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ORIGINAL PAPER

Development of Chromium(III)-selective Potentiometric Sensor by Using Synthesized Pyrazole Derivative as an Ionophore in PVC Matrix and its Applications

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Abstract
A novel poly(vinyl chloride) membrane potentiometric sensor for chromium(III) ions based on the use of 5,5′-(1,4-phenylene) bis(3-(naphthalen-1-yl)-4,5-dihydro-1*H*-pyrazole-1-carbothioamide) as a neutral ionophore was developed. The optimum composition of the best performing membrane contained ionophore, potassium tetrakis (*p*-chlorophenyl) borate (KTpClPB), dibutyl phthalate (DBP), and poly(vinyl chloride) (PVC) in the ratio of 5.5:1.5:55:38 (mg). The sensor exhibits a working concentration range of 1.0×10^{-5}–1.0×10^{-1} mol L^{-1} and a detection limit of 1.7×10^{-6} mol L^{-1}. The sensor shows good selectivity for chromium(III) ions over a number of cations including alkali, alkaline earth, heavy and transition metals. The response time of the sensor is 8 s. In addition, the developed sensor shows good reusability and stability. The sensor operates in the wide pH range of 5.0–11.0. The sensor could be used as an indicator electrode in the quantification of Cr^{3+} ions by potentiometric titration against ethylenediaminetetraacetic acid (EDTA). Finally, this sensor was successfully used for the determination of chromium(III) in commercial water, purification water and wastewater.

Keywords PVC membrane · Chromium(III)-selective · Chromium determination · Sensor

1 Introduction

Chromium is widely used in many fields such as steel manufacturing, metallurgy, leather tanning, wood treatment, electroplating, paint and pigment, metal finishing, and alloy manufacturing industries [1, 2]. Chromium is an essential element for human health in small amounts due to its effect on insulin, carbohydrate, fat and protein levels in the body whereas it is toxic in larger quantities [3–5]. Chromium deficiency may lead to diabetes, cholesterol, immune system and cardio-vascular diseases while its excess may cause epigastria pain, nausea, vomiting, diarrhea, and hemorrhage [6, 7]. In addition, chromium was reported to be mutagenic and carcinogenic for the human body, leading to lung cancer, skin allergy and probably to asthma and renal diseases [8–10].

Until today, a number of different methods of chromium(III) determination have been applied in the field such as atomic absorption spectrometry (AAS) [11, 12], UV–visible spectrophotometry [13], X-ray diffraction (XRD) [14], high performance liquid chromatography (HPLC) [15], and inductively coupled plasma-atomic emission spectroscopy (ICP-AES) [16], neutron activation analysis [17]. These methods are not very preferable for large scale monitoring due to its high cost, complex use, the requirement of trained personnel, high-energy consumption, time consumption and the requirement of sample pretreatment [18–20]. However, ion-selective electrodes (ISEs) offers great advantages including short response time, wide linear working range, low cost, low-energy consumption, ease of preparation, good sensitivity and high selectivity [21–23]. Therefore, ion-selective electrodes are more preferable compared to conventional analytical techniques.

Molecules containing multiple donor atoms such as N, S and O are potentially preferred in the development of chemical sensors [24, 25]. Pyrazole derivatives are well

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known five membered heterocycles with a broad spectrum of biological activity [26]. Also, they have a wide range of physical and chemical properties [27]. In this study, by using a pyrazole derivative organic compound as an ionophore, namely 5,5′-(1,4-phenylene)bis(3-(naphthalen-2-yl)-4,5-dihydro-1*H*-pyrazole-1-carbothioamide) (Fig. 1), we developed a chromium(III)-selective potentiometric sensor. Potentiometric properties of the sensor were also investigated.

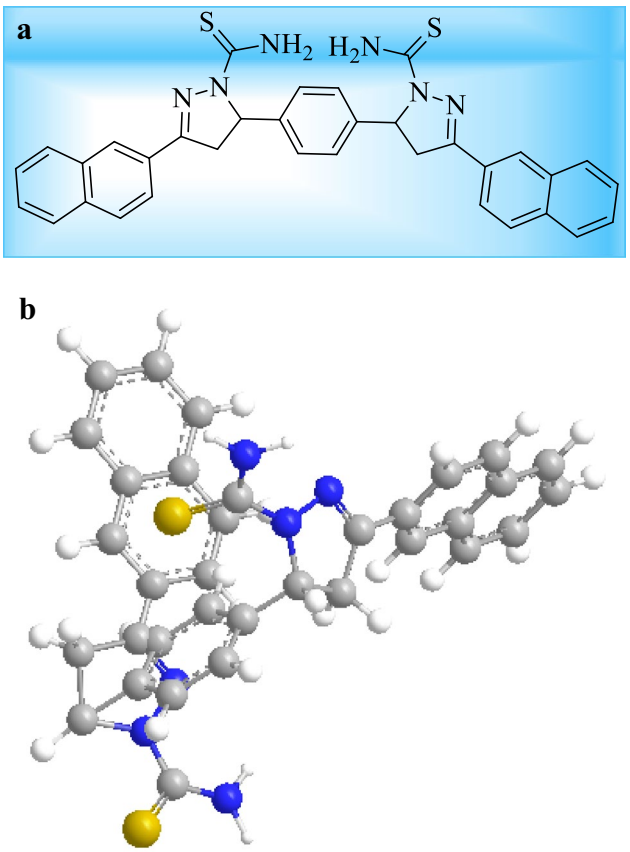

Fig. 1 5,5′-(1,4-phenylene)bis(3-(naphthalen-2-yl)-4,5-dihydro-1*H*-pyrazole-1-carbothioamide). **a** chemical structure of the molecule; **b** 3D structure of the molecule

2 Experimental

2.1 Chemicals and Reagents

Analytical reagent grade DBP, BEHS, KTpClPB, high molecular weight PVC, EDTA, tetrahydrofuran (THF), graphite and nitrate salts of the cations were purchased from Sigma and Fluka. Epoxy (Macroplast Su 2227) was purchased from Henkel (Istanbul, Turkey) and hardener (Desmodur RFE) was purchased from Bayer AG (Darmstadt, Germany), chemicals listed above were used in the preparation of all-state-solid contact. Deionized water was obtained by using a DI 800 Model deionize water system. Cation salt solutions of nitrates were prepared in double distilled water. Solutions of different concentrations (1.0×10^{-1} to 1.0×10^{-5} mol L^{-1}) were prepared by diluting 1.0×10^{-1} mol L^{-1} stock solution.

2.2 Apparatus

Potentiometric measurements were performed at 25 °C ± 0.1 °C using a computer-controlled multichannel potentiometric system. The system has a home-made software program. The potential values as steady-state responses of the PVC membrane chromium(III)-selective sensor were performed for different concentrations of standard solutions of chromium(III). A micro-sized solid Ag/AgCl electrode (Thermo–Orion) was used as a reference electrode with the chromium(III)-selective membrane sensor throughout the measurements. pH measurements were made with a digital pH meter (Mettler Toledo Model S220-K).

2.3 Methods

2.3.1 Synthesis of Ionophore

In this study, the synthesis of 5,5′-(1,4-phenylene)bis(3-(naphthalen-2-yl)-4,5-dihydro-1*H*-pyrazole-1-carbothioamide) molecule was performed according to a previously published method. The synthesis scheme of the ionophore is shown in Fig. 2. The ionophore was synthesized in 70% yield and its melting point was determined as 288–290 °C. The spectroscopic data are identical to that reported in the

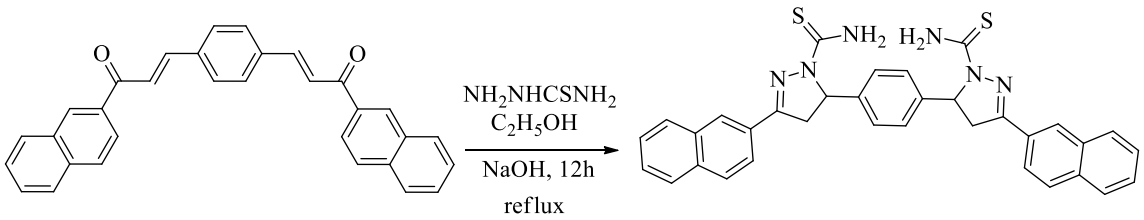

Fig. 2 Synthesis scheme of the ionophore

literature [28]. ^{1}H NMR (400 MHz, DMSO, ppm): δ 9.28 (d, J = 8.8 Hz, 2H), 8.22 (s, 2H), 8.01–7.96 (dd, J = 11.6 Hz, 8.4 Hz 4H), 7.78 (s, 2H), 7.75–7.70 (dd, J = 13.0 Hz, 7.2 Hz, 2H), 7.72–7.68 (m, 2H), 7.62 (t, J = 7.4 Hz, 2H), 7.50–7.46 (dd, J = 13.4 Hz, 7.2 Hz, 2H), 7.23 (s, 2H), 7.21 (s, 2H), 5.98 (d, J = 11.2 Hz, 2H), 4.21–4.11 (m, 2H), 3.29–3.20 (m, 2H). ^{13}C NMR (100 MHz, DMSO, ppm): δ 178.4 (2C), 156.8 (2C), 143.6 (2C), 135.0 (4C), 132.9 (2C), 130.2, 130.0, 129.0 (2C), 128.7 (4C), 127.8, 127.6, 126.6 (2C), 126.4 (2C), 125.8 (4C), 63.7 (2C), 44.1 (2C).

2.3.2 Electrode Preparation

All-solid-state electrodes were prepared according to the literature [29, 30]. First, all-solid-state mixture consisting of 50.0% (*w/w*) graphite, 35.0% (*w/w*) epoxy and 15.0% (*w/w*) hardener was prepared by solving them in approximately 3 mL THF, and then different amounts of the ionophore, KTpClPB, plasticizers (DBF or BEHS) and PVC were dissolved with approximately 3 mL THF. Chromium(III)-selective sensors were prepared by coating the membrane cocktail on the surface of the all-solid-state. The preparation steps of the chromium(III)-selective sensors are summarized in Fig. 3. Compositions of the prepared membranes are listed in Table 1. The data in Table 1 show that the optimum membrane composition was obtained when 5.5% ionophore, 38.0% PVC, 1.5% KTpClPB and 55.0% DBF were used.

2.3.3 Potential Measurements

Potentials were measured using Ag/AgCl reference electrode. All potential studies were carried out at 25 ± 1.0 °C temperature by using the following cell assembly:

$$\mathrm{Ag/AgCl;\ KCl\ (saturated)} \| 10^{-1}\ \mathrm{mol\ L^{-1}\ Cr^{3+}\ sample\ solution} \,|\, \mathrm{Cr^{3+}\ selective\ PVC\ membrane}$$

The potentiometric measurement system of the chromium(III)-selective sensor is shown in Fig. 4.

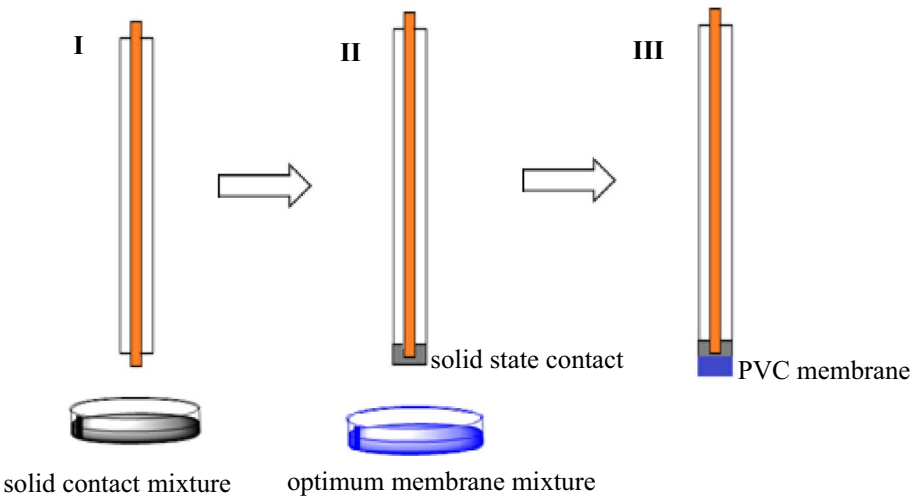

Fig. 3 Schematic diagram for the step-wise preparation of chromium(III)-selective sensors

Table 1 Composition of prepared PVC membrane electrodes

No	Composition (% *w/w*)					
	Ionophore	PVC	KTpClPB	DBF	BEHS	Working concentration range (mol L^{-1})
1	3.0	34.0	1.0	–	62.0	1.0×10^{-2} to 1.0×10^{-5}
2	5.0	33.0	1.0	61.0	–	1.0×10^{-2} to 1.0×10^{-4}
3	3.0	34.0	1.0	62.0	–	1.0×10^{-1} to 1.0×10^{-3}
4	5.0	33.0	1.0	–	61.0	1.0×10^{-1} to 1.0×10^{-4}
5	5.5	31.5	1.0	62.0	–	1.0×10^{-1} to 1.0×10^{-4}
6	4.0	35.0	1.0	–	60.0	1.0×10^{-2} to 1.0×10^{-5}
7	4.5	32.5	1.0	62.0	–	1.0×10^{-1} to 1.0×10^{-5} R^2 = 0.9801
8	4.0	32.0	1.0	63.0	–	1.0×10^{-1} to 1.0×10^{-5} R^2 = 0.9883
9	4.0	37.0	1.0	58.0	–	1.0×10^{-1} to 1.0×10^{-5} R^2 = 0.9902
10	5.5	38.0	1.5	55.0	–	1.0×10^{-1} to 1.0×10^{-5} R^2 = 0.9934

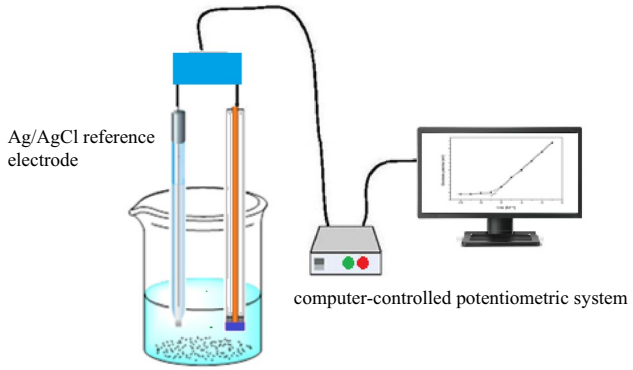

Fig. 4 Potentiometric measurement of chromium(III)-selective sensor

3 Results and Discussion

In this study, by using a pyrazole derivative molecule as an ionophore, all-solid-state chromium(III)-selective PVC membrane sensor was prepared. The potentiometric characteristics of this sensor such as working concentration range, selectivity, reusability, response time and pH working range were further investigated under laboratory conditions.

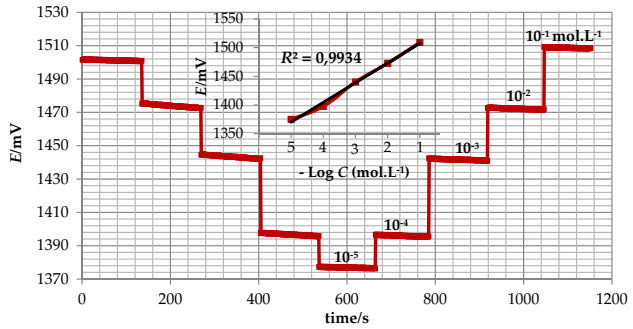

Fig. 5 Potential response of chromium(III)-selective sensor (1.0×10^{-1} to 1.0×10^{-5} mol L^{-1})

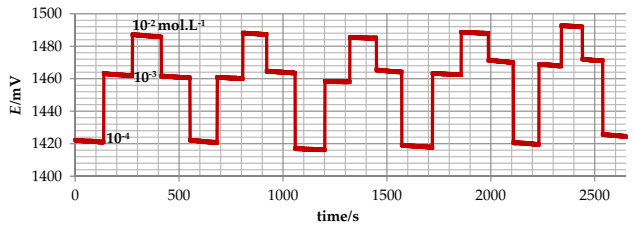

Fig. 6 Reusability of chromium(III)-selective sensor (1.0×10^{-2} to 1.0×10^{-4} mol L^{-1})

3.1 Working Concentration Range

The compositions of prepared membranes and the results obtained for these are presented in Table 1. The membrane No. 10 exhibited the best results and the potentiometric responses of toward chromium(III) ions are shown in Fig. 5. Figure 5 shows that the proposed sensor works linearly ($R^2=0.9934$) in 1.0×10^{-1} to 1.0×10^{-5} mol L^{-1} concentration range. In addition, the limit of detection, as determined from the calibration graph, was 1.7×10^{-6} mol L^{-1}.

3.2 Reusability

Reusability is one of the most important parameters in evaluating a sensor's performance. For this purpose, the developed sensor was exposed repetitively to chromium ion solutions at three different concentrations (1.0×10^{-2} to 1.0×10^{-4} mol L^{-1}). The results observed are shown in Fig. 6. The data shows that the developed chomium(III)-selective sensor is highly reusable.

3.3 Effect of pH

The effect of pH on the potentiometric response of the chromium(III)-selective sensor was studied using 1.0×10^{-2} mol L^{-1} Cr^{3+} ion solution. The pH (2.0–12.0) was adjusted by the addition of hydrochloric acid and sodium hydroxide when appropriate. The potential versus pH graph displayed by the chromium(III)-selective sensor is shown in Fig. 7. As indicated, the potential readings for the membrane sensor are constant over the pH range of 5.0–11.0.

3.4 Potentiometric Selectivity

The selectivity behaviour is one of the most important characteristics of a sensor, which determines its response for primary ion in the presence of other ions. The potentiometric response of chromium(III)-selective sensor was studied in presence of NH_4^+, K^+, Na^+, Ni^{2+}, Sr^{2+}, Pb^{2+}, Cd^{2+}, Ca^{2+}, Cu^{2+}, Mg^{2+}, Zn^{2+}, Co^{2+}, Al^{3+} and Bi^{3+} ions. The potentiometric selectivity coefficients were calculated using the separate solution method [31];

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

The selectivity coefficients against cations in the equation were calculated by taking the potential values corresponding to 1.0×10^{-2} mol L^{-1}. The selectivity coefficients of the chromium(III)-selective sensor are summarized in Table 2. The ionophore is the most significant component of any ion-selective sensor with respect to the selectivity and sensitivity [32]. Table 2 shows that the used ionophore interacts

strongly with Cr^{3+} ion and can be used successfully as a sensing agent for the a chromium sensor and also data show that the developed sensor is highly selective against Cr^{3+} ions even in the presence of other metal ions.

3.5 Response Time

The response time of ion-selective electrodes is an important factor for analytical purposes. The response time was determined by dipping the electrode into the solution until the equilibrium potential was reached, depending on the analyte concentration. Accordingly, the response time of chromium(III)-selective sensor was found to be 8 s.

3.6 Analytical Applications

3.6.1 Potentiometric Titration

Chromium(III)-selective sensor was shown to be an end point indicator electrode for the potentiometric titration of 10 mL of 1.0×10^{-3} mol L^{-1} $Cr(NO_3)_3$ solution with 1.0×10^{-2} mol L^{-1} EDTA solution. The resulting titration curve is shown in Fig. 8. As explained in the literature, the resulting titration graph obtained is not of a S-type (sigmoid) shape due to response of the sodium ions as available from disodium salt of EDTA [7].

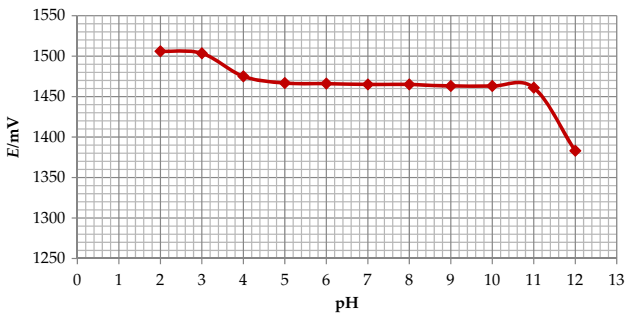

Fig. 7 Effect of pH on potential of chromium(III)-selective sensor

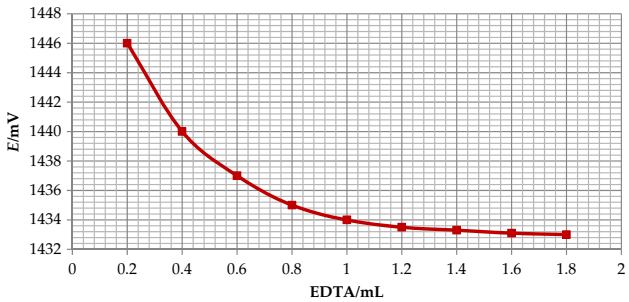

Fig. 8 Potentiometric titration of Cr^{3+} against EDTA

As seen in Fig. 8, the sharp break point of potentiometric titration was determined to be 1.0 mL. Based on these results obtained in the current study, it can be proposed that the developed sensor could be used as an indicator electrode for the potentiometric determination of chromium ions.

3.6.2 Real Samples Applications

The developed chromium(III)-selective sensor was successfully applied to different environmental samples such as purification water, commercial water and waste water to recover chromium present in these samples. The water samples were prepared by the standard addition method. Cr^{3+} solution (1.0×10^{-2} mol L^{-1}) was added to the water samples in known amounts. Potential measurements of water samples were carried out, and their potential values were written in their linear equations and the Cr^{3+} ion concentrations of the water samples were calculated. The results obtained are presented in Table 3. As seen, high recoveries of chromium ion ranging from 90.28% to 97.70% were obtained from the studied samples.

3.7 Comparative Study

The chromium(III)-selective sensor developed in this study was compared with the other Cr^{3+} sensors present in the literature in terms of concentration range, limit of detection, pH working range, response time (Table 4).

Table 2 Selectivity coefficients of various interference metal ions

Interfering ions	Selectivity coefficient, log $K^{pot}_{Cr^{3+},M^{n+}}$	Interfering ions	Selectivity coefficient, log $K^{pot}_{Cr^{3+},M^{n+}}$
Al^{3+}	−2.36	NH_4^+	−3.21
Ni^{2+}	−2.44	K^+	−3.23
Bi^{3+}	−2.51	Cu^{2+}	−3.46
Sr^{2+}	−2.89	Mg^{2+}	−3.50
Pb^{2+}	−2.97	Zn^{2+}	−3.58
Cd^{2+}	−3.01	Co^{2+}	−3.81
Ca^{2+}	−3.11	Na^+	−3.83

Table 3 Different water sample analyses with the chromium(III)-selective sensor

Real sample	Cr^{3+} quantity/(mol L^{-1})		
	Added Cr^{3+}	Mean (±SD) found with sensor[a]	% Recovery
Purification water	4.00×10^{-4}	$3.66\ (0.303)\times10^{-4}$	91.50
Commercial water	7.00×10^{-4}	$6.32\ (0.417)\times10^{-4}$	90.28
Waste water	1.00×10^{-3}	$9.77\ (0.355)\times10^{-4}$	97.70

[a]Results are based on three measurements

According to Table 4, the developed chrome(III)-selective sensor has some advantages. While the response times of previously reported sensors varies between 10 and 20 s, the response time of the sensor developed in this study is 8 s. In addition, the developed sensor works in a wider pH range compared to other sensors. The proposed sensor has very close values in terms of concentration range and detection limit with other sensors reported.

4 Conclusions

In this study, 5,5′-(1,4-phenylene)bis(3-(naphthalen-1-yl)-4,5-dihydro-1*H*-pyrazole-1-carbothioamide) molecule was synthesized according to a previously published study. The synthesized pyrazole derivative molecule was used as an ionophore in the development of chromium(III)-selective sensor. This novel chromium(III)-selective sensor works in the linear concentration range of 1.0×10^{-5} to 1.0×10^{-1} mol L^{-1}. The chromium(II)-selective sensor has certain characteristics such as short response time, wide pH working range, good selectivity and reusability. In addition, the developed sensor operates in a wide pH range compared to the chromium sensors available in the literature and its response time is shorter than those of other chromium(III) sensors. This newly developed sensor can be successfully employed as an indicator electrode of chromium ions in potentiometric titration with EDTA. In addition, we showed that the sensor could be successfully applied in the analysis of chromium ions in various water samples.

Table 4 Comparison of potentiometric characteristic of different chromium electrodes

Ionophore	Electrode or membrane type	Concentration range/(mol L^{-1})	Limit of detection/(mol L^{-1})	pH working range	Response time/s	References
2,3,8,9-Tetraphenyl-1,4,7,10-tetraazacyclododeca-1,3,7,9-tetraene	PVC	1.0×10^{-6} to 1.0×10^{-1}	7.0×10^{-7}	3.0–5.5	15	[33]
4-Dimethylaminoazobenzene	PVC	1.66×10^{-6} to 1.0×10^{-2}	8.0×10^{-7}	3.0–5.5	10	[34]
bis-glyoxal bis(2-hydroxy-anil)	PVC	3.0×10^{-6} to 1.0×10^{-2}	6.3×10^{-7}	2.7–6.5	< 20	[35]
bis-(4-*N*-amino-5-mercapto-1,2,4-triazol-3-yl)alkane	PVC	1.0×10^{-5} to 1.0×10^{-1}	8.6×10^{-6}	3.4–5.2	10	[36]
Tri-*o*-thymotide	PVC	4.0×10^{-6} to 1.0×10^{-1}	2.0×10^{-7}	2.8–5.1	15	[7]
2,2-bis{[(2-benzylaminoformyl) phenxoyl]methyl}-diethylether	PVC	2.8×10^{-6} to 1.0×10^{-1}	8.6×10^{-7}	2.5–6.5	10	[37]
Aurin tricarboxylic acid	PVC	7.0×10^{-6} to 1.0×10^{-1}	7.0×10^{-6}	3.5–6.5	10	[38]
5-Ethyl-6-oxo-5-pentan2-yl-sulfanyl-pyrimidin-4-olate	CPE	1.7×10^{-6} to 1.3×10^{-2}	9.0×10^{-7}	2.3–6.5	< 15	[39]
1,13-bis(8-quinolyl)-l,4,7,10,13-pentaoxatridecane	CPE	1.0×10^{-6} to 1.0×10^{-2}	4.0×10^{-7}	5.0–10.0	10	[40]
N,*N*-bis(salicylidene)-*o*-phenylene diaminate chromium(III)	CPE	7.5×10^{-6} to 1.0×10^{-2}	1.8×10^{-6}	4.5–7.7	5–10	[41]
5,5′-(1,4-Phenylene) bis(3-(naphthalen-1-yl)-4,5-dihydro-1*H*-pyrazole-1-carbothioamide)	PVC	1.0×10^{-5} to 1.0×10^{-1}	1.7×10^{-6}	5.0–11.0	8	This work

CPE carbon paste electrode

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References

1. Kumar P, Shim Y-B. Chromium(III)-selective electrode using p-(4-acetanilidazo)calix[4]arene as an ionophore in PVC matrix. Bull Korean Chem Soc. 2008;29:2471–6.
2. Lu J, Tian J, Wu H, Zhao C. Speciation determination of chromium(VI) and chromium(III) in soil samples after cloud point extraction. Anal Lett. 2009;42:1662–7.
3. Soomro R, Ahmed MJ, Memon N. Simple and rapid spectrophotometric determination of trace level chromium using bis (salicylaldehyde) orthophenylene diamine in nonionic micellar media. Turk J Chem. 2011;35:155–70.
4. Mallah A, Memon SQ, Solangi AR, Khan A, Khuhawar MY, Bhanger MI. Separation and determination of chromium (III) chromium (VI), gold (III) and arsenic (V) by capillary zone electrophoresis using 2-acetylpyridine-4-phenylthiosemicarbazone as complexing reagent. J Chem Soc Pak. 2014;36:255–62.
5. Zhao ZX, Zhang XS. Determination of trace amounts of chromium(III) in water samples using online flow injection catalytic spectrophotometry. J Appl Spectrosc. 2017;83:1084–8.
6. Mao J, He Q, Liu W. An, "off–on" fluorescence probe for chromium(III) ion determination in aqueous solution. Anal Bioanal Chem. 2010;396:1197–203.
7. Gupta VK, Jain AK, Kumar P, Agarwal S, Maheshwari G. Chromium(III)-selective sensor based on tri-o-thymotide in PVC matrix. Sensor Actuat B Chem. 2006;113:182–6.
8. Anthemidis NA, Zachariadis GA, Kougoulis JS, Strati JA. Flame atomic absorption spectrometric determination of chromium(VI) by on-line preconcentration system using a PTFE packed column. Talanta. 2002;57:15–22.
9. Taraba L, Krizek T, Kubickova A, Coufal P. Sample pretreatment for the capillary electrophoretic determination of organic acids in chromium(III) plating baths. J Sep Sci. 2015;38:4255–61.
10. Kumar P, Kumar S, Jain S, Lamba BY, Joshi G, Arora S. All solid state chromium(III) selective potentiometric sensor based on 2-(1-(2-((3-(2-hydroxyphenyl)-1*H*-pyrozol-1-yl)methyl)benzyl)-1*H*-pyrazol-3-yl)phenol. Electroanalysis. 2014;26:2161–7.
11. Tiglea P, Lichtig J. Determination of traces of chromium in foods by solvent extraction flame atomic absorption spectrometry. Anal Lett. 2000;33:1615–24.
12. Sun HW, Kang WJ, Liang SX, Ha J, Shen SG. Determination of chromium(III) and total chromium in water by derivative atomic absorption spectrometry using flow injection on-line preconcentration with a double microcolumn. Anal Sci. 2003;19:589–92.
13. Amin AS, Kassem MA. Chromium speciation in environmental samples using a solid phase spectrophotometric method. Spectrochim Acta. 2012;96:541–7.
14. Magini M. X-ray diffraction study of concentrated chromium (III) chloride solutions. I. Complex formation analysis in equilibrium conditions. J Chem Phys. 1980;73:2499–505.
15. Umesh B, Rajendran RM, Manoharan MT. Method for the determination of chromium in feed matrix by HPLC. Poult Sci. 2015;94:2805–15.
16. Zhu X, Hu B, Jiang Z, Wu Y, Xiong S. Speciation of chromium(III) and chromium(VI) by in situ separation and sequential determination with electrothermal vaporization inductively coupled plasma atomic emission spectrometry. Anal Chim Acta. 2002;471:121–6.
17. Martínez-Gallegos S, Bulbulian S. Neutron activation analysis for chromium(III) and (VI) in lixiviated liquid through a calcined chromium(VI) adsorbed hydrotalcite. J Radioanal Nucl Chem. 2005;266:285–7.
18. Elmosallamy MAF, Fathy AM, Ghoneim AK. Lead(II) potentiometric sensor based on 1,4,8,11-tetrathiacyclotetradecane neutral carrier and lipophilic additives. Electroanalysis. 2008;20:1241–5.
19. Kumar P, Shim Y-B. A novel cobalt(II)-selective potentiometric sensor based on p-(4-n-butylphenylazo)calix[4]arene. Talanta. 2009;77:1057–62.
20. Isildak Ö, Özbek O. Application of potentiometric sensors in real samples. Crit Rev Anal Chem. 2020. https://doi.org/10.1080/10408347.2019.1711013.
21. Isildak Ö, Deligönül N, Özbek O. A novel silver(I)-selective PVC membrane sensor and its potentiometric applications. Turk J Chem. 2019;43:1149–58.
22. Jiang C, Yao Y, Cai Y, Ping J. All-solid-state potentiometric sensor using single-walled carbon nanohorns as transducer. Sens Actuators B. 2019;283:284–9.
23. Özbek O, Isildak Ö, Berkel C. The use of porphyrins in potentiometric sensors as ionophores. J Incl Phenom Macrocycl Chem. 2020. https://doi.org/10.1007/s10847-020-01004-y.
24. Khairul WM, Abu Hasan MF, Daud AI, Zuki HM, Kubulat KH, Abdulkadir M. Theoretical and experimental investigation of pyridyl thiourea derivatives as ionophores for Cu(II) ion detection. Malays J Anal Sci. 2016;20:73–84.
25. Isildak Ö, Özbek O, Gürdere MB, Çetin A. Development of PVC membrane potentiometric sensor for the determination of potassium ion and its applications. Pamukkale Univ Muh Bilim Derg. 2020. https://doi.org/10.5505/pajes.2020.27982.
26. Gürdere MB, Özbek O, Ceylan M. Aluminum chloride–catalyzed C-alkylation of pyrrole and indole with chalcone and bis-chalcone derivatives. Synt Commun. 2016;46:322–31.
27. Ansari A, Ali A, Asif M. Review: biologically active pyrazole derivatives. New J Chem. 2017;41:16–411.
28. Gürdere MB, Kamo E, Budak Y, Sahin Yağlıoğlu A, Ceylan M. Synthesis and anticancer and cytotoxic effects of novel 1,4-phenylene-bis-*N*-thiocarbamoylpyrazole and 1,4-phenylene-bis-pyrazolylthiazole derivatives. Turk J Chem. 2017;41:179–89.
29. Isildak Ö, Özbek O, Yigit KM. Zinc(II)-selective PVC membrane potentiometric sensor for analysis of Zn^{2+} in drug sample and different environmental samples. Int J Environ Anal Chem. 2019. https://doi.org/10.1080/03067319.2019.1691542.
30. Isildak Ö, Özbek O. Silver(I)-selective PVC membrane potentiometric sensor based on 5,10,15,20-tetra(4-pyridyl)-21*H*,23*H*-porphine and potentiometric applications. J Chem Sci. 2020;132:29.
31. IUPAC. Recommendations for nomenclature of ion-selective electrodes. Pure Appl Chem. 1976;48:127–32.
32. Faridbod F, Ganjali MR, Dinarvand R, Norouzi P. The fabrication of potentiometric membrane sensors and their applications. Afr J Biotechnol. 2007;6:2960–87.
33. Ganjali MR, Mizani F, Salavati-Niasari M, Javanbakht M. Novel potentiometric membrane sensor for the determination of trace amounts of chromium(III) ions. Anal Sci. 2003;19:235–8.
34. Abbaspour A, Izadyar A. Chromium(III) ion-selective electrode based on 4-dimethylaminoazobenzene. Talanta. 2001;53:1009–133.
35. Gholivand MB, Sharifpour F. Chromium(III) ion selective electrode based on glyoxal bis(2-hydroxyanil). Talanta. 2003;60:707–13.
36. Kumar P, Sharma HK, Shalaan KG. Development of chromium(III) selective potentiometric sensor by using synthesized triazole derivative as an ionophore. J Chem. 2013;12:1–6.
37. Ma YH, Yuan R, Chai YQ, Liu XL. Potentiometric membrane electrode for Cr(III) ion based on a new aryl amide bifunctional bridging ligand as a neutral carrier. J Chin Chem Soc. 2009;56:676–82.

38. Sharma RK, Goel A. Development of a Cr(III)-specific potentiometric sensor using Aurin tricarboxylic acid modified silica. Anal Chim Acta. 2015;534:137–42.
39. Youssef AFA, Issa YM, Mohamed MS. Carbon paste electrode modified with chromium thiopental for the potentiometric flow injection analysis of chromium (III). Toxicol Environ Chem. 2012;94:220–38.
40. Heidari Z, Masrournia M. A novel modified carbon paste electrode for the determination of chromium(III) in water. J Anal Chem. 2018;73:824–31.
41. Abu-Shawish HM, Saadeh SM, Hartani K, Dalloula HM. A comparative study of chromium(III) ion-selective electrodes based on *N*,*N*-Bis(salicylidene)-*o*-phenylenediaminatechromium(III). J Iran Chem Soc. 2009;6:729–37.