

## A bromide-selective PVC membrane potentiometric sensor

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In this study, a novel poly(vinyl chloride) membrane bromide-selective sensor was developed. The best performance was obtained with a membrane composition of 2.0% ionophore, 33.0% poly(vinyl chloride) (PVC), 64.0% *o*-nitrophenyloctylether (*o*-NPOE) and 1.0% potassium tetrakis (*p*-chlorophenyl) borate (KTpCIPB). The sensor exhibits linear potentiometric response towards bromide ion in the concentration range of  $1.0 \times 10^{-1} - 1.0 \times 10^{-4}$  mol L<sup>-1</sup> and has a detection limit of  $2.2 \times 10^{-5}$  mol L<sup>-1</sup>. The bromide-selective sensor has a fast response time of 10 s and displays a highly selective response towards bromide compared to different anions. The sensor can be used in the pH range from 4.0 to 10.0. Finally, the bromide-selective sensor was successfully used for the determination of bromide in purified and commercial drinking water.

**Keywords:** ion-selective electrode, PVC membrane, all-solid-state, potentiometry, bromide determination

### INTRODUCTION

Bromide is a naturally occurring ion that is commonly present in seawater sources and drinking water. Bromide determination is a very important operation in various areas such as pharmaceutical manufacturing, chemistry, food production and in quality control of water. The presence of high amounts of bromide in environmental samples is considered highly dangerous for human health and thus, its measurement is of high importance for environmental scientists [1].

Different analytical methods have been used for the determination of bromide including ion chromatography [2], capillary electrophoresis [3], colorimetry [4], spectrophotometry [5] inductively coupled plasma mass spectrometry (ICP-MS) [6], high performance liquid chromatography (HPLC) [7] and mass spectrometry (MS) [8]. These methods are not ideal due to their high cost, complexity of use, high energy consumption, long measurement time, requirement for trained personnel and necessity of sample pretreatment [9–12]. Since 1950s, ion-selective electrodes (ISEs) have been widely used in industrial, environmental, pharmaceutical and agricultural analysis. Compared to other analytical methods, ISEs are very simple to use, inexpensive, durable, have good reusability, short response time, wide linear working range, low energy consumption and thus can be considered very suitable for the use in environmental analyses [13–15].

The ionophore, the most important component

of ISEs is responsible for the selective response to the target ion [16]. In sensor studies reported in the literature, thousands of sensors sensitive to either anions or cations have been developed using different ionophores. In the present study, a cobyrinic acid derivative macrocyclic molecule (Fig. 1) was used as an ionophore and a bromide-selective potentiometric sensor was developed. This sensor was evaluated in terms of some potentiometric properties such as linear working range, reusability, selectivity, pH working range and response time in laboratory conditions.

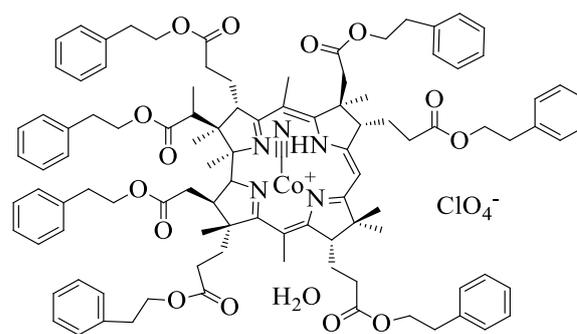


Fig. 1. Structure of the ionophore.

### EXPERIMENTAL

#### Materials

For all-solid-state contact preparation, epoxy (Macroplast Su 2227) and hardener (Desmodur RFE) were obtained from Henkel and Bayer, respectively.

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For bromide-selective sensor preparation, ionophore poly(vinyl)chloride (PVC) of high molecular weight, *o*-nitrophenyloctylether (*o*-NPOE), potassium tetrakis (*p*-chlorophenyl) borate (KTPClPB) and tetrahydrofuran (THF) were purchased from Sigma Aldrich, Merck and Fluka chemical companies. Deionized water was obtained using a DI 800 Model deionized water system. Sodium salts of the anions used in selectivity experiments were obtained from Sigma Aldrich and Merck. All anion stock solutions ( $1.0 \times 10^{-1} \text{ mol L}^{-1}$ ) were prepared using deionized water.

### Apparatus

Potentiometric measurements were performed at room temperature ( $25 \pm 1 \text{ }^\circ\text{C}$ ) using a computer-controlled multichannel potentiometric system. All measurements were performed using a micro-size silver/silver chloride reference electrode (Thermo-Orion). pH measurements were conducted with a digital pH meter (Mettler Toledo Model S220-K).

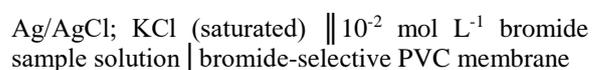
### Method

The preparation of the all-solid-state contact bromide-selective potentiometric sensor was carried out in two steps. We used the same sensor preparation protocol reported in previous studies [17–19]. At the first step, all-solid-state contact was prepared. For this purpose, graphite (50.0%), epoxy (35.0%), and hardener (15.0%) were added to THF in appropriate proportions. After suitable viscosity was obtained, a copper wire was immersed in this mixture 5–6 times and covered with solid-state mixture. Appropriate amounts of ionophore, PVC, *o*-NPOE and KTPClPB were dissolved in 5 mL of

THF. The optimum membrane composition was determined to be 64.0% plasticizer (*o*-NPOE), 33.0% PVC, 2.0% ionophore and 1.0% KTPClPB. This mixture was placed on the all-solid-state electrode surface at a certain thickness and left to dry for 24 h. The schematic diagram for the step-wise preparation of the bromide-selective sensor is shown in Fig. 2. Prior to first use, the prepared sensors were conditioned in a  $1.0 \times 10^{-2} \text{ mol L}^{-1}$  bromide solution for approximately 3 h. The membranes prepared and the optimum membrane composition are summarized in Table 1.

### Potential measurements

Potentials were measured using an Ag/AgCl reference electrode. Potentiometric study of the electrode was carried out by the following cell assembly:



The potentiometric measurement scheme of the bromide-selective sensor is shown in Fig. 2.

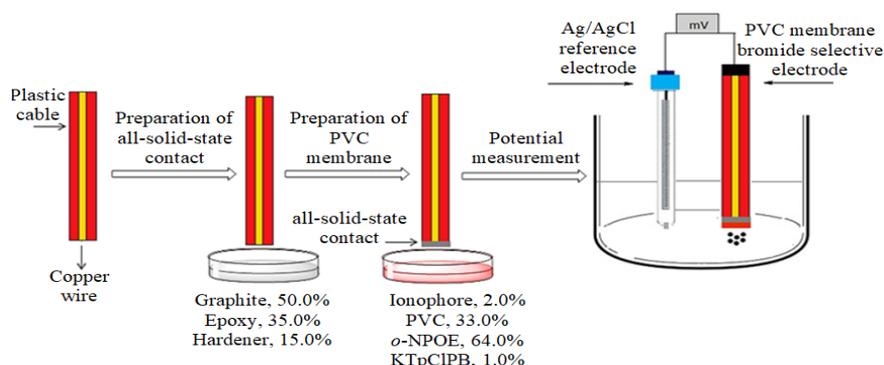
## RESULTS AND DISCUSSION

### Working concentration range and detection limit of the bromide-selective sensor

The PVC membrane bromide-selective sensor was evaluated for its potentiometric performance with optimum membrane composition. Figure 3A shows the calibration curve of the bromide-selective sensor. Figure 3B represents the linear working range of the sensor. Figure 3A shows that the sensitivity of the sensor significantly increases with the increasing concentration.

**Table 1.** Optimization of the bromide-selective membrane (% w/w) with the use of components at varying ratios.

Membrane	Ionophore	PVC	KTPClPB	<i>o</i> -NPOE	Working concentration range
1	1.5	33.0	1.0	64.5	$1.0 \times 10^{-1} - 1.0 \times 10^{-3}$
2	<b>2.0</b>	<b>33.0</b>	<b>1.0</b>	<b>64.0</b>	<b><math>1.0 \times 10^{-1} - 1.0 \times 10^{-4}</math></b>
3	3.0	33.0	1.0	63.0	$1.0 \times 10^{-1} - 1.0 \times 10^{-3}$



**Fig. 2.** Schematic diagram for the step-wise preparation of bromide-selective sensors and potential measurement.

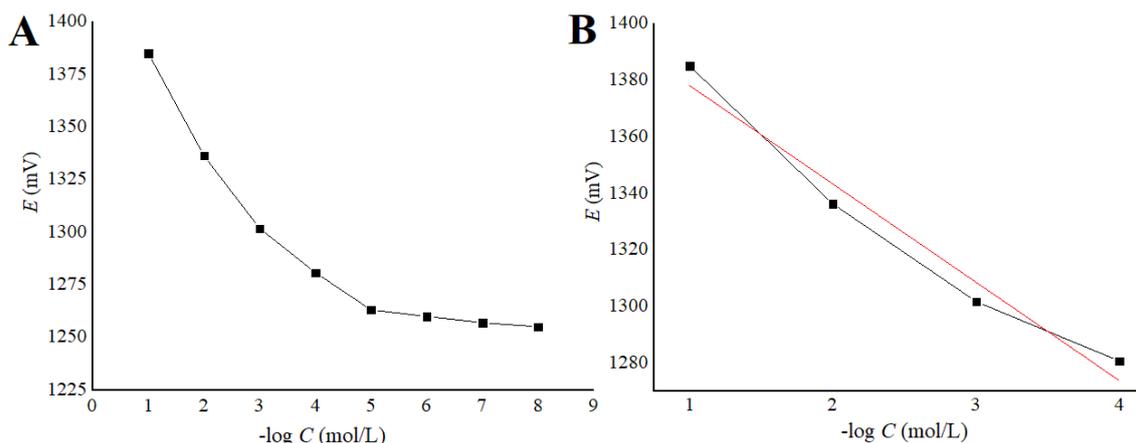


Fig. 3. A) calibration curve; B) potential linear response of the bromide-selective sensor.

This observation can be evaluated as a result of the prepared electrode composition. The developed bromide-selective sensor exhibited a linear response to the bromide ions in the concentration range of  $1.0 \times 10^{-1} - 1.0 \times 10^{-4}$  mol L<sup>-1</sup> (Fig 3B). To calculate the detection limit of the bromide-selective sensor, the potential value corresponding to the point where the extrapolations of the two linear regions in the graph intersect was determined (Fig 3A). The resulting value was written in the correct equation ( $E = 34.9 \log [\text{Br}^-] + 1413$ ) of the graph. Consequently, the detection limit of the sensor was determined to be  $2.2 \times 10^{-5}$  mol L<sup>-1</sup>.

#### Reusability of the bromide-selective sensor

Reusability is considered one of the most important characteristics in evaluating sensor performance [20]. The developed bromide-selective sensor was exposed repetitively to bromide ion solutions at different concentrations ( $1.0 \times 10^{-1} - 1.0 \times 10^{-3}$  mol L<sup>-1</sup>). The results are shown in Fig. 4 and Table 2. Based on these data, it can be seen that the proposed bromide-selective sensor has a good reusability and stability.

#### Selectivity of the bromide-selective sensor

The selectivity is the behavior of the sensor towards the primary ion in the presence of foreign ions, and it is a highly important parameter for the performance of ion-selective electrodes. Thus, the influence of a number of anions ( $\text{ClO}_3^-$ ,  $\text{CH}_3\text{COO}^-$ ,  $\text{PO}_4^{3-}$ ,  $\text{NO}_3^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{CO}_3^{2-}$ ,  $\text{NO}_2^-$ ,  $\text{Cl}^-$ ) on the selectivity behavior of the developed bromide-selective sensor was investigated in the current study. Potentiometric selectivity coefficients of the bromide-selective sensor were calculated according to the IUPAC recommendation by using a separate solution method [21]:

$$\log K_{A,B}^{\text{pot}} = \frac{(E_B - E_A)Z_A F}{RT \ln 10} + \left(1 - \frac{Z_A}{Z_B}\right) \log a_A$$

where  $E_A$  is the potential measured in  $1.0 \times 10^{-2}$  mol L<sup>-1</sup> bromide solution,  $E_B$  the potential measured in  $1.0 \times 10^{-2}$  mol L<sup>-1</sup> interferent anion solutions,  $Z_A$  and  $Z_B$  are the charges of bromide and interfering ions, respectively,  $a_A$  is the activity of bromide and  $R$ ,  $T$ , and  $F$  have the usual meanings. The selectivity coefficients ( $\log K_{\text{Br}^-, X^-}^{\text{pot}}$ ) of the bromide-selective sensor are presented in Table 3. The data show that the sensor is highly selective for bromide ions even in the presence of other anions.

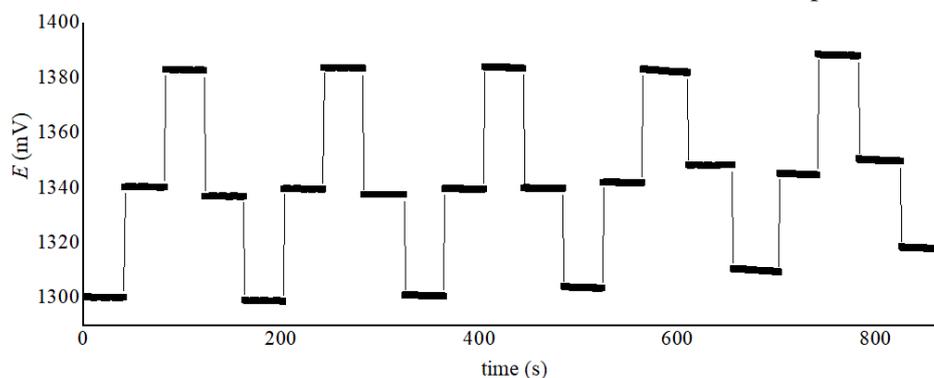


Fig. 4. Reusability of the bromide-selective sensor.

**Table 2.** Reusability results of the bromide-selective sensor.

Br <sup>-</sup> solution	Potential (mV)					Average (± SD) *
	I	II	III	IV	V	
1.0×10 <sup>-1</sup>	1383.2	1383.6	1383.8	1383.3	1387.0	1384.2 (± 1.43)
1.0×10 <sup>-2</sup>	1340.2	1339.8	1340.0	1340.6	1343.8	1340.9 (± 1.48)
1.0×10 <sup>-3</sup>	1300.2	1300.2	1301.2	1303.8	1305.0	1302.0 (± 1.97)

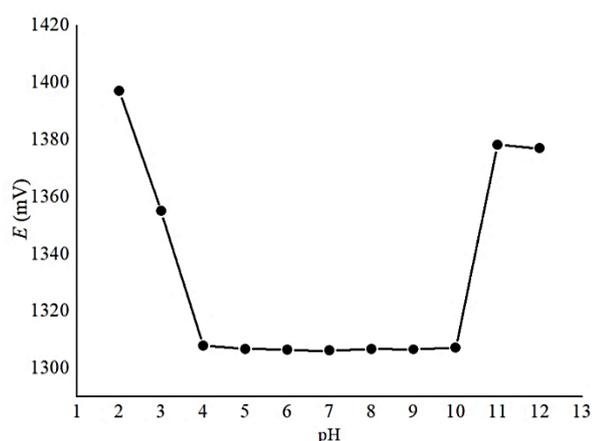
\*Potential values are given for five separate experimental measurements (I-V) (n = 5)

**Table 3.** Selectivity coefficient values for the bromide-selective sensor.

Interfering ions	Selectivity coefficient, $\log K_{Br^-,X^-}^{pot}$
ClO <sub>3</sub> <sup>-</sup>	-1.83
CH <sub>3</sub> COO <sup>-</sup>	-2.32
PO <sub>4</sub> <sup>3-</sup>	-2.34
NO <sub>3</sub> <sup>-</sup>	-2.37
SO <sub>4</sub> <sup>2-</sup>	-2.46
CO <sub>3</sub> <sup>2-</sup>	-2.53
NO <sub>2</sub> <sup>-</sup>	-2.67
Cl <sup>-</sup>	-2.78

#### pH dependence of the bromide-selective sensor

The working pH range of the bromide-selective sensor was obtained by using sodium hydroxide (1.0×10<sup>-2</sup> mol L<sup>-1</sup>) and hydrochloric acid (1.0×10<sup>-2</sup> mol L<sup>-1</sup>) solutions. The bromide solution (1.0×10<sup>-2</sup> mol L<sup>-1</sup>) was added to each pH solution (2.0 – 12.0) and measurements were taken for bromide solutions prepared at different pH values. The working pH range measurement results are shown in Fig. 5. Figure 5 shows that the bromide-selective sensor works in the pH range of 4.0 – 10.0, without being affected by the changes in pH.



**Fig. 5.** Effect of pH on the potential of the bromide-selective sensor.

#### Response time of the bromide-selective sensor

According to the definition made by IUPAC, we determined the response time of the developed sensor [21]. Accordingly, until the sensor reaches 95% of the equilibrium potential, data were obtained after successive immersions of the electrode in a series of bromide ion solutions, each having a ten-fold difference in concentration. The bromide concentration was very rapidly increased from 1.0×10<sup>-4</sup> to 1.0×10<sup>-1</sup> mol L<sup>-1</sup> and values were measured. The static response time for bromide-selective sensor was observed to be 10 s.

#### Analytical applications

The developed sensor was successfully used to determine bromide ions in real samples such as purified and commercial drinking water. Known amounts of bromide solution were added to the water samples according to the standard addition method. Bromide analysis was performed in the water samples with the developed sensor. The results are given in Table 4. It can be clearly seen from the table that high recovery is obtained for the determination of bromide in two different water samples.

**Table 4.** Determination of bromide in water samples.

Real Sample	Added Br <sup>-</sup> (mol L <sup>-1</sup> )	Mean (± SD) found with sensor <sup>a</sup> (mol L <sup>-1</sup> )	% Recovery
commercial drinking water	6.00×10 <sup>-4</sup>	5.75 (± 0.117) ×10 <sup>-4</sup>	95.83
purified drinking water	7.00×10 <sup>-4</sup>	6.03 (± 0.212) ×10 <sup>-4</sup>	86.42

<sup>a</sup>Average value ( $n = 3$ ).

### CONCLUSION

In the literature, many potentiometric sensors have been developed for the detection of cations and anions in various samples. In this study, a new bromide-selective sensor was developed and its working conditions were determined. The developed sensor displays a linear concentration range from  $1.0 \times 10^{-4}$  to  $1.0 \times 10^{-1}$  mol L<sup>-1</sup> with a detection limit of  $2.2 \times 10^{-5}$  mol L<sup>-1</sup>. The sensor has a very fast response time, good reusability and good performance over a wide pH range. In addition, we showed that the sensor could be successfully applied to the determination of bromide in water samples.

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