



Contents lists available at [ScienceDirect](#)

Desalination

journal homepage: www.elsevier.com/locate/desal



Erratum

Erratum to “Construction of barium (II) PVC membrane electrochemical sensor based on 3-deoxy-D-erythro-hexos-2-ulose bis (thiosemicarbazone) as a novel ionophore” [Desalination 250 (2010) 56–61]

Hassan Ali Zamani ^{a,*}, Mohammad Taghi Hamed-Mosavian ^b, Elham Aminzadeh ^c,
Mohammad Reza Ganjali ^{d,e}, Mousa Ghaemy ^f, Hossien Behmadi ^f, Farnoush Faridbod ^d

^a Department of Applied Chemistry, Quchan branch, Islamic Azad University, Quchan, Iran

^b Department of Chemical Engineering, Ferdowsi University of Mashhad, Iran

^c Department of Chemical Engineering, Quchan branch, Islamic Azad University, Quchan, Iran

^d Center for Excellence in Electrochemistry, Faculty of Chemistry, University of Tehran, Tehran, Iran

^e Endocrine & Metabolism Research Center, Tehran University of Medical Sciences, Tehran, Iran

^f Department of Chemistry, Mashhad branch, Islamic Azad University, Mashhad, Iran

The Publisher regrets that an error occurred in affiliation b. This error is now corrected, above. The Publisher apologises for any inconvenience.

DOI of original article: [10.1016/j.desal.2009.09.014](https://doi.org/10.1016/j.desal.2009.09.014).

* Corresponding author. Tel.: +98 581 2224180; fax: +98 581 2226093.

E-mail addresses: haszamani@yahoo.com (H.A. Zamani), mosavian@ferdowsi.um.ac.ir, hmosavian@gmail.com (M.T. Hamed-Mosavian), ganjali@khayam.ut.ac.ir, norouzi@khayam.ut.ac.ir (M.R. Ganjali), ghaemy@umz.ac.ir (M. Ghaemy).

0011-9164/\$ – see front matter © 2010 Elsevier B.V. All rights reserved.

doi:[10.1016/j.desal.2010.02.021](https://doi.org/10.1016/j.desal.2010.02.021)



Construction of barium (II) PVC membrane electrochemical sensor based on 3-deoxy-D-erythro-hexos-2-ulose bis (thiosemicarbazone) as a novel ionophore

Hassan Ali Zamani ^{a,*}, Mohammad Taghi Hamed-Mosavian ^b, Elham Aminzadeh ^c,
 Mohammad Reza Ganjali ^{d,e}, Mousa Ghaemy ^f, Hossien Behmadi ^f, Farnoush Faridbod ^d

^a Department of Applied Chemistry, Quchan branch, Islamic Azad University, Quchan, Iran

^b Department of Chemical Engineering, Ferdowsi University, Mashhad, Iran

^c Department of Chemical Engineering, Quchan branch, Islamic Azad University, Quchan, Iran

^d Center of Excellence in Electrochemistry, Faculty of Chemistry, University of Tehran, Tehran, Iran

^e Endocrine & Metabolism Research Center, Tehran University of Medical Sciences, Tehran, Iran

^f Department of Chemistry, Mashhad branch, Islamic Azad University, Mashhad, Iran

ARTICLE INFO

Article history:

Received 8 March 2008

Accepted 7 June 2009

Keywords:

PVC membrane

Ion-selective electrode

Sensor

Potentiometry

3-Deoxy-D-erythro-hexos-2-ulose bis
 (thiosemicarbazone)

ABSTRACT

In this study, a new ion-selective electrode for Ba²⁺ is described, illustrating 3-deoxy-D-erythro-hexos-2-ulose bis (thiosemicarbazone) (DHUT) in a poly(vinylchloride) (PVC) membrane with benzyl acetate (BA) as a plasticizer and sodium tetraphenyl borate (NaTPB) as an anionic additive. This sensor presented very good selectivity and sensitivity towards the Ba²⁺ ions over a wide variety of cations, including alkali, alkaline earth, transition and heavy metal ions. The electrode revealed a great improvement in the selectivity coefficients for the Ba²⁺ ions in comparison with the formerly reported Ba²⁺ sensors. The proposed electrode exhibited a significantly enhanced response towards the Ba²⁺ ions across the concentration range of 1.0 × 10⁻⁶–1.0 × 10⁻² M for the pH variation from 2.6 to 11 with a lower detection limit of 5.6 × 10⁻⁷ M. Moreover, the sensors displayed the Nernstian slope of 29.6 ± 0.5 mV per decade, having a fast response time within 15 s over the entire concentration range. It could also be used for at least 2 months with no potential divergence. As a result, the developed sensor was successfully applied to the direct barium ion determination in solutions, rock samples and as an indicator electrode in the Ba²⁺ ion potentiometric titration with EDTA.

© 2009 Elsevier B.V. All rights reserved.

1. Introduction

The barium metal does not occur free in nature. However, its compounds are present in small but widely distributed amounts in the earth's crust, especially in igneous rocks, sandstone and shale [1]. High barium levels may lead to a series of medical problems in human beings, some of which include acute gastroenteritis, loss of deep reflexes with onset of muscular paralysis, respiratory failure, rhabdomyolysis, hypophosphatemia and baritosis from inhaled barium [2]. Therefore, because of the increased industrial use of the barium compounds as well as their enhanced discharge, toxic properties and other adverse effects, the assay of the barium ions is necessary.

The available methods for the barium ion monitoring in solution include spectrophotometry, atomic absorption spectroscopy (AAS), inductively coupled plasma-mass spectroscopy (ICP-MS)

and inductively coupled plasma-atomic emission spectrometry (ICP-AES). Potentiometric detection based on ion-selective electrodes (ISEs) offers the advantages of speed and ease of preparation and procedures, relatively fast response, reasonable selectivity thorough judicious choice of the membrane active materials, wide linear dynamic range, and low cost [3–5]. Nevertheless, the literature survey revealed a limited number of ion-selective electrodes (ISEs) for barium. These ISEs illustrated different ion carriers, such as nonylphenoxypoly(ethyleneoxy)ethanol [6], diamide [7], 3,6-dioxaoctanedioic [8], lasalocid [9], 4-(1,1,3,3-tetramethylbutyl)-2,6-dinitrophenoldinonylnaphthalene sulfonate [10], crown ether [11], rose Bengal [12], and nonylphenoxypoly(ethyleneoxy)ethanol [13]. A highly selective and sensitive Ba²⁺-selective PVC membrane, based on dimethyl 1-acetyl-8-oxo-2,8-dihydro-1-hypra-zolo[5,1-a]isoindole-2,3-dicarboxylate, was introduced by Zamani et al. in 2006 [14].

Recently, several selective and sensitive polyvinyl chloride (PVC)-membrane ISEs for various metal ions have been reported [15–40]. At the present work, the development of a highly Ba²⁺-ISE is introduced with 3-deoxy-D-erythro-hexos-2-ulose bis (thiosemicarbazone) (DHUT) as a novel ionophore, for the potentiometric determination of Ba²⁺ ions over a wide concentration range (Fig. 1).

* Corresponding author. Tel.: +98 581 2224180; fax: +98 581 2226093.

E-mail addresses: haszamani@yahoo.com (H.A. Zamani),
mosavian@ferdowsi.um.ac.ir (M.T. Hamed-Mosavian), ganjali@khayam.ut.ac.ir,
norouzi@khayam.ut.ac.ir (M.R. Ganjali), ghaemy@umz.ac.ir (M. Ghaemy).

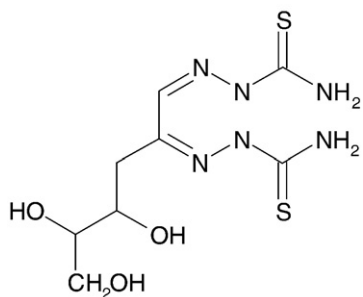


Fig. 1. The DHUT structure.

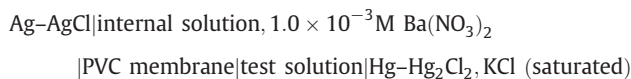
2. Experimental

2.1. Reagents

The Merck and the Aldrich Chemical Co. were the providers of the following reagent grades: benzyl acetate (BA), dibutyl phthalate (DBP), nitrobenzene (NB), sodium tetraphenyl borate (NaTPB), tetrahydrofuran (THF) and high relative molecular weight PVC. All reagents were used without any modification. Ligand 3-deoxy-D-erythro-hexos-2-ulose bis (thiosemicarbazone) (DHUT) was synthesized and purified as described elsewhere [41]. As far as the nitrate and chloride salts of all the employed cations are concerned, they were of the highest available purity and were P₂O₅-vacuum dried. During the experiments, triply distilled deionized water was used.

2.2. EMF measurements

The electromotive force (EMF) measurements with the polymeric membrane electrodes were carried out with the cell assembly of:



A Corning ion analyzer (250 pH/mV meter) was used for the potential measurements at 25.0 ± 0.1 °C. The activities were calculated in agreement with the Debye–Huckel procedure [42].

2.3. Electrode preparation

The PVC membranes were prepared according to a general procedure. The required ingredients for the membrane construction (30 mg PVC, 65 mg BA, 2 mg NaTPB and 3 mg DHUT) were mixed and dissolved in 3 mL of dry THF. The resulting mixture was transferred into a glass dish (2 cm in diameter) and the solvent was evaporated slowly until an oily concentrated mixture could be obtained. A Pyrex tube (3–5 mm in top) was dipped into the oily mixture for about 5 s, so that a transparent film of about 0.3 mm thickness was formed. After the tube removal from this mixture, the tube was kept at room temperature for about 24 h and it was filled with the internal filling solution (1.0×10^{-3} M of Ba(NO₃)₂). In the end, the electrode was conditioned by soaking in a 1.0×10^{-2} M barium nitrate solution for 24 h [43–55]. A silver/silver chloride wire was used as an internal reference electrode.

3. Results and discussion

3.1. Conductometric study

In order to study DHUT selectivity towards the metal ions, its interaction with some metal ions was studied conductometrically in an acetonitrile solution [56].

In all measurements, the cell should be thermostated at the temperature of 25.0 °C, using a Phywe immersion thermostat. In

typical experiments, 25 mL of an ion solution (1.0×10^{-4} M) is placed in a water-jacketed cell, equipped with a magnetic stirrer and connected to the thermostat, circulating water at the desired temperature. Then, a known amount of an ionophore or a ligand (1.0×10^{-2} M) solution is added in a stepwise manner, using a calibrated micropipette. The conductance of the solution is measured after each addition. The ligand addition is continued until the desired ionophore-to-ion mole ratio is achieved. The 1:1 binding of the cations with the ionophore and the complex formation constant in terms of the molar conductance can be expressed as [57]:

$$K_f = \frac{[\text{ML}^{n+}]}{[\text{M}^{n+}][\text{L}]} = \frac{(\Lambda_M - \Lambda_{\text{obs}})}{(\Lambda_{\text{obs}} - \Lambda_{\text{ML}})[\text{L}]} \quad (1)$$

where

$$K_f = C_L - \frac{C_M(\Lambda_M - \Lambda_{\text{obs}})}{(\Lambda_{\text{obs}} - \Lambda_{\text{ML}})} \quad (2)$$

where, Λ_M is the molar conductance of the cation before the addition of the ionophore; Λ_{ML} is the molar conductance of the complexes, Λ_{obs} the molar conductance of the solution during titration, C_L the analytical concentration of the added ionophore and C_M the analytical concentration of the cation salt. The complex formation constant, K_f , and the molar conductance of the complex, Λ_{ML} , were obtained by computer fitting Eqs. (1) and (2) to the molar conductance–mole ratio data, using the nonlinear least-squares program KINFIT [57]. In this experiment, the ligand to cation mole ratio was equal to 1 in all cases. The formation-constant values of the resulting 1:1 complexes in Table 1 show the high selectivity of the proposed ionophore to Ba²⁺ ions.

3.2. Response of the DHUT-based sensors to Ba²⁺ ions

The DHUT suitability as an ion carrier for different metal ions was checked by its utilization in the fabrication of the PVC-membrane-ISEs in preliminary experiments for a wide variety of cations, including alkali, alkaline earth, transition and heavy metal ions. A characterization for the Ba²⁺ sensor selectivity over other metal ions is shown in Fig. 2a and b. It can be evident that the DHUT-based membrane displays a Nernstian response towards the Ba²⁺ ions concentration in a broad concentration range. This is likely due to the quick exchange kinetics of the resulting Ba²⁺-DHUT complex as well as the high ionophore selectivity for barium ions, compared with the other metal ions. Therefore, the ionophore (DHUT) was selected as a suitable sensing material for Ba²⁺ ions in the PVC matrix.

Table 1
The formation constants of DHUT-Mⁿ⁺ complexes.

Ion	Log K _f
K ⁺	<2.0
Na ⁺	<2.0
Cs ⁺	2.12
Mg ²⁺	2.41 ± 0.30
Ca ²⁺	2.0 ± 0.24
Sr ²⁺	2.25 ± 0.14
Ba ²⁺	5.66 ± 0.16
Pb ²⁺	2.74 ± 0.23
Al ³⁺	2.59 ± 0.22
La ³⁺	2.59 ± 0.22
Co ³⁺	2.78 ± 0.20
Cu ²⁺	2.77 ± 0.13
Fe ³⁺	2.54 ± 0.23
Hg ²⁺	2.54 ± 0.23

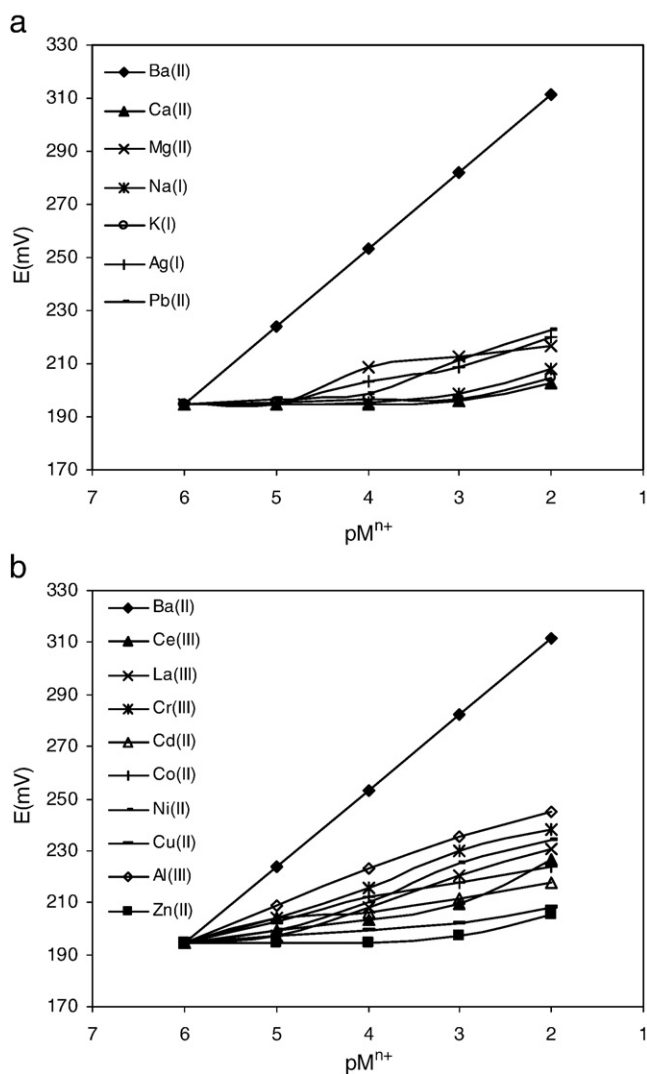


Fig. 2. The potential responses of various ISEs, based on DHUT.

3.3. The membrane composition effect on the potential response of the DHUT-based Ba²⁺ sensor

Some important features of the PVC membranes, such as the properties of the plasticizer, the plasticizer/PVC ratio, the nature and the amount of the ionophore and, especially, the nature and the amount of the used additives, are reported to significantly influence the ISEs sensitivity and selectivity [58–61]. Thus, the influence of the membrane composition, the nature and the amount of the plasticizer along with the NaTPB amount (as a suitable lipophilic additive) was investigated on the potential response of the Ba²⁺ sensor. The corresponding results are provided in Table 2. Clearly, among the three tested plasticizers, BA offers the best sensitivity. It is established that the selectivity and the working concentration range of the membrane sensor are affected by the nature and the amount of the used plasticizer. This phenomenon can be attributed to the plasticizer influence on the dielectric constant of the membrane phase, the ionophore molecules mobility and the state of the ligands [58,62]. Obviously from Table 2, the best electrode response sensitivity is reached with about 3% of DHUT. However, the NaTPB addition of 2% will increase the electrode response sensitivity considerably, so that the membrane electrode demonstrates a Nernstian behavior. It should be noted that the presence of lipophilic anions in the cation-selective membrane electrodes not only diminishes the ohmic resistance [62], but it also enhances their response behavior and selectivity [62–64].

Table 2
Optimization of the membrane ingredients.

Electrode no.	Composition (wt.%)				Slope (mV/decade)	Linear range (M)
	PVC	Plasticizer	NaTPB	DHUT		
1	30	NB, 67	0	3	10.3 ± 0.6	1.0 × 10 ⁻⁴ –1.0 × 10 ⁻²
2	30	NB, 66	1	3	22.2 ± 0.3	1.0 × 10 ⁻⁵ –1.0 × 10 ⁻²
3	30	NB, 65	2	3	27.6 ± 0.5	1.0 × 10 ⁻⁶ –1.0 × 10 ⁻²
4	30	NB, 64	3	3	24.4 ± 0.2	1.0 × 10 ⁻⁶ –1.0 × 10 ⁻²
5	30	NB, 64	2	2	25.3 ± 0.7	1.0 × 10 ⁻⁶ –1.0 × 10 ⁻²
6	30	NB, 66	2	4	23.8 ± 0.6	1.0 × 10 ⁻⁶ –1.0 × 10 ⁻²
7	30	AP, 65	2	3	26.2 ± 0.4	1.0 × 10 ⁻⁶ –1.0 × 10 ⁻²
8	30	BA, 65	2	3	29.6 ± 0.5	1.0 × 10 ⁻⁶ –1.0 × 10 ⁻²
9	30	DBP, 65	2	3	28.1 ± 0.3	1.0 × 10 ⁻⁶ –1.0 × 10 ⁻²

Table 2 displays that the optimum response characteristics were obtained with a membrane composition of 30% PVC, 65% BA, 3% DHUT and 2% NaTPB (no. 8).

3.4. Slope and detection limit

The EMF versus pBa²⁺ plot, obtained under the employment of the optimal membrane ingredients (Fig. 3), indicates that the sensor demonstrates a Nernstian behavior across a wide Ba²⁺ ion concentration range. The detection limit was 5.6 × 10⁻⁷ M, defined as the obtained Ba²⁺ concentration when extrapolating the linear region of the sensor calibration curve with the optimum concentration (Fig. 3) to the baseline potential. The slope of the calibration graph was 29.6 ± 0.5 mV per decade (for one electrode with *n* = 5) of the barium ions concentration.

The reproducibility of the Ba²⁺ electrode was also investigated. The standard deviations of the slope of eight replicate constructed electrodes were ±0.6.

3.5. The pH effect

The pH dependence on the membrane electrode was tested for the pH values (concentrated NaOH or HCl was used for the pH adjustment) from 1.0 up to 12.0 at two certain Ba²⁺ ion concentrations (1.0 × 10⁻³ M and 1.0 × 10⁻⁴ M). The results are illustrated in Fig. 4a and b. As it can be noticed, the potential remains fairly constant in the pH range of 2.6–11.0. At lower pH values than 2.6, a potential increase was observed. This increase was caused by the membrane response to the hydronium ions (the protonation of the nitrogen atoms in acidic media). On the other hand, the observed drift at higher

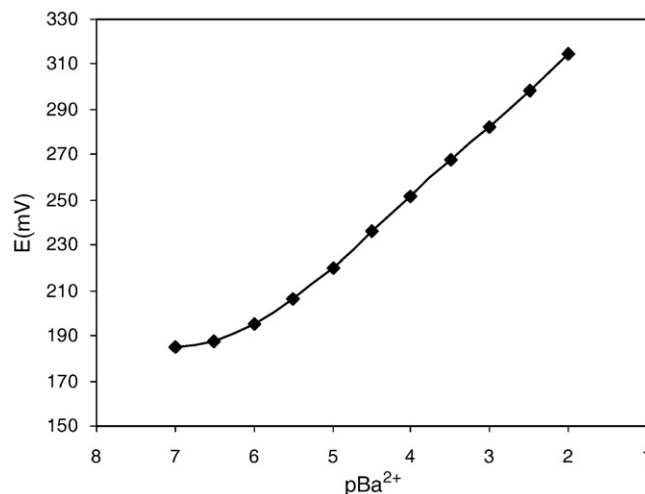


Fig. 3. The calibration curve of the barium electrode based on DHUT.

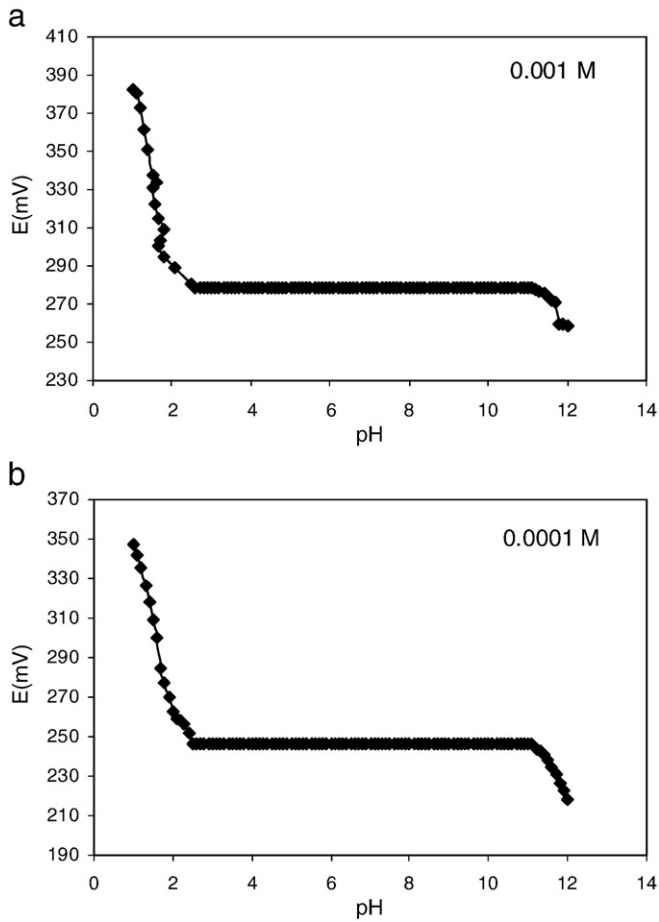


Fig. 4. The pH effect of the test solutions on the potential response of the barium sensor.

pH values could be attributed to the formation of some Ba²⁺ hydroxyl complexes in the solution.

3.6. Dynamic response time

For analytical purposes, response time is one of the most important factors that are taken into account. In this study, the dynamic response time of the membrane was measured at various concentrations (1.0 × 10⁻⁶ to 1.0 × 10⁻² M) of the test solutions. The

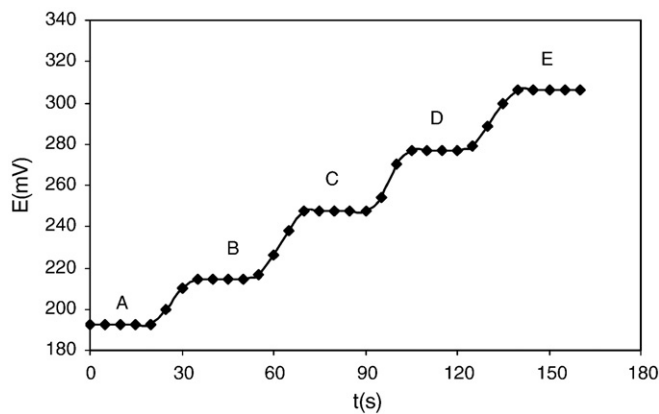


Fig. 5. The dynamic response time of the barium electrode for step changes in the Ba²⁺ concentration: A) 1.0 × 10⁻⁶ M, B) 1.0 × 10⁻⁵ M, C) 1.0 × 10⁻⁴ M, D) 1.0 × 10⁻³ M, E) 1.0 × 10⁻² M.

plot of the actual potential versus the time traces is depicted in Fig. 5, where it is noticed that stable potentials were attained within 15 s.

3.7. Sensor lifetime

The main factor limiting the lifetime of the ion-selective membrane in potentiometric measurements is the leakage of ionophore into the aqueous solutions. The proposed PVC-based membrane sensor could be used for at least 2 months (use of 1 h daily). After its utilization, it was washed and kept dry. During this certain time period, the membrane sensor could be used without any measurable divergence. After 2 months changes were observed in the slope and detection limit (from 29.6 to 25.1 mV per decade and 5.6 × 10⁻⁷ from 7.2 × 10⁻⁶ M, respectively) [65–67].

For long usage of the electrode, ionophore should be sufficiently lipophilic to ensure a long and stable response of the ion-selective electrode [65]. The theoretical lipophilicity of the used ionophore (log P_{octanol/water}) was calculated 1.3 and 1.2 by the chemoffice and hyperchem, respectively. The experimental lipophilicity was calculated to be 1.5.

3.8. Potentiometric selectivity

The potentiometric selectivity coefficients, which reflect the relative response of the membrane sensor towards the primary ions over other ions present in solution, are perhaps the most essential characteristic of an ISE. To investigate the membrane electrode selectivity, its potential response was monitored in the presence of various interfering foreign cations with the help of the matched potential method (MPM) [68].

The MPM was recommended by IUPAC in 1995 [69–72]. In line with MPM, a specified activity (concentration) of primary ions (A) is added to a reference solution and the potential is measured. In a separate experiment, interfering ions (B) are successively added to an identical reference solution, until the measured potential matches the one obtained before the primary ion addition. The MPM selectivity coefficient is then given by the resulting primary ion activity to the interfering ion activity ratio:

$$K_{a,b}^{MPM} = \frac{\Delta a_A}{a_B} = \frac{a'_A - a_A}{a_B} \tag{3}$$

The resulting values are listed in Table 3.

Table 4 summarizes and compares the linearity range, detection limit and selectivity coefficient values of the presented sensor with

Table 3 Selectivity coefficients of the various interfering ions.

Interfering ions	K _{Ba²⁺, B}
Li ⁺	3.8 × 10 ⁻³
Na ⁺	2.9 × 10 ⁻⁴
K ⁺	2.5 × 10 ⁻⁴
Ag ⁺	6.7 × 10 ⁻⁴
Pb ²⁺	1.0 × 10 ⁻³
Hg ²⁺	6.2 × 10 ⁻³
La ³⁺	4.4 × 10 ⁻³
Ce ³⁺	1.8 × 10 ⁻³
Al ³⁺	7.3 × 10 ⁻³
Cr ³⁺	5.6 × 10 ⁻³
Fe ³⁺	5.6 × 10 ⁻⁴
Mg ²⁺	5.7 × 10 ⁻⁴
Ca ²⁺	1.7 × 10 ⁻⁴
Sr ²⁺	8.2 × 10 ⁻⁴
Cu ²⁺	4.2 × 10 ⁻⁴
Ni ²⁺	4.8 × 10 ⁻³
Co ²⁺	3.6 × 10 ⁻⁴
Cd ²⁺	6.2 × 10 ⁻⁴
Zn ²⁺	3.3 × 10 ⁻⁴

Table 4

Comparison of the selectivity coefficients, linearity range and detection limit of the different Ba²⁺ electrodes.

	Ref. [11]	Ref. [12]	Ref. [13]	This work
Selectivity coefficients	FIM	SSM	MSM	MPM
Li ⁺	-1.27	-2.72	-2.04	-2.42
Na ⁺	-1.34	-3.27	-1.64	-3.54
K ⁺	-1.20	-2.03	-1.69	-3.60
Ag ⁺	-1.48	-	-	-3.17
Pb ²⁺	-1.74	-1.60	-	-3.00
Hg ²⁺	-	-	-	-2.21
La ³⁺	-	-	-	-2.36
Ce ³⁺	-1.92	-3.72	-	-2.74
Al ³⁺	-1.79	-3.20	-	-2.14
Cr ³⁺	-1.92	-	-	-2.25
Fe ³⁺	-1.79	-	-	-3.25
Mg ²⁺	-1.74	-2.72	-3.09	-3.24
Ca ²⁺	-1.12	-2.24	-3.09	-3.77
Sr ²⁺	-1.11	-2.09	-1.19	-3.09
Cu ²⁺	-	-2.45	-3.00	-3.38
Ni ²⁺	-	-3.73	-3.09	-2.32
Co ²⁺	-1.92	-3.92	-	-3.44
Cd ²⁺	-1.51	-4.57	-	-3.21
Zn ²⁺	-	-4.55	-	-3.48
Response time (s)	15	20	<60	15
Linearity range (M)	1.4 × 10 ⁻⁵ – 1.0 × 10 ⁻¹	5.0 × 10 ⁻⁵ – 1.0 × 10 ⁻¹	5.0 × 10 ⁻⁵ – 1.0 × 10 ⁻¹	1.0 × 10 ⁻⁶ – 1.0 × 10 ⁻²
Limit of detection (M)	-	2.5 × 10 ⁻⁶	-	5.6 × 10 ⁻⁷

those of the best previously Ba²⁺ electrodes, reported in the literature by other researchers [11–13]. It becomes apparent that the newly-developed sensor is superior to the formerly reported Ba²⁺ sensors in terms of selectivity, detection limit and dynamic concentration range.

3.9. Analytical applications

Barium containing rock samples (e.g. meta-basalt and meta-gabbro) were dissolved as described elsewhere [73]. The test solutions were assessed by direct potentiometry using the DDB barium membrane sensor. These rocks contained other elements such as Rb, Sr, Co, Ni, Cu, Pb, Zn, Cr, Al and V in different proportions. The results were compared with the data obtained by atomic absorption spectrometry (AAS) (Table 5). The results are in good agreement. The designed barium-ISE is preferable to AAS as an alternative method, because it is simple, rapid and relatively inexpensive.

3.9.1. Determination of the Ba²⁺ cations in mixtures of different ions

This electrode was additionally applied to the direct determination of the Ba²⁺ ions in different sample solutions. The resulting data of Table 5 indicate that the accuracy of the Ba²⁺ ions detection in different sample solutions is almost quantitative.

3.9.2. Titration with EDTA

Finally, the Ba²⁺ sensor was successfully used as an indicator electrode in the titration of 25.0 mL of a 1.0 × 10⁻⁴ M Ba²⁺ solution with a 1.0 × 10⁻² M EDTA. The resulting titration curve is given in

Table 5

Potentiometric determination of barium ions from some rocks using the present sensor.

Sample	C _{Ba²⁺} (ppm) by Ba ²⁺ sensors	C _{Ba²⁺} (ppm) by AAS
1	458.5 ± 0.3	456.2 ± 0.3
2	525.6 ± 0.3	523.5 ± 0.4
3	497.2 ± 0.4	491.2 ± 0.2

Table 6

Determination of the Ba²⁺ cations in mixtures of different ions.

Serial no.	Composition	Observed content (M)
1	0.0010 M Ba(NO ₃) ₂ + 0.01 M Ca(NO ₃) ₂ + 0.01 M NaNO ₃ + 0.01 M KNO ₃	0.0092
2	0.0010 M Ba(NO ₃) ₂ + 0.01 M Mg(NO ₃) ₂ + 0.01 M Ca(NO ₃) ₂ + 0.01 M Sr(NO ₃) ₂	0.0094
3	0.0010 M Ba(NO ₃) ₂ + 0.01 M Fe(NO ₃) ₃ + 0.01 M Cr(NO ₃) ₃ + 0.01 M Al(NO ₃) ₃	0.0095
4	0.0010 M Ba(NO ₃) ₂ + 0.01 M Pb(NO ₃) ₂ + 0.01 M Hg(NO ₃) ₂ + 0.01 M AgNO ₃	0.0093
5	0.0010 M Ba(NO ₃) ₂ + 0.01 M La(NO ₃) ₃ + 0.01 M Ce(NO ₃) ₃ + 0.01 M Pb(NO ₃) ₂ + 0.01 M Ca(NO ₃) ₂	0.0097
6	0.0010 M Ba(NO ₃) ₂ + 0.01 M Ni(NO ₃) ₂ + 0.01 M Co(NO ₃) ₂ + 0.01 M Pb(NO ₃) ₂ + 0.01 M Ca(NO ₃) ₂	0.0096
7	0.0010 M Ba(NO ₃) ₂ + 0.01 M Cd(NO ₃) ₂ + 0.01 M Co(NO ₃) ₂ + 0.01 M Zn(NO ₃) ₂ + 0.01 M Cu(NO ₃) ₂	0.001
8	0.0010 M Ba(NO ₃) ₂ + 0.01 M Ca(NO ₃) ₂ + 0.01 M Pb(NO ₃) ₂ + 0.01 M Zn(NO ₃) ₂ + 0.01 M Cd(NO ₃) ₂	0.0098

Fig. 6. Clearly, the amount of Ba²⁺ ions in the solution can be effectively determined with the electrode.

4. Conclusion

The use of the 3-deoxy-D-erythro-hexos-2-ulose bis (thiosemicarbazone) (DHUT) with BA as plasticizer shows the best response characteristics with Nernstian behavior over the concentration range of 1.0 × 10⁻⁶–1.0 × 10⁻² M Ba²⁺, a detection limit of 5.6 × 10⁻⁷ M with very low interference from common alkali, alkaline earth, transition and heavy metal ions and a fast response time of 15 s. The proposed sensor potential responses are independent of pH in the range of 2.6–11.0. The sensor was used as the indicator electrode in the potentiometric titration of barium with EDTA and could be used for the Ba²⁺ determination in rock samples.

Acknowledgement

The authors gratefully acknowledge the financial support of this research proposal from the Research Council of the Quchan Islamic Azad University.

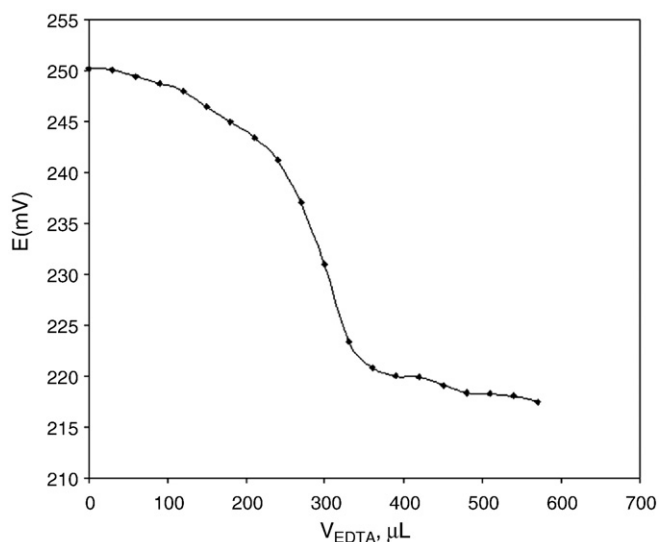


Fig. 6. The potentiometric titration curve of 25.0 mL 1.0 × 10⁻⁴ M solution of Ba²⁺ with 1.0 × 10⁻² M of EDTA.

References

- [1] O.R. Kirk, F.D. Othmer, *Encycl. Chem. Technol.*, Vol. 3, Wiley, New York, 1982.
- [2] A.K. Singh, R. Singh, R.V.P. Singh, P. Saxena, *Sens. Actuators B* 106 (2005) 779–783.
- [3] F. Faridbod, M.R. Ganjali, R. Dinarvand, P. Norouzi, S. Riahi, *Sensors* 8 (2008) 1645–1703.
- [4] M.R. Ganjali, P. Norouzi, F. Faridbod, M. Rezapour, M.R. Pourjavid, *J. Iran. Chem. Soc.* 4 (2007) 1–29.
- [5] F. Faridbod, M.R. Ganjali, R. Dinarvand, P. Norouzi, *Sensors* 8 (2008) 2331–2412.
- [6] D.L. Jones, G.J. Moody, J.D.R. Thomas, *Analyst* 106 (1981) 974–984.
- [7] M. Läeubli, O. Dinten, E. Pretsch, W. Simon, F. Vöegtle, F. Bongardt, T. Kleiner, *Anal. Chem.* 57 (1985) 2756–2758.
- [8] D. Ammann, E. Pretsch, W. Simon, *Anal. Lett.* 5 (1972) 843–850.
- [9] K. Suzuki, K. Tohda, H. Sasakura, T. Shirai, *Anal. Lett.* 20 (1987) 39–45.
- [10] J.C. Moutet, E. Saint-Aman, I. Ion, *J. Electroanal. Chem.* 415 (1996) 187–189.
- [11] V.K. Gupta, A.K. Jain, U. Khurana, L.P. Singh, *Sens. Actuators B* 55 (1999) 201–211.
- [12] A.M. Othman, M.S. El-Shahawi, M. Abdel-Azem, *Anal. Chim. Acta* 555 (2006) 322–328.
- [13] A.M.Y. Jaber, G.J. Moody, J.D.R. Thomas, *Analyst* 101 (1976) 179–186.
- [14] H.A. Zamani, J. Abedini-Torghabeh, M.R. Ganjali, *Electroanalysis* 18 (2006) 888–893.
- [15] H.A. Zamani, G. Rajabzadeh, M.R. Ganjali, S.M. Khatami, *Electroanalysis* 17 (2005) 2260–2265.
- [16] H.A. Zamani, G. Rajabzadeh, M.R. Ganjali, *Sens. Actuators B* 119 (2006) 41–46.
- [17] H.A. Zamani, M.T. Hamed-Mosavian, E. Hamidfar, M.R. Ganjali, P. Norouzi, *Mater. Sci. Eng. C* 28 (2008) 1551–1555.
- [18] H.A. Zamani, M.R. Ganjali, M. Adib, *Sens. Actuators B* 120 (2007) 545–550.
- [19] V.K. Gupta, S. Jain, S. Chandra, *Anal. Chim. Acta* 486 (2003) 199–207.
- [20] H.A. Zamani, *Anal. Lett.* 41 (2008) 1850–1866.
- [21] H.A. Zamani, M.R. Ganjali, P. Norouzi, M. Adib, M. Aceedy, *Anal. Sci.* 22 (2006) 943–948.
- [22] H.A. Zamani, M.R. Ganjali, P. Norouzi, S. Meghdadi, *Anal. Lett.* 41 (2008) 902–916.
- [23] H.A. Zamani, M. Masrournia, M. Rostame-Faroge, M.R. Ganjali, H. Behmadi, *Sens. Lett.* 6 (2008) 759–764.
- [24] H.A. Zamani, M.R. Ganjali, P. Norouzi, S. Meghdadi, *J. Appl. Electrochem.* 37 (2007) 853–859.
- [25] H. Behmadi, H.A. Zamani, M.R. Ganjali, P. Norouzi, *Electrochim. Acta* 53 (2007) 1870–1876.
- [26] H.A. Zamani, M.R. Ganjali, P. Norouzi, A. Tajarodi, Y. Hanifehpour, *J. Chil. Chem. Soc.* 52 (2007) 1332–1337.
- [27] M.R. Abedi, H.A. Zamani, M.R. Ganjali, P. Norouzi, M. Adib, *Sens. Lett.* 5 (2007) 516–521.
- [28] H.A. Zamani, M.R. Ganjali, M. Salavati-Niasari, *Transit. Met. Chem.* 33 (2008) 995–1001.
- [29] H.A. Zamani, M.R. Ganjali, P. Norouzi, M. Adib, *Mater. Sci. Eng. C* 28 (2008) 157–163.
- [30] H.A. Zamani, A. Nezhadali, M. Saghravani, *Anal. Lett.* 41 (2008) 2727–2742.
- [31] H.A. Zamani, M. Mohaddeszadeh, *Anal. Lett.* 41 (2008) 2710–2726.
- [32] F. Faridbod, M.R. Ganjali, B. Larijani, P. Norouzi, S. Riahi, F.S. Mirnaghi, *Sensors* 7 (2007) 3119–3135.
- [33] V.K. Gupta, A.K. Singh, M. Al-Khayat, B. Gupta, *Anal. Chim. Acta* 590 (2007) 81–90.
- [34] V.K. Gupta, S. Chandra, S. Agarwal, H. Lang, *Sens. Actuators B* 107 (2005) 762–767.
- [35] V.K. Gupta, S. Chandra, H. Lang, *Talanta* 66 (2005) 575–580.
- [36] V.K. Gupta, R. Ludwig, S. Agarwal, *Anal. Sci.* 21 (2005) 293–296.
- [37] V.K. Gupta, *Chimia* 59 (2005) 209–217.
- [38] A.K. Jain, V.K. Gupta, J.R. Raison, *Sensors* 4 (2004) 115–124.
- [39] V.K. Gupta, R. Prasad, A. Kumar, *Talanta* 63 (2004) 1027–1033.
- [40] V.K. Gupta, S. Chandra, R. Mangla, *Sens. Actuators B* 86 (2002) 235–241.
- [41] D. Horton, R.G. Nickol, O. Varela, *Carbohydr. Res.* 168 (1987) 295–300.
- [42] S. Kamata, A. Bhale, Y. Fukunaga, A. Murata, *Anal. Chem.* 60 (1988) 2464–2467.
- [43] Y.Q. Chai, J.Y. Dai, R. Yuan, X. Zhong, Y. Liu, D.P. Tang, *Desalination* 180 (2005) 207–215.
- [44] C. Wardak, B. Marczewska, J. Lenik, *Desalination* 163 (2004) 69–75.
- [45] H.A. Zamani, F. Malekzadegan, M.R. Ganjali, *Anal. Chim. Acta* 555 (2006) 336–340.
- [46] S. Chandra, C.K. Singh, H. Agarwal, R.K. Agarwal, *Anal. Sci.* 23 (2007) 683–687.
- [47] H.A. Zamani, G. Rajabzadeh, M.R. Ganjali, P. Norouzi, *Anal. Chim. Acta* 598 (2007) 51–57.
- [48] H.A. Zamani, G. Rajabzadeh, M.R. Ganjali, *Talanta* 72 (2007) 1093–1099.
- [49] T. Ito, C. Coto, J. Trace, *Microprobe Tech.* 19 (2001) 601–613.
- [50] H.A. Zamani, M.R. Ganjali, M. Adib, *Sens. Lett.* 4 (2006) 345–350.
- [51] H.A. Zamani, M.R. Ganjali, P. Norouzi, A. Tadjarodi, E. Shahsavani, *Mater. Sci. Eng. C* 28 (2008) 1489–1494.
- [52] H.A. Zamani, G. Rajabzadeh, A. Firouz, M.R. Ganjali, *J. Anal. Chem.* 62 (2007) 1080–1087.
- [53] S. Khalil, *Anal. Lett.* 36 (2003) 1335–1349.
- [54] G. Ekmekci, D. Uzun, G. Somer, Ş. Kalaycı, *J. Membr. Sci.* 288 (2007) 36–40.
- [55] H.A. Zamani, G. Rajabzadeh, M.R. Ganjali, *Sens. Lett.* 7 (2009) 114–118.
- [56] Z. Pourghobadi, F. Seyyed-Majidi, M. Daghighi-Asli, F. Parsa, A. Moghimi, M.R. Ganjali, H. Aghabozorg, M. Shamsipur, *Pol. J. Chem.* 74 (2000) 837.
- [57] V.A. Nicely, J.L. Dye, *J. Chem. Educ.* 48 (1971) 443.
- [58] E. Ammann, E. Pretsch, W. Simon, E. Lindner, A. Bezegh, E. Pungor, *Anal. Chim. Acta* 171 (1985) 119–129.
- [59] M. Huster, P.M. Gehring, W.E. Morf, W. Simon, *Anal. Chem.* 63 (1990) 1330–1335.
- [60] H.A. Zamani, *Anal. Lett.* 42 (2009) 615–629.
- [61] H.A. Zamani, M. Masrournia, S. Sahebznasagh, M.R. Ganjali, *Anal. Lett.* 42 (2009) 555–570.
- [62] E. Bakker, P. Buhlmann, E. Pretsch, *Chem. Rev.* 97 (1997) 3083–3132.
- [63] T. Rosatzin, E. Bakker, Y. Suzuki, W. Simon, *Anal. Chim. Acta* 280 (1993) 197–208.
- [64] H.A. Zamani, G. Rajabzadeh, M.R. Ganjali, N. Seifi, *Collect. Czech. Chem. Commun.* 72 (2007) 1189–1206.
- [65] A.K. Jain, A.K. Singh, S. Mehtab, P. Saxena, *Anal. Chim. Acta* 551 (2005) 45–50.
- [66] H.A. Zamani, M.R. Ganjali, P. Norouzi, M. Adib, *Sens. Lett.* 5 (2007) 522–527.
- [67] V.K. Gupta, A.K. Singh, B. Gupta, *Anal. Chim. Acta* 575 (2006) 198.
- [68] R.P. Buck, E. Lindner, IUPAC recommendations for nomenclature of ion-selective electrodes, *Pure Appl. Chem.* 66 (1994) 2527.
- [69] Y. Umezawa, K. Umezawa, H. Sato, *Pure Appl. Chem.* 67 (1995) 507–518.
- [70] M. Nekoei, H.A. Zamani, M. Mohammadhossieni, *Anal. Lett.* 42 (2009) 284–297.
- [71] M.R. Abedi, H.A. Zamani, M.R. Ganjali, P. Norouzi, *Intern. J. Environ. Anal. Chem.* 88 (2008) 353–362.
- [72] M.R. Abedi, H.A. Zamani, *Anal. Lett.* 41 (2008) 2251–2266.
- [73] K.A.C. Hassan, G.J. Moody, J.D.R. Thomas, *Analyst* 105 (1980) 147–153.