DETERMINATION OF MERCURY(II) BY SINGLE-WALLED CARBON NANOTUBES PASTE ELECTRODE MODIFIED WITH ZINC/ALUMINIUM LAYERED DOUBLE HYDROXIDE-3(4-METHOXYPHENYL) PROPIONATE NANOCOMPOSITE

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ABSTRACT

This study aimed to develop a mercury(II) sensor and to identify its ability in mercury(II) determination. A mercury(II) sensor was developed by using single-walled carbon nanotubes (SWCNTs) paste electrode modified with Zn/Al layered double hydroxide-3(4-methoxyphenyl)propionate nanocomposite (Zn/Al-LDH-MPP). Determination of optimum conditions for the detector was done by voltammetry method and subsequently confirmed by the double potential-step chronocoulometry. The results show that the optimum conditions were observed at electrode composition 2.5% (w/w) of Zn/Al-LDH-MPP/SWCNTs, 0.4 M potassium chloride, pH 4.0, and scan rate of 100 mV s^{-1}. The sensor exhibited wide linear range from 1.0 $\times 10^{-7}$ M to 1.0 $\times 10^{-3}$ M mercury(II) and 1.0 $\times 10^{-9}$ M to 1.0 $\times 10^{-7}$ M mercury(II), with a detection limit of 1.0 $\times 10^{-10}$ M mercury(II). The high sensitivity of the proposed electrode towards mercury(II) was confirmed by double potential-step chronocoulometry which indicated these values; diffusion coefficient: 1.5445 x 10^{-9} cm^2 s^{-1}, surface charge: 524.5 μC $s^{-½}$ and surface coverage: 4.41 x 10^{-2} mol cm^{-2}. The presence of 25-fold concentration of most metal ions had no influence on the anodic peak current. The analysis of real samples were also compared with those obtained by the proposed electrode and the mercury analyzer, which shows no significant difference between the results obtained by the two methods based on a *t*-test (at 95% confidence level). Thus, it can be concluded that the paste electrode modified with Zn/Al layered double hydroxide-3(4-methoxyphenyl)propionate nanocomposite (Zn/Al-LDH-MPP) is able to detect mercury(II). With characteristics such as high sensitivity, selectivity and repeatability, the electrode is proposed as the appropriate alternative for the determination of mercury(II).

PENENTUAN MERKURI(II) DENGAN ELEKTROD PES NANOTIUB KARBON BERDINDING TUNGGAL TERUBAH SUAI DENGAN NANOKOMPOSIT ZINK/ALUMINIUM LAPISAN BERGANDA HIDROKSIDA-3(4-METOKSIFENIL)PROPIONAT

ABSTRAK

Kajian ini bertujuan untuk membangun satu pengesan merkuri(II) dan mengenal pasti kebolehannya dalam penentuan merkuri(II). Pengesan merkuri(II) telah dibangunkan dengan menggunakan elektrod pes nanotiub karbon berdinding tunggal (SWCNT) terubah suai dengan nanokomposit zink/aluminium lapisan berganda hidroksida-3(4-metoksifenil)propionat (Zn/Al-LDH-MPP). Keadaan optimum pengesan ini kemudiannya ditentukan dengan kaedah voltammetri dan seterusnya disahkan melalui kronokulometri langkah keupayaan berganda. Dapatan menunjukkan keadaan optimum pengesan merkuri(II) adalah pada komposisi elektrod 2.5 % (w/w) Zn/Al-LDH-MPP/SWCNT, 0.4 M kalium klorida, pH 4.0 dan kadar imbasan 100 mV s^{-1}. Pengesan ini mempamerkan julat linear yang luas daripada 1.0×10^{-7} M sehingga 1.0×10^{-3} M merkuri(II) dan 1.0×10^{-9} M sehingga 1.0×10^{-7} M merkuri(II), dengan had pengesanan 1.0×10^{-10} M merkuri(II). Kepekaan yang tinggi oleh elektrod cadangan terhadap merkuri(II) telah disahkan melalui kronokulometri langkah keupayaan berganda yang menunjukkan nilai-nilai ini; pekali pembauran: 1.5445×10^{-9} cm^2 s^{-1}, cas permukaan: 524.5 μC $s^{-1/2}$ dan litupan permukaan: 4.41×10^{-2} mol cm^{-2}. Kehadiran 25 kali ganda kepekatan kebanyakan ion logam tidak memberi sebarang pengaruh terhadap arus puncak anodik. Analisis kajian terhadap sampel sebenar juga dibandingkan dengan yang diperoleh oleh elektrod yang dicadangkan dan penganalisa merkuri, menunjukkan tiada perbezaan yang signifikan antara keputusan yang diperoleh menggunakan kedua-dua kaedah berdasarkan ujian-t (pada 95% tahap keyakinan). Dengan ini dapat disimpulkan bahawa elektrod pes nanotiub karbon berdinding tunggal (SWCNT) terubah suai dengan nanokomposit zink/aluminium lapisan berganda hidroksida-3(4-metoksifenil)propionat (Zn/Al-LDH-MPP) mampu mengesan merkuri(II) dengan baik. Berdasarkan ciri-ciri seperti kepekaan yang tinggi, kepilihan dan keboleh ulangan, elektrod ini dicadangkan sebagai alternatif yang sesuai bagi penentuan merkuri(II).

TABLE OF CONTENTS

CHAPTER 2 LITERATURE REVIEW

CHAPTER 3 METHODOLOGY

CHAPTER 4 RESULTS AND DISCUSSION

CHAPTER 5 CONCLUSION

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

Ag/AgCl	Silver/silver chloride reference electrode
ASV	Anodic stripping voltammetry
AuNPs	Gold nanoparticle
CE	Counter electrode
CME	Chemically modified electrode
CNTs	Carbon nanotubes
CPE	Carbon paste electrode
CV	Cyclic voltammetry
DPV	Differetial pulse voltammetry
E	Measured electrode potential
E°	Standard electrode potential
E_{p}	Peak separation
E_{pa}	Potential of anodic peak
E_{pc}	Potential of cathodic peak
FESEM	Field emission scanning electron microscope
FI	Flow injection
FTIR	Fourier transform infrared spectroscopy
GCE	Glassy carbon electrode
Hg/HgO	Mercury/mercuric oxide reference electrode
ICP-AES	Inductive couple plasma-atomic emission spectrometry
ICP-mass	Inductive couple plasma mass spectrometry

IDICP-mass	Isotopic dilution cold vapour inductive couple plasma mass spectrometry
i_p	Peak current
I_{pa}	Anodic peak current
I_{pc}	Cathodic peak current
LDHs	Layered double hydroxides
LOD	Limit of detection
LSASV	Linear sweep anodic stripping voltammetry
LSV	Linear sweep voltammetry
MWCNT	Multi wall carbon nanotube
RE	Reference electrode
SDS	Sodium dodecyl sulphate
SEM	Scanning electron microscope
SPBiE	Screen printed bismuth electrode
SPCE	Screen printed carbon electrode
SWASV	Square wave anodic stripping voltammetry
SWCNT	Single wall carbon nanotube
WE	Working electrode
Zn/Al-LDH-MPP	Zn/Al layered double hydroxide-3(4-methoxyphenyl)propionate
ΔE_p	Peak potentials separation

CHAPTER 1

INTRODUCTION

1.1 Electrochemical Sensors

A chemical sensor can be defined as a small device operated for direct measurement of analyte in the sample matrix. This device is amazingly adequate to respond continuously and reversibly without disturbing the samples. Since both the sample handling and measurement steps were combined, sample collection and preparation were no longer required in such device (Ardakani & Mohseni, 2011). The transduction element presents in the chemical sensors enable this device to act as a transducer and convert various forms of energy into a measurable signal (Carpenter, Mathur & Kolmakov, 2012). The transduction elements were commonly incorporated with chemically responsive layers that will react to the desired analyte (Ardakani & Mohseni, 2011). This recognition layer is important as there are limitless traceable chemicals that were significantly involved in various industries, such as clinical, mining and automobiles.

To ensure that the chemical sensor is capable in analysing the target compound, it is indeed compulsory for the chemically responsive layer to selectively interact with the trace compounds. This interaction will alter the properties of the transducer, hence any changes on the sensor signal can be observed. If the chemical sensor is applicable to the determination of desired compounds at a very low level, highly selective and great cost-effectiveness, there is a high possibility for the particular chemical sensor to enter a variety of markets (Carpenter et al., 2012).

Chemical sensors may vary from one kind to another due to various combinations of responsive elements and signal transducers in the sensor. Electrochemical sensor which is classified as an important subclass of chemical sensor is practically using an electrode as the transduction element (Zhang, Ju & Wang, 2008). The signals from the sensor can be measured either at the stable or impermanent state (Liu, 2006). This sensor is more prominent compared to the other kind of chemical sensors as it is widely applied in many areas such as medical, industrial, environmental and cultivation analysis (Zhang et al., 2008). This occurrence probably due to several benefits that electrochemical technique seems to offer, including remarkable sensitivity and selectivity (Fu et al., 2010), user-friendliness, cost-effectiveness (Hezard et al., 2012) and highly relevant for in-situ monitoring in environmental waters (Wei et al., 2011).

Electrochemical sensors are commonly classified into several dominant classes, which are; conductivity, potentiometric, amperometric and voltammetric sensors. Both amperometric and voltammetric sensors are distinguished from other sensors on the basis of their current–potential relationship with the electrochemical system. Hence, amperometric sensors may also be categorised as a subclass of voltammetric sensors (Liu, 2006).

1.1.1 Conductometric Sensors

Conductometric sensors refer to the electrochemical sensor that produces signals based on the electrolyte conductivity measured. The signals produced depends on the number of the mobile charge carrier in the electrolyte, and are greatly influenced by the surrounding conditions. The sensor commonly operates using alternating current supply to measure conductivity (Wang et al., 2008). In the conductometric sensors, the conductivity of electrolyte, G is directly proportional to the specific conductivity of the electrolyte σ (cm^{-1}) and cross-sectional area perpendicular to the electrical field A (cm^{2}), but inversely proportional to the segment of the electrolyte along the electrical field, L (cm). This relationship can be simplified as shown in Equation 1.1:

$$G = \sigma A/L \tag{1.1}$$

Equivalent conductance and molar conductivity are two terms which are often used in describing the conductivity of electrolyte. Equivalent conductance is influenced by the concentration and the strength of the electrolyte. If the solution used as the electrolyte is a strong electrolyte, it will completely ionise into ionic forms (Liu, 2006). The molar conductivities increase linearly with the square root of concentration at very low concentration (Gelhaus & Lacourse, 2005). This theory, however, can only be applied for a strong electrolyte as weak electrolyte is only capable to ionise into respective ions until a limited extent. Furthermore, the degree of ionisation for weak electrolyte is greatly influenced by temperature (Liu, 2006).

The conductivity measurement of electrolyte is commonly intricate by the polarization process occurred on the electrode at the operating potential. Since this occurrence may result from the faradaic processes that take place at the electrode surface, it is preferable for the conductometric sensors to operate at potential where faradaic processes is absent. Another factor that should be monitored thoroughly is the formation of double layer adjacent to each electrode surface when a potential is applied to the sensor. This is because the layers might interfere and disturb the interpretation of the conductivity measurement. The effect of both factors can be reduced by using a high-frequency and low amplitude alternating current. Applying greater frequency and lower amplitude of alternating current will lead the measured conductivity closer to the true conductance of the electrolyte (Liu, 2006).

The cross-sectional area practically represents the surface area of the electrodes whereas the segment of the solution along the electrical field refer to the distance between the two electrodes. The specific conductivity of the electrolyte exhibit a linear relationship with the concentration and the magnitude of the charges of the ionic species

(Liu, 2006). Since the conductivity is related quantitatively to the ion concentration, this instrument is capable to be applied for sensing purpose (Wang et al., 2008).

1.1.2 Potentiometric Sensors

Potentiometric sensor is a sensor that measures the activity of desired species in the forms of potential. The potential is often produced in a redox reaction which occurs on the interface of electrode-electrolyte in an electrochemical cell. Even though redox reaction refers to the simultaneous reaction of both oxidation and reduction process that take place in an electrochemical cell, only either one of the half-cell reactions will be considered for sensing purposes. The other half-cell reaction is preferably reversible or non-interfering. (Liu, 2006).

$$E = E^{\circ} + \frac{RT}{nF} \ln \frac{a_{ox}}{a_{red}} \tag{1.2}$$

where E is the measured electrode potential, E^{o} is the standard electrode potential, R is the gas constant, T is the temperature in the absolute scale, n is the number of exchange electrons, F is the Faraday constant, while a_{ox} and a_{red} are the ion activities of oxidation and reduction respectively (Fauvarque & Simon, 2010).

Potentiometric sensor can be divided based on the indicator electrode, whether the electrode is inert or active. An inert electrode such as gold and platinum are not involved in the half-cell reaction. However, the catalytic surface for the reaction will still be provided by this electrode indeed. Unlike inert electrode, active electrode will participate in the half-cell reaction, either as an ion donor or ion accepter. Few types of the active electrodes may include the metal/metal ion, the metal/insoluble salt or oxide and metal/metal chelate electrodes. In order to complete the circuit, it is compulsory for the potentiometric sensor to have a reference electrode, so that a non-interference half-cell reaction can take place. The most often used reference electrodes are silver-silver chloride and calomel (Liu, 2006).

The potential difference between the reference electrode and the indicator electrode of potentiometric sensor is commonly measured without polarising the electrochemical cell, hence only a relatively small amount of current is allowed. The reference electrode is important as it will ensure a constant half-cell potential is achieved, whereas the indicator electrode is necessary to produce a variable potential based on the activity or concentration of desired analyte in the solution. The change in potential and the concentration is associated with a means of a logarithm (Wang et al., 2008).

The potential cannot be applied to quantify the desired ion if more than a single type of ion contributes in the measurement of potential in Equation 1.2. Hence, the surface of the active electrodes is usually integrated with a certain functional membrane that has the ability to selectively allow desired ion to diffuse through (Liu, 2006). The membrane can either in the form of solids, such as glass and inorganic crystal, or plasticised polymer (Wang et al., 2008). Several unique properties of the membrane, including ion-selective, ion-permeable or ion-exchange properties will gradually reduce the ionic interference of the potentiometric sensor. It is necessary for the potential measurement to be conducted under zero-current condition in practical sensing purpose, as the potentiometric sensors work at thermodynamic equilibrium environment (Liu, 2006).

1.1.3 Voltammetric Sensors

Voltammetric sensor is a sensor that applies the current-potential relationship of electrochemical cell for a sensing purpose. Voltammetric sensors generally study the concentration effect of the target analyte toward a current-potential characteristic of the respective redox reaction involved. These characteristics are directly determined by the mass transfer rate of the reaction onto the electrode surface and by the kinetic of the faradaic process which occurred on the electrode surface. The rate of faradaic process in the electrochemical cell, which is determined from the electrode reaction kinetics and mass transfer process has become the fundamental to the operation of the voltammetric sensor (Liu, 2006).

The basic requirements needed for this sensor are electrochemical cell (with three system electrodes immersed in supporting electrolyte), potentiostat and a plotter. Other components may be necessary, depending on the specific voltammetric experiments employed (Wang, 2006). Voltammetric method is conducted by varying the potential difference between a reference electrode and a working electrode

(Rouessac & Rouessac, 2007). The reference electrode is used to measure the potential between the reference electrode and the working electrode, so that the chemical reaction can be controlled (Farrarons & Català, 2011). It is crucial to be particular in choosing a suitable reference electrode, as the performance of a reference electrode is significantly influenced by the medium used. For example, if the electrolyte used is an alkaline aqueous medium, Hg/HgO is preferable. However, if the electrode is in an acidic medium, it is better to use Ag/AgCl as the reference electrode (Fauvarque & Simon, 2010).

This working electrode is the electrode that will serve as a surface for the occurrence of redox reaction (Farrarons & Català, 2011). Therefore, the selectivity and sensitivity of the voltammetric methods greatly depend on the materials of the working electrode. An excellent working electrode should be able to produce a great reproducible response and have high signal-to-noise characteristics. Thus, the selection of working electrode should be based on the redox behaviour of the desired analyte and background current the potential region needed for the measurement. Nevertheless, other crucial characteristics such as potential window, electrical conductivity, surface reproducibility, mechanical properties, cost, availability and toxicity should be considered indeed (Wang, 2006). The working electrode, or also known as an indicator electrode is commonly made up from carbon, platinum, gold or mercury as they may operate in a wide potential range (Rouessac & Rouessac, 2007).

The third electrode, which is made up from inert metal or carbon is called the counter electrodes (Rouessac & Rouessac, 2007). The counter electrode provides the current needed for the reaction at working electrode (Farrarons & Català, 2011). It is better to choose larger double layer capacitor electrode as the counter since this electrode will not contaminate the electrolyte used (Fauvarque & Simon, 2010). The three electrodes systems frequently immersed in a medium that is made up of solvent containing supporting electrolyte. The selection of solvent is commonly based on the solubility and redox reaction of target species. Other considerations may include the solvent properties, such as electrical conductivity, electrochemical activity and chemical reactivity. It is also crucial for the solvent to be unreactive toward target species and will not involve in an electrochemical reaction over a wide potential range.

Although water is frequently used as a solvent, other non-aqueous solvents such as acetonitrile and methanol may also be considered in certain procedures. The supporting electrolyte should as well be added into the medium as it reduces the resistance of the solution, avoids electromigration effect and ensures a constant ionic strength. Potassium chloride, ammonium chloride and hydrochloric acid are some of the commonly used supporting electrolyte in a voltammetric measurement. Buffer system is often applied when pH control is compulsory (Wang, 2006). The schematic diagram of an electrochemical cell for voltammetric measurement is shown in Figure 1.1.

In any electroanalytical voltammetric procedures, the electrochemical cell must be connected to a potentiostat. This instrument will control the voltage that passes through working and a counter electrode pair. This ensures the balance of potential

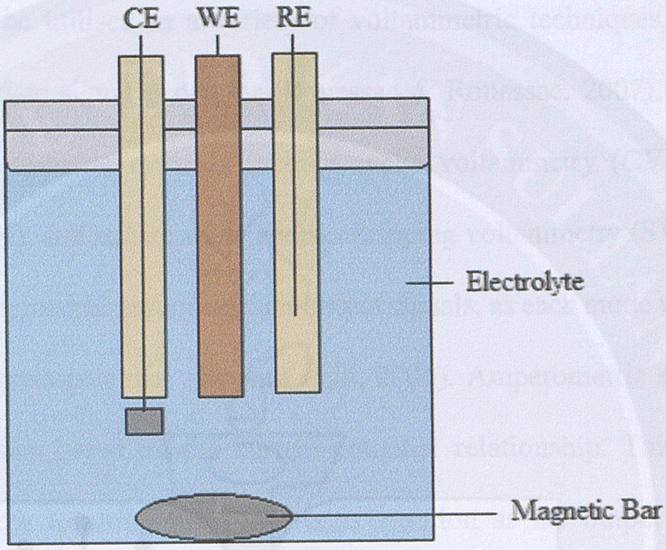

Figure 1.1. Schematic diagram of an electrochemical cell for voltammetric measurement; CE is the counter electrode, WE is the working electrode and RE is the reference electrode