รายงานวิจัยฉบับสมบูรณ์

เซนเซอร์ทางเคมีไฟฟ้าแบบใหม่สำหรับการตรวจหาโลหะปริมาณน้อย

นายสมปอง ทองงามดี

กันยายน 2553

สัญญาเลขที่ MRG5180280

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บทคัดย่อ

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เทคนิคทางเคมีวิเคราะห์เชิงไฟฟ้ากำลังจะมีบทบาทมากทางด้านเซนเซอร์ เพราะเทคนิคนี้ นอกจากจะประยุกต์ใช้กับเซนเซอร์ ซึ่งสามารถวิเคราะห์สารได้โดยตรงในแหล่งสารตัวอย่าง โดยไม่ต้องมีการนำสารตัวอย่างมาวิเคราะห์ในห้องปฏิบัติการแล้ว ยังสามารถประยุกต์ใช้ทำให้เซนเซอร์มีขนาดเล็ก กะทัดรัด มีความว่องไวและจำเพาะในการตรวจวัด งานวิจัยนี้ เป็นการแสวงหาขั้วไฟฟ้าใหม่ที่ไม่ใช่ปรอท มาพัฒนาเป็นเซนเซอร์ พบว่าขั้วไฟฟ้าบิสมัทซึ่งเป็นโลหะที่เป็นมิตรกับสิ่งแวดล้อม เมื่อเคลือบบนเส้นใยคาร์บอน สามารถตรวจวิเคราะห์หาโลหะปริมาณน้อย ๆ ได้ โดยใช้เทคนิคแอดซอร์ฟทีฟสทริพพิงโวลแทมเมทรีมาประยุกต์ร่วม วิธีการใหม่นี้ทำได้โดยการทำให้เกิดการสะสมของสารประกอบเชิงซ้อนของโลหะที่ขั้วบิสมัท หลังจากนั้นใช้คลื่นสแควร์เวฟสแกนไปที่ขั้วบิทมัสทางด้านศักย์ไฟฟ้าลบ ทำให้โลหะหลุดออกจากขั้วเพื่อตรวจหาปริมาณ ปรากฏว่าการวิเคราะห์ได้ผลดีเทียบเท่ากับการใช้ขั้วไฟฟ้าปรอท ซึ่งเป็นขั้วไฟฟ้าที่เป็นอันตรายและนิยมใช้กันอย่างแพร่หลายมานาน จากการวิเคราะห์หาโลหะเบริลเลียมซึ่งเป็นโลหะที่เป็นพิษ พบว่าสารประกอบเชิงซ้อนระหว่างเบริลเลียมกับอาร์เซนนาโซ-III สามารถทำให้เกิดการสะสมบนขั้วไฟฟ้าบิสมัทที่เคลือบอยู่บนเส้นใยคาร์บอนได้ ในสภาวะสารละลายบัฟเฟอร์ของแอมโมเนียมเข้มข้น 0.05 โมล่าร์ พีเอช 9.7 ความเข้มข้นของอาร์เซนนาโซ-III ที่ 10 ไมโครโมล่าร์ ศักย์ไฟฟ้าของการสะสม 0.00 โวลต์ เมื่อวัดเทียบกับขั้วไฟฟ้าอ้างอิงซิลเวอร์-ซิลเวอร์คลอไรด์ การตอบสนองการวิเคราะห์เบริลเลียมช่วงที่เป็นเส้นตรงเมื่อมีการสะสมของเบริลเลียมนาน 60 วินาที อยู่ที่ 10-50 ไมโครกรัมต่อลิตร ขอบเขตต่ำสุดของการวิเคราะห์อยู่ที่ 0.25 ไมโครกรัมต่อลิตร ทำความสะอาดขั้วไฟฟ้าโดยใช้ความต่างศักย์ไฟฟ้าผ่านลงไปนาน 15 วินาที ตรวจสอบความคงทนของขั้วไฟฟ้าบิสมัท โดยตรวจวัดเบริลเลียมที่ความเข้มข้น 100 ไมโครกรัมต่อลิตร ซ้ำ 40 ครั้ง ในช่วงเวลา 2 ชั่วโมง พบว่ามีความเบี่ยงเบนมาตรฐานของการตรวจวัดต่ำมาก อยู่ที่ร้อยละ 3.9 ดังนั้นขั้วไฟฟ้าบิสมัท สามารถใช้เป็นเซนเซอร์ในการตรวจวัดโลหะปริมาณน้อย ๆ ทดแทนขั้วไฟฟ้าปรอทได้เป็นอย่างดี การ

ประยุกต์ใช้ตรวจวัดโลหะในแหล่งน้ำธรรมชาติได้ผลดีเช่นกัน ผลการวิจัยนี้ ชี้ให้เห็นถึงแนวทางที่จะเคลือบขั้วไฟฟ้าบิสมัทบนแผ่นสกรีนพรินต์ เพื่อทำเป็นเซนเซอร์ในโอกาสต่อไป

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Abstract

Project Code : MRG5180280

Project Title : Novel Electrochemical Sensors for Ultratrace Metal Detection

Investigator : Mr. Sompong Thongngamdee Nakhon Pathom Rajabhat University

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Project Period : 2 years

Electrochemical sensing devices have a major impact upon the monitoring of pollutants by allowing the instrument to be taken to the sample rather than bringing the sample to the laboratory. The advancement in miniaturization technology has led to the development of sensitive and selective electrochemical devices for field based and in situ monitoring. Efforts have been focused on the development of bismuth coated carbon electrode for the sensitive adsorptive stripping voltammetric determination of trace metals. A submersible electrode assembly for the real time monitoring of the metals in natural waters has been developed. The new protocol is based on the accumulation of the metal-ligand complex at a preplated bismuth film electrode, followed by a negatively sweeping square wave voltammetric waveform. The resulting performance is examined and compares well with mercury film electrodes. The favorable performance obtained at bismuth electrodes coupled with the negligible toxicity of bismuth makes them extremely attractive for developing the bismuth based submersible sensors for continuous in-situ environmental and industrial monitoring of trace metals. A sensitive adsorptive stripping voltammetric protocol for measuring trace beryllium, for example, in which the preconcentration is achieved by adsorption of the beryllium–arsenazo-III complex at a preplated bismuth-coated carbon fiber electrode, is described. Optimal conditions were found to be a 0.05 M ammonium buffer (pH 9.7) containing 10 μM arsenazo-III, an accumulation potential of 0.0 V (versus Ag/AgCl). The new procedure obviates the need for toxic mercury film electrodes used in early stripping protocols for beryllium. A linear response is observed over the 10–50 $\mu g\ l^{-1}$ concentration range (60 s accumulation), along with a detection limit of 0.25 $\mu g\ l^{-1}$ beryllium. A 15-s electrochemical cleaning enables the same bismuth film to be used for a prolonged operation. High stability is thus indicated from the reproducible response of a 100 $\mu g\ l^{-1}$ beryllium solution (n = 40; RSD = 3.9%) over a 2-h operation. Applicability to a ground water

sample is illustrated. The attractive behavior of the new sensor holds great promise for on-site environmental and industrial monitoring of beryllium. Preliminary data in this direction using bismuth-coated screen-printed electrodes are encouraging.

Keywords : electrochemical sensors, stripping voltammetry, bismuth film electrodes, beryllium

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The help and support of colleagues and friends from Chemistry Program, Faculty of Science and Technology, Nakhon Pathom Rajabhat University will always be remembered.

Sompong Thongngamdee

เอกสารแนบหมายเลข 1

Executive Summary

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1. ความสำคัญและที่มาของปัญหา

A major thrust of the green chemistry research activity is the development of new analytical methodologies. New analytical tools are needed for real-time industrial process monitoring and for preventing the formation of hazardous materials. The development of 'greener' analytical protocols and devices, with negligible waste generation or non-toxic materials is another major goal of green analytical chemistry. The unique features of electrochemical monitoring systems make them particularly attractive for addressing industrial and environmental problems and the challenges of green chemistry. In particular, the new generation of miniaturized electrochemical analyzers offers tremendous potential for obtaining the analytical information in a faster, simpler, and cheaper manner compared to traditional laboratory-based instruments. Also the traditional lab-based atomic absorption spectroscopic techniques are not amenable for on-site metal testing. Among the various trace metal techniques, electrochemical stripping analysis is the most likely candidate to meet the requirements of decentralized metal analysis. The technique combines the advantages of remarkable sensitivity, portability/miniaturization, multi-element capability, low cost, and minimal power requirements. The remarkable sensitivity of stripping analysis is attributed to the combination of an effective preconcentration step with advanced measurement procedures that generates an extremely favorable signal-to-background ratio. Four to six trace metals can thus be measured simultaneously in diverse environmental matrices. Such characteristics have prompted the adaptation of stripping voltammetry for decentralized metal testing.

Proper choice of the working electrode is crucial for the success of the stripping operation. Two basic electrode systems, the mercury film electrode (MFE) and hanging mercury electrode (HMDE), have gained wide acceptance in the development of anodic stripping voltammetry (ASV). In most cases, a glassy carbon electrode, iridium microdisks, or a carbon fiber one are used to support the mercury film. While these small-volume mercury electrodes offer an attractive stripping performance, new alternative electrode materials are urgently desired for addressing growing concerns regarding the toxicity, handling, and disposal of mercury. Future regulations and occupational health considerations may severely limit (or ban) the use of mercury as an electrode material. New alternative electrode materials with a similar performance are highly desired, particularly for meeting the growing demands for on-site environmental analysis. Different bare carbon, gold, or iridium electrodes have been used as possible alternatives to mercury. While offering useful signals for several metals, the overall performance of these non-mercury electrodes has not

approached that of mercury ones, due to a low cathodic potential limit, multiple and/or distorted peaks, or large background contributions. A wide range of ligand- or ion-exchanger modified (preconcentrating) electrodes have also been developed, but their overall sensitivity and reproducibility has not been satisfactory for routine measurements of trace metals. Despite of these intensive efforts, a truly competitive alternative stripping electrode has not emerged, and no major breakthroughs have been reported. A major challenge for deploying electrochemical devices for routine water analysis will thus be the development of effective non-mercury working electrodes for high performance stripping analysis.

This research seeks the development and characterization of new electrochemical sensors for on-site monitoring priority inorganic contaminants (particularly lead and cadmium) in drinking and natural waters. Unfortunately, the technique has traditionally relied on the use of toxic mercury electrodes. Despite of intensive research efforts and growing concerns on the use of mercury, a 'non-mercury' stripping electrode, truly competitive to mercury ones, has not emerged. The proposed research aims at gaining such insights into the behavior of the new non-mercury stripping electrodes, and for using the new knowledge for optimizing the preparation and operation the non-mercury based metal-sensing devices. We will thus critically assess the analytical 'figures of merit' of the 'mercury-free' stripping sensors. We will also develop an easy-to-use hand-held analyzer, compatible with the new disposable non-mercury electrodes, and will extensively test the integrated microsystem with relevant water samples. The effort would thus lead to the emergence of reliable alternative ('non-mercury') sensing electrodes that would have a major impact upon the monitoring of inorganic contaminants in drinking and natural waters and upon the management of water supplies, in general.

2. วัตถุประสงค์

2.1 To explore the non-mercury sensors for ultratrace metal detection

2.2 To optimize the preparation and operation of the mercury-free based devices

3. ระเบียบวิธีวิจัย

3.1 Exploration of the non-mercury sensing elements

The selection of non-mercury sensing elements for ultratrace metals detection is critical to obtain the reliable monitoring of metal contaminant. Therefore, various sensing elements such as bare carbon (in various form of glassy carbon, carbon fiber, carbon paste, carbon graphite rod, boron doped diamond), gold, Iridium, silver and bismuth, will be examined and compared for their voltammetric signal, background current and overall signal-to-background characteristics.

3.2 Electrochemical characterization of the non-mercury sensors

Various voltammetric waveforms can be used to produce the current-potential voltammetric profiles. These differ mainly in the excitation waveform and, hence, yield different signal-to-noise characteristics. The responses of the non-mercury based sensors using linear sweep stripping voltammetry, differential pulse stripping voltammetry and square-wave stripping voltammetry will be compared. The most favorable performance characteristics with the lowest detection limits will be chosen.

3.3 Optimization of the sensor preparation and operation

The parameters for various voltammetric waveforms, such as potential window, initial potential, final potential, step potential, frequency, amplitude etc., will be optimized for new non-mercury based sensors. The best performance characteristics will be used for preparation and operation of the sensors.

3.4 Evaluation of the overall analytical performance of sensors

Analytical 'Figures of Merit'. Following the optimization of the preparation conditions and analytical protocol, we will assess the overall analytical performance. Performance characteristics, including reproducibility, dynamic range, signal/ background characteristics (i.e., detection limits), short-term stability and useful lifetime, renewability will be carefully examined, and the analytical 'figures of merit' will be established.

3.5 Development of a dedicated hand-held analyzer

The operation of the non-mercury sensors will be combined with a miniaturized (pocket-size), user-friendly, battery-operated metal analyzer. We will develop the dedicated hardware and software for such compact unit. The meter will thus consist of a proper potential control, waveform generator, a single computer board, and a display. A new software will be developed for controlling the entire sequence of events (of the deposition/stripping/cleaning cycle), and for a 'smart' data processing (including noise filtration, data smoothing, peak location and integration, and one-point calibration in connection to the 'built-in' non-mercury internal standard). Such signal processing will ensure a high-quality response.

3.6 Extensive testing and validation

The new hand-held meter will undergo extensive testing with a wide range of simulated and real drinking and natural water samples. We will critically assess the precision and accuracy at different levels of metals, will calculate the %recovery and compare the data with those of centralized atomic absorption spectroscopy. Relevant reference materials will also be employed. Appropriate replicates, spikes, standards, calibrations, and recoveries will be employed. Matrix effects will be assessed by comparing the results of simulated and real water samples.

Validation is an important step in the development and acceptance of new analytical devices. The new stripping sensor will be carefully validated. The accuracy of the results will be verified and critically validated by extensive correlation to established EPA reference protocols for the individual metal contaminants, and in connection to relevant reference materials. Proper quality control (QC) and assurance (QA) will be carried out. All measurements will be made so that the results are representative of the water matrix (in connection to a proper sampling and storage). Assessment of the measurement data will rely upon established statistical protocols. Methods used for collecting and assessing the data will be clearly documented. Proper attention will be given also the disposal of used reagents, and to all related safety issues.

4. แผนการดำเนินงานวิจัยตลอดโครงการในแต่ละช่วง 6 เดือน

Activities	2008 (month)								2009 (month)												2010 (month)			
	5	6	7	8	9	10	11	12	1	2	3	4	5	6	7	8	9	10	11	12	1	2	3	4
1. Exploration of the non-mercury sensing elements	◄	—	—	—	►																			
2.Electrochemical characterization of the non-mercury sensors						◄	—	►																
3. Optimization of the sensor preparation and operation									◄	—	►													
4. Evaluation of the overall analytical performance of sensors												◄	—	►										
5. Development of a dedicated hand-held analyzer															◄	—	—	—	—	►				
6. Extensive testing and validation																				◄	—	—	—	►
7. Writing manuscripts and submission									◄	—	—	►									◄	—	—	►

<u>เอกสารแนบหมายเลข 2</u>

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<u>เอกสารแนบหมายเลข 3</u>

การเปิดบัญชีโครงการ

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CHAPTER 1

INTRODUCTION

1.1 Environmental Monitoring

Environmental monitoring for the detection of pollutants is becoming increasingly important to regulatory agencies, the regulated community and the general public. This is true for compounds that pose a potential human health risk or risk to the environment. Especially, environmental contamination by harmful chemicals including explosives, heavy metals, and inorganic, organic and organometallic species is a serious problem due to the possible health threat these contaminants pose to public [1-2]. In recent years, increased concerns with the toxic effects of chemicals in the environment have led to the necessity of monitoring pollutant levels at various points in industrial processes and recycling processes, in effluents and wastewaters, and at industrial, agricultural, and urban sites. Additionally, continuous monitoring of environmental pollution in the field requires portable fast-response sensors that are robust and with sufficient sensitivity and long lifetime. However, the high cost and slow turnaround times typically associated with the measurements of regulated pollutants clearly indicate a need for analytical technologies that are fast, portable and cost effective. To meet this need, a variety of analytical methods have been introduced. Although a very small number of these methods are commercially available, many are under research and development.

1.2 Monitoring of Heavy Metals

Heavy metals are natural constituents of the Earth's crust and are present in varying concentrations in all ecosystems. Human activity has drastically changed the biogeochemical cycles and balance of some heavy metals. Heavy metals are stable and persistent environmental contaminants since they cannot be degraded or destroyed. As trace elements, some heavy metals, e.g. Cu, Se and Zn, are essential to maintain the metabolism of the human body. However, at higher concentrations they can lead to poisoning. Heavy metal poisoning could result, for instance, from drinking-water contamination, high ambient air concentrations near emission sources, or intake via the food chain. Excessive levels of metals in the marine environment can affect marine biota and pose risk to human consumers of seafood. Heavy metals are also known to have adverse effects on the environment and human health [3].

Heavy metals are dangerous because they tend to bioaccumulate. Bioaccumulation means an increase in the concentration of a chemical in a biological organism over time, compared to the chemicals concentration in the environment. Compounds accumulate in living things any time they are taken up and stored faster than they are broken down (metabolized) or excreted. Heavy metals can enter a water supply by industrial and consumer waste, or even from acidic rain breaking down soils and releasing heavy metals into streams, lakes, rivers, and groundwater.

Environmental monitoring of heavy metals is of great importance for ecological assessments as well as for understanding the dissemination of pollutants [4]. Contamination by these metals is indeed widespread all over the world. Due to their toxicity, even at low concentrations, Cr, U, Pb, Cd, As, Hg, Al, are key elements, while Cu, Zn, Ni, Co, Se, Bi are important because they may play a vital or a toxic role, depending on their concentrations and the nature of the considered organisms. Their biogeochemical role also strongly depends on their physico-chemical forms, which include particulate (>1 μm), colloidal (1 nm-1 μm) and dissolved (< 1 nm) species. The latter include free-metal ions, simple inorganic complexes and complexes with anthropogenic and natural organic ligands. Thus, measurements of total metal concentrations alone do not yield sufficient information on the ecotoxicological impact and fate of trace elements. The measurement of specific species or groups of homologous species, denoted as speciation, is therefore essential [5].

1.3 Electrochemical Sensor

Electroanalytical chemistry can play a very important role in the protection of our environment. In particular, electrochemical sensors and detectors are very attractive for on-site monitoring of priority pollutants, as well as for addressing other environmental needs. Such devices satisfy many of the requirements for on-site environmental analysis. They are inherently sensitive and selective towards electroactive species, fast and accurate, compact, portable and inexpensive.

The purpose of an electrochemical sensor is to provide real-time dependable information about the chemical composition of its surrounding environment. Ideally, the sensor is capable of responding continuously and reversibly and does not agitate the sample. Such devices consist of a

transduction element covered with a biological or chemical recognition layer. In the case of electrochemical sensors, they are concerned with the interplay between electricity and chemistry, namely the measurements of electrical quantities, such as current, potential or charge and their relationship to chemical parameters. The analytical information is obtained from the electrical signal that results from the interaction of the target analyte and the recognition layer. Different electrochemical devices can be used for the task of environmental monitoring depending on the nature of the analyte, the character of the sample matrix, and sensitivity or selectivity requirements.

Some of the criteria to be considered for the selection of electrochemical sensors for environmental monitoring are shown in Figure 1.1 [6]. The contribution of electrochemical sensors and electroanalysis can make to this strategy. In general, most of the electrochemical devices used for environmental monitoring fall within three major categories, amperometry and voltammetry, potentiometry and conductimetry.

Amperometry and Voltammetry: The use of a potential applied between a reference and a working electrode causing the oxidation or reduction of an electroactive species. The applied potential thus serves as the driving force for the electron-transfer reaction. The resulting current is a direct measure of the rate of the electron transfer reaction and proportional to the target analyte concentration. The most common example is the oxygen Clark electrode that has been routinely used for monitoring the level of oxygen in water column and sediment pore water.

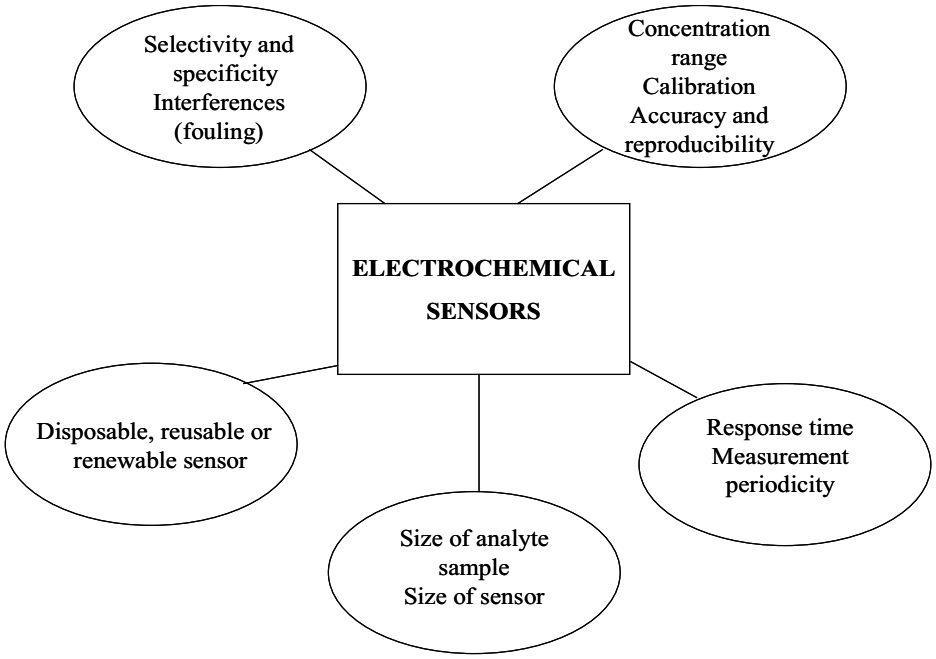

Figure 1.1 Important aspects for choosing electrochemical sensors for environmental monitoring.

Potentiometry: In potentiometric sensors (primarily ion-selective electrodes), the analytical information is obtained by converting an ion-recognition event into a potential signal. A local equilibrium is established across the recognition membrane, leading to a change in the membrane potential. The analytical information is obtained from the potential difference between the ionselective electrode and a reference electrode. Potentials are a function of species activity, not concentration. Typical examples are potentiometric devices for in situ monitoring of pH, pCO_2 or pS.

Conductimetry: Conceptually the simplest of the electroanalytical techniques but inherently non-specific. The concentration of the charge is obtained through measurement of solution resistance and is therefore not species-selective. Conductimetric detectors can, however, be useful in situations where it is necessary to ascertain, for example, whether the total ion concentration is below a certain permissible maximum level or for use as an on-line detector after

separation of a mixture of ions by ion chromatography. Such situations can arise in electroremediation.

1.4 Electroanalytical Methods

1.4.1 Electrode Reaction

The goal of an electroanalytical measurement is to acquire a response, e.g. current, potential, or charge, which is related to analyte concentration in the bulk solution. Voltammetry, potentiometry and amperometry are the three major techniques that are commonly used. The three techniques are based on similar electrochemical reactions that occur at the electrode surface. These reactions can be illustrated, in general, as follows:

$$O + ne^- \rightleftharpoons R \qquad [1.1]$$

Where O and R are the oxidized and reduced forms, respectively, of the redox couple.

The overall electrode reaction can be considered as composed of a series of steps that cause the conversion of the dissolved oxidized species, O, to a reduced form, R, also in solution. Some of the simple reactions involve mass transport of the electroactive species to the electrode surface, the electron transfer across the interface and the transport of the product back to the bulk solution. In general, the net rate of the reaction and thus the current is mainly governed either by mass transport of the reactant from the bulk solution to the electrode surface or by the rate of electron transfer at the electrode surface. The slower rate of these two processes controls the overall rate. Furthermore, the two processes are determined by the analyte and various experimental conditions such as media, electrode material, operating potential, time scale, mode of mass transport, etc.

Thus, if the overall rate is controlled by the electron transfer kinetics, the limiting current, i_l, is given by Buttler-Volmer equation [7]:

$$i_l = nFAk^0 [C_O(0, t)e^{-\alpha nf(E-E0)} - C_R(0, t)e^{(1-\alpha)nf(E-E0)} \qquad [1.2]$$

and

$$f = F/RT \qquad [1.3]$$

where n is the number of electrons per molecule oxidized or reduced, F is the Faraday constant, A is the area of the working electrode, $C_O(0, t)$ and $C_R(0, t)$ are the concentrations of the oxidized and reduced species at the electrode surface at time 0 or t. k^0 is the standard constant, α is the

transfer coefficient, R is the gas constant, T is the temperature, E^0 is the formal potential of the redox couple and E is the potential of the working electrode expressed by the Nernst equation [7]:

$$E = E^0 + RT/nF \ln C_O/C_R \qquad [1.4]$$

Since the kinetics of all electron transfer in most electrode reactions are very rapid compared to those of mass transfer processes, in most cases, the limiting current is mass transfer dependent.

Reactions which are controlled solely by mass transport are called nernstian or reversible, because they obey thermodynamic relationships. The phenomenon of mass transport may occur via three routes: diffusion, convection and migration. While diffusion looks into movement under concentration gradient, i.e. from regions of high concentrations to regions of lower ones, convection deals with gross physical movement to the electrode surface and is minimized via solution (stirring, flowing, sonicating) of electrode (rotating, vibrating). Migration on the other hand deals with movement of charged particle along an electric field, i.e., an electric field is set up at the electrode-solution interface whenever a potential is supplied to a solution, and results in a potential drop across the phase boundary. Such effects are minimized by employing background electrolyte consisting of an electrolytically inert substance (usually an alkali metal salt such as KCl or $NaNO_3$ in aqueous solution). Provided the background electrolyte is concentrated enough (usually 0.1- 1.0 M) the abundance of conducting ions at the electrode interface will effectively prevent the build up of a localized electric field and hence eliminate the contribution of migration to the overall mass transport. Thus, under such diffusion controlled conditions, the limiting current passed through the electrochemical cell and electrode at the time t, $i_l(t)$, can be expressed by the Cottrel equation [7]:

$$i_l(t) = nFA\pi^{-1/2}t^{-1/2}D_i^{1/2}C_i^* \qquad [1.5]$$

Where D_i is the diffusion coefficient and C_i^* is the bulk concentration of species i. Several electroanalytical methods quantitative behavior is based on this equation.

1.4.2 Voltammetry

Voltammetry is a controlled-potential technique which involves measurement of current at a working electrode as an applied potential runs through a limited range which depends on the

electrode material, supporting electrolyte and the reference electrode. In other words, the current is measured as a function of a potential waveform applied to the electrode. The current is proportional to the analyte concentration in the bulk solution. The basic difference between these voltammetric techniques are in their potential-time waveforms. In this thesis, cyclic, linear scan, differential pulse and square wave voltammetry associated with stripping analysis were used.

1.4.2.1 Cyclic Voltammetry (CV)

CV is usually the first experiment performed in an electroanalytical study and the most widely used technique for acquiring qualitative information about electrochemical reactions. The power of CV results from its ability to rapidly provide considerable information on the thermo-dynamics of redox processes, on the kinetics of heterogeneous electron-transfer reactions and on coupled chemical reactions or adsorption processes. Particularly, CV offers a rapid location of redox potentials of the electroactive species, and convenient evaluation of the effect of media upon the redox process [7].

CV thus involves monitoring the current at the working electrode when it is linearly scanned between E_1 to E_2 using a triangular potential waveform at a given scan rate (ν), as shown by the potential-time profile in Figure 1.2. Upon reaching potential E_2 the scan direction is reversed and is often terminated at the start potential, E_1. The gradient of this potential-time plot defines the scan rate, which can vary from a few millivolts per second to millions of volts per second.

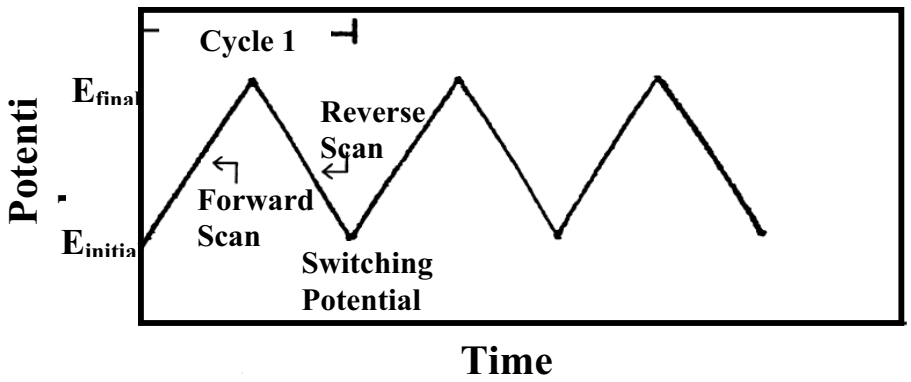

Figure 1.2 A typical potential-time excitation signal in CV.

For an oxidation process, the initial scan direction is positive. There are three main types of electrode process: reversible, irreversible and quasi-reversible. Reversible system (as shown in Figure 1.3) requires fast electrode kinetics compared to the rate of mass transport. An example of this type of process is the oxidation of ferrocene (Fc) to the ferricenium cation (Fc^+) in acetonitrile with 0.1 M $(C_4H_9)_4NClO_4$ as supporting electrolyte [8]. At the initial potential E_1 no current is passed as the magnitude of potential is insufficient to drive electron transfer. As the potential sweeps from E_1 to the oxidizing potential, a current is produced as Fc is converted to Fc^+. The concentration of Fc at the electrode surface ($[Fc]_{x=0}$) decreases as it is converted into Fc^+. This result is an increase in the concentration gradient of Fc at the surface of the electrode and

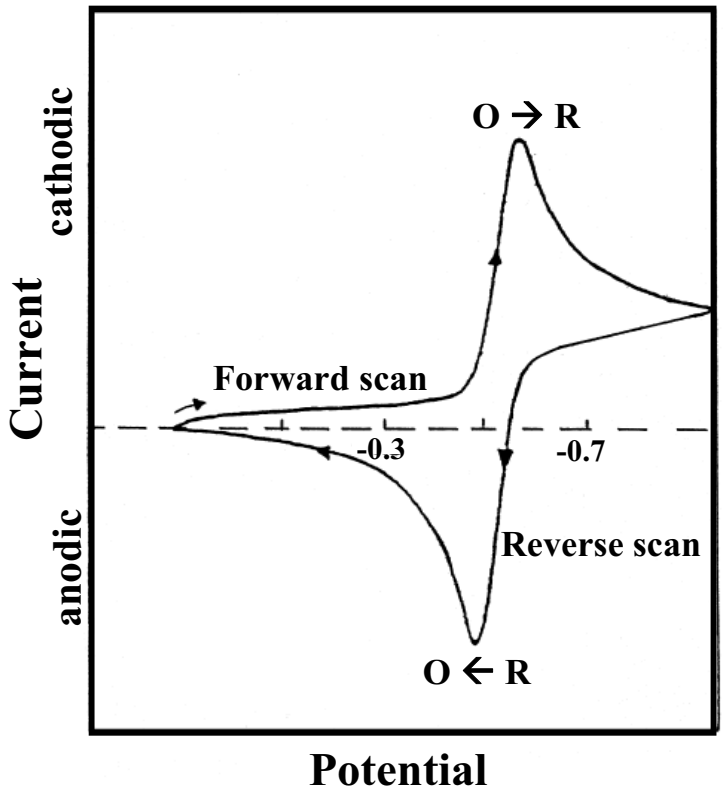

Figure 1.3 A typical cyclic voltammogram showing reversible redox process.

thus the diffusional flux of Fc to the electrode increases. Beyond the formal potential of the redox couple depletion of the reduced species Fc at the electrode surface occurs and more Fc is required

to diffuse in from the bulk. This cause a current maximum (E_p^{ox}) and the subsequent drop in current is controlled by the rate at which a fresh solution can diffuse to the electrode surface.

The magnitude of the peak current, i_p, is predicted by the following equation

$$i_p = (2.69 \times 10^5)\, n^{3/2} A C D^{1/2} \nu^{1/2} \qquad [1.6]$$

Where n is the number of electrons transferred, A is the electrode area (in cm^2), C is the species concentration (in mol cm^{-3}), D is the diffusion coefficient (in $cm^2\ s^{-1}$), and ν is the scan rate (in $V\ s^{-1}$). It should be noted that as the scan rate is increased the value of i_p increases because the diffusion layer becomes thinner and the flux will be greater leading to an enhanced peak current.

At potential E_2 the scan direction is reversed. On this scan an analogous sequence of events occurs. However, in this instance the main reaction is the reductive conversion of Fc^+ back to Fc. A current peak arises at the reduction potential (E_p^{red}). This is where the concentration of Fc^+ has been depleted at the surface and the current depends on the rate of diffusion to the electrode from the bulk. Through scrutinizing the position of the peak potentials and peak heights the reversibility of the redox couple can be assessed.

In these types of processes, the oxidative and reductive peak heights are identical and are separated by a potential of 59 mV (at 25°C), which is independent of scan rate and hence characteristic of an electrochemically reversible couple. If n electrons are transferred in such a system the peak separation is given by [7]:

$$\Delta E_p = E_p^{ox} - E_p^{red} = 0.059/n \qquad [1.7]$$

It should also be noted that the position of the peak on the potential axis (E_p) is related to the formal potential, which is centered between E_p^{ox} and E_p^{red}.

$$E^o = (E_p^{ox} + E_p^{red})/2 \qquad [1.8]$$

Irreversible systems have slow electrode kinetics compared to the mass transport. The increase in the potential E_p^{ox} is due to the over potential required to push the reaction to completion and the loss of a significant reduction peak is because the electrode process does not occur at a measurable rate at potentials close to the formal potential. Unlike the reversible case

the peak potentials depend on scan rate. Quasi-reversible systems are intermediate between the two extremes discussed above.

1.4.2.2 Stripping Voltammetry (SV)

SV is a two-step technique, i.e., preconcentration and stripping steps. In the first step, the species of interest is electrolytically or non-electrolytically accumulated into or onto the working electrode under conditions of forced convection. Stirring the solution increases the efficiency of this process. The concentration of the analyte on or in the electrode is much higher than the concentration in the solution (up to 1000-fold increase). Following a period of inactivity allows homogeneous distribution of the analyte and restoration of quiescent solution conditions. The analyte is electrolytically removed in the stripping step. The preconcentrated species is then stripped back to the solution, under a quiescent condition. The current at a working electrode is measured as a function of a potential waveform applied to the electrode. The response due to a given analyte in the stripping step is proportional to the concentration of that analyte in the solution. The conversion of the response to a concentration can be achieved using a calibration curve, but the method of standard additions is generally used. The dynamic range limits depends on the type of electrode material, the electrolyte solution, and the reference electrode. The detection limit of this technique depends on the length of the preconcentration time.

Based on the excitation potential-time waveforms, the three techniques, linear sweep stripping voltammetry (LSSV), differential pulse stripping voltammetry (DPSV), and square wave stripping voltammetry (SWSV) are commonly used in stripping voltammetry. The stripping peak current is directly proportional to the concentration of the analyte in solution. Determination of the analyte in real samples can be performed by calibration or by standard addition methods. In standard addition, a known amount of the analyte is added to the solution and the experiment is repeated. For each sample, two or more standard additions are often made.

SV techniques differ in their methods of accumulation, electrolytic vs. adsorptive. In general, SV includes three kinds of methods such as Anodic Stripping Voltammetry (ASV), Cathodic Stripping Voltammetry (CSV) and Adsorptive Stripping Voltammetry (AdSV). The basic principles of these methods are explained briefly in the following sections.

1.4.2.2.1 Anodic Stripping Voltammetry (ASV)

ASV is carried out in two steps. Firstly, the deposition step involves the electrolytic reduction of metal ions M^{n+} to their elemental state at a constant potential into/onto the surface of an electrode. During the deposition step analyte is brought to the electrode surface by diffusion and/or convection. Secondly, the stripping step consists of the application of a potential waveform to the electrode which causes dissolution of the deposit, the element state metal stripped off into solution followed by a positive-going (anodic) potential scan and obtained a peak shape voltammogram. The peak potential in this scan is used for identification of the metal, and the peak current is proportional to the concentration. The process can be described as follows (e.g., Hg electrode):

Deposition step: $M^{n+} + ne^- \longrightarrow M(Hg)$ [1.9]

Stripping step: $M(Hg) \longrightarrow M^{n+} + ne^-$ [1.10]

with a positive-going potential scan

ASV is the oldest and best established stripping technique. For most applications, the measuring cell is very simple, and many commercial instruments are available, at relatively low cost, which allow the application of different excitation signals. Procedures using linear sweep anodic stripping voltammetry (LSASV), differential pulse anodic stripping voltammetry (DPASV), or square wave anodic stripping voltammetry (SWASV) at a hanging mercury drop electrode (HMDE), a thin mercury film electrode (TMFE), or a solid microelectrode (SME) show very good performance for many applications. The technique has been widely used in the determinations of trace metals such as Pb, Cu Cd, Zn, Bi, Tl, Sn, Sb, In, Ag, Hg, *etc*., in varies media.

1.4.2.2.2 Cathodic Stripping Voltammetry (CSV)

CSV has been used in the determination of species which can form insoluble derivatives during the pre-electrolysis step. An important group of CSV procedures is devoted to anions, and is based on the formation of sparingly soluble Hg(I) compounds. Like ASV, there are two steps. The first step is the accumulation in which the species is adsorbed on the electrode surface by forming an insoluble salt. Following the preconcentration step, the adsorbed analyte is then

stripped off from the electrode by a negative-going (cathodic) potential scan. The mechanism can be simply described as following:

Accumulation step: $[MO_x]^{m-} - ne^- \rightarrow [MO_x]^{(m-n)-}$ [1.11]

Stripping step: $[MO_x]^{(m-n)-} \rightarrow [MO_x]^{m-} - ne^-$ [1.12]

with a negative-going potential scan

CSV has been used for the determination of inorganic anions such as halides, selenide, and sulfide, and oxyanions such as AsO_3^{3-}, SeO_3^{2-}, TeO_3^{2-}, MoO_4^{2-}, CrO_4^{2-}, WO_4^{2-}, VO_3^{2-} and some organic compounds.

1.4.2.2.3 Adsorptive Stripping Voltammetry (AdSV)

In adsorptive stripping analysis, a spontaneous adsorption process is purposely utilized as a preconcentration step for trace measurements of important species that cannot be accumulated by electrolysis. For instance, trace and ultratrace metals such as Cr, U, Al, Ni, Co, Mo, W, Ti, V, Fe, are impossible, or at least very difficult, to be determined by ASV or CSV. Adsorption generally means the attachment of molecules or ions to the surface of electrodes. The relatively new strategy involves the formation, adsorptive accumulation, and reduction of a surface active complex of the metal. Adsorptive stripping analysis enhances the scope of stripping measurements for numerous trace elements. The voltammetric stripping schemes, with a negative potential scan can be employed for measuring the adsorbed complex. Short adsorptive time (0.5-5.0 min) results in a very effective interfacial accumulation. The resulting voltammetric response of the adsorbed species is significantly larger than that of the solution alone. Hence, the detection limits are improved by several orders of magnitude as compared to the corresponding solution phase voltammetric response. The surface-active characteristics of numerous organic analytes can be exploited for obtaining effective adsorptive accumulation. Low levels of reducible and oxidizable compounds can thus be determined at mercury-based electrodes. The application of adsorptive stripping analysis for measuring organic analytes in various environmental samples is restricted due to the interference and relative poor selectivity.

Alternative preconcentration schemes based on adsorptive accumulation greatly extend the scope of stripping voltammetry towards numerous metals as well as organic molecules of

environmental and biological interest. Adsorption processes of surfactant-active compounds onto the electrode surface involve many mechanisms including electrostatic and hydrophobic interactions as well as $\pi-\pi$ electron interactions and chemisorption. The relationship between the surface and bulk concentrations of an adsorbate is given by the adsorption isotherm. One of the simplest models, the Langmuir isotherm, assumes that there is (a) no interaction between the adsorbed species on the electrode surface, (b) no heterogeneity of the surface, and (c) a saturation coverage at high bulk concentration. The coverage of the electrode surface by species *i*, Γ_i, according to the Langmuir isotherm, is given by the following equation [9]:

$$\Gamma_i = \Gamma_s \alpha_i C_i/(1+\alpha_i C_i) \qquad [1.13]$$

Where Γ_s is the saturation coverage concentration and α_i is the adsorption coefficient of species i. Therefore, in an electrode electrochemical process during which an adsorption action is involved, the relationship between the quantity of electricity *Q* and the adsorption quantity Γ_i can be described as follows,

$$Q = nFA\Gamma_i \qquad [1.14]$$

Where *A* is the surface area of the electrode, *F*, Faraday constant. Thus, the relationship between the measured response *i* and the analyte concentration *Ci* can be given,

$$i = dQ/dt = nFA(\Gamma_s \alpha_i C_i)/(1+\alpha_i C_i) \qquad [1.15]$$

Therefore, the basis of the quantitative analysis using the adsorptive stripping technique can be described as follows [9]:

$$i = k' t_{acc} C_i \qquad [1.16]$$

Where t_{acc} is accumulation time, and k', a constant. A linear relationship between the stripping current and the bulk concentration is expected when the saturation coverage is avoided. This can be achieved by choosing an appropriate accumulation period. For instance, shorter or longer adsorption time is suggested for higher or lower concentration, respectively. However, AdSV is done under conditions of optimum adsorption based on the Langmuir assumptions, and the adsorptive stripping responses, thus, corresponds to the surface coverage which is proportional to the bulk concentration according to equation [1.16].

There are two main advantages related to adsorptive accumulation. The first one is that any oxidation state can be collected rather than only the metallic state. This aspect of AdSV has opened up the technique of electrolysis to any element with a reduction potential falling within the stability range of mercury and hydrogen. The second advantage is that the material is collected as a monomolecular layer on the electrode surface, so almost all the adsorbed species are instantaneously accessible to deduction. Therefore, the reduction current is independent of diffusion of the reactive species and a very fast potential scanning technique can be employed producing larger currents. In addition, the stripping step in AdSV can be anodic or cathodic, so the direction of the potential scan should be specified. A typical electrode reaction based on the adsorption stripping technique can be described in Figure 1.5.

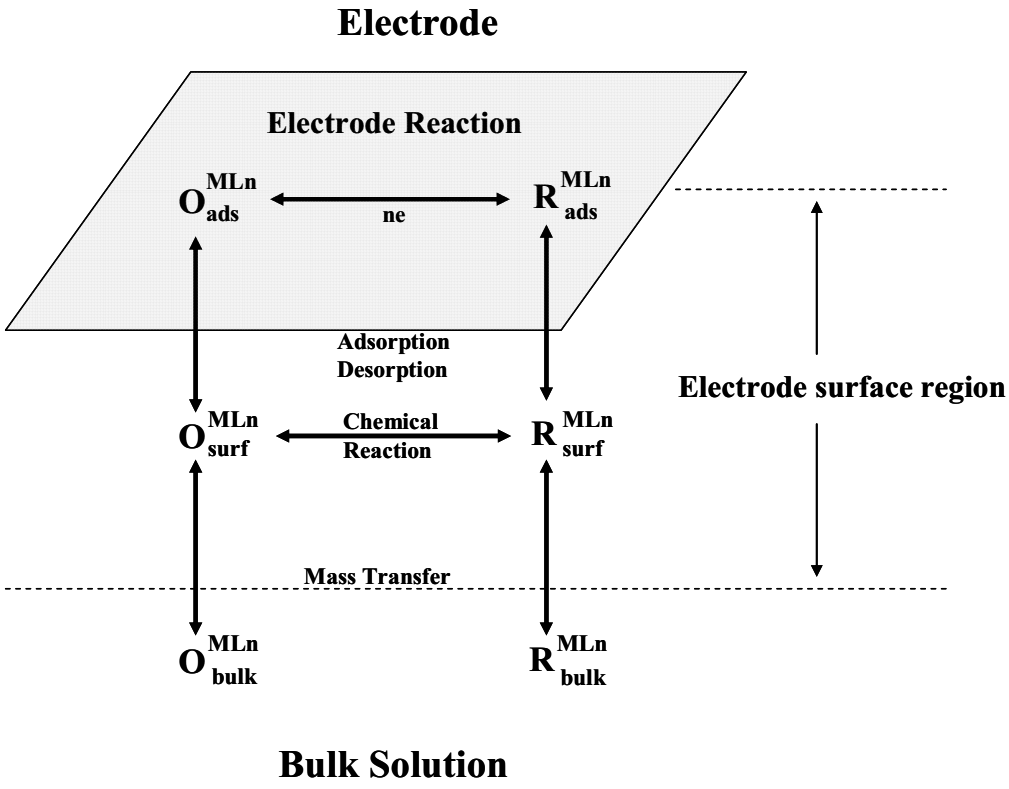

Figure 1.4 A pathway for a typical electrode reaction related to an adsorption reaction.

AdSV has attracted considerable attention for the determination of trace and ultratrace concentration of the metals described above [23, 24, 28-33]. The basis of determination of trace metals by AdSV differs essentially from that of conventional ASV or CSV. The difference is focused on the preconcentration mechanism; according to this mechanism, the metal complex formed, after the addition of the suitable ligand, is accumulated by adsorption on the surface of an electrode. The adsorbed species is subsequently reduced as the potential is scanned to more negative values according to two main mechanisms:

(1) reduction of the elemental species in the adsorbed complex,

Complex step: $M^{n+} + nL \rightarrow ML_n$ [1.17]

Adsorption step: $ML_n \rightarrow [ML_n]_{ads}$ [1.18]

Stripping step: $[ML_n]_{ads} + ne^- \rightarrow M + nL$ [1.19]

(2) reduction of the ligand in the adsorbed complex.

$M^{n+} + nL \rightarrow ML_n$ [1.20]

$ML_n \rightarrow [ML_n]_{ads}$ [1.21]

$[ML_n^O]_{ads} + me^- \rightarrow [ML_n^R]_{ads}$ [1.22]

In AdSV, the surface-active complex that has been collected can be quantified by reduction of metal or ligand in the complex. However, reduction of metal is preferable to ligand reduction as the reduction peak potential is specific to the metal which minimizes interferences by other metals [32]. In addition, the sensitivity of methods employing ligand reduction tends to be lowered by adsorption and reduction of free ligand in addition to that of the chelate. However, reduction of the ligand is convenient if the metal is reduced only at very negative potentials such as Al, Ca, Sr, and some of the rare earths.

1.4.2.2.4 Catalytic Adsorptive Stripping Voltammetry (CAdSV)

Catalytic and adsorptive processes have greatly enhanced the sensitivity of voltammetric procedures. It has been shown that the coupling of catalytic and adsorptive processes, via controlled adsorptive accumulation of a catalyst, yields remarkable sensitivity and detectability down to the picomolar (ppt) level. In general, the main mechanisms in the ultra-sensitive catalytic adsorptive stripping are based on these steps involving complex information,

adsorptive accumulation, complex reduction and oxidant regeneration. More important one is that the products of the electrochemical reduction of the adsorbed species are chemically re-oxidized and reenter the electrochemical reduction cycle.

For instance, a very sensitive procedure for the determination of trace iron by catalytic adsorptive stripping voltammetry of an iron-benzohydroxamic acid-hydrogen peroxide (Fe-HBA-H_2O_2) system has been developed. Figure 1.5 shows the cyclic voltammograms for 0 (a) and 20 (A, b), 2 (B, b) μg/L Fe(III), in the absence (A) and presence of $5x10^{-4}$ M hydrogen peroxide (B), obtained after 120 s stirring at -0.3 V (B, dotted, without preconcentration). The catalytic character of the Fe-BHA-H_2O_2 redox system is indicated in Figure 1.6, which displays differential pulse voltammograms for 5 μg/L iron in the absence (A) and presence (B) of hydrogen peroxide. The addition of hydrogen peroxide results in significant (~20 fold) enhancement of the complex peak. Overall, very large signals and favorable signification effect associated with the coupling of the catalytic process and the adsorptive accumulation. The main mechanisms in this catalytic-adsorptive stripping system can be described as follows,

Complexion $\quad Fe(III) + BHA \rightarrow Fe(III) - BHA$ [1.23]

Adsorption $\quad Fe(III) - BHA + Hg \rightarrow [Fe(III) - BHA]_{ads}(Hg)$ [1.24]

Reduction $\quad [Fe(III) - BHA]_{ads}(Hg) + e^- \rightarrow [Fe(II) - BHA]_{ads}(Hg)$ [1.25]

Oxidation $\quad H_2O_2$

Such use of catalytic adsorption greatly amplifies the response of the accumulated complex, hence permitting convenient quantitation of ng/L (ppt) concentration. Many procedures for the determinations of trace and ultratrace metals by using AdSV and ultra-sensitive CAdSV have been established. It is possible to determine about 40 elements in a great variety of samples [2]. Due to their excellent sensitivity, accuracy, precision, and low cost of instrumentation, the techniques have been successfully and widely used in environmental sample analysis.

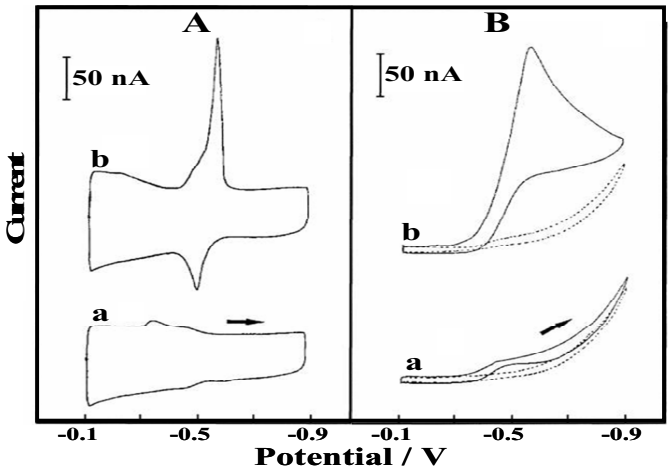

Figure 1.5 Cyclic voltammograms of the Fe-BHA complex. Cyclic voltammograms for 0 (a) and 20 μg/L (A, b), 2 μg/L (B, b) iron(III) in the absence (A) and presence (B) of $5xl0^{-4}$ M hydrogen peroxide, in the presence of $5x10^{-4}$ M BHA and 1 mM HEPES buffer (pH 8.0), obtained after 120 s accumulation at -0.3 V (B, dotted, no preconcentration). Differential pulse scan at 10 mV/s with a 25 mV amplitude.

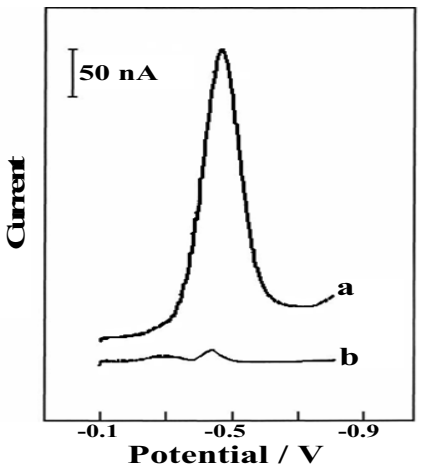

Figure 1.6 Effect of hydrogen peroxide on the Fe-BHA complex adsorptive voltammetry. Stripping voltammograms for 5 μg/L iron(III) in the presence of $5xl0^{-4}$ M BHA, and in (A) the absence and (B) presence of $8xl0^{-4}$M hydrogen peroxide. Accumulation for 2 min at -0.1 V. Differential pulse scan at 10 mV/s with a 25 mV amplitude. Electrolyte, 1 mM HEPES buffer (pH 8.0).

1.5 Research objectives

This research seeks the development and characterization of new electrochemical sensors for on-site monitoring priority inorganic contaminants natural waters. Unfortunately, the technique has traditionally relied on the use of toxic mercury electrodes. Despite of intensive research efforts and growing concerns on the use of mercury, a 'non-mercury' stripping electrode, truly competitive to mercury ones, has not emerged. The proposed research aims at gaining such insights into the behavior of the new non-mercury stripping electrodes, and for using the new knowledge for optimizing the preparation and operation the non-mercury based metal-sensing devices. We will thus critically assess the analytical 'figures of merit' of the 'mercury-free' stripping sensors. We will also develop an easy-to-use hand-held analyzer, compatible with the new disposable non-mercury electrodes, and will extensively test the integrated microsystem with relevant water samples. The effort would thus lead to the emergence of reliable alternative ('non-mercury') sensing electrodes that would have a major impact upon the monitoring of inorganic contaminants in drinking and natural waters and upon the management of water supplies, in general.

CHAPTER 2

SENSOR DESIGN

The use of sensors and detectors to continuously detect important chemical properties has significant analytical advantages. By providing a fast return of the analytical information in a timely, safe and cost effective fashion, such devices offer direct and reliable monitoring of explosive compounds. The real-time electrochemical sensor for explosive monitoring capability has been accomplished through on-line or submersible operations.

2.1 Design Criteria

In general, a useful electrochemical sensor must obey a number of experimental design criteria, many of which are linked to its potential benefits. Among the most important are [6]:

(a) For amperometric and voltammetric sensors, the species to be determined is electroactive within the sensor's potential range and whether there is the addition of an inert supporting electrolyte to carry the current perturbs the equilibria in solution.

(b) For potentiometric sensors, there is an adequate electrode material, free from interferences.

(c) The concentration of electroactive species can be determined with sufficient accuracy and precision.

(d) The measurements are sufficiently reliable and repeatable.

(e) The response time of the sensor is sufficiently fast.

(f) The drift or diminution of sensor response with time due to electrode degradation or surface fouling is sufficiently small.

(g) Calibration is simple and easy to perform, or not necessary.

(h) The detection limit is sufficiently low for the purpose envisaged.

A number of critical design criteria that should be considered when designing and developing robust electrochemical sensors for environmental monitoring is listed in Table 2.1 [8]. These are especially true for the development of submersible sensors where microfabrication, portability, analytical response, sensitivity, selectivity, biofouling, reversibility and power consumption issues are of major concern.

2.2 Remote Carbon Fiber Based Electrochemical Sensor

2.2.1 Sensor Design

A schematic diagram of the typical remote *in-situ* carbon fiber based electrochemical sensor is shown in Figure 2.1. The submersible probe consists of a three-electrode assembly, in a 25 mm i.d. PVC housing tube, connected to a 50 ft (24 m) long shielded cable, via a three-pin environmentally sealed rubber connector. Two female coupling connectors, fixed with epoxy in the PVC tube, served for mounting the microcylinder working electrode and the silver-silver chloride electrode reference electrode. These electrodes were sealed into Teflon male fittings, hence allowing their easy and fast replacement. The platinum wire counter electrode was fixed permanently into the housing. Contact to the working and reference electrodes was made via brass screws and spring assemblies, contained inside 7-mm o.d. copper tubes.

Table 2.1 Criteria for the design and development of electrochemical sensors for environmental monitoring [13].

Macro vs. miniaturized fabrication design
Overall cost, simplicity/complexity of design
Robustness, reliability
Sensitivity and selectivity
Reversibility and stability
Speed
Artifact minimization
Speciation capabilities
Automation, data acquisition
Single vs. multicompound analysis capabilities
Low power consumption

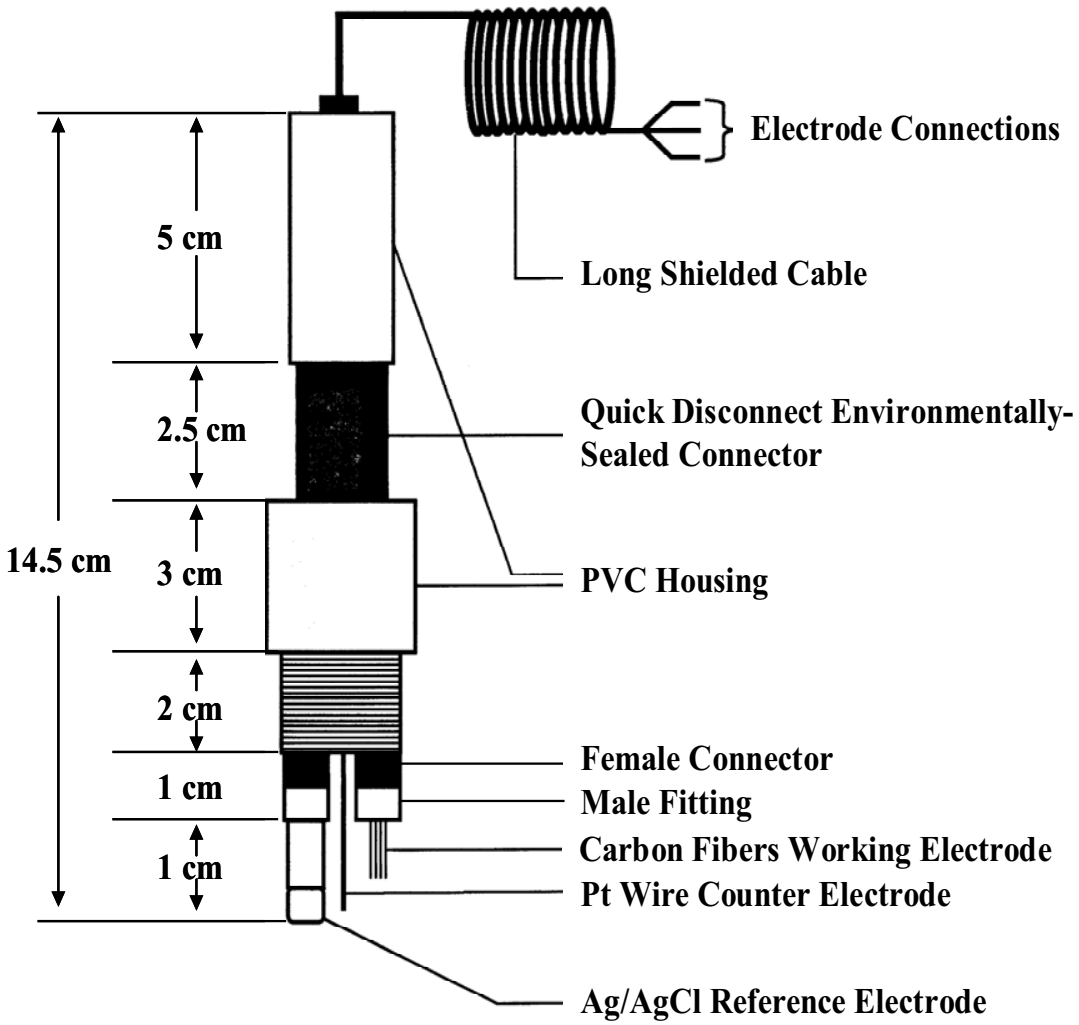

Figure 2.1 Schematic diagram of the remote *in-situ* carbon-fiber based probe.

The latter were placed within the female contacts. The other end of these wires was connected to the male environmentally sealed connector. A similar contact was made to the platinum counter electrode. The male connector was coupled to the receptacle one, which was attached to the shielded cable. Such an arrangement allows rapid disconnection of the electrode housing from the cable. The female connector was also sealed in a PVC tube that provides additional rigidity.

2.2.2 Reference Electrode

The function of the reference electrode is to provide a reference point for working electrode potentials. The reference electrode should, therefore, possess a constant potential value and be chemically stable against solution composition. The commonly employed reference electrode is saturated calomel electrode (SCE) or silver/silver chloride (Ag/AgCl) electrode which has a standard potential of 0.242 or 0.222 V, respectively. In three electrodes system, there is essentially no current drawn through the reference electrode. For the remote carbon fiber based electrochemical sensor, a Ag/AgCl reference electrode (BAS Co.) was used as a reference electrode for all experiments.

2.2.3 Counter/auxiliary Electrode

The function of counter or auxiliary electrode is to complete the electrical circuit where current is allowed to flow between the working and the auxiliary electrodes. The placement of the electrode, with respect to the working electrode, is important as the product of reactions at the electrode may reach the working electrode and interfere. The materials for the counter electrode should be chemically inert. Platinum and carbon are the most commonly employed as the auxiliary electrode. Large surface area, about 50 times larger than the working electrode, is preferable. In the remote carbon fiber based electrochemical sensor, platinum wire was used as the counter electrode for all measurements.

2.2.4 Working Electrode

The carbon fibers microelectrode was used as the working electrode material in the design of remote electrochemical sensor. Due to the number of inherent advantages of carbon fiber microelectrodes of very small dimensions, the use of the microelectrode has become

widespread in electrochemical sensors. The microelectrode possesses the advantage of mass transport of analyte to the electrode surface due to non-linear diffusion. This allows the deposition step to be accomplished without the need for stirring the solution, therefore, random errors often associates with the preconcentration step can be avoided.

According to the fact that the surfaces of carbon fibers are very rich in oxygen containing functional groups such as predominantly carbonyl, carboxyl, hydroxyl and ester groups, these functional groups may play important roles in electrochemical reactions. Carbon fibers electrodes have a wider potential window than metal-based electrodes especially in the anodic range. Carbon fibers (6-20 μm diameter) are produced by the high temperature pyrolysis of polymeric materials and they exhibit interesting surface phenomena that can influence significantly the reversibility of redox reactions and the resulting voltammetric response. Three types of carbon fiber electrode have been mainly used: the exposed single fiber with cylindrical geometry; signal fiber or arrays of fibers, embedded in an insulating material with disk geometry; and brushes, or arrays of exposed fibers.

For fabrication of the carbon fiber micro-working electrodes, carbon fibers (8 m diameter, ALFA AESAR Inc., #1045A) were firstly immersed overnight in 50% ethanol solution, rinsed with distilled water and dried prior to their sealing. Then, a bundle of them (~15 carbon fibers) were placed into a 100 μL standard micropipette tip to a desired distance (usually ~1 cm). The carbon fibers were sealed at the head part of the tip completely with the nail coat insulator and after obtaining the proper part by cutting the tip, it was fixed into a male Teflon fitting. Electrical contact between the carbon fibers and a copper wire was made by back-filling the pipette with the carbon paste and inserting a copper wire (1 mm diameter). Finally, epoxy resin was placed over the carbon paste.

2.3 NPRU Sensor Design

The Nakhon Pathom Rajabhat University (NPRU) sensor consists of three main parts: the electrode unit, the analyzer board and a PC 104 computer. The picture and schematic diagram of the electrode unit is shown in Figure 2.2. The electrode unit has three electrodes: carbon fiber (8

μm diameter, ALFA AESAR Inc., #1045A) working electrode, silver wire reference electrode and platinum wire counter electrode.

To fabricate the electrode unit, cylindrical Plexiglass was used as electrode housing. In the three Teflon male fittings (3 mm diameter) with the screw, the three electrodes were carefully sealed by the epoxy to leave ca. 0.5 cm out and were connected to the copper wires through the graphite powder. The copper wires are long enough for connection with the electrochemical analyzer. The Plexiglass cylinder with the diameter of 3.0 cm and height of 1.5 cm was used to fix the three electrodes. The three electrodes were screwed and fixed in the three holes on the cylinder to leave the three electrodes out for measurement. The distance between every two electrodes was 1 cm. This electrochemical detection system was connected with the interface that can be fixed on the vehicle. In order to detect practical samples such as the sea water, sometimes the three electrodes were protected using plastic tubes with several holes to permit the flow of the sample solution.

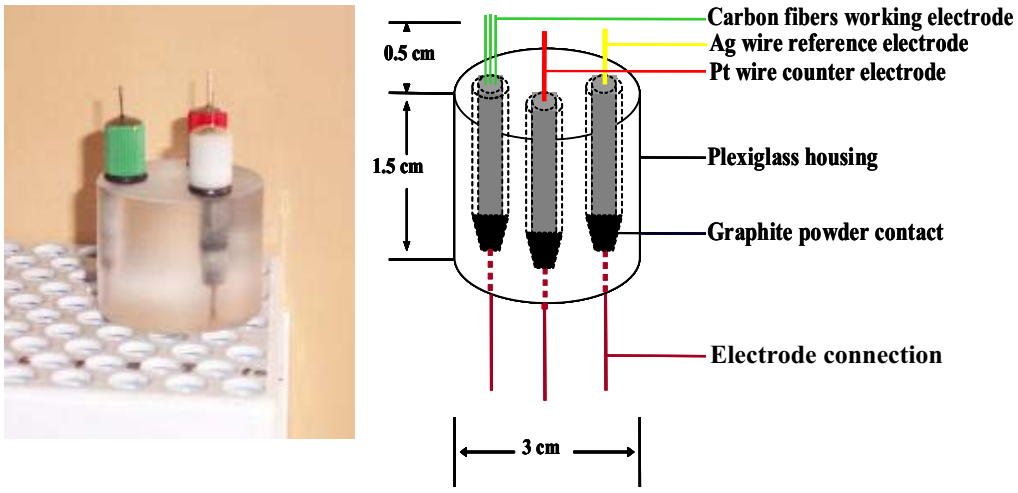

Figure 2.2 The picture and schematic diagram of the *in-situ* carbon-fiber based submersible probe.

The analyzer (also called, potentiostat) performs a function of square-wave voltammetric measurement and is attached to a PC 104 computer via serial connection. Software necessary to control the analyzer board is loaded onto a PC 104 computer which has a Windows operating system. Essentially, voltage is applied between the working and reference electrodes and current is measured between the working and counter electrodes.

2.4 Bismuth Film Electrodes

Over the last two decades, since the invention of polarography by Heyrovsky, mercury has been established as the electrode material of choice for electroanalysis in the negative potential regime, especially for anodic and adsorptive stripping analysis. Starting from the dropping mercury electrode (DME), the hanging mercury drop electrode (HMDE) and later on more robust mercury film electrodes (MFEs), have been used successfully in a lot of applications involving reduction of organic and inorganic electroactive compounds. However, there is a continuous effort to discontinue the use of mercury because of concerns associated with its disposal, leading to potential risks of poisoning and toxicity [10].

As a result, new electrode materials capable of replacing mercury are being continuously searched. In 2000, Wang et al. proposed Bismuth film electrode (BiFE) as an alternate to MFEs. BiFE are prepared by plating a thin bismuth film on a suitable substrate material. Although the most significant advantage of BiFE is their negligible toxicity the analytical properties depicted from voltammetric analysis are roughly comparable to those of MFEs. This phenomenon is attributed to the property of bismuth to form "fused alloys" with heavy metals, which are analogous to the amalgams that mercury forms.

Since the introduction of BiFE, the electroanalytical community has been overwhelmed and there is a concerted effort by several groups to explore the possibility of using bismuth instead of mercury for electroanalysis. Although most of the research has been directed towards understanding the properties of BiFE, some applications in environmental, clinical and food analysis have also started to appear.

2.4.1 Preparation of Bismuth Film Electrode

BiFE primarily uses the same substrates as mercury. One of the widely used substrate is carbon electrode, and different forms of carbon modified with BFE have been reported; glassy carbon, carbon paste wax-impregnated graphite, pencil-lead and screen-printed carbon ink. Although glassy carbon generates a low background current, it is a more expensive material than commercially available pencil-lead and carbon-paste electrodes, which preparation and surface re-generation is easier. Screen-printed electrodes on the other hand can form the basis for disposable, mass-produced sensors. For microelectrode applications, the common substrates that have been used are single carbon fibers, gold and platinum wires. BiFEs based on such microlectrodes are operational in low-conductivity media, give rise to small capacitive currents, allow efficient mass transfer without forced convection and could be applied to small-sample volumes.

For satisfactory performance of the BiFE, it is very important to have a good coating of bismuth on the substrate. There are three general methods of depositing bismuth on the substrate surface; preplating/ex-situ plating, in situ plating and bulk modification of the electrode.

Preplating or ex situ plating, involves prior deposition of a bismuth-film on the electrode surface before transferring the electrode to the sample solution for analysis. An acidic medium is usually recommended for this method to avoid hydrolyzation of Bi(III) ions at higher pH. Since this method requires preplating, a high concentration of the Bi(III) ions in the range of 5-200 mg/L is required. Deposition is performed at a negative potential region in the range -0.5 to -1.2 V with a deposition time of 1-8 min under conditions of forced convection (electrode rotation or stirring).

For in situ plating, a relatively low concentration of Bi(III) ions, typically 400-1000 g/L are added directly into the sample solution and the bismuth film is co-deposited on the electrode surface along with analytes of interest. To avoid saturation of the bismuth film by analytes under analysis, as a general rule, concentration of Bi(III) must be at least 10 fold in excess of the analyte concentration.

Although in situ plating simplifies and shortens the experimental procedure (as an extra preplating step is avoided), it is essentially only useful in fairly acidic pH region since Bi(III) ions are very susceptible to hydrolyze in neutral and alkaline media according to the reaction [11]:

$$Bi^{3+} + 3H_2O \longrightarrow Bi(OH)_3 + 3H^+ \qquad [2.1]$$

However, quite interestingly it has been shown that operation in highly alkaline media is possible under the postulation that Bi(III) does not hydrolyze but forms stable complexes with OH^- ions which are soluble in aqueous media and therefore are electrochemically reduced [11].

$$Bi^{3+} + OH^- \longrightarrow Bi(OH)^{2+} \qquad [2.2]$$

It is worth noting here that unlike Bi(III), Hg(II) ions hydrolyze under such highly alkaline conditions, and therefore are unoperative.

Bulk modification of an electrode involves introducing a bismuth precursor (i.e. a compound of Bi(III), such as Bi_2O_3) into a carbon paste electrode and applying a potential of around -1.0 V. This forms metallic bismuth deposited on the surface of the electrode upon reduction according to the reaction [12]:

$$Bi_2O_{3(S)} + 3H_2O + 6e^- \longrightarrow 2Bi_{(s)} + 6OH^- \qquad [2.3]$$

These bulk electrodes are easy to prepare and simplify the experimental procedure by providing a means of generating a bismuth film in situ without using Bi(III) salts. However, they suffer from low linearity and shifts in the stripping peak potentials).

Scanning electron microscopy (SEM) was used to study the morphology of the bismuth coating and it was shown to be profoundly affected by the substrate material. On glassy carbon, the bismuth film consists of a porous three-dimensional structure, while on carbon-fiber microelectrodes, a more uniform structure was observed. Furthermore, the potential and concentration of the plating solution controls the thickness of the bismuth film that affects peak height and shape in anodic stripping analysis, depending on the target metal ions. BiFEs are expected to be mechanically more stable than MFEs, since the bismuth film forms a solid deposit, whereas the mercury film consists mainly of liquid mercury droplets on the surface of the electrode.

Stripping analysis often requires a series of measurements, and for this application the surface of the electrode must be reactivated by polarization at a potential that facilitates oxidation (anodic stripping) or reduction (adsorptive stripping) of any species. As far as preplated BiFE is concerned, in anodic stripping voltammetry, a "cleaning" potential is chosen which must lie between the oxidation potential of bismuth and metal ions under analysis. Such a potential is applied for a short time of 10-30 s in a stirred solution. In adsorptive stripping voltammetry, the "cleaning" potential chosen is more negative than the reduction potential of the adsorbed species and oxidation potential of bismuth. On the other hand, the "cleaning" potential in in-situ plated BiFEs is rather less precautious since the bismuth film is stripped off electrochemically after each measurement cycle at a potential more positive than the oxidation potential of bismuth and a new bismuth film is re-plated during the next analysis cycle.

It is worth mentioning two related types of electrodes, the so-called bismuth-bulk electrode (BBE) and mixed silver-bismuth alloy electrode. The BBE essentially consists of a polycrystalline pure metallic bismuth rod and its properties and active surface are similar to those of a BiFE. Such an electrode requires no bismuth-plating step and its surface can be easily regenerated by mechanical polishing. Although mixed silver-bismuth alloy electrode has been reported for use in stripping analysis with satisfactory results, there is lack of evidence and discussion towards its analytical utility and advantages.

2.4.2 Performance of Bismuth Film Electrode

2.4.2.1 Potential Window

The accessible potential range of BiFEs is lower than that of MFEs. While there is no significant difference in cathodic limit, BiFEs in comparison to MFEs suffer from limited anodic potential window owing to the easily oxidizable nature of bismuth. Furthermore, the useful potential window is strongly affected by the pH of the solution. Electrolytes with more alkaline pH allow more negative cathodic limit while more positive anodic limit is achieved in more acidic solutions. A narrow anodic potential range limits the utility of BiFEs in not only the anodic stripping analysis (e.g., Cu, Sn and Sb), but adsorptive stripping analysis as well of metal ions

with more positive, or similar, oxidation or accumulation potentials than that of bismuth, respectively.

2.4.2.2 Stripping Modes

The strength of BiFEs is mostly pronounced in applications of trace analysis when coupled to electrochemical stripping methods, which rely on preconcentration of the analytical species on the working electrode prior to a stripping measurement. Stripping methods include stripping voltammetry (linear sweep, differential pulse and square wave) and stripping potentiometry (constant current of chemical as oxidants). In the former, the different techniques are distinguished depending on the nature of the preconcentration process (adsorptive or electrolytic), direction and mode of the voltammetric scan. While most early studies on BiFE have been devoted to ASV measurements, recent activity focused on adsorptive- and potentiometric stripping experiments. In most cases the methodology of detection is adopted from similar procedures on MFEs.

2.4.2.3 Applications of Bismuth Film Electrode

Although most of the earlier work on BiFEs were concerned with insights into their behavior and properties, applications to environmental, clinical and food analysis have started to appear quite recently and are still rather limited. So far the metal ions detected by anodic stripping analysis include Cd, Pb, Zn, Tl, In, and Cu. Within this library, Cd and Pb are probably the most studied metal ions and at trace levels, involving determination in a variety of environmental samples (e.g., hair and tap water, drinking water, and soils), biological fluids (e.g., urine) and food products. Using adsorptive stripping analysis, Ni and Co have been quantified in soils, river water after complexation with dimethylglyoxime, and Cr in tap water, soils, tobacco and certified steel sample (containing 0.7% w/w of Cr) after complexation with cupferron. It is interesting to note Cr determination in certified steel sample showed no interference from co-existing metals (especially from Fe existing in a large excess). There are reports of amperometric and voltammetric determinations of organic compounds on BiFE including 2-nitrophenol and bromofenoxim. BiFE have been further exploited for some novel ideas, for example, using

bismuth peak as an internal "built-in" standard for normalization purposes, the use of electrically heated BiFE and combining with ultrasonic accumulation.

2.4.2.4 Interferences on Bismuth Film Electrodes

Interference studies are an important aspect of any analytical technique. For electroanalysis with BiFE, interferences involve adsorption of surface-active compounds, formation of intermetallic compounds, poor resolution between adjacent peaks and mechanical degradation of the bismuth film. Out of these, interference caused by different surface-active compounds is the most important, and is due to fouling of the electrode surface, lowering sensitivity and erratic behavior of the electrode. In stripping analysis, BiFE are as susceptible as MFEs to the presence of surface-active compounds. An elegant solution to this problem that was explored in this thesis involved covering the surface of the bismuth film with a permselective Nafion membrane. Since Nafion is negatively charged, it rejects the surface-active compounds which are negative charged. Besides avoiding interference, Nafion polymeric film on BiFE imparts mechanical resistance to the electrode and enhances the stripping peaks, leading to an increase in sensitivity.

BiFEs have shown some unique advantages with respect to overlapping peaks since they offer a better separation between the Cd and Pb peaks than MFEs. In cathodic voltammetnc measurements, the reduction of dissolved oxygen had been a common interference and thus deoxygenation of the solution by purging with nitrogen or helium was necessary. The advantage of using BiFEs is that it is less sensitive to the presence of oxygen than MFEs, and therefore the time-consuming deoxygenation step becomes insignificant.

CHAPTER 3

SENSOR OPTIMIZATION

AND

PERFORMANCE CHARACTERISTICS

3.1 Sensor Optimization

3.1.1 Electrode Materials Optimization

The selection of materials for the working electrode is critical to obtain the reliable monitoring of environmental pollutants. Therefore, various electrode materials were examined and compared for their voltammetric signal, background current and overall signal-to-background characteristics. These materials included gold, carbon paste, screen-printed carbon, a Goodfellow carbon fiber, glassy-carbon and a Alfa Aesar™ carbon fiber. The Alfa Aesar™ carbon fiber offered the most attractive performance in terms of signal-to-noise characteristics and was selected for all subsequent work.

3.1.2 Voltammetric Waveform Optimization

Various voltammetric waveforms can be used to produce the current-potential voltammetric profiles. These differ mainly in the excitation waveform and, hence, yield different signal-to-noise characteristics. The responses of the carbon fiber based sensor for heavy metals using linear sweep voltammetry, differential pulse voltammetry and square-wave voltammetry were compared. The square-wave voltammetric profiles yielded the most favorable performance characteristics with detection limits down to 50 ppb. Square-wave scanning rate also can be performed very rapidly (over a 60-second period), thus allowing 60 measurement per hour. No improvements were observed when the square-scan was preceded by a delay time indicating no accumulation of metals onto the carbon fibers working electrode. Most favorable conditions were observed using a square-wave amplitude of 25 mV, a frequency of 15 Hz and a step potential of 4 mV.

Further improvements were obtained using the baseline-subtracted square-wave operation. This effective computer-controlled background-subtraction protocol was developed to correct for high baseline contributions surrounding the metal reduction signal, and allows

convenient quantitation of ppb concentration levels. For example, Figure 3.1(A) and (B) display the square-wave voltammetric for a 500 ppb metal solution. In Figure 3.1(A), the square-wave voltammogram for metal "a" and the background "b" signal without metal is recorded in the conventional mode, and in Figure 3.1(B), it is in the subtractive mode. Such large baseline contribution obscures the signal and prevents convenient quantitation of parts per billion (ppb) concentrations of metal. In contrast, the subtractive mode effectively compensates the background signal and leads to a well-defined response signal, with three reduction peaks of three metals.

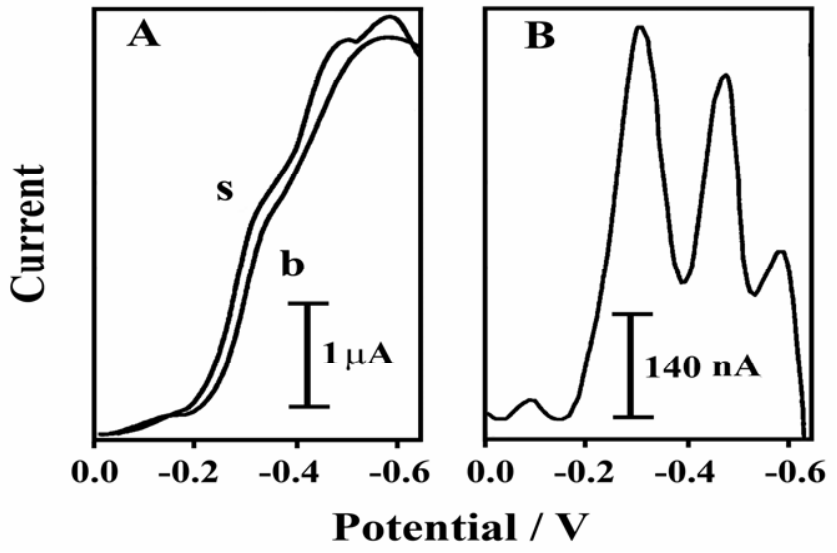

Figure 3.1 Response of the remote *in-situ* carbon-fiber probe: (A) Square-wave voltammograms for the three metals solution of 0.5 ppm each (s) along with the corresponding background (b). (B) Background-corrected voltammogram.

Dramatic improvements, associated with the baseline correction approach, are illustrated also in Figure 3.2 for analogous remote measurements of 0.25 ppm metal. Once again, the effective compensation of the rising background allows convenient monitoring of low parts per billion of metal levels (curves b vs. c). An extremely low detection limit of around 50 ppb can, thus, be estimated.

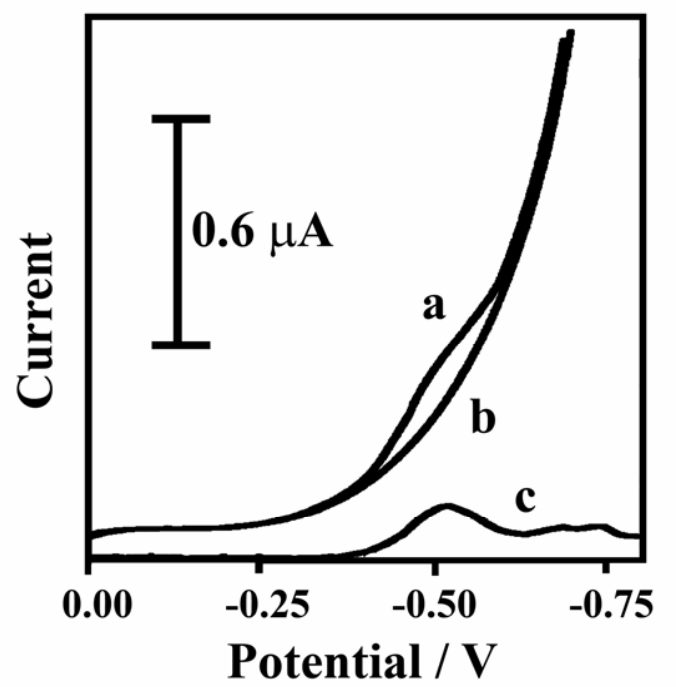

Figure 3.2 Response of the remote *in-situ* carbon-fiber probe to the solution of 0.25 ppm metal solution (a) along with the corresponding background (b) and the background-corrected voltammogram (c)

3.2 Performance Characteristics and Detection Limits

Figures 3.3 and 3.4 depict voltammograms generated with varying concentrations of some heavy metals in laboratory water, respectively. The maximum signal for both metals is directly superimposed onto the oxygen background peak. These results demonstrate small changes in current response relative to large change in metals concentration and results in significantly higher detection limits for these metals.

To improve detection limits and specificity for the metals, one option would be to remove oxygen through purging with an inert gas (e.g. nitrogen or helium) or with the addition of a reducing agent (e.g., sodium dithionite) to the test solution. Figure 3.5 shows the drastic decrease in the oxygen background signal in the voltammogram by simple purging the sample with nitrogen. Based on these results, we anticipate detection limits for the metals on bismuth film electrodes to approach those of the mercury film electrodes.

The analytical utility of the submersible probe is based on the linear dependence between the peak current and the metal concentration. Such dependence was examined for solutions of increasing concentrations over the 100 to 1,000 ppb range (Figure 3.6). Despite these extremely low concentrations, the voltammetric sensor offers convenient detection, particularly when used in the subtractive mode. The peaks are proportional to the metal concentration. The resulting calibration plots (also shown on the right) are linear with a correlation coefficient of 0.979.

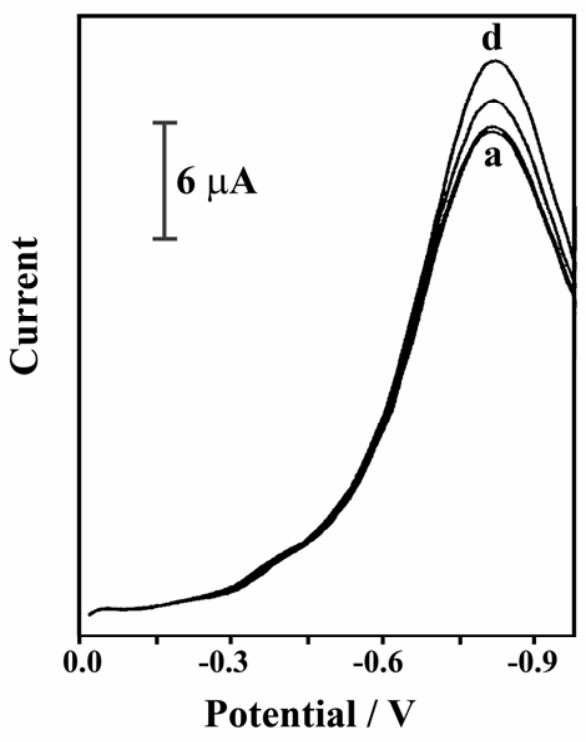

Figure 3.3 Voltammetric response of the remote carbon-fiber submersible probe for 5, 10 and 15 ppm (b-d) metal solution along with corresponding background (a).

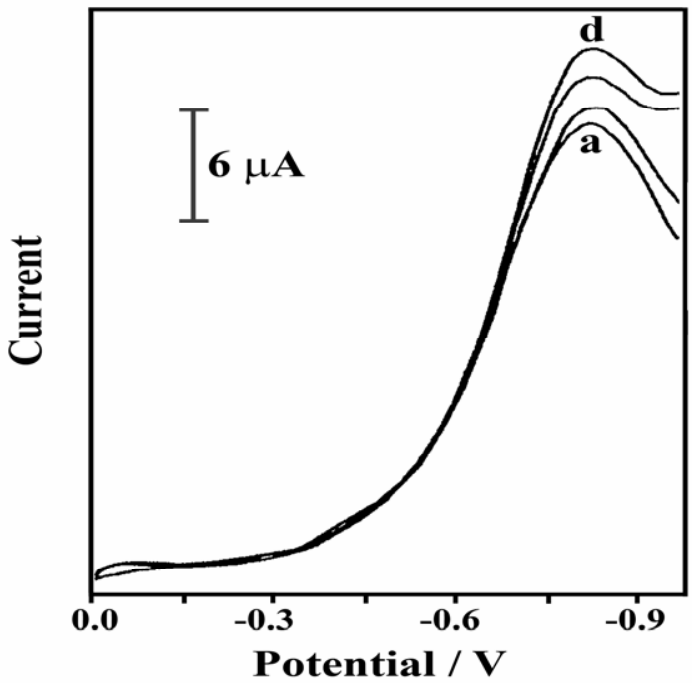

Figure 3.4 Voltammetric response of the remote carbon-fiber submersible probe for 5, 25 and 50 ppm (b-d) metal solution with corresponding background (a).

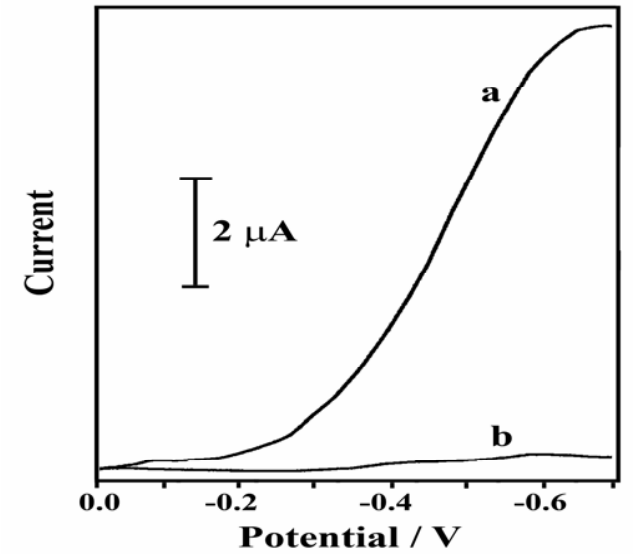

Figure 3.5 Voltammetric response of the remote carbon-fiber submersible probe comparing oxygenated (a) and deoxygenated (b).

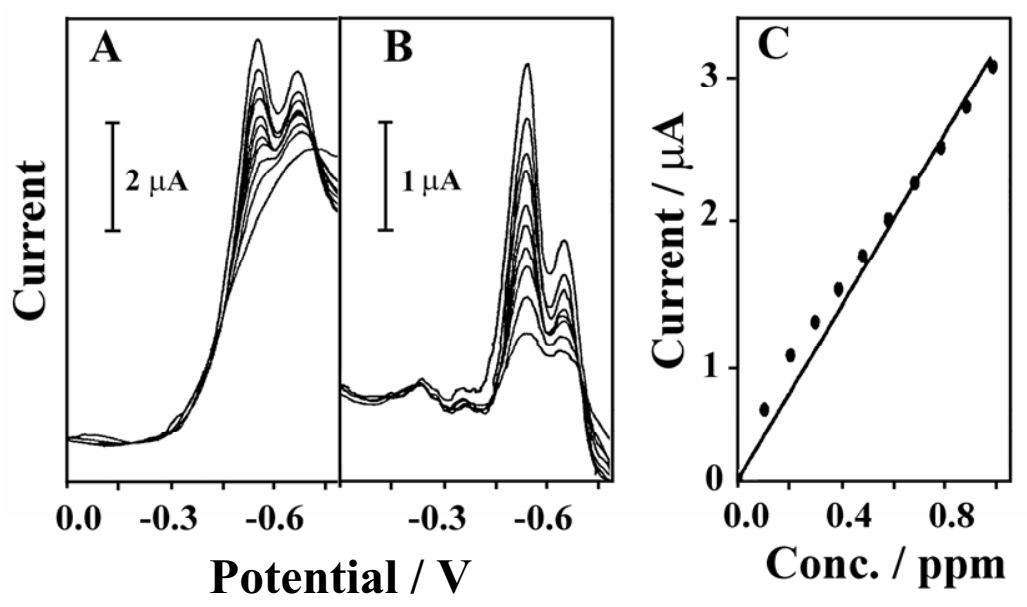

Figure 3.6 Calibration plot (C) obtained with the remote carbon-fiber submersible probe for the increasing levels of 0.1-1.0 ppm metal solution recording with the conventional (A) and subtractive (B) voltammetric mode.

3.3 Stability and Carry Over

The stability of the response has an important bearing on the practical utility of the probe. The carbon-fiber transducer behaved normally over prolonged operations with no apparent surface passivation. The stability was evaluated using a series of 60 repetitive measurements of 2 ppm metal solution over a prolonged (4 hour) period. As indicated from Figure 3.7, such series yielded a highly stable response (for both conventional and subtracted operations, left and right, respectively), with a relative standard deviation of 1.04%. No apparent loss in sensitivity was observed for analogous measurements of 7 ppm metal solution over a 4-hour period using an untreated river water sample. This series of 60 successive runs yielded a relative standard deviation of 1.2%. This indicates that constituents of the natural water sample do not foul the surface, in the short term.

The device responds favorably and rapidly to sudden changes in the metal concentrations level, with no apparent carry over. The lack of memory effect was assessed upon switching between 3-ppm, 10-ppm, and 3-ppm metal solutions. The response decays sharply upon placement in the 3-ppm metal solutions, and rises sharply upon returning to the 10-ppm solution. Such dynamic properties indicate great potential for providing alarm and warning capabilities. Monitoring frequencies as high as 2 runs per minutes are attained in connection to the fast square-wave scanning.

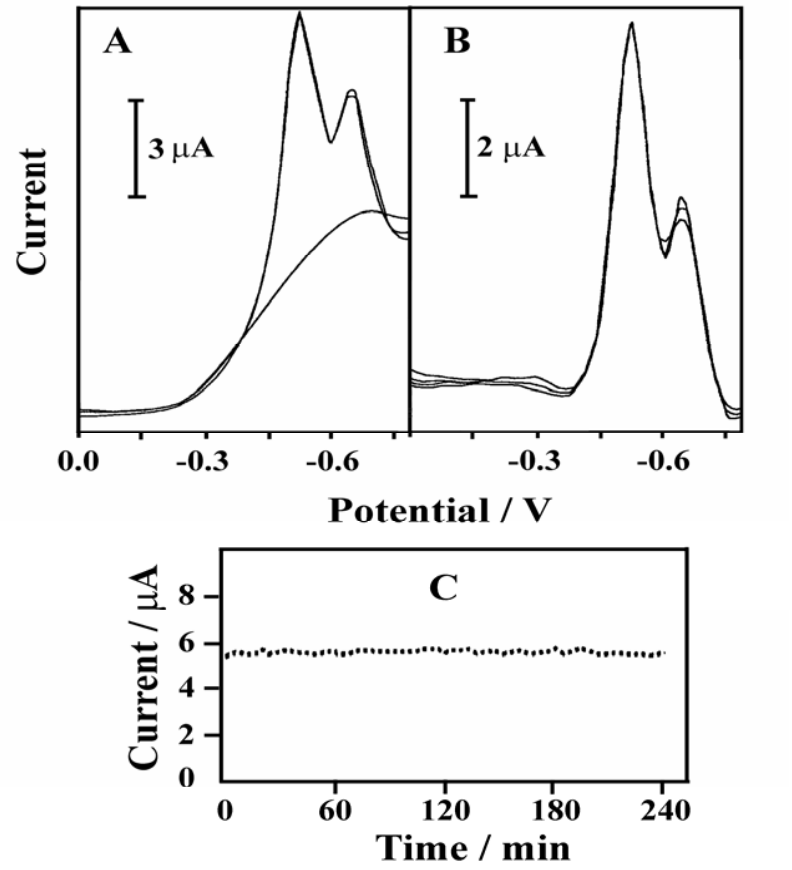

Figure 3.7 Response of the remote carbon-fiber submersible probe to the 15 repetitive measurements of 2 ppm metal solution using conventional (A) and subtractive (B) voltammetric mode along with the resulting stability plot (C).

The above experiments illustrate that trace (ppb and ppm) levels of heavy metal concentration can be monitored continuously and rapidly at large sample-instrument distances by coupling subtractive square wave voltammetric method with a newly designed compact remote probe. The new monitoring capability is characterized with high sensitivity, speed, simplicity, reproducibility and stability for heavy metals. The device responds rapidly and reversibly to sudden changes in the levels of the metals. However, the measurement of some metals will require the removal of oxygen from the samples to provide selectivity and sensitivity.

3.4 NPRU Sensor Performance

Major attention was given to the optimization of variables of the square-wave waveform (including the frequency, potential step, and amplitude) essential for attaining high speed without sacrificing the sensitivity. A computerized baseline subtraction was developed to compensate the oxygen background contribution and hence to facilitate the detection of low ppb levels of metal (see Figure 3.8). The optimal device offered high sensitivity and selectivity, fast response, excellent precision/stability, and absence of matrix effect, and hence meets the demands for underwater sensing of metal. A typical stability data involving 30 repetitive runs of 3 ppm metal solution are displayed in Figure 3.9. As indicated from Figure 3.9, such series yielded a highly stable response with a relative standard deviation of 2.19%.

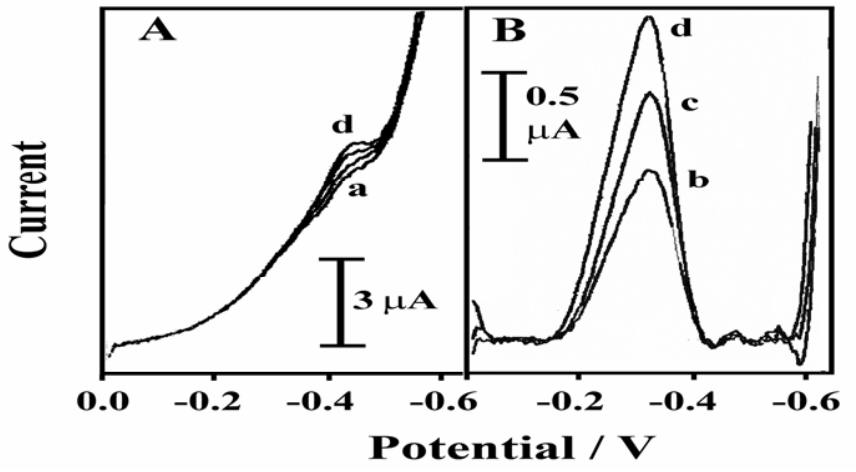

Figure 3.8 Square-wave voltammograms for background (A, a) with the increasing levels of metal in 20 ppb steps (b-d) without (A) and with (B) background correction.

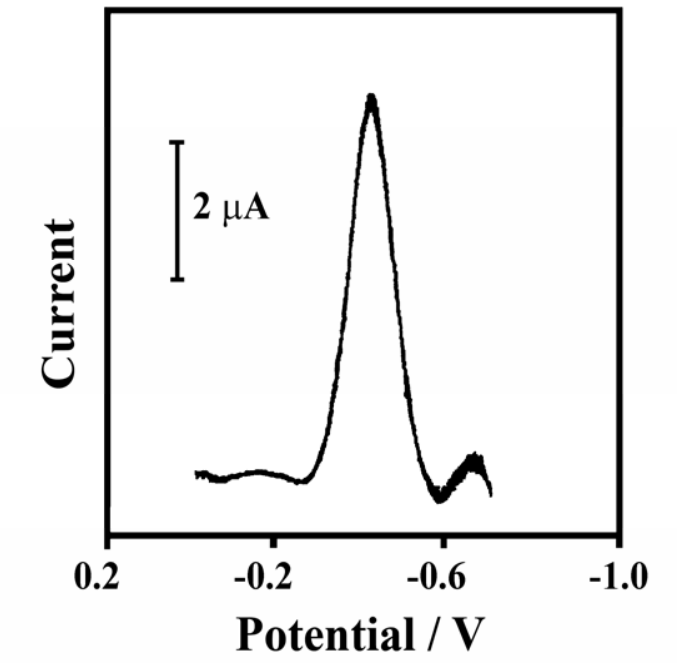

Figure 3.9 Stability of 30 repetitive measurements for 3 ppm of metal solution at submersible carbon fiber based electrode assembly.

3.5 Concluding Remarks

The examples described in this chapter illustrate the power and versatility of modern electrochemical devices for detecting metals. These developments would allow field testing for heavy metals to be performed more rapidly, sensitively, inexpensively and reliably, should greatly facilitate the realization of *in-situ* detection of heavy metals. The resulting *real-time* monitoring capability should thus have a major impact on the way that metals are monitored and upon the prevention of environmental pollution.

CHAPTER 4

SENSOR TESTING AND VALIDATION

4.1 Introduction

An assessment of the metal content in various environmental matrices is of great significance since they are a threat to the environment and human health. What makes them different from other pollutants is that they are not biodegradable and thus are retained indefinitely in the ecological systems and in the food chain, and eventually getting accumulated into the vital organs of humans. The most toxic heavy metals are lead, mercury, cadmium and thallium. Others like zinc, selenium and copper are essential biological elements. Although all of them have the potential to be toxic above a certain threshold concentration, they may also pose potential danger to humans at low levels should they be bioaccumulated into organisms residing at the lower food chain [14].

Such toxicity effects of heavy metals on the environment and humans demand a sensitive and reliable detection system. Electrochemical technique via stripping analysis is an interesting technique for this application. Such technique allows simultaneous measurement of different metals, trace level measurement making use of a preconcentration step, and while taking advantage of cheaper, versatile, reliable and portable instrumentation. One of the things that stripping analysis depends on for its success is the working electrode. While conventional electrochemical cells utilized bulky electrodes making decentralized measurements inconvenient, improvements have been made for their replacement with miniaturized and planar electrodes that could be used as disposable electrode. It is also important to note that traditional electrodes were mainly mercury based, which poses a problem due its toxicity effects. Thus alternate electrodes such as carbon (glassy carbon, carbon paste, carbon fiber and screen printed) and metal (amalgam, bismuth, gold, iridium and silver) have thus been developed. Such mercury free electrodes are highly anticipated, and thus there is ongoing research into optimizing these electrodes to match their analytical performance to the mercury based electrodes. Bismuth based electrodes have been extensively studied for measuring heavy metals, and their stripping performance is similar to that of mercury electrodes, while eliminating toxicity problems. Since

bismuth is a relatively new electrode material, it is vital to understand the factors that influence its favorable stripping performance.

4.2 Bismuth Film Sensor for Adsorptive Stripping Voltammetric Measurements of Ultratrace Beryllium

4.2.1 Introduction

Beryllium is recognized as the most toxic element without radioactivity [15] and its poisoning occurs primarily by inhalation of dust and gas. Beryllium is toxic both as a carcinogen and agent that causes the chronic beryllium disease (CBD). Environmental Protection Agency (EPA) has set a maximum allowable amount of 0.004 mg l^{-1} beryllium in drinking water. Despite the health hazards of beryllium, it is widely used by the aerospace, nuclear and defense industries. Such widespread industrial use reflects the unique properties of beryllium, including its low density, high stiffness and high melting point [16,17]. To protect workers from beryllium-related diseases it is essential to detect and monitor for the presence of trace amounts of beryllium.

Several methods for the determination of beryllium have been reported, including inductively coupled plasma-mass spectrometry [18] electrothermal atomic absorption spectroscopy [19] gas chromatography [20] or liquid chromatography with fluorescence detection [21]. In contrast to these sophisticated and expensive protocols, electrochemical (stripping) procedures offer great promise for obtaining ultra high sensitivity while meeting the portability, speed, cost and low-power demands of field detection of trace beryllium [22]. Since beryllium cannot be readily electrodeposited it has been measured at trace levels using adsorptive stripping voltammetry (AdSV), based on the interacial accumulation and voltammetric determination of its complexes [23,24]. Two complexing agents, thorin [23] and beryllon III [24] have been particularly useful for such AdSV measurements of beryllium. A limitation of these AdSV procedures, particularly for field screening applications, is their reliance on a mercury drop detector. Reliable AdSV sensors, based on preplated film electrodes should particularly benefit field measurements of beryllium.

Although these mercury electrodes offer an attractive AdSV performance, new alternative electrode materials with a similar performance are urgently desired for addressing growing concerns regarding the toxicity, handling, and disposal of mercury. The development of a reliable 'non-mercury' beryllium sensor should particularly benefit on-site (and especially in situ) measurements of beryllium. Bismuth electrodes have attracted considerable attention as an attractive alternative to mercury electrodes used in stripping analysis [25,26]. Most early stripping applications of bismuth film electrodes (BiFEs) focused on measurements of electrodeposited heavy metals. The suitability of BiFEs for AdSV has been demonstrated recently in connection to trace measurements of nickel [27], cobalt [28], uranium [29], chromium [30], molybdenum [31] or vanadium [32].

The aim of this work was to optimize and characterize an effective adsorptive-stripping voltammetric protocol for trace measurements of beryllium at a preplated bismuth film electrode (BiFE), based on the adsorptive accumulation of the arsenazo-III/Be complex. The arsenazo-III complexing agent dye has been shown useful for absorption spectrophotometric measurements of trace beryllium [33]. This dye is commonly used as an indicator for complexometric titrations of alkali earth metals [34].

It has been reported on the measurement of beryllium at mercury electrode [35]. However, there are no early reports on the voltammetric detection of arsenazo-III or related electrochemical measurements of its metal complexes on BiFE. As will be illustrated below, the adsorptive accumulation of Be–arsenazo-III complex onto the BiFE results in a highly sensitive and reproducible AdSV protocol for measuring trace levels of beryllium.

4.2.2 Materials and Methods

Ammonium chloride was obtained from Mallinckrodt Inc. Sodium acetate and stock solutions of beryllium (1000 mg l^{-1}) were purchased from Aldrich. Beryllium solutions were diluted daily as required. The 0.5 mM stock solutions of arsenazo-III (Sigma–Aldrich) were prepared by dissolving the appropriate amount of the ligand in nanopure water. The seawater sample, collected from Cha-Am Bay, Petchburi, was used without any pretreatment. The water

was adjusted to pH 9.7 with ammonium buffer (4:1 volume ratio of water:buffer) before the measurement. All experiments were carried out at room temperature.

Square-wave AdSV measurements were conducted using an Electrochemical Analyzer 621A (CH Instruments, Austin, TX) connected to a personal computer. The 10 ml electrochemical cell assembly (BAS, Model VC-2) consisted of bismuth-coated carbon-fiber working electrode, an Ag/AgCl (3 M KCl) reference electrode (Model CHI111, CH Instruments), and a platinum wire counter electrode. The carbon fibers (Alfa Aesar 10451, Johnson Matthey Co.,Ward Hill, MA) were pretreated first by a 12 h immersion in ethanol. Subsequently, the fibers were dipped into a 6 M nitric acid solution for 30 s, and rinsed with distilled water. This was followed by another wash with acetone, a thorough rinse with distilled water, and an air dry. A bundle of ca. 20 fibers was then glued to a copper wire with a silver conductive paint (SPI Supplies Inc., West Chester, PA). The bundle of carbon fibers was then inserted into a 100 μl plastic pipette tip, exposing a 3 mm length of the fibers at the narrow end of the tip. An internal copper wire provided the electrical contact. The narrow end of the pipette tip was then sealed with a nail polish. All glassware were soaked in 1 M nitric acid and rinsed several times with deionized water prior to use.

The bismuth-coated carbon-fiber electrode was prepared by a 15 min electrodeposition of bismuth at -0.8 V from a 0.1 M acetate buffer (pH 4.5) solution containing 20 mg l^{-1} bismuth. A similar film preparation (but in the presence of 100 mg l^{-1} bismuth) was employed in connection to the screen-printed carbon substrates.

The ammonium buffer (0.05 M, pH 9.7) supporting electrolyte solution contained 5 μM of the arsenazo-III complexing agent. The solution was first purged with nitrogen for 5 min to remove the dissolved oxygen. The electrode was poised at a potential of 0.0 V for 90 s for adsorbing the Be-ligand complex. The stirring was then stopped and after 15 s the square-wave voltammogram (SWV) was recorded over the 0.0 to -1.0 V range (using a step potential of 4 mV, amplitude of 25 mV and a frequency of 25 Hz). A 15 s ‘cleaning’ period (with stirring at -1.0 V) was employed between successive runs.

4.2.3 Results and Discussion

A comparison of a typical linear-sweep (A), square-wave (B) and differential pulse (C) AdSV signals at the bismuth-film electrode for 100 μg l^{-1} beryllium in the presence of 5 μM arsenazo-III recorded following a 90 s accumulation in an ammonium buffer medium (pH 9.7) is illustrated in Figure 4.1. The square-wave (B) and differential pulse (C) stripping modes resulted in well-defined beryllium signals of different sizes (E_p = -0.43 V for both (A) and (B)). A larger background slope and unwell-defined beryllium signal were observed using the linear scan mode. Both differential pulse and square-wave techniques corrected for the charging-current background contribution and yielded better signal-to-background characteristics.

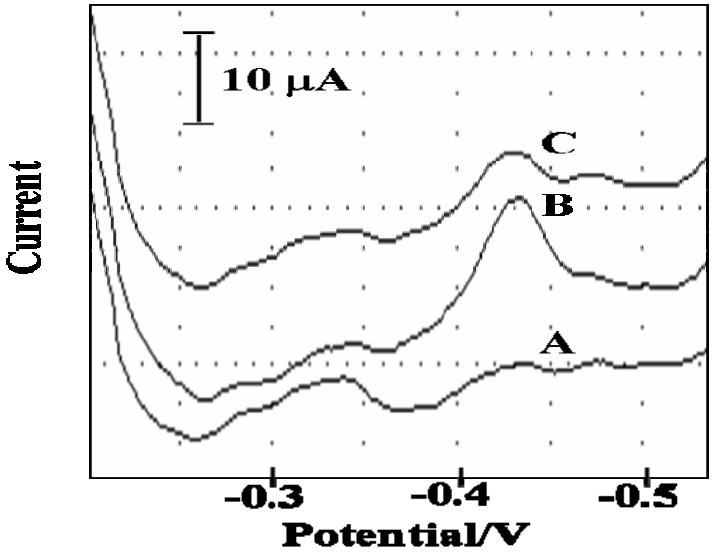

Figure 4.1 Comparison of different stripping modes: linear scan voltammetry (A); square-wave voltammetry (B) and differential pulse voltammetry; (C). Conditions: bismuth-coated carbon-fiber electrode; supporting electrolyte, 0.05 M ammonium buffer (pH 9.7) containing 100 μg l^{-1} beryllium and 5 μM arsenazo-III; nitrogen purging time, 5 min; pre-conditioning potential, -1.0 V; pre-conditioning time, 15 s; accumulation potential, 0.0 V; accumulation time, 90 s; quiet potential, 0 V; quiet time, 15 s; scanning potential window, 0.0 to -1.0 V. Scan rate, 0.1 V/s (A); amplitude, 0.025 V (B); and 0.05 V (C) potential step, 0.004 V (B and C); pulse width, 0.05 s (C); pulse period, 0.2 s (C); frequency, 25 Hz (B).

Square wave voltammetry was selected for all subsequent work due to its distinct speed and sensitivity advantages.

The influence of the pH on the Be AdSV peak current was examined over the 6.0–11.0 range (Figure 4.2A). The response increases slowly between pH 6.0 and 8.3, and very rapidly between pH 8.3 and 9.7. A sharp decrease of the signal is observed at higher pH. Such profile reflects the effect of the pH upon the complexation, adsorption and redox processes. The peak potential of the Be–arsenazo-III complex shifted gradually (from -0.43 to -0.48 V) upon increasing the pH from 6.0 to 9.7 (not shown). All subsequent work involved a solution of pH 9.7.

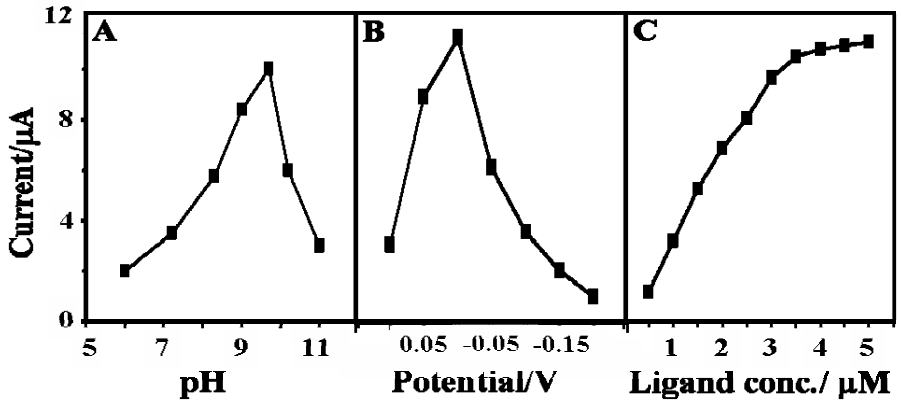

Figure 4.2 Effect of the pH (A), accumulation potential (B) and arsenazo-III concentration (C) upon the square-wave adsorptive stripping response of 100 µg l^{-1} beryllium. Other conditions, as in Figure 4.1B.

The influence of the accumulation potential on the Be stripping peak current was examined over the range of +0.10 to -0.20 V (Figure 2B). The peak rises rapidly between +0.10 and +0.05, and then more slowly up to 0.0 V. The response decreases sharply between 0.0 and -0.05 V and more slowly at more negative potentials. An accumulation potential of 0.0 V led to the highest degree of adsorption and was thus used for the further measurements. The effect of the arsenazo-III concentration upon the Be peak current is shown in Figure 4.2C. As expected for such adsorptive accumulation processes. The response increases rapidly up to around 3 µM arsenazo-III, more slowly up to 4 µM, and levels off thereafter.

The influence of the accumulation time upon the Be–arsenazo-III stripping peak current increases linearly with the accumulation time up to 60 s, then more slowly up to 120 s and starts to level off for longer periods (not shown). The resulting current–time dependence thus displays a curvature characteristic to AdSV measurements, reflecting saturation of the surface at longer accumulation periods.

The coupling of the effective adsorptive accumulation of the Be–arsenazo-III complex at the BiFE with the fast square-wave voltammetric scan results in a highly sensitive beryllium response. Figure 4.3 displays stripping voltammograms for increasing concentrations of beryllium in 10 μg l^{-1} steps following a 90 s preconcentration time and using the optimised parameters. Such short accumulation results in well defined peaks for these low beryllium concentrations. As expected for adsorptive accumulation processes, the response increases linearly with the beryllium concentration up to 50 μg l^{-1}, then more slowly above 60 μg l^{-1}. Although a curvature, characteristic of adsorption processes, is observed above 60 μg l^{-1}, no leveling off is indicated even at high beryllium levels. (see inset for the resulting calibration plot; slope of the linear portion, 80 nA l μg^{-1}; correlation coefficient, 0.998). While the data of Figure 4.3 (curve a) indicate a detection limit of around 3 μg l^{-1} (based on the signal-to-noise characteristics; S/N = 3), a substantially lower detection limit can be obtained in connection to longer accumulation times and a background subtraction operation. Such background-subtraction AdSV response for a 2 μg l^{-1} beryllium solution following a 10 min preconcentration has been investigated (not shown). A well defined response, with favorable signal-to-noise characteristics, is observed, indicating a detection limit of around 0.25 μg l^{-1} (27.8 nM) beryllium. Such detection limit meets the requirements of monitoring of contaminated sites and of most water quality applications.

The new electrochemical detection is suitable for measuring beryllium in natural water systems. The determination of beryllium in such water systems is indicative of the metal uptake through dust or gas sources [16]. Figure 4.4 demonstrates the suitability of the system for monitoring low levels of beryllium in an untreated seawater sample. Well defined peaks (Ep = -0.41 V) are observed for increasing beryllium concentrations in 20 μg l^{-1} steps (a–g). The peak

height increases linearly with the beryllium concentration up to ca. 100 μg l^{-1} and then more slowly (slope of the initial linear portion, 50 nA l μg^{-1}; correlation coefficient, 0.995, not shown). The smaller slope, compared to that observed in the synthetic sample (of Figure 4.3), appears to reflect matrix effects, including coexisting calcium and magnesium ions and surface-active macromolecules. The low background response (unspiked sample; dotted line) indicates the absence of potential interferences.

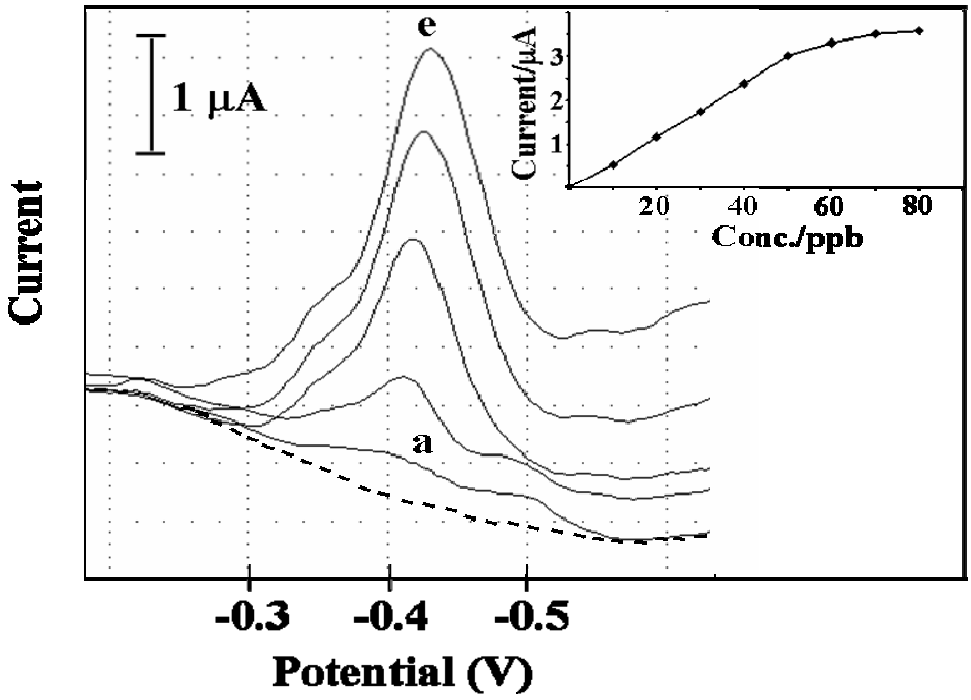

Figure 4.3 Adsorptive stripping square wave voltammograms for increasing levels of beryllium in 10 μg l^{-1} steps (curves a–e) along with the background response (dotted line). Also shown (inset) is the resulting calibration plot. Other conditions, as in Figure 4.1B.

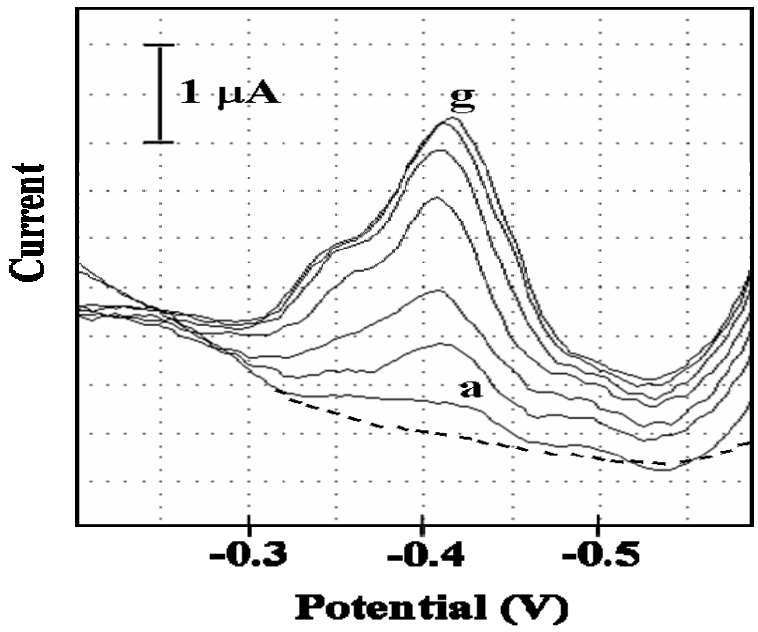

Figure 4.4 Adsorptive stripping square-wave voltammograms for a seawater sample spiked with increasing levels of beryllium in 20 μg l^{-1} steps (a–g) along with the response for the unspiked sample (dotted line). The water sample was adjusted to pH 9.7 with ammonium buffer (4:1 volume ratio of water:buffer) before the measurement. Other conditions, as in Figure 4.1B.

The long-term stability of 40 repetitive voltammograms recorded, for a seawater sample containing 100 μg l^{-1} beryllium, at 3 min intervals over a prolonged (120 min) period is illustrated (not shown). A highly stable response, with a mean peak current of 14.6 μA and a relative standard deviation of 3.9%, is observed for these 40 runs. Such stability indicates no apparent surface fouling by surface-active substances of the seawater matrix.

4.2.4 Conclusions

We have demonstrated a highly sensitive cathodic stripping protocol for detecting trace beryllium based on the adsorptive accumulation of the Be-arsenazo-III complex at a bismuth film electrode. Because of the toxicity, handling, and disposal of mercury, the new procedure obviates the need for the large mercury-drop electrode, mercury film electrode and related mercury

disposal issues. The same pre-plated bismuth film could thus be employed for multiple measurements of beryllium. The new electrochemical protocol offers great promise for meeting the portability, sensitivity, speed, cost and low-power demands of field detection beryllium. Future efforts in this direction will focus on developing single-use screen printed electrode (SPE) for on-site measurements of beryllium.

4.2.5 Acknowledgements

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Output จากโครงการวิจัยที่ได้รับทุนจาก สกว.

1. ผลงานตีพิมพ์ในวารสารวิชาการนานาชาติ

1.1 Thongngamdee, S. and Nacapricha, D. "Bismuth Coated Carbon Fiber Microelectrodes for Square Wave Adsorptive Stripping Voltammetric Measurements of Trace Beryllium" Talanta, Submitted.

2. การนำผลงานวิจัยไปใช้ประโยชน์

2.1 ผลิตบัณฑิตและนักวิจัยในระดับต่าง ๆ

- ระดับปริญญาเอก สาขาวิชาเคมี มหาวิทยาลัยมหิดล จำนวน 1 คน ได้แก่ นางศศิธร มั่นเจริญ

- ระดับปริญญาโท สาขาวิชาวิทยาศาสตรศึกษา มหาวิทยาลัยราชภัฏนครปฐม จำนวน 1 คนได้แก่ นายณัฏฐสิศฏ์ เลาหเรณู

- ระดับปริญญาตรี สาขาเคมี มหาวิทยาลัยราชภัฏนครปฐม จำนวน 5 คน ได้แก่ นางสาวณัฐวิกา ดาวเรือง นางสาวศดานันท์ อัสสาไพร นางสาวอภิญญา แฉล้มนงนุช นางสาวอรอนงค์ แคนจา และ นางสาวชลธิชา พงษ์สุทัศน์

2.2 นำความรู้ที่ได้จากการวิจัยไปให้คำปรึกษาในงานวิจัยต่าง ๆ

- เป็นอาจารย์ที่ปรึกษาวิทยานิพนธ์ นักศึกษาระดับปริญญาเอก สาขาวิชาเคมี (หลักสูตรนานาชาติ) มหาวิทยาลัยมหิดล ได้แก่ นางศศิธร มั่นเจริญ

2.3 นำความรู้ที่ได้จากการวิจัยไปประยุกต์ใช้ในการเรียนการสอนในรายวิชาต่าง ๆ

- รายวิชา หัวข้อพิเศษ (เซนเซอร์) สำหรับนักศึกษาระดับปริญญาเอกและปริญญาโท สาขาวิชาเคมี มหาวิทยาลัยมหิดล

- รายวิชา เคมีวิเคราะห์ขั้นสูง สำหรับนักศึกษาระดับปริญญาโท สาขาวิชาวิทยาศาสตรศึกษา มหาวิทยาลัยราชภัฏนครปฐม

- รายวิชาเคมีวิเคราะห์ สำหรับนักศึกษาระดับปริญญาตรี สาขาวิชาเคมี มหาวิทยาลัยราชภัฏนครปฐม

4. ผลงานตีพิมพ์ในวารสารการประชุมวิชาการระดับนานาชาติ (Proceedings)

4.1 Thongngamdee, S. "Bismuth Film Electrode for Adsorptive Stripping Voltammetric Measurements of Ultratrace Beryllium" **Pure and Applied Chemistry International Conference (PACCON) Proceedings 2009**, 58.

4.2 Ruengsri, S.; Sripanlom, T.; **Thongngamdee, S.** "Effect of carbonizing conditions on electrical resistivity of white popinac, bamboo, coconut shell and eucalyptus charcoal" **Pure and Applied Chemistry International Conference (PACCON) Proceedings 2010**, 467.

5. ผลงานตีพิมพ์ในวารสารวิชาการระดับชาติ

3.1 Thongngamdee, S.; Ruengsri, S.; Sripanlom, T. "Bismuth-modified Electrodes from Eucalyptus Charcoal Powders for Anodic Stripping Voltammetric Determination of Lead and Cadmium" **NPRU Journal of Science and Technology 2010,** *3(1)***,** 1.

3.2 Saowongchan, K.; Sripanlom, T.; Ruengsri, S.; **Thongngamdee, S.** "Frabrication of Graphite Electrodes from Eucalyptus for Trace Analysis of Lead" **NPRU Journal of Science and Technology 2010,** *3(1)*, 13.

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5. การเสนอผลงานปากเปล่า (Oral presentations)

5.1 Thongngamdee, S. "Bismuth-modified Electrodes from Eucalyptus Charcoal Powders for Anodic Stripping Voltammetric Determination of Lead and Cadmium" The 2nd Nakhon Pathom Rajabhat University National Conference, Nakhon Pathom Rajabhat University, Nakhon Pathom, THAILAND (Jun. 2010).

6. การเสนอผลงานภาคโปสเตอร์ (Poster presentations)

6.1 Thongngamdee, S. "Adsorptive Stripping Voltammetric Measurements of Trace Metal at Bismuth Film Electrode" The First Nakhon Pathom Rajabhat University Academic Conference, Nakhon Pathom Rajabhat University, Nakhon Pathom, THAILAND (Oct. 2008).

6.2 Thongngamdee, S. "Bismuth Film Electrode for Adsorptive Stripping Voltammetric Measurements of Ultratrace Beryllium" Pure and Applied Chemistry International Conference 2009 (PACCON 2009) Naresuan University, Phitsanulok, THAILAND (Jan. 2009).

6.3 Thongngamdee, S. "Adsorptive Stripping Voltammetric Measurements on Bismuth Film Electrode for Determination of Ultratrace Beryllium" The Thailand Research Fund (TRF) Academic Conference, Holiday Inn Resort Regent Beach Cha-Am, Cha Am, Phetchaburi, THAILAND (Oct. 2009).

6.4 Ruengsri, S.; Sripanlom, T.; **Thongngamdee, S.** "Effect of Carbonizing Conditions on Electrical Resistivity of White Popinac, Bamboo, Coconut Shell and Eucalyptus Charcoal" Pure and Applied Chemistry International Conference (PACCON) 2010, Ubon Ratchathani University, Ubon Ratchathani, THAILAND (Jan. 2010).

6.5 Muncharoen, S.; **Thongngamdee, S.**; Wilairat, P.; Nacapricha, D. "Simplex Optimization for Simultaneous Analysis of Cobalt and Nickel by Square Wave Voltammetry on Bismuth Film Electrode" Pure and Applied Chemistry International Conference (PACCON) 2010, Ubon Ratchathani University, Ubon Ratchathani, THAILAND (Jan. 2010).

6.6 Thongngamdee, S.; Chidthong, R.; Muncharoen, S. "Electrochemical Flow System for Simultaneous Real-Time Assay of Zinc Cadmium and Lead by Square Wave Anodic Stripping Voltammetry Using Bismuth Film Electrodes" 16th International Conference on Flow Injection Analysis (16th ICFIA) 2010, Pattaya, Chonburi, THAILAND (Apr. 2010).

6.7 Thongngamdee, S.; Chidthong, R. "Bismuth Coated Carbon Fiber Microelectrodes for Square Wave Adsorptive Stripping Voltammetric Measurements of Trace Beryllium" 16th International Conference on Flow Injection Analysis (16th ICFIA) 2010, Pattaya, Chonburi, THAILAND (Apr. 2010).

6.8 Muncharoen, S.; Mantim, T.; **Thongngamdee, S.**; Wilairat, P.; Nacapricha, D. "Development of a Flow-Voltammetric Stripping Measurement of Cobalt and Nickel Using Bismuth Film Electrode" 16th International Conference on Flow Injection Analysis (16th ICFIA) 2010, Pattaya, Chonburi, THAILAND (Apr. 20100).

7. หนังสือและเอกสารประกอบการสอน

7.1 คู่มือปฏิบัติการเคมี โปรแกรมวิชาเคมี คณะวิทยาศาสตร์และเทคโนโลยี มหาวิทยาลัยราชภัฏนครปฐม 2551

7.2 คู่มือปฏิบัติการเคมีวิเคราะห์ขั้นสูง โปรแกรมวิชาเคมี คณะวิทยาศาสตร์และเทคโนโลยี มหาวิทยาลัยราชภัฏนครปฐม 2552

APPENDIX

Submitted Menuscript

Thongngamdee, S. and Nacapricha, D. "Bismuth Coated Carbon Fiber Microelectrodes for Square Wave Adsorptive Stripping Voltammetric Measurements of Trace Beryllium" *Talanta*, Submitted.

Bismuth Coated Carbon Fiber Microelectrodes for Square Wave Adsorptive Stripping Voltammetric Measurements of Trace Beryllium

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Abstract:

A sensitive adsorptive stripping voltammetric protocol for measuring trace beryllium, in which the preconcentration is achieved by adsorption of the beryllium–arsenazo-III complex at a preplated bismuth-coated carbon fiber electrode, is described. Optimal conditions were found to be a 0.05 M ammonium buffer (pH 9.7) containing 10 μM arsenazo-III, an accumulation potential of 0.0 V (versus Ag/AgCl). The new procedure obviates the need for toxic mercury film electrodes used in early stripping protocols for beryllium. A linear response is observed over the 10–50 μg l^{-1} concentration range (60 s accumulation), along with a detection limit of 0.25 μg l^{-1} beryllium. A 15-s electrochemical cleaning enables the same bismuth film to be used for a prolonged operation. High stability is thus indicated from the reproducible response of a 100 μg l^{-1} beryllium solution (n = 40; RSD = 3.9%) over a 2-h operation. Applicability to a ground water sample is illustrated. The attractive behavior of the new sensor holds great promise for on-site environmental and industrial monitoring of beryllium. Preliminary data in this direction using bismuth-coated screen-printed electrodes are encouraging.

Introduction

Beryllium is recognized as the most toxic element without radioactivity [1] and its poisoning occurs primarily by inhalation of dust and gas. Beryllium is toxic both as a carcinogen and agent that causes the chronic beryllium disease (CBD). Environmental Protection Agency (EPA) has set a maximum allowable amount of 0.004 mg l^{-1} beryllium in drinking water. Despite the health hazards of beryllium, it is widely used by the

aerospace, nuclear and defense industries. Such widespread industrial use reflects the unique properties of beryllium, including its low density, high stiffness and high melting point [2,3]. To protect workers from beryllium-related diseases it is essential to detect and monitor for the presence of trace amounts of beryllium.

Several methods for the determination of beryllium have been reported, including inductively coupled plasma-mass spectrometry [4] electrothermal atomic absorption spectroscopy [3,5] gas chromatography [6] or liquid chromatography with fluorescence detection [7]. In contrast to these sophisticated and expensive protocols, electrochemical (stripping) procedures offer great promise for obtaining ultra high sensitivity while meeting the portability, speed, cost and low-power demands of field detection of trace beryllium [8]. Since beryllium cannot be readily electrodeposited it has been measured at trace levels using adsorptive stripping voltammetry (AdSV), based on the interacial accumulation and voltammetric determination of its complexes [9,10]. Two complexing agents, thorin [9] and beryllon III [10] have been particularly useful for such AdSV measurements of beryllium. A limitation of these AdSV procedures, particularly for field screening applications, is their reliance on a mercury drop detector. Reliable AdSV sensors, based on preplated film electrodes should particularly benefit field measurements of beryllium.

Although these mercury electrodes offer an attractive AdSV performance, new alternative electrode materials with a similar performance are urgently desired for addressing growing concerns regarding the toxicity, handling, and disposal of mercury. The development of a reliable ‘non-mercury’ beryllium sensor should particularly benefit on-site (and especially in situ) measurements of beryllium. Bismuth electrodes have attracted considerable attention as an attractive alternative to mercury electrodes used in stripping analysis [11,12]. Most early stripping applications of bismuth film electrodes (BiFEs) focused on measurements of electrodeposited heavy metals. The suitability of BiFEs for AdSV has been demonstrated recently in connection to trace measurements of nickel [13], cobalt [14], uranium [15], chromium [16], molybdenum [17] or vanadium [18].

The aim of this work was to optimize and characterize an effective adsorptive-stripping voltammetric protocol for trace measurements of beryllium at a preplated bismuth film electrode (BiFE), based on the adsorptive accumulation of the arsenazo-III/Be complex. The arsenazo-III complexing agent dye has been shown useful for absorption spectrophotometric measurements of trace beryllium [19]. This dye is commonly used as an indicator for complexometric titrations of alkali earth metals [20].

It has been reported on the measurement of beryllium at mercury electrode [21]. However, there are no early reports on the voltammetric detection of arsenazo-III or related electrochemical measurements of its metal complexes on BiFE. As will be illustrated below, the adsorptive accumulation of Be–arsenazo-III complex onto the BiFE results in a highly sensitive and reproducible AdSV protocol for measuring trace levels of beryllium.

Materials and Methods

Ammonium chloride was obtained from Mallinckrodt Inc. Sodium acetate and stock solutions of beryllium (1000 mg l^{-1}) were purchased from Aldrich. Beryllium solutions were diluted daily as required. The 0.5 mM stock solutions of arsenazo-III (Sigma–Aldrich) were prepared by dissolving the appropriate amount of the ligand in nanopure water. The seawater sample, collected from Cha-Am Bay, Petchburi, was used without any pretreatment. The water was adjusted to pH 9.7 with ammonium buffer (4:1 volume ratio of water:buffer) before the measurement. All experiments were carried out at room temperature.

Square-wave AdSV measurements were conducted using an Electrochemical Analyzer 621A (CH Instruments, Austin, TX) connected to a personal computer. The 10 ml electrochemical cell assembly (BAS, Model VC-2) consisted of bismuth-coated carbon-fiber working electrode, an Ag/AgCl (3 M KCl) reference electrode (Model CHI111, CH Instruments), and a platinum wire counter electrode. The carbon fibers (Alfa Aesar 10451, Johnson Matthey Co.,Ward Hill, MA) were pretreated first by a 12 h immersion in ethanol. Subsequently, the fibers were dipped into a 6 M nitric acid solution for 30 s, and rinsed with distilled water. This was followed by another wash with acetone, a thorough rinse with distilled water, and an air dry. A bundle of ca. 20 fibers was then glued to a copper wire with a silver conductive paint (SPI Supplies Inc., West Chester, PA). The bundle of carbon fibers was then inserted into a 100 μl plastic pipette tip, exposing a 3 mm length of the fibers at the narrow end of the tip. An internal copper wire provided the electrical contact. The narrow end of the pipette tip was then sealed with a nail polish. All glassware were soaked in 1 M nitric acid and rinsed several times with deionized water prior to use.

The bismuth-coated carbon-fiber electrode was prepared by a 15 min electrodeposition of bismuth at -0.8 V from a 0.1 M acetate buffer (pH 4.5) solution containing 20 mg l^{-1} bismuth. A similar film preparation (but in the presence of 100 mg l^{-1} bismuth) was employed in connection to the screen-printed carbon substrates.

The ammonium buffer (0.05 M, pH 9.7) supporting electrolyte solution contained 5 μM of the arsenazo-III complexing agent. The solution was first purged with nitrogen for 5 min to remove the dissolved oxygen. The electrode was poised at a potential of 0.0 V for 90 s for adsorbing the Be-ligand complex. The stirring was then stopped and after 15 s the square-wave voltammogram (SWV) was recorded over the 0.0 to -1.0 V range (using a step potential of 4 mV, amplitude of 25 mV and a frequency of 25 Hz). A 15 s 'cleaning' period (with stirring at -1.0 V) was employed between successive runs.

Results and Discussion

A comparison of a typical linear-sweep (A), square-wave (B) and differential pulse (C) AdSV signals at the bismuth-film electrode for 100 μg l^{-1} beryllium in the presence of 5 μM arsenazo-III recorded following a 90 s

accumulation in an ammonium buffer medium (pH 9.7) is illustrated in Figure 1. The square-wave (B) and differential pulse (C) stripping modes resulted in well-defined beryllium signals of different sizes (Ep = -0.43 V for both (A) and (B)). A larger background slope and unwell-defined beryllium signal were observed using the linear scan mode. Both differential pulse and square-wave techniques corrected for the charging-current background contribution and yielded better signal-to-background characteristics. Square wave voltammetry was selected for all subsequent work due to its distinct speed and sensitivity advantages.

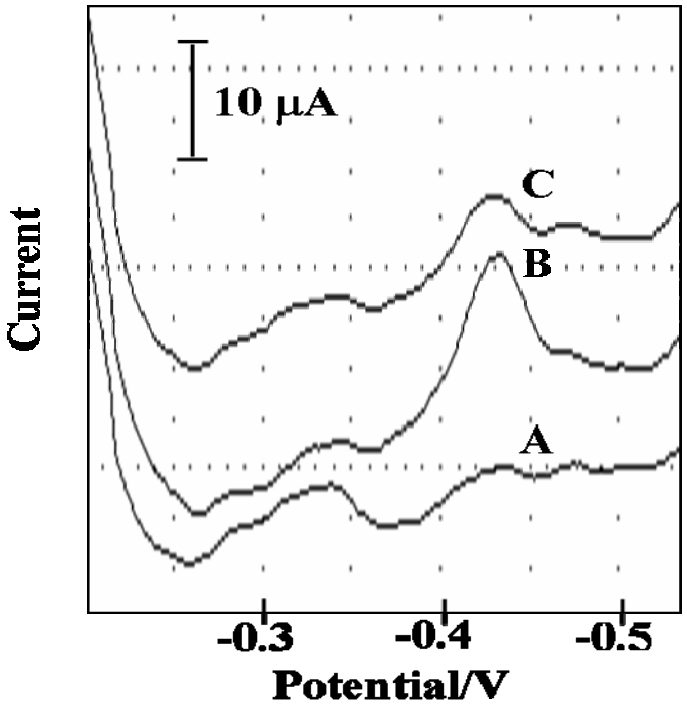

Figure 1. Comparison of different stripping modes: linear scan voltammetry (A); square-wave voltammetry (B) and differential pulse voltammetry; (C). Conditions: bismuth-coated carbon-fiber electrode; supporting electrolyte, 0.05 M ammonium buffer (pH 9.7) containing 100 μg l^{-1} beryllium and 5 μM arsenazo-III; nitrogen purging time, 5 min; pre-conditioning potential, -1.0 V; pre-conditioning time, 15 s; accumulation potential, 0.0 V; accumulation time, 90 s; quiet potential, 0 V; quiet time, 15 s; scanning potential window, 0.0 to -1.0 V. Scan rate, 0.1 V/s (A); amplitude, 0.025 V (B); and 0.05 V (C) potential step, 0.004 V (B and C); pulse width, 0.05 s (C); pulse period, 0.2 s (C); frequency, 25 Hz (B).

The influence of the pH on the Be AdSV peak current was examined over the 6.0–11.0 range (Figure 2A). The response increases slowly between pH 6.0 and 8.3, and very rapidly between pH 8.3 and 9.7. A sharp decrease of the signal is observed at higher pH. Such profile reflects the effect of the pH upon the complexation, adsorption and redox processes. The peak potential of the Be–arsenazo-III complex shifted gradually (from -0.43 to -0.48 V) upon increasing the pH from 6.0 to 9.7 (not shown). All subsequent work involved a solution of pH 9.7.

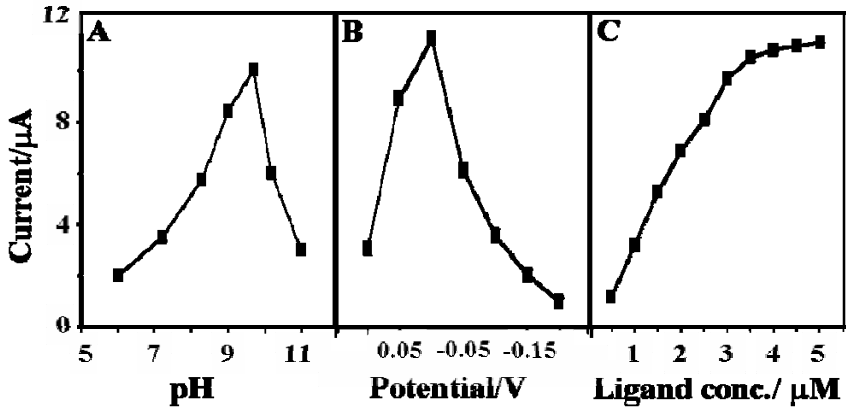

Figure 2. Effect of the pH (A), accumulation potential (B) and arsenazo-III concentration (C) upon the square-wave adsorptive stripping response of 100 μg l^{-1} beryllium. Other conditions, as in Figure 1B.

The influence of the accumulation potential on the Be stripping peak current was examined over the range of +0.10 to -0.20 V (Figure 2B). The peak rises rapidly between +0.10 and +0.05, and then more slowly up to 0.0 V. The response decreases sharply between 0.0 and -0.05 V and more slowly at more negative potentials. An accumulation potential of 0.0 V led to the highest degree of adsorption and was thus used for the further measurements. The effect of the arsenazo-III concentration upon the Be peak current is shown in Figure 2C. As expected for such adsorptive accumulation processes. The response increases rapidly up to around 3 μM arsenazo-III, more slowly up to 4 μM, and levels off thereafter.

The influence of the accumulation time upon the Be–arsenazo-III stripping peak current increases linearly with the accumulation time up to 60 s, then more slowly up to 120 s and starts to level off for longer periods (not shown). The resulting current–time dependence thus displays a curvature characteristic to AdSV measurements, reflecting saturation of the surface at longer accumulation periods.

The coupling of the effective adsorptive accumulation of the Be–arsenazo-III complex at the BiFE with the fast square-wave voltammetric scan results in a highly sensitive beryllium response. Figure 3 displays stripping voltammograms for increasing concentrations of beryllium in 10 μg l^{-1} steps following a 90 s preconcentration time and using the optimised parameters. Such short accumulation results in well defined peaks for these low beryllium concentrations. As expected for adsorptive accumulation processes, the response increases linearly with the beryllium concentration up to 50 μg l^{-1}, then more slowly above 60 μg l^{-1}. Although a curvature, characteristic of adsorption processes, is observed above 60 μg l^{-1}, no leveling off is indicated even at high beryllium levels. (see inset for the resulting calibration plot; slope of the linear portion, 80 nA l μg^{-1}; correlation coefficient, 0.998). While the data of Figure 3 (curve a) indicate a detection limit of around 3 μg l^{-1} (based on the signal-to-noise characteristics; S/N = 3), a substantially lower detection limit can be obtained in

connection to longer accumulation times and a background subtraction operation. Such background-subtraction AdSV response for a 2 μg l^{-1} beryllium solution following a 10 min preconcentration has been investigated (not shown). A well defined response, with favorable signal-to-noise characteristics, is observed, indicating a detection limit of around 0.25 μg l^{-1} (27.8 nM) beryllium. Such detection limit meets the requirements of monitoring of contaminated sites and of most water quality applications.

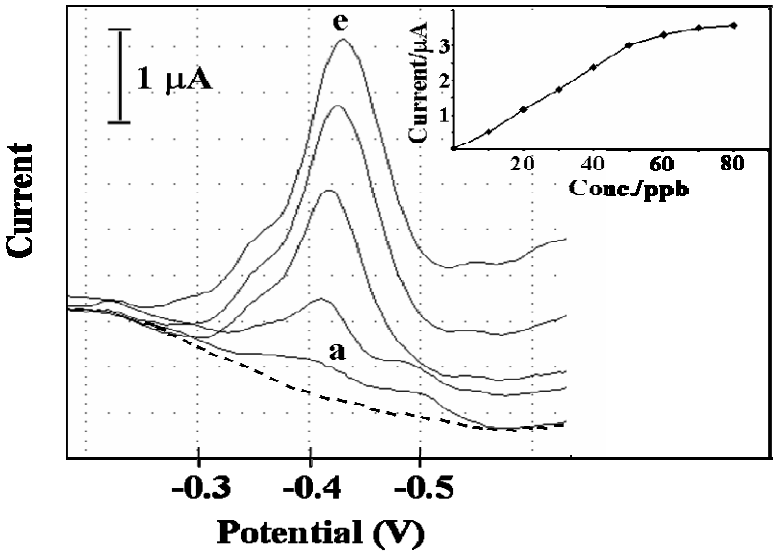

Figure 3. Adsorptive stripping square wave voltammograms for increasing levels of beryllium in 10 μg l^{-1} steps (curves a–e) along with the background response (dotted line). Also shown (inset) is the resulting calibration plot. Other conditions, as in Figure 1B.

The new electrochemical detection is suitable for measuring beryllium in natural water systems. The determination of beryllium in such water systems is indicative of the metal uptake through dust or gas sources [2]. Figure 4 demonstrates the suitability of the system for monitoring low levels of beryllium in an untreated seawater sample. Well defined peaks (Ep = -0.41 V) are observed for increasing beryllium concentrations in 20 μg l^{-1} steps (a–g). The peak height increases linearly with the Be concentration up to ca. 100 μg l^{-1} and then more slowly (slope of the initial linear portion, 50 nA l μg^{-1}; correlation coefficient, 0.995, not shown). The smaller slope, compared to that observed in the synthetic sample (of Figure 3), appears to reflect matrix effects, including co-existing calcium and magnesium ions and surface-active macromolecules. The low background response (unspiked sample; dotted line) indicates the absence of potential interferences.

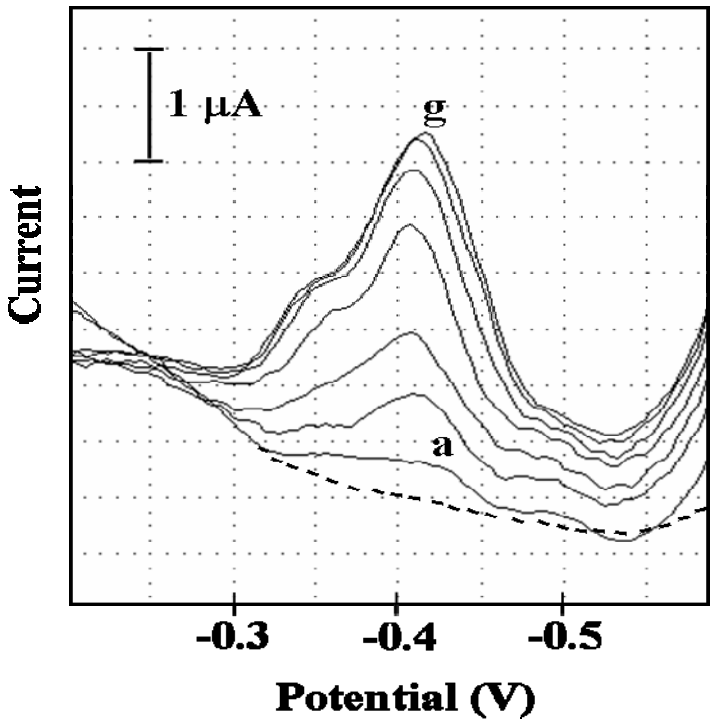

Figure 4. Adsorptive stripping square-wave voltammograms for a seawater sample spiked with increasing levels of beryllium in 20 μg l^{-1} steps (a–g) along with the response for the unspiked sample (dotted line). The water sample was adjusted to pH 9.7 with ammonium buffer (4:1 volume ratio of water:buffer) before the measurement. Other conditions, as in Figure 1B.

The long-term stability of 40 repetitive voltammograms recorded, for a seawater sample containing 100 μg l^{-1} beryllium, at 3 min intervals over a prolonged (120 min) period is illustrated (not shown). A highly stable response, with a mean peak current of 14.6 μA and a relative standard deviation of 3.9%, is observed for these 40 runs. Such stability indicates no apparent surface fouling by surface-active substances of the seawater matrix.

Conclusions

We have demonstrated a highly sensitive cathodic stripping protocol for detecting trace beryllium based on the adsorptive accumulation of the Be-arsenazo-III complex at a bismuth film electrode. Because of the toxicity, handling, and disposal of mercury, the new procedure obviates the need for the large mercury-drop electrode, mercury film electrode and related mercury disposal issues. The same pre-plated bismuth film could thus be employed for multiple measurements of beryllium. The new electrochemical protocol offers great promise for meeting the portability, sensitivity, speed, cost and low-power demands of field detection beryllium. Future efforts in this direction will focus on developing single-use screen printed electrode (SPE) for on-site measurements of beryllium.

Acknowledgements

This work was financially supported by the Thailand Research Fund (TRF) and Nakhon Pathom Rajabhat University (NPRU). Useful discussions with J. Wang at the Center for Bioelectronics and Biosensors, the Biodesign Institute, Arizona State University, is gratefully acknowledged.

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BISMUTH FILM ELECTRODE FOR ADSORPTIVE STRIPPING VOLTAMMETRIC MEASUREMENTS OF ULTRATRACE BERYLLIUM

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Ammonium chloride was obtained from Mallinckrodt Inc. Sodium acetate and stock solutions of beryllium (1000 mg l^{-1}) were purchased from Aldrich. Beryllium solutions were diluted daily as required. The 0.5 mM stock solutions of arsenazo-III (Sigma–Aldrich) were prepared by dissolving the appropriate amount of the ligand in nanopure water. The seawater sample, collected from Cha-Am Bay, Petchburi, was used without any pretreatment. The water was adjusted to pH 9.7 with ammonium buffer (4:1 volume ratio of water:buffer) before the measurement. All experiments were carried out at room temperature.

Square-wave AdSV measurements were conducted using an Electrochemical Analyzer 621A (CH Instruments, Austin, TX) connected to a personal computer. The 10 ml electrochemical cell assembly (BAS, Model VC-2) consisted of bismuth-coated carbon-fiber working electrode, an Ag/AgCl (3 M KCl) reference electrode (Model CHI111, CHInstruments), and a platinum wire counter electrode. The carbon fibers (Alfa Aesar 10451, Johnson Matthey Co.,Ward Hill, MA) were pretreated first by a 12 h immersion in ethanol. Subsequently, the fibers were dipped into a 6 M nitric acid solution for 30 s, and rinsed with distilled water. This was followed by another wash with acetone, a thorough rinse with distilled water, and an air dry. A bundle of ca. 20 fibers was then glued to a copper wire with a silver conductive paint (SPI Supplies Inc., West Chester, PA). The bundle of carbon fibers was then inserted into a 100 µl plastic pipette tip, exposing a 3 mm length of the fibers at the narrow end of the tip. An internal copper wire provided the electrical contact. The narrow end of the pipette tip was then sealed with a nail polish. All glassware were soaked in 1 M nitric acid and rinsed several times with deionized water prior to use.

The bismuth-coated carbon-fiber electrode was prepared by a 15 min electrodeposition of bismuth at −0.8 V from a 0.1 M acetate buffer (pH 4.5) solution containing 20 mg l^{-1} bismuth. A similar film preparation (but in the presence of 100 mg l^{-1} bismuth) was employed in connection to the screen-printed carbon substrates.

The ammonium buffer (0.05 M, pH 9.7) supporting electrolyte solution contained 5 µM of the arsenazo-III complexing agent. The solution was first purged with nitrogen for 5 min to remove the dissolved oxygen. The electrode was poised at a potential of 0.0 V for 90 s for adsorbing the Be-ligand complex. The stirring was then stopped and after 15 s the square-wave voltammogram (SWV) was recorded over the 0.0 to −1.0 V range (using a step potential of 4 mV, amplitude of 25 mV and a frequency of 25 Hz). A 15 s 'cleaning' period (with stirring at −1.0 V) was employed between successive runs.

Results and Discussion

A comparison of a typical linear-sweep (A), square-wave (B) and differential pulse (C) AdSV signals at the bismuth-film electrode for 100 µg l^{-1} beryllium in the presence of 5 µM arsenazo-III recorded following a 90 s accumulation in an ammonium buffer medium (pH 9.7) is illustrated in Figure 1. The square-wave (B) and differential pulse (C) stripping modes resulted in well-defined beryllium signals of different sizes (Ep = −0.43 V for both (A) and (B)). A larger background slope and unwell-defined beryllium signal were observed using the linear scan mode. Both differential pulse and square-wave techniques corrected for the charging-current background contribution and yielded better signal-to-background characteristics.

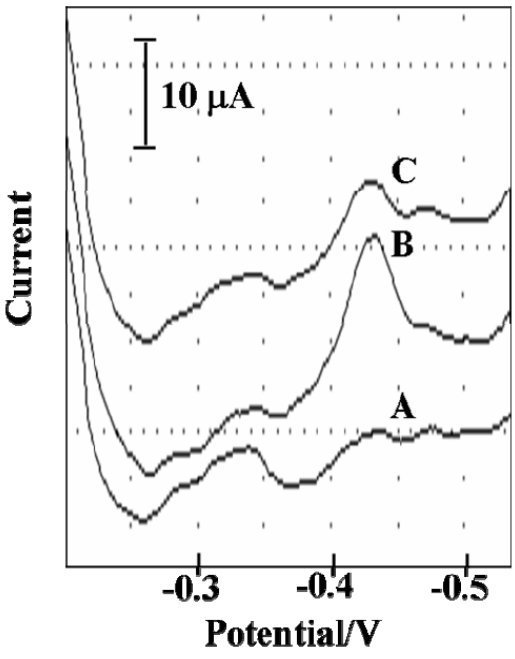

Figure 1. Comparison of different stripping modes: linear scan voltammetry (A); square-wave voltammetry (B) and differential pulse voltammetry; (C). Conditions: bismuth-coated carbon-fiber electrode; supporting electrolyte, 0.05 M ammonium buffer (pH 9.7) containing 100 µg l^{-1} beryllium and 5 µM arsenazo-III; nitrogen purging time, 5 min; pre-conditioning potential, −1.0 V; pre-conditioning time, 15 s; accumulation potential, 0.0 V; accumulation time, 90 s; quiet potential, 0 V; quiet time, 15 s; scanning potential window, 0.0 to −1.0 V. Scan rate, 0.1 V/s (A); amplitude, 0.025 V (B); and 0.05 V (C) potential step, 0.004 V (B and C); pulse width, 0.05 s (C); pulse period, 0.2 s (C); frequency, 25 Hz (B).

Square wave voltammetry was selected for all subsequent work due to its distinct speed and sensitivity advantages.

The influence of the pH on the Be AdSV peak current was examined over the 6.0–11.0 range (Figure 2A). The response increases slowly between pH 6.0 and 8.3, and very rapidly between pH 8.3 and 9.7. A sharp decrease of the signal is observed at higher pH. Such profile reflects the effect of the pH upon the complexation, adsorption and redox processes. The peak potential of the Be–arsenazo-III complex shifted gradually (from −0.43 to −0.48 V) upon increasing the pH from 6.0 to 9.7 (not shown). All subsequent work involved a solution of pH 9.7.

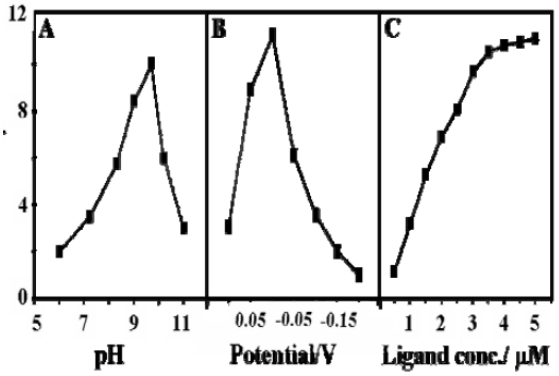

Figure 2. Effect of the pH (A), accumulation potential (B) and arsenazo-III concentration (C) upon the square-wave adsorptive stripping response of 100 µg l^{-1} beryllium. Other conditions, as in Figure 1B.

The influence of the accumulation potential on the Be stripping peak current was examined over the range of +0.10 to −0.20 V (Figure 2B). The peak rises rapidly between +0.10 and +0.05, and then more slowly up to 0.0 V. The response decreases sharply between 0.0 and −0.05 V and more slowly at more negative potentials. An accumulation potential of 0.0 V led to the highest degree of adsorption and was thus used for the further measurements. The effect of the arsenazo-III concentration upon the Be peak current is shown in Figure 2C. As expected for such adsorptive accumulation processes. The response increases rapidly up to around 3 µM arsenazo-III, more slowly up to 4 µM, and levels off thereafter.

The influence of the accumulation time upon the Be–arsenazo-III stripping peak current increases linearly with the accumulation time up to 60 s, then more slowly up to 120 s and starts to level off for longer periods (not shown). The resulting current–time dependence thus displays a curvature characteristic to AdSV measurements, reflecting saturation of the surface at longer accumulation periods.

The coupling of the effective adsorptive accumulation of the Be–arsenazo-III complex at the BiFE with the fast square-wave voltammetric scan results in a highly sensitive beryllium response. Figure 3 displays stripping voltammograms for increasing concentrations of beryllium in 10 µg l^{-1} steps following a 90 s preconcentration time and using the optimised parameters. Such short accumulation results in well defined peaks for these low beryllium concentrations. As expected for adsorptive accumulation processes, the response increases linearly with the beryllium concentration up to 50 µg l^{-1}, then more slowly above 60 µg l^{-1}. Although a curvature, characteristic of adsorption processes, is observed above 60 µg l^{-1}, no leveling off is indicated even at high beryllium levels. (see inset for the resulting calibration plot; slope of the linear portion, 80 nA l µg^{-1}; correlation coefficient, 0.998). While the data of Figure 3 (curve a) indicate a detection limit of around 3 µg l^{-1} (based on the signal-to-noise characteristics; S/N = 3), a substantially lower detection limit can be obtained in connection to longer accumulation times and a background subtraction operation. Such background-subtraction AdSV response for a 2 µg l^{-1} beryllium solution following a 10 min preconcentration has been investigated (not shown). A well defined response, with favorable signal-to-noise characteristics, is observed, indicating a detection limit of around 0.25 µg l^{-1} (27.8 nM) beryllium. Such detection limit meets the requirements of monitoring of contaminated sites and of most water quality applications.

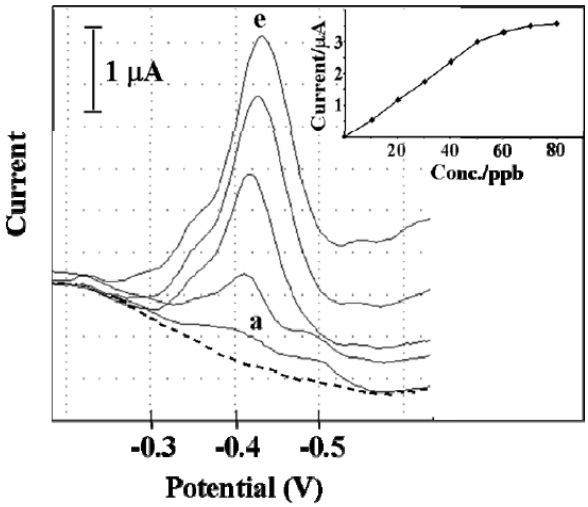

Figure 3. Adsorptive stripping square wave voltammograms for increasing levels of beryllium in 10 µg l^{-1} steps (curves a–e) along with the background response (dotted line). Also shown (inset) is the resulting calibration plot. Other conditions, as in Figure 1B.

The new electrochemical detection is suitable for measuring beryllium in natural water systems. The determination of beryllium in such water systems is indicative of the metal uptake through dust or gas sources [2]. Figure 4 demonstrates the suitability of the system for monitoring low levels of beryllium in an

untreated seawater sample. Well defined peaks (Ep = −0.41 V) are observed for increasing beryllium concentrations in 20 μg l^{-1} steps (a–g). The peak height increases linearly with the Be concentration up to ca. 100 μg l^{-1} and then more slowly (slope of the initial linear portion, 50 nA 1 μg^{-1}; correlation coefficient, 0.995, not shown). The smaller slope, compared to that observed in the synthetic sample (of Figure 3), appears to reflect matrix effects, including co-existing calcium and magnesium ions and surface-active macromolecules. The low background response (unspiked sample; dotted line) indicates the absence of potential interferences.

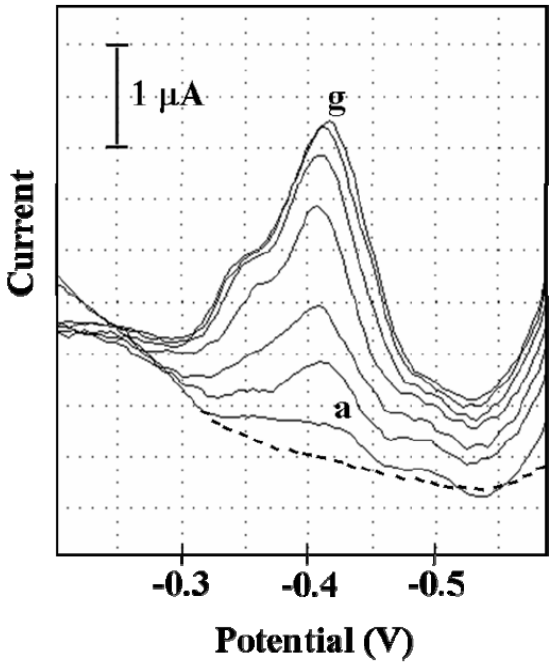

Figure 4. Adsorptive stripping square-wave voltammograms for a seawater sample spiked with increasing levels of beryllium in 20 μg l^{-1} steps (a–g) along with the response for the unspiked sample (dotted line). The water sample was adjusted to pH 9.7 with ammonium buffer (4:1 volume ratio of water:buffer) before the measurement. Other conditions, as in Figure 1B.

The long-term stability of 40 repetitive voltammograms recorded, for a seawater sample containing 100 μg l^{-1} beryllium, at 3 min intervals over a prolonged (120 min) period is illustrated (not shown). A highly stable response, with a mean peak current of 14.6 μA and a relative standard deviation of 3.9%, is observed for these 40 runs. Such stability indicates no apparent surface fouling by surface-active substances of the seawater matrix.

Conclusions

We have demonstrated a highly sensitive cathodic stripping protocol for detecting trace beryllium based on the adsorptive accumulation of the Be-arsenazo-III complex at a bismuth film electrode. Because of the toxicity, handling, and disposal of mercury, the new procedure obviates the need for the large mercury-drop electrode, mercury film electrode and related mercury disposal issues. The same pre-plated bismuth film could thus be employed for multiple measurements of beryllium. The new electrochemical protocol offers great promise for meeting the portability, sensitivity, speed, cost and low-power demands of field detection beryllium. Future efforts in this direction will focus on developing single-use screen printed electrode (SPE) for on-site measurements of beryllium.

Acknowledgements

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Effect of carbonizing conditions on electrical resistivity of white popinac, bamboo, coconut shell and eucalyptus charcoal

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Abstract: Electrical resistivity of *White Popinac, Bamboo, Coconut Shell* and *Eucalyptus* wood charcoal produced under different carbonizing conditions were determined. The results showed that electrical resistivity of the charcoal indicated strong and systematic dependence on the calcination temperature. The appropriate conditions for all were started from 400, 700 and up to 1000 •€. The soaking time at the highest temperature were 30 minutes for all samples, while the electrical resistivity of the charcoal powders were found to be 5.1, 9.7, 19.8 and 4.1 • •for White Popinac, Bamboo, Coconut Shell and Eucalyptus, respectively. After that the prepared powders were placed in containers, electrical resisitivity were also determined.

Introduction

Wood charcoal is an important functional materials [1] which are widening use in structural applications such as carbon fibres [2], carbon fuel cells and carbon electrodes [3]. During 1970's, Stanford Research Institute (RSI) developed a coal base fuel cell in molten lead at temperature of 500 to 900 •€ [4,5], while Gur and Huggins constructed a high temperature fuel cell (725 to 955 •€) that employed stabilized zirconia as a solid electrolyte and a graphite anode [6]. In 1810 carbonized charcoal electrodes were use in arc lamp, and in 1830 carbonized charcoal was used as an electrode for primary batteries. These electrodes were made from powdered charcoal or coke bonded with sugar syrup or coal tar, pressed and carbonized at high temperatures [7].

Charcoal is the carbon residue from thermal decomposition with insufficient oxygen. Good quality of charcoal has fixed carbon content, measured by ASTM D 1762-84, to about 70%. These charcoals prepared by heating up to 400-500 •€. Chemical formula for charcoal is $CH_{0.60}O_{0.13}$ [8]. Higher quality of charcoal corresponded to the higher carbon content, which prepared by treated higher carbonizing temperature to above 500 •€. Carbon content can have in excess of 94% in high temperature carbonized charcoal. Some carbonized charcoals are purer than natural graphite [9], and electrical properties are closely related to degree of graphitization in wood charcoals [10].

Accordingly, the objective of this work was to find out the suitable carbonizing conditions of White Popinac, Bamboo, Coconut Shell and Eucalyptus charcoal which affected to their electrical resistivity.

Materials and Methods

Wood samples of *White Popinac, Bamboo, Coconut Shell* and *Eucalyptus* were cut into 12 cm^2. The samples were carbonized from 30 to 400 •€ at the starting rate of 4 •€/min and then to 600, 700, 800, 900 and 1000•€ at the heating rate of 12•€/min and the holding time was 30 min. After that the charcoals were allowed to cool in the furnace, electrical resistivity were measured using digital multimeter.

The charcoal powders were ground and placed in pipette tips, which used as containers for voltammetric electrode. Mineral oil was used as binder. Electrical resistivities of the charcoal powders were determined. Two probes of multimeter were hold between the two copper wires. The first wire was touched to the contact surface to eliminate the resistant at the surface, while the other was inserted to the charcoal powders at the different height of 1 to 4 cm, as see in figure 1.

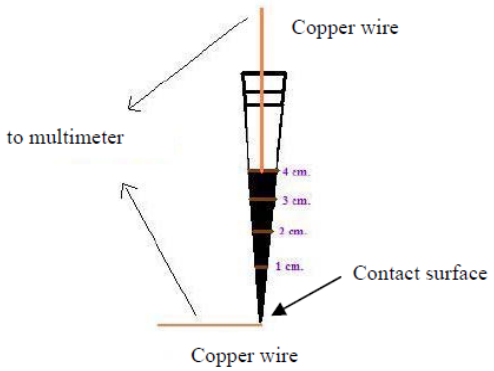

Figure 1. Apparatus for electrical resistivity measurement