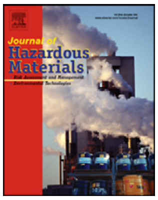
Journal of Hazardous Materials 178 (2010) 157–163

Contents lists available at ScienceDirect

Journal of Hazardous Materials

journal homepage: www.elsevier.com/locate/jhazmat



Preparation of a new chromium(III) selective electrode based on 1-[(2-hydroxy ethyl) amino]-4-methyl-9H-thioxanthen-9-one as a neutral carrier

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ARTICLE INFO

Article history:
Received 10 October 2009
Received in revised form 2 January 2010
Accepted 9 January 2010
Available online 18 January 2010

Keywords:
Chromium-selective electrode
Potentiometric sensor
Carbon paste electrode
1-[(2-hydroxy ethyl) amino]-4-methyl-9H-thioxanthen-9-one

ABSTRACT

A new chromium carbon paste electrode sensor based on a carbon paste electrode containing 1-[(2-hydroxy ethyl) amino]-4-methyl-9H-thioxanthen-9-one (AMTX) as new carrier has been prepared. The influence of carbon paste ingredients including sodium tetraphenylborate (NaTPB), ionophore, Nujol and graphite powder on the electrode response has been investigated. The best performance characteristics for the electrode was obtained with a carbon:NaTPB:Nujol:AMTX in the mass ratio of (400:1.43:57.2:3 mg) (86.65:0.31:12.39:0.65%). At the optimum value of all variables, the response of electrode is linear in range of 3.2×10^{-7} to 1.0×10^{-1} mol L^{-1} with a Nernstian slope of 20.51 mV decade^{-1} of Cr^{3+} ion concentration with detection limit of 1.6×10^{-7} mol L^{-1}. The electrode response is independent of pH in the range of 4.8–6.3, while the response time of the electrode was ~8 s. The potentiometric selectivity coefficients of proposed chromium-selective electrode towards various interfering ions were determined by fixed interference method (FIM), separate solution method (SSM) and matched potential method (MPM).

1. Introduction

Due to wide application of chromium compounds in modern industries, a large quantity of this element is being discharged into the environment. Chromium occurs in wastewaters in both trivalent Cr(III) and hexavalent Cr(VI) forms. The chromium toxicity depends critically on its oxidation state. While chromium (III) is considered essential for mammals for the maintenance of glucose, lipid and protein metabolism, chromium (VI) is known to be toxic for humans [1]. Therefore, development of accurate and reliable method for determination of chromium ion is very important [2–5].

Among the various applied analytical methods in this regard, ion-selective electrode as a simple method due to unique advantages such as speed and ease of electrode preparation and procedure, simple instrumentation, relatively fast response, wide dynamic range, reasonable selectivity and low cost widely has been used for this purpose [6].

Due to urgent need for accurate and selective determination of trace amounts of Cr^{3+} ions in food and water samples many coordination compounds have been used as ionophores in the construction of chromium-selective electrodes (ISEs) [7–14] (Table 1). Some of these electrodes suffer from limitations such as poor detection limit [7,9,10], narrow working concentration range [9,10,13] and narrow useful pH range.

A selective agent (ionophore) mixed thoroughly with carbon powder and paraffin oil which are named chemically modified carbon paste electrodes (CMCPEs) are easy to construct and present a stable electrochemical response while their surface can be renewed by removing an outer layer of the paste by re-smoothing the electrode surface. They have lower resistance than that of ion-selective electrodes based on polymeric membranes although in both of them selectivity and operation mechanism may be attributed to the modifier materials incorporated in carbon paste. These electrodes are superior to polymeric membranes electrode in terms of lower ohmic resistance and producing very stable response [15].

The operation mechanism of chemically modified electrodes (CMEs) depends on the properties of the modifier materials used to import selectivity towards the target species [16–25].

Our survey through literature reveals that thioxantone (TX) derivatives have been used efficiently as good ion carriers for preparation of ion-selective.

Hear in, we applied 1-[(2-hydroxy ethyl) amino]-4-methyl-9H-thioxanthen-9-one (Scheme 1) with unique ability to form highly selective 2:1 (TX:Cr ion) complex with Cr $^{3+}$ ion in a DMSO solvent for construction of chromium carbon paste electrode. The proposed electrode at optimum value of all effective variables has good characteristic performance without need to cut the dried membrane in the desired pieces and then glue it to one end of a Pyrex glass tube.

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0304-3894/$ – see front matter © 2010 Published by Elsevier B.V.
doi:10.1016/j.jhazmat.2010.01.057

Table 1
General performance characteristics of some chromium (III) ion sensors based on various organic ionophore.

Ionophore	L.R.[a]	Slope[b]	D.L. (μM)	pH	R.T.[d]	Reference
DMAAB	1.66–0.01	19.5 ± 0.6	0.8	3.0–5.5	10	[7]
GBHA	3–0.01	19.8 ± 0.5	0.63	2.7–6.5	<20	[9]
NBDA	1–0.1	19.9 ± 0.3	0.7	3.0–6.6	<12	[10]
AHMTO	1–0.1	19.7 ± 0.3	0.58	2.7–6.6	<10	[11]
NDAE	0.089–0.1	19.8	0.056	2.0–7.0	10	[12]
NTETA	0.83–0.1	19.5	0.63	2–5.5	22	[12]
ATCA	7–0.1	19.0	7.0	3.5–6.5	10	[13]
TOT	4–0.1	20.0 ± 0.1	0.2	2.8–5.1	15	[14]

[c] Interference; DMAAB 4-dimethylaminoazobenzene. GBHA, Glyoxal bis(2-hydroxyanil). NBDA, N-(1-thien-2-ylethylidene)benzene-1,2-diamine (SNS). AHMTO, 4-amino-3-hydrazino-6-methyl-1,2,4-triazin-5-one. NBAE, N-(acetoacetanilide)-1,2-diaminoethane. NTETA, N,N_-bis(acetoacetanilide)-triethylenetetraammine. ATCA, Aurin tricarboxylic acid modified silica. TOT, tri-*o*-thymotide.

[a] Linear range (μM-M).

[b] mV per decade concentration.

[d] Response time (s).

2. Experimental

2.1. Apparatus

All the potential and pH measurements were carried out with a pH/Ion meters model 691 (Metrohm). The UV–vis absorbance spectra were recorded on a PerkinElmer (Lambda 25) spectrophotometer with 1.0 cm glass cell.

2.2. Reagents and materials

All chemicals used were of analytical reagent-grade and doubly distilled water was used throughout. Graphite powder from Fluka (Buchs, Switzerland), sodium tetraphenylborate (NaTPB), dimethyl sulfoxide (DMSO) and tetrahydrofuran (THF) Dermasdat, Germany. Different surfactants including cetyl trimethyl ammonium bromide (CTAB), sodium dodecyl sulfate (SDS), Triton X-100 and Triton X-114 were purchased from Merck, the analytical grade nitrate and chloride salts of all the cations were purchased from Merck and Aldrich without any further purification. High purity Nujol oil was purchased from Fluka (Buchs, Switzerland) and used as received. The stock solution of 0.5 M chromium (III) ion was prepared by dissolving appropriate amount of chromium (III) nitrate form Merck in 100 mL of doubly distilled water.

2.2.1. Synthesis of 1-[(2-hydroxyethyl)amino]-4-methyl-9H-thioxanthen-9-one

An excess amount of 2-aminoethanol (3 mmol) was added to a solution of 1-fluoro-4-methyl-9H-thioxanthen-9-one (1 mmol) in dimethyl formamid (DMF) and was heated in an oil bath at 120 °C for 10 h till the color of the reaction mixture changed from yellow to red. The progress of reaction was monitored by thin layer chromatography (TLC). The obtained red solution was cooled and a yellow resulted suspension was diluted with cool water. The solid was filtered and washed with water and then dried at room temperature. The schematic diagram of ligand synthesis was pointed in Fig. 1. The ligand information is pointed out as following.

mp = 179–181 °C; IR (KBr, cm^{-1}): 3458 (b), 1600 (s), 1510 (s), 1271 (s), 1226 (s), 1068 (s); 1H NMR (CDCl3, 250 MHz) δ 10.46 (1H, s), 8.43 (1H, d, J = 7.9), 7.47–7.43 (1H, m), 7.37–7.31 (2H, m), 7.18 (1H, d, J = 8.5), 6.56 (1H, d, J = 8.5), 3.90 (2H, t, J = 5.4), 3.41 (2H, t, J = 5.4), 2.35 (3H, s); 13C NMR (DMSO-d6, 62.9 MHz) δ 181.9, 152.0, 136.4, 135.9, 135.0, 132.1, 129.4, 128.5, 126.4, 125.7, 117.3, 111.6, 107.3 59.1, 44.8, 18.4; MS: m/z (%) 285 (20.6, M^+), 254 (100), 226 (11.9), 149 (14.6). Anal. calc. for C16H15NO2S (258.36): C, 67.34; H, 5.30. Found: C, 67.38; H, 5.33.

2.3. Electrode preparation and potential measurements

Unmodified carbon paste was prepared by hand mixing of 86.7% (w/w) of reagent-grade graphite powder and 13.3% (w/w) of Nujol oil with a mortar and pestle. A modified paste was maxid the roughy according to optimum value of ingredients (graphite, Nujol, NaTPB and ligand in the ratio) pastes were packed into 5.0 mL polyethylene syringes, which electrical contact of the paste (2.5 mm diameter) was established via inserting a thin copper wire thorough flank. The surplus of paste was cut out with a glass rod and the exposed-end polished on a paper until the surface showed shiny appearance.

2.4. Cell potential measurements

The Cell potential measurements of proposed carbon paste electrode were carried out with the following cell assemblies: MCPE |sample solution| reference electrode [28]. All the potential observations were made relative to a double junction Ag/AgCl electrode with a pH/mV meter. The performance of the electrodes was investigated by measuring the cell potential of chromium nitrate solutions in the concentration range of 1×10^{-1} to 1×10^{-7} M by serial dilution. Each solution was stirred and the potential reading was recorded when it became stable and then plotted as a logarithmic function of Cr^{3+} ion concentration.

2.5. Spectrophotometric titrations

Standard stock solutions of ligands (1.0×10^{-3} M) and metal ions (1.0×10^{-3} M) and 0.05 M tetraethyl ammonium perchlorate (TEAP) for investigation of the effect of structure by spectrophotometric methods were prepared by dissolving exactly weighed (with an accuracy of 0.0001 g) pure solid compounds in 25.0 mL volumetric flasks and diluted up to mark with dimethyl sulfoxide (DMSO) as stock solution. Working solutions were prepared by appropriate dilution of the stock solutions. Titration of the ligand solution (3.8×10^{-5} M, 2.6 mL) was carried out by the addition of microliter amounts of a concentrated standard solution of the metal ion in solvent (1.0×10^{-3} M) using a pre-calibrated microsyringe [29,30].

2.6. Pre-treatment of real sample

2.6.1. Tea and coffee

1 g of the sample was placed in a beaker and 10 mL of HNO_3 and 4 mL of $HClO_4$ were added, followed by digestion on a hot plate until the organic residue was completely oxidized. The solution was finally diluted to 100 mL after filtering it through a filter paper (Whatman No. 1) [9,12].