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Preparation and properties of a new solid state borate ion selective electrode and its application

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ABSTRACT

A new borate ion selective electrode using solid salts of Ag_3BO_3, Ag_2S and Cu_2S has been developed. Detailed information is provided concerning the composition, working pH and conditioning of the electrode. An analytically useful potential change occurred from 1×10^{-6} to 1×10^{-1} M borate ion. The slope of the linear portion was 31 ± 2 mV/10-fold changes in borate concentration. The measurements were made at constant ionic strength (0.1 M $NaNO_3$) and at room temperature. The effect of Cl^-, Br^-, $NO_3{}^-$, $SO^={}_4$, $H_2PO_4{}^-$ anions and K^+, Na^+, Cu^{2+}, Ag^+, Ca^{2+} cations on borate response is evaluated and it was found that only Ag^+ had a small interference effect. The lifetime of the electrode was more than two years, when used at least 4–5 times a day, and the response time was about 20–30 s. Borate content in waste water of borax factory, tap water of a town situated near to the borax factory and city tap water far from these mines were also determined. The validation was made with differential pulse polarography for the same water sample, and high consistency was obtained.

1. Introduction

For the determination of low levels of boron, inductively coupled plasma optical emission spectrometry (ICP OES) and electrothermal atomic absorption spectrometry (ETAAS) are used most frequently, although they suffer from interferences, memory effects and insufficient sensitivity. On the other hand, with the use of ion selective electrode, measurement of low levels of boron maybe achieved without any pretreatment of the sample. Thus, it was the aim of this research to prepare an ion selective electrode for borate ($B_4O_7{}^=$) ion.

Potentiometric detection with the use of ion-selective electrodes (ISEs) is nowadays a commonly used analytical technique due to a number of its advantages, such as analysis speed, their selectivities on specific ions, wide working range, ease of handling and low cost. These electrodes are being used in clinical analysis and in routine control analysis of some ions and some biological species [1,2]. They can simply be produced with a very low cost and above all they allow us to analyze the solution without pre-treatments.

Silver salts of spare solubility are used mostly for their preparation. It was found that solid state electrodes prepared from silver halogenides were sensitive to halogenides, however these electrodes could also be used for the determination of some cations such as mercury indirectly [3,4] Pungor and Hollos-Rokosingi [5] determined iodide ion in the presence of chloride ion using an electrode prepared from silver iodide and paraffin. It was found that the electrodes made from two sulfide salts such as Ag_2S–PbS and Ag_2S–CdS were sensitive to lead and cadmium ions, respectively [6]. The correlation found between the crystalline structure of the sensing material and the potentiometric response made possible the controlled preparation of several precipitate based electrodes such as cadmium, lead and copper selective electrodes [7–9]. The mixtures of less soluble salts such as Ag_2S, PbS, $PbSO_4$ and Cu_2S in different combinations when prepared as solid state pellet electrodes responded well against sulfate and sulfide ions [10]. The response of the sulfide-selective electrode to sulfide, iodide and cyanide was investigated [11] and the slopes were found to be 57 mV for I^-, 28 mV for $S^=$ and 115 mV for CN^-. Halide and sulfide selective electrodes were prepared using a slightly soluble silver salt together with silicon rubber [12] and linear relationship was observed in the range of 10^{-1}–10^{-4} M with a slope of 30 mV/activity decade. For fluoride ion detection, LaF_3 membrane electrode [13] has been developed which is widely used for practical measurements. A solid state ion selective electrode was prepared using Ag_2Se and Cu_2S which was selective to selenite [14]. Some of the ion selective electrodes are in solid state such as lead, cadmium, copper [7–9], selenite [14], and hydroxide electrodes [15], some of them are prepared using PVC or silicon rubber membrane such as halide and sulfide [16], selenite [17], ferric ion [18], iodide [4] and glucose electrodes [1]. A new solid state fluoride sensitive electrode

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was prepared from Ag_2S, Cu_2 S and CaF_2 salts. The slope of the linear portion (1×10^{-1}–1×10^{-5} M) was about 26 ± 2 mV/10-fold concentration changes in fluoride [19].

Boron and its compounds have wide usage and they have strategic importance. Boron is an essential element for plants and it is an essential micronutrient for humans. The tendency of boron to accumulate in animal and vegetable tissues [20] constitutes a potential hazard to the health of those consuming food and water with high boron (B) content. Therefore, accurate determination of boron concentration is very important [20–22]. The most common methods are spectrophotometric and plasma source spectrometric [21,22], although they suffer from interferences, insufficient sensitivity and need of preconcentration and extraction procedures.

Only, a few electrochemical methods have been used for the determination of boron, the reason may be that it is not electroactive. However, an indirect differential pulse polarographic (DPP) method has been established using its complex formation with copper [23]. In one other work borohydride was determined using its DPP peak in phosphate buffer and KNO_3 at pH 9 with high precision [24].

Tetrafluoroborate liquid membrane electrode was prepared for BF_4^- determination [25]. The electrode is satisfactorily used for the determination of 0.5–500 μg/ml of boron after conversion to BF_4^-. Fluoroborate ion formation, following addition of hydrofluoric acid to the sample, requires about 2 h. Samples should not be analyzed before this complexation time has elapsed. Fluoroborate ion sensitive PVC membrane electrode based on chloro[tetra(*m*-amino-phenyl)porphinato]-manganese as neutral carrier exhibits Nernstian response to fluoroborate ion [26].

Although there are many investigations about pellet electrodes prepared from solid salts, none of these were subject for borate ion determination. From the literature survey it maybe be seen that there are very few electrodes for the indirect determination of boron [25,26]. Since these electrodes are selective only for BF_4^-, the borate in sample has to be first transformed into this form using hydrofluoric acid which takes long time and is not easy. Also prolonged storage of fluoroborate solutions results in a loss of the ion from the solution.

The aim of this work was to fulfill this gap and to prepare an electrode selective for borate ion which is easy to prepare, easy to handle and has long lifetime. The present work describes the preparation and application of a new solid state borate ion selective electrode, which fulfills the above given futures. It was used for the determination of borate content in tap waters of two different cities, one of which is situated near to the borax mines. A water sample from the waste water of Kırka borax factory was also analyzed with the new electrode.

2. Experimental

2.1. Apparatus and reagents

Potential measurements were made with a Hanna HI 8521 pH meter. All potential values reported, are taken with respect to an HI 5412 saturated calomel electrode which was hold in a Luggin–Haber capillary. Reagent grade chemicals were used without further purification. All solutions were prepared with triple distilled water. For the preparation of pH buffers proper known solutions are used.

Stock 0.1 M solution of borate was prepared by dissolving 9.53 g of $Na_2B_4O_7{\cdot}10H_2O$ (BDH pro analysis) in 250.0 ml distilled water.

Preparation of Ag_2S: about 3 g of $AgNO_3$ (Fluka) is dissolved in distilled water, 40 ml 1 M Na_2S (Merck) is added. Precipitate formed is filtered, washed several times, dried in an oven at 110 °C. It was stored in a desiccator in dark.

Preparation of Cu_2S: to protect from air oxidation this reaction was carried out under nitrogen atmosphere. About 2 g of CuCl was dissolved in 100 ml de-aerated water, in order to protect from oxidation. To this solution Na_2S prepared also with de-aerated water is added. It was left waiting for 30 min at 60 °C. Black precipitate formed is filtered, washed several times and dried in an oven at 110 °C. It was stored in a desiccator.

Preparation of Ag_3BO_3: for this purpose $Na_2B_4O_7{\cdot}10H_2O$ is dissolved in distilled water and it is precipitated with the addition of $AgNO_3$. The precipitate formed is filtered, washed several times and dried in an oven at 110 °C. It was stored in a desiccator in dark.

2.2. Preparation of the electrodes

Precipitated solid salts such as Cu_2S, Ag_3BO_3 and Ag_2S were dried and then mixed in varying compositions. A certain amount of the salt or salt mixture (10–15 mg) was taken and pellets were made by holding first under a pressure of 5000 kg cm^{-2} for 5 min and then under a pressure of 8000 kg cm^{-2} for 10 min using the hydraulic press of IR instrument. The pellets of 7 mm diameter and 0.1–0.3 mm thickness were sealed with epoxy resin (0.7 g epoxy and 0.9 g hardener).

To obtain a good sealing the epoxy resin (0.7 g epoxy_0.9 g hardener) on the edge of the tubing had to wait for about 10 min and then the pellet was sealed. One day after the pellet was sealed a silver wire with a flat end is connected. For this purpose the inside of the glass tube was filled to about 1 cm with a mixture of 0.5 g graphite powder, epoxy resin and hardener. The electrode prepared had to wait for about 2 days so that the resin can get dry. The surface of the electrode is washed and then polished with a soft paper. These electrodes should wait in air and in a dark place when they are not in use. The lifetime of these electrodes can be at least 2 years, when they are used 4–5 times a day.

3. Results and discussion

3.1. Calibration curves of the electrodes

The potentiometric response of electrodes prepared in different compositions, were investigated against borate ion concentration. For this purpose, appropriate spikes of borate solution (prepared from Na_2 $B_4O_7{\cdot}10H_2O$) were introduced to the cell and corresponding potentials were recorded. For a fixed ionic strength all measurements were made in 20 ml 0.1 M $NaNO_3$ solution. This is very important since during the formation of calibration curve or during standard additions the change in concentration will be 10 times.

The response of each borate electrode was measured after the additions of 0.2 ml $Na_2B_4O_7$ solutions so that borate ion concentrations changed from 0.1 M to 1×10^{-6} M. For the calibration curve the potential readings were plotted against −log of borate ($B_4O_7^{=}$) concentration. The calibration curve for the electrode with the 1% Ag_3BO_3, 89% Ag_2S, 10% Cu_2S composition is given in Fig. 1 as an example. As expected for anions, with increasing concentration of borate ion the potential becomes more negative.

3.2. Effect of electrode compositions and thickness

Membrane composition has a great effect over the sensitivity, selectivity and stability of the ion selective membrane electrodes. In this study, electrodes using Ag_3BO_3, Cu_2S and Ag_2S in 5 different compositions were prepared in which the percentage of Ag_3BO_3 varied from 90, 10, 5, 1 and 0.5. Cu_2S generally is used to increase the dynamic properties of the electrode.

Two electrodes prepared in 90% Ag_3BO_3 and 10% Cu_2S (without Ag_2S) composition had nearly no response against the change

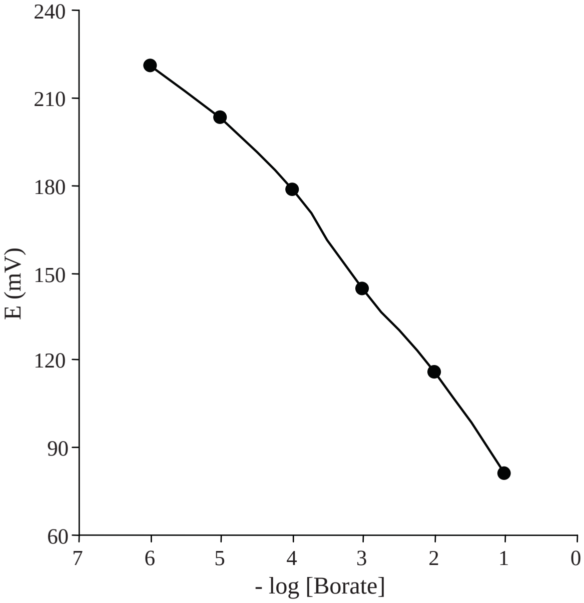

Fig. 1. Calibration curve for the newly prepared borate electrode (in 0.1 M $NaNO_3$). Response to $Na_2B_4O_7$ standard additions (1% Ag_3BO_3, 89% Ag_2S, 10% Cu_2S).

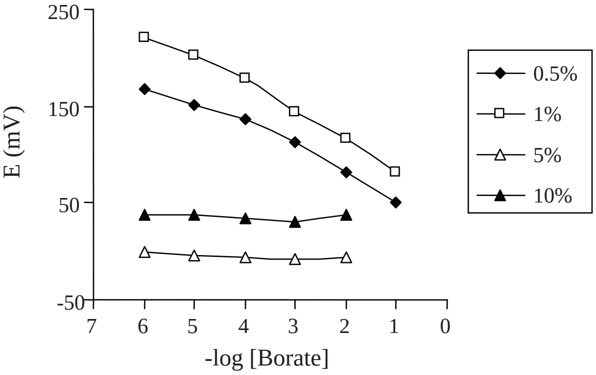

Fig. 2. Calibration curves for borate electrodes prepared in different compositions (in 0.1 M $NaNO_3$) (the percentages belong to Ag_3BO_3 in electrode).

in borate concentration. Electrodes of various compositions (three of each) were prepared each containing Ag_2S. For an electrode with 10% Ag_3BO_3, 10% Cu_2S and 80% Ag_2S composition, there was nearly no response. The highest slope was obtained for the electrode having 1% Ag_3BO_3, 10% Cu_2S and 89% Ag_2S composition. The average slope for three electrodes, prepared in same composition, was 31 ± 2 mV ($R^2 = 0.9923$) in 1×10^{-5} M–1×10^{-1} M borate concentration range.

The electrodes prepared in 0.5% Ag_3BO_3, 10% Cu_2S and 89.5% Ag_2S composition, had a slope of 26 ± 2 mV, slightly smaller than obtained with 1% Ag_3BO_3 electrode The results obtained for the electrodes in different compositions are summarized in Table 1 and the calibration curves are given in Fig. 2.

When the thickness of the electrode was increased by changing its mass from 0.1 g to 0.2 g, there was nearly no response. In further studies the electrodes with a mass of 0.1 g have been used. All of these electrodes were cleaned and wiped with a soft and wet paper and they were left wait in air and dark when not in use. The lifetime of the electrode was more than two years when it was left in air and in dark between measurements.

3.3. Conditioning of the electrode

The electrodes prepared in 1% Ag_3BO_3, 10% Cu_2S and 89% Ag_2S composition were left in air (in dark), in distilled water and in 10^{-4} M $Na_2B_4O_7$ solution under same duration of time and then their responses to borate ion were measured. It was found that the electrode had a highest slope when it was used just after preparation or when it was left wait in air (in dark), when it was washed and wiped thoroughly after its usage. But when it was left wait in distilled water or in tetraborate solution the slope decreased drastically. The calibration curves obtained for various conditions are given in Fig. 3.

Table 1
Effect of composition on the response of the electrode (potentials are measured against Ag/AgCl reference electrode) (the percentages belong to Ag_3BO_3 in electrode).

[Borate ($B_4O_7^{=}$)]	^aE (mV)			
	0.5%	1%	5%	10%
1×10^{-6}	168	221	−0.1	38
1×10^{-5}	151	203	−3.5	38
1×10^{-4}	137	178	−7.0	34
1×10^{-3}	113	144	−8.0	31
1×10^{-2}	81	116	−7.0	38
1×10^{-1}	51	81	–	–
Slope (1×10^{-6}–1×10^{-1})	24 ± 2	30 ± 2	–	–
Slope (1×10^{-5}–1×10^{-1})	26 ± 2	31 ± 2	–	–

[a] Electrodes prepared with Ag_2S.

3.4. The response time

The response time of the electrode depends to the concentration change. After each addition the time until the change in potential was constant is taken as the response time. When borate concentration was changed from 1×10^{-6} to 1×10^{-5}, from 1×10^{-5} to 1×10^{-4}, from 1×10^{-4} to 1×10^{-3}, from 1×10^{-3} to 1×10^{-2}, and from 1×10^{-2} to 1×10^{-1} M, the response of the electrode was about 15–20 s, which is a short period and it is an advantage. For this reason, this electrode can easily be used for routine analysis. All of these measurements were made at constant temperature and the electrode with the highest slope has been used throughout the work.

3.5. Effect of pH

Effect of pH on the potential readings in the presence of 10^{-4} M borate, were investigated. For this purpose to 20 ml 0.1 M $NaNO_3$ solutions 0.02 ml aliquots of 1 M HCl was added and the potentials after each addition was measured. The same procedure was applied for the NaOH additions. The electrode with the highest slope (1% Ag_3BO_3) was used during the measurements. The change

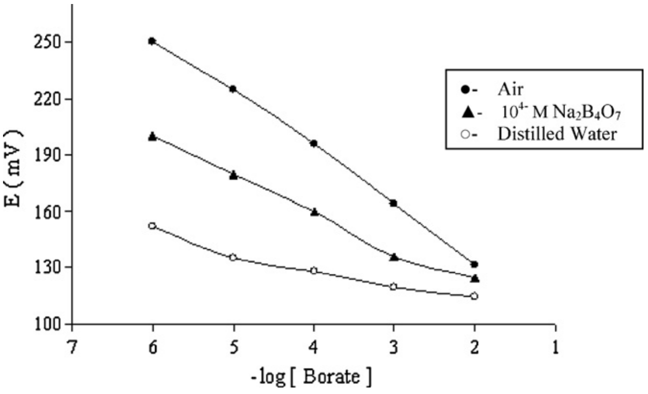

Fig. 3. The effect of medium in which the electrode was stored (1% Ag_3BO_3, 89% Ag_2S, 10% Cu_2S).

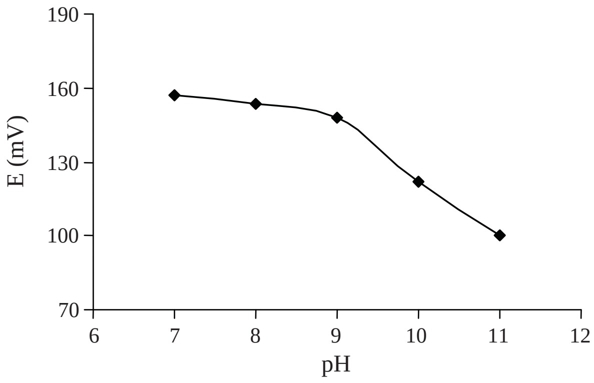

Fig. 4. The pH dependence of 1% Ag_3BO_3, 10% Cu_2S and 89% Ag_2S electrode in the presence of 1×10^{-4} M borate ($B_4O_7^{=}$) (in 0.1 M $NaNO_3$).

in potential with pH was only 2–3 mV for each pH unit change from pH 6 to 9. As can be seen from Fig. 4, this electrode can be used between pH 6 and 9 safely. Since 0.1 M $NaNO_3$ was used to keep the ionic strength constant, the pH will be around this range. The pH for various concentrations of borate ($B_4O_7^{=}$) was measured to see whether its standard addition had an effect on pH of the solution. It was found that the pH of 1×10^{-6} and 1×10^{-5} M borate solutions were about 8.1 and for borate solutions of 1×10^{-4} M, 1×10^{-3} M and 1×10^{-2} M concentrations the pH values were 8.5, 8.9 and 9.1, respectively. Thus, during standard additions there will be no potential change because of pH.

The reason of the potential change at pH values higher than 9, may be because of the slight dissolution of Cu_2S, oxidation of Cu(I) and then formation of Cu(II) complexes with hydroxide ion. As expected the potential increased in negative direction with pH because of OH^- (anion) complexes of copper (II), with negative oxidation state.

3.6. *Interference studies*

It usually is not possible to obtain an ISE which is only specific for one ion. Thus, in order to achieve correct and sensitive results in analysis it is important to know the effects of all other ions in the medium. These effects are identified through selectivity coefficients. In this study mixed solutions method was used to determine selectivity coefficient, $k_{A,B}^{pot}$ as it usually corresponds more closely to the situation in samples. In this method, solutions were prepared with a constant activity of the main ion and varying activity of interfering ion. Selectivity coefficient values were calculated via making use [27] of the below given equation:

$$k_{A,B}^{pot} a_B^{nA/nB} = a_A \left\{ \text{anti} \quad \log[(E_1 - E_2)/S] \right\} - a_A$$

Here, $S = 2.303RT/nAF$ (the slope of borate electrode), a_A is the activity of the primary ion (here borate), a_B the activity of the interfering ion, E_1 the potential measured when only A is present, E_2 the potential responsive to the primary ion in the presence of interfering ion, the selectivity coefficient, ($k_{A,B}^{pot}$) and nA, nB are the charges of A (borate) and B (interfering ion).

Possible interferences by a number of anions, Cl^-, Br^-, NO_3^-, $SO^{=}_4$, $H_2PO_4^-$ and some cations, K^+, Na^+, Cu^{2+}, Ag^+, Ca^{2+} were studied. In this work interfering ion was added into 0.1 M $NaNO_3$, containing 10^{-5} M borate solution, so that the interfering ion concentration was 10^{-2}–10^{-5} M, and after each addition, the change of potential was measured.

The potentials obtained at different concentrations of interfering ions are plotted against concentrations as shown in Fig. 5 for cations and in Fig. 6 for anions. For comparison the curve obtained for borate is also given in the same figure.

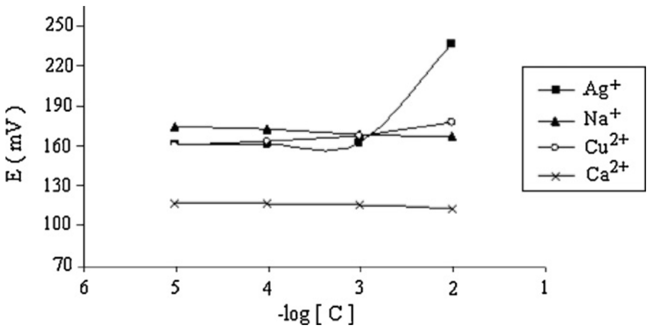

Fig. 5. The response of electrode against some cations in the presence of 1×10^{-5} M borate ($B_4O_7^{=}$) (1% Ag_3BO_3, 10% Cu_2S and 89% Ag_2S).

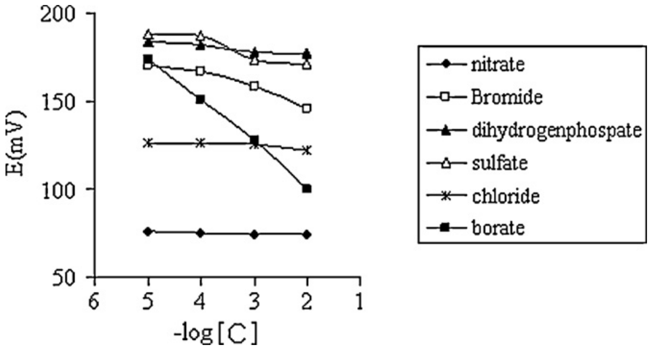

Fig. 6. The response of electrode against some anions in the presence of 1×10^{-5} M borate ($B_4O_7^{=}$) (1% Ag_3BO_3, 10% Cu_2S and 89% Ag_2S).

While no interference was observed for sodium, potassium, calcium and copper, slight interference was observed for silver ions. As can be seen nearly no interference was observed for chloride, nitrate, sulfate and dihydrogen phosphate ions. Only, bromide has shown slight effect when its concentration was about 10^{-3} M. The selectivity coefficients calculated for above mentioned ions are summarized in Table 2.

3.7. *Determination of borate (as B) content in tap waters of two different cities and waste water*

Tap water samples were taken from two different cities for comparison. One of the cities (Eskişehir, Kırka) was situated near to the borax mines and the second city was Ankara which is far away. For the determination of borate, first the potential of 20 ml of 0.1 M $NaNO_3$ is measured using borate ion selective electrode. Then, appropriate volumes of water samples were added and once more potential was measured. (In case of lower concentrations of borate, $NaNO_3$ had to be added into larger volumes of water sample.) The borate (as B) content of this water was determined by standard additions. As can be seen from Table 3 the B content in tap water of a city situated near to borax mines was quite larger

Table 2
Selectivity coefficients ($k_{A,B}^{pot}$) for the borate electrode in mixed solutions[a] (in the presence of 1×10^{-5} M borate).

B (anions)[b]	$k_{A,B}^{pot}$	B (cations)[b]	$k_{A,B}^{pot}$
NO_3^-	2×10^{-4}	Ag^+	2×10^{-2}
SO_4^{2-}	3×10^{-5}	K^+	1×10^{-4}
$H_2PO_4^-$	3×10^{-5}	Na^+	1×10^{-4}
Br^-	4×10^{-4}	Cu^{2+}	2×10^{-4}
Cl^-	4×10^{-4}	Ca^{2+}	3×10^{-4}

[a] A: borate ion.
[b] B: interfering ion.

Table 3
Determination of B contents in tap water samples taken from two different cities and waste water from Kırka borax factory.

Sample taken	DPP [23] mol/L	Borate electrode, B mol/L
Eskişehir, Kırka (tap water)	$(5.1 \pm 0.3) \times 10^{-4}$	$(4.7 \pm 0.2) \times 10^{-4}$
Ankara (tap water)	–	$(1.1 \pm 0.1) \times 10^{-5}$
Eskişehir, Kırka (waste water)	–	$(2.3 \pm 0.1) \times 10^{-3}$

than the one which was taken far from the mines. To check the validity of the method, the same water sample from Kırka was analyzed also by differential pulse polarographic (DPP) method [23]. Good agreement was obtained between two different methods. The waste water taken from Kırka borax mines was also determined using the newly established electrode. The results are summarized in Table 3 together with the result obtained using DPP.

4. Conclusions

Although there are many investigations about pellet electrodes prepared from solid salts, none of these were subject for borate ion determination. In this work a new borate ion ($B_4O_7^=$) selective electrode using solid salts of Ag_3BO_3, Ag_2S and Cu_2S has been prepared. The preparation of the electrode is simple, it displays very good performance in regard to reproducibility, sensitivity and lifetime. The slope of the linear portion (1×10^{-1}–1×10^{-6} M) was 31 ± 2 mV/decade change in borate ion. This electrode displayed very good selectivity for borate ion with respect to Cl^-, Br^-, NO_3^-, $SO^=_4$, $H_2PO_4^-$ anions and K^+, Na^+, Cu^{2+}, Ca^{2+} cations. It was found that only Ag^+ had a small interference effect. The lifetime of the electrode was more than two years, when used at least 4–5 times a day.

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