



## Determination of plant available boron in agricultural soil by using voltammetric method

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### Abstract

In this study, a novel voltammetric method has been developed to determine the amount of boron in soil. 50 soil samples were collected from 5 typical sites of agricultural area. After hot water extraction of available boron in the soil samples, all boron is complexed by addition of Alizarin Red S (ARS) to the extraction solutions. Differential pulse anodic stripping voltammetry was used to determine the amount of the boron complexes. The electrochemical parameters have been optimized according to the experimental results. The optimum scan rate, stirring rate, deposition potential, deposition time and pH values were determined as 5 mVs<sup>-1</sup>, 200 rpm, -0.5 V (vs. Ag/AgCl, sat.), 15sec. and 7.5, respectively. An oxidation peak was occurred at the peak potential of -0.45 V for Boron-Alizarin complex. The limit of detection, limit of quantification and linear working range were determined for the voltammetric soil-boron analysis. In addition, the interference effects of coexisting ions were successfully investigated. Comparison of the analytical data for analyzing real samples was carried out between the differential pulse anodic stripping voltammetric method and the Azometine H spectrophotometric method have shown good agreement. A great advantage of voltammetry over the spectrophotometric method is found to be simplicity, selectivity and shortening of the analysis time.

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### Introduction

Boron is an essential micronutrient for plants. Plants need a constant supply of boron (B) to maintain growth (Lehto et al, 2010). Boron shows basic role on transportation and metabolism of carbohydrate for plants (Uygan, 2004). Important parameters would be affected by boron deficiency such as shoot growth, barrier function of leaf surfaces, vessel formation, photosynthesis and root growth (Wimmer, 2013). On the other hand, boric acid can easily pass directly across phospholipid bilayers, so that boron is toxic for plants at higher concentrations (Reid 2010; Ibekwe et al, 2010). For these reasons, the determination of plant available boron in soil is an important workspace for modern agriculture.

Soils may contain 0.5-20 mg.L<sup>-1</sup> of plant available boron and hot water extraction method is convenient for establishing the available boron in soil (Kelling, 2010). Inductive Coupled Plasma (ICP) technique is widely used for trace boron analysis. ICP technique is applicable to the large number of elements with high reliability. However, this method is not suitable for on-site environment monitoring analysis due to its bulky size, high cost, and long analysis time. Besides, ICP technique only allows measurements of total concentration (Jang et al, 2011; Buffle, 2005). Spectrophotometric method can be used for determination of boron in soil extracts after the addition of specific reagents. Azomethine-H method is perhaps the most

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commonly used spectrophotometric method on boron determination. However, Azomethine-H method suffers from some interferences even if it is known as the most sensitive method (Sah, 1997; Seyhan et al, 2009).

Stripping voltammetry is an alternative method for spectroscopy to determine trace metal contents in various soil extracts (Opydo, 2008; Nedeltcheva et al, 2005; Serrano et al, 2013; Kumar et al, 2005). Zn, Cd, Pb, Cu, Ni, Co, Cr metals were determined in  $\mu\text{g.L}^{-1}$  levels with anodic, cathodic and adsorptive stripping voltammetry methods with glassy carbon working electrode (Farghaly, 2005). Pb, Zn and Cd metals were analyzed with mercury and bismuth modified pencil graphite working electrodes in anodic stripping voltammetry (Economou, 2004). Nowadays, pencil graphite is commonly used as working electrode for voltammetric measurements due to simple use, low cost and commercial availability (Özcan, 2011; Şahin, 2010). Adsorptive stripping voltammetry has been applied to determination of trace organic species and metal complexes in various media either with mercury drop and solid electrodes (Şahin, 2009; Lehto et al, 2010).

Since boron species are not electrochemically active, they cannot be oxidized or reduced when voltage or current applied. Due to this reason, boron cannot be determined by voltammetry directly. However, boron in water samples could be quantified with anodic adsorptive stripping voltammetry using hanging mercury working electrode after adding Alizarin Red S (ARS) boron complexing agent because of the electroactivity of Alizarin Red S-Boron (ARS-Boron) complex (Nakiboğlu, 2006).

In this paper, a simple and rapid voltammetric method has been applied for determination of boron in soil extracts with pencil graphite working electrode by using Alizarin Red S (ARS) complexing agent. This is the first time to use of pencil graphite as working electrode for the determination of Alizarin Red S-Boron (ARS-Boron) complex. Several parameters such as scanning rate, stirring rate, deposition potential, deposition time and pH were optimized for voltammetric technique. Interference of coexisting ions was successfully investigated. Finally, a new method has been applied on real soil samples. The reached sensitivity in this study is suitable for the determination of low levels of boron in soil samples without an extra pretreatment.

## Material and Methods

Electrochemical studies were performed by Gamry Reference 3000 potentiostat/galvanostat with Gamry Framework and Echem Analyst softwares. Pencil graphite, Pt wire and Ag/AgCl electrodes were used as working, counter and reference electrodes, respectively. Pencil graphite electrodes (PGEs) were Faber Castell leads with a diameter of 0.5 mm. A pencil holder stem was soldered with copper wire for electrical contact. Boron was determined by using Shimadzu UV-1800 UV-Vis spectrophotometer with Azometine H as described in soil analysis for comparison.

All chemicals used were of analytical grade and were used as received without any further purification (Merck). Aqueous solutions were prepared by using ultra deionized water. Polyethylene or polytetrafluoroethylene vessels were used for all procedures and optimizations even with simple dilution operations.

### Soil Analysis

Fifty soil samples were collected at different depths (0-20, 20-40, 40-60 cm) from the regions of Samsun, Tekirdağ, Kırklareli (Turkey). The collected soil samples were stored in polyethylene container for transportation to the laboratory, dried at room temperature, grounded and passed through a 10 mesh sieve.

10 g samples of soil was weighted and mixed with 20 mL of 10 mM  $\text{CaCl}_2$  (hot water extraction) solution. Mixture was boiled in polytetrafluoroethylene vessel for 10 minutes. The mixture was centrifuged for 15 minutes with 2700 rpm, and filtered after 2 minutes. Then, 0.1 g activated coal was added, mixed and filtered again when yellow colored solutions were obtained after first filtration.

1 mL of soil extract was pipetted and mixed with 2 mL of ammonium acetate/ acetic acid/ EDTA (2.5:1.31:0.15) masking buffer solution and 2 mL of azomethine H ( $1.01 \times 10^{-3} \text{ mol.L}^{-1}$ ). Spectrophotometric measurements were performed after 30 minutes.

8 mL of phosphate buffer solution (pH 7.5) -EDTA was added into 1 mL of soil extract for voltammetric experiments. Solution was diluted to 10 mL with  $10^{-4} \text{ mol.L}^{-1}$  ARS and voltammetric measurements were carried out with three electrode conventional system.

## Results and Discussion

### Optimization of voltammetric parameters

Firstly, ARS-Boron complex formation parameters and electrochemical behavior of the complex have been studied by cyclic voltammetry (CV) (Figure 1). Cyclic voltammograms of  $5 \times 10^{-4} \text{ mol.L}^{-1}$  ARS solution were taken with and without boron. One oxidation and one reduction peaks have been seen in the cyclic voltammograms. After the addition of boron into the ARS solution, the oxidation peak of ARS shifted to more cathodic potentials and the intensity of the reduction peak decreased.

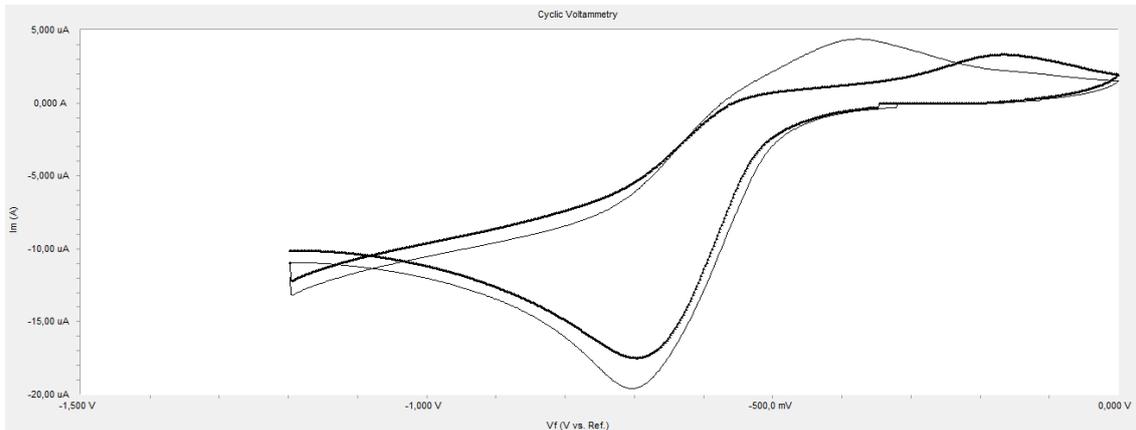


Figure 1. Cyclic voltammograms of  $5 \times 10^{-4} \text{ mol.L}^{-1}$  ARS a) with (thin line) and b) without (bold line) boron in phosphate buffer solution at pH: 7.5.

Differential pulse voltammetric (DPV) response of complexing agent was evaluated in the phosphate buffer solution (PBS) with and without boron (Figure 2). DPV method was used for the determination of the oxidation peak of ARS and ARS-Boron complex. An oxidation peak of ARS was obtained at the peak potential of -500 mV with pencil graphite working electrode in PBS. When boron was added to the ARS solutions, a new peak occurs at -0.400 mV and increasing amount of boron leads to decrease of ARS peak current intensity. These results show that pencil graphite is suitable to sense ARS-Boron complex in soil extracts.

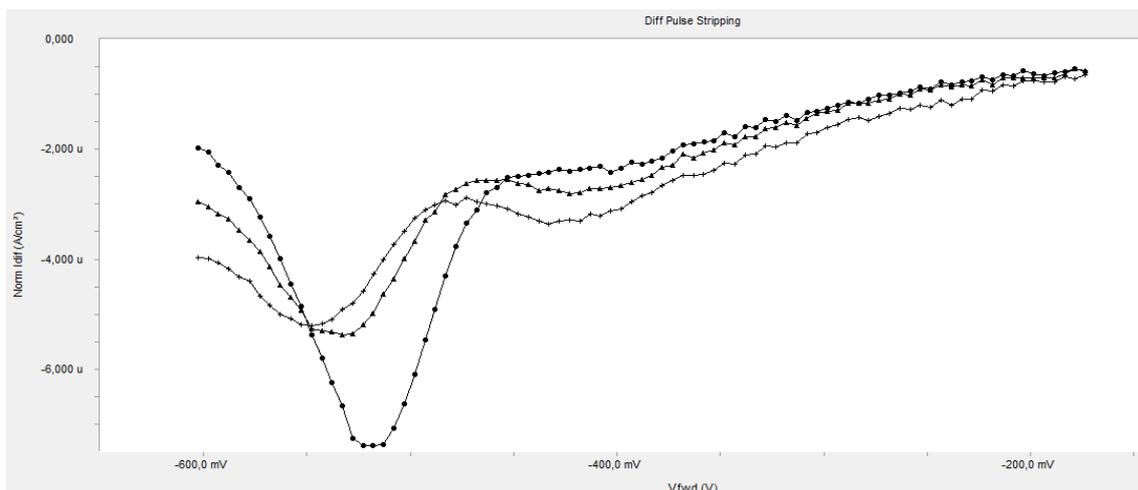


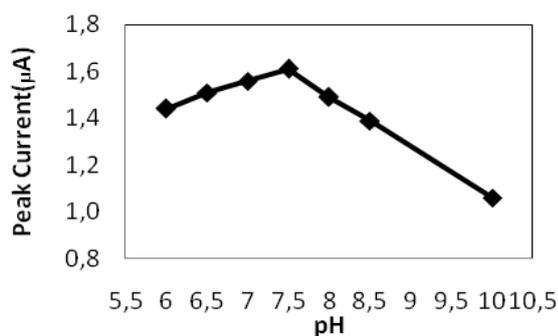
Figure 2. Differential pulse stripping voltammograms of a)  $\bullet$   $5 \times 10^{-4} \text{ mol.L}^{-1}$  ARS, b)  $\blacktriangle$   $5 \times 10^{-4} \text{ mol.L}^{-1}$  ARS +  $0.54 \text{ mg.L}^{-1}$  B, c)  $\blacksquare$   $5 \times 10^{-4} \text{ mol.L}^{-1}$  ARS +  $0.81 \text{ mg.L}^{-1}$  B

Differential pulse anodic stripping voltammetry (DPASV) and square wave anodic stripping voltammetry (SWASV) methods were used to determine the amount of ARS-Boron complex. The complex gives response

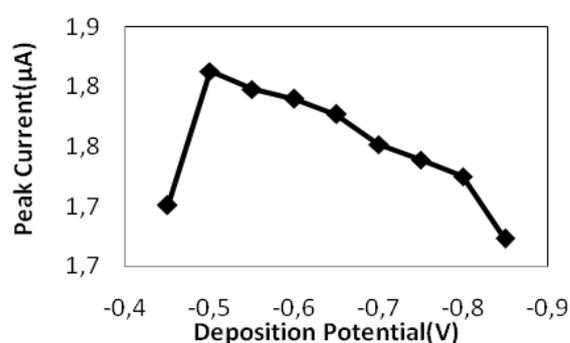
to both voltammetric methods. However, SWASVs were not selective as much as DPASV method for the determination of ARS-Boron complex. Therefore DPASV is decided to be a suitable stripping mode for determination of ARS-Boron complex.  $5 \text{ mV}\cdot\text{s}^{-1}$  was determined as convenient scanning rate on differential pulse stripping voltammetry. Several parameters such as pH, preconcentration potential, preconcentration time, stirring rate have been optimized before soil analysis.

**Effect of pH and supporting electrolyte type:** The pH of solution has a significant influence on the stability of complex. The pH and type of supporting electrolyte affect the complex formation parameters and stability of a complex (Segura et al, 2008). In order to verify the influence of the supporting electrolyte on the efficiency of electrochemical activity, ammonium acetate, phosphate, ammonium chloride and potassium chloride were used as supporting electrolyte and the best resolution was gained by using phosphate supporting electrolyte. The effect of pH on the peak currents of ARS-Boron complexes have been studied by a series of voltammetric analysis (Figure 3a). The highest peak current was obtained at pH 8. The signal has disappeared at the pH range of 4.5-5.5. We believe that complex is formed even at pH 4.5. However, ARS and ARS-Boron peaks could be overlapped. The measurements were also carried out at pH 8.5-10, but the voltammograms exhibited a poor profile; this may be attributed to the low formation of complex in basic media or overlapping of the peaks. Enhanced peak currents were achieved in phosphate buffer solution of pH 8. Therefore, phosphate buffer solution has been chosen as a supporting electrolyte in the rest of the present analytical study.

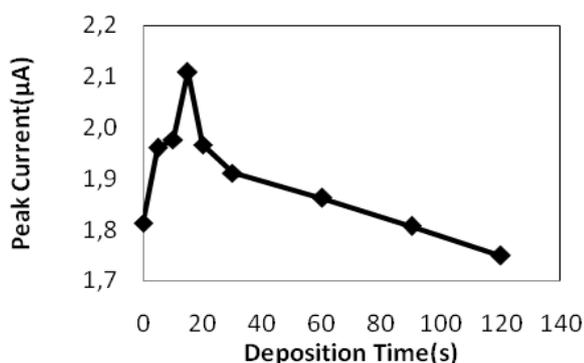
**Preconcentration potential:** Preconcentration is an important step on stripping voltammetry analysis. For this reason, preconcentration potential have been optimized by a series of experiments in this work. The resulting peak current-accumulation potential profile is exhibited in Figure 3b. The peak currents of ARS-Boron complex increased from -0.45 V to -0.5 V. However, the S/N ratio has started to decrease when the magnitude of voltage was raised, due to the hydrogen evolution and saturation of electrode surface. The optimum potential was determined as -0.5 V and this potential is used for all the consequent measurements. The optimum potential is also suitable to minimize the interference effect of coexisting ions due to the low deposition on pencil graphite working electrode at this potential.



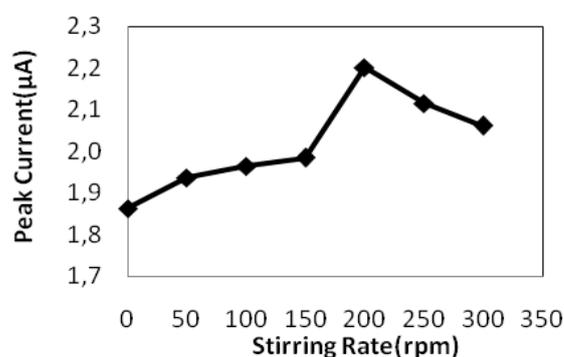
(a)



(b)



(c)



(d)

Figure 3. Influence of a) pH, b) deposition potential, c) deposition time, d) stirring rate on peak current values. (Optimization of voltammetric parameters)

**Preconcentration time:** The effect of accumulation time on peak current of complex was studied in the range of 0-120 seconds. As can be seen in Figure 3c., the peak current of ARS-Boron complex increases distinctly with increasing the accumulation time up to 15 seconds. After that value, a gradual decrease has been seen due to the saturation of pencil graphite surface. When the deposition time takes place longer than required, the complex would be stripped from the surface of the electrode spontaneously. 15 seconds were determined as the optimum deposition time for ARS-Boron complex on pencil graphite working electrode.

**Stirring rate:** Stirring rate is another important factor to obtain sufficient transport of analyte to the working electrode while electrolysis is performed. The peak currents of electrodeposition at 0, 50, 100, 150, 200, 250, 300 rpm stirring rates were obtained from DPAS voltammograms (Figure 3d). Increasing the stirring rate yields a higher diffusion rate, which appears to be beneficial to the regular deposition of analyte molecules. On the other hand, too high stirring rate disperses the analyte molecules in aqueous media and restricts the interactions of analyte with pencil graphite working electrode. Furthermore, variation of stirring rate over the range from 0-300 rpm at 15 seconds accumulation time and -0.5 V accumulation potential revealed that a stirring rate of 200 rpm was the ideal choice for optimal sensitivity (Figure 3d).

**Method validation and interferences:** Calibration was performed on pencil graphite electrode for the determination of boron using following conditions-accumulation potential of -0.5 V; preconcentration time of 15 s; stirring rate of 200 rpm. The curve is linear in the concentration range of 0-160  $\mu\text{g.L}^{-1}$ . Detection and quantification limit values were found as  $0.016 \pm 0.001 \text{ mg.L}^{-1}$  and  $0.053 \pm 0.001 \text{ mg.L}^{-1}$ , respectively. Relative standard deviation was calculated as 6.4 % for 0.08  $\text{mg.L}^{-1}$  boron level (n=10).

Interference of various ions such as  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  were examined in the presence of 0.16  $\text{mg.L}^{-1}$  boron. 100  $\text{mg.L}^{-1}$   $\text{Cu}^{2+}$  and  $\text{Zn}^{2+}$  ions show positive influence on the peak current. 100  $\text{mg.L}^{-1}$   $\text{Mn}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$ ,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  did not show significant change on the peak current. However, remarkable change on the peak current has been seen with excess  $\text{Pb}^{2+}$  ions added to the working solution. The interference effect of  $\text{Pb}^{2+}$  ions could be removed by adding 0.01  $\text{mol.L}^{-1}$  of EDTA complexing agent.

## Soil Analysis

In order to validate the electrochemical detection, we have compared the obtained results with both detection methods, by using the optimal spectrophotometric conditions. Table 1 and Table 2 show the data obtained by the spectrophotometry and differential pulse anodic stripping voltammetry using pencil graphite working electrode.

Table 1. Some physical and chemical characteristics of soil samples obtained from Tekirdağ and Kirklareli areas.

	ID	Sand %	Clay %	Silt %	pH (1:1)	EC (1:1) dSm-1	Lime content, %	Boron* mg/L	Boron** mg/L
Velimeşe, Tekirdağ	1	36	50	14	7.49	0.432	0.99	0.641	0.7739
	2	40	44	16	7.5	0.46	0.64	0.939	0.94
	3	38	50	12	6.85	0.55	1.18	1.24	1.18
	4	30	60	10	6.31	0.25	0.47	0.908	0.899
	6	16	42	42	4.8	0.18	0.48	0.69	0.89
Vize, Kirklareli	7	42	36	22	7.97	0.53	7.63	0.96	0.99
	9	46	32	22	8.43	0.46	0.178	1.32	1.04
	10	36	42	22	7.95	0.46	3.36	0.503	0.521
	11	38	44	18	7.52	0.46	1.39	0.7186	0.711
	12	38	46	16	7.6	0.45	0.65	1	0.935
Yağcı, Tekirdağ	13	40	38	22	7.64	0.54	0.73	0.612	0.592
	14	42	34	24	6.09	0.23	0.82	1.12	1.156
	15	46	32	22	6.8	0.5	0.34	0.812	0.473
	16	50	26	24	8.01	0.55	0.173	0.49	0.544
	17	52	24	24	7.95	0.57	0.262	0.711	0.718
	18	54	24	22	7.9	0.5	0.334	0.95	0.872

\*Available boron detection with Voltammetric Method

\*\* Available boron detection with Spectrophotometric Method

The electroanalytical procedure for the determination of available boron contents of soil samples were developed by using DPASV. Available amount of boron in soil samples were determined by standard calibration method. Therefore, Azomethine H method was used to check the accuracy of improved the DPASV method. Both voltammetric and spectrophotometric results are given in Table.1 and Table 2. Comparative results between DPASV and UV-Vis techniques (Figure 4) indicate that there is a good agreement between the two methods ( $r^2=0.8852$ ).

Table 2. Some physical and chemical characteristics of soil samples obtained from Samsun.

	ID	Sand %	Clay %	Silt %	pH (1:1)	EC (1:1) dSm-1	Lime %	Boron* mg/L	Boron** mg/L
Çarşamba, Samsun	Ç-5	52.4	20.9	26.8	5.81	0.328	0.27	0.102	0.996
	Ç-10	40.8	19.8	39.4	5.6	0.311	0.2	0.651	0.679
	Ç-11	26.7	38.2	35.2	5.96	0.279	0.4	1.26	1.149
	Ç-12	21.3	49.8	28.9	5.81	0.322	0.5	0.486	0.49
	Ç-13	52.3	20.4	27.3	4.94	0.29	0.48	BDL	
	Ç-16	16.7	52.1	31.1	4.92	0.193	0.1	0.5	0.52
	Ç-17	25.7	46.1	28.2	5.8	0.631	0.4	0.704	0.639
	Ç-18	17.0	39.2	43.8	5.14	0.199	0.3	0.241	0.292
	Ç-19	28.3	46.4	25.3	6.01	0.296	0.48	1.04	1.04
	Ç-25	19.1	54.5	26.4	5.42	0.2521	0.231	1.755	1.71
	Ç-30	25.3	49.9	24.8	5.9	0.312	0.4	1.47	1.392
	Ç-31	12.5	57.5	30.1	7.27	0.311	0.7	0.993	0.906
	Ç-32	18.1	54.5	27.5	7.23	0.433	2.6	0.57	0.641
	Ç-33	17.0	51.2	31.9	6.96	0.458	1.19	0.98	0.96
	Ç-36	16.4	63.3	20.3	4.67	0.228	0.1	1.19	1.36
	Ç-38	16.4	63.3	20.3	4.67	0.228	0.1	0.922	0.702
Samsun, Samsun	Ç-41	10.8	60.3	28.9	6.85	0.418	0.4	1.47	1.255
	Ç-42	9.2	56.8	34.0	6.68	0.246	0.4	0.694	0.695
	Ç-44	12.1	64.0	23.9	6.54	0.439	0.63	1.11	1.1
	Ç-45	40.6	29.6	29.8	7.23	0.319	0.73	1.35	1.25
	Ç-48	32.2	29.1	38.8	5.4	0.407	0.4	0.478	0.495
	Ç-49	10.2	57.2	32.6	5.87	0.486	0.48	1.01	1.01
	Ç-51	29.9	29.1	41.0	7.63	0.437	5.7	0.808	0.895
	Ç-55	13.0	55.0	32.0	5.44	0.404	0.56	BDL	
	Ç-62	64.6	6.5	28.9	6.66	0.304	0.7	0.328	0.537
	Ç-64	8.9	59.0	32.1	6.1	0.412	0.24	0.87	0.82
	Ç-70	17.6	46.4	36.0	6.17	0.451	0.32	0.99	0.95
	Ç-71	17.5	47.7	34.8	7.43	0.423	1.4	BDL	
	Ç-74	69.4	8.9	21.7	6.89	0.311	0.2	1.13	1.12
	Ç-85	15.9	46.6	37.6	7.2	0.342	0.4	0.601	0.605
	Ç-93	16.3	57.8	25.8	7.2	0.371	0.461	0.903	0.959
	Ç-144	61.6	21.3	17.1	7.44	0.414	3.92	1.56	1.35
Ç-156	61.6	40.9	47.5	6.93	0.467	0.58	0.616	0.722	
Ç-163	61.6	29.8	14.8	6.14	0.199	0.423	0.4	0.352	

\*Voltammetric Method

\*\*Spectrophotometric Method BDL-Below Detection Limit

## Conclusion

Pencil graphite was used as working electrode for the determination of available boron in soil samples in this study. Differential pulse anodic stripping voltammetry has been developed for the determination of available boron in soil samples. The method would be used also for the determination of boron in soil samples at total concentrations. The results of the voltammetric method are in good agreement with those obtained by spectrophotometric method. The proposed voltammetric technique can be used as an alternative method for spectrophotometric azomethine H method. In fact, azomethine-H method consumes time at least 30 minute for the complexation reaction. Already proposed method requires 5 minutes to test the sample.

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