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INDIRECT DETERMINATION OF BORON IN WATER BY CATHODIC STRIPPING VOLTAMMETRY

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SUMMARY

An indirect cathodic stripping voltammetric method for the determination of boron was described. The method is based on monitoring the peak current decrease of As(V) in the presence of mannitol, copper and selenium in sulphuric acid medium. The chemical and instrumental parameters affecting this peak current decrease were investigated and optimized. The calibration plot for boron was linear in the range of 9–100 mg/L. Limit of detection was calculated from the calibration curve to be 2.7 mg/L, and a relative standard deviation of 2.6 % at the 10 mg/L boron level (n = 7) was found. The method was applied to high boron-containing top water samples with recoveries in the range of 97–105%.

KEYWORDS:
Boron, mannitol, arsenic, water analysis.

INTRODUCTION

The essentiality of boron to animals and human beings has not been identified, but it is essential for plants. Boron deficiency affects plant growth and yield, but substantial amounts of boron are toxic to plants and reduce plant yield. Boron has been classified to be hazardous by the Agency for Toxic Substances and Disease Registry (ATSDR), and minimal risk level for boron was given as 0.01 mg/kg/day for oral exposure [1]. Therefore, it is suggested that excess boron is toxic for all living organisms [1-3], and, therefore, its determination is important in water, soil, food and some industrial fields, such as metallurgy, electronics, glass manufacture and the nuclear industry.

Various spectrometric methods, including UV-VIS spectrophotometry [3-7], atomic absorption spectrometry [3, 8], atomic emission spectrometry [3, 9], inductively coupled plasma-atomic emission spectrometry [3, 10, 11], inductively coupled plasma-mass spectrometry [12-16], and X-Ray fluorescence spectrometry [17] have been reported to determine boron in various samples. Advantages and disadvantages of these methods have been well-discussed by Sah and Brown [3]. On the other hand, only few can be found on voltammetric determination of boron, based on adsorption of the boron-Beryllon(III) complex [18, 19]. In spite of its good sensitivity, this method is time-consuming and difficult for routine analysis, due to a boiling step for 15 min and a waiting step for ca. 15 h.

In this study, an indirect determination of boron, for samples containing mg/L levels of boron, by cathodic stripping voltammetry is described. The principle of the method is based on monitoring the decrease of As(V) peak current, obtained in the presence of mannitol, copper and selenium in sulphuric acid. As(V) is electrochemically inactive, but can be reduced to As(III) using mannitol in acidic medium [20, 21]. The As(V)-peak current depends linearly on the concentration of mannitol. On the other hand, it is well-known that boron (B) reacts with mannitol to form a complex compound. Hence, the arsenic peak currents were measured with and without adding boron to the solution containing As(V) and mannitol. Then, the difference between two peak current values was used as a signal to determine the amount of boron indirectly in the solution, by cathodic stripping voltammetry.

MATERIALS AND METHODS

A Radiometer Pol 150 Polarographic Analyzer, connected with a MDE 150 polarographic stand, was used for measurements. The analyzer was controlled with Trace Master 5 software. Three electrode systems with a hanging mercury drop electrode (HMDE) as working electrode, a Ag/AgCl one with saturated KCl as reference electrode, and a platinium wire as auxiliary electrode, were used. Hexa-distilled mercury (Radiometer-Copenhagen) was used through-out the study for HMDE.

As(V) and B working solutions were prepared from 1000 mg/L (Merck, Darmstadt) standard solutions after appropriate dilution with deionized water. Sulphuric acid

(Merck) was used for acidification without further purification. The other chemicals used throughout the study were of analytical grade. All the solutions were prepared with deionized water having the resistivity of 18.2 MΩ.

Various public water samples were collected from Bigadiç district of Balıkesir City, and stored in a refrigerator below 4 ^{0}C.

In all experiments, the required amounts of As(V), mannitol, copper(II), selenium(IV) and sulphuric acid were transferred to the jacketed voltammetric cell, and the volume was completed to 10 mL with deionized water to give final concentrations of 0.8 mg/L, 0.1 mol/L, 22.5 mg/L, 60 µg/L, and 0.1 mol/L, respectively. Then, the cell temperature was adjusted to 35 ^{o}C using a thermostat. The voltammetric cell was put into place and stripping carried out using the square wave mode after the deposition step without stirring (I_{pA}). For the calibration curve, aliquots of the B standard solutions were transferred to the voltammetric cell containing As(V), mannitol, copper(II), selenium(IV) and sulphuric acid. Then, after dilution to 10 mL with deionized water, the voltamograms were recorded (I_{pB}). The difference of the peak current, (I_{pA})- (I_{pB}), was used as signal for B determination. All measurements were done in the presence of dissolved oxygen without nitrogen-purging, to shorten the analysis time. The same procedure was used for samples analysis.

RESULTS AND DISCUSSION

It has been reported that As(V) becomes electro-active, when mannitol is used for its reduction to As(III) in acidic medium. Greulach and Henze [19] described a cathodic stripping voltammetric method for As(V) determination in the presence of mannitol (0.5 mol/L), copper sulphate ($2x10^{-3}$ mol/L), sodium perchlorate and perchloric acid, at pH 1.7. Henze *et al.* [21] modified this method by using sulphuric acid and selenium, instead of sodium perchlorate and perchloric acid. In both methods, a linear relationship between As(V) peak current and concentration of mannitol has been observed. Starting from this point, the principle of our method is based on the reaction between mannitol and boron that causes a decrease in arsenic peak current. The decrease, which allows the indirect determination of B by cathodic stripping voltammetry, varies proportionally with B concentration in the solution.

Our first attempt was to obtain best conditions for a reproducible peak current of arsenic, depending on mannitol concentration. For this purpose, instrumental and experimental parameters, such as deposition potential, deposition time, and concentrations of copper(II), sulphuric acid, selenium and mannitol, were re-optimized.

Dependence of the peak current on the deposition potential in the presence of mannitol, Cu(II), sulphuric acid and selenium is shown in Table 1. The peak current increases with increase of deposition potential towards the negative direction, but peak deterioration was observed at further negative potential. Therefore, deposition potential was selected to be –550 mV for subsequent experiments. This value is the same as given in the literature [18].

The effects of Cu concentration and deposition time were investigated together, because these parameters are interrelated (Fig. 1), and determined to be 22.5 mg/L and 90 s, respectively, corresponding to the highest peak current.

TABLE 1 - The variation of peak current with deposition potential (conditions: 250 µg/L As(V), 0.15 mol/L mannitol, 0.1 mol/L H_2SO_4,, 40µg/L Se(IV), 22.5 mg/L Cu(II), t_d= 90 s, scan rate 25 mV/s).

Deposition potential (mV)	-450	-475	-500	-525	-550	-575	-600	-625
Peak current (nA)	-73.5	-145	-258	-403	-581	-776	-956	-1145

It is proposed that Se(IV) forms an inter-metallic compound in deposition step, having a significant effect on the As peak [21]. Therefore, the relationship between As peak current and Se concentration was investigated. The peak current increased with Se concentration to a maximum at 40 µg/L Se, and then slightly decreased until 60 µg/L. In addition to this, the optimum sulphuric acid level was found to be 0.4 mol/L, to obtain a significant As peak current. But, the reaction between mannitol and B was not quantitative, as desired in strongly acidic solution. For this reason, 0.1 mol/L sulphuric acid was used for the subsequent studies to make the boron-mannitol reaction nearly quantitative.

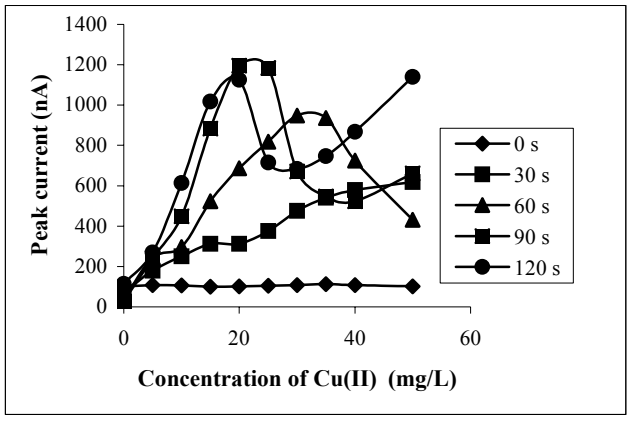

FIGURE 1 - Effect of varying Cu(II) for different deposition times (conditions: 0.15 mol/L mannitol, 0.4 mol/L sulphuric acid, 250 µg/L As(V), 100 µg/L Se(IV), E_d=–550 mV, scan rate: 25 mV/s, pulse amplitude: –50 mV).

Fig. 2 shows the effect of mannitol on arsenic peak current, and there is a linear relationship between 0.01-0.15 mol/L of mannitol. Hence, 0.1 mol/L mannitol was chosen for subsequent experiments. Ten independent As

signals were measured under these conditions and the relative standard deviation was calculated to be 2%.

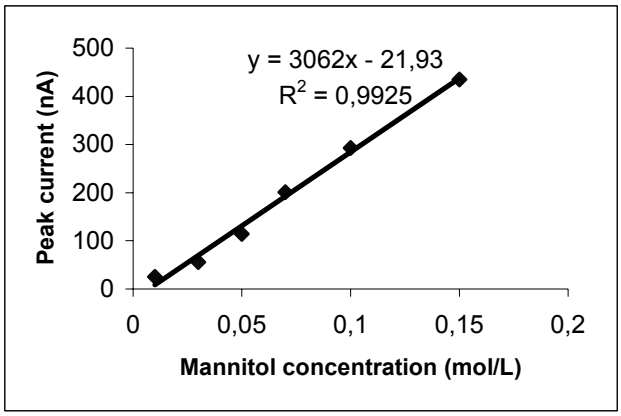

FIGURE 2 - The variation of As(V) peak current with concentration of mannitol (0.1 mol/L sulphuric acid, 250 µg/L As(V); 40 µg/L Se(IV), 22.5 mg/L Cu(II); E_d=-550 mV, t_d=90 s, scan rate= 25 mV/s, without stirring).

After a reproducible peak current was recorded for As, our second attempt was to obtain a decrease in As peak current, due to boron-mannitol complex formation, when B was added to the solution. Indeed, As peak current decreased after B addition, linearly with B concentration. Additionally, the temperature effect was investigated and results are given in Fig. 3. The peak current difference (ΔI_p) increased with cell temperature, giving a maximum at 35 ^oC, and then decreased.

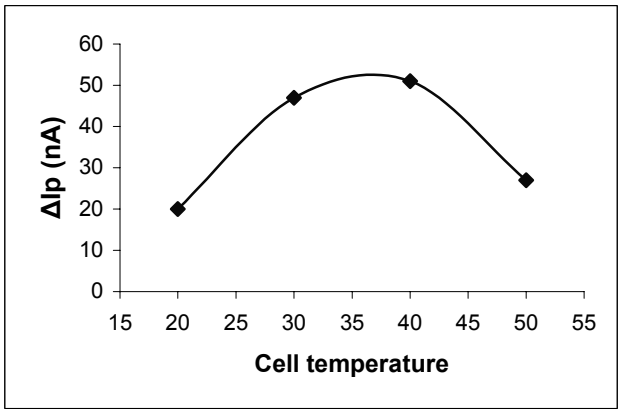

FIGURE 3 - The variation of peak current difference (ΔI_p) as a function of cell temperature (conditions: (0.1 mol/L sulphuric acid, 0.8 mg/L As(V); 40 µg/L Se(IV), 22.5 mg/L Cu(II); E_d=-550 mV, t_d=90 s, scan rate= 25 mV/s, without stirring).

Under the above selected conditions, a calibration curve for B was constructed. Fig. 4 shows the voltammograms obtained for calibration. The calibration curve was linear in the range 9–100 mg/L B, and was described by the regression equation:

$$\Delta I_p = 2.76(\pm 0.14)\, C_B + 2.38(\pm 2.82),$$

where ΔI_p is the difference between two peak (in nA) and C_B is the concentration of boron (in mg/L). The correlation coefficient was 0.998. The limit of detection was calculated from calibration curve procedure as described in reference [20], and found to be 2.7 mg/L.

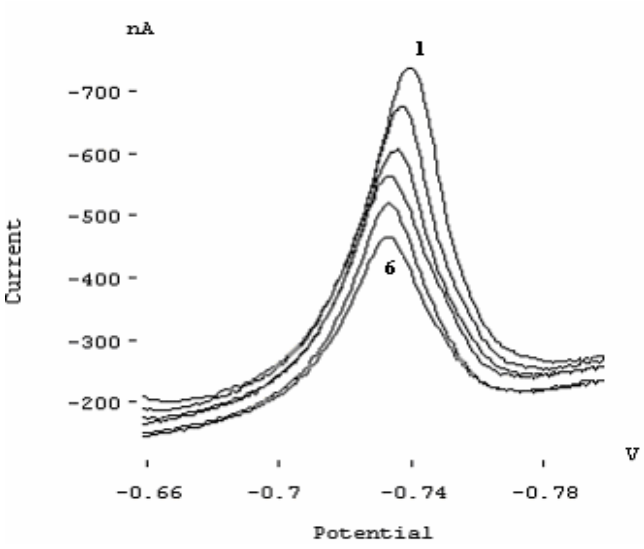

FIGURE 4 - Voltammograms obtained for calibration curve: (1) blank (0.1 mol/L sulphuric acid, 0.8 mg/L As(V); 60 µg/L Se(IV), 22.5 mg/L Cu(II); E_d=-550 mV, t_d=90 s, scan rate= 25 mV/s, cell temperature,35 ^{0}C, without stirring); (2) 1+20 mg/ L boron; (3) 1+40 mg/L boron (4) 1+60 mg/L boron; .(5) 1+ 80 mg/L boron; (6) 1+100 mg/L boron.

The proposed method was applied to various top water samples containing high B concentrations. The accuracy of the proposed method was checked using the azomethine-H method. Additionally, a recovery test was performed and recovery rates for the samples were calculated to be 97–105%. For this purpose, water samples were analyzed with and without B addition in different concentrations, and the results obtained are summarized in Table 2. Statistical evaluations of the results using Student's t test (for 95% confidence level) show that there are no significant differences in the mean concentrations obtained by the two methods.

TABLE 2 - Results obtained from two methods for the determination of boron in water samples.

Sample	Boron added	Boron found	R %	Azomethine H Method
A	- 5	4.3 (± 0.5)* 9.55	- 105	4.1 (± 0.2)
B	- 10	7.5 (± 0.6) 17.8	- 103	7.2 (± 0.4)
C	- 15	8.7 (± 0.7) 23.3	- 97	8.1 (± 0.4)
D	- 20	9.1 (± 0.8) 19.6	- 98	9.6 (± 0.5)
E	-	29.4 (± 2.2)	-	30.2 (± 1.4)

*($\bar{x} \pm s$) mg B/L (N=3)

CONCLUSIONS

The present study described an alternative method for indirect determination of boron by cathodic stripping voltammetry. This method has been successfully applied in water samples with high boron contents. Interferences caused by organic compounds can be avoided by using UV irradiation. Additionally, separation and pre-concentration method based on ester generation, such as the volatile methyl borate, may be used to eliminate possible interferences and for determination of boron in samples with contents lower than detection limit of the method.

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REFERENCES

[1] Agency for toxicological substances and diseases registry, July 1992, Toxicological profile for boron, http://www.atsdr.cdc.gov/toxprofiles/tp26.html, 2005/09/02.

[2] World Health Organization, (1998), Guidelines for Drinking Water Quality. Second Edition. Volume 1. Recommendations.Addendum, Geneva.

[3] Sah, R.N. and Brown P.H. (1997) Boron Determination-A Review of Analytical Methods. Microchemical Journal 56, 285-304.

[4] Zaijun, L., Yuling, Y., Jiaomai, P. and Jan, T. (2001) 1-(2-hydroxy-3-methoxybenzylideneamino)-8-hydroxynaphthalene-3,6-disulfonic acid as a reagent for the spectrophotometric determination of boron in ceramic materials. Analyst 126, 1160-1163.

[5] Tumang, C.D.A., Luca, G.C.D., Fernandes, R.N., Reis, B.F. and Krug, F.J. (1998) Multicommutation in flow analysis exploiting a multizone trapping approach: spectrophotometric determination of boron in plants. Analytica Chimica Acta 374, 53-59.

[6] Hanay, A., Boncukoğlu, R., Kocakerim, M.M. and Yılmaz, A.E. (2003) Boron removal from geothermal waters by ion exchange in batch reactor. Fresenius Environmental Bulletin, Vol 12 (10), 1190-1194.

[7] Öztürk N. and Kavak D. (2003) Boron removal from aqueous solutions by adsorption using full factorial design. Fresenius Environmental Bulletin, Vol 12 (12), 1450-1456.

[8] Burguera, M., Burguera, J.L., Rondon, C. and Carrero, P. (2001) Determination of boron in blood, urine and bone by electrothermal atomic absorption spectrometry using zirconium and citric acid as modifiers. Spectrochimica Acta Part B 56, 1845-1857.

[9] Sarıca, D.Y. and Ertaş, N. (2001) Flow Injection Analysis for Boron Determination by Using Methyl Borate Generation and Flame Atomic Emission Spectrometry. Turkish Journal of Chemistry 25, 305-310.

[10] Sun, D.H., Waters, J.K. and Mawhinney, T.P. (1997) Microwave digestion and ultrasonic nebulization for determination of boron in animal tissues by inductively coupled plasma atomic emission spectrometry with internal standardization and addition of mannitol. Journal of Analytical Atomic Spectrometry 12, 675-679.

[11] Probst, T.U., Berryman, N.G., Lemmen, P., Weissfloch, L., Auberger, T., Gabel, D., Carlsson, J. and Larsson, B. (1997) Comparison of inductively coupled plasma atomic emission spectrometry and inductively coupled plasma mass spectrometry with quantitative neutron capture radiography for the determination of boron in biological samples from cancer therapy. Journal of Analytical Atomic Spectrometry 10, 1115-1122.

[12] Wilke, T., Wildner, H. and Wünsch, G. (1997) Ester Generation for the Determination of Ultratrace Amounts of Boron in Volatile High-purity Process Chemicals by Inductively Coupled Plasma Mass Spectrometry. Journal of Analytical Atomic Spectrometry 9, 1083-1086.

[13] Sun, D.H., Ma, R.L., McLeod, C.W., Wang, X.R. and Cox, A.G. (2000) Determination of boron in serum, plasma and urine by inductively coupled plasma mass spectrometry (ICP-MS). Use of mannitol-ammonia as diluent and for eliminating memory effect. Journal of Analytical Atomic Spectrometry 15, 257-261.

[14] Al-Ammar, A.S., Gupta, R.K. and Barnes, R.M. (2000) Elimination of boron memory effect in inductively coupled plasma-mass spectrometry by ammonia gas injection into the spray chamber during analysis. Spectrochimica Acta Part B 55, 629-635.

[15] Kozono, S., Takahashi, S. and Haraguchi, H. (2002) Determination of boron in high-purity tantalum materials by on-line matrix separation/inductively coupled plasma mass spectrometry. Analyst 127, 930-934.

[16] Park, C.J. and Song, S. (2003) Determination of boron in high-purity sulfuric acid by ester generation and isotope dilution inductively coupled plasma mass spectrometry. Journal of Analytical Atomic Spectrometry 18, 1248-1251.

[17] Ramos, S.S., Reig, F.B., Adelantado, J.V.G., Marco, D.J.Y., Carbo, A.D. and Perez, J.A.B. (2000) Validation of a method for the determination of boron in ceramic materials by X-ray fluorescence spectrometry. Spectrochimica Acta Part B 55, 1669-1677.

[18] Zhang, Y. and Yue, G. (1995) Study of the enhancement of the boron-beryllon III system by anion surfactant using oscillopolarography. Analytica Chimica Acta 309, 63-71.

[19] Thunus, L. (1996) Voltammetric determination of boron in plasma using Beryllon(III) as a ligand. Analytica Chimica Acta 318, 303-308.

[20] Greulach, U. and Henze, G. (1995) Analysis of arsenic(V) by cathodic stripping voltammetry. Analytica. Chimica Acta 306, 217-223.

[21] Henze, G., Wagner, W. and Sander, S. (1997) Speciation of arsenic(V) and arsenic(III) by cathodic stripping voltammetry in fresh water samples. Fresenius Journal of Analytical Chemistry, 358, 741-744.

[22] J.C. Miller and J.N. Miller (1993) Statistics for Analytical Chemistry. Third Ed., Ellis Horwood, Chichester, UK, p117.

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