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A selective modified carbon paste electrode for determination of cyanide using tetra-3,4-pyridinoporphyrazinatocobalt(II)

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Abstract

A chemically modified carbon paste electrode with 3,4-tetra pyridinoporphirazinatocobalt(II) (Co(3,4 tppa) was applied to the determination of free cyanide ion. The electrode has a linear range between 1.5×10^{-5} M and 1.0×10^{-2} M with a Nernstian slope of 60 ± 1.5 mV/decade and its detection limit is 9×10^{-6} M. The response time of electrode is 5 min. The proposed electrode was applied successfully for the determination of cyanide in commercially available spring water. Some anions, such as SCN^-, I^-, Cl^-, Br^- and oxalate that are usually serious interfering species for most of cyanide selective electrodes, did not have any interfering effect for this proposed electrode.

Keywords: Carbon paste electrode; Cyanide; Potentiometry; Co(3,4 tppa)

1. Introduction

Sodium cyanide is used in the industrial extraction for silver and gold [1], for case hardening of steel, and as an intermediate in the chemical industry. Hydrogen cyanide is used in the manufacture of acrylic fibers, nylon-66, methyl methacrylate, pesticide and agricultural chemical production [2].

The extreme toxic hazards of cyanides are well known. In the case of HCN, the maximum permissible exposure level over an 8 h working day is 10 ppm [2].

Therefore, a great deal of research has been done for cyanide determination using various techniques and methods, for example, its determination and evaluation by volumetric, gravimetric and complexometric titrations [2], high performance liquid chromatography (HPLC) [3–10], ion chromatography (IC) [11–19], voltammetry [20–25], amperometry [26–31], plarography [32–36], potentiometry (solid state membrane ion selective electrodes) [37–42], atomic absorption spectroscopy (AAS) [43–48] and fluorimetry [49,50].

Few reports for determination of cyanide by carbon paste electrodes (CPE) are available in literature, but all of them are based on voltammetric methods. For example, voltammetric determination of cyanide by use of pre-concentration at a carbon paste electrode modified with liquid crystals [51] or cyanide determination using a carbon paste amperometric biosensor based on cytochrome oxidase inhibition [52].

In this work, we applied a Co(3,4 tppa)-modified carbon paste electrode (MCPE) for determination of free cyanide anions using potentiometry method. According to our knowledge this is the first report on cyanide selective electrode based on the chemically modified carbon paste electrode using potentiometry method. Not only the method is simple and inexpensive, the electrode has the advantages of being selective for cyanide in the presence of variety of anions, such as SCN^-, I^-, Cl^-, Br^- and oxalate that usually one or some of them are serious interfering species for most of cyanide ion selective electrodes [39,40,51,53]. In addition, voltammetric cyanide selective carbon paste electrodes may have good detection limits, but comparing to this proposed electrode their linear ranges are shorter.

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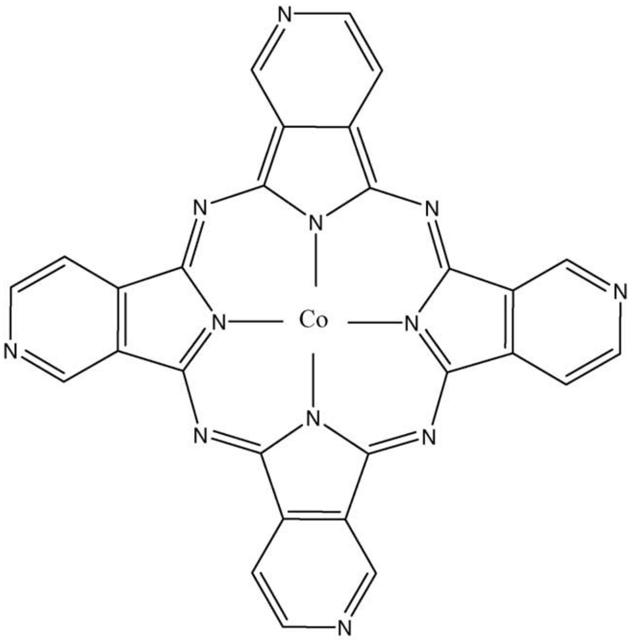

Fig. 1. Chemical structure of tetra-3,4-pyridinoporphirazinatocobalt(II).

2. Experimental

2.1. Materials

Pure graphite powders (Merck) and paraffin oil (Fluka) were used for the preparation of carbon paste electrode. Co(3,4 tppa) (Fig. 1) was synthesized and purified according to the literature [54]. All anion salts were of analytical reagent grade from Merck. Solutions were prepared with doubly distilled water.

Since cyanide is easily oxidized [1] (Eq. (1)) and also to avoid of cyanide adsorption on the walls of glass vessels [55], a stock solution of 0.1 M KCN was prepared daily in a polyethylene vessel by dissolving an appropriate amount of KCN in borax buffer (pH of 10).

$$CN^{-} + 2H_2O + O_2 \leftrightarrow NH_3 + HCO_3^{-} \quad (1)$$

Solutions of interferences were prepared by dissolving appropriate amounts of each compound in borax buffer.

2.2. Preparation of MCPE

The general procedure for preparing MCPE is similar to our previous works [56–60]. The electrode was prepared by mixing 0.1054 g of pure graphite powder and 0.0250 g of Co(3,4 tppa) complex in a 5-mL beaker and grinding the mixture in an IR mortar. Then, 0.0560 g of liquid paraffin was added, and the mixture was completely mixed in to a uniform paste.

Electrode bodies were made from disposable 1-mL polyethylene syringes the tip of which had been cut off with a razor blade. These bodies were filled with approximately 0.1 mL of modified paste materials. Smooth surfaces were obtained by applying manual pressure to the piston while holding the electrode surface against a flat solid support and were polished with the very smooth paper. After polishing, the working surface of the electrode was checked for pinholes by a usual lens.

When packing the well, we avoided applying too much pressure, since high pressure may result in separation of the carbon and oil, with a resulting high resistance contact between paste and metal [61]. The electrical connection was made with a copper wire.

A fresh electrode surface can be obtained by cutting approximately 1 mm of paste and polishing the fresh surface over a smooth paper.

2.3. Apparatus

A corning model of 125-pH/mV meter was used for potentiometric measurements. The reference electrode was a double junction saturated calomel electrode. A Metrohm potentiometer (pH meter model of 780) was used for pH controlling, and a thermostatic water bath model of Huber polystate cc2 was used for temperature controlling. All spectroscopy studies were down with a Cintra5 spectrophotometer.

2.4. Procedure

The electrode was immersed directly in test solution. The pH of this solution was adjusted to 10 by borax buffer (0.025 M), and 0.1 M Na_2SO_4 was used as supporting electrolyte, and the temperature was controlled at $25 \pm 0.1\,^{\circ}C$. The solution stirred (100 rpm) for about 50–60 min until the response of the potentiometer became stable. Then certain amounts of stock solution were added to the test solution. After 5 min (response time of electrode), the potential of each solution was measured. To avoiding of cyanide adsorption on the wall of vessels, all experiments were done into a polyethylene beaker.

3. Results and discussion

3.1. Optimization of the amount of modifier in the electrode

For this purpose, seven electrodes with different percentage of modifier were prepared. The proportions of modifier in these seven electrodes were 8.1, 9.9, 11.2, 12.7, 13.4, 14.8 and 15.5% (w/w). The slopes and correlation coefficients of the above electrodes are given in Table 1. According to these results, optimum amount of the modifier was 13.4%. In this optimum proportion, the slope of the electrode was Nernstian.

3.2. Effect of the ionic strength on the response of the electrode

The effect of ionic strength on the calibration curve was studied by using sodium sulfate salt as a supporting electrolyte. The lower limit of linear range was im-

Table 1
Optimization of the amount of modifier

Modifier percent (%, w/w)	Slope (mV/decade)	Linear range (M)	*R*
8.1	−65.7	3.0×10^{-5} to 1×10^{-2}	0.995
9.9	−65.5	3.0×10^{-5} to 1×10^{-2}	0.993
11.2	−64.6	3.0×10^{-5} to 1×10^{-2}	0.995
12.7	−64.6	3.0×10^{-5} to 1×10^{-2}	0.996
13.4	−60.3	3.0×10^{-5} to 1×10^{-2}	0.992
14.8	−51.4	1.3×10^{-4} to 1×10^{-2}	0.995
15.5	−51.0	1.3×10^{-4} to 4×10^{-3}	0.990

Conditions: borax buffer 0.025 M and pH = 10 without Na_2SO_4 supporting electrolyte.

proved (1.5×10^{-5} M) when we used 0.1–0.2 M of Na_2SO_4 (Table 2).

3.3. Optimization of pH and conditioning time

Cyanide is a weak base ($pK_b = 4.79$) and in pH values below 9.5, more than 50% of cyanide species changed to HCN, which is a volatile weak acid. To obtain the optimum pH, we accomplish cyanide titration in three pH values of 10.0, 10.5 and 11.0 and their results are given in Table 2. As this Table shows, the electrode has a better characteristic response at the pH of 10.0, for this reason, this pH value was chosen as the optimum pH for the system. Since hydroxide is a serious interference for carbon paste electrode, therefore, in pH values higher than 10.0 the sensitivity of decreases and this makes the linear range shorter. In addition, the electrode response becomes supernernstian in these pH values.

3.4. Response characteristics of modified and unmodified carbon paste electrode

The unmodified electrode showed no significant response under the optimum conditions (Fig. 2). The response time of the modified electrode was measured by using IUPAC recommendation [62]. The response time in variation of concentration from 1.5×10^{-4} to 1.5×10^{-3} M cyanide was measured and was about 5 min. The limit of detection (9×10^{-6} M) was evaluated from the intersection of two extrapolated segments of the calibration graph according to IUPAC recommendations [62].

3.5. Homogeneity and reproducibility of the electrode

For examination of paste homogeneity, the proposed electrode was applied six times for cyanide measurement in a solution with cyanide concentration of 4×10^{-5} M. It should be mentioned that after each measurement the electrode surface was renewed as explained in the experimental section. The results show an average of 171.5 mV for potential measurements with R.S.D. of 0.61, which can be an acceptable value. To examine reproducibility of the electrode, four different electrodes with the same paste composition were prepared and from the results four calibration plots for cyanide were obtained as are illustrated in Fig. 3. According to Fig. 3, the reproducibility for this proposed electrode is also reasonable (the average slope of the four plots is 59.8 ± 1.1 mV/decade).

Table 2
Optimization of pH at three different pH values of 10, 10.5, 11 and using 0.1 M Na_2SO_4 as supporting electrolyte

pH value	Linear range (M)	Slope (mV/decade)	*R*
10	1.5×10^{-5} to 1.0×10^{-2}	−60.5	0.994
10.5	6.4×10^{-5} to 1.0×10^{-2}	−64.3	0.995
11	5×10^{-4} to 1.0×10^{-2}	−72.1	0.994

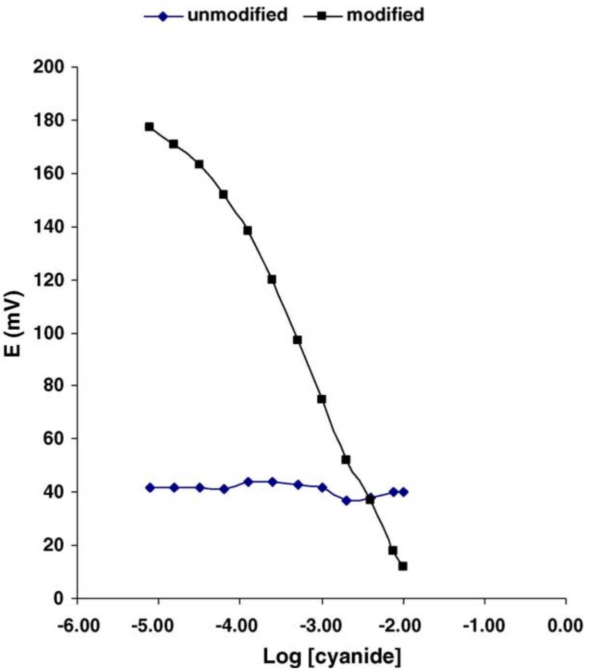

Fig. 2. Response of modified and unmodified carbon paste electrode under the optimum conditions. *Conditions:* pH = 10, 13.4% modifier, 0.1 M Na_2SO_4 assupporting electrolyte, concentration = 0.1 M.

3.6. Selectivity and interference

Probably one of the most important characteristics of an ion selective electrode is its relative response to other ions present in solution, which expressed in terms of selectivity coefficients. The selectivity coefficients of the modified carbon paste electrode were evaluated by the match potential method (MPM) [63]. This method has two advantageous [64]: the first one is that when ions of unequal charges are involved, the MPM is recommended, as it gives practical $K_{A,B}$ values. Secondly, when interfering ions and/or the primary ion do not satisfy the Nernstian condition, the matched potential method is also recommended, even if the charges of the primary and interfering ions are equal. According to this method, the potententiometric selectivity coefficient is defined as the activity ratio of primary and interfering ions that give the same potential change under identical conditions. At first, a known activity (a'_A) of the primary ion solution

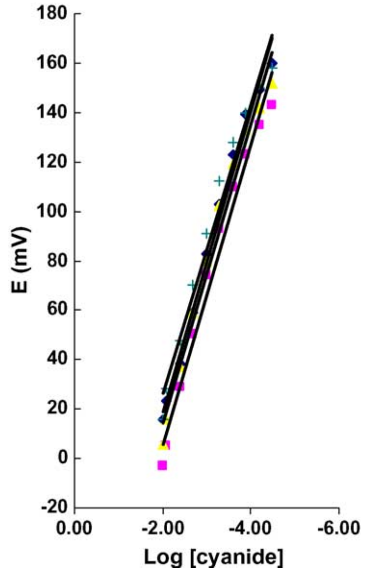

Fig. 3. Four calibration curves for electrode reproducibility investigation. *Conditions:* pH = 10, 13.4% modifier, 0.1 M Na_2SO_4 assupporting electrolyte.

is added into reference solution that contained a fixed activity (a_A) of primary ions, and the corresponding potential change (ΔE) is recorded. Next, a solution of interfering ion (B) is added to the reference solution until the same potential change (ΔE) is recorded. According to this method, the selectivity coefficient ($K_{A,B}$) is defined as:

$$K_{A,B} = \frac{a'_A - a_A}{a_B}$$

$K_{A,B}$ for several common anions were measured and the results are shown in Table 3. It should be noted that in this study, a very low concentration of cyanide solution (3×10^{-5} M) was used as a primary solution (a'_A). A comparison between this chemically modified carbon paste electrode and some of cyanide ion selective electrodes are given in Table 4. As Table 4 shows the present electrode is more selective than the previously reported cyanide electrodes.

Table 3
Selectivity coefficients for some common anions by match potential method

Interference (j)	K_{ij}
HPO_4^-	2.9×10^{-4}
I^-	3.4×10^{-4}
Br^-	$<10^{-4}$
SCN^-	1.7×10^{-3}
Cl^-	1.6×10^{-4}
SO_4^{2-}	$<10^{-4}$
SO_3^{2-}	6×10^{-4}
S^{2-}	1.6
CO_3^{2-}	1.9×10^{-4}
$C_2O_4^{2-}$	$<10^{-4}$
N_3^-	2.1×10^{-3}
NO_2^-	4.9×10^{-3}
NO_3^-	$<10^{-4}$
F^-	1.5×10^{-4}
CH_3COO^-	$<10^{-4}$

Note: The primary concentration of cyanide is 3×10^{-5} M.

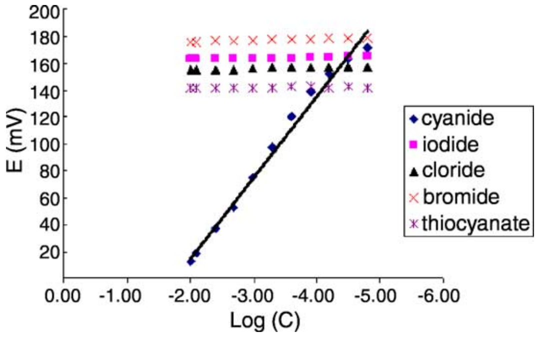

Fig. 4. The electrode responses for CN^-, Br^-, Cl^-, I^- and SCN^-. *Conditions:* pH = 10, 13.4% modifier, 0.1 M Na_2SO_4 assupporting electrolyte.

Fig. 4 illustrates the responses of this electrode to cyanide and four important interferences (Br^-, Cl^-, I^- and SCN^-) of most available cyanide ion selective electrodes. As Fig. 4 shows except cyanide ion for cyanide the electrode does not response to any other species. The high selectivity of this electrode for cyanide anion is because of that the pre-existing of negative charge on the cyanide increases the σ-donor propensity but weakens its effectiveness as a π-acceptor. There-

Table 4
Comparison between cyanide MCPE and some other cyanide ion selective electrodes

Type of electrode	Linear range (M)	Slope (mV/decade)	Interference	Ref.
Solid state (topac commercial electrode)	5×10^{-5} to 1×10^{-2}	57 ± 2	I^-, Br^-, Cl^-, S^{2-}	[65]
Solid state (Radiometer commercial electrode)	5×10^{-7} to 10^{-3}	–	I^-, Br^-, S^{2-}	[66]
Solid state (Sentek commercial electrode)	10^{-5} to 10^{-2}	–	I^-, S^{2-}	[67]
pHoenix commercial cyanide electrode	5×10^{-6} to 10^{-2}	57 ± 2	S^{-2}, I^-, Br^-	[52]
Solid state (Orion 96-06 commercial electrode)	8×10^{-6} to 10^{-2}	58 ± 2	I^-, S^{2-}	[68]
Solid state (ELIT 8291 commercial electrode)	3.8×10^{-4} to 10^{-2}	56 ± 5	I^-, S^{2-}	[69]
Solid state (Ag_2S/Ag)	4×10^{-4} to 8×10^{-3}	–	—-	[70]
Solid state (Ag_2S/Ag)	$4 \times 10^{-4+}$ to 4×10^{-2}	120	—-	[54]
Solid state (AgI)	10^{-5} to 10^{-1}	∼57	I^-	[39]
Solid state (HgS/Hg_2I_2)	–	–	I^-, S^{2-}	[71]
Solid state (HgS/AgI)	–	–	I^-, S^{2-}	[71]
Solid state (Ag_2S/AgI)	–	–	I^-, S^{2-}, SCN^-	[71]
This electrode (CMCPE)	1.5×10^{-5} to 1×10^{-2}	60 ± 1.5	S^{2-}	

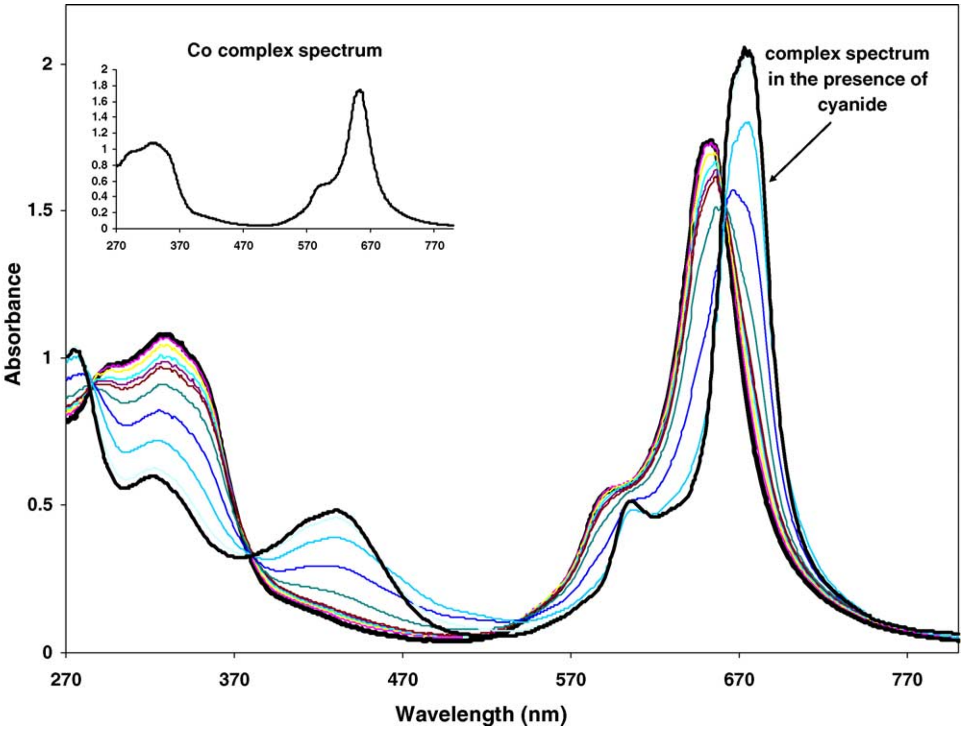

Fig. 5. Spectra of Co(3,4 tppa) in the absence and presence of CN^- ion in DMSO.

fore, CN^- as a strong donor and its implication as a weak π-acceptor manifest in the strong interaction of CN^- with the cobalt center of ionophore.

3.7. *Spectroscopic studies*

The UV–vis spectra of Co(3,4 tppa) in the absence and presence of cyanide ions in DMSO as solvent is demonstrated in Fig. 5. As shown in this figure the cobalt complex spectrum has a red shift when cyanide ligand coordinates to cobalt complex.

3.8. *Practical application*

For this purpose, we chose a commercially available spring water sample (Sepidan) and spiked some certain amounts of cyanide solution into it. The sample compositions of the Sepidan spring water are given in Table 5. Before spiking cyanide into sample solution, the pH value was adjusted by adding appropriate amounts of disodiumtetraborate salt and concentrated NaOH solution as buffering species, and suitable amounts of Na_2SO_4 as supporting electrolyte into certain volume of spring water sample. The amount of cyanide was measured for two spring water samples with cyanide concentrations of 5.98×10^{-5} and 7.94×10^{-4} M. The results of these measurements are shown in Table 6. As results show, this electrode can be used successfully for determination of cyanide in a real sample solution.

Table 5
Composition of Sepidan commercial spring water sample

Species	Concentration (ppm)
Magnesium	4
Calcium	55
Sodium	2
Potassium	0.4
Iron	0.048
Bicarbonates	171
Sulphate	6
Chlorides	8
Florides	0.5
Nitrates	6
Total hardness	130–150

Table 6
Determination of spiked cyanide in Sepidan commercial spring water

Concentration (mol/L)	No. of measurements	Average ($\bar{X}$)	Error (%)	R.S.D. (S.D./$\bar{X}$ × 100)
5.98×10^{-5}	6	5.92×10^{-5}	1.00	4.57
7.94×10^{-4}	5	8.09×10^{-4}	1.89	7.88

Conditions: pH = 10, 13.4% modifier, 0.1 M Na_2SO_4 assupporting electrolyte.

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