize and characterize a voltammetric procedure using a disposable PGE for boron determination in real samples. The instrumental and chemical parameters such as pH, type and concentration of supporting electrolyte, ionic strength, Tiron concentration, scan rate, step amplitude, pulse amplitude, and type of pencil graphite lead were investigated. The method was applied to water and steel samples. The results were compared with those obtained from the ICP-OES method and no statistically significant difference between the methods was found.

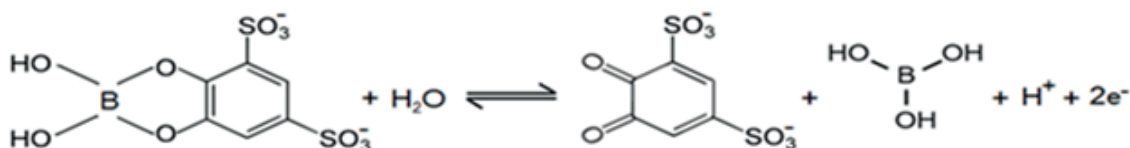


Scheme 1. Chemical structure of Tiron (disodium 4,5-dihydroxy-1,3-benzenedisulfonate).

2. Results and discussion

2.1. Voltammetric behavior of boron–Tiron complex at the pencil graphite electrode

The stoichiometry, structure, and electrochemical oxidation mechanism of the boron–Tiron complex have been reported in the literature.²⁸ According to this study, boron forms a 1:1 complex with Tiron. The oxidation mechanism of the complex formed in the solution is given in Scheme 2.



Scheme 2. Oxidation mechanism of boron–Tiron complex.

The DP voltammograms of 5 mM Tiron in the absence (a and a') and presence (b and b') of 3 M boron in phosphate buffer at pH 7.5 are shown in Figure 1A. A very small peak is present at 825 mV in a solution of 5 mM Tiron. After addition of boron to the solution, the peak current increases while the peak potential remains almost constant. The peak proportionally increased with increasing boron concentration and was used as a signal for determination of boron. On the other hand, voltammetric behavior of the boron–Tiron complex was investigated using a bare GCE and PGE. For this purpose, cyclic voltammograms of the boron–Tiron complex were recorded in 0.06 M phosphate buffer (pH 7.5) containing 10 mM Tiron and 20 mg/L B at 100 mV/s scan rate at the GCE and PGE (Figure 1B). It is clear from the voltammograms that the peak current obtained from the PGE is higher compared to the peak at the GCE. The PGE showed about a six times higher signal and 75 mV lower oxidation potential (from 900 mV to 825 mV) than the GCE for boron. Moreover, the peak potential value of the boron–Tiron complex at the GCE shifted in the negative direction from 900 mV to 825 mV in the case of the PGE. Furthermore, cyclic voltammograms were recorded for 5, 10, 20, 50, 100, and 200 mV/s scan rates and the logarithm of peak current was plotted as a function of scan rate (data not shown here). The linear relationship was observed obeying the equation of $\log I_p = 0.4902\nu + 0.4813$ ($R^2 = 0.9962$). The slope of the equation is very close to 0.5, indicating that the electrochemical oxidation process of the boron–Tiron complex is a diffusion-controlled reaction. Additionally, the process is quasireversible at both PGE and GCE electrodes.

2.2. Effect of pH, type of supporting electrolyte, and ionic strength

pH and type of supporting electrolyte are important solution parameters affecting both formation of the boron–Tiron complex and its anodic oxidation reaction at the electrode surface. Therefore, these parameters should be optimized. The pH effect on peak height (I_p) was investigated by recording differential pulse voltammograms at a scan rate of 5 mV s⁻¹ in the range of 6–8 in 0.03 M phosphate buffer containing 4 mM Tiron, 0.2 M KCl, and 3 mg/L B. The peak current–pH graph was plotted and is shown in Figure 2. The peak height dramatically increased with increasing pH up to 7.5 and reached almost a plateau after that. No significant

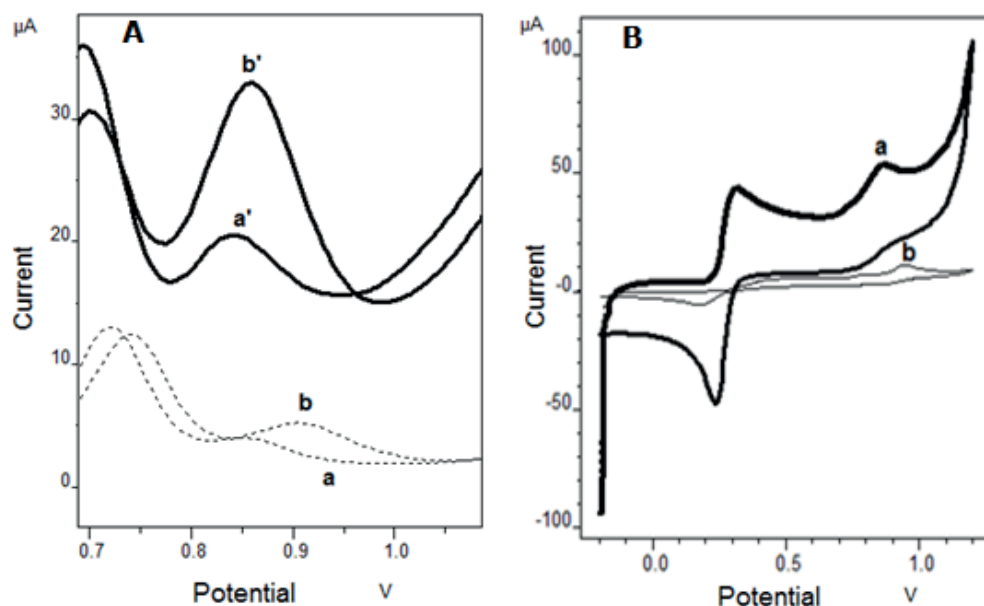


Figure 1. (A) Differential pulse voltammograms of Tiron with and without boron in phosphate buffer (pH 7.5) at PGE (black line) and GCE (dashed line). (a and a') 5 mM Tiron and 0.2 M KCl (b and b') a + 5 mg/L B. (B) Cyclic voltammograms obtained for the solution containing 0.06 M phosphate buffer (pH 7.5), 10 mM Tiron, 20 mg/L B, and 0.2 M KCl at PGE (a) and GCE (b).

peak was observed at pH lower than 6. An optimal pH was selected as 7.5 for further experiments. Additionally, ammonium acetate was used as supporting electrolyte instead of phosphate buffer. It was reported by Fujimoro et al. that a reproducible peak belonging to the boron–Tiron complex was observed only in the case of phosphate buffer. However, we obtained a peak at the same peak potential when ammonium acetate at pH 7.5 was used instead of phosphate buffer. The use of ammonium acetate instead of phosphate buffer can overcome a problem caused by the precipitation of magnesium phosphate in samples with high magnesium content. Nevertheless, boron concentration higher than 4 mg/L is required for obtaining a significant peak in ammonium acetate solution. Therefore, ammonium acetate solution can be recommended as an alternative to phosphate buffer for samples containing high boron and magnesium. The effect of concentration of phosphate buffer on peak current was also investigated in the range of 0.01–1.00 M (Figure 3). The peak current increased up to 0.05 M and then

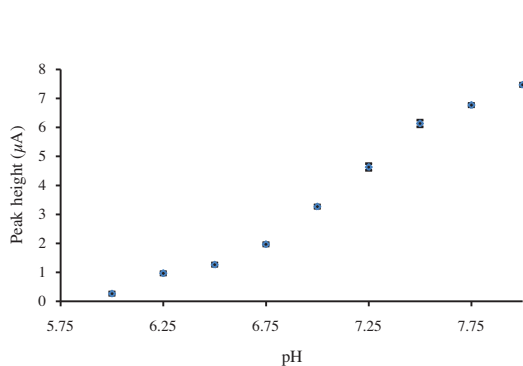


Figure 2. Effect of pH on the peak height in 0.06 M phosphate buffers. Conditions: 4 mM Tiron, 0.2 M KCl, 3 mg/L B, scan rate 5 mV s^{-1} , pulse amplitude 60 mV.

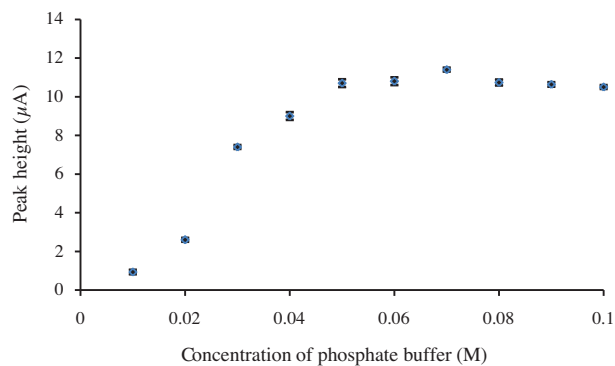


Figure 3. Dependence of phosphate buffer concentration on the peak height. Other conditions are the same as in Figure 2.

remained almost constant at high concentrations. The concentration of phosphate buffer was chosen as 0.06 M for subsequent studies.

Ionic strength is the other solution parameter affecting peak current and thus the sensitivity of the method. Various concentrations of potassium chloride were used for this purpose and the results are shown in Figure 4. The peak current increases with increasing potassium chloride concentration up to 0.2 M and then remains almost constant for higher values. Therefore, 0.2 M potassium chloride was used in the measurements.

2.3. Effect of Tiron concentration

Tiron concentration is the other important solution parameter affecting the peak current of the boron–Tiron complex. The effect of Tiron concentration on peak current is given in Figure 5. The peak current increased virtually linearly with increasing Tiron concentration up to 4 mM and then slightly increased at higher concentrations. The higher background current and increase in oxidation peak current of free Tiron caused resolution problems at concentrations higher than 5 mM. For this reason 5 mM was selected as optimum.

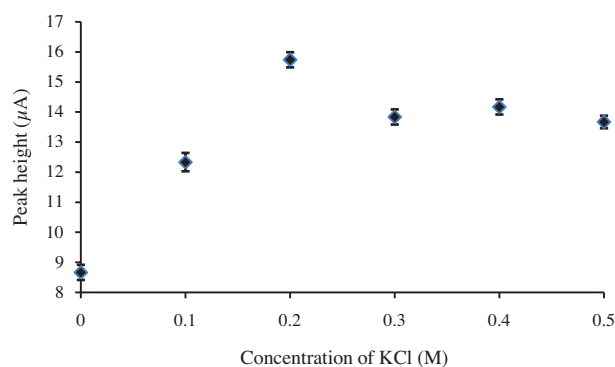


Figure 4. The effect of ionic strength on the peak height in 0.06 M phosphate buffer at pH 7.5. Other conditions are the same as in Figure 2.

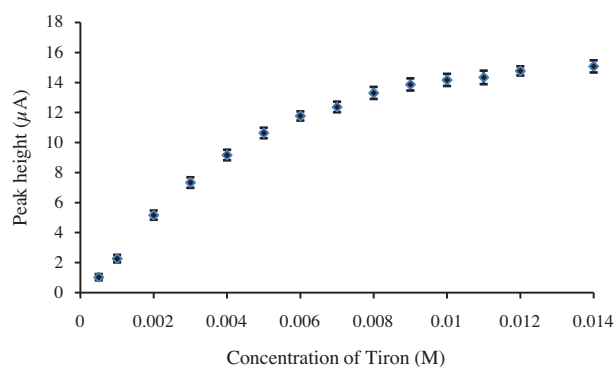


Figure 5. Effect of Tiron concentration on the peak height in 0.06 M phosphate buffer at pH 7.5. Other conditions are the same as in Figure 2.

2.4. Effect of scan rate and pulse amplitude

Scan rate and pulse amplitude are instrumental parameters affecting the peak current and hence sensitivity. Accordingly, the effect of scan rate and pulse amplitude was examined and the results are given in Figures 6 and 7, respectively. The peak current increased with scan rate up to 5 mV/s and then slightly decreased at higher values. Thus, 5 mV/s was used for sensitivity in the measurements. On the other hand, the peak current increased up to 60 mV when the pulse amplitude was increased. No peak deterioration or resolution problem was observed in the voltammograms recorded. Therefore, 60 mV was used for pulse amplitude.

2.5. Effect of pencil grade

Pencils are graded on the European Letter Scale using H (hardness) and B (blackness) letters with a number representing degree of hardness or blackness. A pencil graphite can be regarded as a composite electrode because it is composed of graphites, clays, and waxes as ingredients in varying proportions to obtain different pencil grades. Therefore, the effect of pencil grades on peak current using H, HB, B, and 2B pencil leads was studied and the results are given in Figure 8. It is clear from the figure that the proportion of graphite increased the

peak current up to B grade and then decreased it. Therefore, B grade pencil lead was selected as the working electrode material.

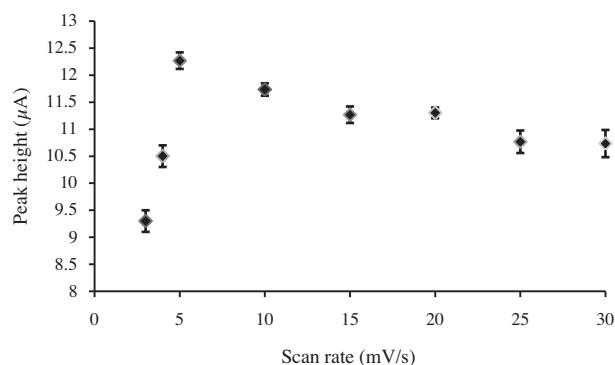


Figure 6. The effect of scan rate on the peak height. Conditions: 4 mM Tiron, 3 mg/L B, and 0.2 M KCl.

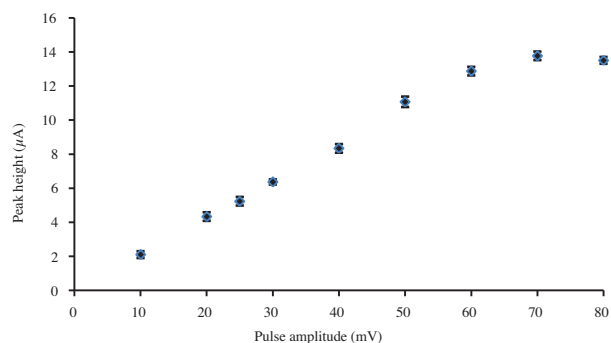


Figure 7. The effect of pulse amplitude on the peak height in phosphate buffer. Conditions: 4 mM Tiron, 3 mg/L B, and 0.2 M KCl.

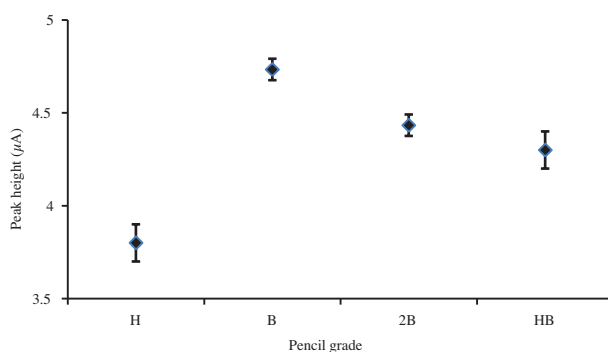


Figure 8. Plot of peak height values versus different grade pencil graphites (5 mM Tiron, 2.5 mg/L B, and 0.2 M KCl in 0.06 M phosphate buffer at pH 7.5).

2.6. Validation and application of the method

Using the selected conditions, voltammograms were recorded for constructing the calibration curve (Figure 9). After a blank subtraction was made, the linear relationship was obtained between 0.28 and 12 mg/L boron. The regression data are given in Table 1. The limit of detection ($3s$) and the limit of quantification ($10s$) calculated from the standard deviation of blank data ($n = 7$) were 0.084 mg/L and 0.28 mg/L, respectively. The relative standard deviation was calculated as 4.6% for the 1 mg/L boron level ($n = 7$).

Table 1. Regression data of the calibration graph.

Parameter	Value
Slope ($\mu\text{A L/mg}$)	2.507
Intercept (μA)	0.556
Standard deviation of slope ($\mu\text{A L/mg}$)	0.174
Standard deviation of intercept (μA)	1.182
Standard error of estimate (μA)	0.849
Determination coefficient (R^2)	0.9929

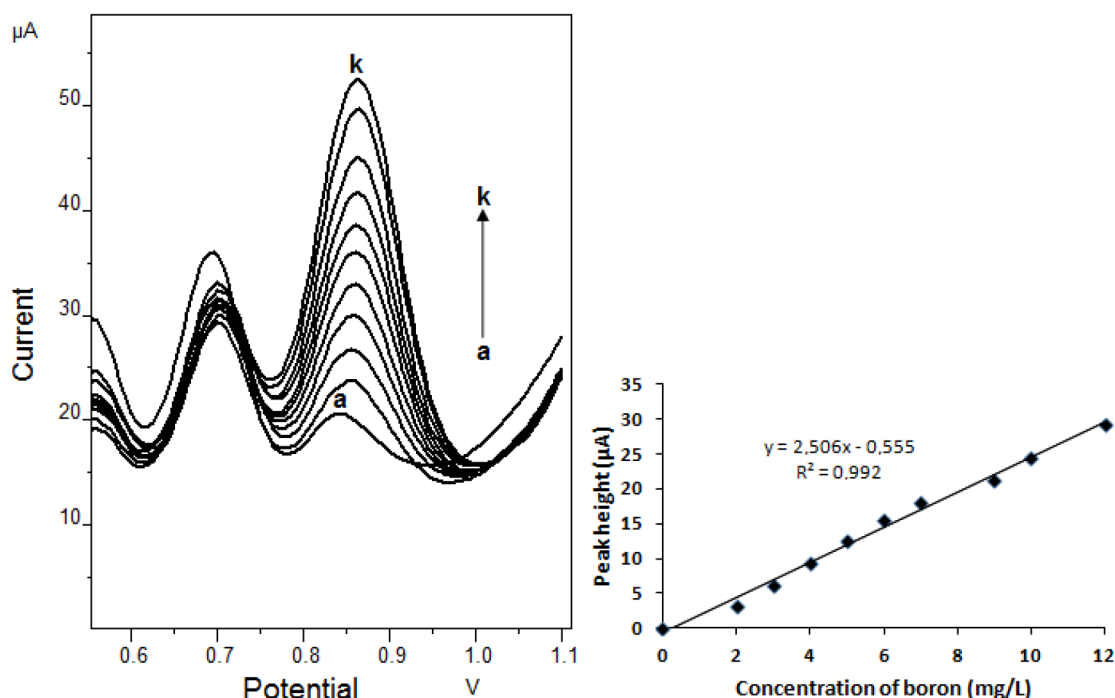


Figure 9. Some voltammograms and calibration graphs obtained for various boron concentration. (a) 0 mg/L, (b) 2 mg/L, (c) 3 mg/L, (d) 4 mg/L, (e) 5 mg/L, (f) 6 mg/L, (g) 7 mg/L, (h) 9 mg/L, (i) 10 mg/L, (j) 12 mg/L, and (k) 14 mg/L.

The interference effects of Zn^{2+} , Sb^{3+} , Pb^{2+} , Ni^{2+} , Mn^{2+} , Mg^{2+} , Fe^{3+} , Cu^{2+} , Cr^{3+} , Co^{2+} , Cd^{2+} , Ca^{2+} , Bi^{3+} , and Al^{3+} ions on the determinations of boron were investigated under the optimum conditions with 0.10 mg/L boron and in the presence of 0.10 mg/L investigated ion. The interference criterion was $\pm 5\%$ change in the peak current. The results showed that Zn^{2+} , Pb^{2+} , Ni^{2+} , Mn^{2+} , Mg^{2+} , Cr^{3+} , Co^{2+} , Cd^{2+} , Ca^{2+} , and Al^{3+} did not affect the peak current, while Bi^{3+} , Cu^{2+} , Fe^{3+} , and Sb^{3+} caused about 9%, 13%, 8%, and 15% signal decrease, respectively.

The method was applied for boron determination in drinking water and steel samples by using the standard addition method. A steel sample (code number K110 1.2379) containing C (1.55%), Si (0.30%), Mn (0.30%), Cr (11.3%), Mo (0.75%), and V (0.75%) was used as the steel matrix in the experiments. There was no information about the boron content of the steel sample. For this reason, the accuracy of the method was confirmed by comparing the obtained results with those found by ICP-OES as well by the use of the recovery test. The results are summarized in Table 2. The results obtained by the proposed method for both water and steel samples were in agreement with the ICP-OES, and satisfactory recoveries were obtained.

In conclusion, voltammetric determination of boron in water and steel samples using a disposable PGE was examined for the first time. The disposable PGE is a good alternative to toxic mercury electrodes and the other expensive carbon-based electrodes requiring time-consuming preparation and cleaning steps. However, the whole measurement for a sample in the proposed method can be completed using only one PGE lead without electrochemical and mechanical cleaning steps and hence it is simple and rapid. The recovery and comparison tests showed that the proposed method is applicable to water and steel samples for the simple, rapid, selective, and accurate determination of boron. The method is sufficient for monitoring of water drinkableness in terms of boron according to the WHO guideline.

Table 2. The results achieved by the proposed and ICP-OES methods for the determination of boron in water and steel samples.

Samples	Proposed method				ICP-OES method
	Boron added (mg/L)	Boron found (mg/L) ($\bar{x} \pm s, N = 3$)	RSD%	R %	Boron found (mg/L) ($\bar{x} \pm s, N = 3$)
Tap water	-	0.71 \pm 0.07	7.0		0.74 \pm 0.01
	0.50	1.15 \pm 0.05	4.3	90	1.23 \pm 0.03
	1.00	1.64 \pm 0.11	6.7	93	1.76 \pm 0.03
Well water	-	1.06 \pm 0.06	5.7	-	1.05 \pm 0.02
	0.50	1.52 \pm 0.03	2.0	92	1.60 \pm 0.02
	1.00	2.12 \pm 0.16	7.5	103	2.11 \pm 0.03
Steel	Boron added (μg)	Boron found (μg)	(RSD%)	R %	Boron found (μg)
	37.5	40.5 \pm 3.5	8.6	108	39.0 \pm 0.5
	75.0	73.5 \pm 2.0	2.7	98	71.5 \pm 0.5
	100.0	93.5 \pm 3.0	3.2	94	94.5 \pm 1.5

3. Experimental

3.1. Chemicals and equipment

Atomic spectroscopic standard solutions from $1000 \pm 0.2 \text{ mg L}^{-1}$ stock solutions (as H_3BO_3 in water) were used for standard boron solution and the other solutions were used for interference studies after appropriate dilution with deionized water. All the other chemicals were analytical reagent grade. Deionized water (18.2 M Ω) obtained from a Sartorius Arium 611 ultrapure water purification system was used for preparation all the solutions.

Voltammetric measurements were performed using an Ivium CompactStat voltammetric analyzer connected to a BASi C3 electrode stand and controlled by a PC. A three-electrode system consisting of a disposable PGE with a surface area of 2.24 mm^2 (Tombow 07, Japan) as working electrode, a platinum electrode as auxiliary electrode, and a Ag/AgCl/KCl (3 M) as reference electrode was used. Pencil graphite leads were purchased from a local market in the city of Balıkesir in Turkey. An ONAS MP 775 model mechanical pencil body (China) was used as a graphite lead holder. A copper wire was coiled onto the metallic tip of the pencil for supplying electrical contact with the graphite lead. pH measurements was performed using a Hanna HI-121 model pH-meter combined with a glass electrode. The meter was adjusted with standard buffer solutions prior to measurements.

3.2. Measurement procedure

Voltammetric measurements were carried out in a quartz voltammetric cell. Before measurements, the electrochemical treatment of the PGE was performed in a solution containing 0.1 M of KCl and 0.05 M of phosphate buffer at pH 7.5 by applying a potential of 1.4 V for 60 s followed by cycling of the potential between -1.00 V and $+1.00 \text{ V}$ with a scan rate of 50 mV/s until a stable background was obtained. Then nitrogen was purged for 5 min after addition of Tiron or Tiron and the required amount of boron (or 5 mL sample). The final volume was completed to 10 mL with deionized water. Differential pulse modulation in the potential range between 0.50 and 1.00 V was used for obtaining current measurements. The instrumental parameters such as step amplitude, pulse amplitude, and scan rate were 10 mV, 60 mV, and 5 mV/s, respectively. All of the measurements were obtained at room temperature.

3.3. Sample preparation procedure

Drinking water and well water samples were collected from the Bigadiç district of Balıkesir in Turkey. The samples were stored in polycarbonate bottles at 4 °C. The measurement procedure was directly applied to water samples without any sample preparation step. The steel sample (ca. 1 g) was weighed accurately and transferred to a beaker and decomposed by heating on a hot plate after adding a concentrated nitric acid and hydrochloric acid (1:1) mixture. Then the solution was boiled to remove nitrogen oxides. After cooling, the solution was transferred into a 50-mL volumetric flask and completed to the mark with deionized water. Sodium hydroxide was added to the solution to separate iron as iron(III) hydroxide. The precipitate was filtered using Whatman Grade No 2 filter paper. A 5-mL aliquot of the filtrate was used for voltammetric measurements. Various amounts of boron were spiked to the sample prior to the decomposition step.

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