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A Novel Borate Ion Selective Electrode Based On Carbon Nanotube-Silver Borate

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A novel miniaturized borate selective composite membrane electrode based on carbon nanotube-silver borate is described. The developed electrode exhibited a stable and linear potentiometric behavior over the concentration range of 1×10^{-1} M and 1×10^{-4} M borate ion with a Nernstian slope of 34 mV/decade and a limit of detection of 2×10^{-5} M. The electrode showed a clear selectivity to borate ion over sulfate, chloride, nitrate and many other inorganic acid anions. The response time of the electrode was found less than 14 s. Potentiometric readings of the electrode were consistent, when pH was between 4 and 8, through almost 3 months. The developed borate-selective composite membrane electrode was directly applied for the quantification of borate ions in real water samples. The results obtained by the developed electrode method was statistically analyzed and compared with those obtained by ICP-MS method. No significant differences for either accuracy or precision were observed.

Keywords: Borate selective composite membrane electrode, Borate in environmental waters, Potentiometry, Carbon nanotube-silver borate

1. INTRODUCTION

Boron as a naturally occurring element and its compounds have been widely used in agricultural and industrial fields such as glass manufacture, domestic washing agents and agricultural fertilizers [1]. The excess boron is accepted as toxic for plants and humans. The maximum limit value for boron in drinking water is decided 2.4 mg/L by WHO [2]. Also, this value is valid for irrigation waters and wastewater [3]. Therefore, the determination of boron in industrial and environmental samples is necessary. Several analytical methods have been developed for the determination of boron. Among the methods, spectrophotometry [4-6], spectrofluorimetry [7], atomic absorption spectrometry [8], inductively coupled plasma-atomic emission spectrometry [9,10], inductively coupled plasma-mass spectrometry [11, voltammetry [12] and potentiometry have been used. Among them, spectrometric methods are applicable to the determination of borate at concentrations down to 0.01 mg/L and the widely used method for the analysis of boron in water [13-17]. However, all these techniques require sophisticated and expensive equipment which is not affordable for smaller laboratories.

Since the quantitative detection of boron is important in both environmental samples, ion selective electrodes (ISEs) as mobile, miniaturized, simple, rapid, and low-cost devices can be used to monitor boron. However, in recent years, the number of reports on developing boron-selective electrodes are limited [18,19]. Thus, it is challenging and still interest to design boron-selective electrodes. Solid state membrane electrodes offer an alternative platform by eliminating inner reference solution to achieve better response properties as compared to conventional polymeric membrane electrodes [20-24]. Most of the ion selective electrode methods use the conversion of the boron in a sample into the fluoroborate form with concentrated hydrogen fluoride [25]. In the determination of the boron by the converting method using concentrated hydrogen fluoride, the conversion to the fluoroborate form in the sample takes much longer time and a suitable fluoroborate-selective electrode is required [26]. A few is used for the direct determination in the form of tetraborate or borate without any conversion [18]. In the form of tetraborate, it can be determined quickly and reliably with a direct tetraborate-sensitive electrode without any conversion process. To assess the quality of field water samples, onsite measurement of boron is crucial. The challenge lies in developing a simple standardized method for which the sample preparation and operation process are minimized in order to reduce measurement errors and cost. The method must be capable of measuring selectively the boron from less than 1 mg/L to more than 500 mg/L in water samples often rich in metals, chloride and sulfates. However, the present work describes the preparation and application of a new composite borate-selective electrode for the direct determination of borate content in soil, rock and water samples from different locations were taken for real sample analysis. The results obtained by the developed electrode method were statistically analyzed and compared with those obtained by ICP-MS.

2. MATERIALS AND METHODS

2.1. Reagents

Tetrahydrofuran (THF) and graphite, used in the preparation of solid contacts, from Sigma-Aldrich, epoxy (Ultrapure SU 2227), Hardener (Desmodur RFE) from Victor (Italy) All other salts used in the study (Bayer, Alkaline, alkaline, alkaline) transition metal salts and other salts) and solvents from Sigma-Aldrich. Silver borate salt used in the study. It was precipitated using aqueous solutions of silver nitrate and sodium tetraborate (borax) salts from Sigma-Aldrich and obtained after necessary filtration-drying. The used carbon nanotube (CNT) is TN-MWNTs (OD: 20-30nm, L: 50 BETM) 95% BET:> 110m2 / g MFD: Z0410428M has catalog and grain size numbers.

2.2. Instrumentation

A computer-controlled high-input impedance multi-channel potentiometric measurement system (sensitivity ±0.1 mV) with a custom-made software program (Medisen Ar-Ge, Turkey) was used in order to carry out the potentiometric measurements. All electrode potentials were measured against the potential of a Ag/AgCl reference electrode (RE) (MF-2052 model, BASi) with a 3 M NaCl aqueous filling solution that has been saturated with AgCl. HI9126 (Hanna Instruments) waterproof portable pH/mV meter including the HI1230B double junction pH electrode was used to monitor the pH of the solutions. Branson ultrasonic bath (USA) was used to homogenize solutions at essential concentrations. Dissolved oxygen (DO) was measured using an Oakton DO 300 Series field meters. Temperature, pH, and oxidation-reduction potential (ORP) were measured with Beckman U265 pH/Temp/mV meters, and an Oakton CON 400 series field meter was used to measure conductivity. Agilent 7700X model ICP-MS was applied for comparison analysis of environmental samples. The deionized water used in the preparation of the solutions was obtained from the ZENEER Power II Water Purification System.

2.3. Preparation of standard solutions

Standard anion solutions used in our experimental studies were prepared from sodium salts of different anionic species and cation solutions from nitrate salts of different cationic species. Thus, the cation type for the anion solutions and the anion type for the cation solutions were kept constant. Primarily, 0.1 M stock solutions of anions and cations were prepared precisely. The standard solutions used were then prepared by diluting these stock solutions.

2.4. Preparation of carbon nanotube and silver borate-based borate selective composite electrodes

The preparation of carbon nano tube-based borate-selective composite membrane electrodes was carried out in two stages. In the first stage, the active material containing carbon nanotube and silver borate was filled into a plastic tube and compressed. In the second stage, the appropriate length sections were taken from the plastic tube containing the active material to be compressed and dried, and a copper wire with the appropriate length was attached to the end with a solid contact material, and then isolated. The stages of preparation of the carbon nanotube-silver borate composite membrane electrodes are shown in Figure 1.

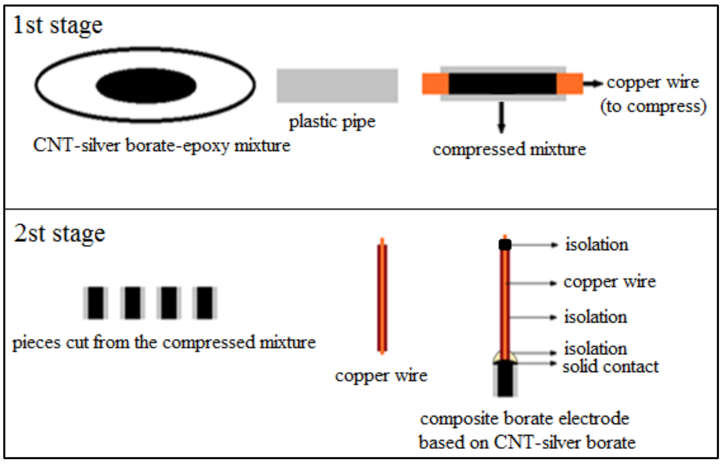

Figure 1. Preparation steps of carbon nanotube-silver borate-based borate-selective composite membrane electrodes.

3. RESULTS AND DISCUSSION

3.1. Potentiometric performance characteristics of carbon nanotube-silver borate-based borate-selective composite membrane electrodes

In the study, firstly, silver borate was formed on the carbon nanotube surface to be used in the construction of borate selective composite membrane electrodes. For this purpose, 0.1 g carbon nanotube in a 100 ml 0.1 M of $AgNO_3$ solution, at a constant mixing speed for 1 hour at 1.5 V constant current applied, the Ag^+ ions were reduced to Ag^0 on the surface of the carbon nanotubes. The carbon nanotube with reduced silver was then removed from the solution by filtration. The filtered carbon nanotube-Ag was then placed in a 100 mL 0.1 M $Na_2B_4O_7$ solution under a direct current flow of 1.5 V for 1 hour was applied in a reverse direction at a constant mixing speed. With the $B_4O_7^{2-}$ ions contained in the solution, the silver on the surface of the carbon nanotube was again allowed to form silver borate on the carbon nanotube surface.

Table 1. Carbon nanotube-silver borate-based borate selective composite membrane electrode compositions tested.

Compositions	CNT-silver borate	Ag_2S (g)	Cu_2S (g)	Epoxy (g)	Total mixture (g)
Composition A	0.205	0.085	0.010	0.700	1.000
Composition B	0.201	0.089	0.010	0.700	1.000
Composition C	0.201	0.089	0.010	0.800	1.000
Composition D	0.105	0.085	0.010	0.800	1.000
Composition E	0.110	0.080	0.010	0.800	1.000
Composition F	0.210	0.080	0.010	0.700	1.000
Composition G	0.220	0.070	0.010	0.700	1.000

After silver borate formation on the carbon nanotube surface the mixture was re-filtered, dried and carbon nanotube-silver borate-based borate-selective composite membranes were prepared using matrix mixtures in the different compositions shown in Table 1. After the necessary pressing and drying processes were done, the sections taken from the composite matrix were fixed to the appropriate length of copper wire, and carbon nanotube-silver borate-based borate-selective composite membrane electrodes were prepared. Membrane composition affects the sensitivity and selectivity of the borate-selective electrode prepared as above. Measurements were made in standard solutions comprising borate. The calibration curves for the prepared electrodes are given in Figure 2. As a result of the calibration measurements of the electrodes prepared. The electrode with the composition E was chosen for this study, as it depicted analytical stability and better sensitivity in the borate concentration range under investigation. All potentiometric performance tests made after this stage were however performed with the electrode prepared by the Composition E.

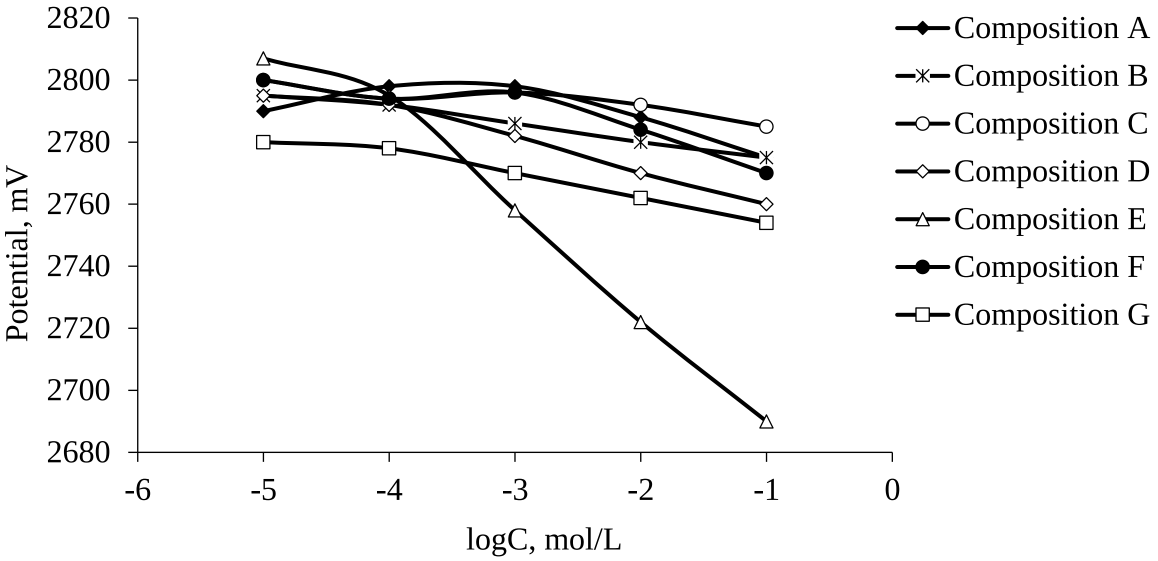

Figure 2. Potentiometric behaviors of carbon nanotube-silver based borate-selective composite membrane electrodes against borate ions prepared in different compositions.

The aim of the work is to develop a standard method for routine boron determination in water using the fluoroborate-selective electrode. Prior to applying the electrode to soil, rock and water samples, it was therefore necessary to evaluate the suitibility and analytical performance of the electrode. Potentiometric determination methods involve separation of borate from the sample matrix, treatment with HF and the resulting fluoroborate ion which is measured potentiometrically with a suitable fluoroborate-selective electrode (27,28). Potentiometric methods that do not require borate separation from the sample have also been reported (29-31).

In the study, the potentiometric behavior of carbon nanotube-silver borate-based borate-selective composite membrane electrode prepared by the composition E against the standard borate ions as well as different anions which are widely used were investigated. Standard solutions of $1.0x10^{-1}$ to $1.0x10^{-5}$ M of each anion solution were prepared for these measurements. Carbon nanotube-silver borate-based borate-selective composite membrane electrode was dipped directly into these standard solutions and the observed potential values were recorded. The data obtained was plotted against the concentration. The potentiometric performance characteristics of the electrode, such as the linear study range, response time, calibration and limit of determination, were determined.

As can be seen from the potentiometric performance characterictics, the obtained results obtained during this study, it is possible to confirm that the borate-selective electrode based on carbon nanotube-silver borate provides better selectivity, reproducibility, lower response time and longer lifetime. [18, 32-35]. This is probably due to the appropriate heterogenous membrane matrix including carbon nanotube-silver borate. For boron determination, electrodes used for the fluoroborate ion determination was reviewed by Olmos et al in 1994. There were few papers published about potentiometric boron determination in the past period from 1994 up to present. There is only one paper that uses borate-selective electrode for the direct determination of boron as borate 18. All the others use fluoraborate-selective electrode for the boron determination after treatment borate with HF. Data on an evaluation of the potentiometric perfomance characteristics of the borate and fluoroborate ion-selective electrodes used by other authors, cited in the literatüre form 1994 to present, are limited and are shown in Table 2.

Table 2. Comparison of analytical parameters for borate and fluoroborate-selective electrodes

Method	Borate-selective electrodes			Fluoroborate-selective electrodes		
	Present study	Somer et al Ref [18]	Wood and Nicholson Ref [33]	Jezkova et al. Ref [34]	Zhang et al. Ref [35]	Studenyak et al Ref [36]
Potential response (mV)	34±1	31±2	58	8	58.1	
Lineal range (M)	10^{-1}-10^{-4}	10^{-1}-10^{-6}	10^{-1}-10^{-4}	10^{-1}-10^{-5}	10^{-1}-$5.1x10^{-7}$	10^{-1}-10^{-4}
Limit of detection (M)	$5.6x10^{-5}$	10^{-6}	10^{-5}	$2x10^{-5}$	10^{-6}	$5x10^{-4}$
Response time (s)	14	20-30	60-600	10-60	15	
Lifetime (w)	18	24	8			
Working pH range	4-8	7-9	4-6		5.3-12.1	2-8
Principal interferences	No	Ag^+ and Br^-		Cl^- and I^-	No	ClO_4^-, SCN^-, I^-

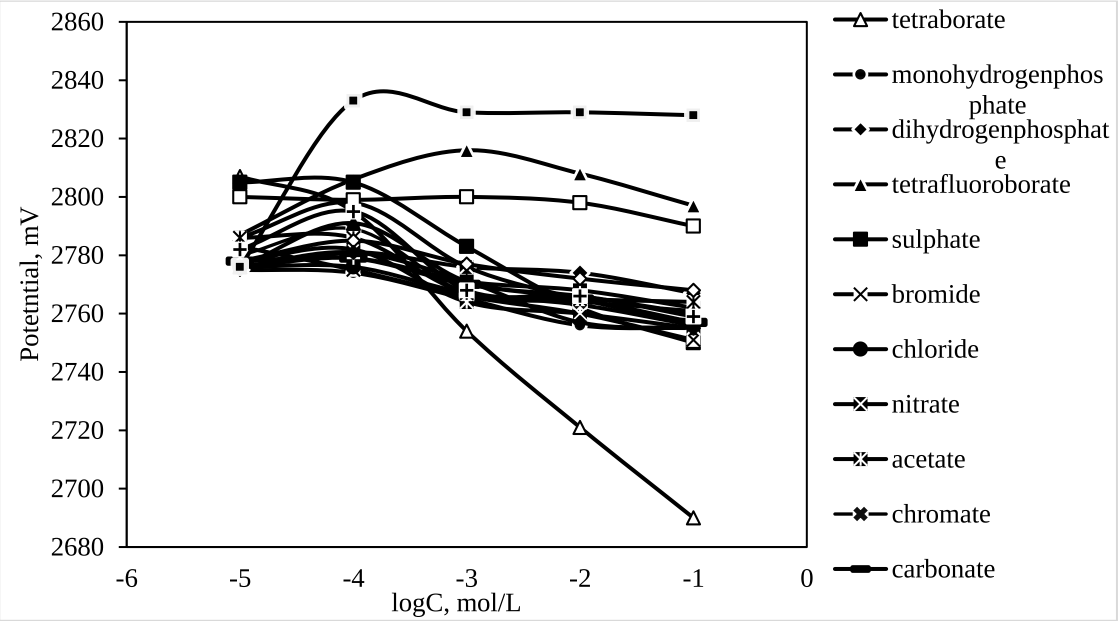

Figure 3. Potentiometric behavior of carbon nanotube-silver borate-based borate-selective composite membrane electrode towards standard anion solutions.

Figure 3 shows the potentiometric behavior of carbon nanotubes-silver borate-based borate-selective composite membrane electrode against different anionic species. In Figure 3, it can be seen that carbon nanotubes-silver borate-based borate-selective composite membrane electrode showed a highly sensitive and selective behavior for borate ion.

Figure 4 shows the calibration graph and linear working range of carbon nanotube-silver borate-based borate-selective composite membrane electrode.

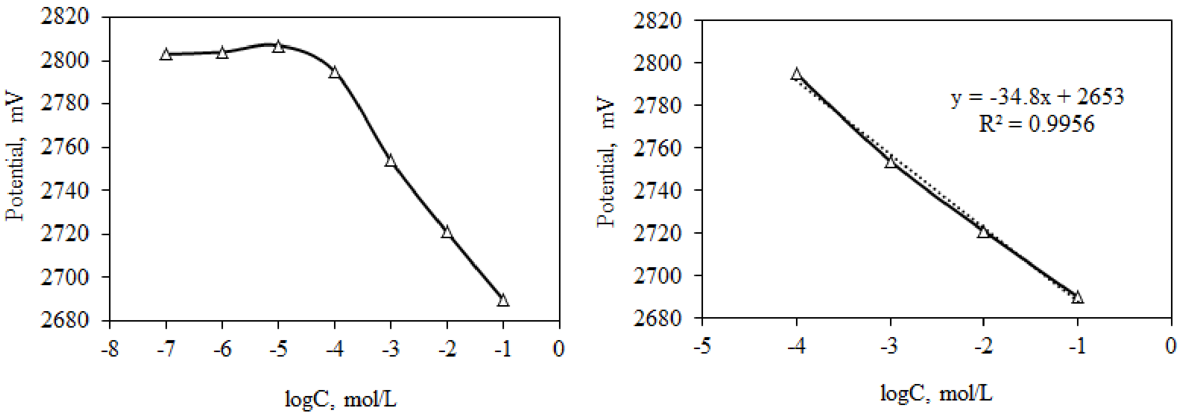

Figure 4. Calibration graph and linear working range of carbon nanotube-silver borate-based borate-selective composite membrane electrode.

In Figure 4, it was observed that carbon nanotubes-silver borate-based borate-selective composite membrane electrode showed linear behavior with 34 ± 1 mV slope versus standard borate ions between 1.0×10^{-1} - 1.0×10^{-4} M. In addition, the determination limit of the electrode was calculated as 5.6×10^{-5} M. In the linear study range, the calibration equation and R^2 values were determined as $y = -34.8x + 2653$ and 0.9956, respectively.

3.2. Potentiometric Selectivity

Selectivity coefficients of the electrode for each anion were determined in order to better express the selectivity behavior of the carbon nanotube-silver borate-based borate-selective composite membrane electrode against borate ions. For this study, a calibration graph was created with standard borate solutions ranging in concentration from 1.0×10^{-1} to 1.0×10^{-6} M using the carbon nanotube-silver borate-based borate-selective composite membrane electrode and the calibration equation was obtained. Then 0.1 M standard solutions of each anionic species were prepared. The electrode was dipped directly into these prepared standard solutions and the observed potential value was recorded. These obtained potential values were written in the calibration equation obtained from the calibration graph, and the corresponding concentration values were calculated. Finally, the selectivity coefficient calculated by using these values were determined. In Table 3, selectivity coefficients of carbon nanotube-silver borate-based borate-selective composite membrane electrode are given according to the separate solution method. In the study, the composite membrane electrode, as heterogeneous membrane, was made from relatively insoluble ionically conducting inorganic salts (Ag_2S, Cu_2S and CNT-$Ag3BO_3$) which were incorporated in the epoxy binder. As can be seen in Table 3, nearly no interference was observed for all ions tested. The prepared electrode showed a good selectivity towards borate due to only borate ions effectively introduced into the crystal lattice of the heterogeneous membrane interface. This means the other ions tested did not effectively introduce the crystal lattice of the membrane since the ion-exchange process lead to the formation of the potential at the heterogeneous membrane interface [18, 37-39].

Table 3. Selectivity coefficients of carbon nanotube-silver borate-based borate-selective composite membrane electrode.

Separate Solution Method		
Ions	$K^{pot}_{A,B}$	$-\log K^{pot}_{A,B}$
SO_4^{2-}	$1.66 x 10^{-2}$	1.78
Br^-	$1.55 x 10^{-2}$	1.81
CH_3COO^-	$1.17 x 10^{-2}$	1.93
SCN^-	$1.17 x 10^{-2}$	1.93
HPO_4^{2-}	$1.17 x 10^{-2}$	1.93
Cl^-	$1.12 x 10^{-2}$	1.95
NO_3^-	$1.05 x 10^{-2}$	1.98
CO_3^{2-}	$1.05 x 10^{-2}$	1.98
NO_2^-	$9.12 x 10^{-3}$	2.04
HCO_3^-	$8.51 x 10^{-3}$	2.07
CrO_4^{2-}	$7.94 x 10^{-3}$	2.10
SO_3^{2-}	$7.41 x 10^{-3}$	2.13
$C_2O_4^{2-}$	$6.46 x 10^{-3}$	2.19
$H_2PO_4^-$	$5.37 x 10^{-3}$	2.27
F^-	$5.01 x 10^{-3}$	2.30
$Cr_2O_7^{2-}$	$1.14 x 10^{-3}$	2.94
BF_4^-	$7.41 x 10^{-4}$	3.13
HSO_4^-	no interference	no interference

The repeatability of carbon nanotube-silver borate-based borate-selective composite membrane electrode was tested using $1.0 x 10^{-2}$ - $1.0 x 10^{-3}$ - $1.0 x 10^{-4}$ M standard borate solutions. The electrode was dipped directly into these solutions. Potential-time graph was drawn with the obtained data. Care was taken thoroughly wash the electrode with deionized water while passing from one solution to another. In Figure 5, the repeatability of carbon nanotube-silver borate-based borate-selective composite membrane electrode is given.

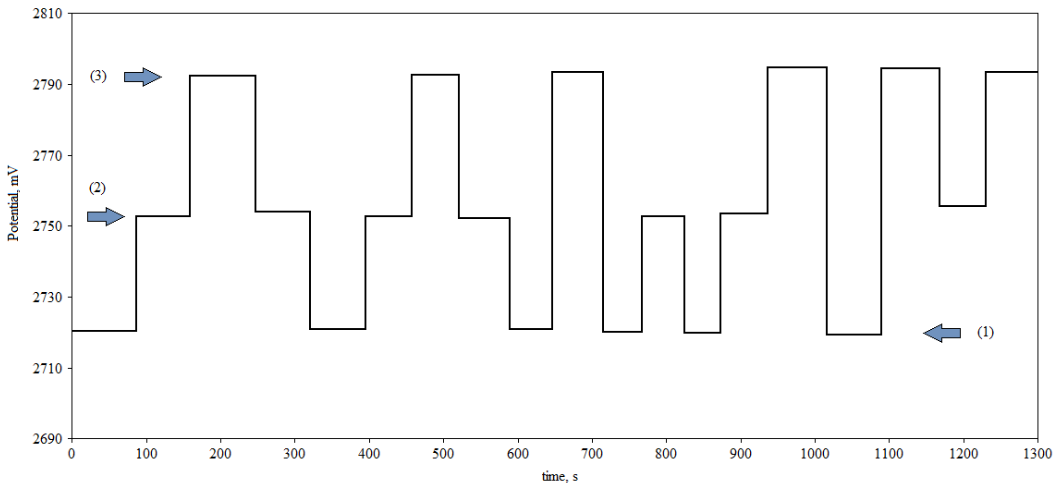

Figure 5. Repeatability of carbon nanotube-silver borate-based borate-selective composite membrane electrode [(1): 1.0x10^{-2}, (2): 1.0x10^{-3}, (3): 1.0x10^{-4} M $B_4O_7^{2-}$]

3.3. Response Time

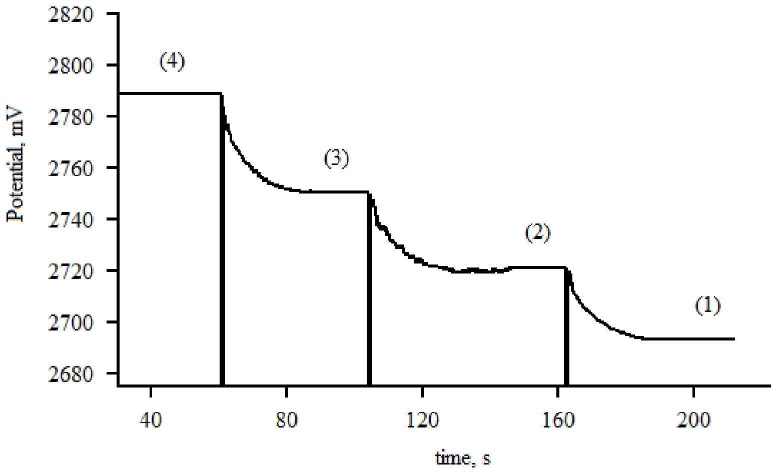

Figure 6. Response time of carbon nanotube-silver borate-based borate-selective composite membrane electrode [(1): 1.0x10^{-1}, (2): 1.0x10^{-2}, (3): 1.0x10^{-3}, (4): 1.0x10^{-4} M $B_4O_7^{2-}$]

The transition time of the electrode to the equilibrium potential from the standard borate solution between 1.0x10^{-1} M to 1.0x10^{-4} M concentrations was measured in order to observe the response time of carbon nanotubes-silver borate-based borate-selective composite membrane electrode (Figure 6). The transition time to the equilibrium potential with a repeatable and linear (34 ± 1mV difference) response at the 1.0x10^{-1} to 1.0x10^{-4} M concentrations was calculated less than 14 s which is a short period and it is an advantage when compared to the borate-selective electrode in the literature [18].

3.4. pH Working Range

At concentrations of 1.0x10^{-2} M and 1.0x10^{-3} M $B_4O_7^{2-}$ ion was kept constant and the potential changes were observed in each solution by immersing carbon nano-silver borate-based borate-selective composite membrane electrode directly into the pH adjusted solutions. The obtained data were transferred to potential-pH graph, and pH working range of the electrode was determined. As can be seen from the Figure 7, the potential of the electrode decreased at low pH values than 5 and increased at high pH values than 8. The reason of the potential change at pH values higher than 8, may be because of the slight dissolution of Cu_2S, oxidation and then formation of Cu(II) complexes with hydroxide ion. As expected the potential increased in negative direction with pH because of OH^- complexes of copper (II) [18]. From the Figure 7, the pH working range of carbon nanotube-silver borate-based borate-selective composite membrane electrode at both concentrations was found between pH 5 and 8.

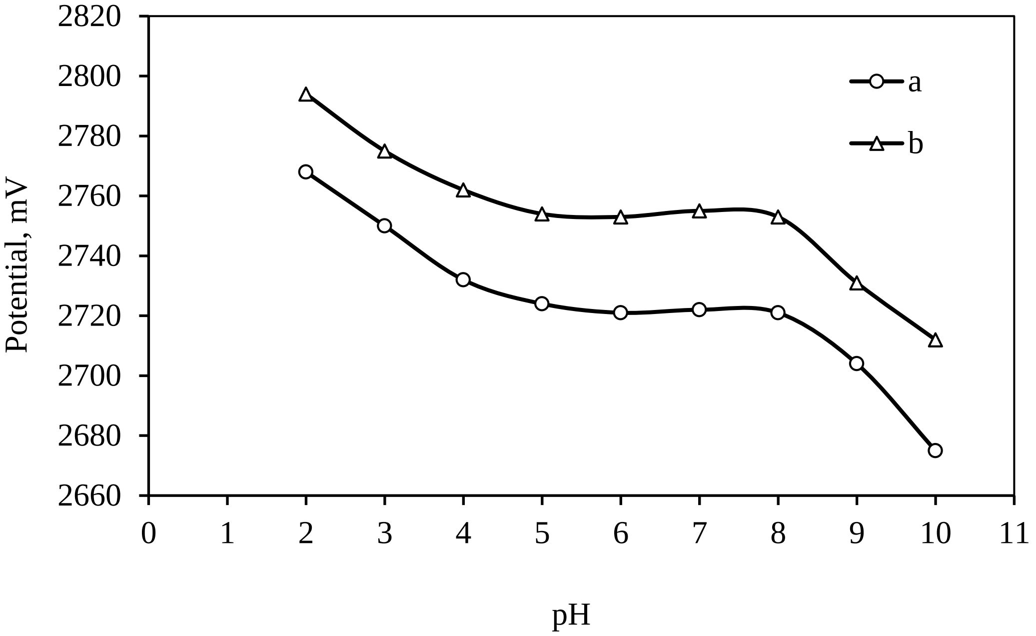

Figure 7. The working range of carbon nanotube-silver borate-based borate-selective composite membrane electrode [a: $1.0x10^{-2}$, b: $1.0x10^{-3}$ M $B_4O_7^{2-}$]

3.5. Lifetime

In order to determine the useful lifetime of carbon nanotube-silver borate-based borate-selective composite membrane electrode, measurements were performed with the same $B_4O_7^{2-}$ solutions at the same day and time, under the same conditions using the same electrode, and the slopes were recorded. The slope-time (week) graph was drawn with the obtained slope values and the useful life of the carbon nanotube-silver borate-based borate-selective composite membrane electrode was determined. As can be seen from Figure 8, the lifetime of the carbon nanotube-silver borate-based borate-selective composite membrane electrode was found about 18 weeks.

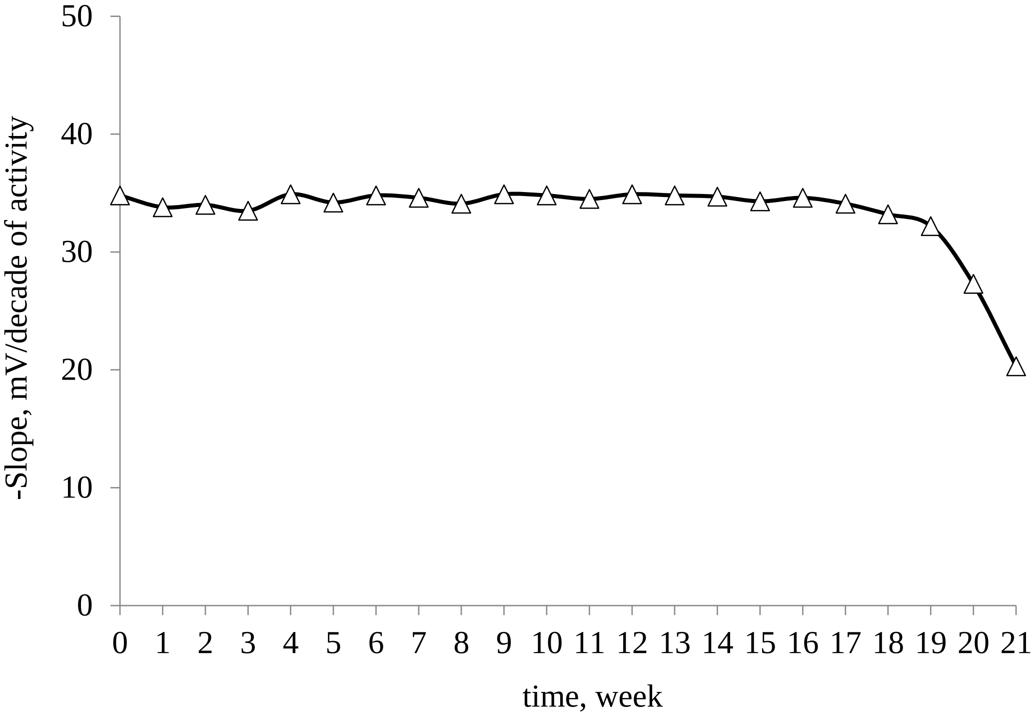

Figure 8. Life cycle of carbon nanotube-silver borate-based borate-selective composite membrane electrode.

3.6. Analytical Applications

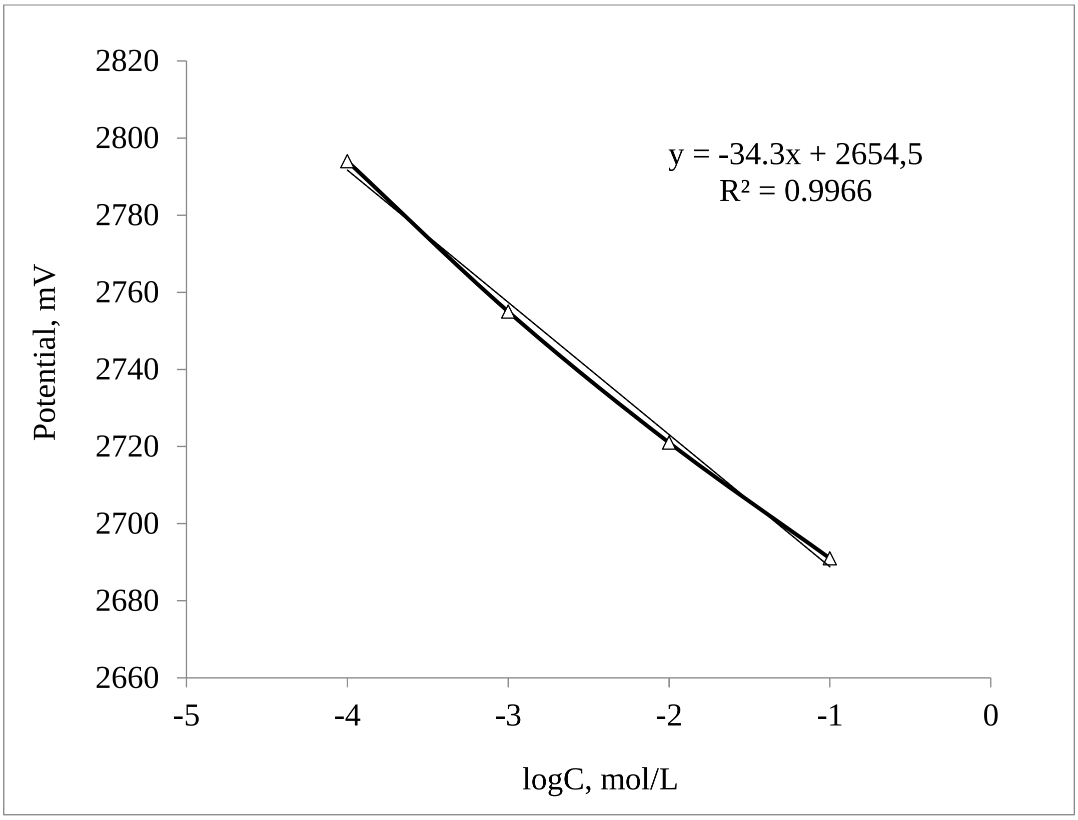

Figure 9. Calibration graph and correct equation used in real sample analysis.

In this study, soil samples from 12 different locations, water samples from 7 different locations and rock samples from 3 different regions were taken for real sample analysis. After powdering soil and rock samples, 3 grams of sample was added to 15 mL of deionized water. The resulting mixture was shaken for 1 hour at a constant stirring speed at 25°C in a shaking water bath. After one hour, the sample mixtures were filtered to extract boron compounds which may be present in soil and rock samples. Water samples were only filtered, and the solid particles were removed. For the application of real sample analysis, a calibration graph was first plotted by using standard $B_4O_7^{2-}$ solutions ranging from $1.0x10^{-1}$ M to $1.0x10^{-4}$ M, and a correct equation was obtained. This calibration graph and its equation are given in Figure 9.

3.6.1 Determination of boron in rock, soil and water samples

There are numerous reports of applications of potentiometric methods for borate or fluoroborate determination in soil, rock and water samples. A partial list of published methods is given in Table 2. Most of these methods suffrer several interferences, lack of sensitivity and response time that limit the application of this methods for samples for low borate concentartions and complex sample matrices. The carbon nanotube-silver borate-based borate-selective composite membrane electrode was directly immersed into the samples prepared for analysis and the observed potential values were recorded. The potential reading was performed 5 times per sample and the average potential value was calculated for each sample. These calculated potential values were written in the equation which was resulted from the calibration graph, and the corresponding concentration values were calculated. Consequently, the amount of borate contained in each sample was determined by standard addition. Figure 10 shows the potential values obtained from rock and soil samples. Figure 11 shows the analysis of water samples

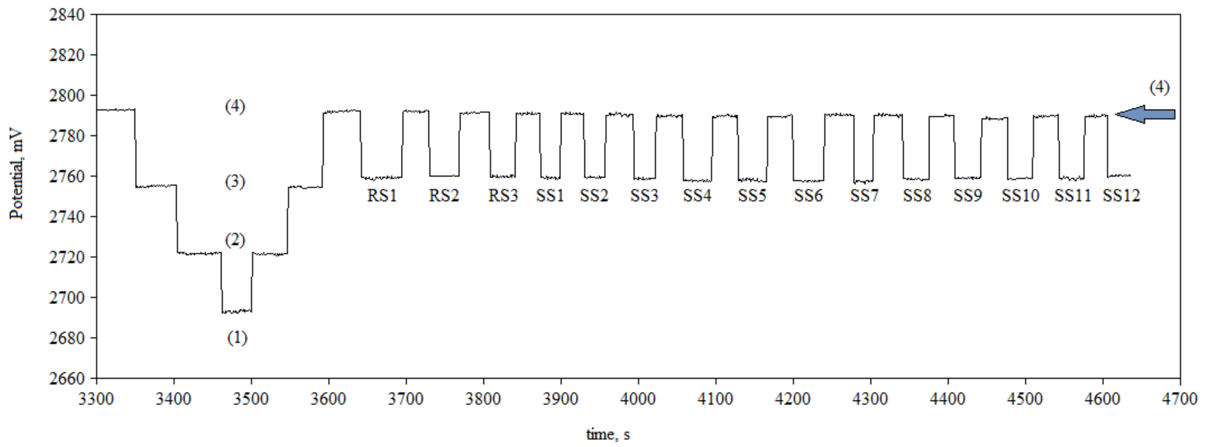

Figure 10. Analysis of rock and soil samples with carbon nanotube-silver borate-based borate-selective composite membrane electrode [(1): $1.0x10^{-1}$, (2): $1.0x10^{-2}$, (3): $1.0x10^{-3}$, (4): $1.0x10^{-4}$ M $B_4O_7^{2-}$].

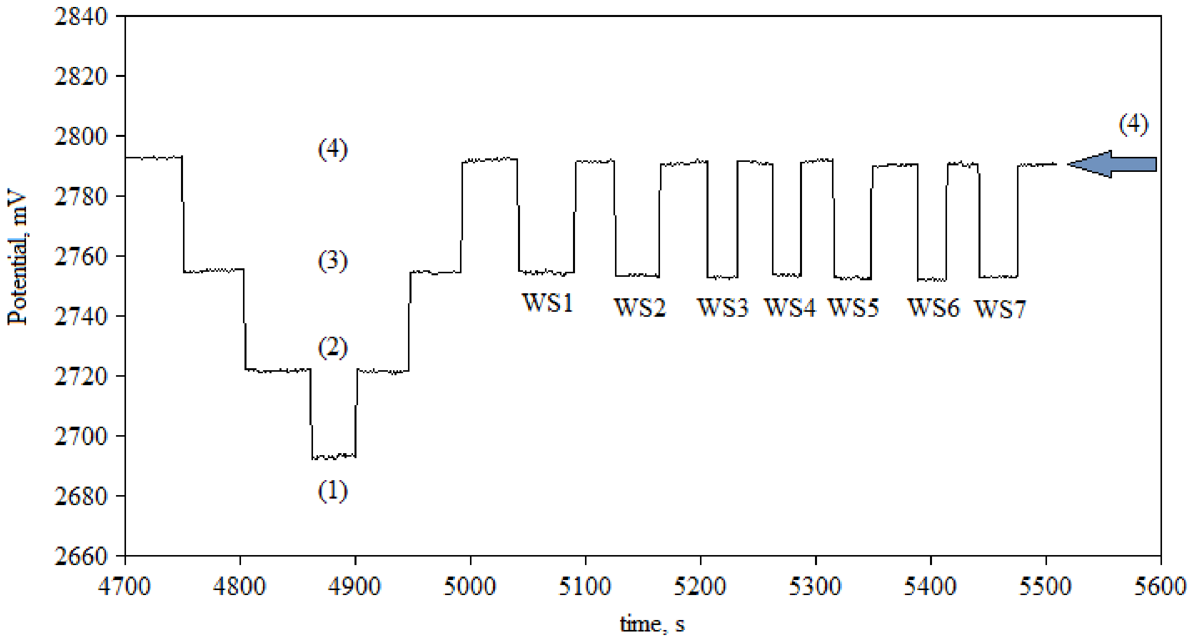

Figure 11. Analysis of water samples with carbon nanotube-silver borate-based borate-selective composite membrane electrode [(1): 1.0x10^{-1}, (2): 1.0x10^{-2}, (3): 1.0x10^{-3}, (4): 1.0x10^{-4} M $B_4O_7^{2-}$].

The samples used were also determined by the ICP-MS method for comparison and validity of the present electrode method. Since ICP-MS performs elemental analysis, it gives the boron content in the sample as ppm. In order to make a comparison with this method, the amount of borate found by the electrode method was calculated as the ppm amount of boron. The data obtained are given in Table 4.

Table 4. Real sample analysis results with carbon nanotube-silver borate-based borate-selective composite membrane electrode

Samples	Electrode method Calculated B, (ppm)*	ICP-MS method B, (ppm)
Rock sample 1 (RS1)	47.31	45.66
Rock sample 2 (RS2)	48.91	48.74
Rock sample 3 (RS3)	47.61	47.30
Soil sample 1 (SS1)	46.93	46.68
Soil sample 2 (SS2)	46.30	45.31
Soil sample 3 (SS3)	47.24	46.30
Soil sample 4 (SS4)	51.72	53.81
Soil sample 5 (SS5)	45.93	46.40
Soil sample 6 (SS6)	46.61	46.10
Soil sample 7 (SS7)	48.61	47.44

Soil sample 8 (SS8)	50.25	51.19
Soil sample 9 (SS9)	48.88	48.55
Soil sample 10 (SS10)	46.87	47.84
Soil sample 11 (SS11)	48.93	49.08
Soil sample 12 (SS12)	46.62	46.94
Water sample 1 (WS1)	48.81	48.77
Water sample 2 (WS2)	46.62	46.33
Water sample 3 (WS3)	46.55	46.14
Water sample 4 (WS4)	46.19	46.69
Water sample 5 (WS5)	46.87	45.81
Water sample 6 (WS6)	47.42	47.11
Water sample 7 (WS7)	46.55	46.87

*values are mean values calculated for n = 5

In order to compare the results of quantitative analysis of boron amount by electrode method and ICP-MS method [40], double-sided t-test was applied between the two methods. There was no significant difference between the two methods. Since the theoretical t value is 1.721 within the range of 95% confidence limits (P = 0.05) and the degree of freedom of 21, the calculated t value *of* 0,148 is smaller than this value. As a result, there is no significant difference between the results of actual sample analysis using carbon nanotube-silver borate-based borate-selective composite membrane electrode and the results of ICP-MS method. Thus, the acceptability of the results of the analysis with the electrode method was determined statistically.

4. CONCLUSIONS

As a result of the experiments conducted in this study, we conclude that a new boron-selective membrane electrode was developed for the determination of boron in soil, rock and water samples. The developed electrode method was found as precise and accurate as compared to ICP-MS technique which is widely used in boron determination in environmental samples. Short response time of the developed electrode enhances the electrode’s reliability as a detector in a flow injection analysis system, however, the developed borate-selective electrode will be attempted to use in flow injections systems to get monitoring glucose and glycated protein levels in blood streams.

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