Original Article

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

Hilal Eren, Harun Uzun, Muberra Andac*, Seda Bilir

Department of Chemistry, Faculty of Science, Ondokuz Mayis University, Kurupelit-Samsun, Turkey

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, time-consuming, 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-Nitrophosphonyl octyl ether (NPOE), dibuthyl phthalate, Diocetyl 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 saturated Ag-AgCl reference electrode. The pH of the solutions 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.

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 $1 \times 10^{-2}$ 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 $1.0 \times 10^{-2}$ 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 Diocetyl 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...
The potentiometric performance characteristics of the solid contact cobalt selective membrane 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 1.0 \( \times 10^{-2} M \) 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 PVC membrane electrode is 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 \( \times 10^{-7} \) mol/L), a linear response with a characteristic Nernstian slope, was observed for a broader concentration range (1 \( \times 10^{-7} \)–1 \( \times 10^{-6} \) 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 \( \times 10^{-2} \) M and 1.0 \( \times 10^{-4} \) M Co(II) 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 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  | 1.5   | 62   | 69  | 62  |
| 2            | 3.5       | 33  | 1.5   | 62   | 69  | 62  |
| 3            | 3.5       | 33  | 1.5   | 62   | 69  | 62  |
| 4            | 3.5       | 33  | 1.5   | 62   | 69  | 62  |

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

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

| Parameter | Co(II)-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 \( \times 10^{-1} \)–1 \( \times 10^{-6} \) |
| Limit of detection (mol/L) | 3.5 \( \times 10^{-7} \) mol L\(^{-1}\) |
| Response time for 10\(^{-2}\) mol/L (s) | <10 |
| Working pH range | 3.50–6.50 |
| Life span (wk) | 16 |
| Selectivity coefficient \( K_{Co^{2+}, A}^{pot} \) Interferent (A) | \( K_{Co^{2+}, A}^{pot} \) |
| Ca\(^{2+}\) | 1.42 \( \times 10^{-3} \) |
| Cr\(^{3+}\) | 6.12 \( \times 10^{-3} \) |
| Cu\(^{2+}\) | 9.68 \( \times 10^{-4} \) |
| Fe\(^{3+}\) | 3.98 \( \times 10^{-4} \) |
| Mg\(^{2+}\) | 5.02 \( \times 10^{-3} \) |
| Na\(^{+}\) | 3.82 \( \times 10^{-3} \) |
| K\(^{+}\) | 6.12 \( \times 10^{-3} \) |
| Mn\(^{2+}\) | 7.15 \( \times 10^{-4} \) |
| NH\(_4\)\(^{+}\) | 2.32 \( \times 10^{-4} \) |
| Ni\(^{2+}\) | 4.63 \( \times 10^{-3} \) |
| Pb\(^{2+}\) | 3.38 \( \times 10^{-3} \) |
| Cd\(^{2+}\) | 2.42 \( \times 10^{-3} \) |
| Ca\(^{2+}\) | 1.76 \( \times 10^{-3} \) |
| Pd\(^{2+}\) | 4.45 \( \times 10^{-3} \) |

NaTPB = sodium tetraphenylborate; NPOE = nitrophenyl octyl ether; PVC = poly(vinyl chloride).
Effect of partially nonaqueous medium on the determination of cobalt in beer by direct selective sensor.

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 Co²⁺ 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                 |

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 Co²⁺ ions against 1.0 × 10⁻³ 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 testb |
|--------|-------------------------|---------|
|        | Proposed sensor | AAS method |
| 1      | 2.63 × 10⁻⁶ ± 8.5 × 10⁻⁸ | 2.00 × 10⁻⁶ | 2.15 |
| 2      | 3.58 × 10⁻⁶ ± 2.7 × 10⁻⁷ | 1.50 × 10⁻⁶ | 2.74 |
| 3      | 2.52 × 10⁻⁶ ± 2.7 × 10⁻⁷ | 2.20 × 10⁻⁶ | 1.62 |
| 4      | 2.35 × 10⁻⁶ ± 5.7 × 10⁻⁷ | 2.10 × 10⁻⁶ | 0.63 |
| 5      | 3.16 × 10⁻⁶ ± 2.3 × 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.

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

Fig. 4 — Potentiometric titration curve of 20 mL of 1 × 10⁻³ M Co²⁺ solution with 1 × 10⁻² M EDTA at pH 4.0.
of $3.5 \times 10^{-7}$ mol L$^{-1}$ over the concentration range of $1 \times 10^{-1}$–$1 \times 10^{-6}$ 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**

We gratefully acknowledge the financial support of Ondokuz Mayis University Research Foundation (BAP), Kurupelit-Samsun, Turkey (Project number PYO.Fen. 1904.11.019).

**References**

[1] Geierab DA, Geiercd MR. An autism cohort study of cobalt levels following vitamin B12 injections. Toxicol Environ Chem 2010;92:1025–37.
[2] Concise International Chemical Assessment Document 69. Cobalt and inorganic cobalt compounds. World Health Organization; 2006.
[3] Cobalt facts—environment, cobalt exposure and heart disease; 2006.
[4] Pais I, Benton Jr J. The handbook of trace elements. Florida: St. Lucie Press; 1996. p. 240.
[5] Baghban N, Shabani AMH, Shayessteh DS, et al. Flame atomic absorption spectrometric determination of trace amounts of cobalt. J Braz Chem Soc 2009;20:832–8.
[6] Ribeiro AS, Vieira MA, Da Silva AF, et al. Determination of cobalt in biological samples by line-source and high-resolution continuum source graphite furnace atomic absorption spectrometry using solid sampling or alkaline treatment. Spectrochim Acta B 2005;60:693–8.
[7] Todorovska N, Karadjova I, Arpadjan S. Electrothermal atomic absorption spectrometric-determination of cobalt in human serum and urine. Acta Pharmacol 2003;53:83–90.
[8] Zhang L, Zhou J, Hao Y, et al. Determination of Co$^{2+}$ based on the cobalt(II)-catalyzed electrochemiluminescence of luminol in acidic solution. Electrochim Acta 2005;50:3414–9.
[9] Vanstaden JF, Talijaard RE. Determination of lead(II), copper(II), zinc(II), cobalt(II), cadmium(II), iron(III), mercury(II) using sequential injection extractions. Talanta 2004;64:1203–12.
[10] Korolczuk M, Moroziewicz A, Grabarczyk M, et al. Determination of traces of cobalt in the presence of nioxime and cetyltrimethylammonium bromide by adsorptive stripping voltammetry. Talanta 2005;65:1003–7.
[11] Yun J, Choi H. Micellar colorimetric determination of iron, cobalt, nickel and copper using 1-nitroso-2-naphthol. Talanta 2000;52:893–902.
[12] Ma Q, Cao QE, Zhao Y, et al. Two sensitive fluorescence methods for the determination of cobaltous in food and hair samples. Food Chem 2000;71:129–7.
[13] Singh AK, Singh P. Determination of cerium ion by polymeric membrane and coated graphite electrode based on novel pendant armed macrocycle. Anal Chim Acta 2010;675:170–80.
[14] Bobacka J, Ivaska A, Lewenstam A. Potentiometric ion sensors. Chem Rev 2008;108:329–51.
[15] Abu Shawish HM, Khedr AM, Abed-Almonem KI, et al. A comparative study of solid and liquid inner contact benzalkonium chloride ion-selective electrode membranes. Talanta 2012;101:211–9.
[16] Jianfeng P, Yixian W, Jian W, et al. Development of an all-solid-state potassium ion-selective electrode using graphene as the solid-contact transducer. Electrochem Commun 2011;13:1529–32.
[17] Zhu J, Qin Y, Zhang Y. Preparation of all-solid-state potentiometric ion sensors with polymer—CNT composites. Electrochem Commun 2009;11:1684–7.
[18] Mousavi Z, Bobacka J, Lewenstam A, et al. Ion-selective organic electrochemical junction transistors based on poly(3,4-ethylenedioxythiophene) doped with poly(styrene sulfonate). J Electroanal Chem 2009;633:246–52.
[19] Michalska A, Wojciechowski M, Bulska E, et al. Experimental study on stability of different solid contact arrangements of ion-selective electrodes. Talanta 2010;82:151–7.
[20] Górski L, Matusевич A, Pietrzak, et al. Influence of inner transducer properties on EMF response and stability of solid-contact anion selective membrane electrodes based on metalloporphyrin ionophores. J Solid State Electrochem 2009:13:157–64.
[21] Gupta VK, Jain AK, Khayat Al, et al. Electroanalytical studies on cobalt(II)-selective potentiometric sensor based on bridge modified calixarene in poly(vinyl chloride). Electrochim Acta 2008;53:5409–14.
[22] Coldur F, Andac M. All-solid-state polyvinyl chloride membrane lithium-selective electrode with improved selectivity and its application in serum lithium assay. Sensor Lett 2011;9:1738–44.
[23] Andac M, Eren H, Coldur F. Determination of nitrate in leafy vegetables by flow injection analysis with potentiometric detection. J Food Drug Anal 2011;19:457–62.
[24] IUPAC Analytical Chemistry Division. Commission on Electroanalytical Chemistry. Recommendations for nomenclature of ion. Pure Appl Chem 1994;66:2527–36.
[25] IUPAC Analytical Chemistry Division. Commission on Electroanalytical Chemistry. Potentiometric selectivity coefficients of ion-selective electrodes. Pure Appl Chem 2000;72:1851–2082.