A SELECTIVE COPPER(II) ELECTRODE BASED ON 2–ACETYLPYRIDINE –(1R)–(-)–FENCHONE AZINE LIGAND AND 2,6–DIACETYLPYRIDINE –DI–(1R)–(-)–FENCHONE DIAZINE LIGAND

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ABSTRACT

This study describe the construction and characteristics of polymeric membrane electrodes based on 2–acetylpyridine–(1R)–(-)–fenchone azine ligand (A) and 2,6–diacetylpyridine–di–(1R)–(-)–fenchone diazine ligand (B) for determination of copper(II) ions. Optimum performance was observed with a membrane composition (w/w) of A (6): PVC (40): DOP (56): NaTPB (1) for ionophore A and B (7): PVC (50): TMDP (86): NaTPB (1) for ionophore B. Membrane electrode A works satisfactorily in the concentration range of 1.0×10^{-5} to 1.0×10^{-1} M with a detection limit of 4.0×10^{-6} M and Nernstian slope of 30.0±0.2 mV/decade. Meanwhile, membrane electrode B works in the concentration range of 1.0×10^{-5} to 1.0×10^{-1} M with detection limit 2.5×10^{-6} M and Nernstian slope of 29.1±0.4 mV/decade. Both of these membrane electrodes exhibit wide pH range (4.0–5.0 and 6.0–10.0 for ligand A and 4.0–8.0 for ligand B) and posses a fast response time of below 20 s and also shelf life period of 3 months. The potentiometric selectivity coefficient values as determined by fixed interference method indicate excellent selectivity for copper(II) ions over interfering cations. Both electrodes was used in the determination of copper(II) in wastewater samples and the results were in agreement with an atomic absorption spectrometry method.

ELEKTROD PEMILIH KUPRUM(II) BERASASKAN LIGAN 2–ASETILPIRIDINA–(1R)–(-)–FENCON AZIN DAN LIGAN 2,6–DIASETILPIRIDINA–DI–(1R)–(-)–FENCON DIAZIN

ABSTRAK

Kajian ini menghuraikan pembinaan dan ciri-ciri elektrod membran polimer berasaskan ligan 2–asetilpiridina–(1R)–(-)–fencon azin (A) dan ligan 2,6–diasetilpiridina–di–(1R)–(-)–fencon diazin (B) bagi penentuan ion kuprum(II). Keupayaan optimum telah didapati dengan komposisi membran (w/w) A (6): PVC (40) : DOP (56): NaTPB (1) bagi inofor A dan B (7): PVC (50): TMDP (86): NaTPB (1) bagi inofor B. Elektrod membran A bekerja dengan baik dalam julat kepekatan 1.0×10^{-5} hingga 1.0×10^{-1} M dengan had pengesanan 4.0×10^{-6} M dan kecerunan Nernstian sebanyak 30.0±0.2 mV/dekad. Manakala, elektrod membran B pula bekerja dengan baik dalam julat kepekatan 1.0×10^{-5} hingga 1.0×10^{-1} M dengan had pengesanan 2.5×10^{-6} M dan kecerunan Nernstian sebanyak 29.1±0.4 mV/dekad. Kedua-dua elektrod membran menunjukkan julat pH yang luas (4.0–5.0 dan 6.0–10.0 untuk A dan 4.0–8.0 untuk B) dan memberikan masa gerak balas yang cepat di bawah 20 saat dan juga tempoh jangka hayat selama 3 bulan. Nilai pekali kepilihan potensiometrik ditentukan dengan kaedah penetapan gangguan menunjukkan kepilihan yang sangat baik terhadap kuprum(II) mengatasi kation-kation gangguan. Kedua-dua elektrod digunakan dalam penentuaan kuprum(II) di dalam sampel air buangan dan keputusan adalah setara dengan kaedah sprektrometri penyerapan atom.

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LIST OF ABBREVIATIONS

AAS	Atomic absorption spectrometry
Ag/AgCl	Silver-silver chloride
Ag_2S	Silver sulfide
APPT	2-acetylpyridine-4-phenyl-3-thiosemicarbazone
ARS	Alizarin red S
ASV	Anodic stripping voltammetry
BA	Benzyl acetate
BBPA	Bis(butylpentyl) adipate
BCB	Brilliant cresyl blue
BEHA	Bis(2-ethylhexyl) adipate
BEHS	Bis(2-ethylhexyl) sebacate
BHAB	Bis(2-hydroxyacetophenone) butane-2,3-dihydrazone
BHAPDMPDI	Bis(2-hydroxyacetophenone)-2,2-dimethyl-1,3-propanediimine
Br-PADAP	2-(5-bromo-2-pyridylazo)-5-(diethylamino-phenol)
CASV	Catalytic adsorptive stripping voltammetric
CNPE	Carbon nanotubes paste electrode
CPE	Cloud point extraction
CWEs	Coated wire electrodes
DBE	Dibenzyl ether
DBP	Dibutyl phthalate
DBS	Dibutyl sebacate
DDP	Didecyl phthalate
DMTD SAM	2,5-Dimercapto-1,3,4-thiadiazol self-assembled monolayer
DNP	Dinonylphthalate
DOP	Dioctyl phthalate
DOPP	Dioctylphenylphosphonate
DPASV	Differential pulse anodic stripping voltammetry
EDTA	Ethylenediaminetetraacetic acid
Emf	Electromotive force
ET-AAS	Electrothermal atomization-atomic absorption spectrometry

FAAS	Flame atomic absorption spectrometry
FDS	First-order derivative spectrophotometry
FETs	Field effect transistors
FIA	Flow injection analysis
FIM	Fixed interference method
FTIR	Fourier transform infrared
HCl	Hydrochloric acid
HDPB	Hexadecylpyridinium bromide
Hg/HgCl$_2$	Mercury-mercury chloride
HPLC	High performance liquid chromatography
HPSAM	H-point standard addition method
HTAB	Hexadecyltrimethylammonium bromide
ICP-MS	Inductively coupled plasma-mass spectrometry
ISEs	Ion selective electrodes
ISFETs	Ion selective field effect transistors
IUPAC	International union of pure and applied chemistry
KCl	Potassium chloride
KTpClPB	Potassium tetrakis(4-chlorophenyl)borate
LaF	Lanthanum fluoride crystal
LSASV	Linear scan anodic stripping voltammetry
MPM	Matched potential method
NaCl	Sodium chloride
NaF	Sodium fluoride
NaOH	Sodium hydroxide
NaTFPB	Sodium tetrakis(4-fluorophenyl)borate
NaTPB	Sodium tetraphenylborate
NMR	Nuclear magnetic resonance
o-NPOE	*Ortho*-nitrophenyloctyl ether
PAN	1-(2-pyridylazo)-2-naphthol
PCC	Phosphorylated cotton chelator
PVC	Poly (vinyl chloride)
RDS	Relative standard deviation
SAL-BH	Salicylaldehy debenzoyl hydrazone

SBs	Schiff bases
SPE	Solid phase extraction
SSM	Separate solution method
SWASV	Square wave anodic stripping voltammetry
T2EP	Tris(2-ethylhexyl) phosphate
TBP	Tributyl phosphate
T_g	Transition temperature
THF	Tetrahydrofuran
TMDP	Tetraethyl methylenediphosphonate
TOMACI	Trioctylmethylammonium chloride
TS-FF-AAS	Thermospray flame furnace atomic absorption spectrometry
UMEs	Ultra-microelectrodes

CHAPTER 1

INTRODUCTION

1.1 Introduction to Copper

Copper is a chemical element with the symbol Cu and atomic number 29. It is a ductile metal, with very high thermal and electrical conductivity. Pure copper is rather soft and malleable, and a freshly exposed surface has a pinkish or peachy color. Copper compounds are commonly encountered as salts of Cu^{2+}, which often impart blue or green colors to minerals such as turquoise and have been used historically widely as pigments.

Copper occurs naturally in the environment and spreads through the environment through natural phenomena. Humans widely use copper in the industries and in agriculture. Copper is often found near mines, industrial settings, landfills and waste disposals. Pure copper usually found in such minerals as azurite, malachite and bornite and in sulfides as in chalcopyrite, coveline, chalcosine or oxides like cuprite. Its unique chemical and physical properties have made it one of the most commercially important metals. Copper compounds are used as an agricultural pesticide, and to control algae in lakes and reservoirs. Copper can be released into the environment by both natural sources and human activities. Examples of natural sources are wind-blown dust, decaying vegetation, forest fires and sea spray. Examples of human activities that contribute to copper release are mining, metal production, wood production and phosphate fertilizer production.

The copper that released into environment will spread widely into either water sediment or soil particles. Copper also can be found in many kinds of food, in drinking water and in air. In food, copper can be found in whole grain cereals, legumes, oysters, organ meats, dark chocolate, vegetables, nuts, and shellfish. Copper also can be found in a trace element in every cell of the human body. Liver is the main store of copper, so the concentration of these mineral are highest in liver and less amounts found in the brain, heart, kidney and muscles.

One property of Cu that drives its diverse roles in structure and catalysis is its existence in either a reduced (Cu^+) state or an oxidized (Cu^{2+}) state. Although Cu is essential for many biological processes, Cu is also a potent anti-microbial weapon against invading pathogens. Indeed, Cu has been used as a bactericidal and fungicidal agent for over a century, with a notable use as the active ingredient in Bordeaux mixture, which protects grapes from fungal infection. Copper-containing amine oxidases, located around plant cell walls, utilize diamines and polyamines as substrates to produce hydrogen peroxide which has microbicidal activity. Copper also an essential micronutrient that plays a vital role as a catalytic co-factor for a variety of metalloenzymes. Approximately 90% of the copper in the blood is incorporated into a compound called ceruloplasmin, which is a transport protein responsible for carrying copper to tissues that need the mineral. In addition to its role as a transport protein, ceruloplasmin also acts as an enzyme, catalyzing the oxidation of minerals, most notably iron. The oxidation of iron by ceruloplasmin is necessary for iron to be bound to its transport protein so that it can be carried to tissues where it is needed (Brewer, 2010; Percival & Harris, 1990).

Superoxide dismutase is a copper-dependent enzyme that catalyzes the removal of superoxide radicals from the body. Superoxide radicals are generated during normal metabolism, as well as when white blood cells attack invading bacteria and viruses. If not eliminated quickly, superoxide radicals cause damage to cell membranes. When copper is not present in sufficient quantities, the activity of superoxide dismutase is diminished, and the damage to cell membranes caused by superoxide radicals is increased. When functioning in this enzyme, copper works together with the mineral zinc, and it is actually the ratio of copper to zinc, rather than the absolute amount of copper or zinc alone, that helps the enzyme function properly (Danks, 1988).

Copper also a component of lysyl oxidase, an enzyme that participates in the synthesis of collagen and elastin, two important structural proteins found in bone and connective tissue. Tyrosinase, a copper-containing enzyme, converts tyrosine to melanin, which is the pigment that gives hair and skins its color. As a part of the enzymes cytochrome c oxidase, dopamine hydroxylase, and Factor IV, copper plays a role in energy production, the conversion of dopamine to norepinephrine and blood clotting, respectively. Copper is also important for the production of the thyroid hormone called thyroxine and is necessary for the synthesis of phospholipids found in myelin sheaths that cover and protect nerves.

Copper deficiency produces an extensive range of symptoms. These symptoms include iron deficiency anemia, ruptured blood vessels, osteoporosis, joint problems, brain disturbances, increased susceptibility to infections due to poor immune function, loss of pigment in the hair and skin, weakness, fatigue, breathing difficulties, skin sores, poor thyroid function, and irregular heartbeat (Bonham, Connor, Hannigan, & Strain, 2002). Certain medical conditions including chronic diarrhea, celiac sprue, and Crohn's disease result in decreased absorption of copper and may increase the risk of developing a copper deficiency. In addition, copper requires sufficient stomach acid for absorption, so if you consume antacids regularly you may increase your risk of developing a copper deficiency. Inadequate copper status is also observed in children with low protein intake and in infants fed only cow's milk without supplemental copper.

Copper is an essential micronutrient involved in a variety of biological processes indispensable to sustain life. At the same time, it can be toxic when present in excess. Potent, efficient regulatory mechanisms control copper absorption in the digestive tract and copper biliary excretion; absorption ranges between 12% and 60% in humans, depending on copper intake, presence of other factors in the diet that may promote or inhibit its absorption and on the copper status of the individual (de Romana, Olivares, Uauy, & Araya, 2011).

1.2 Significance of Study

The existence of copper in our environment is very important as it is used for many industrial, agricultural and domestic purposes and also plays an important role in various biological processes (Mittal, Kumar, Gupta, Kaur, & Kumar, 2007). The Cu^{2+} ion at lower concentrations is an essential trace nutrient to all higher plant and animal life. In animals, including humans, it is found widely in tissues, with concentration in liver, muscle, and bone. It functions as superoxide dismutase, which detoxifies free radicals and as a co-factor in various enzymes and in copper-based pigments (Tyrala, Brodsky, & Auerbach, 1982).

Humans ingest about 1.0-3.0 mg/day. Copper may be stored in the liver, bound in part to metallothionein or secreted into plasma bound to ceruloplasmin, which transports 80% of plasma copper, or may be excreted in bile, perhaps bound to ceruloplasmin fragments. Our body can receive maximum level up to 2.0 mgL^{-1} of copper ions (Faust & Aly, 1987). Excessive intake of copper can cause abdominal pain and cramps, nausea, diarrhea, vomiting, and liver damage. In addition, some experts believe that elevated copper levels, especially when zinc levels are also low, may be a contributing factor in many medical conditions including schizophrenia, hypertension, stuttering, autism, fatigue, muscle and joint pain, headaches, childhood hyperactivity, depression, insomnia, senility, and premenstrual syndrome (Bertinato &

L'Abbé, 2004). Postpartum depression has also been linked to high levels of copper. This is because copper concentrations increase throughout pregnancy to approximately twice normal values, and it may take up to three months after delivery for copper concentrations to normalize (Stern, 2010).

Since excess copper is excreted through bile, copper toxicity is most likely to occur in individuals with liver disease or other medical conditions in which the excretion of bile is compromised. The toxic effects of high tissue levels of copper are seen in patients with Wilson's disease, a genetic disorder characterized by copper accumulation in various organs due to the inadequate synthesis of ceruloplasmin by the liver. Wilson's disease primarily affects the liver, kidneys, and brain causing degenerative physiological changes that are fatal if untreated (Gupta, Jain, Maheshwari, Lang, & Ishtaiwi, 2006; Gholivand, Rahimi-Nasrabadi, Ganjali, & Salavati-Niasari, 2007). Thus, in view of widespread use of Cu^{2+} ions, it is important to determine the copper ion in environmental samples in view of its utility as well as toxicity.

A necessary source of the information for the evaluation of the ecology state of the environment is the analytical control. The most critical characteristic in performing timely ecological monitoring of the objects of environment is analysis rapidity. A number of instrumental techniques such as atomic absorption spectrometry (AAS) (Hassan, Elnemma, & Mohamed, 2005; Stafilov, 2000; Zendelovska, Pavlovska, Cundeva, & Stafilov, 2001), inductively coupled plasma-optical emission spectroscopy (ICP-OES) (Takara, Pasini-Cabello, Cerutti, Gasquez, & Martinez, 2005; Bezerra, dos Santos, Lemos, Korn, & Ferreira, 2007), anodic stripping voltammetry (Lima, Rangel, & da Silva, 1990), flame atomic absorption spectroscopy (FAAS) (Elci, Soylak, & Ozcan, 2003; Saber-Tehrani, Rastegar, Parchehbaf, & Rezvani, 2005), stripping voltammetry (Safavi, Maleki, Shams, & Shahbazi, 2002), and inductively coupled plasma-mass spectrometry (ICP-MS) (Jungová, Navrátilová, Peš, Vaculovič, Kanický, Šmarda et al., 2010) are used for determination of trace metal ions in environmental. Even, these techniques provide accurate results but are time consuming and require adequate expertise, large scale infrastructure back up. Further their maintenance and operational cost is high and therefore not very appropriate for routine analysis for large number of environmental samples. Thus, a reliable, low cost, quick and portable analytical technique is needed and such requirements are generally met with ion selective electrodes (ISEs) to a significant extent.

ISE are versatile device with variety of chemical and medical application for analysis of inorganic and organic ion. Since they are often non-destructive, adaptable to small sample volume and require minimum chemical manipulation in sample preparation (Buhlmann, Pretsch, & Bakker, 1998). ISE are potentiometry sensor characterized by the fact that the electrochemical response is usually dominated by one ionic species presented in the solution, known as the primary ion (analyte ion, target ion) and the potential of the electrode depend on the concentration of the primary ion following Nernst equation (Fakhari, Raji, & Naeimi, 2005; Pungor, 1997).

Since the 1970s, it has been reported that ion selective electrodes (ISE) are part of a group of relatively simple and inexpensive analytical tools which are commonly referred to as sensors (Khuri, Hajjar, & Agulian, 1972; Buhlmann, Pretsch, & Bakker, 1998; Gupta & Kumar, 1999; Gupta, Pal, & Sharma, 2010). Numerous publications on neutral-carrier and ion-exchanger based ISEs and their application can be found in specialized publications as a part of the general area of chemical sensors (Janata, Josowicz, & DeVaney, 1994; Janata & Bezegh, 1988) or as a class of its own (Solsky, 1990). Other reviews discuss the use of potentiometric selective electrodes for water analysis (MacCarthy, Klusman, Cowling, & Rice, 1991) and biochemical applications (Wang, Lin, Eremenko, Kurochkin, & Mineyeva, 1993). General guidelines for the use of ISEs in environmental applications (Fucskó, Tóth, Pungor, Kunovits, & Puxbaum, 1987) and as detectors for flow systems (Pungor, Tóth, & Hrabéczy-páll, 1984) have also been reported.

It has not been possible to develop a good ISE for Cu^{2+} mainly owning to non-availability of selective ionophores. To prepare a good ISE for Cu^{2+}, an ionophores which shows high affinity for copper and poor for other is required. Such ionophores if present in a membrane would only allow copper ions to pass through and restricts the passage of others. Recently, a number of attempts have been made to develop Cu^{2+} selective sensors. A literature survey revealed that the sensor developed for copper make use of calixazacrown ethers, thiacrown ethers, bis(acetylacetone) propylenediimine, and Schiff Base complexes (Park, Shon, Rim, Lee, Kim, Nam et al., 2001; Brzozka, 1988; Gupta, Goyal, Bachheti, Singh, & Agarwal, 2005; Singh & Bhatnagar, 2004). However most of them suffer from disadvantages such as narrow working concentration range, high response time, poor detection limits and poor interfering effect of cations such as Li^{+}, K^{+}, Hg^{2+}, Cd^{2+}, Zn^{2+}, Ca^{2+}, Pb^{2+}, and Co^{2+}.

1.3 Electrochemistry

Electrochemistry is the branch of chemistry concerned with the interrelation of electrical and chemical effects. A large part of this field deals with the study of chemical changes caused by the passage of an electric current and the production of electrical energy by chemical reactions. In fact, the field of electrochemistry encompasses a huge array of different phenomena, devices and technologies. Scientists make electrochemical measurements on chemical systems for a variety of reasons. They may be interested in obtaining thermodynamic data about a reaction. They may want to generate an unstable intermediate such as a radical ion and study its rate of decay or its spectroscopic properties. They may seek to analyze a solution for trace amounts of metal ions or organic species. In these examples, electrochemical methods are employed as tools in the study of chemical systems in just the way that spectroscopic methods are frequently applied.

There are also investigations in which the electrochemical properties of the systems themselves are of primary interest, for example, in the design of a new power source or for the electrosynthesis of some product. Many electrochemical methods have been devised. Their application requires an understanding of the fundamental principles of electrode reactions and the electrical properties of electrode–solution interfaces.

Electroanalytical chemistry encompasses a group of qualitative and quantitative analytical methods based on the electrical properties of a solution or the analyte when it is made part of an electrochemical cell. Electroanalytical chemistry plays a very important role in the protection of our environment. In particular, electrochemical sensors and detectors are very attractive for on-site monitoring of priority pollutants, as well as for addressing other environmental needs. Such devices satisfy many of the requirements for on-site environmental analysis. They are inherently sensitive and selective towards electro-active species, fast and accurate, compact, portable and inexpensive. Such capabilities have already made a significant impact on decentralized clinical analysis. Yet, despite their great potential for environmental monitoring, broad applications of electrochemical sensors for pollution control are still in their infancy (Skoog, Holler, & Crouch, 2007).

Electrochemical sensors are essentially an electrochemical cell which employs a two or three electrode arrangement. Electrochemical sensor measurement can be made at steady-state or transient. The applied current or potential for electrochemical sensors may vary according to the mode of operation, and the selection of the mode is often intended to enhance the sensitivity and selectivity of a particular sensor (Liu, 2000). Several electrochemical devices have been used routinely for years in environmental analysis. Recent advances in electrochemical sensor technology will certainly expand the scope of these devices towards a wide range of organic and inorganic contaminants and will facilitate their role in field analysis. These advances include the introduction of modified or ultramicroelectrodes, the design of highly selective chemical or biological recognition layers, of molecular devices or sensor arrays, and developments in the areas of microfabrication, computerized instrumentation and flow detectors.

The purpose of a chemical sensor is to provide real-time reliable information about the chemical composition of its surrounding environment. Ideally, such a device is capable of responding continuously and reversibly and does not perturb the sample. Such devices consist of a transduction element covered with a biological or chemical recognition layer. In the case of electrochemical sensors, the analytical information is obtained from the electrical signal that results from the interaction of the target analyte and the recognition layer (Bard & Faulkner, 2001; Koryta, Dvorak, & Kavan, 1993). According to Frant and Ross (1970) electrochemical sensor can be categorized by their mode of measurements, that is into potentiometric (measurement of voltage), amperometric (measurement of current) and conductimetric (measurement of conductivity) sensors. Potentiometry is the most commonly used of the electrochemical sensor and involves the measurement of potential generated by a cell under essentially equilibrium condition.

1.3.1 Potentiometry

Potentiometry is an electroanalytical method which is based on measurement of potential of an electrode system and measured under the conditions of no current flow. Potentiometric measurements enable selective detection of ions in presence of other substances. The measured potential may then be used to determine the analytical quantity of interest, generally the concentration of some component of the analyte solution. The potential that develops in the electrochemical cell is the result of the free energy change that would occur if the chemical phenomena were to proceed until the equilibrium condition has been satisfied (Bakker & Pretsch, 2002).

This concept is typically introduced in quantitative analysis courses in relation to electrochemical cells that contain an anode and cathode. For these electrochemical cells, the potential difference between the cathode electrode potential and the anode electrode potential is the potential of the electrochemical cell. If the reaction is conducted under standard state conditions, it allows the calculation of the standard cell potential. When the reaction conditions are not standard state, however, one must utilize the Nernst equation (equation 1.1) to determine the cell potential, as:

$$E_{cell} = E^{\circ} - \frac{RT}{nF} \ln Q \qquad (1.1)$$

Where E_{cell} is a cell potential, E° is a standard cell potential at the temperature of interest, n is the number of moles of electrons transferred in the cell reaction and Q represent the reaction quotient. Respectively R, T and F have their conventional meanings as gas constant, absolute temperature and Faraday constant.

Physical phenomena which do not involve explicit redox reactions, but whose initial conditions have a non-zero free energy, also will generate a potential. An example of this would be ion concentration gradients across a semi-permeable membrane. This can also be potentiometric phenomena, and is the basis of measurements that use ion-selective electrodes.

Potentiometric sensors are essentially passive electrochemical devices, in which changes in the electromotive force (emf) are monitored under virtually zero current conditions. In so-called direct potentiometry, the emf is ideally a function of the activity of only one chosen sample ion so that it can be selectively assessed in the