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DETERMINATION OF SULFUR COMPOUNDS IN PETROLEUM DISTILLATES BY VOLTAMMETRY USING BISMUTH ELECTRODE

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A Thesis Submitted in Partial Fulfillment of the Requirements
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ศิริพรรณ สาคร : การตรวจวัดสารประกอบซัลเฟอร์ในปิโตรเลียมดิสทิลเลตด้วยเทคนิคโวลแทมเมทตรี บนขั้วไฟฟ้าบิสมัต. (DETERMINATION OF SULFUR COMPOUNDS IN PETROLEUM DISTILLATES BY VOLTAMMETRY USING BISMUTH ELECTRODE) อ. ที่ปรึกษาวิทยานิพนธ์หลัก : อ.ดร.เจริญขวัญ ไกรยา, 86 หน้า.

งานวิจัยนี้จึงได้อธิบายการตรวจวัดปริมาณสารประกอบซัลเฟอร์ในปิโตรเลียมดิสทิลเลตด้วยเทคนิคโวลแทมเมตรี โดยใช้ขั้วไฟฟ้าบิสมัตเป็นขั้วไฟฟ้าใช้งาน อิทธิพลของความเข้มข้นของบิสมัต ศักย์ไฟฟ้าที่ใช้ในการเกาะติด และเวลาที่ใช้ในการเกาะติดเพื่อ ให้ได้มาถึงภาวะการเตรียมขั้วไฟฟ้าบิสมัตที่เหมาะสม ผลการศึกษาพบว่าภาวะที่เหมาะสมสำหรับเตรียมขั้วไฟฟ้าบิสมัต คือ ความเข้มข้นบิสมัตที่ 0.5 พีพีเอ็ม บนขั้วไฟฟ้ากล๊าสซีคาร์บนที่ศักย์ไฟฟ้า –1.2 โวลต์ เป็นเวลา 60 วินาที จากนั้นตรวจสอบพื้นผิวของขั้วไฟฟ้าบิสมัตด้วยเทคนิคกล้องจุลทรรศน์แบบส่องกราด และภายใต้ภาวะที่เหมาะสมขั้วไฟฟ้าแบบอิน-ซิทูและเอกซ์-ซิทูได้ถูกตรวจสอบ พบว่าขั้วไฟฟ้าแบบอิน-ซิทูให้ช่วงความเป็นเส้นตรงในช่วง 49.9 – 248.8 นาโนโมลาร์ และ 2.5 – 20 ไมโครโมลาร์ สำหรับไดเฟนิลไดซัลไฟด์และบิวเทนไธออล ตามลำดับ ในขณะที่ขั้วไฟฟ้าแบบเอกซ์-ซิทูมีช่วงความเป็นเส้นตรงที่ 25.0 – 149.5 นาโนโมลาร์ สำหรับไดเฟนิลไดซัลไฟด์ และ 2.5 – 20 ไมโครโมลาร์ สำหรับบิวเทนไธออล มีขีดจำกัดการตรวจวัดที่ 19.1 และ 12.5 นาโนโมลาร์ สำหรับไดเฟนิลไดซัลไฟด์ และ 1.2 และ 1.4 สำหรับบิวเทนไธออล สุดท้ายได้นำขั้วไฟฟ้าบิสมัตไปใช้วิเคราะห์ปรมาณสารประกอบซัลเฟอร์ในตัวอย่างน้ำมันเครื่องบินและน้ำมันก๊าด พบว่าน้ำมันเครื่องบินและน้ำมันก๊าด มีปริมาณไดเฟนิลไดซัลไฟด์และบิวเทนไธออลประมาณ 230.4 ± 0.1, 102.9 ± 0.1 นาโนโมลาร์ 12.2 ± 0.3 และ 5.2 ± 0.3 ไมโครโมลาร์ ตามลำดับ

สาขาวิชา...ปิโตรเคมีและวิทยาศาสตร์พอลิเมอร์...ลายมือชื่อนิสิต ……………………………………..

ปีการศึกษา......................2553..........................ลายมือชื่อ อ.ที่ปรึกษาวิทยานิพนธ์หลัก…………

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KEYWORDS : SULFUR COMPOUNDS/ PETROLEUM DISTILLATED/ BISMUTH ELECTRODE / SQUARE WAVE VOLTAMMETRY

SIRIPUN SAKORN: DETERMINATION OF SULFUR COMPOUNDS IN PETROLEUM DISTILLATES BY VOLTAMMETRY TECHNIQUE ON BISMUTH ELECTRODE. ADVISOR: CHAROENKWAN KRAIYA, Ph.D., 86 pp.

This research describes a trace level sulfur determination in petroleum distillated using voltammetry technique. A bismuth electrode was a working electrode. To obtain an optimal conditions for bismuth modified electrode, the influences of bismuth concentration, deposition potential and time on the analyte signal were investigated. The result shown that the bismuth modified electrode was best prepared by electrodeposition of 0.5 ppm bismuth onto the glassy carbon electrode (GCE) at -1.2 V vs. Ag/AgCl for 60 s. The electrode surface was, then, characterized by SEM. Under optimal conditions, the *in situ* and *ex situ* bismuth electrode were examined. The *in situ* bismuth electrode displayed linear dynamic range of 49.9 – 248.8 nM and 2.5 -20 μM for Ph-S-S-Ph and Bu-SH, respectively. While, the *ex situ* bismuth electrode showed linear dynamic range of 25.0 – 149.5 nM for Ph-S-S-Ph and 2.5 -20 μM for Bu-SH. Detection limit of 19.1 and 12.5 nM were found for the Ph-S-S-Ph and 1.2 and 1.4 μM for Bu-SH, respectively. Finally, the bismuth electrode was applied for kerosene and jet fuel for analysis of Ph-S-S-Ph and Bu-SH. The analysis reviewed that jet fuel and kerosene contain Ph-S-S-Ph and Bu-SH at 230.4 ± 0.1, 102.9 ± 0.1 nM, 12.2 ± 0.3 and 5.2 ± 0.3 μM, respectively.

Field of Study :..Petrochemistry and Polymer Science.. Student's Signature ....
Academic Year : ....2010………………… Advisor's Signature ....

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LIST OF ABBREVIATIONS

SO_2 : Sulfur dioxide
US : United Satat of America
µM : micro-molar
GC : Gas chromatography
WD-XRF : waveleng-dispersive X-ray fluorescence spectroscopy
ICP-MS : Inductive-couple-plasma-mass spectroscopy
HMDE : Hanging mercury drop electrode
MDE : Mercury drop electrode
MFE : Mercury film electrode
e.g. : Example
BiFE : Bismuth film electrode
SWV : Square wave voltammetry
%v/v : Percent volume by volume
CH_3COOH : Acetic acid
CH_3COONa : Sodium acetate
N_2 : Nitrogen
M : Molar
µm : Micro-mater
GCE : Glassy carbon electrode
V : Volt
s : Seconds
SWASV : Square wave anodic stripping voltammetry
O_2 : Oxygen
H_2S : Hydrogen sulfide
S_x^{2-} : Polysulfide
I- : Iodide ion using
CV : cyclic voltammetry
Ph-S-S-Ph : Diphenyldisulfide
Bu-SH : Butanethiol
SWV : Square wave voltammetry
SEM : Scanning electron microscopy

CHAPTER I

INTRODUCTION

1.1 Statement of problem

Sulfur compounds are considered to be one of the main problems in the petroleum industry. They caused damaging effects even at very low concentration because the sulfur compounds are corrosive. They could react with the catalyst that used in the distillation process, which results in deactivation of catalyst and equipment corrosion. Moreover, the oxidation of sulfur compounds to sulfur dioxide (SO_2) when fuel combusted causes serious environmental pollution. Thus, the sulfur levels were used to indicate the quality of petroleum products. In 2005, the international regulations on the highest sulfur concentration contained in petroleum products in Europe and the US has been set to 50 ppm and reduced to 10 ppm in 2008. Thus, the allowable sulfur levels in petroleum products and distillates have been drastically in the future to combat the air pollution [1, 2]. Therefore, the determination of sulfur compound in trace analysis is essential.

Commonly, the measurement of sulfur compounds are performed by the use of conventional analytical techniques such as titration [3], colorlorimetry [4], gas chromatography [5], waveleng-dispersive X-ray fluorescence spectroscopy [6] and inductive-couple-plasma-mass spectroscopy [7]. These techniques require skillful analysts as well as high acquisition and maintenance cost for routine operation. Hence, there have been need a facile analytical system for sulfur determination in petroleum. Electrochemical techniques, especially voltammetry, satisfy many of the requirements for quantitative analysis because of the simple instrumentation and operation, affordable, high sensitivity and reproducibility with low detection limit. Square wave voltammetry one of methods has been widely used for trace determination.

Hanging mercury drop electrode (HMDE) [8], dropping mercury electrode (DME) [9] and mercury film electrode (MFE) [10] have been traditional electrodes for many determinations since mercury possesses valuable properties for analysis such as low background and noise, excellent resolution and reproducibility, and wide range of reduction. However, the risks associated with the use, manipulation, and disposal mercury salts have led to research for alternative electrodes with environmentally friendly quality. Several electrodes, e.g., gold have been developed in order to substitute the use of mercury electrodes in analysis [11, 12], but none approach favorable properties of the mercury electrodes.

In 2000, bismuth film electrode (BiFE), prepared by deposition a thin film of bismuth on carbon substrate, was introduced as an alternative electrode for analysis in aqueous since it showed comparable performance with mercury electrode [13]. The performance characteristics of BiFE as its inherent low toxicity, insensitive to oxygen, undistorted signal peaks, and excellent signal resolution have made the bismuth electrode to be the superior than the mercury electrode.

In this work, the attractive square wave voltammetry behavior of bismuth modified electrode for determining the sulfur compound in petroleum distillates is described.

1.2 Scope of the research work

This research aims to fabricate the bismuth modified electrode for the determination of diphenyldisulfide (Ph-S-S-Ph) and butanethiol (Bu-SH) in petroleum distillates using square wave voltammetry (SWV). Several experimental parameters have been optimized to improve the ability of bismuth modified electrode toward the determination of both compounds in petroleum distillates. The thesis is divided into four parts. For the first part, the comparison of bismuth modified electrode and mercury electrode is investigated. The second part presents the parameters that influence on diphenyldisulfide (Ph-S-S-Ph) signal. The third part shows the analytical performance of the *in situ* and *ex situ* bismuth modified electrodes in comparison with hanging mercury drop electrode (HMDE). Finally, the determination of diphenyldisulfide (Ph-S-S-Ph) and butanethiol (Bu-SH) in petroleum distillates samples is displayed in the fourth part.

CHAPTER II

THEORY AND LITERATURE REVIEWS

For understanding of this thesis, the definition and theories of the following term will be described. The petroleum is explained in the initial section of chapter. Then, sulfur compounds present in the petroleum that studied in this work are described. Consideration is then given to electrochemical chemistry and finally the detail of characterization technique is described.

2.1 Petroleum [19]

Petroleum or crude oil is a naturally occurring, toxic, flammable liquid consisting of a complex mixture of hydrocarbons of various molecular weights and other liquid organic compounds which are found in geologic formations below the Earth's surface. Petroleum is recovered mostly through oil drilling. It is refined and separated, most easily by boiling point, into a large number of consumer products, from petrol and kerosene to asphalt and chemical reagents used to make plastics and pharmaceuticals.

The petroleum consists of the mostly hydrocarbons while the other organic compounds contain nitrogen, oxygen and sulfur, and trace amounts of metals such as iron, nickel, copper and vanadium. The exact molecular composition varies widely from formation to formation but the proportion of chemical elements varies over fairly narrow limits as follows in Table 2.1.

Small amount of sulfur presence in petroleum, causes many problems such as a corrosion of equipment that used in storage, distillation and transportation. Moreover, sulfur could deactivate the catalysts that are used in the distillation process results in lower the product quality.

Table 2.1 Composition by weight of petroleum before refinery process

Element	Percent range
Carbon	83 to 87%
Hydrogen	10 to 14%
Nitrogen	0.1to 2.0%
Oxygen	0.1 to 1.5%
Sulfur	0.5 to 6.0%
Metals	< 0.1%

2.1.1 Sulfur compounds in petroleum [10, 20, 21]

Sulfur has been the most abundant element in petroleum after carbon and hydrogen for many years. Nowadays, in the case of the products resulting from the degradation of organisms, oxygen and nitrogen are more abundant than sulfur. It has been demonstrated that sulfur penetrates into organic matter before crude oil is extracted and also after the sedimentation process. For a long period, reducing bacteria in sediments have made changes in sulfate salts and have altered the formation of sulfur reducing compounds as shown in Table 2.2. In other words, these sulfur species are produced by anaerobic bacteria reduction of sedimentary sulfate (SO_4^{2-}) deposits (mainly anhydrite or gypsum). The anaerobic bacteria consumed sulfur instead of oxygen (O_2) as a source of energy and a hydrogen acceptor to produce these sulfur compounds. Apparently the reactions of these sulfur species and the formation of C–S bonds causes the occurrence of organosulfur compounds in petroleum derivatives. Changlong Yin [22, 23] reported that thiol, sulfide, disulfide and thiophene are the most common sulfur forms presence in petroleum. The another sulfur compound, disulfide and thiol presence at the least amount.

Table 2.2 Type and structure of sulfur compounds in petroleum [21]

Sulfur compound	**Structure**
Hydrogen sulfide	H_2S
Mercaptans (thiol)	
- Aliphatic	R-SH
- Aromatic	R-Ph-SH
Sulfides	
- Aliphatic	R-S-R
- Cyclic	CH_2-S-$(CH_2)_n$
Disulfideulfides	
- Aliphatic	R-S-S-R
- Aromatic	Ph-S-S-R
Thiophene	CH=S=CH

When petroleum is subjected to distillation and the uncondensable gases and moisture have gone over, a series of hydrocarbon compounds such as liquefied petroleum gas (LPG), naphtha, gasoline, kerosene, gas oil and lubricants are obtained as shown in Figure 2.1 which are the petroleum products. Although in this process, sulfur is removed, however it may still remain in a few. As the combustion of transportation oil that contained the sulfur emitted the sulfur dioxide ($S0_2$) in to the atmospheres which cause the air pollution. Therefore, the sulfur level is a determinant to control the quality of transportation fuel.

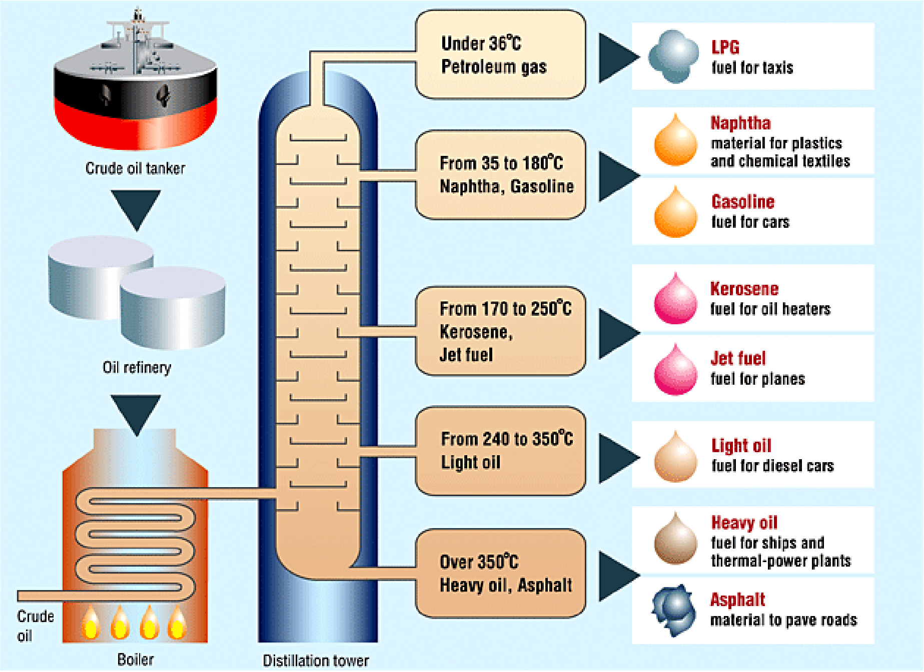

Figure 2.1 Oil refinery diagrams [22].

2.1.2 Sulfur level of petroleum products in Thailand

In Thailand, the sulfur levels in petroleum products were defined by the ministry of energy. In this section some petroleum products used in this work are described.

2.1.2.1 Kerosene [21, 23]

Kerosene is obtained from the fractional distillation of petroleum between 150 °C and 275 °C. It is widely used to power jet-engine aircraft (jet fuel) and some rockets, but is also commonly used as a heating fuel and for fire toys such as poi. The properties of kerosene is shown in Table 2.3

Table 2.3 The Kerosene properties of optimal condition product [23]

Properties	**Units**	**Min/Max**	**Limit**	**ASTM Test-Method**
Density	g/cm^3	Max	0.84	1298
Flash Point	°C	Max	37	56
Smoke Point	Mm	Min	22	1322
Sulfur Content	%wt	max	0.20	1266

2.1.2.2 Jet fuel [21, 24]

Jet fuel is a type of aviation fuel designed for use in aircraft powered by gas-turbine engines. It is clear to straw-colored in appearance. The most commonly used fuels for commercial aviation are Jet JP-4 and Jet A-1 which are produced to a standardized international specification. The only other jet fuel commonly used in civilian turbine-engine powered aviation is Jet B which is used for its enhanced cold-weather performance. Table 2.4 displays the properties of jet fuel.

Table 2.4 The Jet fuel properties of optimal condition product [24]

Properties	**Units**	**Min/Max**	**Limit Jet A-1**	**ASTM Test-Method**
Density	g/cm^3	Max	0.775	1298
Flash Point	°C	Max	38	56
Smoke Point	Mm	Min	25	1322
Sulfur Content	%wt	max	0.30	1266

As the sulfur is the cause of the air pollution resulted to the analysis should be accurate.

2.2 Electroanalytical chemistry (EC) [25]

Electroanalytical chemistry encompasses chemical and physical processes that involve the transfer of charge. There are two categories of electrochemical processes, potentiometric and electrolytic methods, that are applied to quantitative measurements.

Potentiometry is the field of electroanalytical chemistry in which potential is measured under the conditions of no current flow. The measured potential may then be used to determine the analytical quantity of interest, generally the concentration of some component of the analyte solution. Unlike potentiometry, which the free energy contained within the system generates the analytical signal. Electrolytic method is an area of electroanalytical chemistry in which an external source of energy is supplied to drive an electrochemical reaction which would not normally occur. The externally applied driving force is either applied potential or current. When the potential is applied, the resultant potential is the analytical signal. Techniques which utilize applied potential are typically referred to as galvanic method. Unlike potentiometric measurements, which employed only two electrodes, voltammetric measurement utilized a three electrode electrochemical cell. The use of three electrodes along with the potentiostat instrument allows accurate application of potential functions and the measurement of the resultant current.

In this research, the voltammetry was used. The details of these methods are described as the following:

2.2.1 Voltammetry

Voltammetry is one of the electroanalytical methods that based on the measurement of current as a function of potential. Voltammetry is typically comprised of three electrodes: working electrode (WE), reference electrode (RE) and counter electrode (CE). The potential is applied to working electrode as a function of time, and then the signal in the form of current as a function of potential obtained is call voltammogram.

2.2.1.1 General theory

In voltammetry, the effects of the applied potential and the behavior of the redox current are described by several well-known laws. The applied potential controls the concentrations of the redox species at the electrode surface (CO_0 and CR_0) and the rate of the reaction (k_0), as described by the Nernst or Butler–Volmer equations, respectively. In the cases where diffusion plays a controlling part, the current resulting from the redox process (known as the faradaic current) is related to the material flux at the electrode–solution interface and is described by Fick’s law. The interplay between these processes is responsible for the characteristic features observed in the voltammograms of the various techniques.

For a reversible electrochemical reaction (that is, a reaction so fast that equilibrium is always reestablished as changes are made), which can be described by $O + ne^- \longrightarrow R$, the application of a potential E forces the respective concentrations of O and R at the surface of the electrode (that is, c_O^0 and c_R^0) to a ratio in compliance with the Nernst equation:

$$E = E^0 - \frac{RT}{nF} \ln \frac{c_R^0}{c_O^0} \qquad (2.1)$$

where R is the molar gas constant (8.3144 J/mol·K), T is the absolute temperature (K), n is the number of electrons transferred, F = Faraday constant (96,485 C/equiv), and E_0 is the standard reduction potential for the redox couple. If the potential applied to the electrode is changed, the ratio c_R^0/c_O^0 at the surface will also change so as to satisfy Eq. (2.1). If the potential is made more negative the ratio becomes larger (that is, O is reduced) and, conversely, if the potential is made more positive the ratio becomes smaller (that is, R is oxidized).

For some techniques it is useful to use the relationship that links the variables for current, potential, and concentration, known as the Butler–Volmer equation:

$$\frac{i}{nFA} = k^0\{c_O^0 \exp[-\alpha\theta] - c_R^0 \exp[(1-\alpha)\theta]\} \qquad (2.2)$$

where q = nF(E – E_0)/RT, k_0 is the heterogeneous rate constant, a is known as the transfer coefficient, and A is the area of the electrode. This relationship allows us to obtain the values of the two analytically important parameters, i and k_0.

Finally, in most cases the current flow also depends directly on the flux of material to the electrode surface. When new O or R is created at the surface, the increased concentration provides the force for its diffusion toward the bulk of the solution. Likewise, when O or R is destroyed, the decreased concentration promotes the diffusion of new material from the bulk solution. The resulting concentration gradient and mass transport is described by Fick’s law, which states that the flux of matter (F) is directly proportional to the concentration gradient

$$\Phi = -AD_O(\partial c_O/\partial x) \qquad (2.3)$$

where D_O is the diffusion coefficient of O and x is the distance from the electrode surface. An analogous equation can be written for R. The flux of O or R at the electrode surface controls the rate of reaction, and thus the faradaic current flowing in the cell. In the bulk solution, concentration gradients are generally small and ionic migration carries most of the current. The current is a quantitative measure of how fast a species is being reduced or oxidized at the electrode surface. The actual value of this current is affected by many additional factors, most importantly the concentration of the redox species, the size, shape, and material of the electrode, the solution resistance, the cell volume, and the number of electrons transferred.

In addition to diffusion, mass transport can also occur by migration or convection. Migration is the movement of a charged ion in the presence of an electric field. In voltammetry, the use of a supporting electrolyte at concentrations 100 times that of the species being determined eliminates the effect of migration.

Convection is the movement of the electroactive species by thermal currents, by density gradients present in the solution, or by stirring the solution or rotating the electrode. Convection must be eliminated or controlled accurately to provide controlled transport of the analyte to the electrode.

Many voltammetric techniques have their own unique laws and theoretical relationships that describe and predict in greater detail the various aspects of the i–E behavior (such as curve shape, peak height, width, and position). When appropriate, these are discussed in more detail.

2.2.1.2 Instrument of voltammetry

The basic instrumentation of voltammetry consist of an electrochemical cell (with a three-electrode system), a voltammetric analyzer (a potentiostatic circuitry and a voltage ramp generator).

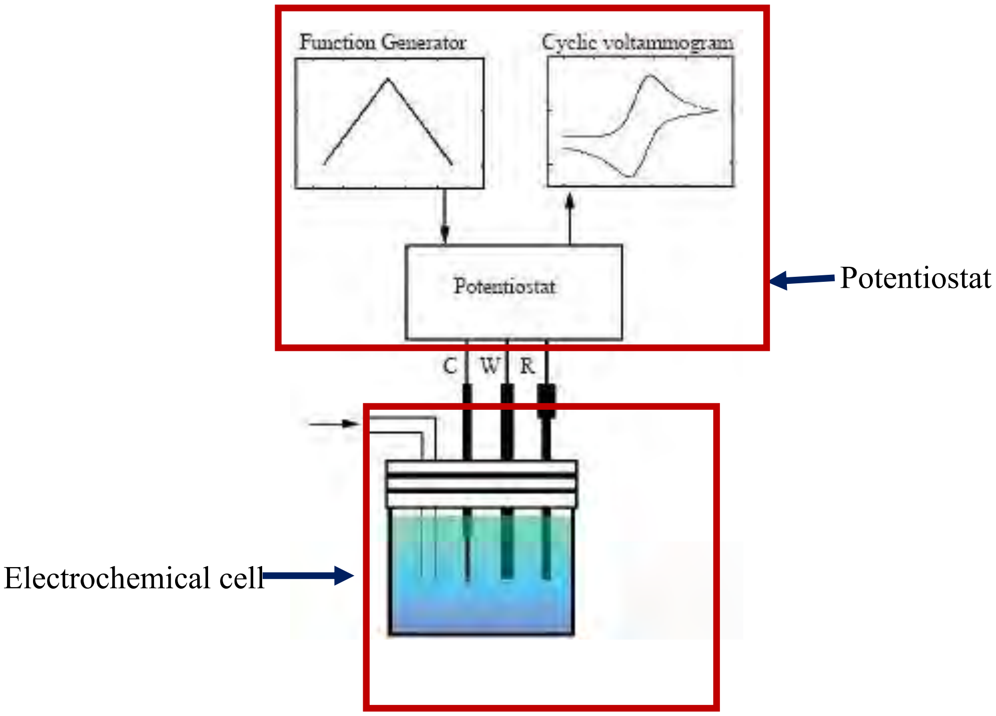

Figure 2.2 Basic instruments of voltammetry [26]

2.2.1.2.1 Voltammetric anlyzer/ potentiostats

The task of applying a known potential and monitoring the current falls to the potentiostat. The most widely used potentiostats today are assembled from discrete integrated-circuit operational amplifiers and other digital modules. In many cases, especially in the larger instruments, the potentiostat package also includes electrometer circuits, A/D and D/A converters, and dedicated microprocessors with memory.

A simple potentiostat circuit for a three-electrode cell with three operational amplifiers (OA) is shown in Figure 2.3.

The output of OA-1 is connected to the counter electrode with feedback to its own inverting input through the reference electrode. This feedback decreases the difference between the inverting and noninverting inputs of OA-1 and causes the reference electrode to assume the same potential as Ein of OA-1. Because the potential difference between the working electrode and the reference electrode is zero the working electrode is set to the same potential as applied to the OA-1 input. With the reference electrode connected to Ein through the high impedance of OA-3, the current must flow through the counter electrode. Current flow through the reference not only is undesirable because of its higher resistance but also would eventually cause its potential to become unreliable. A three electrode system is normally used in voltammetry for currents in the range of microamperes to milliamperes. With the use of micron-sized electrodes, currents are in the pico to nanoampere range, and thus two electrodes are often used (that is, the counter and reference are tied together). An OA acting as a current-to-voltage converter (OA-2) provides the output signal for the A/D converter.

Most voltammetric techniques are dynamic (that is, they require a potential modulated according to some predefined waveform). Accurate and flexible control of the applied potential is a critical function of the potentiostat. In early analog instruments, a linear scan meant just that, a continuous linear change in potential from one preset value to another. Since the advent of digital electronics almost all potentiostats operate in a digital (incremental) fashion. Thus, the application of a linear scan is actually the application of a “staircase” modulated potential with small enough steps to be equivalent to the analog case. Not surprisingly, digital fabrication of the applied potential has opened up a whole new area of pulsed voltammetry, which gives fast experiments and increased sensitivity. In the simpler standal-one potentiostats the excitation signal used to modulate the applied potential is usually provided by an externally adjustable waveform generator. In the computer-controlled instruments, the properties of the modulation and the waveform are under software control and can be specified by the operator. The most commonly used waveforms are linear scan, differential pulse, and triangular and square wave. The use of micro and nanometer size electrodes has made it necessary to build potentiostats with very low current capabilities. Microelectrodes routinely give current responses in the pico to nanoampere range. High-speed scanning techniques such as square wave voltammetry require very fast response times from the electronics. These diverse and exacting demands have pushed potentiostat manufacturers into providing a wide spectrum of potentiostats tailored to specific applications.

2.2.1.2.2 Electrochemical cell

The electrochemical cell consists of a three electrodes (working, reference and counter electrode) immersed into an electrolyte as show in Figure 2.4. The first electrode is the working electrode which the reaction interest occurs. The second electrode is reference electrode. Reference electrode provides a stable potential (independent of the sample composition) against which the potential of working electrode is compared. Such buffering against potential change is achieved by constant position of both form of its redox couple, e.g., Ag/AgCl or Hg/Hg_2Cl_2, as common with the silver-silver chloride and the saturated calomel reference electrode, respectively. To minimize contamination of the sample solution, the reference electrode may be insulated from the sample through and intermediate bridge. The third electrode is the counter or auxiliary electrode which serves as a source for electrons so that current can be passed from the external circuit through the cell.

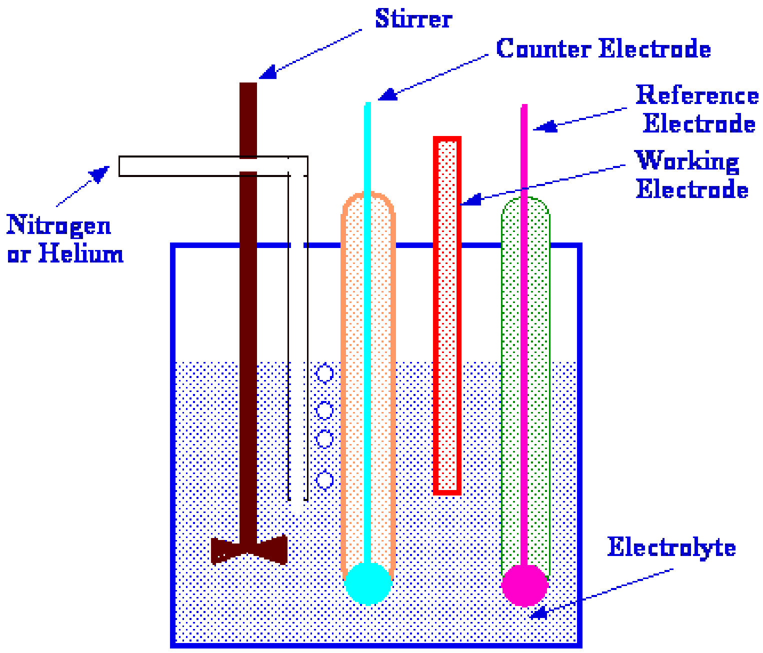

Figure 2.3 Schematic diagram of a cell for voltammetric measurements [27]

2.3 Electrode for electrochemical cell

For electrochemical measurement, the tree electrode system consisted of working, auxiliary and reference electrodes are commonly used. Working electrode is the electrode at which the reaction of interest occurs whereas the reference electrode provide a stable, constant and well-know potential, allowed the potential of working electrode to be determined. An inert conducting material such as platinum or carbon can be used as the current-carrying auxiliary electrode. The performance of the electrochemical measurement is strongly influenced by the material of the working electrode. Popular materials for working electrodes are mercury, carbon and noble materials.

2.3.1 Glassy carbon electrode (GCE)

The limited anodic potential range of mercury electrode has precluded their utility for monitoring oxidizable compounds. Accordingly, solid electrodes with extended anodic potential window have attracted considerable analytical interest. Of the difference solid materials that can be used as working electrodes, the most often used are carbon, platinum and gold. Silver, nickel and copper can also be used for specific applications. Glassy carbon electrode (GCE) has been used for many electrochemical techniques. It was use to measure the concentration and to detect the presence of electrochemical species because of its good electrical and thermal conductivity, low density, corrosion resistance, low thermal expansion and high purity. In addition, carbon materials can be produced in a variety of structure such as powders, fiber and thin solid sheet. Furthermore, carbon materials are generally available at low-cost. The most common shape for glassy carbon electrodes are rod, typically 0.5 cm or less in diameter. However, rectangular plates and circular disk of glassy carbon are also used for electrodes. In this research, glassy carbon electrode is used as a substrate for plated bismuth particle.

2.3.2 Mercury electrode

Mercury electrode is a very attractive choice of electrode materials because it has a high hydrogen overvoltage that great extends the cathodic potential window and processes a highly reproducible, smooth and readily renewable surface. Disadvantages of the use of mercury are its limited anodic range (due to the oxidation of mercury) and toxicity.

2.3.3 Bismuth electrode

Bismuth electrode was a new type of electrode which was proposed as an alternative to mercury electrode in 2000. Bismuth electrodes, one of the most widely use electrode for analysis, consists of a very thin bismuth film or precursor of metallic bismuth covering a suitable substrate material. Bismuth film can form fused alloys with metals, which analogous to the amalgams that mercury form. The attractive properties of bismuth electrode are that they are environmentally friendly, high sensitivity, insensitive to oxygen and simple preparation. Bismuth electrodes can be classified into two main types; *in situ* bismuth electrode and *ex situ* bismuth electrode [28].

2.3.3.1 *In situ* bismuth electrode

In situ bismuth electrode is often employed for stripping analysis. The electrode is prepared by simultaneous deposition of bismuth (III) ions and the measured interest ions (analyte) on conducting substrate. According to equations 2.1 and 2.2, the bismuth ions and interested ions can be achieved [29]:

$$Bi^{3+}\,(aq) + 3e^{-} \longrightarrow Bi\,(s) \qquad (2.1)$$

$$M^{2+}\,(aq) + 2e^{-} + Bi\,(s) \longrightarrow M(Bi)\,(s) \qquad (2.2)$$

when M^{2+} and M(Bi) represent interest ions (analyte) and formation of bismuth and interest ions (analyte), respectively. Therefore, in order to prepare *in situ* bismuth electrode, the solution of bismuth (III) ions must be present in the sample solution containing interest ions (analyte).

2.3.3.2 *Ex situ* bismuth electrode

Ex situ bismuth electrode is made by reducing bismuth (III) ions to metallic bismuth on suitable supporting material, as equation 2.1. Subsequently, this *ex situ* bismuth electrode is immersed in the sample solution which contains only interest ion (analyte).

In comparison the advantage of *in situ* and *ex situ* bismuth electrodes, the *ex situ* bismuth electrode is more complicated and time consuming than *in situ* bismuth electrode (since it requires a separate bismuth-plating step from a Bi(III) solution and subsequent transfer of the electrode to the sample solution). However, the *ex situ* bismuth electrode is portable analytical system than *in situ* bismuth electrode. Thus, the *in situ* and *ex situ* bismuth electrodes were prepared in this research.

Each electrodes have been difference the potential windows as solvent and supporting electrolytes as show in Figure 2.6. Therefore, the selection of working electrode also considers the solvent and supporting electrolyte.

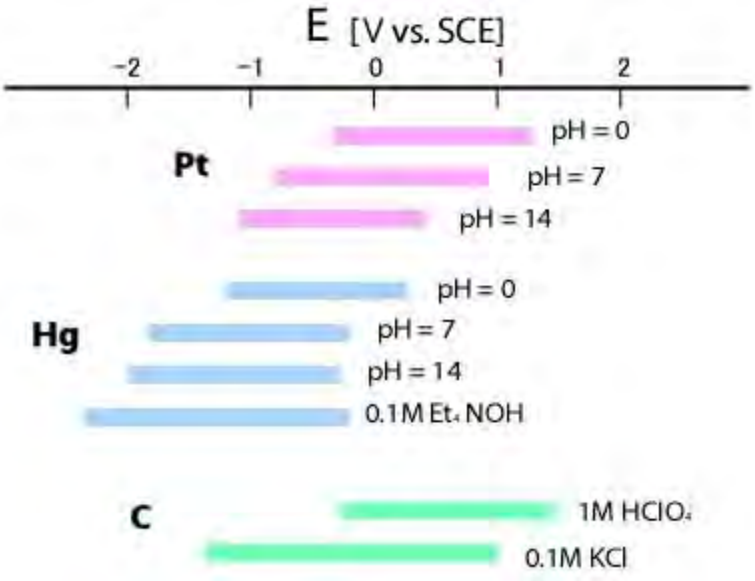

Figure 2.4 Potential windows of platinum, mercury and carbon electrodes in various supporting electrolytes [29].

2.4 Solvent and supporting electrolytes [25]

Electrochemical measurements are commonly carried out in a medium which consists of solvent containing a supporting electrolyte. The choice of the solvent is dictated primarily by the solubility of the analyte and its redox activity, and by solvent properties. The solvent should not react with the analyte and should not undergo electrochemical reaction over a wide potential range.

While water has been used as a solvent more than any other medium, non-aqueous solvent have also been frequently used. Mix solvents may also be considered for application. Double distillated water is adequate for most work in aqueous media. Organic solvents often require drying or purification procedures.

Supporting electrolytes are required in controlled-potential experiments to decrease the resistance of the solution, to eliminate electromigration effects, and to maintain a constant ionic strength. The inert supporting electrolyte may be an inorganic salt, a mineral acid or a buffer. While potassium chloride or nitrate, ammonium chloride, sodium hydroxide or hydrochloric acid is widely used when using water as a solvent, tetraalkylammonium salts are often employed in organic media. Buffer systems are used when pH control is essential. The composition of the electrolyte may affect the selectivity of electrochemical measurement. The supporting electrolyte should be prepared from highly purified reagents and should not be easily oxidized or reduced. The usual electrolyte concentration range is 0.1 – 1.0 M.

2.5 Electrochemical techniques [25]

Electrochemical techniques are formally classified by International Union for Oure and Applied Chemistry (IUPAC) on the basis of their working principles. Figure 2.2 shows the common waveform of the voltammetry. Although many electrochemical techniques are available, only striping analysis and square wave voltammetry are discussed in this thesis.

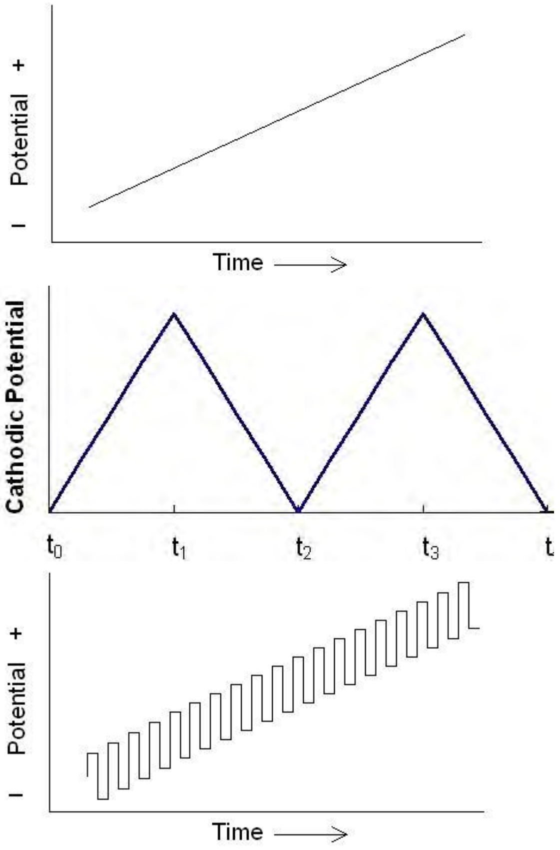

Figure 2.5 Potential-time waveforms used in various electroanalytical methods. Waveforms based on (a) square, (b) linear and (c) triangular potential-time patterns are used in linear sweep, cyclic and square wave voltammetry, respectively [30, 31, 32]

2.5.1 Stripping analysis

Stripping is an excellently sensitive electrochemical technique for measuring trace analytes. It consists of two steps: deposition step and stripping step. The first step involves the electrolytic deposition or accumulation of a small portion of interest ions (analyte ions) in solution to the working electrod in order to preconcentrate analytes. Next step is the stripping or measurement step which involves the dissolution or stripping of the deposition analytes. Different versions of stripping sanalysis can be used, depending upon the nature of deposition and stripping steps. In this thesis, stripping voltammetry (CSV) with square wave form was employed for prepared *in situ* and *ex situ* bismuth electrode.

2.5.1.1 Stripping voltammetry (SV)

Stripping voltammetry (SV) is an analytical technique that ions are preconcentrated by electrodeposition on the working electrode via oxidation or reduction process. During this step, the solution is continuously stirred to produce the force convection, allowing more analyte deposition. Following the deposition step, the stirred is stopped and the voltammogram is recorded by applying a potential scan. Thus, stripping voltammogram will display peak for deposited analyte.

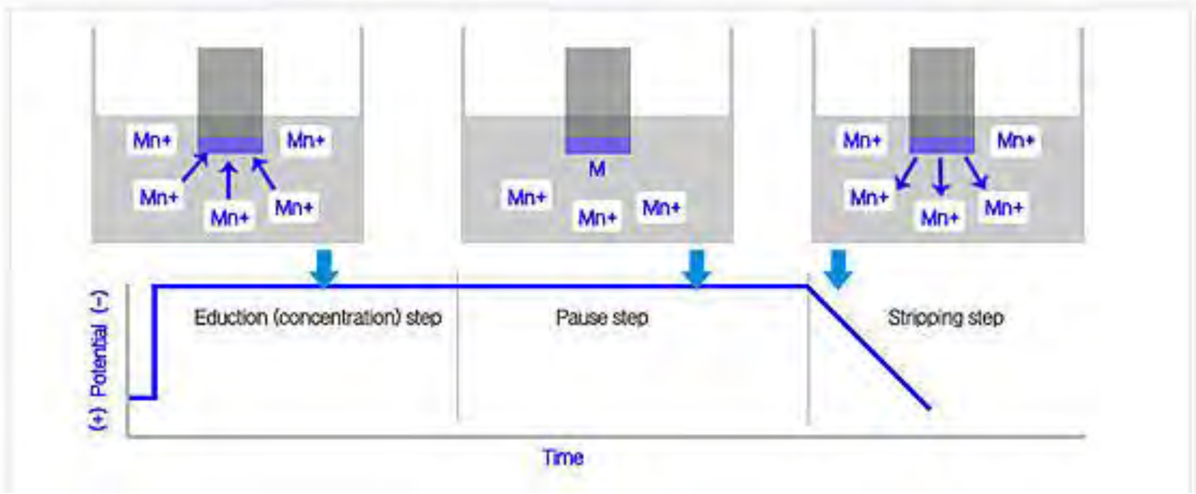

Figure 2.6 (a) Process of stripping analysis and (b) potential-time waveform of stripping voltammetry [33].

Figure 2.6 shows potential wave form of sripping voltammetry and a plot of current versus applied potential or a stripping voltammogram. The voltammetric peaks reflect the time-dependent concentration gradient of analytes deposited on the working electrode.

2.5.2 Square wave voltammetry [32]

Square wave voltammetry (SWV) is a large-amplitude differential technique in whick a waveform composed of a symmetrical square wave, superimposed on a base staircase potential, is applied to the working electrode as show in Figure 2.6. The current is sampled twice during each square-wave cycle, once at the end of the forward pulse and once at the end of the reverse pulse. Since, the square-wave modulation amplitude is very large, the reverse pulses cause the reverse reaction of the product (of the forward pulse). The difference between the two measurements is plotted vs. the base staircase potential. A dimensionless plot of the theoretical forward, reverse, and difference

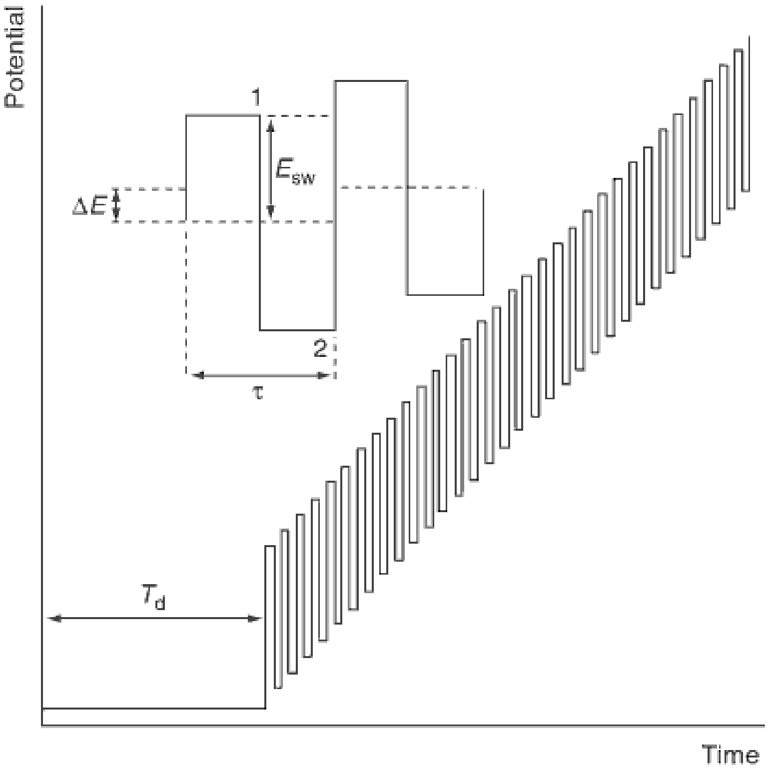

Figure 2.7 Potential wave form for sampled current polarography [32]

current is given in Figure 2.7 for a rapid reversible redox system. The resulting peak-shaped voltammogram is symmetrical about the half-wave potential, and the peak current is proportional to the concentration. Excellent sensitivity accrues from the fact that the net current is larger than either the forward or reverses components; coupled with effective discrimination against the charging background current, very low detection limits near 1 x 10^{-8} M can be attained. Comparison of square wave and differential pulse voltammetry for reversible and irreversible cases indicated that the square wave currents are 4 and 3.3 times higher, respectively, than the analogous differential pulse response. The major advantage of square wave voltammetry is its speed. The effective scan rate is given by fE_S. The term f is aquare wave frequency (in Hz). E_s is the step height. Frequencies of 1 to 100 cycles per second permit the use of extremely fast potential scan rate. For example, if = 10 mV and = 50 Hz. The effective scan rate is 0.5 V/s. As the results, an analysis time is drastically reduced; a complete voltammogram can be recorded within a few seconds, as compared with about 2 – 3 min. in differential pulse voltammetry.

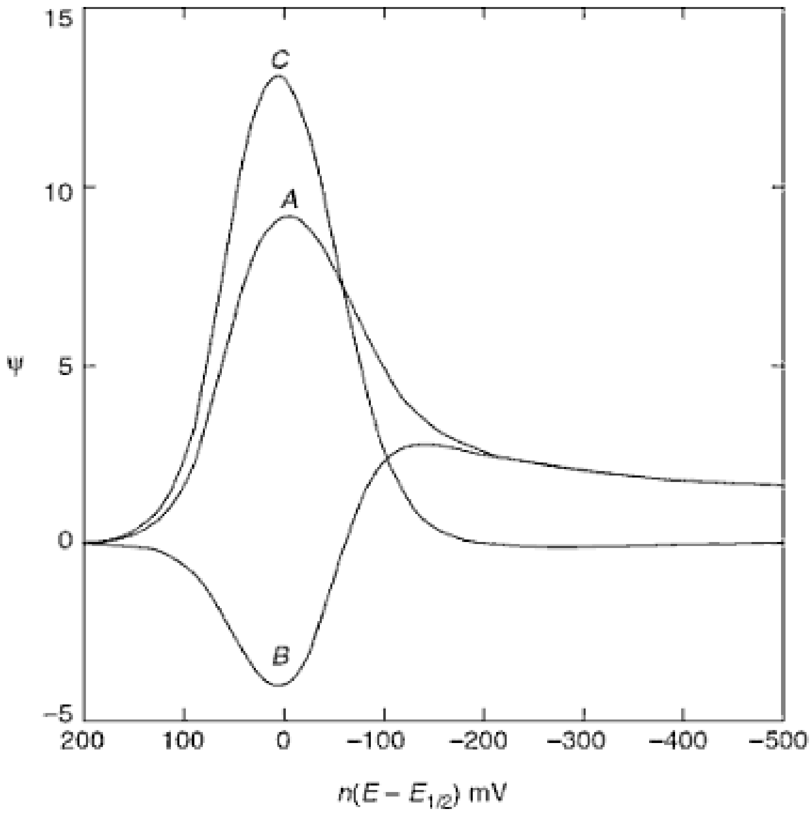

Figure 2.8 Square wave voltammogram for reversible electrode transfer (curve A) forward current; (curve b) reverse current and (curve c) net current [32]

2.6 Characterization technique

2.6.1 Scanning electron microscopy (SEM) [34]

The Scanning electron microscopy (SEM) is an instrument that produces a largely magnified image by using electrons instead of light to form an image. Figure 2.9 show the Schematic diagram of SEM. A beam of electrons is produced at the top of the microscope by an electron gun. The electron beam follows a vertical path through the microscope, which is held within a vacuum. The beam travels through electromagnetic fields and lenses, which focus the beam down toward the sample. Once the beam hits the sample, electrons and X-rays are ejected from the sample as shown in Figure 2.9.

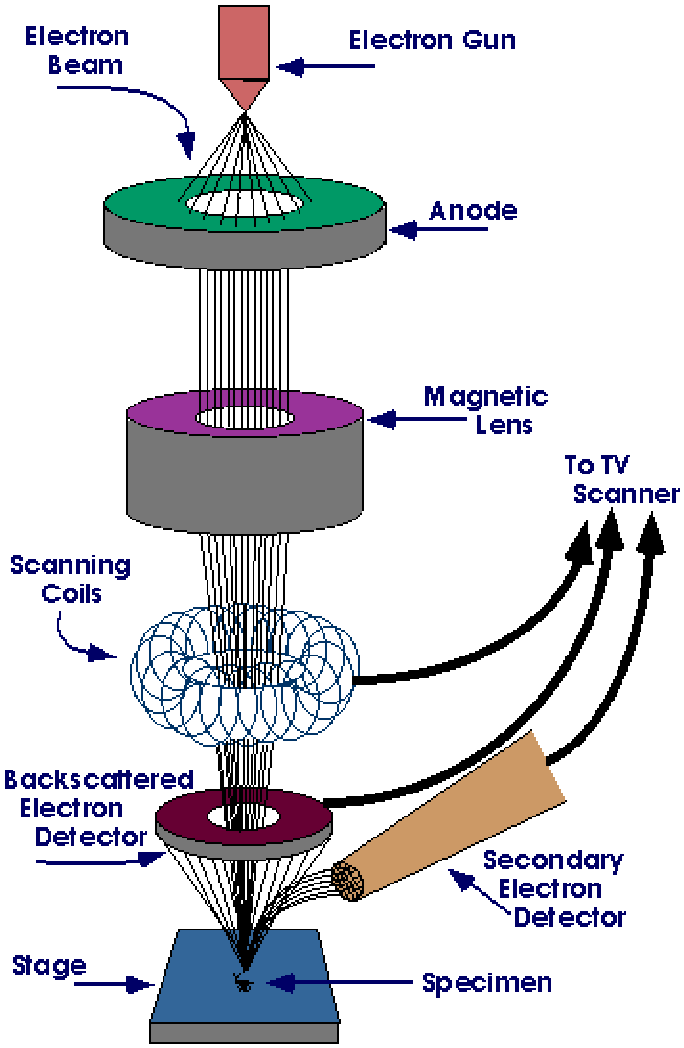

Figure 2.9 Schematic diagram of an SEM [34]

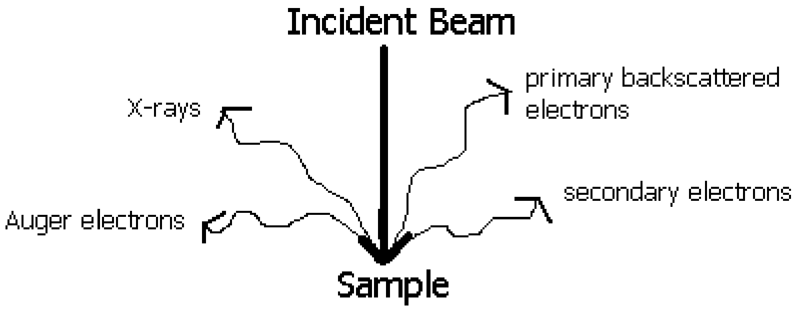

Figure 2.10 The scattering of light on the sample[34]

Detectors collect these X-rays, backscattered electrons, and secondary electrons and convert them into a signal that is sent to a screen similar to a television screen. This produces the final image.

2.7 Literature reviews

Various research have been determined the sulfur compounds in petroleum distillates and petroleum products using electrochemical technique.

In 1996, Kashiki et al. [9] reported the suitable electrolyte for the determination of the disulfide, mercaptane and elemental sulfur in petroleum naphtha using square wave polarography technique. The results report that 2%v/v acetic acid (CH_3COOH) mixed with 1.4 M sodium acetate (CH_3COONa) in methanol was a suitable electrolyte for the determination of disulfide, butanethiol and elemental sulfur in petroleum with satisfied sensitivity and reproducibility. Before analysis, the nitrogen (N_2) was flow over 5 mins for deoxygen.

In 2007, Serafil et al. [10] determined sulfur compound in gasoline using square wave voltammetry by mercury film electrode. A 2%v/v CH_3COOH mixed with 1.4 M CH_3COONa in methanol as an electrolyte. A mercury film electrode was deposited on glassy carbon at -0.9 V vs. Ag/AgCl for 10 mins which result 4.3 µm mercury film thicknesses. Then, gasoline was determined. Elemental sulfur, disulfide and butanethiol were found at $3.9x10^{-9}$, $1.6x10^{-7}$ and $4.9x10^{-7}$ M, respectively.

Up to present, the mercury electrode has been only used as a working electrode. There have been no reports regarding the use of bismuth electrode for the voltammetric detection of sulfur compounds in petroleum distillates.

The first bismuth electrode is *in situ* bismuth film electrodes which were generated by depositing the bismuth film and the metal ions via reduction onto substrate. Firstly, J. Wang's group [13] introduced bismuth coated glassy carbon and carbon fiber electrodes for measurement of cadmium (II), lead (II), thallium (I) and zinc (II) ions in non-deaerated condition. The performance of bismuth film electrodes as high sensitivity, well-defined signals and good electrodes as high sensitivity, well-defined signals and good resolution peaks were obtained In the following year, was confirmed by comparison with mercury electrodes [14].

In 2001, Hutton et al. [15] studied a preparation of bismuth film electrode for direct determination of organic compounds. The research used a 2-nitrophenol and bromophenoxym as a model analyze. A bismuth film electrode was prepared by deposited 5 ppm bismuth (III) on glassy carbon electrode (GCE) at -1.0 V vs. Ag/AgCl for 60 s. Then, the effect of electrolyte pH was studied in term of potential windows. The result showed and electrochemical behavior of 2-nitrophenol. The results indicated that high pH result to wild reduction potential windows. Then, a performance of bismuth film electrode for organic compounds determination was compared with GC and mercury film. A bismuth film electrode showed a well-define peak current same a GCE and mercury film. A lower background current was present at bismuth film electrode. Moreover, the performance of bismuth film electrode for non-aqueous system was studies. The result indicated that the bismuth electrode could be used in non-aqeous system.

In 2003, Kefala et al. [16] reported the simulataneous determination of cadmium (II), lead (II) and zinc (II) ions at low ppb levels by square wave anodic stripping voltammetry (SWASV) using *in situ* plated bismuth film on glassy carbon electrodes. This electrode was applied to trace measurements of cadmium (II), lead (II) and zinc (II) ions in tab water and human hairs. Moreover, the results were in agreement with atomic absorption spectroscopic (AAS) observation.

In 2005, Charalambous et al. [17] studied the utility of in situ bismuth film modified glassy carbon electrode for measurements of indium (II) ions in the presence of other metal cations (cadmium (II) and lead (II) ions) by square wave anodic stripping voltammetry (SWASV). Using the optimized choice of instrumental conditions, the bismuth film electrode provided better separation between cadmium and indium signals than mercury film ones.

In 2006, Waite et al. [18] studied the performance of bismuth coat gold electrode and mercury coat gold electrode for oxygen (O_2), hydrogen sulfide (H_2S), polysulfide (S_x^{2-}), $S_2O_3^{2-}$, Fe^{2+}, Fe^{3+}, Mn^{2+} and iodide ion (I^-) using cyclic voltammetry (CV). The results indicated that a bismuth coat gold electrode could not be used for O_2, $S_2O_3^{2-}$, I^- and low sulfide level (less than 10 μM). Moreover, the potential window of bismuth coat gold electrode narrow than mercury coat gold electrode.

CHAPTER III

EXPERIMENTAL

3.1 Instruments and equipments

The following is the list of instruments and equipments used in these studies.

3.1.1 Poralography (VA 757, Metrohm, Swizerland)
3.1.2 Glassy Carbon Electrode I.D. 1 mm
3.1.3 Silver/Silver Choride (Ag/AgCl) electrode
3.1.4 Platinum wire
3.1.5 pH meter (Metrohm 744 pH meter, Metrohm, Switzerland)
3.1.6 Polish wheel
3.1.7 10.00, 50.00 and 100.00 mL volumetric flasks
3.1.8 10.00, 100.00, 500.00 and 1000.00 mL beakers
3.1.9 Micro-pipettes (Efpendroft)
3.1.10 Digital balance; 4 digitals
3.1.11 Scanning electron microscopy (JEM-2100)

All glasswares were washed with detergent, and rinsed with de-ionization (DI) water and acetone before used.

3.2 Chemicals

All chemicals used in this work were analytical grade and were used as recieved. List of chemicals and their suppliers are shown below:

3.2.1 Diphenyldisulfide (Sigma – Aldrich; Germany)
3.2.2 Butanethiol (Sigma – Aldrich; Germany)
3.2.3 Sodium acetate anhydrous (Qrec; New Zealand)
3.2.4 1000 ppm Bismuth nitrate standard for AAS

3.2.5 Toluene (J. T. Baker; USA)
3.2.6 Methanol (Merck; Germany)
3.2.7 Acetic acid (Merck; Germany)
3.2.8 Acetone (Merck; Germany)
3.2.9 1.0 μm and 0.3 μm alumina powder
3.2.10 Hydrochloric acid (Merck; Germany)
3.2.11 Kerosene
3.2.12 Jet fuel

3.3 Solution preparation

Electrolyte and standard solutions were daily prepared as described in the following procedures.

3.3.1 Sodium acetate (CH_3COONa) buffer pH 4.5

A 0.7545 g sodium acetate (CH_3COONa; $M_W = 82.03$ g/mol) was dissolved with 1:1 methanol:toluene in a 100.00 mL volumetric flask. A pH of the solution was adjusted to 4.5 with acetic acid. Then, the volume was adjusted to the mark with 1:1 methanol:toluene. This solution was used as an electrolyte.

3.3.2 Diphenyldisulfide (Ph-S-S-Ph) standard solution 50 mM

A 0.1092 g diphenyldisulfide (Ph-S-S-Ph) crystal (218.36 g/mol) was dissolved by 1:1 methanol:toluene solution in a 10.00 mL volumetric flask.

3.3.3 Diphenyldisulfide (Ph-S-S-Ph) standard solution 50 μM

A 10.00 μL of 50 mM diphenyldisulfide (Ph-S-S-Ph) was pipetted and diluted with 1:1 toluene:methanol solution in a 10.00 mL volumetric flask.

3.3.4 Butanethiol (Bu-SH) standard solution 50 mM

A 54.00 µL 100%v/v butanethiol (Bu-SH; M_w = 90.19 g/mol; D = 0.84 g/mL) was carefully pipetted and diluted with 1:1 toluene:methanol solution in a 10.00 mL volumetric flask.

3.3.5 Bismuth solution 50 ppm

A 500 µL of 1000 ppm bismuth nitrate ($Bi(NO_3)_3$) standard for AAS was diluted with the sodium acetate solution (pH 4.5) in a 10.00 mL volumetric flask. This solution was used to prepare 0.5 ppm bismuth solution.

3.3.6 Bismuth solution 0.5 ppm

A 1.00 mL of the 50 ppm bismuth solution was diluted with the sodium acetate solution (pH 4.5) in a 100.00 mL volumetric flask. This solution was used to prepared bismuth electrode.

3.4 Electrochemical method

3.4.1 Electrode cleaning

A glassy carbon electrode (GCE) was polished using 1.0 and 0.3 µm alumina slurry on polishing microcloth (Bueher), respectively by machine. Then, the electrode was immersed in 2 %v/v hydrochloric acid about 2 minutes prior to be used.

3.4.2 Electrochemical cell

Electrochemical cell was set up as showed in Figure 3.1. A glassy carbon electrode (GCE) was used as a substrate electrode for bismuth or bismuth co-deposited particles. This electrode is called a bismuth modified electrode and used as a working electrode. The silver/silver chloride (Ag/AgCl) and platinum wire were employed as reference and counter electrodes, respectively. All electrodes were immersed into an acetate buffer pH 4.5. Except where note, all measurements were carried out in the square wave voltammetric mode; 50 mV pulse amplitude (E_p), 15 mV voltage step (E_s) at 70 Hz frequency. At the end of each scan a cleaning potential of +0.3 V was applied for 180 s to remove any probable memory effects from previous experiments.

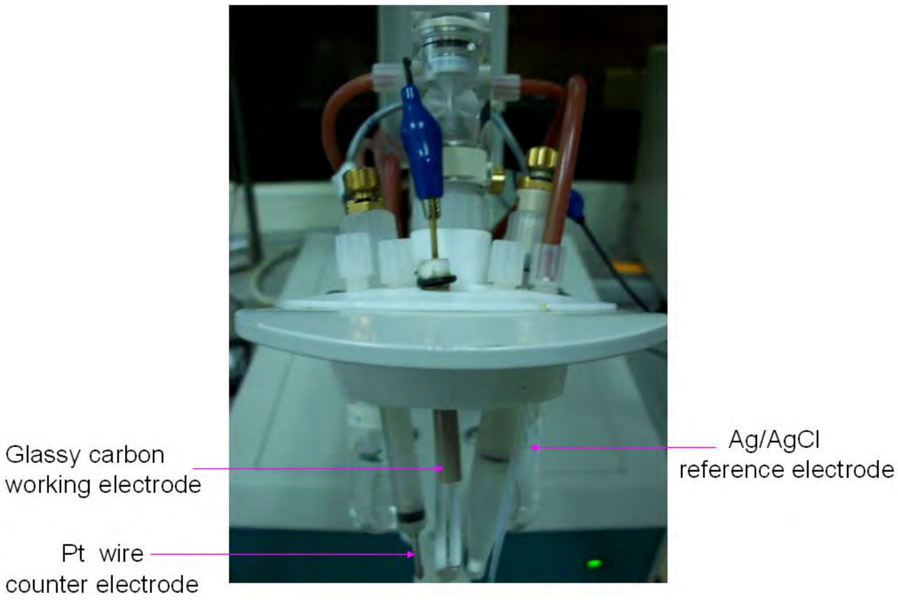

Figure 3.1 The electrochemical cell for square wave voltammetric study

3.5 Experimental procedures

This section consists of experimental procedures for studying a) the electrochemical behavior of diphenyldisulfide (Ph-S-S-Ph) and butanethiol (Bu-SH), b) parameters that influence on the voltammetric signal, c) analytical performance of *in situ* and *ex situ* bismuth modified electrodes in comparison with hanging mercury drop electrode (HMDE) and d) determination of diphenyldisulfide (Ph-S-S-Ph) and butanethiol (Bu-SH) in real samples.

3.5.1 Electrochemical behavior of diphenyldisulfide (Ph-S-S-Ph) and butanethiol (Bu-SH) on the bismuth modified electrode in comparison with mercury electrode

3.5.1.1 Experimental procedure on an *in situ* bismuth modified electrode

An analyt solution; 10.00 μL of 50 mM Ph-S-S-Ph or 10.00 μL of 50 mM Bu-SH, was pipetted into 20.00 mL of 0.5 ppm bismuth solution that contained in an electrochemical cell. A potential of -1.2 V vs. Ag/AgCl was applied through the glassy carbon electrode for 60 s. Then, the square wave potential form was scanned from -0.2 to -1.0 V vs. Ag/AgCl; 50 mV E_p, 15 mV E_s at 70 Hz. The responding current was recorded during the scan.

3.5.1.2 Experimental procedure on an *ex situ* bismuth modified electrode

A glassy carbon electrode was immersed in 20.00 mL of 0.5 ppm bismuth solution that contained in an electrochemical cell. A deposition potential of -1.2 V vs. Ag/AgCl was applied for 60 s. Then the electrode, now referred as an *ex situ* bismuth modified electrode, was transferred into another electrochemical cell that contained an analyte; 10.00 μL of 50 mM Ph-S-S-Ph or 10.00 μL of 50 mM Bu-SH, in 20.00 mL acetate buffer pH 4.5. A potential of -0.9 V vs. Ag/AgCl was applied for 60 s. Then, the square wave potential form was scanned from -0.2 to -1.0 V vs. Ag/AgCl; 50 mV E_p, 15 mV E_s at 70 Hz. The responding current was recorded during the scan.

3.5.1.3 Experimental procedure on a hanging mercury drop electrode (HMDE)

An analyt solution; 10.00 μL of 50 mM Ph-S-S-Ph or 10.00 μL of 50 mM Bu-SH, was pipetted into 20.00 mL of acetate buffer pH 4.5 that contained in an electrochemical cell. A potential of -0.9 V vs. Ag/AgCl was applied for 60 s. Then, the square wave potential form was scanned from -0.2 to

-1.0 V vs. Ag/AgCl; 50 mV E_p, 15 mV E_s at 70 Hz. The responding current was recorded during the scan.

3.5.2 Studies of parameters that influence on the voltammetric signal

3.5.2.1 Effect of applied pulse amplitude

3.5.2.1.1 *In situ* method

1) A glassy carbon electrode was immersed in a mixed solution of 10.00 µL of 50 mM Ph-S-S-Ph and 20.00 mL of 0.5 ppm bismuth solution.

2) A -1.2 V vs. Ag/AgCl deposition potential was applied on the glassy carbon electrode for 60 s.

3) A square wave potential form was scanned from -0.2 to -1.0 V vs. Ag/AgCl with the setting parameters as follow; 50 mV E_p, 15 mV E_s at 70 Hz. The responding current was recorded during the scan.

4) Then, a cleaning potential of +0.3 V vs. Ag/AgCl was applied for 180 s.

5) Steps 2) to 4) were repeated at least two times. Latter, the measured peak current were averaged and standard deviation value was calculated.

6) Steps 2) to 5) were repeated with different values of E_p; 10, 15, 20, 25, 30, 35, 40, 45, 50, 75, and 500 mV.

3.5.2.1.2 *Ex situ* method

1) A glassy carbon electrode was immersed in 20.00 mL of 0.5 ppm bismuth solution.

2) A -1.2 V vs. Ag/AgCl deposition potential was applied on the glassy carbon electrode for 60 s. After this step, the electrode was named as *ex situ* bismuth modified electrode.

3) The *ex situ* bismuth modified electrode was , then, transfered into another electrochemical cell that contained a mixed solution of 10.00 µL of 50 mM Ph-S-S-Ph and 20.00 mL acetate buffer pH 4.5.

4) A -0.9 V vs. Ag/AgCl deposition potential was applied on the glassy carbon electrode for 60 s.

5) A square wave potential form was scanned from -0.2 to -1.0 V vs. Ag/AgCl with the setting parameters as follow; 50 mV E_p, 15 mV E_s at 70 Hz. The responding current was recorded during the scan.

6) Steps 4) to 5) were repeated at least two times. Latter, the measured peak current were averaged and standard deviation value was calculated.

7) A cleaning potential of +0.3 V vs. Ag/AgCl was applied for 180 s. Then, the glassy carbon electrode was polish as described in Section 4.2.1.

8) Steps 1) to 7) were repeated with different values of E_p; 10, 15, 20, 25, 30, 35, 40, 45, 50, 75, and 500 mV.

3.5.2.2 Effect of applied voltage step

3.5.2.2.1 *In situ* method

1) A glassy carbon electrode was immersed in a mixed solution of 10.00 µL of 50 mM Ph-S-S-Ph and 20.00 mL of 0.5 ppm bismuth solution.

2) A -1.2 V vs. Ag/AgCl deposition potential was applied on the glassy carbon electrode for 60 s.

3) A square wave potential form was scanned from -0.2 to -1.0 V vs. Ag/AgCl with the setting parameters as follow; 50 mV E_p, 15 mV E_s at 70 Hz. The responding current was recorded during the scan.

4) Then, a cleaning potential of +0.3 V vs. Ag/AgCl was applied for 180 s.

5) Steps 2) to 4) were repeated at least two times. Latter, the measured peak currents were averaged and standard deviation value was calculated.

6) Steps 2) to 5) were repeated with different values of E_s; 7.5, 10, 15, 20, 25, 30, 35 and 40 mV.

3.5.2.2.2 *Ex situ* method

1) A glassy carbon electrode was immersed in 20.00 mL of 0.5 ppm bismuth solution.

2) A -1.2 V vs. Ag/AgCl deposition potential was applied on the glassy carbon electrode for 60 s. After this step, the electrode was named as *ex situ* bismuth modified electrode.

3) The *ex situ* bismuth modified electrode was , then, transfered into another electrochemical cell that contained a mixed solution of 10.00 µL of 50 mM Ph-S-S-Ph and 20.00 mL acetate buffer pH 4.5.

4) A -0.9 V vs. Ag/AgCl deposition potential was applied on the glassy carbon electrode for 60 s.

5) A square wave potential form was scanned from -0.2 to -1.0 V vs. Ag/AgCl with the setting parameters as follow; 50 mV E_p, 15 mV E_s at 70 Hz. The responding current was recorded during the scan.

6) Steps 4) to 5) were repeated at least two times. Latter, the measured peak currents were averaged and standard deviation value was calculated.

7) A cleaning potential of +0.3 V vs. Ag/AgCl was applied for 180 s. Then, the glassy carbon electrode was polish as described in Section 4.2.1.

8) Steps 1) to 7) were repeated with different values of E_s; 7.5, 10, 15, 20, 25, 30, 35 and 40 mV.

3.5.2.3 Effect of applied frequency

3.5.2.3.1 *In situ* method

1) A glassy carbon electrode was immersed in a mixed solution of 10.00 µL of 50 mM Ph-S-S-Ph and 20.00 mL of 0.5 ppm bismuth solution.

2) A -1.2 V vs. Ag/AgCl deposition potential was applied on the glassy carbon electrode for 60 s.

3) A square wave potential form was scanned from -0.2 to -1.0 V vs. Ag/AgCl with the setting parameters as follow; 50 mV E_p, 15 mV E_s at 70 Hz. The responding current was recorded during the scan.

4) Then, a cleaning potential of +0.3 V vs. Ag/AgCl was applied for 180 s.

5) Steps 2) to 4) were repeated at least two times. Latter, the measured peak currents were averaged and standard deviation value was calculated.

6) Steps 2) to 5) were repeated with different values of frequency; 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 Hz.

3.5.2.3.2 *Ex situ* method

1) A glassy carbon electrode was immersed in 20.00 mL of 0.5 ppm bismuth solution.

2) A -1.2 V vs. Ag/AgCl deposition potential was applied on the glassy carbon electrode for 60 s. After this step, the electrode was named as *ex situ* bismuth modified electrode.

3) The *ex situ* bismuth modified electrode was , then, transfered into another electrochemical cell that contained a mixed solution of 10.00 µL of 50 mM Ph-S-S-Ph and 20.00 mL acetate buffer pH 4.5.

4) A -0.9 V vs. Ag/AgCl deposition potential was applied on the glassy carbon electrode for 60 s.

5) A square wave potential form was scanned from -0.2 to -1.0 V vs. Ag/AgCl with the setting parameters as follow; 50 mV E_p, 15 mV E_s at 70 Hz. The responding current was recorded during the scan.

6) Steps 4) to 5) were repeated at least two times. Latter, the measured peak currents were averaged and standard deviation value was calculated.

7) A cleaning potential of +0.3 V vs. Ag/AgCl was applied for 180 s. Then, the glassy carbon electrode was polish as described in Section 4.2.1.

8) Steps 1) to 7) were repeated with different values of frequency; 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 Hz.

3.5.2.4 Effect of applied deposition potential

1) A glassy carbon electrode was immersed in a mixed solution of 10.00 µL of 50 mM Ph-S-S-Ph and 20.00 mL of 0.5 ppm bismuth solution.

2) A -1.2 V vs. Ag/AgCl deposition potential was applied on the glassy carbon electrode for 60 s.

3) A square wave potential form was scanned from -0.2 to -1.0 V vs. Ag/AgCl with the setting parameters as follow; 50 mV E_p, 15 mV E_s at 70 Hz. The responding current was recorded during the scan.

4) Then, a cleaning potential of +0.3 V vs. Ag/AgCl was applied for 180 s.

5) Steps 2) to 4) were repeated at least two times. Latter, the measured peak currents were averaged and standard deviation value was calculated.

6) Steps 2) to 5) were repeated with different values of deposition potential; -0.7, -0.8, -0.9, 1.0, -1.1, -1.2, -1.3, -1.4 and -1.5 V.

3.5.2.5 Effect of applied deposition time

1) A glassy carbon electrode was immersed in a mixed solution of 10.00 µL of 50 mM Ph-S-S-Ph and 20.00 mL of 0.5 ppm bismuth solution.

2) A -1.2 V vs. Ag/AgCl deposition potential was applied on the glassy carbon electrode for 60 s.

3) A square wave potential form was scanned from -0.2 to -1.0 V vs. Ag/AgCl with the setting parameters as follow; 50 mV E_p, 15 mV E_s at 70 Hz. The responding current was recorded during the scan.

4) Then, a cleaning potential of +0.3 V vs. Ag/AgCl was applied for 180 s.

5) Steps 2) to 4) were repeated at least two times. Latter, the measured peak currents were averaged and standard deviation value was calculated.

6) Steps 2) to 5) were repeated with different values of deposition time; 5, 10, 15, 30, 60, 90, 120, 180, 240 and 300 s

3.5.2.6 Effect of applied bismuth concentration

1) A glassy carbon electrode was immersed in a mixed solution of 10.00 µL of 50 mM Ph-S-S-Ph and 20.00 mL acetate buffer pH 4.5.

2) A 100.00 µL of 50 ppm bismuth solution was added into the previous solution and its diluted concentration is shown in Table 3.1.

3) A -1.2 V vs. Ag/AgCl deposition potential was applied on the glassy carbon electrode for 60 s.

4) A square wave potential form was scanned from -0.2 to -1.0 V vs. Ag/AgCl with the setting parameters as follow; 50 mV E_p, 15 mV E_s at 70 Hz. The responding current was recorded during the scan.

5) Then, a cleaning potential of +0.3 V vs. Ag/AgCl was applied for 180 s.

6) Steps 3) to 5) were repeated at least two times. Latter, the measured peak currents were averaged and standard deviation value was calculated.

7) Step 2) to 6) were repeated with different volumes of bismuth concentration; 100, 200, 300, 400, 500, 600 and 700 µL.

Table 3.1 Bismuth concentrations used in the studies of bismuth concentration effect

Volume of 50 ppm bismuth solution (μL)	Total volume (mL)	Final bismuth concentration in the electrochemical cell (ppm)
100.00	20.00	0.3
200.00	20.00	0.5
300.00	20.00	0.7
400.00	20.00	1.0
500.00	20.00	1.2
600.00	20.00	1.5
700.00	20.00	2.0

3.5.2.7 Electrode morphological studies

3.5.2.7.1 Bare glassy carbon electrode

1) A glassy carbon electrode was cleaned as described in Section 3.4.1

2) Then, the electrode was rinsed with DI water and kept in the DI water prior to be investigated by scanning electron microscopy (SEM)

3.5.2.7.2 Adsorped bismuth particle

1) A glassy carbon electrode was immersed in 20.00 mL of 0.5 ppm bismuth solution.

2) A -1.2 V vs. Ag/AgCl deposition potential was applied on the glassy carbon electrode for 60 s.

3) Then, the electrode was removed from the electrochemical cell, rinsed with DI water and kept in the DI water prior to be investigated by SEM.

3.5.2.7.3 Adsorped bismuth-analyte co-deposition

1) A glassy carbon electrode was immersed in a mixed solution of 10.00 µL of 50 mM Ph-S-S-Ph and 20.00 mL of 0.5 ppm bismuth solution.

2) A -1.2 V vs. Ag/AgCl deposition potential was applied on the glassy carbon electrode for 60 s.

3) Then, the electrode was removed from the electrochemical cell, rinsed with DI water and kept in the DI water prior to be investigated by SEM.

3.6 Analytical performance

3.6.1 Experimental procedure on the *in situ* bismuth modified electrode

1) A glassy carbon electrode was immersed in a mixed solution of analyte; 10.00 µL of 50 µM Ph-S-S-Ph solution or 1.00 µL of 50 mM Bu-SH, 200.00 µL of 50 ppm bismuth solution and 20.00 mL acetate buffer pH 4.5.

2) A -1.2 V vs. Ag/AgCl deposition potential was applied on the glassy carbon electrode for 60 s.

3) A square wave potential form was scanned from -0.2 to -1.0 V vs. Ag/AgCl with the setting parameters as follow; 50 mV E_p, 15 mV E_s at 70 Hz. The responding current was recorded during the scan.

4) Then, a cleaning potential of +0.3 V vs. Ag/AgCl was applied for 180 s.

5) Steps 2) to 4) were repeated at least two times. Latter, the measured peak currents were averaged and standard deviation value was calculated.

6) Steps 1) to 5) were repeated with different analyte volume as shown in Table 3.2 and Table 3.3

7) A calibration curve of each analyte was constructed and the linearity range was determined.

8) A lowest detection of each analyte was examined by 3SD method. The acetate buffer pH 4.5 was measured 10 times under optimal condition and then, the average of Ph-S-S-Ph and Bu-SH signals at -0.7 and -0.4 V vs Ag/AgCl and standard deviation value were calculated. Then, changed the unit from micro-ampere (μA) to molar (M) using the linear equation obtained calibration curve (Figure 4.12). Latter, the limit of detection was determined using equation 3.1;

$$\text{Limit of detection} = \bar{x} + 3SD \qquad (3.1)$$

When $\bar{x}$ is average concentration and SD is standard deviation value.

Table 3.2 Various Ph-S-S-Ph concentrations used in the analytical performance studies on the *in situ* bismuth modified electrode

Volume of 50 μM Ph-S-S-Ph (μL)	Total volume (mL)	Final Ph-S-S-Ph concentration in the electrochemical cell (nM)
10.00	20.21	24.74
20.00	20.22	49.4
30.00	20.23	74.1
40.00	20.24	98.8
50.00	20.25	123.4
60.00	20.26	148.1
70.00	20.27	172.7
80.00	20.28	197.2
90.00	20.29	221.8
100.00	20.30	246.3
110.00	20.31	270.8
120.00	20.32	295.3

Table 3.3 Various Bu-SH concentrations used in the analytical performance studies on the *in situ* bismuth modified electrode

Volume of 50 mM Bu-SH (µL)	**Total volume (mL)**	**Final Bu-SH concentration in the electrochemical cell (µM)**
1.00	20.20	2.5
2.00	20.20	5.0
3.00	20.20	7.4
4.00	20.20	9.9
5.00	20.20	12.4
6.00	20.21	14.8
7.00	20.21	17.3
8.00	20.21	19.8
9.00	20.21	22.3
10.00	20.21	24.7

3.6.2 Experimental procedure on the *ex situ* bismuth modified electrode

1) A glassy carbon electrode was immersed in 20.00 mL of 0.5 ppm bismuth solution.

2) A -1.2 V vs. Ag/AgCl deposition potential was applied on the glassy carbon electrode for 60 s. After this step, the electrode was named as *ex situ* bismuth modified electrode.

3) The *ex situ* bismuth modified electrode was , then, transfered into another electrochemical cell that contained a mixed solution of 10.00 µL of 50 µM Ph-S-S-Ph solution or 1.00 µL of 50 mM Bu-SH and 20.00 mL acetate buffer pH 4.5.

4) A -0.9 V vs. Ag/AgCl deposition potential was applied on the glassy carbon electrode for 60 s.

5) A square wave potential form was scanned from -0.2 to -1.0 V vs. Ag/AgCl with the setting parameters as follow; 50 mV E_p, 15 mV E_s at 70 Hz. The responding current was recorded during the scan.

6) Steps 3) to 5) were repeated at least two times. Latter, the measured peak currents were averaged and standard deviation value was calculated.

7) A cleaning potential of +0.3 V vs. Ag/AgCl was applied for 180 s. Then, the glassy carbon electrode was polished as described in Section 4.2.1.

8) Steps 1) to 7) were repeated with different analyte volume as shown in Table 3.4 and Table 3.5

9) A calibration curve of each analyte was constructed and the linearity range was determined

10) A lowest detection of each analyte was examined by 3SD method. The acetate buffer pH 4.5 was measured 10 times under optimal condition and then, the average of Ph-S-S-Ph and Bu-SH signals at -0.7 and -0.4 V vs Ag/AgCl and standard deviation value were calculated. Then, changed the unit from micro-ampere (µA) to molar (M) using the linear equation obtained calibration curve (Figure 4.12). Latter, the limit of detection was determined using equation 3.1.

Table 3.4 Various Ph-S-S-Ph concentrations used in the analytical performance studies on the *ex situ* bismuth modified electrode

Volume of 50 µM Ph-S-S-Ph (µL)	Total volume (mL)	Final Ph-S-S-Ph concentration in the electrochemical cell (nM)
10.00	20.00	25.0
20.00	20.00	50.0
30.00	20.00	74.9
40.00	20.00	99.8
50.00	20.00	124.7
60.00	20.01	149.5
70.00	20.01	174.4
80.00	20.01	199.2
90.00	20.01	224.0
100.00	20.10	248.5
110.00	20.11	273.5
120.00	20.12	298.2

Table 3.5 Various Bu-SH concentrations used in the analytical performance studies on the *ex situ* bismuth modified electrode

Volume of 50 µM Bu-SH (µL)	Total volume (mL)	Final Bu-SH concentration in the electrochemical cell (µM)
1.00	20.00	2.5
2.00	20.00	5.0
3.00	20.00	7.5
4.00	20.00	10.0
5.00	20.00	12.5
6.00	20.01	15.0
7.00	20.01	17.5
8.00	20.01	20.0
9.00	20.01	22.5
10.00	20.01	25.0

3.6.3 Experimental procedure on the HMDE

1) An analyt solution; 10.00 µL of 50 µM Ph-S-S-Ph solution or 1.00 µL of 50 mM Bu-SH, was pipetted into 20.00 mL acetate buffer pH 4.5 that contained in an electrochemical cell.

2) A -0.9 V vs. Ag/AgCl deposition potential was applied on the glassy carbon electrode for 60 s.

3) A square wave potential form was scanned from -0.2 to -1.0 V vs. Ag/AgCl with the setting parameters as follow; 50 mV E_p, 15 mV E_s at 70 Hz. The responding current was recorded during the scan.

4) Steps 2) to 3) were repeated at least two times. Latter, the measured peak currents were averaged and standard deviation value was calculated.

5) Steps 1) to 4) were repeated with different analyte volume as shown in Table 3.6 and Table 3.7

6) A calibration curve of each analyte was constructed and the linearity range was determined

7) A lowest detection of each analyte was examined by 3SD method. The acetate buffer pH 4.5 was measured 10 times under optimal condition and then, the average of Ph-S-S-Ph and Bu-SH signals at -0.7 and -0.4 V vs Ag/AgCl

and standard deviation value were calculated. Then, changed the unit from micro-ampere (μA) to molar (M) using the linear equation obtained calibration curve (Figure 4.12). Latter, the limit of detection was determined using equation 3.1.

Table 3.6 Various Ph-S-S-Ph concentrations used in the analytical performance studies on HMDE

Volume of 50 μM Ph-S-S-Ph (μL)	Total volume (mL)	Final Ph-S-S-Ph concentration in the electrochemical cell (nM)
8.00	20.0	20.0
10.00	20.0	25.0
20.00	20.0	50.0
30.00	20.0	75.0
40.00	20.0	100.0
50.00	20.0	125.0
60.00	20.0	150.0
70.00	20.0	175.0
80.00	20.0	200.0
90.00	20.0	225.0
100.00	20.0	250.0
110.00	20.0	275.0
120.00	20.0	300.0

Table 3.7 Various Bu-SH concentrations used in the analytical performance studies on HMDE

Volume of 50 μM Bu-SH (μL)	Total volume (mL)	Final Bu-SH concentration in the electrochemical cell (μM)
1.00	20.00	2.5
2.00	20.00	5.0
3.00	20.00	7.5
4.00	20.00	10.0
5.00	20.00	12.5
6.00	20.01	15.0
7.00	20.01	17.5
8.00	20.01	20.0
9.00	20.01	22.5
10.00	20.01	25.0

3.7 Determination of diphenyldisulfide (Ph-S-S-Ph) and butanethiol (Bu-SH) in real sample

The standard addition method was used to determine the amount of diphenyldisulfide (Ph-S-S-Ph) and butanthiol (Bu-SH) in jet fuel and kerosene

3.7.1 Experimental procedure on the *in situ* bismuth modified electrode

1) A glassy carbon electrode was immersed in a mixed solution of 20.00 mL acetate buffer pH 4.5, 200.00 µL of 50 ppm bismuth solution and 1.00 mL sample solution.

2) The 20.00 µL of 50 µM Ph-S-S-Ph and 1.00 µL of 50 mM Bu-SH were added into the previous solution.

3) A -1.2 V vs. Ag/AgCl deposition potential was applied on the glassy carbon electrode for 60 s.

4) A square wave potential form was scanned from -0.2 to -1.0 V vs. Ag/AgCl with the setting parameters as follow; 50 mV E_p, 15 mV E_s at 70 Hz. The responding current was recorded during the scan.

5) Then, a cleaning potential of +0.3 V vs. Ag/AgCl was applied for 180 s.

6) Steps 3) to 5) were repeated at least two times. Latter, the measured peak currents were averaged and standard deviation value was calculated.

7) Steps 1) to 6) were repeated with different standard volumes as show in Table 3.8.

Table 3.8 Various Ph-S-S-Ph and Bu-SH standard volumes used in the standard addition method on the *in situ* bismuth modified electrode

Addition number	**Volume of (µL)**		**Standard concentration in the electrochemical cell**	
	50 µM Ph-S-S-Ph	50 mM Bu-SH	Ph-S-S-Ph (nM)	Bu-SH (µM)
1	20.00	0.80	47.1	1.9
2	30.00	1.60	70.6	3.8
3	40.00	3.20	94.1	7.5
4	50.00	3.60	117.6	8.5
5	60.00	4.00	141.1	9.4

3.7.2 Experimental procedure on the *ex situ* bismuth modified electrode

1) A glassy carbon electrode was immersed in 20.00 mL of 0.5 ppm bismuth solution.

2) A -1.2 V vs. Ag/AgCl deposition potential was applied on the glassy carbon electrode for 60 s. After this step, the electrode was named as *ex situ* bismuth modified electrode.

3) The *ex situ* bismuth modified electrode was , then, transfered into another electrochemical cell that contained a mixed solution of 20.00 mL acetate buffer pH 4.5 and 1.00 mL sample solution.

4) The 20.00 µL of 50 µM Ph-S-S-Ph and 1.00 µL of 50 mM Bu-SH were added into the previous solution.

5) A -0.9 V vs. Ag/AgCl deposition potential was applied on the glassy carbon electrode for 60 s.

6) A square wave potential form was scanned from -0.2 to -1.0 V vs. Ag/AgCl with the setting parameters as follow; 50 mV E_p, 15 mV E_s at 70 Hz. The responding current was recorded during the scan.

7) Steps 5) to 6) were repeated at least two times. Latter, the measured peak currents were averaged and standard deviation value was calculated.

8) A cleaning potential of +0.3 V vs. Ag/AgCl was applied for 180 s. Then, the glassy carbon electrode was polish as described in Section 4.2.1.

8) Steps 1) to 8) were repeated with different standard volumes as show in Table 3.9.

Table 3.9 Various Ph-S-S-Ph and Bu-SH standard volumes used in the standard addition method on the *ex situ* bismuth modified electrode

Addition number	**Volume of (μL)**		**Standard concentration in the electrochemical cell**	
	50 μM Ph-S-S-Ph	50 mM Bu-SH	Ph-S-S-Ph (nM)	Bu-SH (μM)
1	20.00	2.00	47.6	4.7
2	40.00	4.00	95	9.5
3	60.00	6.00	142.4	14.2
4	80.00	8.00	189.7	19.0
5	100.00	10.00	236.8	23.7

3.7.3 Experimental procedure on the hanging mercury drop electrode (HMDE)

1) The 1.00 mL of sample solution was pipette into 20.00 mL acetate buffer pH 4.5 that contained in an electrochemical cell.

2) The 10.00 μL of 50 μM Ph-S-S-Ph solution and 1.00 μL of 50 mM Bu-SH were added into previous solution.

3) A -0.9 V vs. Ag/AgCl deposition potential was applied on the HMDE for 60 s.

4) A square wave potential form was scanned from -0.2 to -1.0 V vs. Ag/AgCl with the setting parameters as follow; 50 mV E_p, 15 mV E_s at 70 Hz. The responding current was recorded during the scan.

4) Steps 2) to 3) were repeated at least two times. Latter, the measured peak currents were averaged and standard deviation value was calculated

.

5) Steps 3) to 4) were repeated with different analyte volume as shown in Table 3.10.

Table 3.10 Various Ph-S-S-Ph and Bu-SH standard volumes used in standard addition method by HMDE

Addition number	**Volume of (µL)**		**Standard concentration in the 20.00 mL electrochemical**	
	50 µM Ph-S-S-Ph	**50 mM Bu-SH**	**Ph-S-S-Ph**	**Bu-SH**
1	20.00	1.00	50.0	2.5
2	40.00	2.00	100.0	5.0
3	60.00	3.00	150.0	7.5
4	80.00	4.00	200.0	10.0
5	100.00	5.00	250.0	12.5
6	120.0	6.00	300	15.0

CHAPTER IV

RESULTS AND DISCUSSION

This chapter describes an electrochemical behavior of two sulfur compounds; the diphenyldisulfide (Ph-S-S-Ph) and butanethiol (Bu-SH), in petroleum medium measured on the *in situ* and *ex situ* bismuth electrodes in comparison with the classic hanging mercury drop electrode (HMDE). The diphenyldisulfide (Ph-S-S-Ph) represents those sulfur compounds contained in petroleum distillates at nano-molar level where butanethiol (Bu-SH) represents the sulfurs compound in micro-molar level. Parameters influence on the voltammetric signal would be studied and optimized. Then, an analytical performance of each electrode was investigated under the optimized conditions. Finally, the determination of diphenyldisulfide (Ph-S-S-Ph) and butanethiol (Bu-SH) in petroleum distillated samples by the developed electrode were performed.

4.1 Electrochemical behavior of diphenyldisulfide (Ph-S-S-Ph) and butanethiol (Bu-SH) on the bismuth modified electrodes in comparison with mercury electrode

The electrochemical reductions of diphenyldisulfide (Ph-S-S-Ph) and butanethiol (Bu-SH) were investigated on the *in situ* and *ex situ* bismuth modified electrodes, in comparison with the hanging mercury drop electrode (HMDE) using square wave voltammetry (SWV). The voltammetric responses obtained on those three electrodes were compared in Figure 4.1.

Figure 4.1(a) demonstrates the Ph-S-S-Ph responses measured on the *in situ* bismuth modified electrode, *ex situ* bismuth modified electrode and HMDE. Peaks located at -0.62, -0.76 and -0.56 V correspond to the reduction of Ph-S-S-Ph on the *in situ* bismuth modified electrode, *ex situ* bismuth modified electrode and HMDE, respectively. The peaks obtained on the bismuth modified electrode are board and located about 6 to 20 mV negative to that obtained on the HMDE. However, the heights of peak measured from the bismuth modified electrodes were slightly higher than one measured from the HMDE.

The voltammetric response of the Bu-SH is presented in Figure 4.1(b). Peaks located at -0.42, -0.47 and -0.30 V correspond to the reduction of Bu-SH on the *in situ* bismuth modified electrode, *ex situ* bismuth modified electrode and HMDE, respectively. Similar to the Ph-S-S-Ph response, the Bu-SH peaks obtained on these bismuth modified electrodes located at a few millivolts more negative than that obtained on the HMDE. The peak heights measured by the bismuth modified electrode were higher than that measured by the HMDE.

By the fact that both sulfur compounds were electrochemically detected on the bismuth modified electrodes in a similar manner as on the HMDE [10]; in term of peak position, shape and height, therefore, an analogous mechanism is proposed as show in equations (4.1) and (4.2) for Ph-S-S-Ph and (4.3) and (4.4) for Bu-SH;

$$\mathrm{RSSR} + \mathrm{Bi}^{3+} + 3e^{-} \longrightarrow [(\mathrm{RS})_2\mathrm{Bi}]_{\mathrm{ads}} \tag{4.1}$$

$$[(\mathrm{RS})_2\mathrm{Bi}]_{\mathrm{ads}} + 2e^{-} + 2\mathrm{H}^{+} \longrightarrow 2\mathrm{RSH} + \mathrm{Bi(s)} \tag{4.2}$$

$$\mathrm{RSH} + \mathrm{Bi}^{3+} + 2e^{-} \longrightarrow [\mathrm{Bi(RS)}]_{\mathrm{ads}} + \mathrm{H}^{+} \tag{4.3}$$

$$[\mathrm{Bi(RS)}]_{\mathrm{ads}} + e^{-} + \mathrm{H}^{+} \longrightarrow \mathrm{RSH} + \mathrm{Bi(s)} \tag{4.4}$$

where RSSR represents disulfide compound and RSH represents sulfide compound.

The above results lead us to a conclusion that the bismuth modified electrodes could be used as a mercury electrode replacement for sulfide compounds determination in petroleum medium.

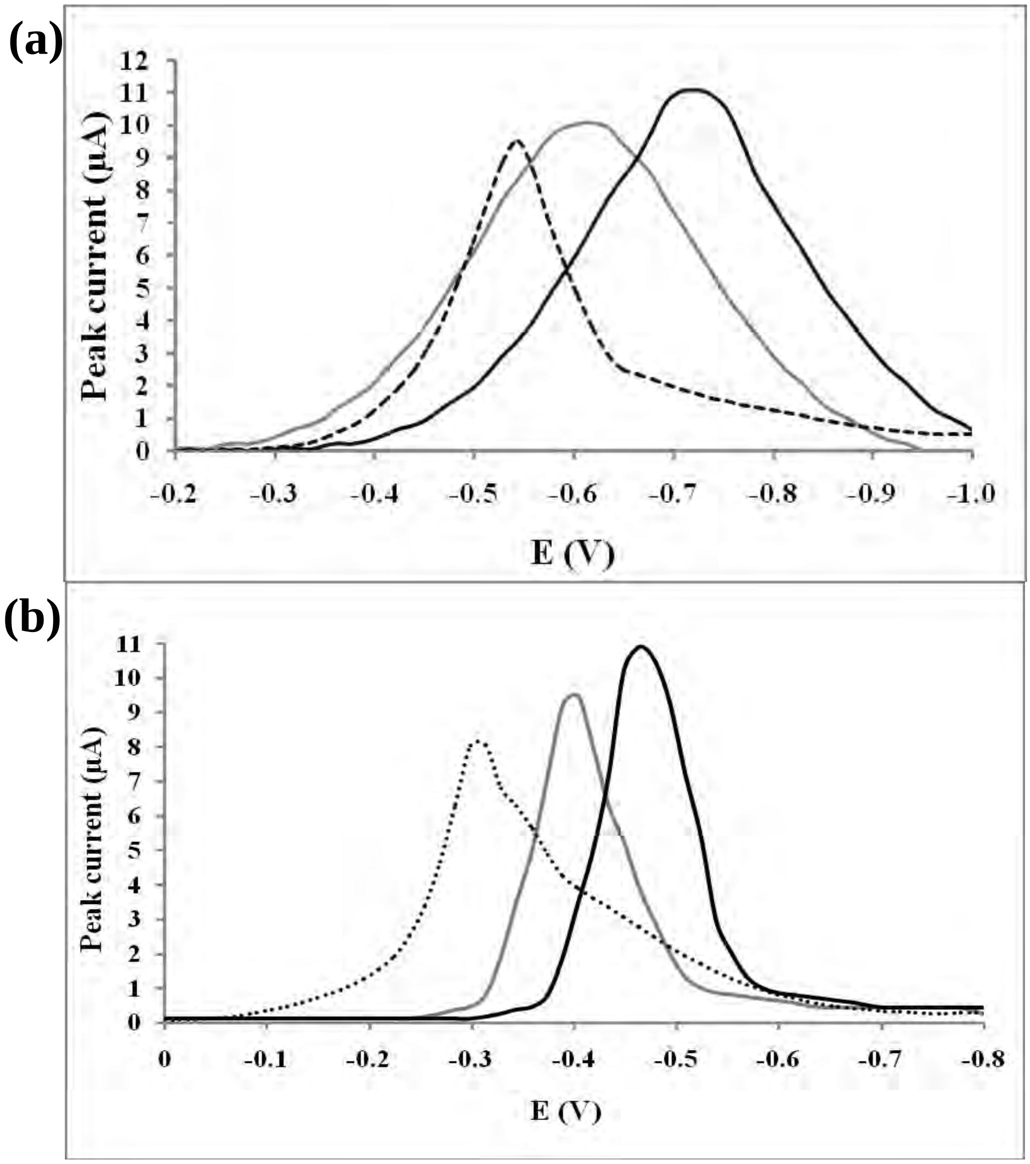

Figure 4.1 Square wave voltammograms of (a) 25 µM diphenyldisulfide (Ph-S-S-Ph) and (b) 25 µM butanethiol (Bu-SH) on the *in situ* bismuth modified electrode (grey solid line), *ex situ* bismuth modified electrode (black solid line) and HMDE (dash line); amplitude 50 mV, voltage step 15 mV at frequency 70 Hz

4.2 Studies of parameters that influence on the voltammetric signal

The square wave voltammetric signal in this studies alter upon variation of pulse amplitude, voltage step, applied frequency, deposition potential and time as well as bismuth concentration used in the electrode preparation procedure. Therefore, studied of these parameter effects and obtained the experimental optimum that maximize the response of the target analytes is importance. As the diphenyldisulfide (Ph-S-S-Ph) contained at the least amount among another sulfur compounds present in petroleum distillated [22, 23], it was, then, chosen as a model analyte throughout the studies in this section. In addition, since the measured voltammetric signal corresponds to the amount of bismuth-analyte particles accumulated on the electrode surface (discussed later), thus, the studies of effect due to the deposition potential and time including the bismuth concentration would be focused on the *in situ* bismuth modified electrode.

4.2.1 Effect of applied pulse amplitude (E_p)

Figure 4.2(a) shows an effect of pulse amplitude on square wave voltammograms of 25 μM diphenyldisulfide (Ph-S-S-Ph) measured on the *in situ* bismuth modified electrode. The peak heights were determined and plotted against the applied pulse amplitude as shown in Figure 4.2(b). Linear increasing of the peak height with increasing of the pulse amplitude was observed in a range of 10 – 50 mV. Beyond the 50 mV pulse amplitude, the peak height was not improved and the precision of the peak height measurement trends to decrease with larger pulse amplitude. The same result effect was obtained on the *ex situ* bismuth modified electrode (Figure 4.3). Therefore, the pulse amplitude of 50 mV was considered to be used in the further measurements.

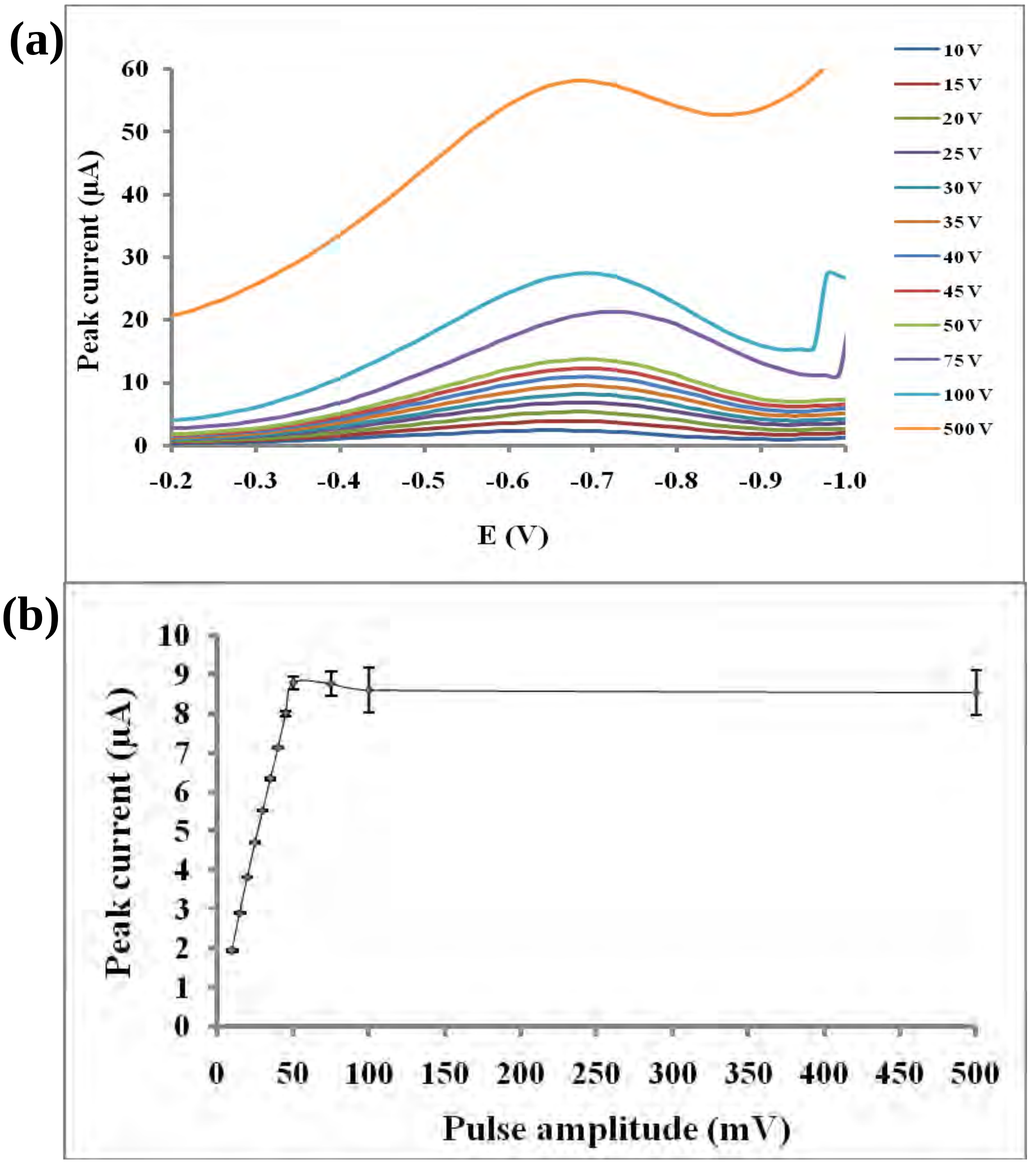

Figure 4.2 (a) Square wave voltammograms of 25 µM diphenyldisulfide (Ph-S-S-Ph) at various pulse amplitudes measured on the *in situ* bismuth modified electrode and (b) effect of pulse amplitude on 25 µM diphenyldisulfide (Ph-S-S-Ph) peak current; voltage step of 15 mV at 70 Hz

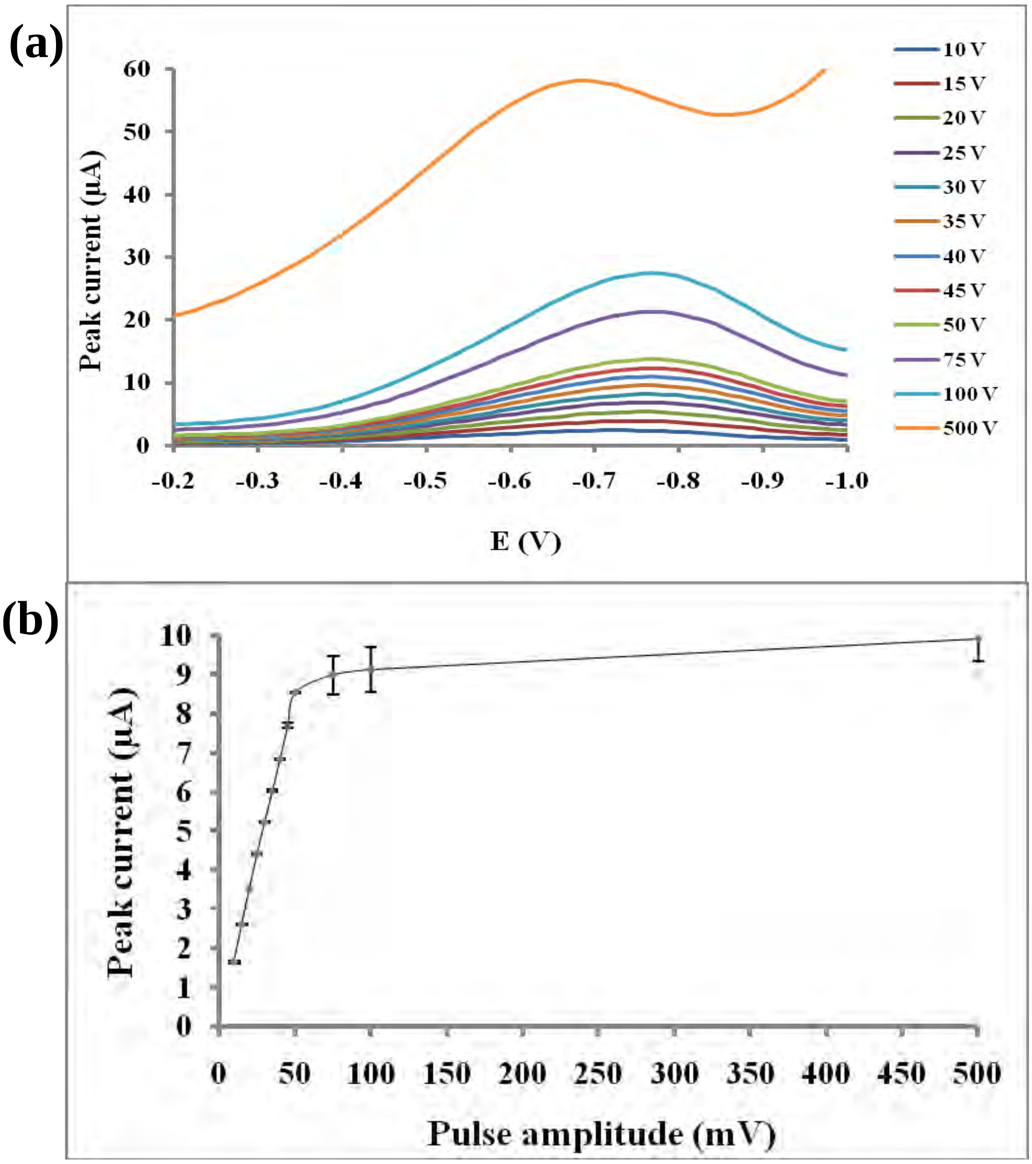

Figure 4.3 (a) Square wave voltammograms of 25 µM diphenyldisulfide (Ph-S-S-Ph) at various pulse amplitudes measured on the *ex situ* bismuth modified electrode and (b) effect of pulse amplitude on 25 µM diphenyldisulfide (Ph-S-S-Ph) peak current; voltage step of 15 mV at 70 Hz

4.2.2 Effect of applied voltage step (E_s)

An effect of applied voltage step on the diphenyldisulfide (Ph-S-S-Ph) peak height was monitored from 7.5, 10, 15, 20, 25, 30 and 40 mV. An increasing of the peak height with the voltage step was observed upto

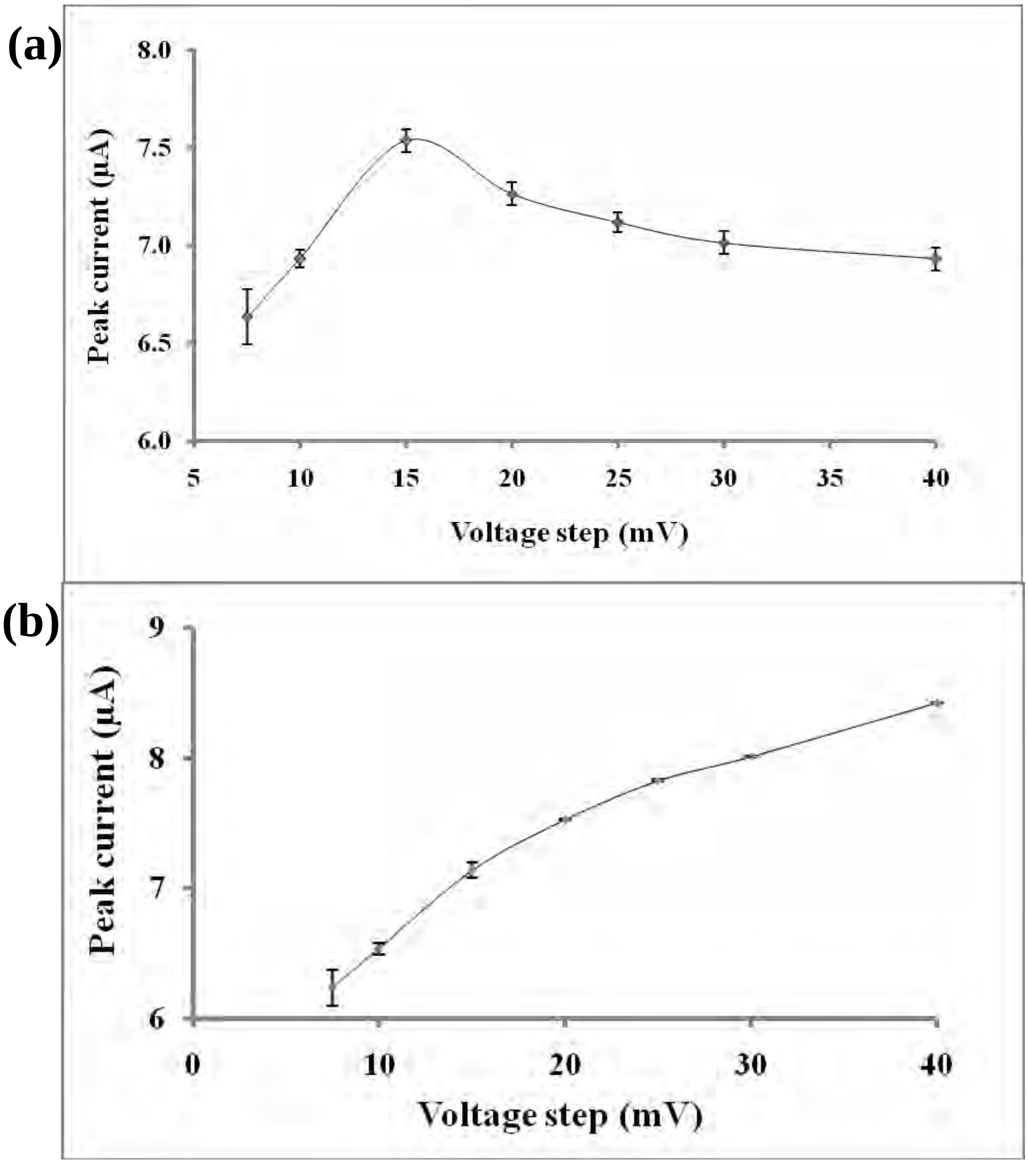

Figure 4.4 Effect of voltage step on 25 µM diphenyldisulfide (Ph-S-S-Ph) measured by (a) *in situ* bismuth modified electrode and (b) *ex situ* bismuth modified electrode; 50 mV pulse amplitude at 70 Hz

15 mV on the *in situ* bismuth modified electrode (Figure 4.4(a)). Beyond this point, the peak height slowly decreased as the voltage step increased. Unlike the *in situ* bismuth modified electrode, the decreasing of peak height at high voltage step did not occur on the *ex situ* bismuth modified electrode (Figure 4.4(b)). However slow increasing of the peak height was found when the applied voltage step was larger than 15 mV. Therefore, the voltage step of 15 mV was considered to be used in the further measurements.

4.2.3 Effect of applied frequency

An effect of applied frequency on the diphenyldisulfide (Ph-S-S-Ph) peak height was studied at 10, 20, 30, 40, 50, 60, 70, 80, 90 and 100 Hz. An increasing of the peak current with the frequency was observed upto 70 mV on both the *in situ* and *ex situ* bismuth modified electrodes (Figure 4.5). At the frequency higher than 70 Hz, the peak current seem to be independent on the applied frequency. The peak current did not change much when 80, 90 and 100 Hz was applied, while less precision on the peak current measurement occurred in that high frequency range. Therefore, the frequency of 70 Hz was considered to be use in the further measurements.

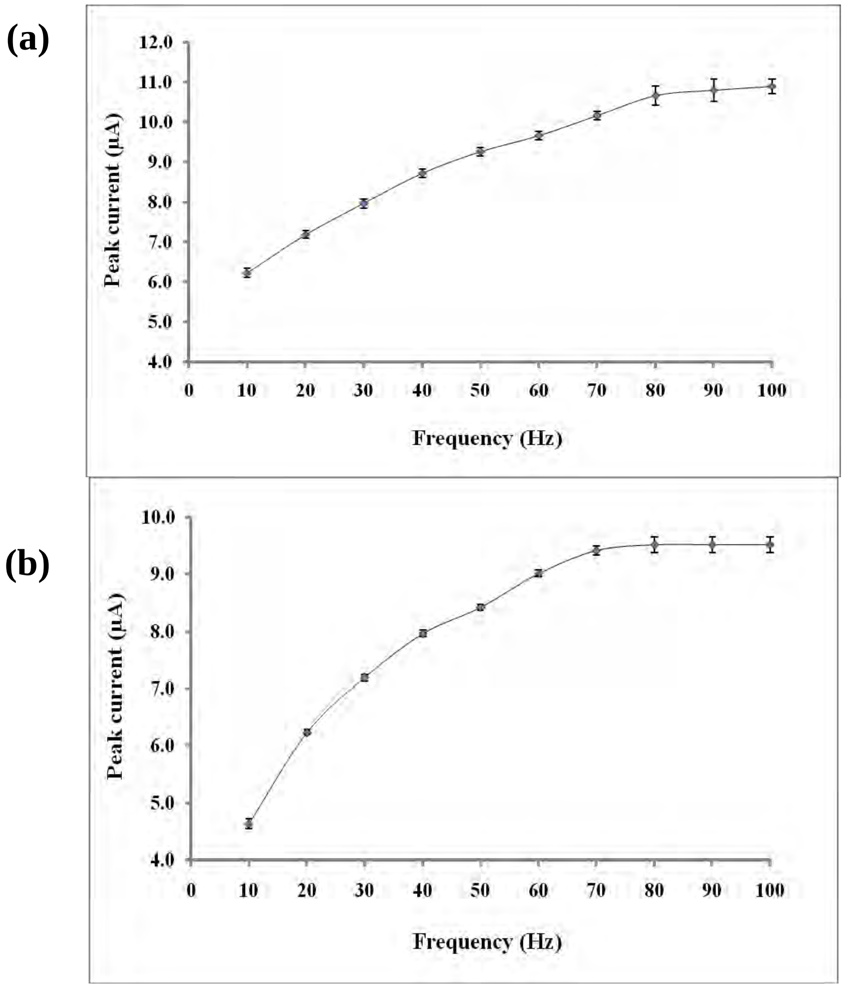

Figure 4.5 Effect of frequency on 25 µM diphenyldisulfide (Ph-S-S-Ph) measured by (a) *in situ* bismuth modified electrode and (b) *ex situ* bismuth modified electrode; 50 mV pulse amplitude at 70 Hz

4.2.4 Effect of applied deposition potential

Voltammograms of 25 μM diphenyldisulfide (Ph-S-S-Ph) obtained at difference deposition potentials on the *in situ* bismuth modified electrode is presented in Figure 4.6(a). The diphenyldisulfide (Ph-S-S-Ph) peak located about -0.6 V and begun to shift to more position potential direction when the deposition potential increased from -1.1 to -1.5 V. In the same potential range, a small shoulder of bismuth peak was also observed about -0.4 V. Heights of the diphenyldisulfide (Ph-S-S-Ph) peak were also measured and plotted against the applied potential (Figure 4.6(b)). An increasing of the diphenyldisulfide (Ph-S-S-Ph) peak current with the applied deposition potential was observed from -0.7 to -1.2 V. This due to the more $[(PhS)_2Bi]_{ads}$ particle accumulated on the electrode surface during the more negative deposition potential applied. This hypothesis is confirmed by SEM images of the electrode surface taken right after the applied deposition potential completed. It is clearly demonstrated in Figure 4.7(a) and 4.7(b) where the applied deposition potentials were -0.7 and -1.2 for 60 s, respectively, that the number of particles accumulated on the electrode surface increased with the deposition potential of -0.7 to -1.2 V. The particle size in Figure 4.7(a) were in a range of 478 to 516 nm where the size in the Figure 4.7(b) was not possible to determine due to the highly aggregation of the particles. However, from Figure 4.7(d) and 4.7(e) where bismuth particles, from a solution contained no analyte, adsorped on the electrode surface by electrode position at -0.7 V and -1.2 V, respectively, it was found that the bismuth particles size were mostly the same; 218 – 236 nm. This result indicates that the applied deposition potential has a strong effect on the particles aggregation and less effect on the size of the accumulated particle.

Once the applied deposition potential was more negative than -1.2 V, the decreasing in peak current was found in Figure 4.6(b). This account could resulted from many more particles accumulated on the electrode surface due to very large negative potential applied and these particles located very close to each other or, perhaps, adjustment to each other, resulting in film formation on the electrode surface (Figure 4.7(c) and 4.7 (f)) instead of small particle size formation. This leads to a change of electrode surface phenomena and therefore, the sensitivity of the electrode. It obvious that once the film phenomena started to form at the deposition potential of -1.3 V, the peak current was 11.7% reduced and it was hardly alter with the large negative deposition potential anymore (Figure 4.6(b)).

Figure 4.7(c) and 4.7(f) demonstrate SEM images of electrode surface covered with the $[(PhS)_2Bi]_{ads}$ film and bismuth film, respectively, after an electrodeposition was applied at -1.5 V for 60 s. Small size particles were no larger found on the electrode surface. Therefore, to maintain the electrode morphology of nano-particle size formation and obtained the highest sensitivity of the electrode, the deposition potential of -1.2 V was chosen for the further measurements.

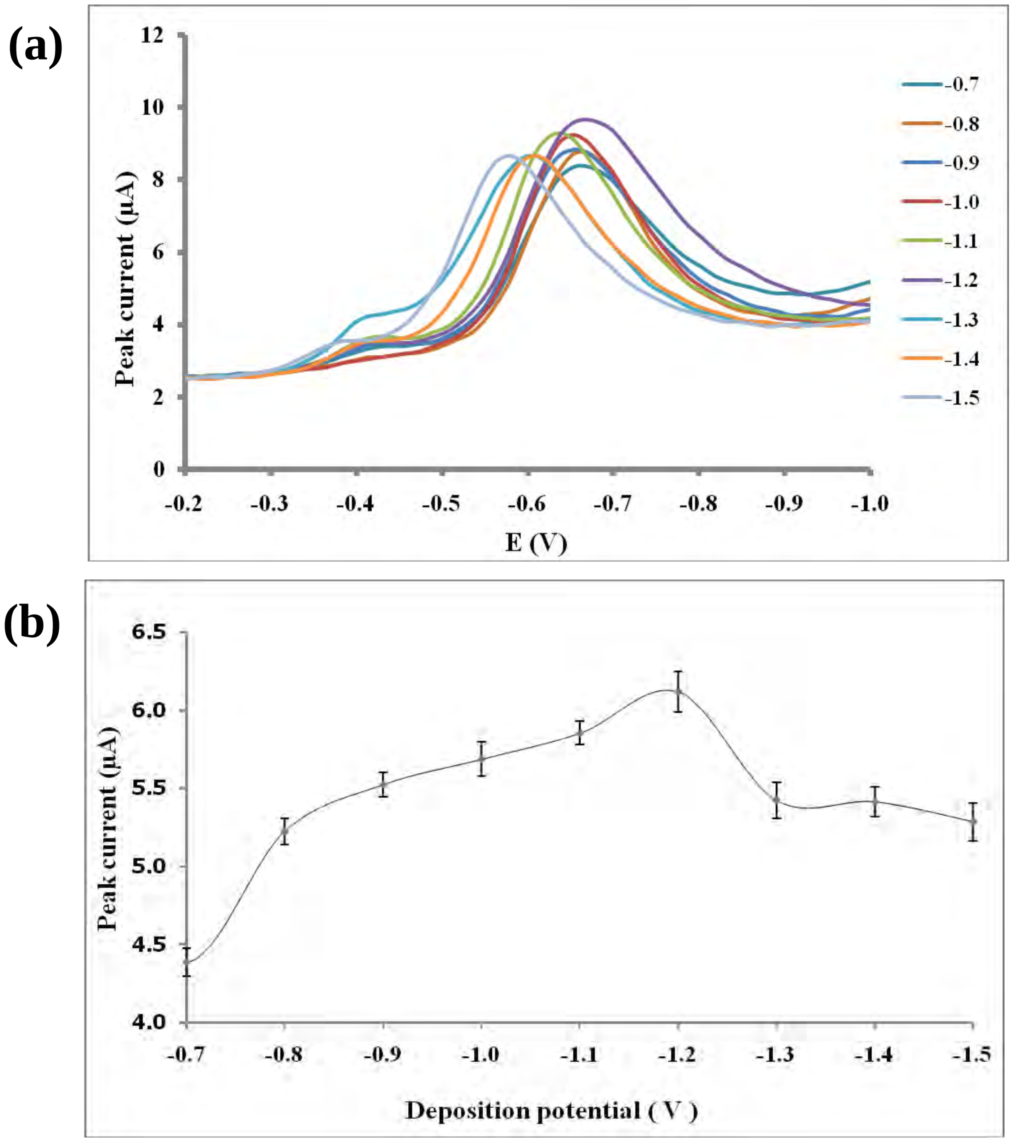

Figure 4.6 (a) Square wave voltammograms of 25 µM diphenyldisulfide (Ph-S-S-Ph) at various deposition potentials measured on the *in situ* bismuth modified electrode and (b) effect of deposition potential on 25 µM diphenyldisulfide (Ph-S-S-Ph) peak current; 0.5 ppm bismuth solution and 60 s deposition time

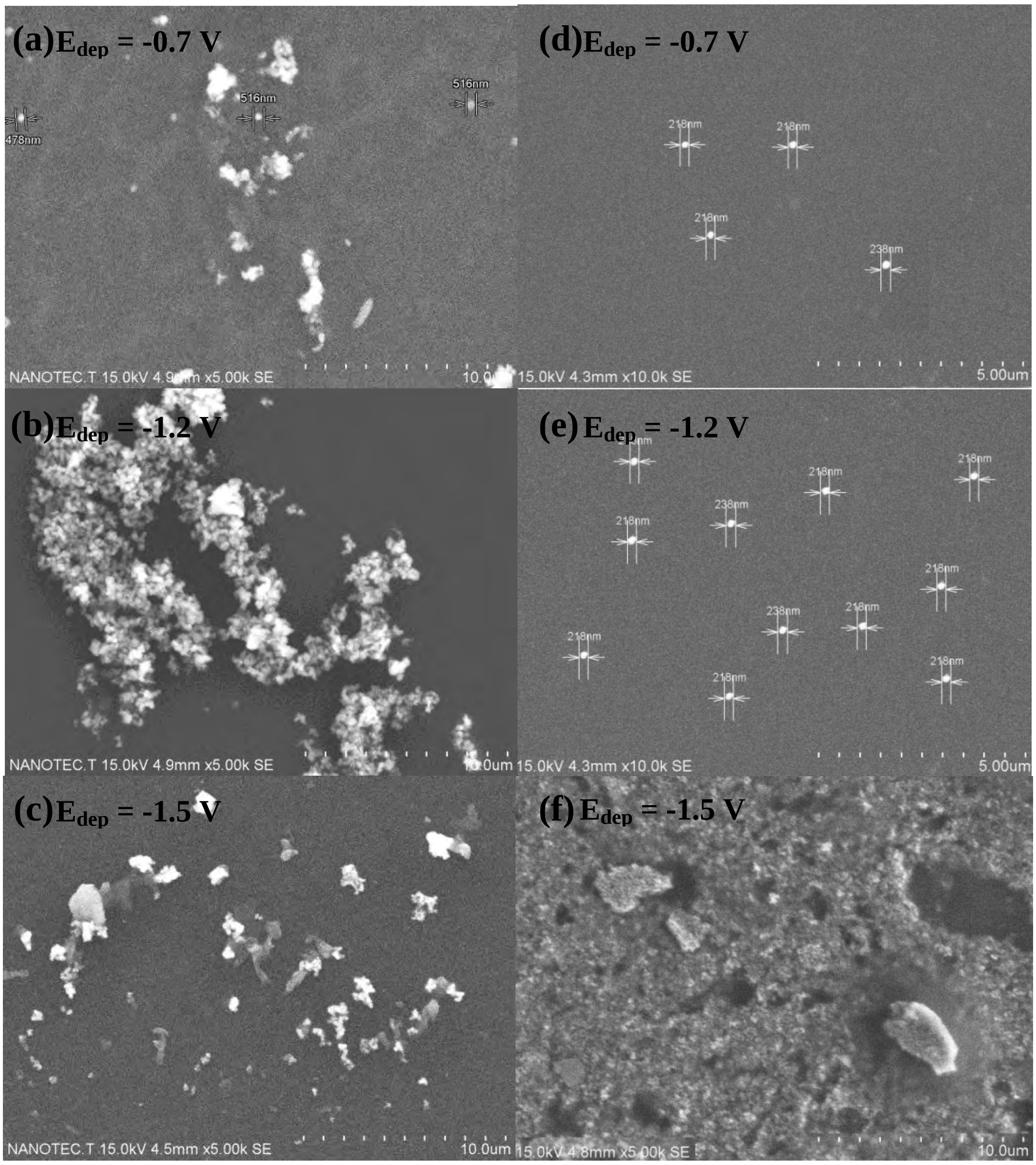

Figure 4.7 SEM images of (a-c) $[(PhS)_2Bi]_{ads}$ and (d-f) bismuth particles accumulated on the electrode surface at -0.7 V, -1.2 V and -1.5 V deposition potential for 60 s in 0.5 ppm bismuth solution

4.2.5 Effect of applied deposition time

An effect of deposition time on the diphenyldisulfide (Ph-S-S-Ph) peak currents was studied at -1.2 V in fixed concentrations of bismuth and diphenyldisulfide (Ph-S-S-Ph) solution; 0.5 ppm and 25 µM, respectively. The square wave voltammetric responses of diphenyldisulfide (Ph-S-S-Ph) at various applied deposition times are shown in Figure 4.8(a). Change of the peak current was determined and plotted against the applied deposition time in Figure 4.8(b). Note here that bismuth peak at about -0.4 V appeared when the deposition time was longer than 90 s. From Figure 4.8(b), a linear increasing of the peak current with increasing of the deposition time was observed in a range of 5 to 60 s. The result agrees well with SEM images shown in Figure 4.9(a) and 4.9(b) where higher aggregate particle was found at 60 s deposition time when compares with one at 5 s deposition time. Note that from Figure 4.9(e) and 4.9(f) the particle size also developed as the deposition time increased. For deposition time longer than 60 s, the film phenomena was observed on the electrode surface and this resulted in reducing of the peak current. Once the film phenomena formed at 90 s deposition time, the maximum of the peak current was 13.5% reduced and begun to be independent on the deposition time (Figure 4.8(b)). Similar to the reasons given in section 4.2.4, the deposition time of 60 s was consider to be suitable for applying in the further measurements.

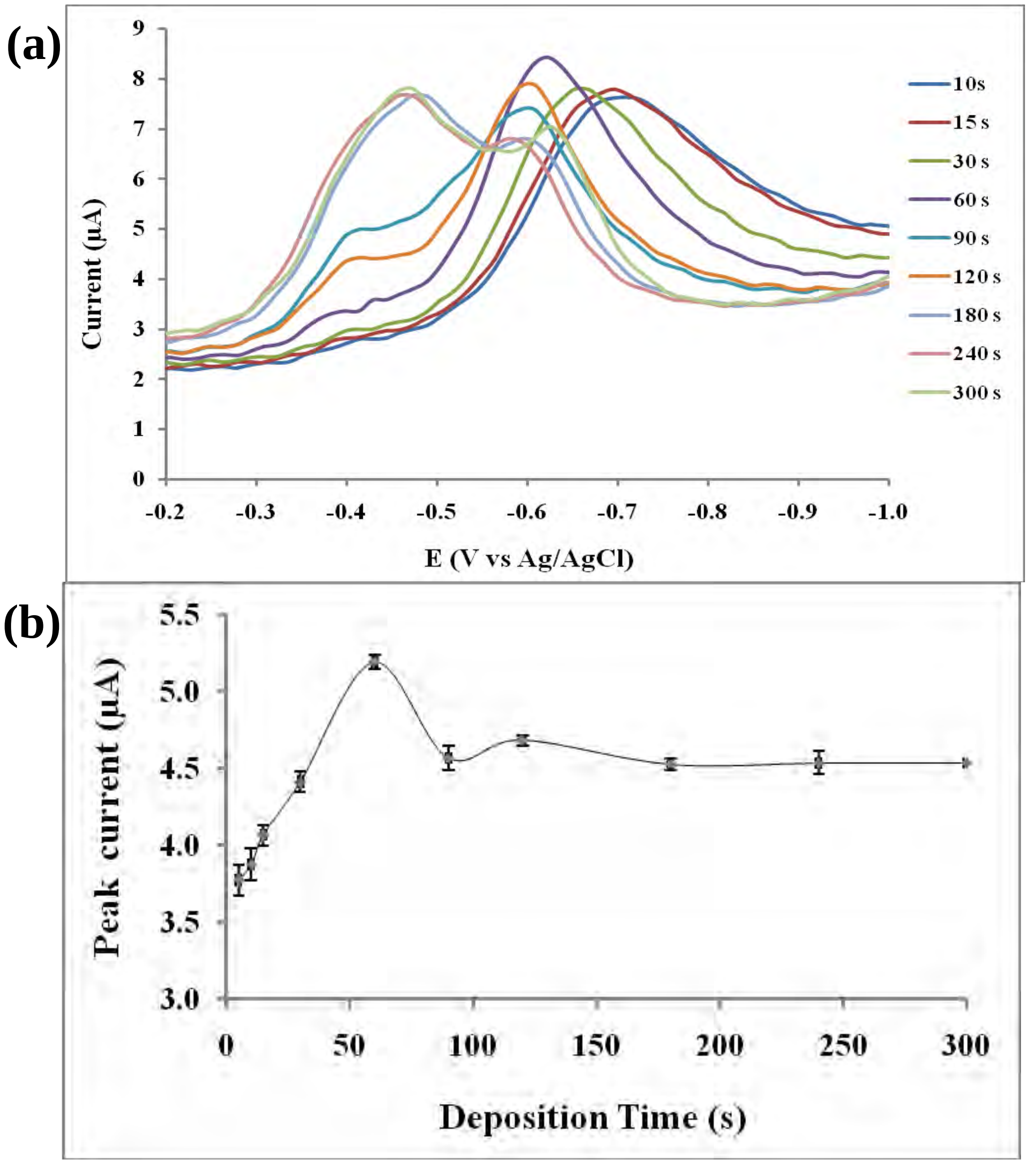

Figure 4.8 (a) Square wave voltammograms of 25 µM diphenyldisulfide (Ph-S-S-Ph) at various deposition times measured on the *in situ* bismuth modified electrode and (b) effect of deposition time on 25 µM diphenyldisulfide (Ph-S-S-Ph) peak current; 0.5 ppm bismuth solution and -1.2 V deposition potential

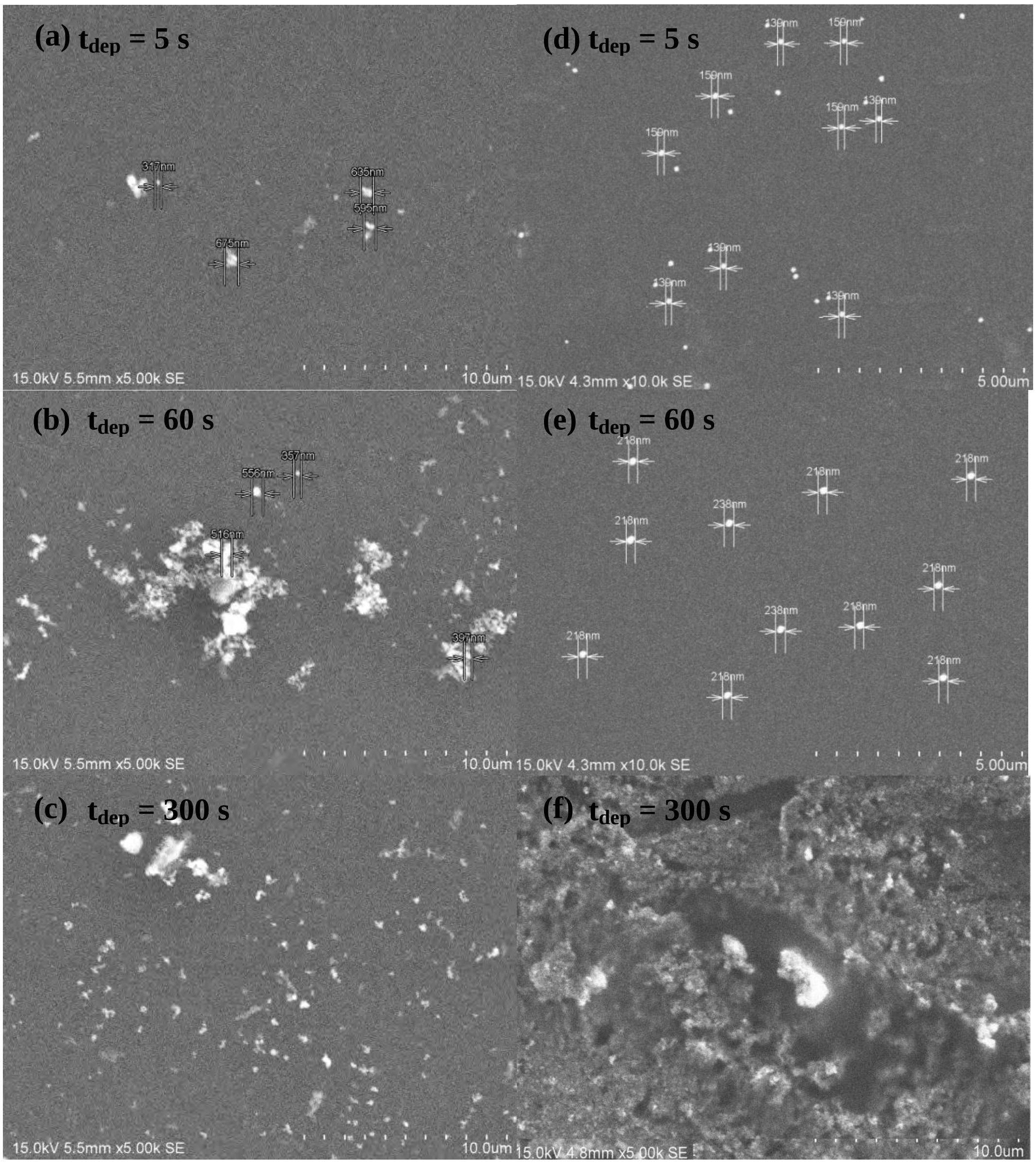

Figure 4.9 SEM images of (a-c) $[(PhS)_2Bi]_{ads}$ and (e-f) bismuth particles accumulated on the electrode surface at -1.2 V deposition potential for 5, 60 and 300 s in 0.5 ppm bismuth solution

4.2.6 Effect of bismuth concentration

A series of bismuth concentration in a range of 0.2, 0.5, 0.7, 1.0, 1.2, 1.5 and 2.0 ppm were used to investigate on *in situ* diphenyldisulfide (Ph-S-S-Ph) measurement. Square wave voltammetric responses of 25 μM diphenyldisulfide (Ph-S-S-Ph) in the various bismuth concentrations are shown in Figure 4.10(a). The diphenyldisulfide (Ph-S-S-Ph) peak locate at about -0.6 V slightly shift to negative potential direction when the bismuth concentration was higher than 1.2 ppm and the bismuth peak at about -0.4 was observed. The diphenyldisulfide (Ph-S-S-Ph) peak heights were determined and plotted against the bismuth concentration presented in the solution (Figure 4.10(b)). The highest peak current was found when bismuth concentration was 0.5 ppm. The results agree with SEM images shown in Figure 4.11 where the particles aggregated on the electrode surface more from solution contained 0.5 ppm bismuth than 1.0 ppm bismuth. Therefore, the bismuth concentration of 0.5 ppm was considered to be suitable for applying in the further measurements.

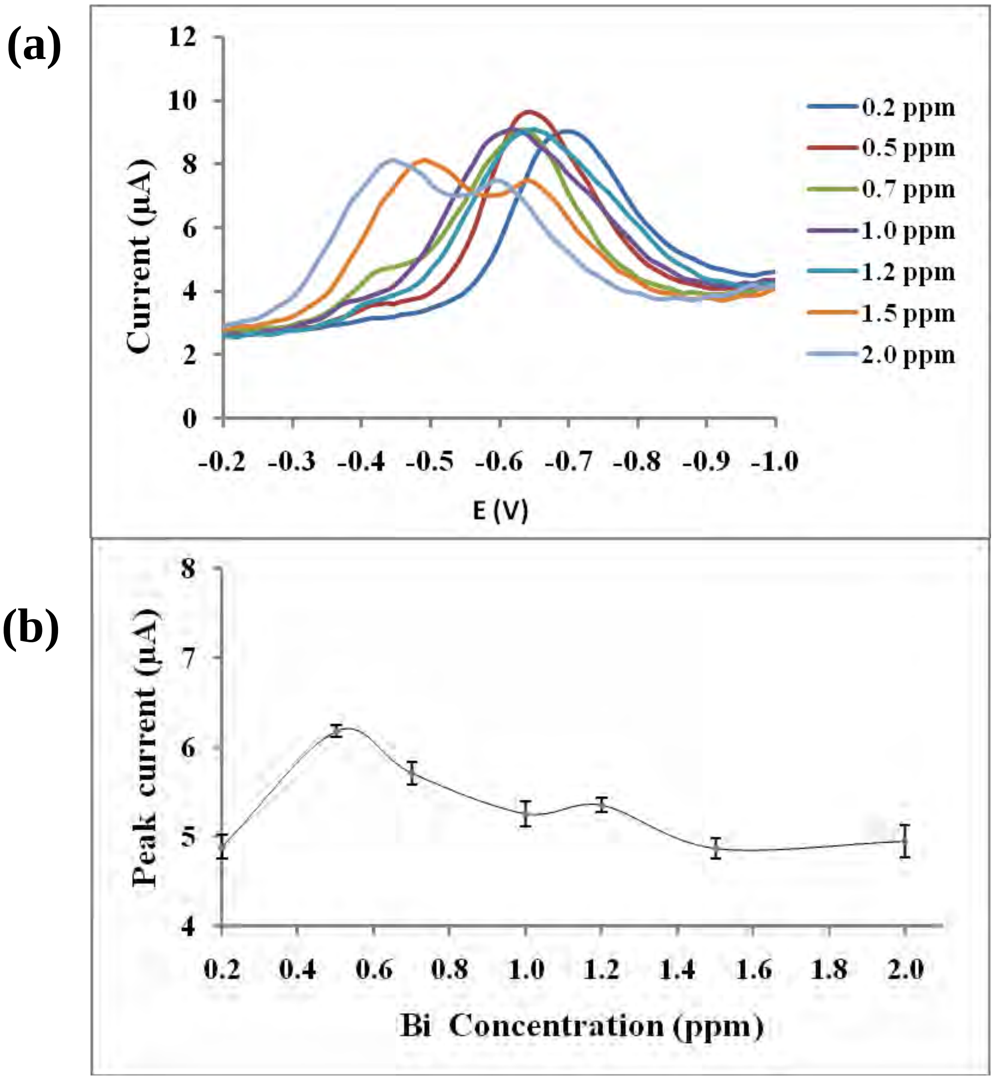

Figure 4.10 (a) Square wave voltammograms of 25 µM diphenyldisulfide (Ph-S-S-Ph) in various bismuth concentrations measured on the *in situ* bismuth modified electrode and (b) effect of bismuth concentration on 25 µM diphenyldisulfide (Ph-S-S-Ph) peak current; -0.9 V deposition potential for 60 s

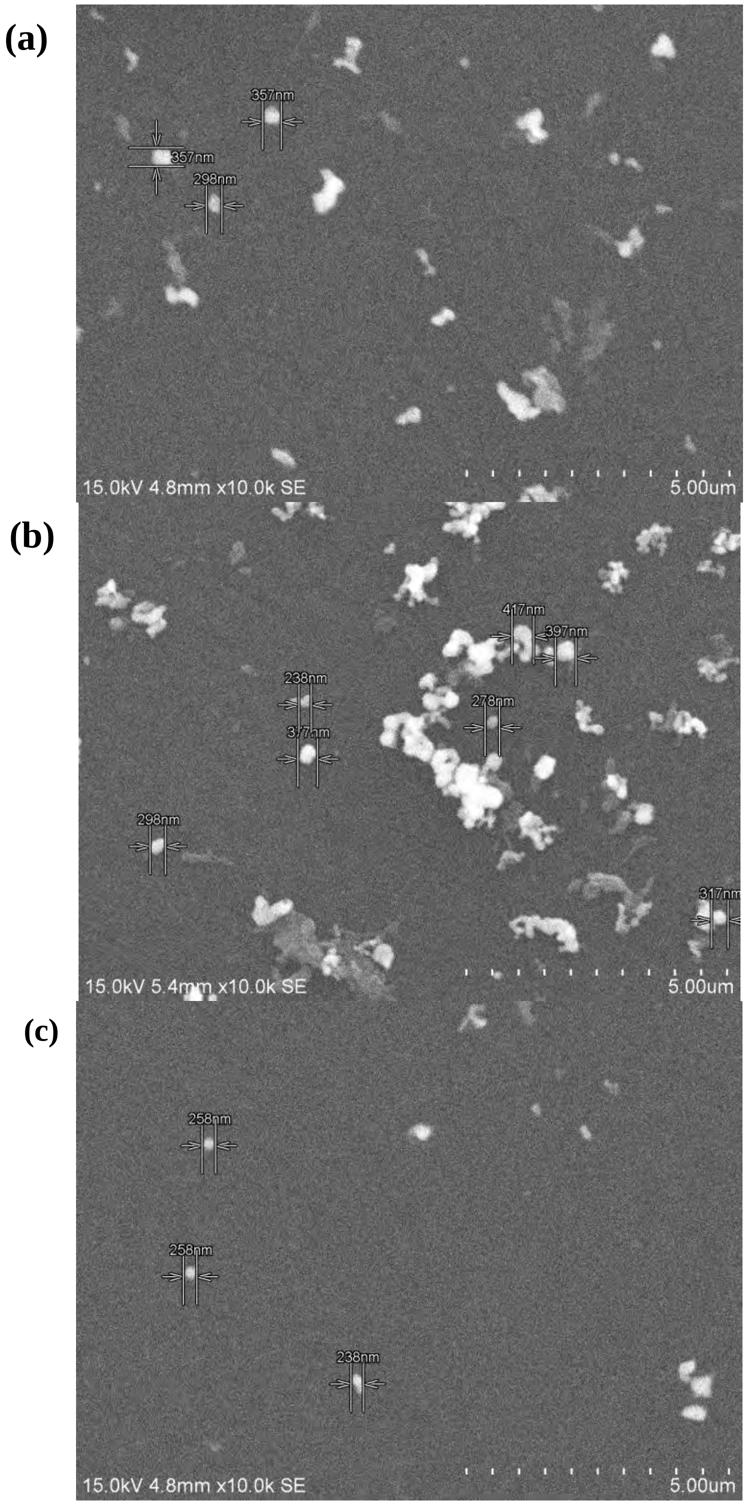

Figure 4.11 SEM images of $[(PhS)_2Bi]_{ads}$ accumulated on the electrode surface at -1.2 V deposition potential for 60 s in (a) 0.2, (b) 0.5 and (c) 1.0 ppm bismuth solution

In conclusion of this section, the optimal conditions that results in the highest sensitive square wave signal of sulfur compound were 50 mV pulse amplitude, 15 mV voltage step at 70 Hz in a solution contained 0.5 ppm bismuth contained solution by using -1.2 V deposition potential for 60 s.

4.3 Analytical performance

Under the optimum conditions found in section 4.2, the *in situ* and *ex situ* determinations of standard diphenyldisulfide (Ph-S-S-Ph) and butanethiol (Bu-SH) were performed in the petroleum medium; 1:1 toluene: methanol. Calibration curves and lowest detection limit were examined in compared with those obtained by the classic hanging mercury drop electrode (HMDE).

Figure 4.12 demonstrates voltammograms and calibration curves measured on the *in situ* and *ex situ* bismuth modified electrodes. It was found that linear ranges of diphenyldisulfide (Ph-S-S-Ph) were 49.4 – 246.3 nM and 25.0 - 149.5 nM when measured on the *in situ* and *ex situ* bismuth modified electrodes, respectively. Slop of calibration curve refers to a method sensitivity. In this case, it was found that the *ex situ* bismuth method (slop = 0.026 mM/A) provided 2-time higher in the sensitivity on the diphenyldisulfide (Ph-S-S-Ph) measurement when compare to the *in situ* bismuth method (slop = 0.010 mM/A). Lowest detection limit (LDL) determined by 3SD method indicates that 19.6 nM and 12.5 nM are the lowest detection limit of diphenyldisulfide (Ph-S-S-Ph) on the *in situ* and *ex situ* bismuth modified electrodes, respectively. Note here that the *ex situ* bismuth modified electrode provides a better sensitivity and detection limit for diphenyldisulfide (Ph-S-S-Ph) while the *in situ* cover a wider linear range in the diphenyldisulfide (Ph-S-S-Ph) calibration curve.

Unlike the diphenyldisulfide (Ph-S-S-Ph), the butanethiol (Bu-SH) linearity obtained in a range of 2.5 – 19.8 µM on the *in situ* bismuth modified electrode and 2.5 – 20.0 the *ex situ* bismuth modified electrode (Figure 4.12(d) and 4.12(e)) with a similar calibration slop. This implies that both electrodes have about the same sensitivity to the Butanethiol (Bu-SH). The butanethiol (Bu-SH) lowest detection limit (LDL) were 1.2 and 1.4 µM on the *in situ* and *ex situ* bismuth modified electrodes, respectively.

These data are summarized in Table 4.1, in comparison with those obtained via hanging mercury drop electrode (HMDE). The voltammograms and calibration curves obtained from the hanging mercury drop electrode (HMDE) are shown in Figure 4.12(c) and 4.12(f). From the Table 4.1, the linear ranges obtained on the bismuth modified electrodes cover most of the concentration that obtained on the hanging mercury drop electrode (HMDE) and extend wider to a higher concentration range. This is true for both diphenyldisulfide (Ph-S-S-Ph) and butanethiol (Bu-SH). However, the sensitivity of bismuth electrode is not better than one obtained on the hanging mercury drop electrode (HMDE).

The analytical performance of voltammetry with the bismuth modified electrodes was compared with other techniques. For the comparison with the gas chromatography (GC) technique[35], the linear rang and lowest detection limit (LDL) obtained from voltammetry with bismuth modified electrode for butanethiol are lower and wilder range than GC technique (LDL = 186 nM and linearity range = 186 μM – 930 μM). For the comparison with the inductive-couple plasma (ICP) technique, Jens et. al. [1] reported that the lowest detection limit (LDL) were found at 1.25 nM and linearity range from 0.3 – 3.1 μM for sulfur determination. Thus, these results demonstrate that the voltammetry with bismuth modified electrode is better than gas chromatography (GC) technique but is not better than with the inductive-couple plasma (ICP) technique. Moreover, the voltammetry with bismuth modified electrode is simple preparation and convenient operation and low cost of instrument. Thus, the voltammetry with bismuth modified electrode is attention to determine the sulfur compound in petroleum distillates.

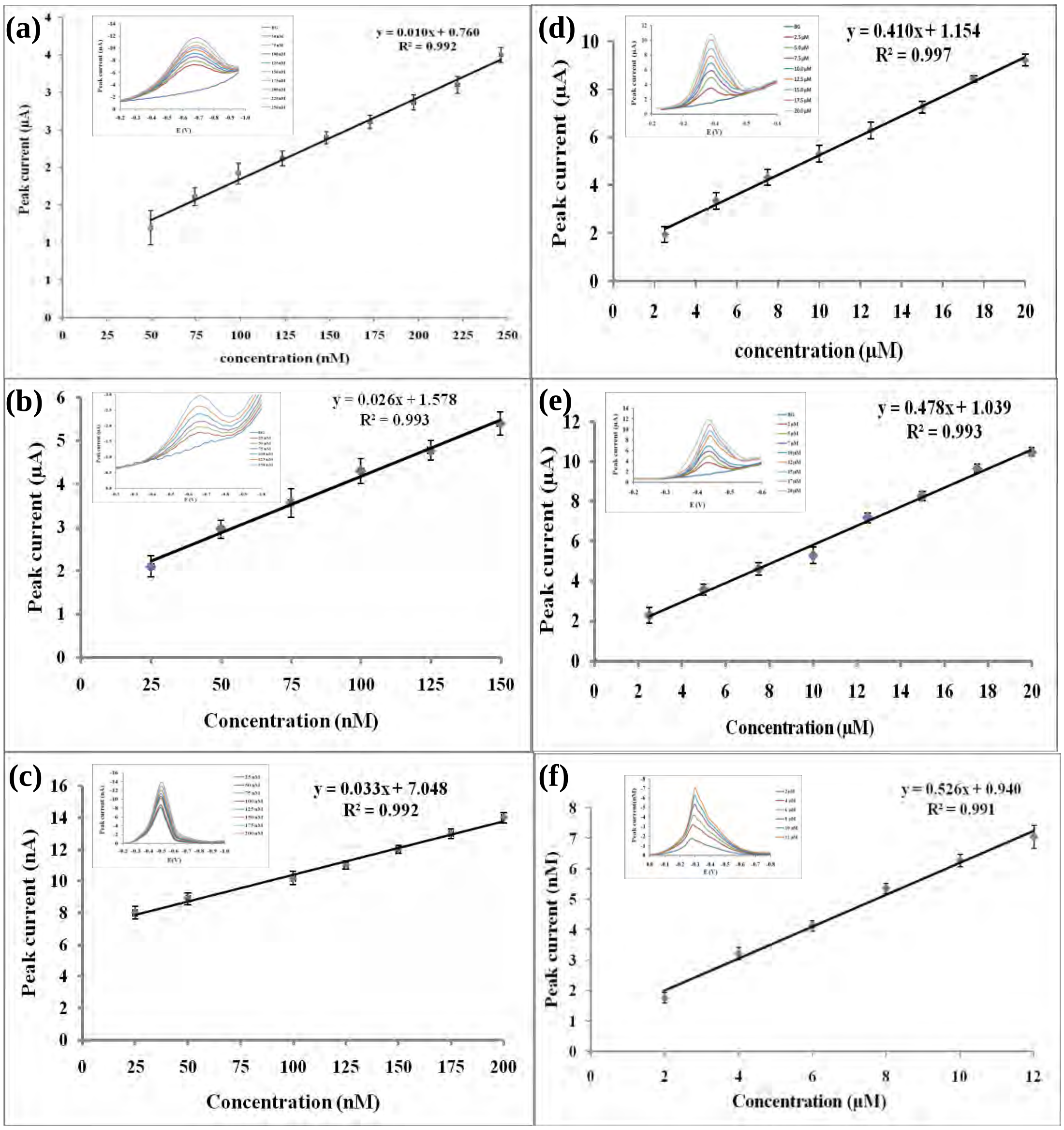

Figure 4.12 Diphenyldisulfide (Ph-S-S-Ph) calibration curves obtained on the (a) *in situ* bismuth modified electrode, (b) *ex situ* bismuth modified electrode and (c) hanging mercury drop electrode (HMDE) and butanethiol (Bu-SH) calibration curve obtained on the (d) *in situ* bismuth modified electrode, (e) *ex situ* bismuth modified electrode and (f) hanging mercury drop electrode (HMDE)

Table 4.1 Analytical performance of the *in situ* bismuth modified electrode and *ex situ* bismuth modified electrode

Sulfur compound	**Linearity range**			**Slop**			**R^2**			**Detection limit**		
	*In situ**	*Ex situ***	HMDE	*In situ**	*Ex situ***	HMDE	*In situ**	*Ex situ***	HMDE	*In situ**	*Ex situ***	HMDE
Ph-S-S-Ph	49.9 – 246.3 nM	25.0 – 149.5 nM	20.0 – 200 nM	0.010 A/mM	0.026 A/mM	0.033 A/mM	0.992	0.993	0.992	19.4 nM	12.5 nM	11. 7nM
Bu-SH	2.5 – 19.8 μM	2.5 – 20.0 μM	2.0 – 12.0 μM	0.410 A/M	0.478 A/M	0.526 A/M	0.997	0.993	0.991	1.2 μM	1.4 μM	0.5 μM

**in situ* = *in situ* bismuth modified electrode

**ex situ* = *ex situ* bismuth modified electrode

4.4 Determination of diphenyldisulfide (Ph-S-S-Ph) and butanethiol (Bu-SH) in Petroleum distillated

Jet fuel and kerosene were petroleum distillated samples used in this study. The developed *in situ* and *ex situ* bismuth modified electrodes were applied for the determination using standard addition method and results were compared with one measured by the hanging mercury drop electrode (HMDE).

Figure 4.13 shown the square wave voltammograms of the sample measured on *in situ* and *ex situ* bismuth modified electrodes including their standard addition curve**s.** When measured by *in situ* bismuth modified electrode, it indicated that 104.9±0.2 nM diphenyldisulfide (Ph-S-S-Ph) and 5.6±0.3μM butanethiol (Bu-SH) contained in kerosene and 230.9±0.1 nM diphenyldisulfide (Ph-S-S-Ph) and 12.6±0.3μM butanethiol (Bu-SH) contained in jet fuel. These results were reported in Table 4.2, in comparison with values found on the hanging mercury drop electrode (HMDE). Percent error was also calculated by using these values obtained on hanging mercury drop electrode (HMDE) as a reference. The amount of diphenyldisulfide (Ph-S-S-Ph) and butanethiol (Bu-SH) that contained in jet fuel and kerosene obtained from the *in situ* bismuth modified electrode were in a good agreement with mercury electrode HMDE.

Similar to values reported from using *in situ* bismuth modified electrode 100.9±0.1 nM diphenyldisulfide (Ph-S-S-Ph) and 4.9±0.3μM butanethiol (Bu-SH) contained in kerosene and 230.0±0.1 nM diphenyldisulfide (Ph-S-S-Ph) and 11.8±0.3μM butanethiol (Bu-SH) contained in jet fuel were found by using *ex situ* bismuth modified electrode. Then these results were compared with those from hanging mercury drop electrode (HMDE) and reported in Table 4.2, same way as described above.

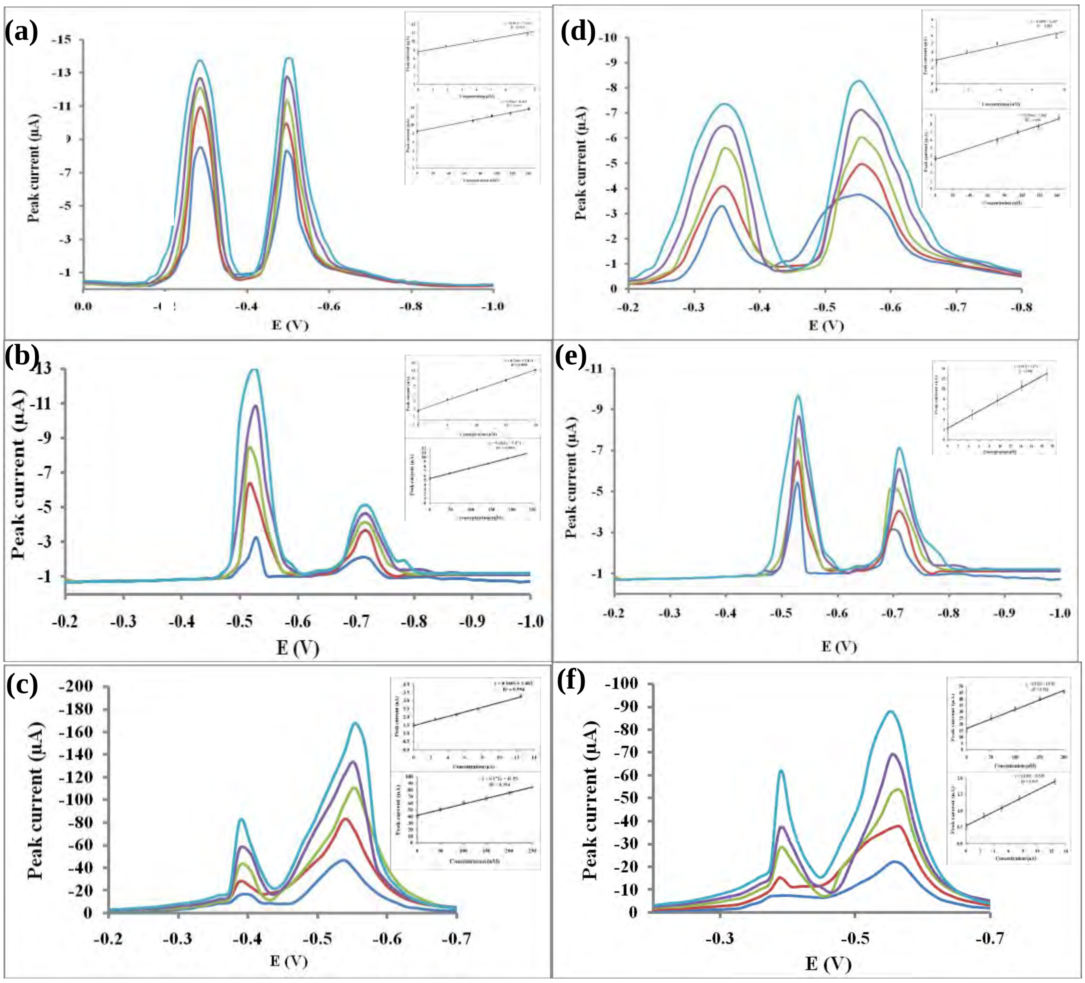

Figure 4.13 Square wave voltammograms of jet fuel on (a) the *in situ* bismuth modified electrode, (b) the *ex situ* bismuth modified electrode and (c) the HMDE and square wave voltammograms of kerosene on (d) the *in situ* bismuth modified electrode, (e) the *ex situ* bismuth modified electrode and (f) the HMDE

Table 4.2 Diphenyldisulfide and butanethiol concentrations detected in jet fuel and kerosene

Sample	***in situ* bismuth modified electrode**						***ex situ* bismuth modified electrode**					
	Diphenyldisulfide			**Butanethiol**			**Diphenyldisulfide**			**Butanethiol**		
	[C]* (nM)	**SD**	**%error**	**[C]* (µM)**	**SD**	**%error**	**[C]* (nM)**	**SD**	**%error**	**[C]* (µM)**	**SD**	**%err**
Jet fuel	230.9	0.1	10.6	12.6	0.3	10.5	230.0	0.1	10.6	11.8	0.3	3.5
Kerosene	104.9	0.2	1.1	5.6	0.3	7.7	100.9	0.1	2.8	4.9	0.3	5.8

[C] *= concentration

CHAPTER V

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The bismuth modified electrode has successfully been investigated to use as a mercury electrode replacement for trace sulfur compound determination in petroleum medium under optimal conditions as follow; apply -1.2 V for 60 s and scan with square wave voltammetry mode where 50 mV pulse amplitude and 15 mV voltage step at 70 Hz frequency is applied. A bismuth concentration of 0.5 ppm was considered as a suitable amount to use for the *in situ* and *ex situ* measurements. An analytical performance of the bismuth modified electrode, in comparison with the hanging mercury drop electrode (HMDE) shows that the bismuth modified electrodes have a wider linearity range than that of the hanging mercury drop electrode (HMDE). However, the hanging mercury drop electrode (HMDE) provides a better sensitivity and limit of detection (LOD) than those bismuth modified electrodes. In comparison with GC, the low detection limits obtained from this work were lower[32]. The developed bismuth modified electrodes were finally applied for diphenyldisulfide (Ph-S-S-Ph) and butanethiol (Bu-SH) determinations in petroleum distillated samples; kerosene and jet fuel. For the kerosene, the values reported from using the *in situ* bismuth modified electrodes were 104.9±0.2 nM diphenyldisulfide (Ph-S-S-Ph) and 5.6±0.3μM butanethiol (Bu-SH) and from using the *ex situ* bismuth modified electrodes were 100.9±0.1 nM diphenyldisulfide (Ph-S-S-Ph) and 4.9±0.3μM butanethiol (Bu-SH) While, the amount of diphenyldisulfide (Ph-S-S-Ph) and butanethiol (Bu-SH) contained in jet fuel were 230.9±0.1 nM and 12.6±0.3μM, respectively, when measured with the *in situ* bismuth modified electrode and 230.0±0.1 nM and 11.8±0.3μM, respectively, when measured with the *ex situ* bismuth modified electrodes. Then, these results were compared with the data obtained from the hanging mercury drop electrode (HMDE). The percent error of diphenyldisulfide (Ph-S-S-Ph) and butanethiol (Bu-SH) obtained on the *in situ* bismuth modified electrode were larger than from the *ex situ* bismuth modified electrode. It is likely that the co-deposition effect could affect the voltammetric signal. However, the bismuth modified electrodes were in a good agreement with classic hanging mercury electrode (HMDE). Thus, the bismuth modified electrode could be used as a mercury electrode replacement for sulfur determination in petroleum distillates.

5.2 Suggestion for Further Work

It is known that petroleum distillated consists of many sulfur compounds. Interference or matrices in the sample solution may affect to the analytical performance. The determination of total sulfur and investigation of interference and matrix effect to the determination of total sulfur present in petroleum distillates must be continued. Furthermore, new modified or preparation of bismuth modified electrode is an interesting aspect to be developed in order to obtain the electrode with better sensitivity and higher stability.

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APPENDIX

APPENDIX A

The average peak current data and square wave voltammogram

Table A1 The average peak current for diphenyldisulfide (Ph-S-S-Ph) at various pulse amplitudes by *in situ* bismuth modified electrode

Pulse amplitude (mV)	**Peak current (μA)**
10	1.91±0.02
15	2.89±0.03
20	3.76±0.02
25	4.63±0.03
30	5.44±0.03
35	6.22±0.02
40	7.19±0.01
45	7.93±0.07
50	8.89±0.10
75	8.56±0.50
100	8.43±0.56
500	8.02±0.56

Table A2 The average peak current for diphenyldisulfide (Ph-S-S-Ph) at various pulse amplitudes by *ex situ* bismuth modified electrode

Pulse amplitude (mV)	**Peak current (µA)**
10	1.65±0.03
15	2.61±0.02
20	3.55±0.01
25	4.41±0.02
30	5.24±0.02
35	6.04±0.02
40	6.84±0.01
45	7.72±0.05
50	8.56±0.01
75	13.00±0.50
100	16.13±0.56
500	16.33±0.56

Table A3 The average peak current for diphenyldisulfide (Ph-S-S-Ph) at various voltage steps by *in situ* bismuth modified electrode

Voltage step (mV)	**Peak current (µA)**
7.5	6.64±0.14
10.0	6.78±0.04
15.0	7.44±0.06
20.0	7.23±0.01
25.0	7.18±0.01
30.0	7.02±0.01
40.0	6.82±0.01

Table A4 The average peak current for diphenyldisulfide (Ph-S-S-Ph) at various voltage steps by *ex situ* bismuth modified electrode

Voltage step (mV)	**Peak current (µA)**
7.5	6.24±0.14
10.0	6.53±0.04
15.0	7.14±0.09
20.0	7.53±0.01
25.0	7.83±0.01
30.0	8.02±0.04
40.0	8.42±0.01

Table A5 The average peak current for diphenyldisulfide (Ph-S-S-Ph) at various frequencies by *in situ* bismuth modified electrode

Frequency (Hz)	**Peak current (µA)**
10	6.10±0.07
20	7.05±0.03
30	7.91±0.03
40	8.43±0.07
50	9.02±0.03
60	9.22±0.01
70	10.10±0.08
80	10.89±0.24
90	10.92±0.23
100	10.94±0.15

Table A6 The average peak current for diphenyldisulfide (Ph-S-S-Ph) at various frequencies by *ex situ* bismuth modified electrode

Frequency (Hz)	**Peak current (µA)**
10	4.70±0.07
20	6.15±0.03
30	6.99±0.03
40	7.8±0.07
50	8.46±0.03
60	9.02±0.01
70	9.39±0.08
80	9.49±0.17
90	9.51±0.15
100	9.45±0.15

Table A7 The average peak current for 25 µM diphenyldisulfide (Ph-S-S-Ph) at various deposition potentials

Deposition potential (V)	**Peak current (µA)**
-0.7	4.37±0.15
-0.8	5.21±0.08
-0.9	5.53±0.08
-1.0	5.70±0.11
-1.1	5.85±0.07
-1.2	6.13+0.13
-1.3	5.42±0.12
-1.4	5.41±0.10
-1.5	5.32+0.12

Table A8 The average peak current for 25 µM diphenyldisulfide (Ph-S-S-Ph) at various deposition times

Deposition time (s)	**Peak current (µA)**
5	3.77±0.16
10	3.88±0.14
15	4.07±0.07
30	4.41±0.07
60	5.20±0.10
90	4.57±0.35
120	4.68+0.04
180	4.53±0.04
240	4.54±0.07
300	4.59±0.10

Table A9 The average peak current for 25 µM diphenyldisulfide (Ph-S-S-Ph) at various bismuth concentrations

Bismuth concentration (ppm)	**Peak current (µA)**
0.2	4.89±0.37
0.5	6.18±0.06
0.7	5.71±0.13
1.0	5.26±0.14
1.2	5.36±0.08
1.5	4.87±0.11
2.0	4.95+0.48

Table A10 The average peak current of various diphenyldisulfide (Ph-S-S-Ph) concentrations on *in situ* bismuth modified electrode

Concentration (nA)	**Peak current (µA)**
49.4	1.20±0.23
74.1	1.61±0.12
98.8	1.92±0.14
123.4	2.12±0.10
148.1	2.40±0.08
172.7	2.61±0.09
197.2	2.87±0.10
221.8	3.10±0.11

Table A11 The average peak current of various diphenyldisulfide (Ph-S-S-Ph) concentrations on *ex situ* bismuth modified electrode

Concentration (nA)	**Peak current (µA)**
25.0	1.90±0.23
50.0	2.96±0.12
74.9	3.57±0.14
99.8	4.30±0.10
124.7	4.78±0.08
149.5	5.20±0.09

Table A12 The average peak current of various diphenyldisulfide (Ph-S-S-Ph) concentrations on HMDE

Concentration (nA)	**Peak current (µA)**
25	8.04±0.40
50	8.89±0.37
75	10.20±0.40
100	11.01±0.26
125	12.96±0.30
150	14.03±0.34

Table A13 The average peak current for butanethiol (Bu-SH) at various concentrations by *in situ* bismuth modified electrode

Concentration (µA)	**Peak current (µA)**
2.5	1.95±0.37
5.0	3.35±0.38
7.4	4.33±0.31
9.9	5.31±0.26
12.4	6.29±0.40
14.8	7.26±0.26
17.3	8.45±0.15
19.8	9.22±0.17

Table A14 The average peak current for butanethiol (Bu-SH) at various concentrations by *ex situ* bismuth modified electrode

Concentration (nA)	**Peak current (µA)**
2.5	2.27±0.39
5.0	3.58±0.28
7.5	4.62±0.33
10.0	5.29±0.41
12.5	7.17±0.26
15.0	8.26±0.22
17.5	9.65±0.21
20.0	10.48±0.21

Table A15 The average peak current for butanethiol (Bu-SH) at various concentrations by HMDE

Concentration (µA)	**Peak current (µA)**
2.0	1.76±0.39
4.0	3.21±0.20
6.0	4.12±0.15
8.0	5.35±0.14
12.0	6.27±0.26

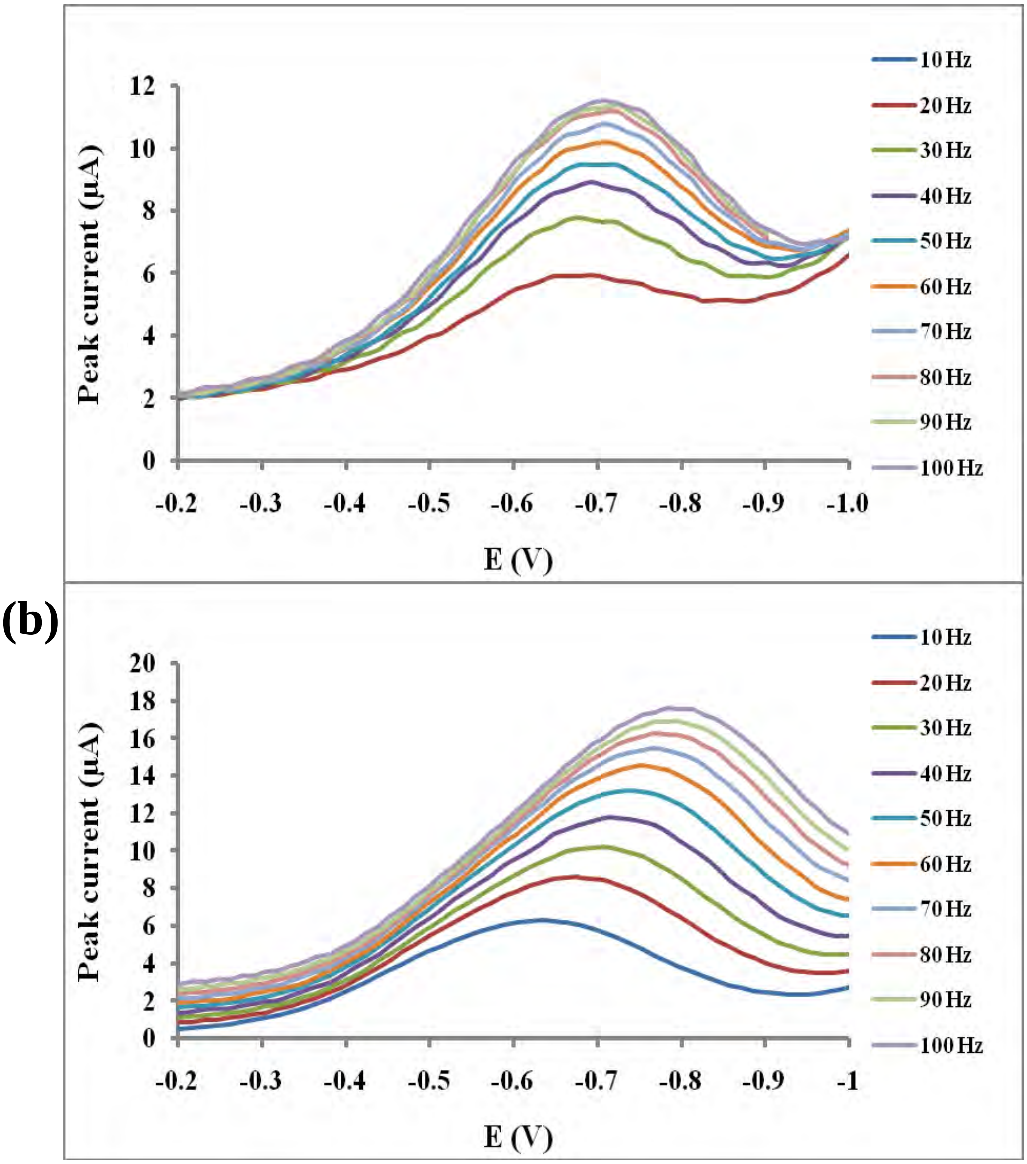

Figure A1 Square wave voltammograms of 25 µM diphenyldisulfide (Ph-S-S-Ph) at various frequencies on (a) *in situ* bismuth modified electrode and (b) *ex situ* bismuth modified electrode

VITA

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