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Potentiometric monitoring of cobalt in beer sample by solid contact ion selective electrode

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ABSTRACT

A new solid contact cobalt selective electrode was constructed with 4-*tert*-butylthiacalix[4] arene as ionophore. The best performance was observed with the membrane having an ionophore/polyvinyl chloride/sodium tetraphenylborate/nitrophenyl octyl ether ratio of 3.5:33:1.5:62 (w/w; mg). The electrode, under steady-state conditions, exhibited a working concentration range of $1 \times 10^{-1} - 1 \times 10^{-6}$ mol/L with a near-Nernstian slope of 25.3 mV/ decade and a detection limit of 3.5×10^{-7} mol/L. The electrode had a very short response time (<10 seconds) and good reproducibility at a working pH range of 4.0–6.5. The electrode was used for 4 months without any significant change in its sensitivity. The potentiometric performance of the electrode in partially nonaqueous medium [up to 20 % (v/v) alcohol] was found satisfactory. The performance of the prepared electrode for the analysis of beer samples using direct potentiometric method is very encouraging.

1. Introduction

Cobalt is a naturally occurring element in soil, rock, air, water, plants, and animals. Plants can accumulate very small amounts of cobalt from the soil, especially in fruit, grain, and seeds. Cobalt is an essential element at trace levels, but is toxic at high concentration levels. It is required for good health in animals and humans and therefore, it is important that foodstuffs contain adequate quantities of cobalt. However, oral cobalt exposure in humans and/or animals has resulted in adverse effects [1–4]. For these reasons, an accurate and rapid procedure is of considerable interest for the determination of cobalt ion in food, environmental, biological, and industrial samples. Several techniques have been used for the determination of cobalt in solution including flame/ graphite furnace/electrothermal atomic absorption spectrometry (AAS) [5–7], electrochemiluminescence [8], thin film sequential injection [9], cyclic voltammetry [10], spectrophotometry [11], and spectrofluorimetry [12].

Most of the mentioned methods have drawbacks such as high cost of equipment and expensive materials, timeconsuming, and complicated operation. Potentiometric detection based on ion selective electrodes (ISEs), which is the simplest method, offers several advantages such as portability, low energy consumption, and low cost, and may also be suitable for online analysis [13,14]. Among these ISEs, the solid-contact ones (SC-ISEs) have attracted significant attention for genomics, clinical diagnosis, and practical pharmacy applications [15,16]. In recent years, research has intensified

to develop solid contact electrodes as a feasible alternative to conventional ISEs with an inner solution arrangement [17]. Solid contact electrodes offer several advantages over conventional electrodes particularly their promise in robust systems, free maintenance, miniaturization, and zero risk of inner filling solution leakage [14,18–20]. However, to the best of our knowledge, as alternatives to present electrodes for cobalt, no work has been done on the development of potentiometric solid contact cobalt sensors to date.

This study describes the preparation, characterization, and analytical application of a new solid contact cobalt selective electrode based on 4-*tert*-butylthiacalix[4]arene as an alternative cobalt selective electrode for monitoring of cobalt in beer samples. 4-*tert*-Butylthiacalix[4]arene has been used for the preparation of cobalt selective electrodes [21]. However, the results obtained in this study revealed that the solid contact electrode, prepared using modified carbon-based materials as the solid-contact ion-to-electron transducers, surpassed the typical poly(vinyl chloride) (PVC) membrane electrodes with inner solution arrangement in linear dynamic range and response time.

2. Materials and methods

2.1. Reagents

All chemicals used were of analytical reagent grade and used without further purification. Tetrahydrofuran (THF), high molecular weight PVC, 2-Nitrophenyl octyl ether (NPOE), dibuthyl phthalate, Dioctyl sebacate (DOS), sodium tetraphenylborate (NaTPB), 4-*tert*-butylthiacalix[4]arene, and graphite were purchased from Fluka (Buchs, Switzerland). Chloride or nitrate salts of all cations used (from Merck, Darmstadt, Germany) were of the highest purity available. Epoxy (Macroplast Su 2227) and hardener (Desmodur RFE) were purchased from Henkel (Istanbul, Turkey) and Bayer AG (Darmstadt, Germany). Doubly distilled deionized water was used for the preparation of all solutions.

2.2. Apparatus and electromotive force (EMF) measurements

A laboratory-made, computer-controlled, high-input impedance eight-channel potentiometric system was used for the potential measurement. The data output was recorded by a home-made software program. Throughout the measurements, a saturated Ag-AgCl reference electrode (Gamry, USA) was used as the reference electrode. The pH of the solutions was adjusted by using a glass pH electrode (Schott) with a Jenway 3040 model Ion Analyzer (UK). Solutions at required concentrations were homogenized using an Ultrasonic LC30 stirrer (Germany).

Potentiometric measurements were carried out with the following cell assembly: SC-ISE test solution Ag-AgCl, KCl (sat'd). The cell consists of SC-ISE as the indicator electrode, a saturated Ag-AgCl reference electrode, and a magnetic stirrer. All measurements were carried out at room temperature. Reference and indicator electrodes were washed with deionized water and dried with an adsorbent tissue prior to each measurement of the solutions. Calibration was performed from higher to lower activities.

2.3. Preparation of ISEs

Cobalt selective electrode was prepared as described in our previous works [22,23]. A conductive material was prepared by mixing 50% (w/w) graphite, 35% (w/w) epoxy, and 15% (w/w) hardener in sufficient THF. The mixture was allowed to stand in air until the appropriate viscosity was attained. A shielded copper wire was dipped into this mixture a few times to obtain a uniform solid contact with a coating thickness of about 0.2 mm and then allowed to stand overnight in room temperature.

The ion selective membrane contained ionophore/PVC/NaTPB/NPOE at a ratio of 3.5:33:1.5:62 (w/w; mg). The membrane solution was prepared by dissolving of the membrane components in 2.0 mL THF. After the preparation of membrane, solid contacts were dipped into the membrane solution at least three times, and then the coated membranes were allowed to dry in air for at least 1 day. Next, the dried membrane electrodes were soaked in a 1×10^{-2} mol/L Co(NO$_3$)$_2$ solution for 1 day before use. When not in use, the electrode was stored under laboratory conditions. Before the individual measurement process, the electrode was reconditioned by at least 30 minutes in a 1.0×10^{-2} mol/L Co(NO$_3$)$_2$ solution.

2.4. Sample preparation and determination

Commercial beer samples, which normally contain a minute concentration of cobalt, were selected for analysis. All samples were bought in a marketplace. There is a need to develop a potentiometric method to check whether a beer sample contains cobalt. For beer analysis, 1 mL of 18 N H$_2$SO$_4$ was added to 50 mL degassed beer. The beer was evaporated to dryness, and 10 mL distilled water was added. The pH was adjusted to 4.5 using either 0.1 N HCl or 0.1 N NaOH. The solution was filtered, and a constant volume (5 mL) of the beer solution was transferred to 25-mL calibrated volumetric flasks. Finally, each flask was made up to the mark with water and mixed. The pH for all samples was adjusted to 4.5. The concentration of cobalt was then determined for each sample using ISE.

3. Results and discussion

A number of characteristics such as selectivity, sensitivity, response, and low detection limit are required for a sensor to be considered suitable for ion determination. The sensitivity and selectivity of any membrane electrode are significantly related with the composition of the ion selective membrane and the used mediators plasticizer (DBP, NPOE, and Dioctyl sebacate) and lipophilic additives (NaTPB). The results given in Table 1 show that ionophore/PVC/NaTPB/NPOE at a ratio of 3.5:33:1.5:62 (w/w; mg) gives the best sensitivity among the three studied plasticizers, most probably because of the better solubility of the ligand in NPOE.

The potentials were measured by varying the concentration of the cobalt test solution in the range of

Table 1 – Composition of PVC-based membranes of 4-*tert*-butylthiacalix[4]arene and their performance as Co(II)-selective electrodes.

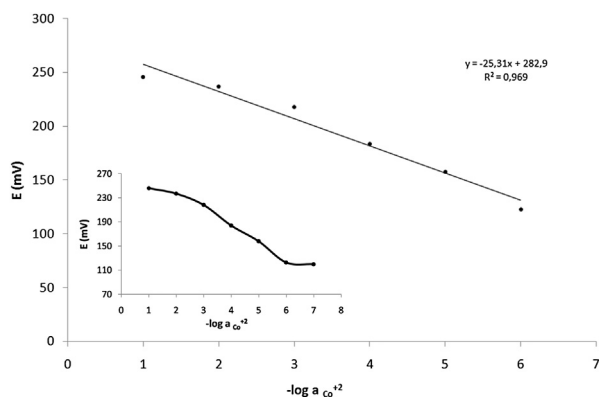| Membrane no.	Composition of membrane (w/w) (ratio of components)						Working concentration range (M)	Slope mV per decade of concentration	Response time (s)
	Ionophore	PVC	NaTPB	NPOE	DOS	DBP			
1	3.5	33		63.5			1×10^{-1}–5×10^{-5}	23.2 ± 1.5	15
2	3.5	33	1.5	62			1×10^{-1}–1×10^{-6}	25.3 ± 1	<10
3	3.5	33	1.5		62		1×10^{-1}–1×10^{-5}	20.2 ± 2	20
4	3.5	33	1.5			62	1×10^{-1}–5×10^{-4}	24.5 ± 2.3	25

DBP = dibuthyl phthalate; DOS = dioctyl sebacate; NaTPB = sodium tetraphenylborate; NPOE = nitrophenyl octyl ether; PVC = poly(vinyl chloride).

1.0×10^{-7} – 1.0×10^{-1} M. The calibration plot of the electrode is presented in Fig. 1. For the electrolyte activities from 1.0×10^{-1} mol/L and 1.0×10^{-6} mol/L, the solid contact cobalt selective electrodes exhibit linear responses with a near-Nernstian slope of 25.3 mV/decade ($R^2 = 0.964$).

The electrochemical performance characteristics of the solid contact cobalt selective electrode were systematically evaluated according to the recommendations of the International Union of Pure and Applied Chemistry [24,25]. Response times were determined after the potential of a solution of cobalt(II) nitrate had become constant, and similar measurements were carried out in another solution of 10-fold lower concentration. The response time was defined as the time it takes to reach a potential of 90% of the potential difference in two measurements.

The potentiometric performance characteristics of the solid contact cobalt selective membrane electrode are summarized in Table 2.

As shown in Table 2, the performance of the prepared electrode is almost comparable with the results of a reported PVC membrane electrode constructed with 4-*tert*-butylthiacalix[4]arene as ionophore [21]. In addition, our electrode surpassed the typical PVC membrane electrode in terms of linear dynamic range and response time. The sensitivity of the proposed electrode (limit of detection 3.5×10^{-7} mol/L), a linear response with a characteristic Nernstian slope, was observed for a broader concentration range (1×10^{-1}–1×10^{-6} mol/L) than that reported in a previous study [21].

The effect of pH on the potential response of the sensor has been tested over the range 1.0–7.0 for 1.0×10^{-3} M and 1.0×10^{-4} M Co^{2+} solution. The pH of the test solutions was adjusted with nitric acid or ammonia. Fig. 2 shows that the response of the electrode is independent of the solution pH in the range of 3.5–6.5.

The performance of the sensor was also investigated in partially nonaqueous medium using 10%, 20%, and 30% (v/v) methanol–water and acetonitrile–water mixtures. As shown in Table 3, the electrode membrane did not show any appreciable change in the working concentration range and slope in methanol–water mixtures up to 20% (v/v) nonaqueous contents, whereas in the acetonitrile–water mixture, the

Table 2 – Potentiometric performance characteristics of the solid contact cobalt selective membrane electrode.

Parameter	Co^{2+}-selective PVC membrane electrode
Membrane composition	2% (w/w) ionophore, 4-*tert*-butylthiacalix[4]arene, 66% (w/w) PVC, 127% (w/w) NPOE, 1.5% (w/w) NaTPB
Slope (mV/decade)	25.3 ± 0.1
Correlation coefficient (r)	0.964
Limit of linear range (mol/L)	1×10^{-1}–1×10^{-6}
Limit of detection (mol/L)	3.5×10^{-7} mol L^{-1}
Response time for 10^{-2} mol/L (s)	<10 s
Working pH range	3.50–6.50
Life span (wk)	16
Selectivity coefficient $K_{Co^{2+},A^{+n}}^{pot}$	Interferent (A) $K_{Co^{2+},A^{+n}}^{pot}$
	Cr^{3+} 1.42×10^{-3}
	Cu^{2+} 6.12×10^{-3}
	Mg^{2+} 9.68×10^{-4}
	Fe^{3+} 3.98×10^{-4}
	Na^{+} 5.02×10^{-3}
	K^{+} 3.82×10^{-3}
	Zn^{2+} 6.12×10^{-3}
	Ba^{2+} 1.75×10^{-4}
	NH_4^{+} 2.32×10^{-4}
	Hg^{2+} 4.63×10^{-3}
	Ni^{2+} 3.38×10^{-3}
	Cd^{2+} 2.42×10^{-3}
	Ca^{2+} 1.76×10^{-3}
	Pb^{2+} 4.45×10^{-3}

NaTPB = sodium tetraphenylborate; NPOE = nitrophenyl octyl ether; PVC = poly(vinyl chloride).

Fig. 1 – The potentiometric response of the Co^{2+}-selective electrode.
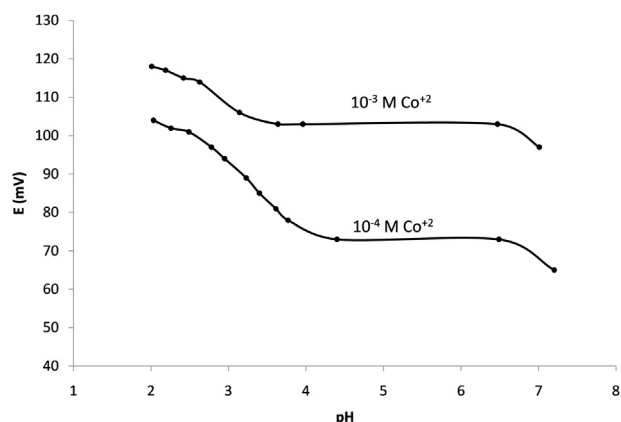
Fig. 2 – Effect of the pH of the test solution on the potential response of the electrode.

Table 3 – Effect of partially nonaqueous medium on the potentiometric characteristics of Co^{2+} selective sensor.

Nonaqueous content (% v/v)	Slope (mV/decade of activity)	Working concentration range (mol L^{-1})
0	25.3 ± 0.1	1.0×10^{-6}–1.0×10^{-1}
Methanol		
5	25.3 ± 0.1	1.0×10^{-6}–1.0×10^{-1}
10	25.2 ± 0.1	1.1×10^{-6}–1.0×10^{-1}
20	25.1 ± 0.1	1.2×10^{-6}–1.0×10^{-1}
30	21.2 ± 0.1	6.8×10^{-6}–1.0×10^{-1}
Acetonitrile		
5	25.2 ± 0.1	1.0×10^{-6}–1.0×10^{-1}
10	25.1 ± 0.1	1.3×10^{-6}–1.0×10^{-1}
20	24.5 ± 0.1	6.4×10^{-6}–1.0×10^{-1}
30	20.2 ± 0.1	9.5×10^{-6}–1.0×10^{-1}

membrane could tolerate up to 10% (v/v) nonaqueous content. However, above these mentioned nonaqueous contents, the slope decreased appreciably; consequently, reliable measurements could not be obtained. The drift in potentials in the organic phase may be attributable to swelling in the membrane, which made it mechanically weak, and leaching of ionophore from the membrane to the nonaqueous solution took place.
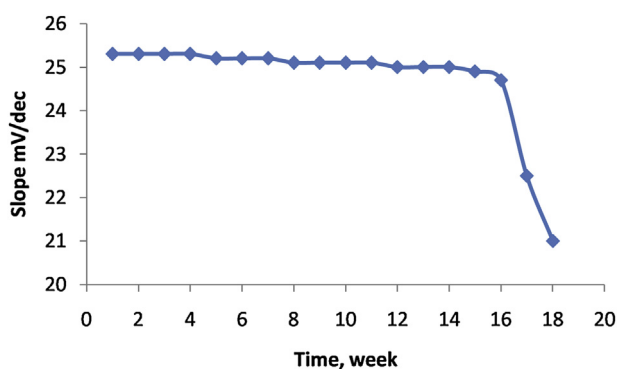

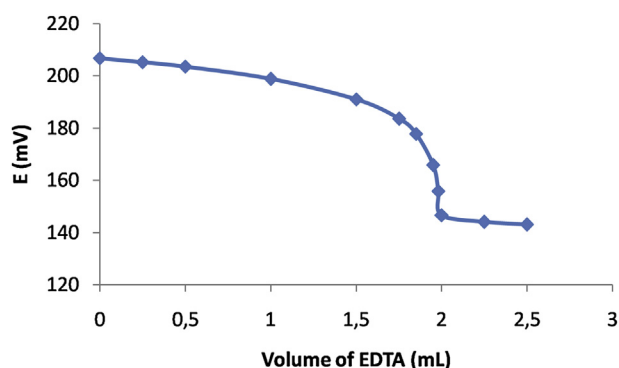Fig. 3 – Lifetime of the constructed cobalt selective electrodes.

Fig. 4 – Potentiometric titration curve of 20 mL of 1×10^{-3} M Co^{2+} solution with 1×10^{-2} M EDTA at pH 4.0.

The lifetime of the sensor was investigated. As displayed in Fig. 3, the membrane showed deterioration in the response to a Nernstian of 25.83 mV/decade for cobalt. The primary reason for this deterioration is the leaching of membrane components into the sample.

3.1. Application

The analytical applicability of the electrode was evaluated by carrying out a potentiometric titration of 20 mL of 1.0×10^{-3} M Co^{2+} ions against 1.0×10^{-2} M EDTA at pH 4. The titration plot in Fig. 4 shows a conventional sigmoid shape. The inflexion point of the plot corresponds to 1:1 stoichiometry of the Co–EDTA complex.

The prepared electrode was successfully used for the monitoring of cobalt ion in beer samples. Three samples of each beer were analyzed using the direct potentiometric method under steady-state conditions and AAS. The results obtained by the proposed cobalt sensor, together with those obtained by AAS and with t test, are summarized in Table 4. As can be seen in Table 4, there is a good agreement between the results obtained by the developed electrode and AAS within the 95% confidence level.

4. Conclusion

The sensor shows favorable performance characteristics with a short response time (<10 seconds) and a low detection limit

Table 4 – Determination of cobalt in beer by direct potentiometry using solid contact ion selective electrode.

Sample	Cobalt content (mol/L)[a]		t test[b]
	Proposed sensor	AAS method	
1	$2.63 \times 10^{-6} \pm 8.5 \times 10^{-8}$	2.00×10^{-6}	2.15
2	$3.58 \times 10^{-6} \pm 2.7 \times 10^{-7}$	1.50×10^{-6}	2.74
3	$2.52 \times 10^{-6} \pm 2.7 \times 10^{-7}$	2.20×10^{-6}	1.62
4	$2.35 \times 10^{-6} \pm 5.7 \times 10^{-7}$	2.10×10^{-6}	0.63
5	$3.16 \times 10^{-6} \pm 2.3 \times 10^{-7}$	2.80×10^{-6}	2.25

AAS = atomic absorption spectrometry.
[a] Average of three replicate measurements ± standard deviation.
[b] The theoretical values of t at $p = 0.05$ is 2.78.

of 3.5×10^{-7} mol L^{-1} over the concentration range of 1×10^{-1}–1×10^{-6} mol L^{-1}. The sensor is superior to existing sensors in terms of concentration range and response time. The analysis of real samples indicated that the constructed potentiometric sensor is capable of monitoring cobalt in beer, providing a handy alternative for routine analysis.

Conflicts of interest

All authors declare no conflicts of interest.

Acknowledgments

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