



# Fabrication of a novel iron(III)–PVC membrane sensor based on a new 1,1'-(iminobis(methan-1-yl-1-ylidene))dinaphthalen-2-ol synthetic ionophore for direct and indirect determination of free iron species in some biological and non-biological samples

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## ABSTRACT

In this novel, the iron(III)–PVC membrane sensor was investigated based on a new 1,1'-(iminobis(methan-1-yl-1-ylidene))dinaphthalen-2-ol (IBMYD) synthetic ionophore as a suitable carrier. The best performance was observed for the membrane composition including 33.0% PVC, 65.0% TEHP, 1.0% NaTPB and 1.0% ionophore. The electrode displayed a linear potential response over a wide concentration range from  $1.0 \times 10^{-7}$  to  $1.0 \times 10^{-1}$  mol L<sup>-1</sup>, with a detection limit of  $5.0 \times 10^{-8}$  mol L<sup>-1</sup> and a good Nernstian slope of  $19.9 \pm 0.3$  mV decade<sup>-1</sup>. The sensor possessed some advantages such as short conditioning time, very fast response time (<12 s) and especially good discriminating ability towards Fe(III) ions over a wide variety of alkali, alkaline earth, transition, and heavy metal ions. The potential response of the proposed sensor was independent of the pH of the test solution, in the pH working range from 3.0 to 6.3. The fabricated electrode was applied for at least 2 months, without any measurable divergence in the potential characteristics. The optimized sensor was used successfully for direct and indirect determination of free iron species in some different synthetic and real samples with satisfactory results.

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## 1. Introduction

Iron plays important roles in biological systems. With only a few possible exceptions in the bacterial world, there will be no life without iron [1]. If the iron concentration exceeds the normal level in the body, it may become a potential health hazard. Excess amounts of iron ions in the body cause liver and kidney damages. Some iron compounds are realized to be carcinogens. Hence, the need to iron ion determination in clinical, medicinal, environmental and different industrial samples has created several methods to measure this analyte [2–7].

Among analytical available techniques, the carrier based ion-selective electrodes are well established analytical tools that can be used to measure different ions with the most important properties such as high speed and non-destructive sample analysis, portability

of the device, online monitoring, cost effectiveness and large measuring range. Despite the urgent need to iron-selective sensors for the potentiometric monitoring of Fe(III) ions, only limited reports have been published related to Fe(III) ion-selective electrodes in the literatures [8–16].

Compared to these previously mentioned sensors, the new Fe(III)–PVC based ion-selective electrode revealed the better characteristics in working activity range, Nernstian slope, response time, stability and selectivity towards Fe(III) ions over a wide variety of alkali, alkaline earth, transition and heavy metal ions. The recommended potentiometric sensor could also be used successfully for the direct and indirect determination of free iron species in some different synthetic and real samples with satisfactory results. We have recently reported the successful use of some PVC based membrane sensors for the different cations such as Zn<sup>2+</sup>, Cu<sup>2+</sup>, Pb<sup>2+</sup>, Cr<sup>3+</sup>, Al<sup>3+</sup> and zirconium ion based on different neutral ionospheres [17–21]. In this study, we were also motivated to investigate the fabrication and characterization of a new ISE based on 1,1'-(iminobis(methan-1-yl-1-ylidene))dinaphthalen-2-ol (IBMYD) as a suitable ionophore (Fig. 1).

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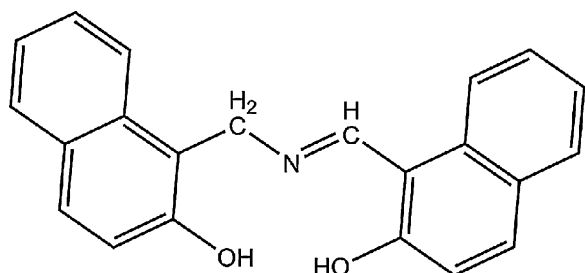


Fig. 1. Structure formula of 1,1'-(iminobis(methan-1-yl-1-ylidene))dinaphthalen-2-ol.

## 2. Experimental

### 2.1. Chemicals

Analytical grade reagents such as 2-nitrophenyloctylether (O-NPOE), dibutylphthalate (DBP), dioctylphthalate (DOP), tris(2-ethylhexyl)phosphate (TEHP), dioctylsebasate (DOS), benzylacetate (BA), acetophenone (AP), tetrahydrofuran (THF), sodium tetraphenylborate (NaTPB), oleic acid (OA), metal ion nitrate salts and high relative molecular weight poly(vinyl chloride) (PVC) were used as received from Merck or Fluka. Biological standard reference materials such as NIES, No. 1 pepperbush; NIES, No. 5 human hair; NIES, No. 6 mussels; and NIES, No. 2 pond sediment were purchased from National Institute for Environmental Studies (NIES) Japans Company. Alloy standard reference materials such as NKK No. 916 Aluminum Alloy; NKK No. 1021 Al, Si, Cu, Zn, Alloy and NKK No. 920 Aluminum Alloy were also obtained from Nippon Keikin-zoku Kogyo (NKK) Japans Company. The stock solution of Fe(II) was prepared by dissolution of  $\text{Fe}(\text{SO}_4)_2(\text{NH}_4)_2$  (reagent grade, Merck) in 10% HCl to obtain a stable  $0.01 \text{ mol L}^{-1}$  of Fe(II) standard solution. A mixed buffer solution pH at 4.5, containing appropriate amount of  $0.1 \text{ mol L}^{-1}$  acetic acid and  $0.1 \text{ mol L}^{-1}$  sodium acetate was also used to adjust the pH of the test solutions. Doubly distilled water was used to prepare all the metal ion solutions throughout.

### 2.2. Synthesis and characterization of 1,1'-(iminobis(methan-1-yl-1-ylidene))dinaphthalen-2-ol

A new 1,1'-(iminobis(methan-1-yl-1-ylidene))dinaphthalen-2-ol ionophore was synthesized based on the condensation of 2-naphthol with hexamethylenetetramine in acetic acid solvent medium in accordance with Duff's method [22]. 10 g of 2-naphthol and 4.9 g of hexamethylenetetramine were heated in acetic acid solvent medium for an hour at  $100^\circ\text{C}$  temperature. The resulting product was collected and well washed in ethanol. After evaporation of ethanol, a purified sharp pale yellow powder was obtained with a melting point of  $220\text{--}222^\circ\text{C}$  (yield, 70%). The ligand structure was finally characterized by infrared and  $^1\text{H}$  NMR spectra. IR (KBr): 3050–3200, 1640, 1600, 1512, 1442, 1362, 1276, 1181, 1020, 994, 815,  $743 \text{ cm}^{-1}$ ,  $^1\text{H}$  NMR (DMSO): 6.5–8.5 (phenyl protons, 12); 5.25 ( $\text{CH}_2$ , 1); 9.35 (CH, 1); 10.29 (OH, 1); 14.2 (OH, 1); 3.3–2.4 (solvent).

### 2.3. Spectrophotometric study of the complex formation between IBMYD and some metal ions

The stoichiometry and stability constants of the resulting complex formations between IBMYD and some metal ions were checked spectrophotometrically. The spectra from a series of solutions containing a constant concentration of  $5.0 \times 10^{-5} \text{ mol L}^{-1}$  of ligand in acetonitrile solution were individually recorded by changing the concentration of the metal ions at  $25^\circ\text{C}$ . The typical results for

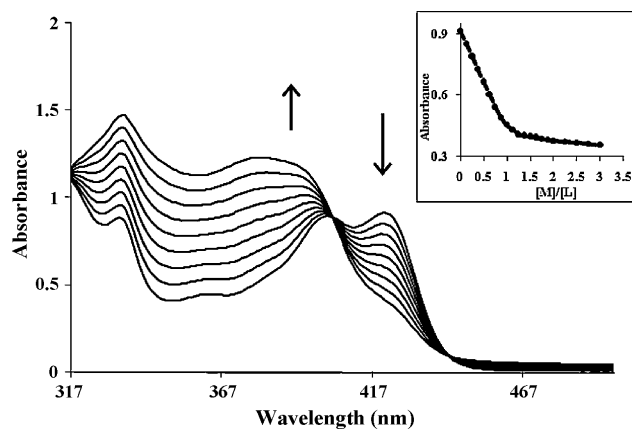


Fig. 2. Electronic absorption spectra of IBMYD ionophore in  $5.0 \times 10^{-5} \text{ mol L}^{-1}$  of acetonitrile by increasing Fe(III) ion concentration. Corresponding mole ratio plot at 421 nm is shown in the inset.

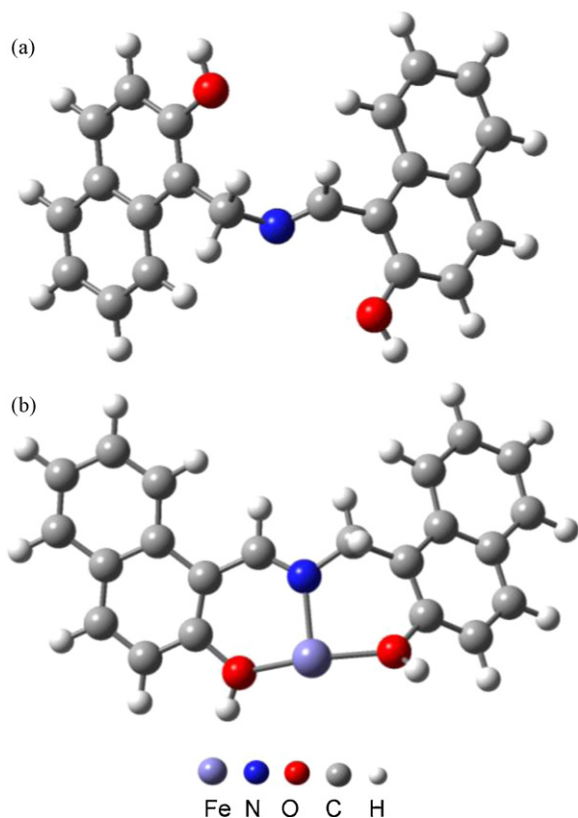
Fe(III) target ion and IBMYD are shown in Fig. 2. As it can be seen, the complex formation between Fe(III) and IBMYD was accompanied by decreasing in the absorption band of the IBMYD at 421 nm and by increasing in a new absorption band at about 377 nm. The obtained mole ratio plot (absorbance vs  $[\text{Fe}^{3+}]/[\text{IBMYD}]$ ) at wavelength of 421 nm for IBMYD–Fe(III) complex formation is shown in the inset of Fig. 2. The stability constant results for the 1:1 complex formations between IBMYD and other metal ions tested are listed in Table 1. As it can be shown, the IBMYD with the most stable complex with Fe(III) ion was expected to act as a selective ionophore to prepare Fe(III)-selective membrane electrodes. The formation constants of the resulting complexes between cations and IBMYD were calculated by computer fitting of the corresponding mole ratio data in accordance with a previously derived equation [23] and by using a non-linear curve-fitting program, KINFIT [24].

### 2.4. Computational details

All calculations were carried out using Gaussian 98 program [25]. Full geometry optimizations of the metal ion–ligand complexes were performed at the Hartree-Fock (HF) level of theory. The Hay-Wadt LANL2MB effective core potential (ECP), was used for the iron ion (calculated in its +2 and +3 states) [26] and the 6-31G (d) basis set was used for all other atoms [27]. The structure of free IBMYD was optimized using the same method with 6-31G (d) basis set. The ab initio quantum-mechanical (QM) calculations at HF level were checked to calculate the interaction between ligand and iron ion in its +2 and +3 states. Interaction energies for Fe(II)–IBMYD and Fe(III)–IBMYD complexes were

Table 1  
Stability formation constants of different metal ions with IBMYD.

Metal	$\log K_f$
Fe(III)	$6.05 \pm 0.02$
Ag(I)	$2.11 \pm 0.03$
Cu(II)	$4.93 \pm 0.02$
Pb(II)	$2.05 \pm 0.03$
Zn(II)	$2.63 \pm 0.04$
Cd(II)	$2.46 \pm 0.03$
Al(III)	$4.01 \pm 0.03$
Ni(II)	$2.82 \pm 0.03$
Co(II)	$2.35 \pm 0.04$
Mn(II)	$2.41 \pm 0.02$
Cr(II)	$4.13 \pm 0.03$
Hg(II)	$2.44 \pm 0.03$



**Fig. 3.** Full geometry optimization of the complex formation between the iron metal ions with IBMYD ionophore using Gaussian 98 program. Optimized structures of (a) free and (b) iron(III)–IBMYD complexed.

–0.469 and –1.412 a.u., respectively. This indicates that the IBMYD interacts more strongly with Fe(III) than Fe(II). The optimized geometries of IBMYD and its Fe(III) complex is presented in Fig. 3.

### 2.5. Electrode preparation

A polymeric casting solution was prepared by dissolving 33.0 mg of PVC, 65.0 mg of TEHP plasticizer, 1.0 mg of NaTPB and 1.0 mg of ionophore in 2–3 ml of THF solvent. The resulting mixture was poured into a glass dish of about 2 cm in diameter. The solvent was permitted to evaporate until an oily concentrated mixture was obtained. A Teflon tube (3–5 mm on top) was dipped into the oily mixture for about 10 s to form a thin film of about 0.3 mm in thickness. Then, the tube was pulled out from the mixture, kept at room temperature for about 1 h, filled with the internal filling solution  $1.0 \times 10^{-3} \text{ mol L}^{-1}$  of iron(III) nitrate solution and conditioned for 24 h by its soaking in a  $1.0 \times 10^{-3} \text{ mol L}^{-1}$  solution of  $\text{Fe}(\text{NO}_3)_3$  before use.

### 2.6. Standard alloy sample preparation

The proposed method was applied to determine iron content in some alloy standard reference materials such as NKK No. 916 Aluminum Alloy; NKK No. 1021 Al, Si, Cu, Zn, Alloy and NKK No. 920 Aluminum Alloy as received from Nippon Keikin-zoku Kogyo (NKK) Japans Company. A 1.0 g sample of standard alloy samples described in Section 3.5, were individually dissolved in 10–15 ml of hydrochloric acid (1:1) and heated on a water-bath. Then, 2–3 ml of 30% (v/v) hydrogen peroxide was added to them. The excess of peroxide was decomposed by heating the samples. The solutions were cooled and filtered. The filtrated solutions were diluted to

100 ml with doubly distilled water in a standard flask. The total iron contents of the alloy samples were measured by using the standard addition method at pH 4.5.

### 2.7. Biological samples preparation

The proposed method was applied to determine iron content in some biological standard reference materials such as NIES, No. 1 pepperbush; NIES, No. 5 human hair; NIES, No. 6 mussels; and NIES, No. 2 pond sediment as received from Japanese National Institute for Environmental Studies (NIES) reference materials Japans Company. A 1.0 g of biological samples described in Section 3.5, were individually transferred into a beaker and dissolved in 5.0 ml concentrated nitric acid by the heating. The resulting solutions were cooled, diluted and filtered. The filtrated solutions were diluted to 100 ml with doubly distilled water in a calibrated flask. The pH of the test solution was kept on 4.5. The total free iron contents were measured by using the standard addition method.

### 2.8. General procedure to determine free iron species in some different synthetic samples

The proposed sensor was used successfully to determine free iron content in some synthetic Fe(II)/Fe(III) mixture solutions at different proportions by keeping the pH at 3.7. This pH value was suitable for the quantitative determination of Fe(II) because at pH higher than 4.2, Fe(II) ion species were properly converted to Fe(III) due to its oxidation with  $\text{OH}^-$  and  $\text{O}_2$  or by its hydrolysis in these mediums [28].

Found concentration values for initial Fe(III) ion concentrations present in the resulting mixtures and containing both target ions were directly calculated based on the potential signals taken by the proposed sensor at pH 3.7. Then, 5 ml of oxidizing agent (concentrated nitric acid) was added to the resulting mixtures to convert the initial Fe(II) to Fe(III) ion species and the total free Fe(III) ion concentrations were measured at pH 3.7. The initial Fe(II) ion concentrations present in the resulting mixture solutions were indirectly measured by subtracting the found values for the initial Fe(III) and total iron contents. In all these measurements, the standard addition method was applied at pH 3.7.

### 2.9. EMF measurements

The representative electrochemical cell for the EMF measurements was as follows:  $\text{Ag}/\text{AgCl}, \text{KCl} (3 \text{ mol L}^{-1}) | \text{internal solution: } \text{Fe}(\text{NO}_3)_3 (1.0 \times 10^{-3} \text{ mol L}^{-1}) | \text{PVC membrane} | \text{test solution} | \text{Hg}/\text{Hg}_2\text{Cl}_2, \text{KCl} (\text{satd})$ . A Metrohm-692 pH/mV meter was also used during the experiments at  $25.0 \pm 0.1^\circ\text{C}$ . Absorbance spectra were recorded using a HP spectrophotometer (Agilent 8453) equipped with a thermostated bath (Huber polystat cc1). In the complexation studies, the temperature of the cell holder was maintained at  $25 \pm 0.1^\circ\text{C}$ .

## 3. Results and discussion

The structure of IBMYD as a ferric ion-selective ionophore is presented in Fig. 1. The complex formation constants between IBMYD ionophore and some metal ions were checked spectrophotometrically (Table 1). The results showed that the IBMYD synthesized ionophore had a good discriminating ability towards Fe(III) ions over a wide variety of alkali, alkaline earth, transition, and heavy metal ions. The theoretical Gaussian studies showed that the ionophore was also a three dentate ligand and formed the most stable complex with Fe(III) as ML complex formation compared to Fe(II) and other metal ions tested.

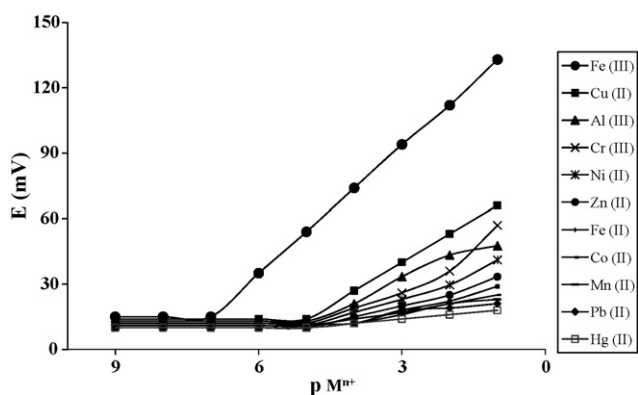


Fig. 4. Potential response of the Fe(III) ion-selective electrode based on IBMYD to various metal ions.

The existence of two donating hydroxyl atom groups as well as one donating nitrogen atom in the structure of IBMYD molecule was expected to increase the stability of the complex formation between Fe(III) and IBMYD ionophore, and its selectivity towards target ions. Thus, the proposed IBMYD ionophore was understood to be a suitable neutral carrier to prepare the Fe(III)-selective membrane electrodes. Consequently, the potential response of the electrode to various metal ions was checked. A typical potential response curve is presented in Fig. 4. As it can be shown, among the different cations tested, Fe(III) with the most sensitive response seemed suitable to be determined with the PVC membrane electrode based on IBMYD. The EMF responses obtained for all other cations were much lower than those expected by the Nernstian equation. This was probably due to both the selective behavior of the ionophore against Fe(III) compared to some other metal ions and the rapid exchange kinetics of the resulting complexes [21]. It was well known that the sensitivity and selectivity obtained for a given ion-selective electrode depends not only on the nature of ionophore used, but also significantly on the membrane composition and the properties of the plasticizer used [29,30].

Thus, the effect of different proportions of the membrane components, such as ionophore, PVC, plasticizer and additive materials were examined (Table 2). The best performance was observed with the membrane electrode No. 9, comprising the percent ratio as 33:65:1:1 for PVC:TEHP:IBMYD:NaTPB constituents, respectively. Plasticizers should gather certain properties and characteristics such as high lipophilicity and molecular weight, low tendency to exudation from the polymeric matrix, low vapor pressure and high capacity to dissolve the substrate and other additives present in the

polymeric membrane. Additionally, its viscosity and dielectric constant should be adequate [31]. The values of the dielectric constant, lipophilicity, viscosity and molecular weight of some plasticizers used had been illustrated previously [32,33]. In this study, the best results were observed when TEHP was used as a solvent mediator (Table 2). These results seemed to indicate a synergism between lipophilicity and polarity of TEHP to reach an intermediate value.

The lipophilic negatively charged additive salts such as NaTPB and oleic acid are also required to add into the membrane compositions to decrease the ohmic resistance, response time and anionic interference of cation-selective membrane. Moreover, the use of additives may enhance the response behaviors, sensitivity and selectivity in which the extraction capacity is poor or even if insufficient amount of ionophore present improve the selectivity, sensitivity and extraction capacity for the certain selective electrodes [29,34]. Additives may also catalyze the exchange kinetic at the sample-membrane surface and increase significant changes in the selectivity [34]. Thus, the PVC membranes (No. 1–7) with out additive used showed the sub-Nernstian slopes. Addition of ionophore more than 1%, resulted in the diminished and sluggish response of the electrode that was most probably due to possible saturation of the membrane [35]. The proposed electrode also revealed a good wide working concentration range from  $1.0 \times 10^{-7}$  to  $1.0 \times 10^{-1}$  mol L<sup>-1</sup> with the Nernstian compliance slope of  $19.9 \pm 0.3$  mV decade<sup>-1</sup>.

### 3.1. Effect of pH on the potential response of the electrode

The pH dependence of the electrode's potential was investigated over a pH range 1.0–9.0, for  $1.0 \times 10^{-3}$  and  $1.0 \times 10^{-5}$  mol L<sup>-1</sup> of Fe(III) ion concentrations. The results are summarized in Fig. 5. As it can be shown, the potential was almost independent of pH within the range 3.0–6.3. The observed drift at pH values higher than 6.3 could be due to the formation of some hydroxyl complexes of Fe(III) ions in the test solution. At pH values lower than 3.0, the potential decreased because the protonated ionophore possessed a poor response to Fe(III) ions in the test solution. Thus, a mixed buffer solution pH at 4.5 was used to adjust the pH of the whole solutions tested.

### 3.2. Influence of the inner filling solution concentration and condition time

The phase boundary potential theory was more acceptable model to explain responses in the ion-selective membrane electrodes with the conventional inner filling solution [36–38]. The proposed membrane electrode was also examined with differ-

Table 2  
Optimization of membrane ingredients for the iron(III)-sensor ( $n = 5$ ).

Membrane number	Composition (%)				Slope (mV decade <sup>-1</sup> )	Dynamic range (mol L <sup>-1</sup> )
	PVC (mg)	Plasticizer (mg)	Additive (mg)	Ionophore (mg)		
1	34	65 (NPOE)	0	1	24.6 ± 0.5	$1.0 \times 10^{-4}$ – $1.0 \times 10^{-1}$
2	34	65 (DOS)	0	1	10.3 ± 0.4	$1.0 \times 10^{-5}$ – $1.0 \times 10^{-2}$
3	34	65 (AP)	0	1	12.5 ± 0.4	$1.0 \times 10^{-4}$ – $1.0 \times 10^{-1}$
4	34	65 (DBP)	0	1	11.4 ± 0.3	$1.0 \times 10^{-4}$ – $1.0 \times 10^{-1}$
5	34	65 (BA)	0	1	14.0 ± 0.5	$1.0 \times 10^{-5}$ – $1.0 \times 10^{-1}$
6	34	65 (DOP)	0	1	15.6 ± 0.4	$1.0 \times 10^{-5}$ – $1.0 \times 10^{-1}$
7	34	65 (TEHP)	0	1	17.2 ± 0.3	$1.0 \times 10^{-6}$ – $1.0 \times 10^{-1}$
8	33	65 (TEHP)	1.0 (OA)	1	18.8 ± 0.4	$6.0 \times 10^{-7}$ – $1.0 \times 10^{-1}$
9	33	65 (TEHP)	1.0 (NaTPB)	1	19.9 ± 0.3	$1.0 \times 10^{-7}$ – $1.0 \times 10^{-1}$
10	32	65 (TEHP)	1.0 (NaTPB)	0.5	19.1 ± 0.4	$3.0 \times 10^{-7}$ – $1.0 \times 10^{-1}$
11	32	65 (TEHP)	0.5 (NaTPB)	1	19.3 ± 0.5	$5.0 \times 10^{-7}$ – $1.0 \times 10^{-1}$
12	31	65 (TEHP)	0.5 (NaTPB)	0.5	18.0 ± 0.3	$8.0 \times 10^{-7}$ – $1.0 \times 10^{-1}$
13	30	65 (TEHP)	1.0 (NaTPB)	1.5	18.7 ± 0.4	$6.0 \times 10^{-7}$ – $1.0 \times 10^{-1}$
14	30	65 (TEHP)	1.5 (NaTPB)	1	18.4 ± 0.4	$5.0 \times 10^{-7}$ – $1.0 \times 10^{-1}$
15	34	65 (TEHP)	1.0 (NaTPB)	0	3.8 ± 0.5	$1.0 \times 10^{-4}$ – $1.0 \times 10^{-2}$

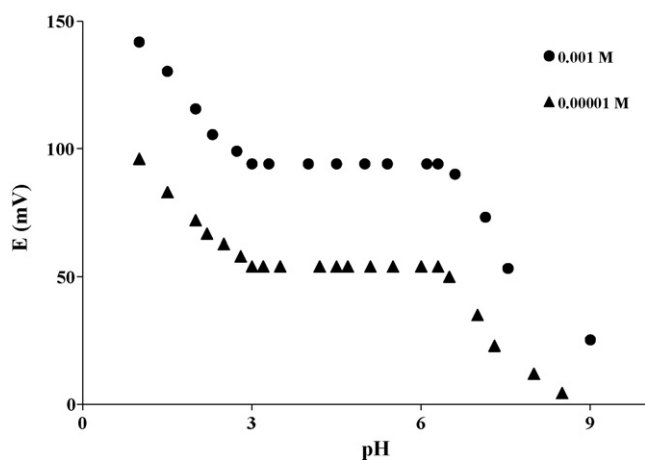


Fig. 5. Effect of pH on the response of the Fe(III) ion-selective electrode.

ent concentrations of the inner filling solution from  $1.0 \times 10^{-5}$  to  $1.0 \times 10^{-2}$  mol L<sup>-1</sup> of Fe(III) ion concentration. It was found that changing the concentration of the internal solution caused no significant difference in the potential response, except an expected change in the intercept of the resulting Nernstian plots. Thus, a  $1.0 \times 10^{-3}$  mol L<sup>-1</sup> of Fe(NO<sub>3</sub>)<sub>3</sub> ion concentration was quite appropriate to smooth functioning of the electrode with the conditioning time about 24 h.

### 3.3. Response time, life time, calibration curve and reproducibility of the proposed electrode

The average response time required for the Fe(III) ion-selective electrode (No. 9) to reach a potential within  $\pm 0.5$  mV of the final equilibrium value was investigated for the test solutions each having a 10-fold difference in concentration from  $1.0 \times 10^{-7}$  to  $1.0 \times 10^{-1}$  mol L<sup>-1</sup> after successive immersion in a series of iron(III) ion solutions. The result is given in Fig. 6. As it can be presented, in the whole concentration range, the static response times of the membrane electrode were obtained in the short response times (<12 s). The potentials remained constant for at least 5 min while the potentials were recorded from low to high concentrations and vice versa.

The PVC membrane electrode prepared, filled by conventional inner filling solution and operated under best experimental conditions showed a linear response to the activity (concentration) of

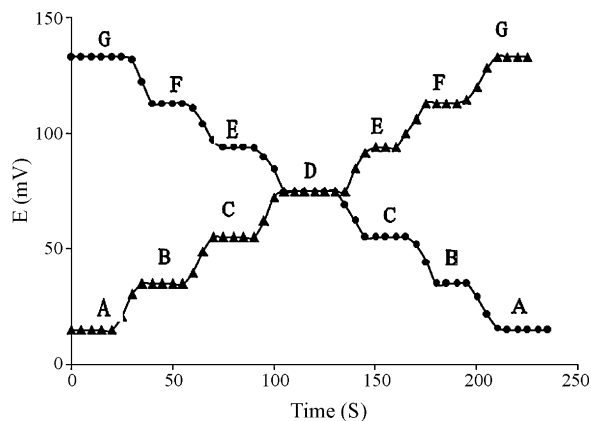


Fig. 6. Dynamic response time of the proposed electrode for the step changes in the concentration (from low to high and vice versa): (A)  $1.0 \times 10^{-7}$  mol L<sup>-1</sup>, (B)  $1.0 \times 10^{-6}$  mol L<sup>-1</sup>, (C)  $1.0 \times 10^{-5}$  mol L<sup>-1</sup>, (D)  $1.0 \times 10^{-4}$  mol L<sup>-1</sup>, (E)  $1.0 \times 10^{-3}$  mol L<sup>-1</sup>, (F)  $1.0 \times 10^{-2}$  mol L<sup>-1</sup> and (G)  $1.0 \times 10^{-1}$  mol L<sup>-1</sup>.

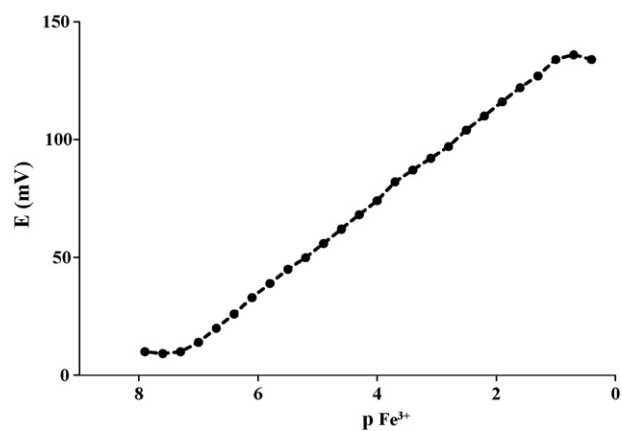


Fig. 7. Calibration curve for Fe(III) ion-selective electrode based (composition No. 6), at pH 4.5.

Fe(III) ion concentration in the range  $1.0 \times 10^{-7}$ – $1.0 \times 10^{-1}$  mol L<sup>-1</sup> with a Nernstian slope of  $19.9 \pm 0.3$  mV decade<sup>-1</sup> of Fe(III) ion concentration (Fig. 7).  $1.0 \times 10^{-1}$ – $1.0 \times 10^{-1}$  mol L<sup>-1</sup> with a Nernstian slope of  $19.9 \pm 0.3$  mV decade<sup>-1</sup> of Fe(III) ion concentration (Fig. 7). The detection limits of about  $5.0 \times 10^{-8}$  mol L<sup>-1</sup> was determined by the intersection of the two extrapolated segments of the calibration graph. To evaluate the reproducibility of this electrode, a series of membranes (seven) with the similar composition (No. 6) were prepared and the response of these electrodes to Fe(III) ion concentration was tested. The results showed that the average of slopes, detection limits and linear dynamic ranges were  $19.9 \pm 0.3$  mV decade<sup>-1</sup>,  $5.0(\pm 0.4) \times 10^{-8}$  mol L<sup>-1</sup> and  $1.0(\pm 0.3) \times 10^{-1}$ – $1.0(\pm 0.3) \times 10^{-7}$  mol L<sup>-1</sup>, respectively. The standard deviation of eight replicate measurements was  $\pm 0.3$  mV. Reproducibilities of these electrodes were also checked to recover five replicate measurements of  $2.0 \times 10^{-3}$  and  $3.0 \times 10^{-5}$  mol L<sup>-1</sup> of iron(III) ion concentrations using the proposed sensor. The results showed that there are good reproducibilities for all cases (RSDs <5.5). The main lifetime factors of the proposed sensor were also checked. The prepared membrane electrode was very stable and could be used over a period of at least 2 months without observing any measurable changes in the response characteristics. This prominent feature was properly due to the best lipophilicity of the ionophore and plasticizer which results in potential stability and long lifetime of the membrane electrode [39,40].

### 3.4. Potentiometric selectivity

One of the most important characteristic of a membrane electrode was its response to the target ion to be measured over other ions and species present in the solution. This characteristic was expressed in terms of the potentiometric-selectivity coefficient. In this study, potentiometric-selectivity coefficients for some cations, amino acids, sugars, vitamins and surfactants tested were determined by the mixed-solution method (MSM) [41,42]. A fixed concentration of iron(III) ( $1 \times 10^{-3}$  M) and different amounts of interfering species (*x*) were used to check the selectivity coefficients in accordance with Eq. (1).

$$K_{\text{Fe(III)},x}^{\text{pot}} a_x^{(1/n)} = a_{\text{Fe(III)}} \left[ \exp(E_2 - E_1) \frac{F}{RT} \right] - a_{\text{Fe(III)}} \quad (1)$$

where,  $E_1$  and  $E_2$  were the electrode potentials for the solution of iron(III) alone and for the solution containing interfering species and iron(III), respectively. The potentiometric-selectivity coefficient values ( $K_{\text{Fe(III)},x}^{\text{pot}}$ ) could be evaluated from the slope of the graph of  $a_{\text{Fe(III)}} [\exp(E_2 - E_1) F/RT] - a_{\text{Fe(III)}}$  vs  $a_x^{(1/n)}$ . The resulting selectivity coefficients are summarized in Table 3.

**Table 3**  
Selectivity coefficient of various interfering ions for the proposed sensor based on the MSM method ( $n = 3$ ).

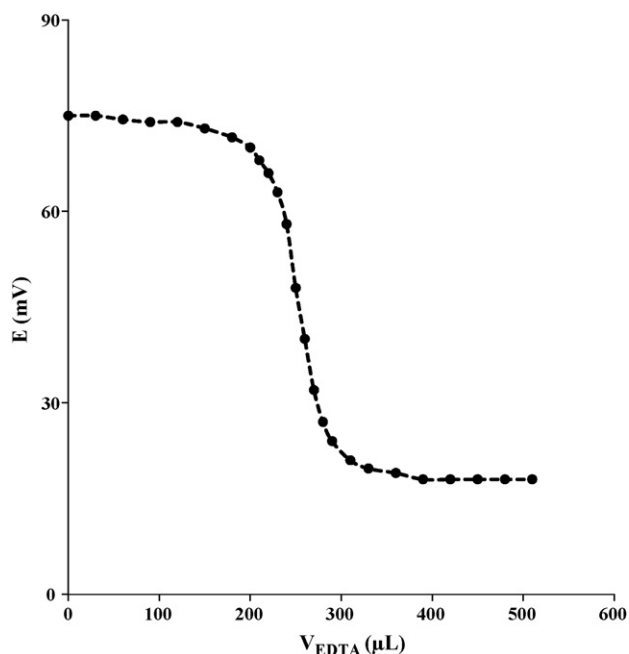
Interfering	K	Interfering	K	Interfering	K
Fe <sup>2+</sup>	$4.62 \times 10^{-4}$	Al <sup>3+</sup>	$3.21 \times 10^{-2}$	Vitamin A	$1.24 \times 10^{-5}$
Pb <sup>2+</sup>	$8.59 \times 10^{-4}$	Mn <sup>2+</sup>	$2.65 \times 10^{-3}$	L-Lysine	$9.31 \times 10^{-6}$
Cd <sup>2+</sup>	$5.35 \times 10^{-4}$	Co <sup>2+</sup>	$1.93 \times 10^{-3}$	TritonX-100	$4.70 \times 10^{-4}$
Ni <sup>2+</sup>	$7.16 \times 10^{-3}$	Sr <sup>2+</sup>	$5.41 \times 10^{-5}$	Glucose	$2.94 \times 10^{-5}$
Cr <sup>3+</sup>	$8.23 \times 10^{-2}$	Ba <sup>2+</sup>	$6.74 \times 10^{-5}$	D-Arginine	$8.78 \times 10^{-6}$
Cu <sup>2+</sup>	$6.45 \times 10^{-2}$	Mg <sup>2+</sup>	$3.12 \times 10^{-4}$	CTAB	$5.33 \times 10^{-4}$
Zn <sup>2+</sup>	$6.70 \times 10^{-3}$	K <sup>+</sup>	$4.13 \times 10^{-5}$	Vitamin E	$1.53 \times 10^{-5}$
Ag <sup>+</sup>	$2.18 \times 10^{-4}$	Ca <sup>2+</sup>	$1.01 \times 10^{-4}$	Fructose	$4.04 \times 10^{-5}$
Hg <sup>2+</sup>	$4.36 \times 10^{-4}$	Pd <sup>2+</sup>	$3.26 \times 10^{-4}$	Vitamin B6	$3.19 \times 10^{-5}$

**Table 4**  
Determination of the iron(III) ion concentrations in some different samples ( $n = 5$ ).

Sample	Added (mol L <sup>-1</sup> )	Found by ISE (mol L <sup>-1</sup> )	Found by AAS (mol L <sup>-1</sup> )
Tap water	$2 \times 10^{-2}$	$(2.03 \pm 0.03) \times 10^{-2}$	$(2.02 \pm 0.02) \times 10^{-2}$
	$4 \times 10^{-4}$	$(4.13 \pm 0.12) \times 10^{-4}$	$(4.11 \pm 0.10) \times 10^{-4}$
	$3 \times 10^{-6}$	$(2.79 \pm 0.19) \times 10^{-6}$	$(3.21 \pm 0.22) \times 10^{-6}$
Mineral water	$2 \times 10^{-2}$	$(2.04 \pm 0.04) \times 10^{-2}$	$(2.05 \pm 0.05) \times 10^{-2}$
	$4 \times 10^{-4}$	$(3.87 \pm 0.12) \times 10^{-4}$	$(3.85 \pm 0.14) \times 10^{-4}$
	$3 \times 10^{-6}$	$(2.77 \pm 0.20) \times 10^{-6}$	$(2.79 \pm 0.19) \times 10^{-6}$
Waste water	$2 \times 10^{-2}$	$(2.03 \pm 0.03) \times 10^{-2}$	$(2.04 \pm 0.04) \times 10^{-2}$
	$4 \times 10^{-4}$	$(4.15 \pm 0.14) \times 10^{-4}$	$(4.15 \pm 0.13) \times 10^{-4}$
	$3 \times 10^{-6}$	$(3.25 \pm 0.27) \times 10^{-6}$	$(3.26 \pm 0.27) \times 10^{-6}$

**Table 5**  
Analysis of total iron content in the standard alloy by the proposed sensor ( $n = 7$ ).

Sample	Composition (%)	Concentration certified value (%)	Found value (%)
NKK No. 916 Aluminum Alloy	Si, 0.41; Mg, 0.10; Cr, 0.05; B, 0.0006; Ni, 0.06; Ti, 0.10; Sn, 0.05; Cu, 0.27; V, 0.02; Sb, 0.01; Zr, 0.05; Bi, 0.03; Co, 0.03; Mn, 0.11; Zn, 0.30; Pb, 0.04	0.54	$0.50 \pm 0.04$
NKK No. 1021 Al, Si, Cu, Zn, Alloy	Si, 5.56; Mg, 0.29; Cr, 0.03; Ni, 0.14; Ti, 0.04; Sn, 0.10; Pb, 0.18; Sb, 0.01; Zr, 0.01; Bi, 0.01; V, 0.007; Ca, 0.004; Mn, 0.11; Cu, 2.72; Zn, 1.76	0.99	$0.95 \pm 0.06$
NKK No. 920 Aluminum Alloy	Si, 0.78; Mg, 0.46; Cr, 0.27; Ni, 0.29; Sb, 0.10; Bi, 0.06; Ga, 0.05; Ca, 0.03; Zn, 0.80; Co, 0.1; Mn, 0.20; Cu, 0.71; V, 0.15	0.72	$0.76 \pm 0.05$

**Fig. 8.** Potentiometric titration curve of 25 ml of a  $1.0 \times 10^{-4}$  mol L<sup>-1</sup> solution of iron(III) with  $1.0 \times 10^{-2}$  mol L<sup>-1</sup> of EDTA.

As it can be shown, all the cations, sugars, surfactants, amino acids and vitamins tested were not expected to interfere on applicability of the proposed iron(III)-selective sensor except vitamin C. In this study, we preferred to check the real samples that contained no vitamin C or properly had less amounts of vitamin C. A typical general procedure was suggested to measure iron contents in biological samples which included vitamin C or may be any other interferences by the authors as follow: you may heat appropriate amounts of real samples in a furnace to dryness using dry ashing method at the desired temperature. The remainder is dissolved in nitric acid and diluted to 25 ml by triply distilled water. The resulting solution is followed by the proposed sensor to estimate iron contents without any side interferences.

### 3.5. Analytical applications

The proposed sensor was examined successfully for the potentiometric titration of 25 ml of a  $1.0 \times 10^{-4}$  mol L<sup>-1</sup> of Fe(III) ion concentration with  $1.0 \times 10^{-2}$  mol L<sup>-1</sup> of EDTA, at pH 4.5. As it can be presented from Fig. 8, the end point on the graph (250 μL) closely agreed to the calculated equivalent point (253 μL). To assess the applicability of the proposed electrode to real samples, an attempt was made to determine the Fe(III) ion concentration in waste and tap water as spiked, alloy and biological samples (Tables 4–6). The samples were pre-treated by the suitable methods described in this paper and analyzed by the ISE at pH 4.5. The results obtained by the proposed sensor were in accordance with the data taken

**Table 6**  
Analysis of total iron content in the biological samples by the proposed sensor ( $n=7$ ).

Sample	Composition	Certified value ( $\mu\text{g g}^{-1}$ )	Found value ( $\mu\text{g g}^{-1}$ )
NIES, No. 1 (pepper bush)	K, $1.51 \pm 0.06$ ; Mn, $0.203 \pm 0.107$ ; Mg, $0.408 \pm 0.020$ ; Cu, $12 \pm 1$ ; Co, $23 \pm 3$ ; Pb, $5.5 \pm 0.8$ ; Ni, $8.7 \pm 0.6$ ; Ti(0.13); Rb, $75 \pm 4$ ; Ba, $165 \pm 10$ ; Na, $106 \pm 13$ ; Sr, $36 \pm 4$ ; Hg(0.056); As, $2.3 \pm 0.3$ ; P(1100); Cr(1.3); Cs(1.2); Ca, $1.38 \pm 0.07\%$ ; Cd, $6.7 \pm 0.05$ ; Zn, $340 \pm 20$	$205.0 \pm 17$	$219.0 \pm 13.6$
NIES, No. 5 (human hair)	Pb, 6.0; Cd, 0.2; Sb, 0.07; Ni, 1.8; Al, 240; Co, 0.10; Hg, 4.4; K, 34; Rb, 0.19; Sc, 0.05; Se, 1.4; Na, 26; Mg, 208; Sr, 23; Ti, 3.2; Ca, 728; Cr, 1.4; Ba, 2.2; Cu, 163; Zn, 169	225.0	$210.7 \pm 12.2$
NIES, No. 6 (muscle)	Na, $1.00 \pm 0.03$ ; K, $0.54 \pm 0.02$ ; Ca, $0.13 \pm 0.01$ ; As, $9.2 \pm 0.5$ ; Mg, $0.21 \pm 0.01$ ; P(0.77%); Mn, $16.3 \pm 1.2$ ; Zn, $106 \pm 6$ ; Cu, $4.9 \pm 0.3$ ; Ni, $0.93 \pm 0.06$ ; Hg(0.05); Cr, $0.63 \pm 0.07$ ; Ag, $0.027 \pm 0.003$ ; Pb, $0.91 \pm 0.04$ ; Cd, $0.82 \pm 0.03$ ; Al(220); Sr(17); Se(1.5); Co(0.37)	$158 \pm 8$	$168.0 \pm 10.6$
NIES, No. 2 (pond sediment)	Al, $10.6 \pm 0.5$ ; Ca, 0.81; K, 0.68; Cu, 210; Zn, $0.82 \pm 0.03$ ; Cr, 75; Ni, 40; Cd, 0.82; Co, 27; Pb, 105; AS, 12	$6.53 \pm 0.03$	$7.07 \pm 0.56$

**Table 7**  
Analysis of synthetic Fe(II)–Fe(III) mixture solutions at different proportions by the proposed sensor, ( $n=7$ )<sup>a</sup>.

Certified values ( $\text{mol L}^{-1}$ ) Fe(II)/Fe(III)	Found values ( $\text{mol L}^{-1}$ ) Fe(II)/Fe(III)	Recovery (%) Fe(II)/Fe(III)
$1.0 \times 10^{-5}/1.0 \times 10^{-5}$	$(1.07 \pm 0.08) \times 10^{-5}/(1.06 \pm 0.07) \times 10^{-5}$	107.0/106.0
$1.0 \times 10^{-5}/1.0 \times 10^{-4}$	$(1.08 \pm 0.02) \times 10^{-5}/(0.96 \pm 0.04) \times 10^{-4}$	108.0/96.0
$1.0 \times 10^{-4}/1.0 \times 10^{-5}$	$(1.03 \pm 0.02) \times 10^{-4}/(1.06 \pm 0.06) \times 10^{-5}$	103.0/106.0
$1.0 \times 10^{-3}/1.0 \times 10^{-5}$	$(0.98 \pm 0.03) \times 10^{-3}/(1.06 \pm 0.05) \times 10^{-5}$	98.0/106.0
$1.0 \times 10^{-5}/1.0 \times 10^{-3}$	$(1.08 \pm 0.03) \times 10^{-5}/(1.04 \pm 0.04) \times 10^{-3}$	108.0/104.0

<sup>a</sup> Initial concentration of Fe(II)/Fe(III) in the synthetic mixture with the pH 3.7.

by flame atomic absorption spectrometry (FAAS). Finally, the proposed sensor was used for direct and indirect determination of free iron concentrations in some different synthetic sample solutions containing both target ions at different concentration ratios. The results obtained by the proposed sensor are listed in Table 7. As it can be shown, the proposed electrode was also quite precise and accurate.

#### 4. Conclusion

The PVC-based membrane electrodes incorporating 1,1'-(iminobis(methan-1-yl-1-ylidene))dinaphthalen-2-ol carrier revealed some inherent advantages including easy preparation, low cost, wide dynamic range, low detection limit, suitable pH range, Nernstian behavior and good reproducibility. The sensors were used successfully for the titration of iron(III) ion concentration with EDTA and could also be used to estimate free iron ion concentrations in some real and synthetic samples with satisfactory results.

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#### References

- [1] N.N. Greenwood, A. Earns Haw, Chemistry of the Elements, Pergamum Press, Oxford, 1984, p. 1243.
- [2] A.F. Oliverra, J.A. Nobrega, O. Fatibello-Filho, Asynchronous merging zones system: spectrophotometric determination of Fe(II) and Fe(III) in pharmaceutical products, *Talanta* 49 (1995) 505–510.
- [3] J.M.T. Carneiro, A.C.B. Dias, E.A.G. Zagatto, R.S. Honorato, Spectrophotometric catalytic determination of Fe(III) in estuarine waters using a flow-batch system, *Anal. Chim. Acta* 455 (2002) 327–333.
- [4] A. Safavi, H. Abdollahi, M.R. Hormozi-Nezhad, Simultaneous kinetic determination of Fe(III) and Fe(II) by H-point standard addition method, *Talanta* 56 (2002) 699–704.
- [5] B. Nagabhushana, G. Chandrappa, B. Nagappa, N. Nagaraj, Diformylhydrazine as analytical reagent for spectrophotometric determination of iron(II) and iron(III), *Anal. Bioanal. Chem.* 373 (2002) 299–303.
- [6] J. Zolgharnein, H. Abdollahi, D. Jaefarifar, G.H. Azimi, Simultaneous determination of Fe(II) and Fe(III) by kinetic spectrophotometric H-point standard addition method, *Talanta* 57 (2002) 1067–1073.
- [7] R.C.C. Costa, A.N. Araujo, Determination of Fe(III) and total Fe in wines by sequential injection analysis and flame atomic absorption spectrometry, *Anal. Chim. Acta* 438 (2001) 227–233.
- [8] H.A. Zamani, M.R. Ganjali, H. Behmadi, M.A. Behnajady, Fabrication of an iron(III) PVC-membrane sensor based on bis-benzilthiocarbohydrazide as a selective sensing material, *Mater. Sci. Eng.* 29 (2009) 1535–1539.
- [9] R. Maleki, R. Hosseinzadeh, H. Mehrabi, A. Hassanzadeh, K. Farhadi, Ketomethyl phenanthridine as a new carrier in the construction of a highly selective Fe(III) ion-selective membrane electrode, *Turk. J. Chem.* 33 (2009) 1–10.
- [10] M.U. Naushad, A new ion-selective electrode based on aluminum tungstate for Fe(III) determination in rock sample, pharmaceutical sample and water sample, *Mater. Sci. B* 31 (2008) 957–965.
- [11] H.A. Zamani, M.R. Ganjali, M. Salavati-Niasari, Fabrication of an iron (III)-selective PVC membrane sensor based on a bis-bidentate Schiff base ionophore, *Transit. Metal. Chem.* 33 (2008) 995–1001.
- [12] E. Duzgun, M. Tastekin, O. Atakol, *Rev. Anal. Chem.* 27 (2008) 83–90.
- [13] G. Ekmekci, D. Uzun, G. Somer, S. Kalayci, A novel iron (III) selective membrane electrode based on benzo-18-crown-6 crown ether and its applications, *J. Membr. Sci.* 288 (2007) 36–40.
- [14] W.H. Mahmoud, Iron ion-selective electrodes for direct potentiometry and potentiometric titrimetry in pharmaceuticals, *Anal. Chim. Acta* 436 (2001) 199–206.
- [15] M.H. Mashhadizadeh, I. Sheikh-Shoaei, N. Monadi, A novel ion selective membrane potentiometric sensor for direct determination of Fe(III) in the presence of Fe(II), *Talanta* 64 (2004) 1048–1052.
- [16] R. De Marco, D.J. Mackey, Calibration of a chalcogenide glass membrane ion-selective electrode for the determination of free Fe(III) in seawater: I. Measurements in UV photooxidised seawater, *Mar. Chem.* 68 (2000) 283–294.
- [17] M.B. Gholivand, Y. Mozaffary, PVC-based bis(2-nitrophenyl)disulfide sensor for zinc ions, *Talanta* 59 (2003) 399–407.
- [18] M.B. Gholivand, N. Nozari, Copper (II)-selective electrode using 2,2'-dithiodianiline as neutral carrier, *Talanta* 54 (2001) 597–602.
- [19] M.B. Gholivand, F. Raheedayat, Chromium (III) ion selective electrode based on oxalic acid bis (cyclohexylidene) hydrazide), *Electroanalysis* 16 (2004) 1330–1335.
- [20] M.B. Gholivand, F. Ahmadi, E. Rafiei, A novel Al(III)-selective electrochemical sensor based on N,N-bis(salicylidene)-1,2-phenylenediamine complexes, *Electroanalysis* 18 (2006) 1620–1626.
- [21] M.B. Gholivand, A. Babakhanian, M. Joshaghani, Zirconium ion selective electrode based on bis(diphenylphosphino) ferrocene incorporated in a poly(vinyl chloride) matrix, *Anal. Chim. Acta* 584 (2007) 302–307.
- [22] W.J. Burkem, J. Kolbezen, J. Reynolds, G.A. Short, Study of 2-naphthol-hexamethylenetetramine condensation products, *J. Am. Chem. Soc.* 78 (1956) 805–808.

- [23] J. Ghasemi, M. Shamsipur, Spectrophotometric study of thermodynamics of interaction of some metal ions with murexide in binary acetonitrile–dimethylsulfoxide mixtures, *J. Coord. Chem.* 36 (1995) 183–194.
- [24] V.A. Nicely, J.L. Dye, A general purpose curve fitting program for class and research use, *J. Chem. Educ.* 49 (1971) 443–447.
- [25] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.J.A. Montgomery, R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B. Johnson, W. Chen, M.W. Wong, J.L. Andres, C. Gonzalez, M. Head-Gordon, E.S. Replogle, J.A. Pople, Gaussian 98, Gaussian Inc., Pittsburgh, PA, 1998.
- [26] P.J. Hay, W.R. Wadt, Ab initio effective core potentials for molecular calculations. Potentials for the transition metal atoms Sc to Hg, *J. Chem. Phys.* 82 (1985) 270–278.
- [27] W.J. Hehre, R. Ditchfield, J.A. Pople, Self-consistent molecular orbital method. XII. Further extensions of Gaussian-type basis sets for use in molecular orbital studies of organic molecules, *J. Phys.* 56 (1972) 2257–2265.
- [28] S. Blain, P. Trkguer, Iron(II) and iron(III) determination in sea water at the nanomolar level with selective on-line preconcentration and spectrophotometric determination, *Anal. Chim. Acta* 308 (1995) 425–432.
- [29] R. Eugster, P.M. Gehring, W.E. Morf, U. Spichiger, W. Simon, Selectivity-modifying influence of anionic sites in neutral-carrier-based membrane electrodes, *Anal. Chim. Acta* 63 (1991) 2285–2289.
- [30] T. Rosatzin, E. Bakker, K. Suzuki, W. Simon, Lipophilic and immobilized anionic additives in solvent polymeric membranes of cation-selective chemical sensors, *Anal. Chim. Acta* 280 (1993) 197–208.
- [31] R. Eugster, T. Rosatzin, B. Rusterholz, A. Aebersold, U. Pedrazza, D. Ruegg, A. Schmid, U.E. Spichiger, W. Simon, Plasticizers for liquid polymeric membranes of ion-selective chemical sensors, *Anal. Chim. Acta* 289 (1994) 1–13.
- [32] M. de-los, A.A. Perez, L.P. Marin, J.C. Quintana, M. Yazdani-Pedram, Influence of different plasticizers on the response of chemical sensors based on polymeric membranes for nitrate ion determination, *Sens. Actuators B* 89 (2003) 262–268.
- [33] P.K. Mohapatra, P.N. Pathak, A. Kelkar, V.K. Manchanda, Evaluation of a supported liquid membrane containing a macrocyclic ionophore for selective removal of strontium from nuclear waste solution, *New J. Chem.* 28 (2004) 1004–1009.
- [34] P.M. Gehrig, W.E. Morf, M. Weltic, E. Pretsch, W. Simon, Catalysis of ion transfer by tetraphenylborates in neutral carrier-based ion-selective electrodes, *Helv. Chim. Acta* 73 (1990) 203–212.
- [35] X. Yang, N. Kumar, H. Chi, D.B. Hibbert, P.W. Alexander, Lead-selective membrane electrodes based on dithiophenediazacrown ether derivatives, *Electroanalysis* 9 (1997) 549–553.
- [36] P.C. Meier, W.E. Morf, M.L. Ubbi, W. Simon, Evaluation of the optimum composition of neutral-carrier membrane electrodes with incorporated cation-exchanger sites, *Anal. Chim. Acta* 156 (1984) 1–8.
- [37] R. Eugster, P.M. Gehrig, W.E. Morf, U.E. Spichiger, W. Simon, Selectivity-modifying influence of anionic sites in neutral-carrier-based membrane electrodes, *Anal. Chim. Acta* 63 (1991) 2285–2289.
- [38] E. Bakker, P. Buhlmann, E. Pretsch, Carrier-based ion-selective electrodes and bulk optodes, *Chem. Rev.* 97 (1997) 3083–3132.
- [39] S.T. Ceresa, A. Zwickl, T.E.J. Pretsch, Large improvement of the lower detection limit of ion-selective polymer membrane electrodes, *J. Am. Chem. Soc.* 119 (1997) 11347–11348.
- [40] O. Dinten, U.E. Spichiger, N. Chaniotakis, P. Gehrig, B. Rusterholz, W.E. Morf, W. Simon, Lifetime of neutral-carrier-based liquid membranes in aqueous samples and blood and the lipophilicity of membrane components, *Anal. Chim. Acta* 63 (1991) 596–603.
- [41] K. Srinivasan, G.A. Rechnitz, Selectivity studies on liquid membrane ion-selective electrodes, *Anal. Chim. Acta* 41 (1969) 1203–1208.
- [42] Y. Umezawa, K. Umezawa, H. Sato, Selectivity coefficients for ion-selective electrodes: recommended methods for reporting  $K_{A,Bpot}$  values (Technical Report), *Pure Appl. Chem.* 67 (1995) 507–518.