รายงานวิจัยฉบับสมบูรณ์

โครงการ การตรวจสอบสารประกอบซัลเฟอร์ในน้ำมันด้วยขั้วบิสมัทโดยใช้เทคนิคโวลแทมเมทตรี

โดย ดร.เจริญขวัญ ไกรยา

กรกฎาคม 2554

สัญญาเลขที่ MRG 5180230

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ดร.เจริญขวัญ ไกรยา
ภาควิชาเคมี คณะวิทยาศาสตร์
จุฬาลงกรณ์มหาวิทยาลัย

สนับสนุนโดยสำนักงานกองทุนสนับสนุนการวิจัย

กิตติกรรมประกาศ

ผู้วิจัยขอขอบพระคุณ สำนักงานกองทุนสนับสนุนการวิจัย (สกว.) และสำนักงานคณะกรรมการอุดมศึกษา (สกอ.) ที่ให้การสนับสนุนทุนวิจัยในการดำเนินงานวิจัยโครงการการตรวจสอบสารประกอบซัลเฟอร์ในน้ำมันด้วยขั้วบิสมัทโดยใช้เทคนิคโวลแทมเมทตรีนี้ ภายใต้เงินทุนพัดนาศักยภาพในการทำงานวิจัยของอาจารย์รุ่นใหม่ ประจำปี 2551 (สัญญาเลขที่ MRG 5180230) รวมถึงอำนวยการต่าง ๆ ซึ่งส่งผลให้การดำเนินงานสามารถสำเร็จลุล่วงได้ด้วยดี

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โดยใช้เทคนิคโวลแทมเมทตรี

ชื่อนักวิจัย : ดร.เจริญขวัญ ไกรยา
ภาควิชาเคมี คณะวิทยาศาสตร์ จุฬาลงกรณ์มหาวิทยาลัย

E-mail Address : Kraiya@bluehen.udel.edu

ระยะเวลาโครงการ : 2 ปี

งานวิจัยนี้ได้อธิบายการตรวจวัดปริมาณสารประกอบซัลเฟอร์ในปิโตรเลียมด้วยเทคนิคโวลแทมเมตรี โดยใช้ขั้วไฟฟ้าบิสมัตเป็นขั้วไฟฟ้าใช้งาน อิทธิพลของความเข้มข้นของบิสมัต ศักย์ไฟฟ้าที่ใช้ในการเกาะติด และเวลาที่ใช้ในการเกาะติด ได้ถูกศึกษาและปรับค่า เพื่อให้ได้มาถึงภาะการเตรียมขั้วไฟฟ้าบิสมัตที่เหมาะสม ผลการศึกษาพบว่าภาวะที่เหมาะสมสำหรับเตรียมขั้วไฟฟ้าบิสมัต คือความเข้มข้นบิสมัตที่ 0.5 ppm บนขั้วไฟฟ้ากล๊าสซีคาร์บนที่ศักย์ไฟฟ้า –1.2 V เป็นเวลา 60 s จากนั้นตรวจสอบพื้นผิวของขั้วไฟฟ้าบิสมัตด้วยเทคนิคกล้องจุลทรรศน์แบบส่องกราด และภายใต้ภาวะที่เหมาะสม พบว่าขั้วไฟฟ้าแบบอิน-ซิทูให้ช่วงความเป็นเส้นตรงในช่วง 49.9 – 248.8 นาโนโมลาร์ และ 2.5 – 20 ไมโครโมลาร์ สำหรับไดเฟนิลไดซัลไฟด์และบิวเทน-ไธออล 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 บนขั้วไฟฟ้าแบบอิน-ซิทูและเอกซ์-ซิทูตามลำดับ สุดท้ายได้นำขั้วไฟฟ้าบิสมัตไปใช้วิเคราะห์ปริมาณสารประกอบซัลเฟอร์ในตัวอย่างน้ำมันเครื่องบินและน้ำมันก๊าด พบว่าน้ำมันเครื่องบินและน้ำมันก๊าดมีปริมาณไดเฟนิลไดซัลไฟด์ 230.4 ± 0.1 และ 102.9 ± 0.1 นาโนโมลาร์ ตามลำดับ และบิวเทนไธออล 12.2 ± 0.3 และ 5.2 ± 0.3 ไมโครโมลาร์ ตามลำดับ

คำหลัก : ซัลเฟอร์, ปิโตรเลียม, บิสมัต, โวลแทมเมตรี

Abstract

Project Code : MRG 5180230

Project Title : Determination of sulfur compounds in petroleum on bismuth electrode by voltammetric technique

Investigator : Dr. Charoenkwan Kraiya
Department of Chemistry, Faculty of Science, Chulalongkorn University

E-mail Address : Kraiya@bluehen.udel.edu

Project Period : 2 Years

This research describes a trace level sulfur determination in petroleum 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 results 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 provide linear dynamic ranges of 49.9–246.3 nM and 2.5-19.8 μM for Ph-S-S-Ph and Bu-SH, respectively and the *ex situ* bismuth modified electrode showed linear dynamic ranges of 25.0–149.5 nM for Ph-S-S-Ph, and 2.5-20.0 μM for Bu-SH. Detection limits of 19.4 and 12.5 nM were found for the Ph-S-S-Ph and 1.2 and 1.4 μM for Bu-SH, on the *in situ* and *ex situ* bismuth modified electrodes, respectively. Finally, the bismuth electrodes were applied for the analysis of Ph-S-S-Ph and Bu-SH in real samples. The analysis reviewed that jet fuel and kerosene contain about 230.4±0.1 and 102.9±0.1 nM Ph-S-S-Ph, respectively and Bu-SH 12.2 ±0.3 and 5.2±0.3 μM, respectively.

Keywords : Sulfur, Petroleum, Bismuth, Voltammetry

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.

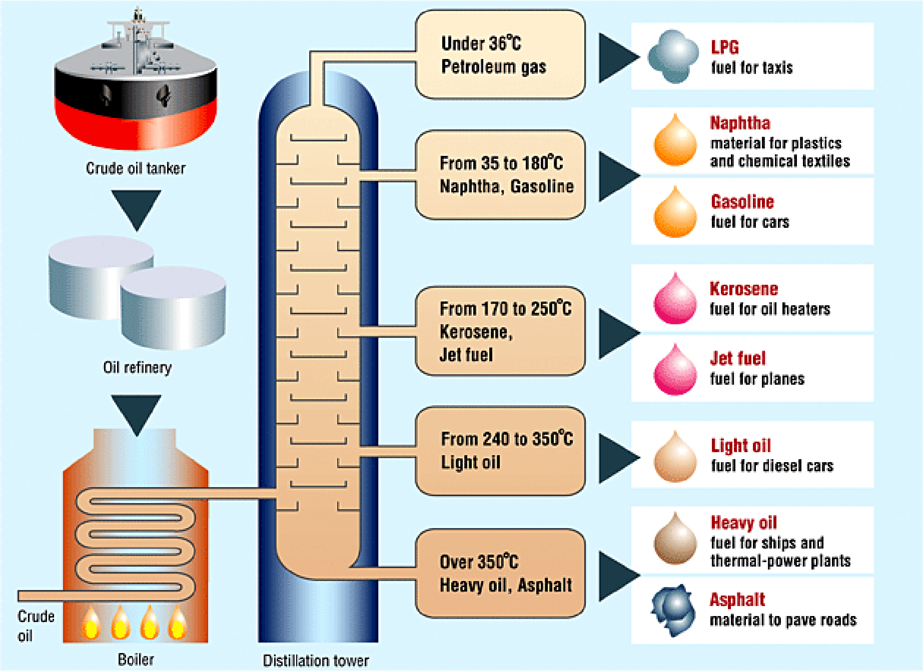

Figure 2.1 Oil refinery diagrams [22].

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.

2.3 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 2.2. Therefore, the selection of working electrode also considers the solvent and supporting electrolyte.

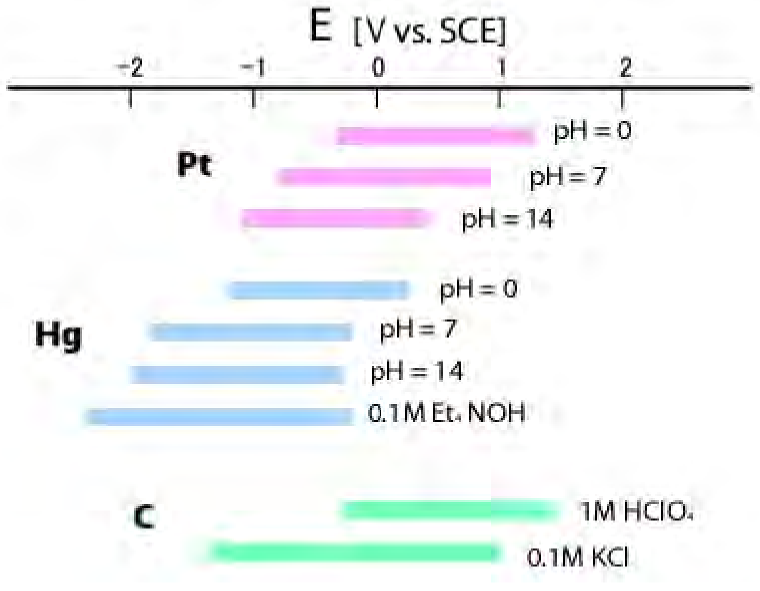

Figure 2.2 Potential windows of platinum, mercury and carbon electrodes in various supporting electrolytes [29].

2.4 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 2.3 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.

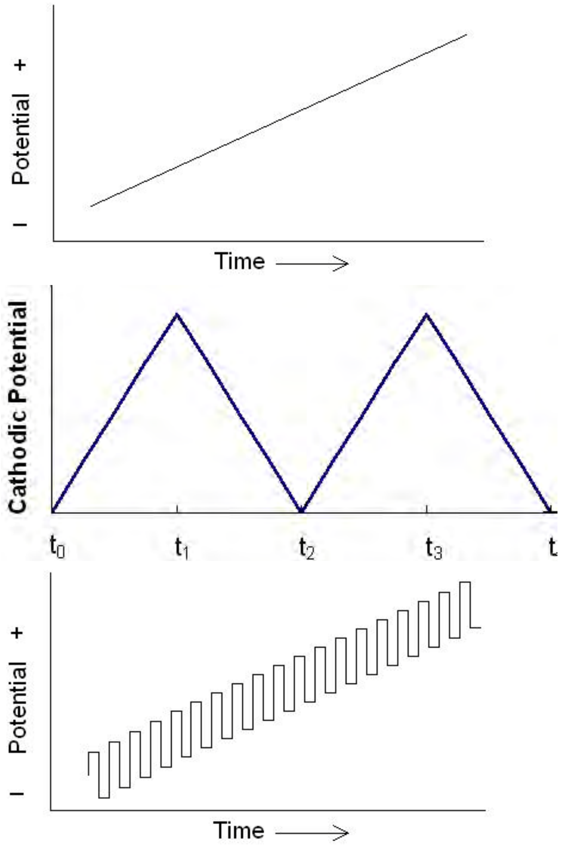

Figure 2.3 Potential-time waveforms used in various electroanalytical methods. Waveforms based on (a) square, (b) linear and (c) triangular potential-time patterns are used in linear sweep, cyclic and square wave voltammetry, respectively [30, 31, 32]

2.4.1 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.

2.4.1.1 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.

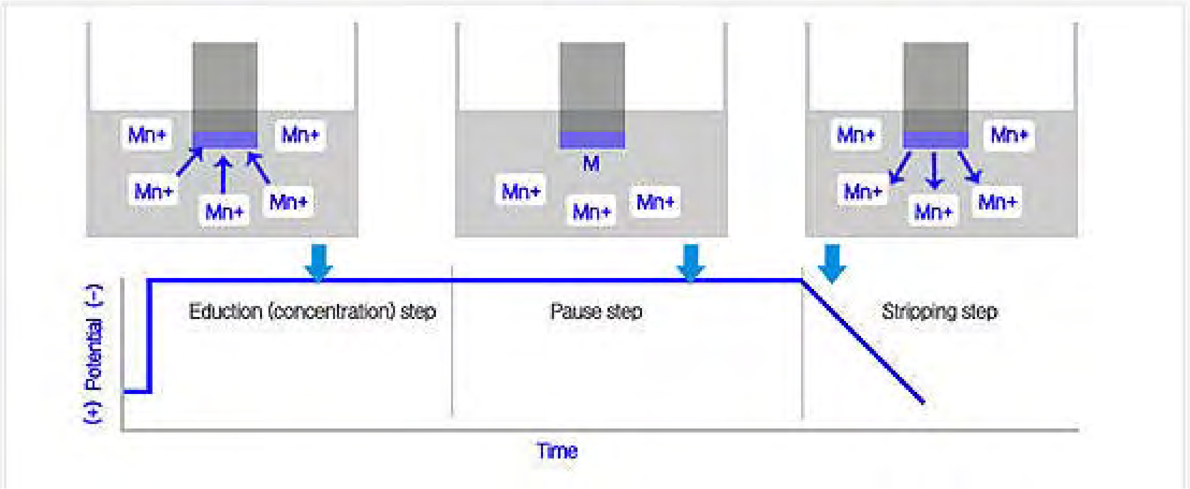

Figure 2.4 (a) Process of stripping analysis and (b) potential-time waveform of stripping voltammetry [33].

Figure 2.4 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.

2.4.2 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 2.5. 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 current is given in Figure 2.6 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

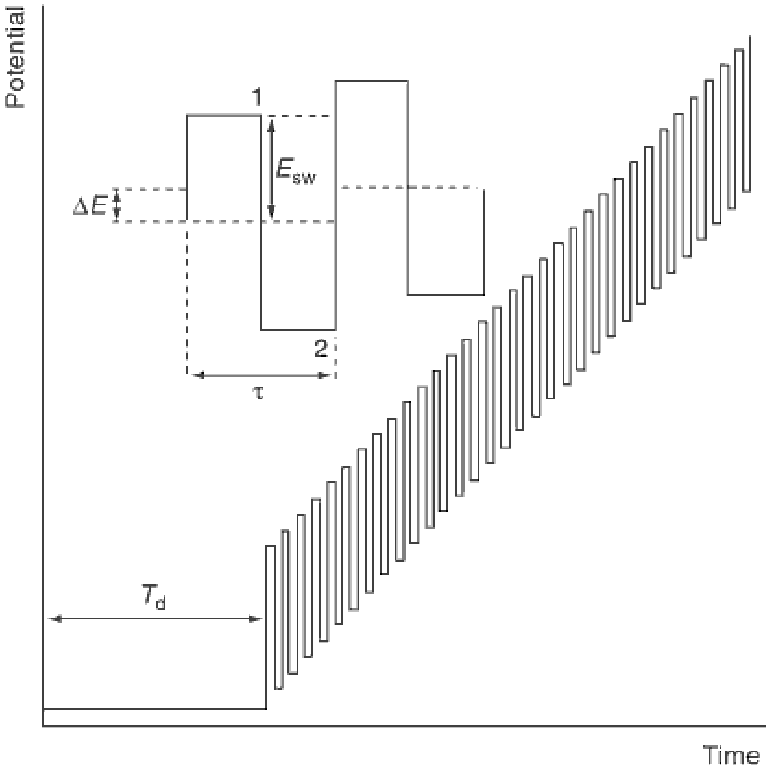

Figure 2.5 Potential wave form for sampled current polarography [32]

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.

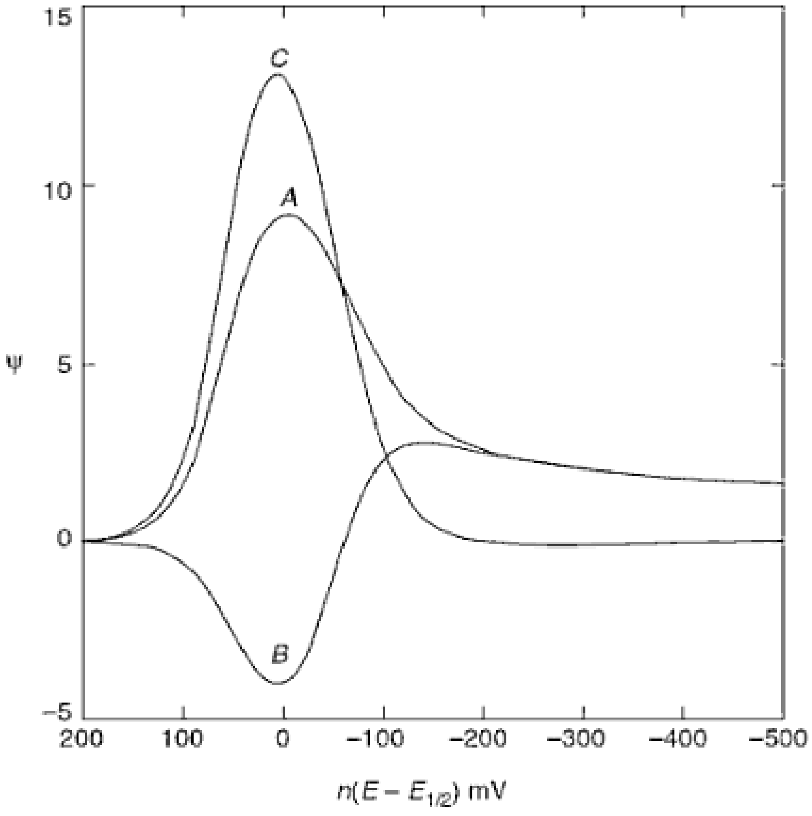

Figure 2.6 Square wave voltammogram for reversible electrode transfer (curve A) forward current; (curve b) reverse current and (curve c) net current [32]

2.5 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 3.9×10^{-9}, 1.6×10^{-7} and 4.9×10^{-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 Reagents and instruments

Analytical grade reagents were used throughout as recieved. A 0.1 M acetate buffer at pH 4.5 prepared in 1:1 toluene:methanol was used as a supporting electrolyte. Standard solutions of Ph-S-S-Ph and Bu-SH were daily prepared in 1:1 toluene:methanol. The bismuth standard for AAS (Atomic Absorption Standard) solution was used for bismuth-modified-electrode preparation.

A VA 757 electrochemical analyzer (Metrohm, Switzerland) was used to perform square wave voltammetry (SWV) in a convectional three-electrode cell containing bismuth modified electrode, Ag/AgCl and Pt as working, reference and auxiliary electrodes, respectively. Scanning electron microscopy; SEM (JEM-2100) was used to characterize the morphologic of electrode surface.

3.2 Experimental procedure

Each modified electrode along with its measurement method was separately described. 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. Under each study condition, experiments were performed with triplicate scans.

3.2.1 *in situ* bismuth modified electrode

A 1.0-mm-dia glassy carbon electrode was polished with 1.0 and 0.3 µm alumina slurry, respectively, prior to be placed in the electrochemical cell containing 0.5 ppm Bi (III) and analyte solution in the electrolyte solution. 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. At the end of each scan, a cleaning potential of +0.3 V was applied for 180 s.

3.2.2 *Ex situ* bismuth modified electrode

A 1.0-mm-dia GCE was polished with 1.0 and 0.3 µm alumina slurry, respectively, prior to be 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. 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.

3.2.3 HMDE

An analyte solution was pipetted into 20.00 mL 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. The responding current was recorded during the scan.

3.3 Characterization of electrode surface

3.3.1 *In situ* bismuth modified electrode

A GCE was immersed in the electrochemical cell containing 0.5 ppm Bi (III) and analyte solution in the electrolyte solution. A -1.2 V vs. Ag/AgCl deposition was applied through the glassy carbon electrode for 60 s. 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.

3.3.2 *Ex situ* bismuth modified electrode

A GCE 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 was removed from the electrochemical cell, rinsed with DI water and kept in the DI water prior to be investigated by SEM.

3.4 Analytical performance and sample analysis

Under optimized conditions, the Ph-S-S-Ph and Bu-SH calibration curves were constructed on each electrode. A lowest detection of each analyte was also examined by 3SD method.

The standard addition method was employed for Ph-S-S-Ph and Bu-SH determinations in jet fuel and kerosene**.**

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;

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

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

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

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

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.

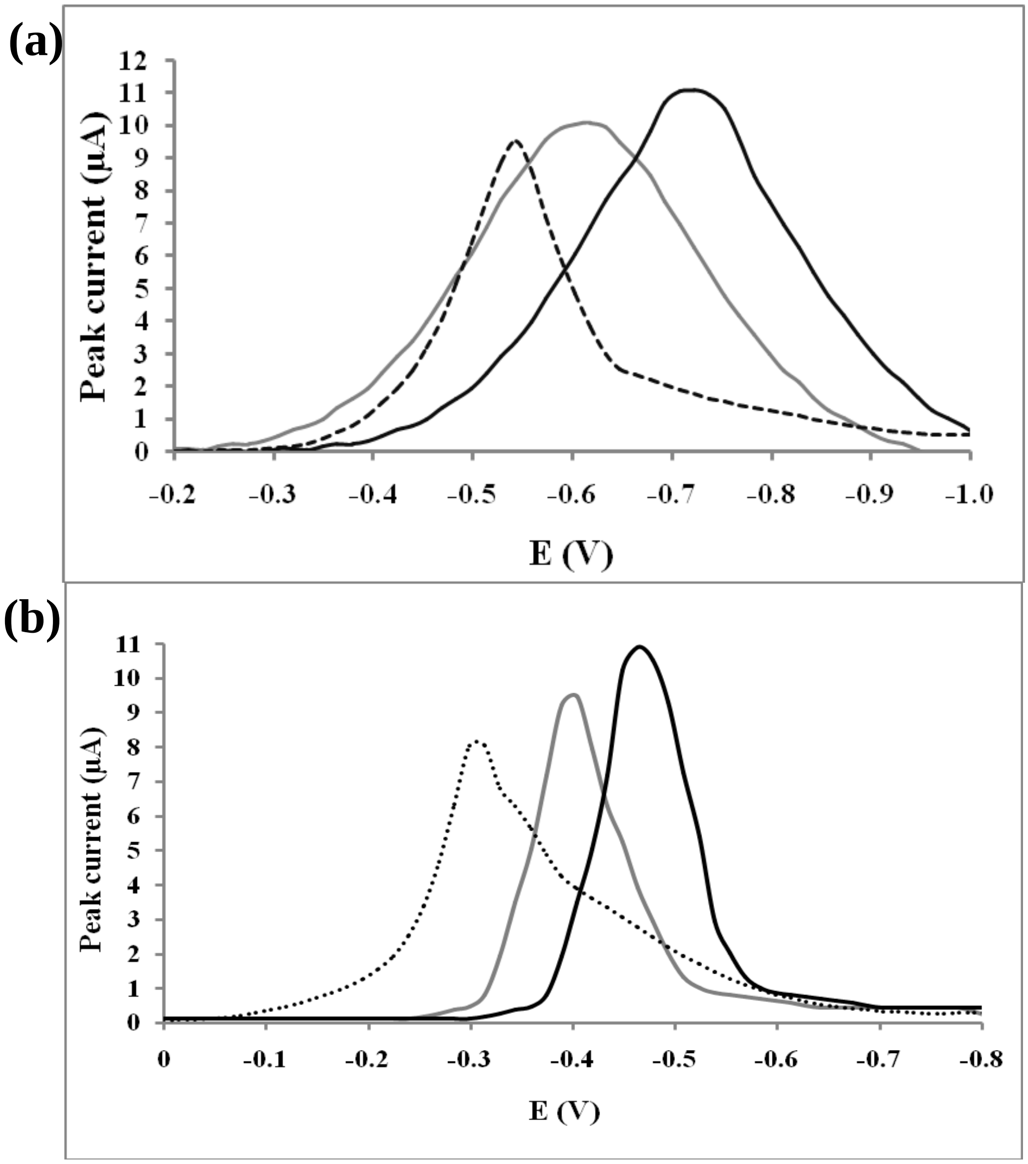

Figure 4.1 Square wave voltammograms of (a) 25 µM diphenyldisulfide (Ph-S-S-Ph) and (b) 25 µM butanethiol (Bu-SH) on the *in situ* bismuth modified electrode (grey solid line), *ex situ* bismuth modified electrode (black solid line) and HMDE (dash line); amplitude 50 mV, voltage step 15 mV at frequency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

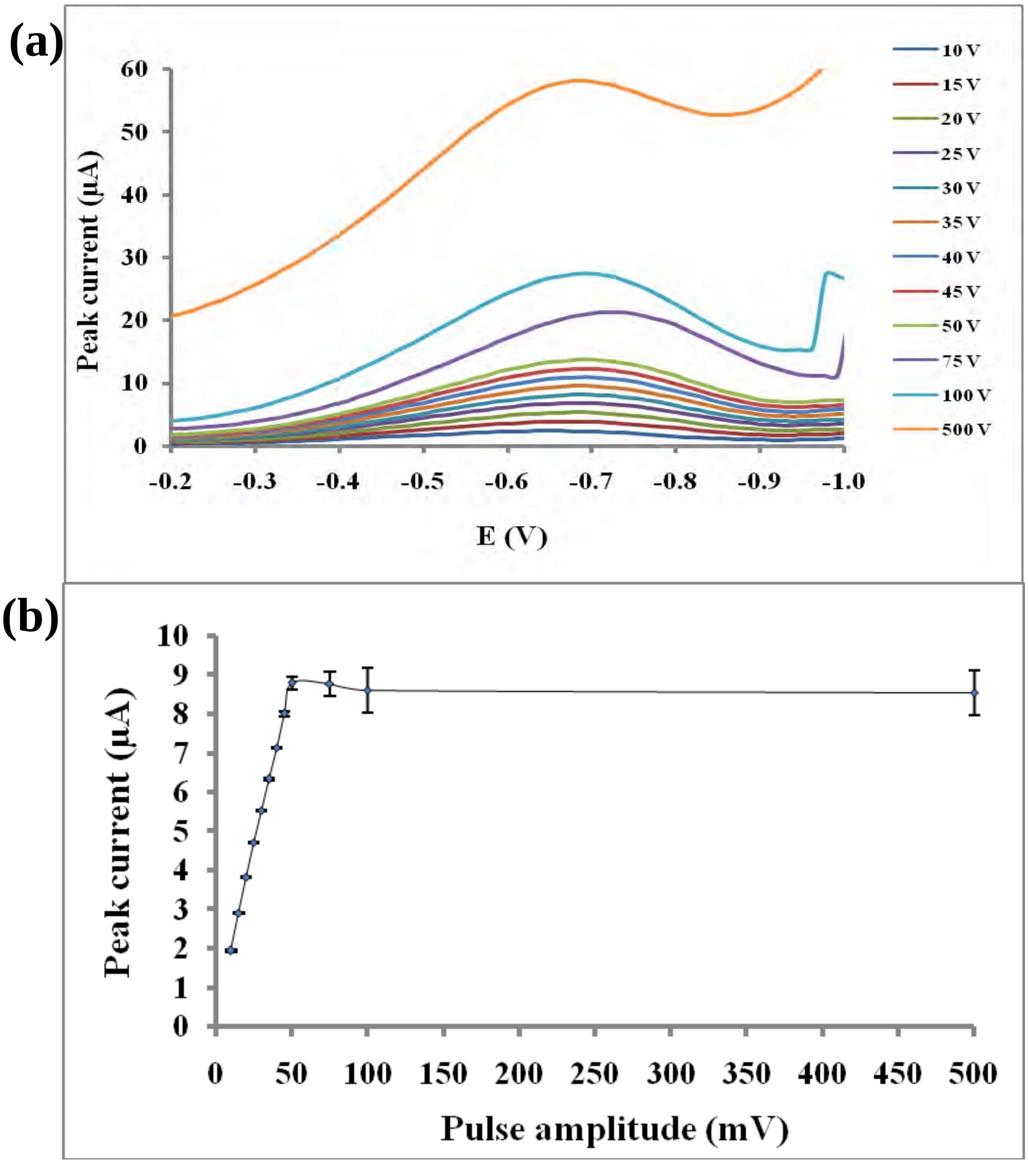

Figure 4.2 (a) Square wave voltammograms of 25 µM diphenyldisulfide (Ph-S-S-Ph) at various pulse amplitudes measured on the *in situ* bismuth modified electrode and (b) effect of pulse amplitude on 25 µM diphenyldisulfide (Ph-S-S-Ph) peak current; voltage step of 15 mV at 70 Hz

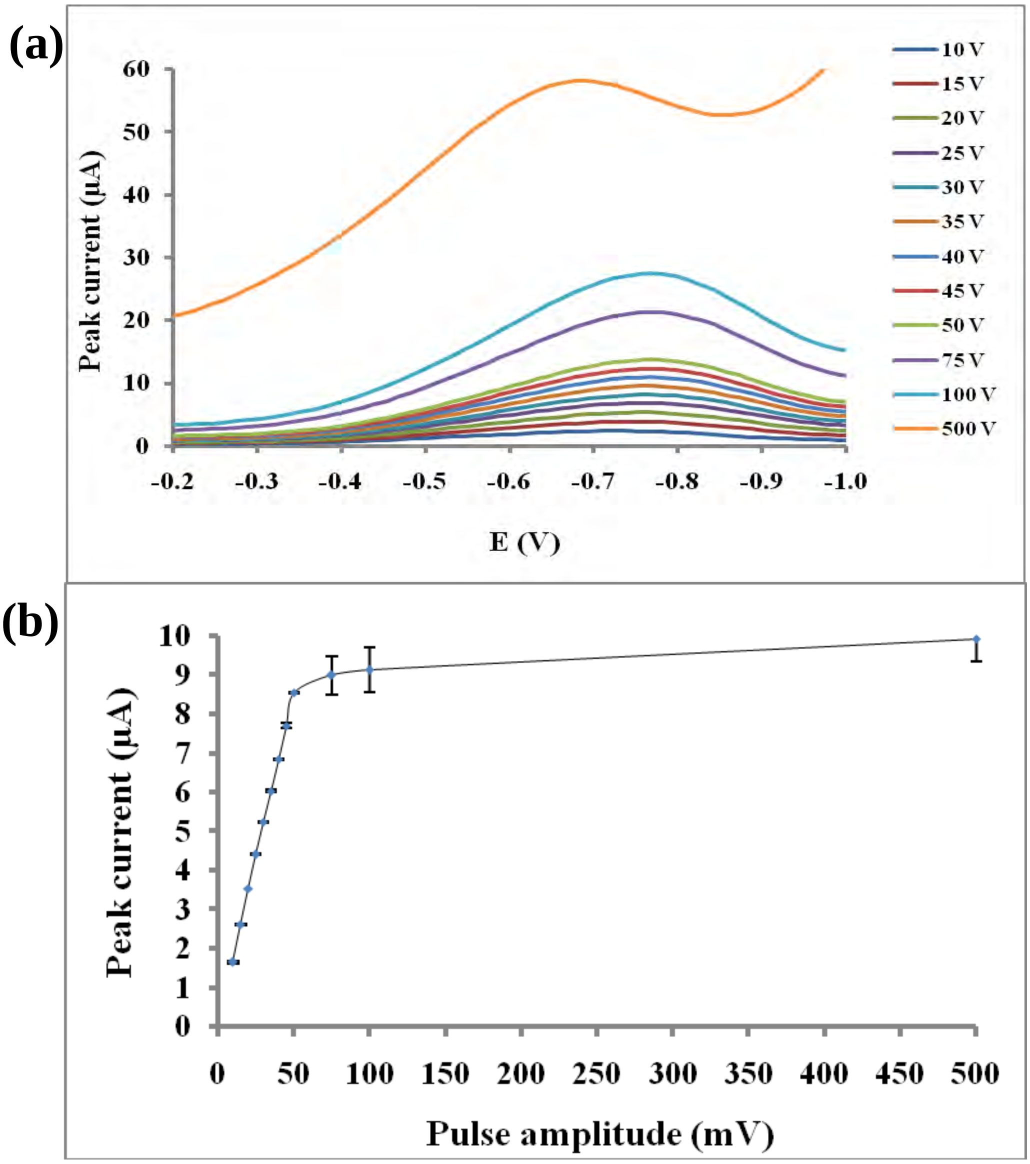

Figure 4.3 (a) Square wave voltammograms of 25 µM diphenyldisulfide (Ph-S-S-Ph) at various pulse amplitudes measured on the *ex situ* bismuth modified electrode and (b) effect of pulse amplitude on 25 µM diphenyldisulfide (Ph-S-S-Ph) peak current; voltage step of 15 mV at 70 Hz

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

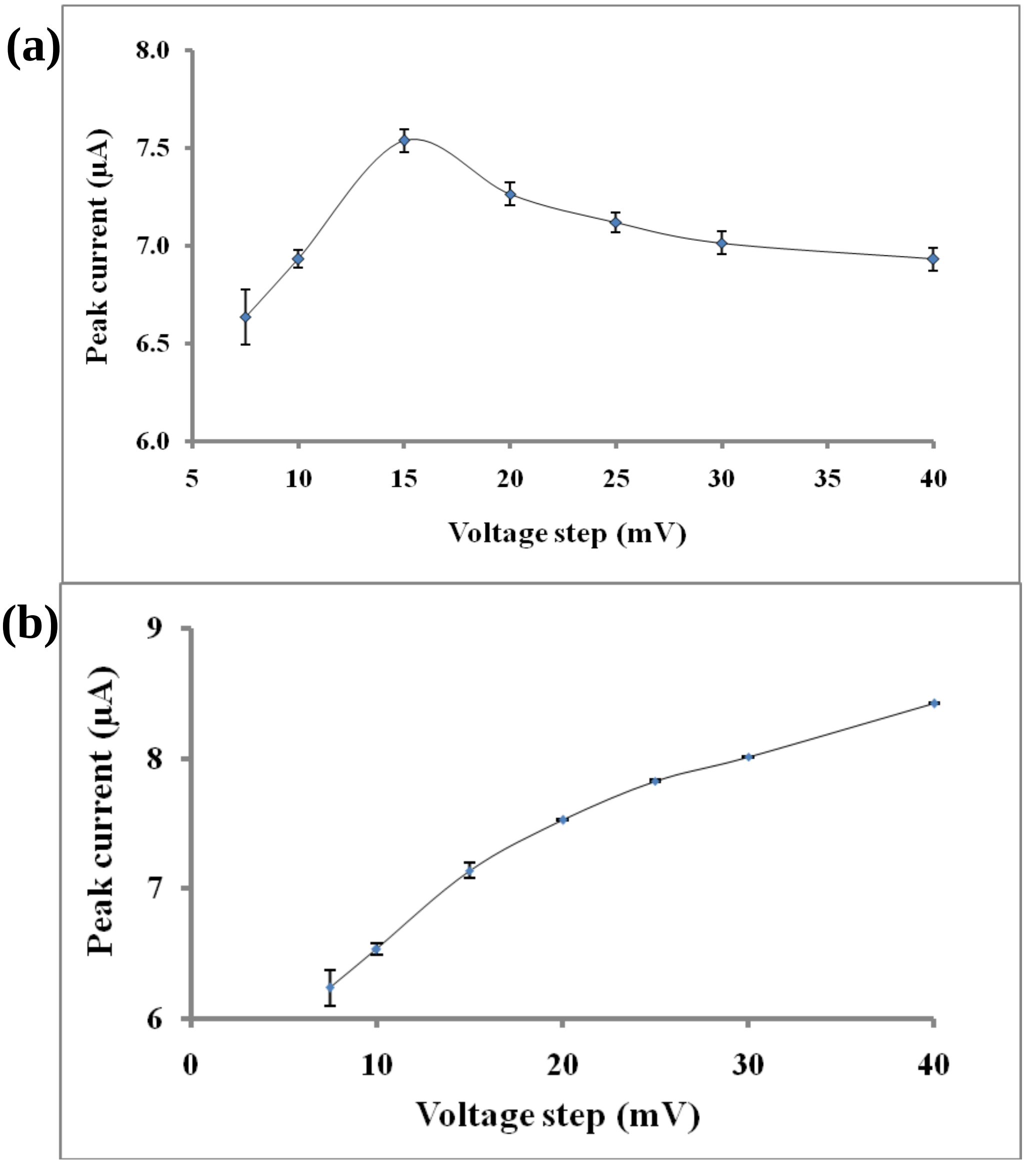

Figure 4.4 Effect of voltage step on 25 µM diphenyldisulfide (Ph-S-S-Ph) measured by (a) *in situ* bismuth modified electrode and (b) *ex situ* bismuth modified electrode; 50 mV pulse amplitude at 70 Hz

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.

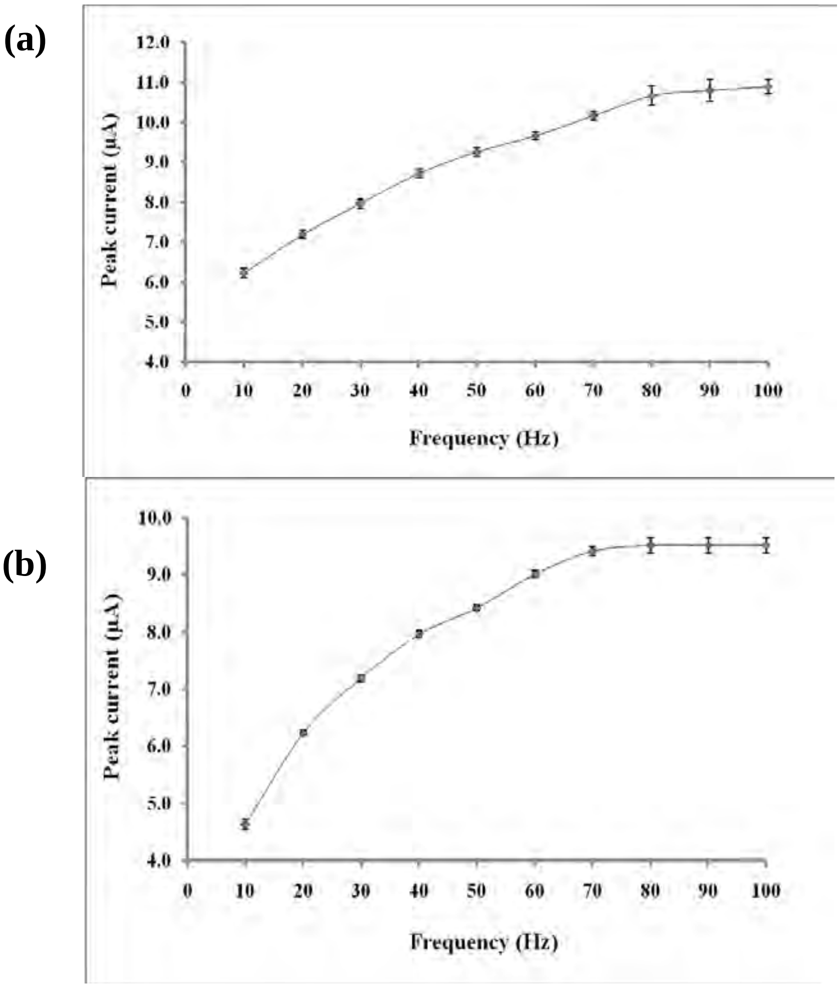

Figure 4.5 Effect of frequency on 25 µM diphenyldisulfide (Ph-S-S-Ph) measured by (a) *in situ* bismuth modified electrode and (b) *ex situ* bismuth modified electrode; 50 mV pulse amplitude at 70 Hz

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.

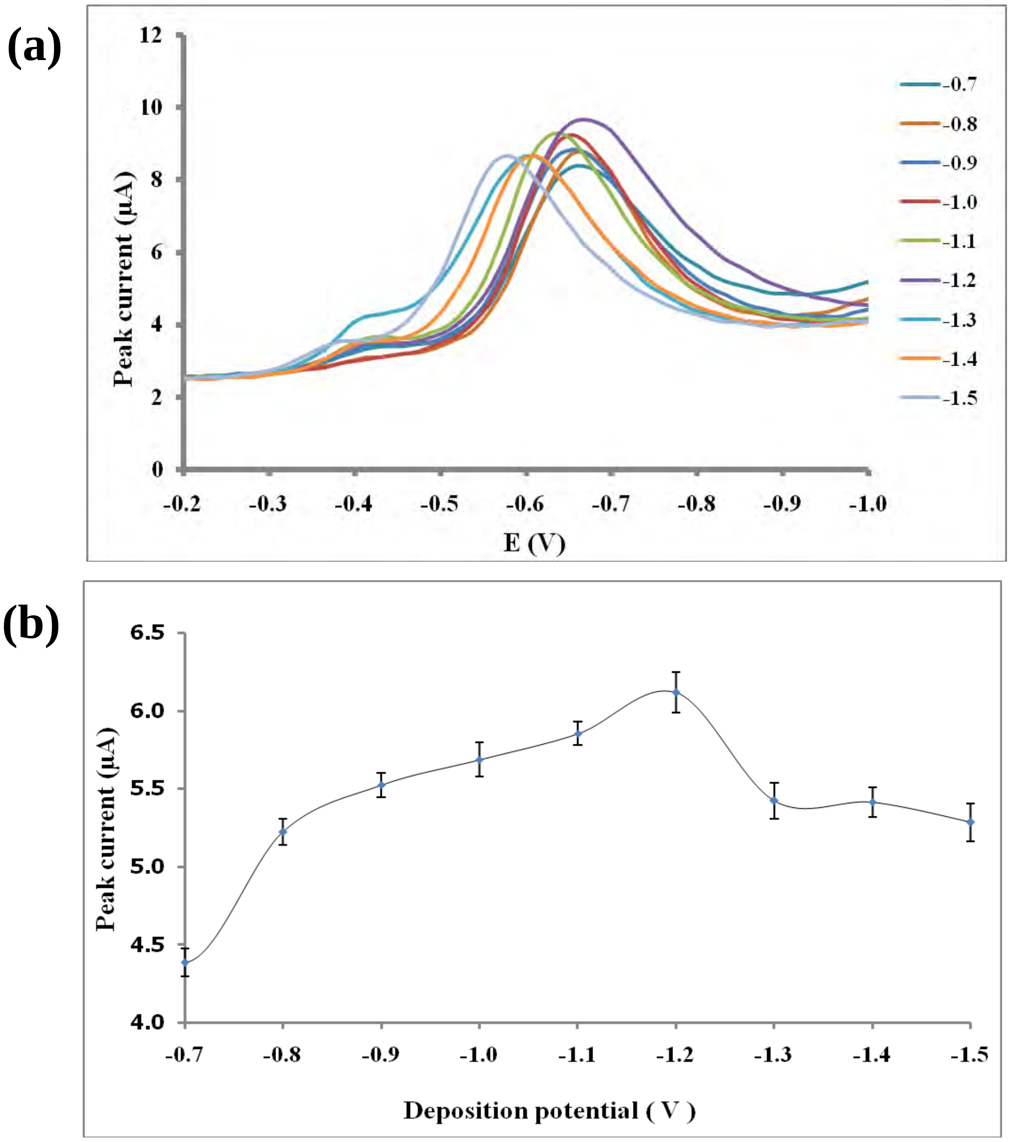

Figure 4.6 (a) Square wave voltammograms of 25 µM diphenyldisulfide (Ph-S-S-Ph) at various deposition potentials measured on the *in situ* bismuth modified electrode and (b) effect of deposition potential on 25 µM diphenyldisulfide (Ph-S-S-Ph) peak current; 0.5 ppm bismuth solution and 60 s deposition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

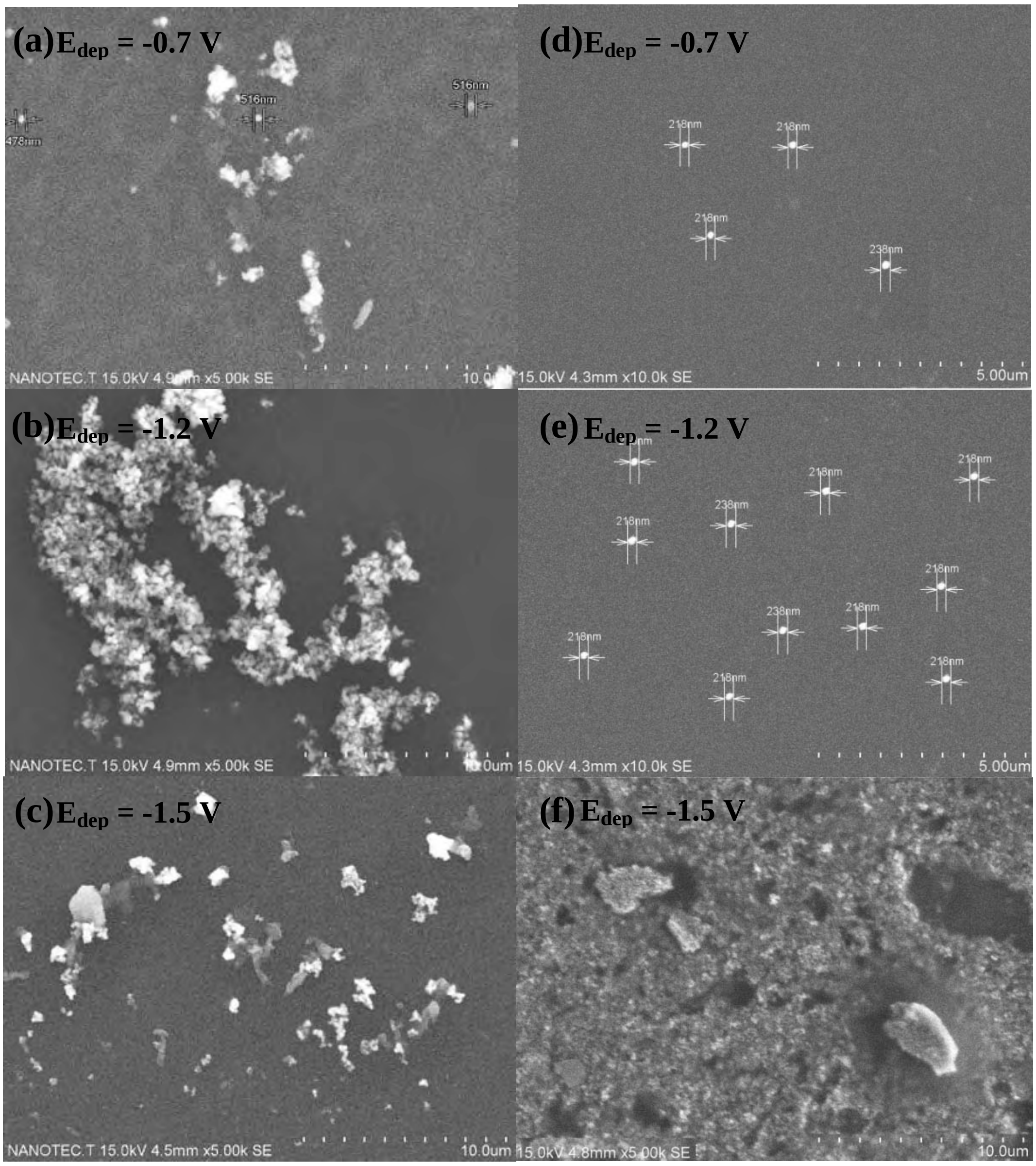

Figure 4.7 SEM images of (a-c) $[(PhS)_2Bi]_{ads}$ and (d-f) bismuth particles accumulated on the electrode surface at -0.7 V, -1.2 V and -1.5 V deposition potential for 60 s in 0.5 ppm bismuth solution

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.

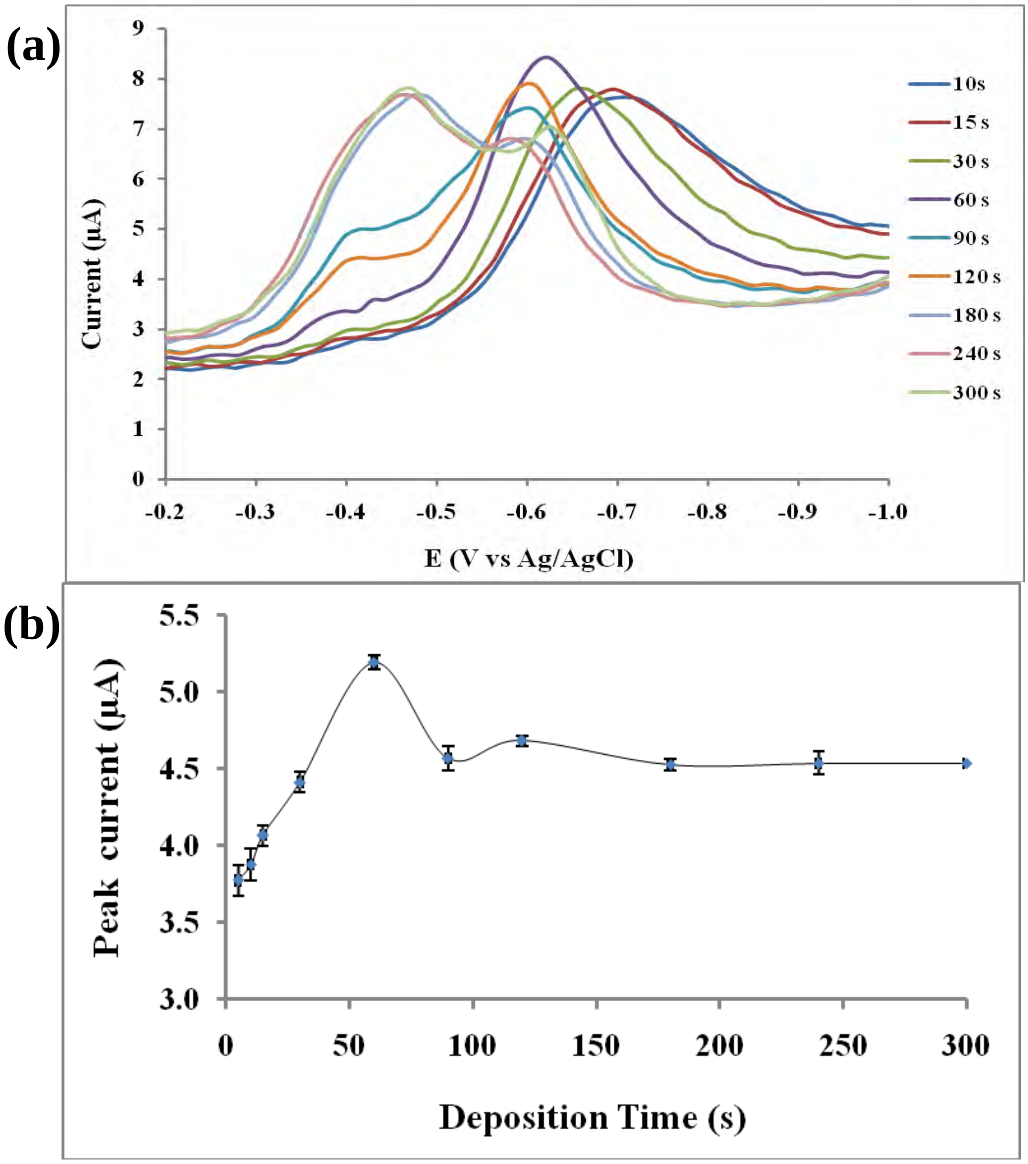

Figure 4.8 (a) Square wave voltammograms of 25 µM diphenyldisulfide (Ph-S-S-Ph) at various deposition times measured on the *in situ* bismuth modified electrode and (b) effect of deposition time on 25 µM diphenyldisulfide (Ph-S-S-Ph) peak current; 0.5 ppm bismuth solution and -1.2 V deposition potential

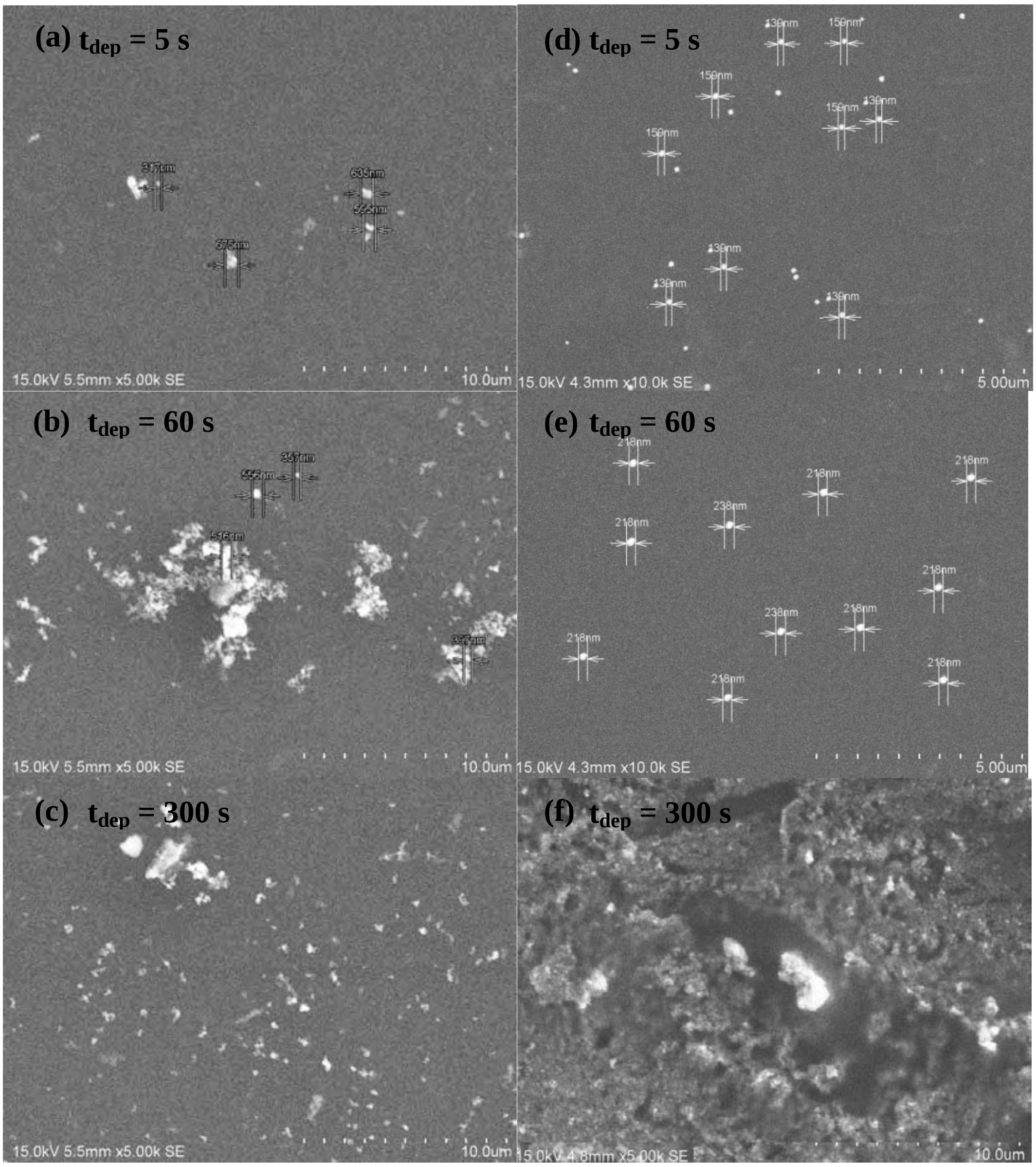

Figure 4.9 SEM images of (a-c) $[(PhS)_2Bi]_{ads}$ and (e-f) bismuth particles accumulated on the electrode surface at -1.2 V deposition potential for 5, 60 and 300 s in 0.5 ppm bismuth solution

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.

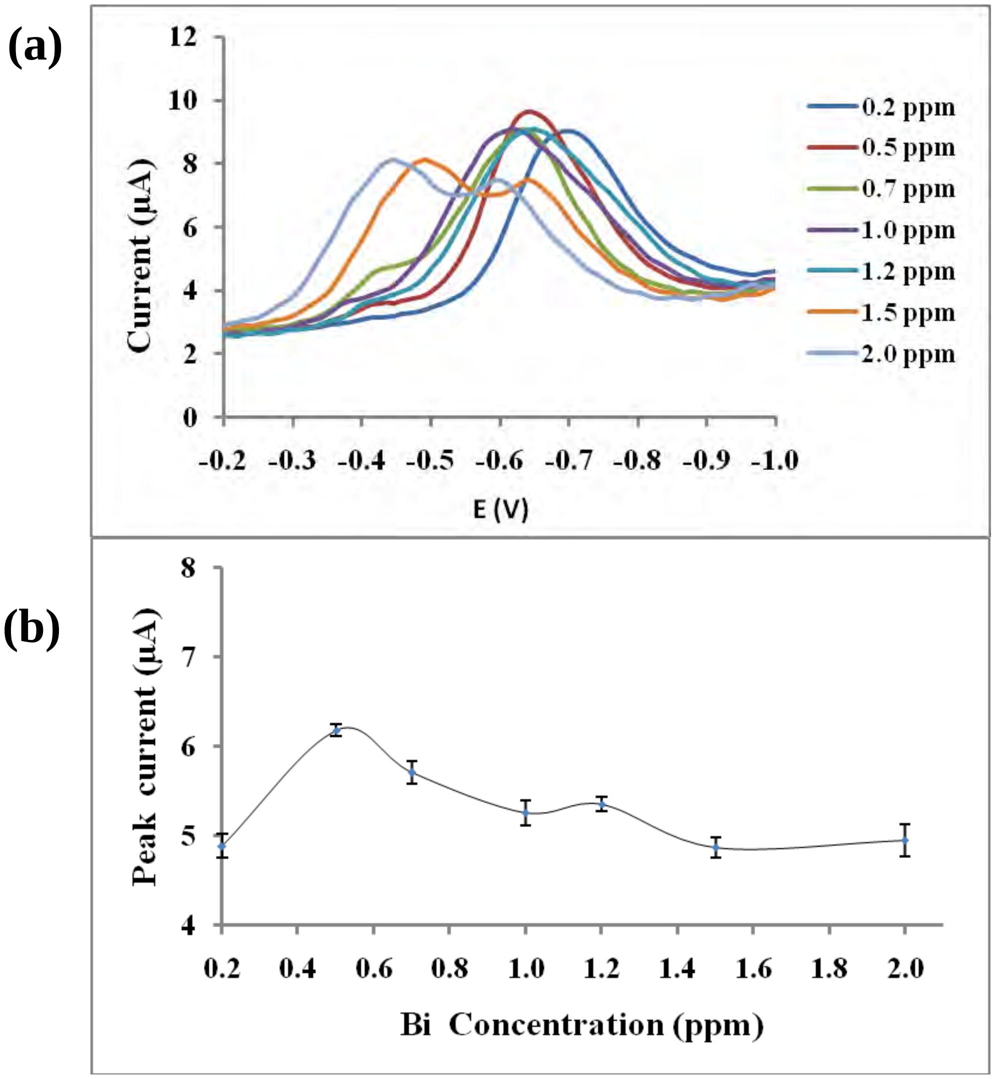

Figure 4.10 (a) Square wave voltammograms of 25 µM diphenyldisulfide (Ph-S-S-Ph) in various bismuth concentrations measured on the *in situ* bismuth modified electrode and (b) effect of bismuth concentration on 25 µM diphenyldisulfide (Ph-S-S-Ph) peak current; -0.9 V deposition potential for 60 s

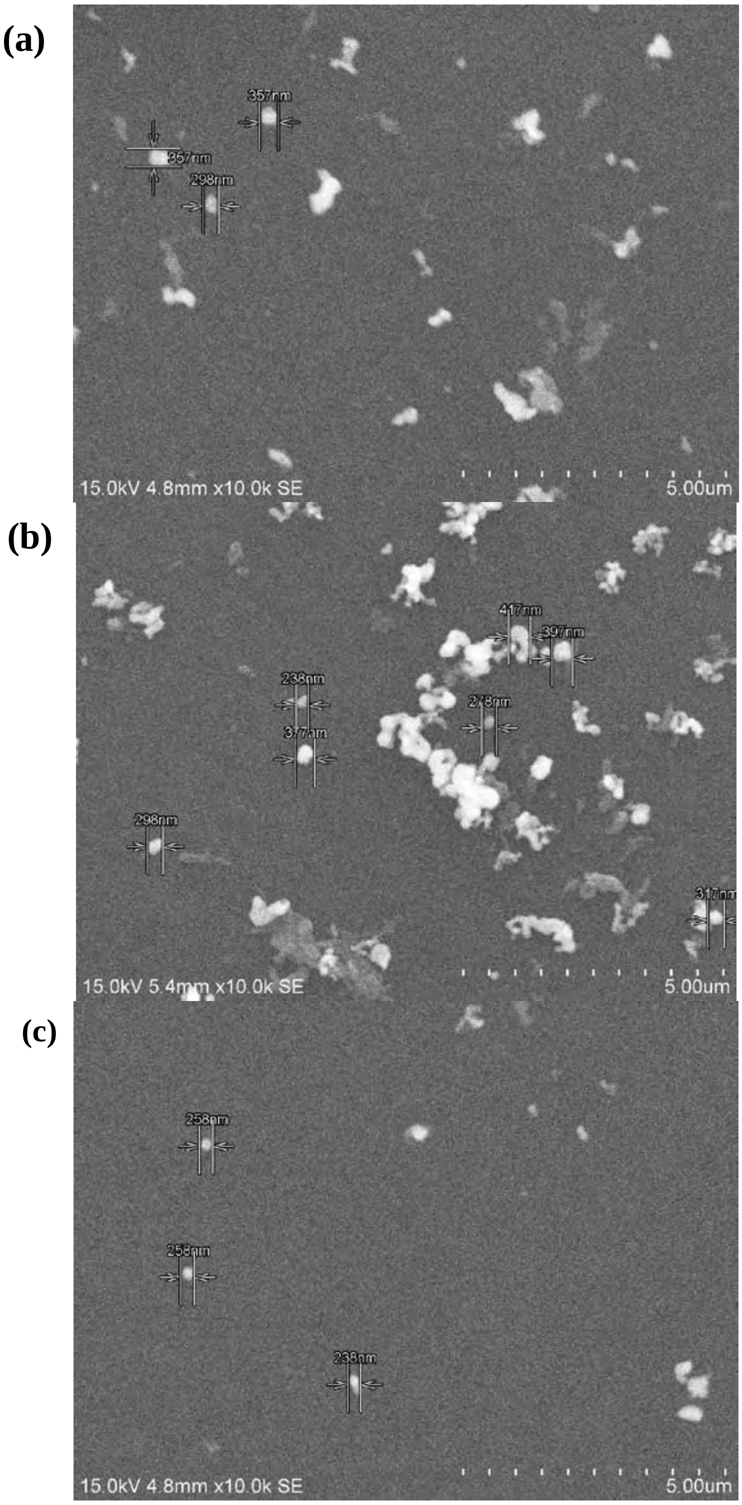

Figure 4.11 SEM images of $[(PhS)_2Bi]_{ads}$ accumulated on the electrode surface at -1.2 V deposition potential for 60 s in (a) 0.2, (b) 0.5 and (c) 1.0 ppm bismuth solution

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.

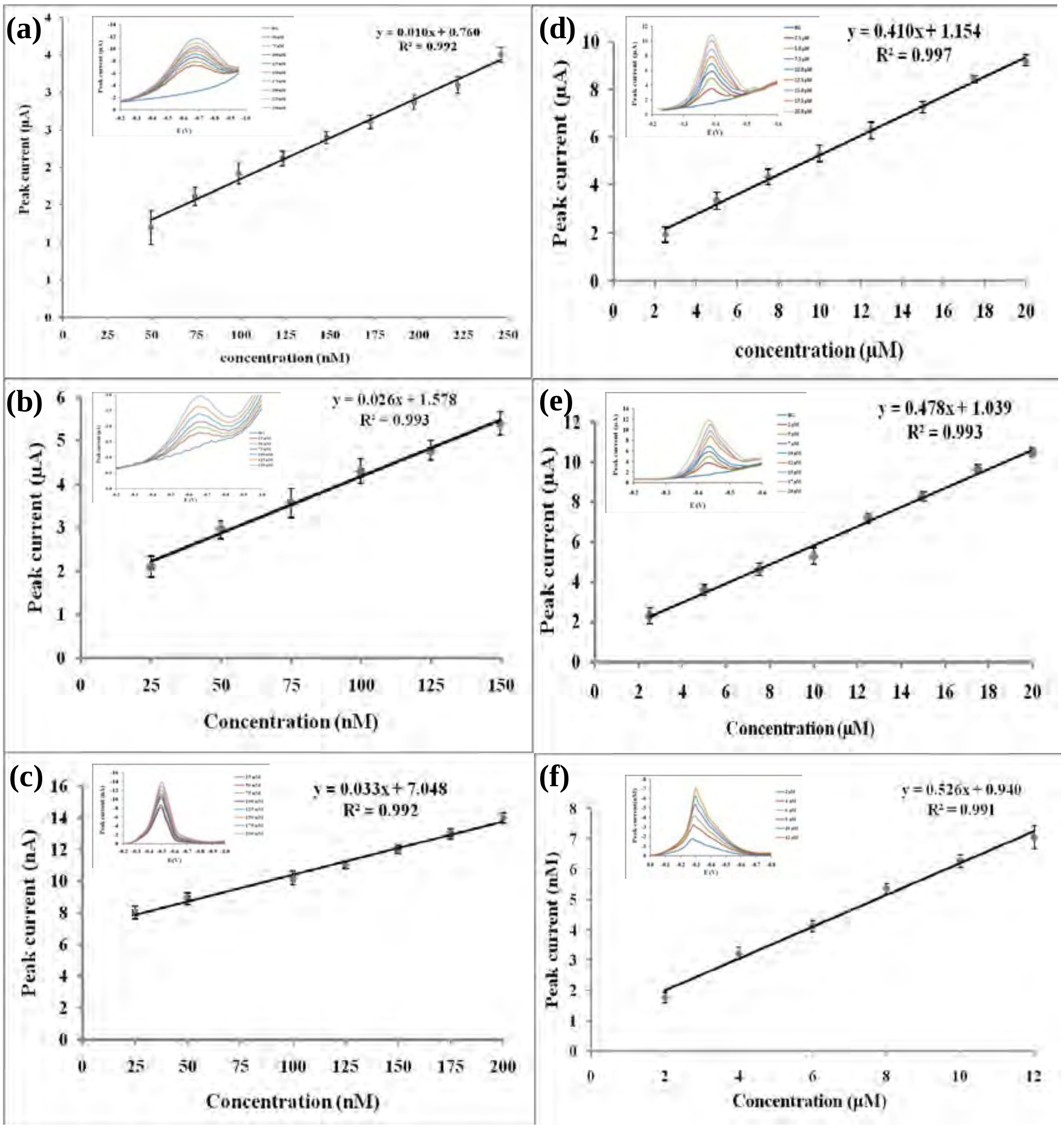

Figure 4.12 Diphenyldisulfide (Ph-S-S-Ph) calibration curves obtained on the (a) *in situ* bismuth modified electrode, (b) *ex situ* bismuth modified electrode and (c) hanging mercury drop electrode (HMDE) and butanethiol (Bu-SH) calibration curve obtained on the (d) *in situ* bismuth modified electrode,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

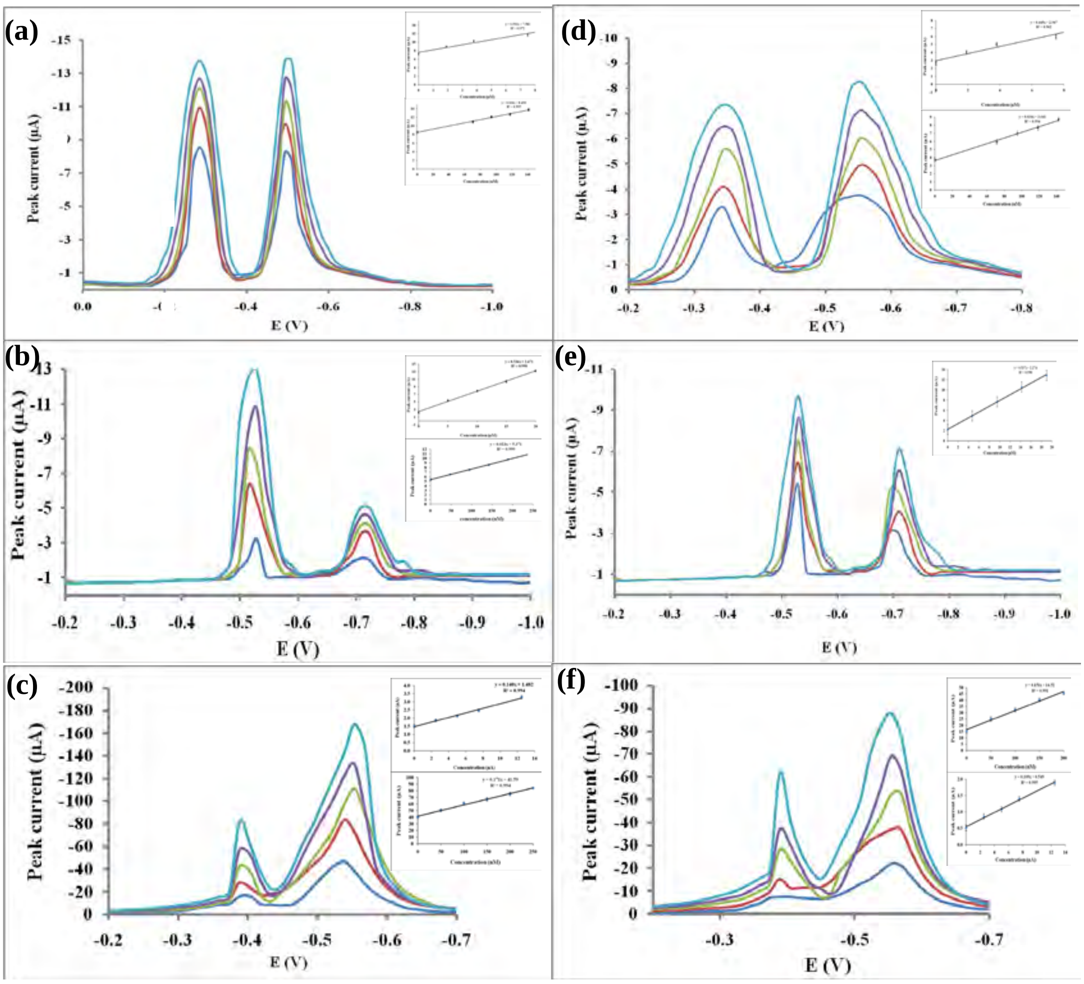

Figure 4.13 Square wave voltammograms of jet fuel on (a) the *in situ* bismuth modified electrode, (b) the *ex situ* bismuth modified electrode and (c) the HMDE and square wave voltammograms of kerosene on (d) the *in situ* bismuth modified electrode, (e) the *ex situ* bismuth modified electrode and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

9 -10 July 2010	Poster presentation at The Symposium on Advance Polymer and Nanomaterials, Pratumwan Hotel, Bangkok, Thailand.
26 -27 August 2010	Oral presentation at The International Sustainable Greater Mekong Subregion (The GMSTEC 2010), Imperial Queen Park Hotel, Bangkok, Thailand
16 – 19 November 2010	Poster presentation at The International Conference for The 2nd Regional Electrochemical South East Asia (The 2nd REMSEA), Chulalongkorn University, Bangkok, Thailand.
13 – 15 December 2010	Poster presentation at The 6th Mathematic and Physical Science Graduate Congress (The 6th MPSGC), University of Malaya, Malaysia.