

UNIVERSITI SAINS MALAYSIA



Optimization of the Differential Pulse Cathodic Stripping Voltammetry Technique for the Determination of Nickel in Pengkalan Chepa River, Kelantan

Dissertation submitted in partial fulfillment for the Degree of Bachelor of
Science (Health) in Forensic Science

AZLINA BINTI MAT SHARIFF

School of Health Sciences
Universiti Sains Malaysia
Health Campus
16150, Kubang Kerian Kelantan
Malaysia

2009

CERTIFICATE

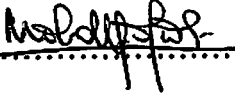
This is to certify that the dissertation entitled

**Optimization of the Differential Pulse Cathodic Stripping
Voltammetry Technique for the Determination of
Nickel in Pengkalan Chepa River, Kelantan**

is the bonafide record of research work done by

Azlina binti Mat Shariff

During the period of 21th December 2008 to 6nd May 2009 under my supervision

Signature of Supervisor:.....

Name and address of Supervisor: Dr. Mohammad Hadzri b. Yaacob
Lecturer,
School of Health Science,
Universiti Sains Malaysia,
Healthy Campus.

Date;.....

ACKNOWLEDGEMENT

In the name of Allah, the Most Gracious and Most Merciful. First of all, all praise be to Allah S.W.T and blessing be upon His Prophet S.A.W because with His blessing and ultimate guidance, I have completed this work by research without having any problem with patiently and creates more meaningful purpose to this work.

I would like to express my millions and special thanks with an appreciation to my supervisor, Dr. Mohamad Hadzri bin Yaacob for all of his advices, guidances and also his supports during this study for his efforts developing my understanding and knowledge towards this study.

Along the duration of this study also, I would like to express also my special thanks especially to Prof. Madya Dr. R. Kuppuswamy and also to all the lecturers of Pusat Pengajian Sains Kesihatan, the Science Officers and the laboratory staffs who's directly or indirectly contribute their efforts to the completion of this research project.

The very special with million of thanks is given to Encik Zulkhairi bin Othman for the assistance in handling voltammetric instrument with full of patient, Encik Wan Mohd Sahnusi for the preparation of nickel standard solution and Ms. Izzati for the river water samples.

Not forgotten also to my parents and my entire partner, Nor Amalina Zulkipli who give me the supports especially moral support in build up the patient and confident and the assistance in the completion of this research project and the dissertation writing.

TABLE OF CONTENTS

Contents	Page
List of tables, charts and figures	i-vi
Abbreviations	vii-viii
Abstract	1
Introduction	2
Review of Literature	9
Objectives	16
Materials and Reagents	17
Methodology	20
Results	25
Discussion	50
Conclusion	54
References	55
Appendix	

LIST OF TABLES, CHARTS AND FIGURES

List of Tables	Page
-----------------------	-------------

Table 1: The finding for height of the peak, nA with the series of
the concentration of the nickel stock solution.....37

Table 2: DPCSV analysis results of nickel determination in the eight
samples of the Pengkalan Chepa River.....41

List of Chart	Page
----------------------	-------------

Chart 1: Flow Chart of Methodology.....20

Figure 1: The typical arrangement for voltammetric electrochemical cell.....	6
Figure 2: pH Meter.....	17
Figure 3: Metrohm 757 VA Computrace Voltammetric Analyzer combined with Multimode Electrode (MME) System.....	18
Figure 4: The river water samples of Pengkalan Chepa River.....	19
Figure 5: Voltammogram of the optimized condition of the supporting electrolyte (pH).....	25
Figure 6: The graph for the peak height of nickel standard solution in different pH of supporting electrolyte.....	26
Figure 7: Voltammogram of Ni at the initial potential, E_i at -0.70 V and Final potential, E_f at -1.15 V.....	27
Figure 8: Voltammogram of the optimized parameter for the scan rate, ν	28
Figure 9: The graph for the Peak Height, I_p versus Scan Rate, ν	29

Figure 10: Voltammogram of the optimized parameter for the deposition potential, E_{acc}.....	30
Figure 11: The graph for the Peak Height, I_p versus Deposition Potential, E_{acc} in the optimization of deposition potential, E_{acc}.....	31
Figure 12: Voltammogram of the optimized parameter for the deposition time, t_{acc}.....	32
Figure 13: The graph for the Peak Height, I_p versus Deposition Time, t_{acc} in the optimization of the deposition potential, E_{acc}.....	33
Figure 14: Voltammogram of the optimized parameter for the equilibrium time, t_{eq}.....	34
Figure 15: The graph for the Peak height, I_p versus Equilibrium Time, t_{eq} in the optimization of the deposition potential, E_{acc} and deposition time, t_{acc}.....	35
Figure 16: Voltammogram of series volume of 5ppm nickel standard solution....	37
Figure 17: Calibration Curve of Peak Height, I_p versus Concentration of the Nickel Standard Solution.....	38

Figure 18: Voltammogram of determination of nickel in the Sample 1:	
Pengkalan Chepa River (surface).....	42
Figure 19: Voltammogram of determination of nickel in the Sample 1:	
Pengkalan Chepa River (surface) after a series of internal	
standard addition.....	42
Figure 20: Voltammogram of determination of nickel in the Sample 2:	
Pengkalan Chepa River (bottom).....	43
Figure 21: Voltammogram of determination of nickel in the Sample 2:	
Pengkalan Chepa River (bottom) after a series of internal	
standard addition.....	43
Figure 22: Voltammogram of determination of nickel in the Sample 3:	
Pengkalan Chepa River 2 (surface).....	44
Figure 23: Voltammogram of determination of nickel in the Sample 3:	
Pengkalan Chepa River 2 (surface) after a series of internal	
standard addition.....	44
Figure 24: Voltammogram of determination of nickel in the Sample 4:	
Pengkalan Chepa River 2 (bottom).....	45

Figure 25: Voltammogram of determination of nickel in the Sample 4:	
Pengkalan Chepa River 2 (bottom) after a series of internal	
standard addition.....	45
Figure 26: Voltammogram of determination of nickel in the Sample 5:	
Alor Lintah River (surface).....	46
Figure 27: Voltammogram of determination of nickel in the Sample 5:	
Alor Lintah River (surface) after a series of internal	
standard addition.....	46
Figure 28: Voltammogram of determination of nickel in the Sample 6:	
Alor Lintah River (bottom).....	47
Figure 29: Voltammogram of determination of nickel in the Sample 6:	
Alor Lintah River (bottom) after a series of internal	
standard addition.....	47
Figure 30: Voltammogram of determination of nickel in the Sample 7:	
Alor B River (surface).....	48
Figure 31: Voltammogram of determination of nickel in the Sample 7:	
Alor B River (surface) after a series of internal standard addition.....	48

Figure 32: Voltammogram of determination of nickel in the Sample 8:

Keladi River (surface).....49

Figure 33: Voltammogram of determination of nickel in the Sample 8:

**Keladi River (surface) after a series of internal
standard addition.....49**

ABBREVIATIONS

AAS	- Atomic Absorption Spectroscopy
AADC	- ammonium 2-aminocyclopentene-1-dithiocarboxylate
AdCSV	- Adsorptive Cathodic Stripping Voltammetry
AdSV	- Adsorptive Stripping Voltammetry
Ag/AgCl	- Argentum/Argentum Chloride
ASV	- Anodic Stripping Voltammetry
BRB	- Britton-Robinson Buffer
CSV	- Cathodic Stripping Voltammetry
DME	- Dropping Mercury Electrode
DMG	- Dimethylglyoxime
DPAdSV	- Differential Pulse Adsorptive Stripping Voltammetry
DPASV	- Differential Pulse Anodic Stripping Voltammetry
DPCSV	- Differential Pulse Cathodic Stripping Voltammetry
DPSV	- Differential Pulse Sweep Voltammetry
E_{acc}	- Deposition Potential
E_f	- Final Potential
E_i	- Initial Potential
HMDE	- Hanging Mercury Dropped Electrode
ICP-AES	- Inductively Coupled Plasma Atomic Emission Spectroscopy
ICP-MS	- Inductively Coupled Plasma Mass Spectrometry
IKAN	- National Water Quality Index

I_p	- Peak Height
JAS	- Jabatan Alam Sekitar
LOD	- Limit of Detection
MME	- Multimode System
Ni	- Nickel
ppb	- parts per billion
ppm	- parts per million
RSD	- Relative Standard Deviation
SD	- Standard deviation
t_{acc}	- Deposition time
t_{eq}	- Equilibrium time
WHO	- World Health Organization

ABSTRACT

Nickel is a very toxic heavy metal which is significant subject of environmental surveillance, food control and occupational medicine, toxicology and hygiene. Various techniques have been used for the determination of this heavy metal including inductively-coupled plasma mass spectrometry (ICP-MS), flame atomic absorption spectrometry (FAAS) and atomic emission spectrometry (AES). However, these methods are having disadvantages particularly time consuming in sample preparation. A voltammetric method as an alternative method for the determination of the nickel in the river water samples of Pengkalan Chepa River is described. In this study the determination of nickel in the river water samples collected from Pengkalan Chepa River was performed by using Differential Pulse Cathodic Stripping Voltammetry (DPCSV) analysis. All samples were collected from Pengkalan Chepa River at various places including those from surface and the bottom of the river. From the study, the optimum condition for the supporting electrolyte, Britton-Robinson Buffer (BRB), 0.04 M was determined to be at pH 4. The optimum voltammetric parameters with initial potential, E_i was -0.70 V, final potential, E_f was -1.15 V, scan rate, ν was 0.020 V/s, deposition potential, E_{acc} was -0.70 V, deposition time, t_{acc} was 0 second and equilibrium time, t_{eq} was 10 seconds. The calibration curve was constructed, using peak height, I_p versus concentration of nickel standard solution (5 ppm). A linear graph with regression equation, $Y = 20.131X + 0.743$ and correlation coefficient, r was 0.999. Standard deviation (SD) was 1.063, sensitivity 20.131 nA/ppm and limit of detection was 0.158 ppm or 158 ppb. The results from this study show that nickel was not detected in all samples using our experimental conditions.

INTRODUCTION

1.1. Overview

Development is one of the important agenda in developing country such as Malaysia. However, development also often associates with adverse effects to the nature including atmospheric system, aquatic system and also flora and fauna. In Kelantan, Water Quality Index of Kelantan rivers was indicated at two levels which are at clean and medium level of polluted from year 2001 until 2006 (JAS, 2007).

In 2001, total clean rivers were 17 rivers while four more were categorized as medium polluted, while a total of 20 rivers were clean level and one river detected as medium polluted in 2006. Quality of river waters indicated in a medium level only for several rivers especially those flow through development and industrial areas, such as Pengkalan Chepa River (JAS, 2007).

One source of Pengkalan Chepa River pollution originates from municipal sewage. A previous study showed that all stations sampled from this river content a very high in total faecal colliform bacteria and solid suspended resulting National Water Quality Index (IKAN) from Sungai Pengkalan Chepa to be in range of 60 - 80 (JAS, 2003). It is unknown about the level if heavy metal contamination and therefore it is worth investigating the level of heavy metal contamination. In this study voltammetry technique will be used to analyze nickel, one of the selected heavy metals in water from Pengkalan Chepa River.

1.2. Nickel as General

Heavy metals are highly toxic and dangerous pollutants following a wide range of human activities releasing them to aquatic environments such as rivers, oceans, lakes and also drinking waters. Nickel is among the toxic heavy metal of significance for environmental surveillance, food control and occupational medicine, toxicology and hygiene (Stulik & Kalvoda, 1995).

Nickel is a naturally occurring metal existing in various mineral forms which may be found throughout the environment including rivers, lakes, oceans, soils, air drinking waters, plants and animals. It is released into atmosphere from burning fossil fuels, mining and refining operation and incinerations of municipal waste. It is also found in soil and sewage sludge, and as well as in cigarettes.

Nickel is compounds that are usually important in modern industry and are used in electroplating, electroforming and also for production of nickel-cadmium batteries and electronic equipment. Nickel alloy like stainless steel are used in the production of tools, machinery, armaments and appliances. They also used in coins and medical prostheses (Garrett, 2000).

Sources of nickel contamination include the production and processing of nickel and its by-products, the recycling nickel-containing products and nickel-containing waste disposal. From anthropogenic sources, nickel is emitted as oxides, sulfides, silicates, soluble

compounds and to a lesser extent as metallic nickel. Combustion of fossil fuels produces the greatest contribution of nickel (Osumex 2008).

Nickel has no known biological function and is of medium toxicity to humans. The organic form of nickel is much more toxic than its inorganic forms (Osumex, 2008). It is highly irritant to the skin and toxic to the cardiovascular system as well as being carcinogenic. Once it is in the body, nickel can replace metals in metallo-enzymes and cause disruption of metabolic pathways. Skin exposure may occur when jewellery which contains nickel is worn.

Generally, we daily ingest nickel averaging about 170 micrograms of nickel per day. This may come from air that we breathe, water that we have drunk and food that we have eaten. Most ingested nickel absorbed goes to our kidneys. Nickel consumed is usually excreted in faeces quickly while those in the bloodstream are eliminated through the urine.

Nickel in air is attached to small particles that can be in the range of 1-86 ng/m³. Nickel in water is generally as low as 10 parts per billion (ppb). In soils, nickel contains generally about 4-80 parts per million (ppm). Nickel which is in the food naturally has a high content in chocolate and soy beans (Osumex, 2008).

The most common harmful health effect of nickel in humans is an allergic reaction. Approximately 10-20% of the population is sensitive to nickel (Niguel, 2005). The most common reaction is skin rash at the site of contact with nickel-containing products. Dermatitis

may develop in an area of the skin that is away from the site of contact. For example, hand eczema is fairly common among people sensitized to nickel.

Adverse health effects from exposure to nickel include chronic bronchitis, reduced lung function, cancer of the lung and nasal sinus. This is likely to people who have breathed dust containing certain nickel compounds, or those working in nickel refineries or nickel processing plants. Lung and nasal sinus cancers associated with nickel exposure of more than $10 \text{ mg/m}^3 \text{ Ni}$ is high.

A variety of methods has been used in determine nickel concentrations in different media. For studying environmental problems and environmental control, simple and sufficiently sensitive methods for the determination of the heavy metal like nickel are necessary. For the determination of trace elements in aquatic systems such as rivers, lakes, oceans, sediments, waste water and others, voltammetric technique is suitable.

1.3. Voltammetry as General

In voltammetry, time-dependent potential is applied to an electrochemical cell and the current flowing through the cell is measured as a function of that potential. A plot of current as a function of applied potential is called voltammogram. It is the electrochemical equivalent of a spectrum in spectroscopy, providing quantitative and qualitative information about the species involved in the oxidation or reduction reaction.

The shape of a voltammogram is determined by several factors. The most important of which of how the current is measured and whether the convection is included as a means of transport. The voltammogram is characterized by a current to a limiting current at which the analyte is oxidized or reduced. Since the magnitude of a faradaic current is inversely proportional to δ , a limiting current implies that the thickness of the diffusion layer remains constant.

Modern voltammetry makes use of a three electrode potentiostat, auxiliary electrode (AE), working electrode (WE) and reference electrode (RE) as shown in Figure 1. A time-dependent potential excitation signal is applied to the working electrode, changing its potential relative to the fixed potential of the reference electrode. The resulting current between working and auxiliary electrode is then measured.

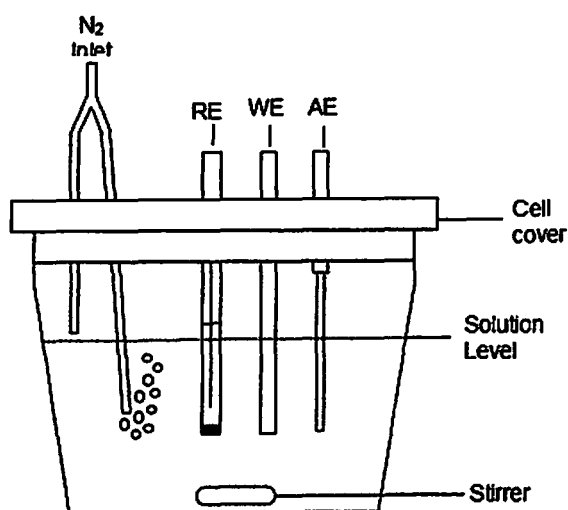


Figure 1: The typical arrangement for voltammetric electrochemical cell.

The auxiliary electrode is generally a platinum wire and Standard Calomel Reference (SCE) and Ag/AgCl electrodes are the common reference electrode. The electrode can be solid which there are several different materials have been used as working electrodes, including mercury, platinum, gold, silver, and carbon formed by a drop of mercury hanging from a tip of capillary. The earliest voltammetric techniques, including polarography, used mercury as the working electrode.

The most common characteristic of all voltammetric techniques is that they involve the application of a potential (E) to an electrode and the monitoring of the resulting current (i) flowing through the chemical cell. Thus, all voltammetric techniques can be described as some function of E , i and t . Voltammetry is considered an active technique because it applies potential which forces a change in concentration of electroactive species.

One of the most important quantitative voltammetric technique is stripping voltammetry, which is composed of three related technique; anodic, cathodic and adsorptive stripping voltammetry. Anodic stripping voltammetry is very sensitive to experimental conditions, which must be carefully controlled if results are to be accurate and precise. It is using hanging mercury drop electrode (HMDE).

Even though ASV, CSV and AdSV each have their own unique features, all have two steps in common. First the analyte species in the sample solution is concentrated onto or into a working electrode. During the second step, the pre-concentrated analyte is measured or stripped from the electrode by the application of a potential scan. Any number of potential

waveforms can be used for the stripping step. The most common are differential pulse and square wave due to the discrimination against charging current.

Voltammetric technique is advantageous as being a versatile technique with excellent sensitivity and allows a wide linear concentration range for both inorganic and organic species (10^{-2} to 10^{-1} M). It can use a large number of useful solvents and electrolytes, accommodate a wide range of temperatures, has rapid analysis times (seconds), and allows simultaneous determination of several analytes.

There are also many other analytical advantages of the voltammetric techniques including their ability to determine kinetic and mechanistic parameters. This allows us to reasonably estimate the values of unknown parameters. Different potential waveforms can be generated and small currents measured. One of the most important applications of voltammetry is the quantitative analysis of trace metals down to ppm levels.

The advantages and disadvantages of advanced electroanalytical techniques versus AAS, ICP-AES and ICP-MS in environmental analysis have been reviewed elsewhere. A few methods allow the simultaneous determination of all five metals in water samples, mainly voltammetric methods (Golimowski & Tykarska, 1994). This means that the AAS, ICP-AES and ICP-MS are difficult to analyze an analyte simultaneously.

REVIEW OF LITERATURE

2.1. Overview

The determination of nickel in the environment is important due to its toxic nature as well as its important role in metallurgy is for the production of various types of ferrous and non-ferrous alloys. Nickel is widely used in various industries such as electroplating industry, storage batteries and catalytic hydrogenation of vegetable oils. Its occurrence in various effluents is a potential source to environment pollution.

Many analytical procedures have been proposed for the nickel determination such as spectrophotometry, flame atomic absorption spectrometry (AAS) after preconcentration, inductively coupled plasma (ICP), atomic emission spectrometry (AES) following a preconcentration step (Ferreira et. al.,1996), potentiometry using nickel selective electrodes and adsorptive cathodic stripping voltammetry (A. A. Ensafi & K.Zarei, 2000).

Among the techniques, the most popular and powerful technique is voltammetry technique involve stripping analysis for the heavy metal analysis. Most other techniques are generally required time consuming preconcentration of extraction steps for the trace and ultratrace analysis of nickel before the determination step can be performed. On the otherhand, voltammetry techniques might take less than 1 minute for the sample analysis (J. Wang, 1985)

2.2. Nickel

Nickel is metallic element which is found in several oxidation states, ranging from -1 to +4. However, the +2 oxidation state is most prevalent form of nickel in biosystems. Solubilized Ni^{2+} ions in aqueous media at neutral pH are hydrated to the greenish hexahydrated $[\text{Ni}(\text{H}_2\text{O}_6)]^{2+}$. There are also several polynuclear nickel species which are having no direct biological significance.

Nickel is human poison by ingestion and inhalation of its finely divided powders and dusts. It is a confirmed carcinogen in animals causing lung and nasal tumors. Nickel can replace essential metals in metallo-enzymes and causes disruption of metabolic pathways (Vincoli, 2003). In the study of nickel in river sediment, I_{geo} value was determined and was found that the principal natural source of heavy metals in the environment is from crustal material.

Nickel levels in terrestrial and aquatic organisms can vary over several orders of magnitude. Typical atmospheric nickel levels for human exposure range from about 5 to 35 ng/m^3 at rural and urban sites. Drinking-water generally contains less than 10 $\mu\text{g}/\text{L}$ of nickel, but occasionally nickel may be released from the plumbing fittings, resulting in concentrations of up to 500 $\mu\text{g}/\text{L}$ of nickel (WHO, 1991).

The atmospheric concentration of nickel in industrialized areas has been estimated to be range 120-170 ng/m^3 while 6-17 ng/m^3 in suburban areas (Nordberg et. al., 1979). Direct leaching from rocks and sediments can produce significant concentrations of nickel in water.

Nickel concentration in deep sea water usually range from 0.1 to 0.5 ppb whereas surface water contains 15-20 ppb. Divalent nickel is the predominate form of nickel in aquatic sources (Nielson, 1987).

Trace element such as nickel (Ni), cadmium (Cd), copper (Co), zinc (Zn), manganese (Mn) and aluminum (Al) analysis in freshwater and seawater is one of the most difficult fields in analytical chemistry. Since 1975, however, seawater and freshwater concentrations of many trace elements have been shown to be factor of 10 to 100 lower than those previously accepted (Leyalen & Wegscheider, 1981).

Nickel was found in the United States (U.S.) waters with a frequency of 16% and at an overall mean concentration of 19 $\mu\text{g/L}$. The detection limit for nickel in water with total dissolved solids of 400 $\mu\text{g/L}$ was 20 $\mu\text{g/L}$. If the dissolved solids amounted to 200 $\mu\text{g/L}$, the detection limit would be 10 $\mu\text{g/L}$. The Missouri River and Western Gulf basins had the lowest frequency of nickel detection and among the lowest mean concentrations, at 5 and 3 $\mu\text{g/L}$, respectively. The highest mean concentration was 130 $\mu\text{g/L}$, which is in the Cuyahoga River at Cleveland, Ohio. The mean concentration of the nickel is based only on occurrences that must be interpreted in light of the frequency of detection (Kopp & Kroner, 1967).

2.3. Voltammetric Determination of Nickel

The existing polarographic methods for the determination of Ni (and Co) are limited by the irreversible electrode process (Crow & Rose, 1979). Even the usage of supporting electrolytes providing a higher reversibility of Ni(II) reduction due to the formation of appropriate complex species did not allow to improve the sensitivity of the determination by differential pulse polarography at the Dropping Mercury Electrode (DME) to more than about 10 µg/L (Peker, Herlem, & Badoz-Lambling, 1967).

A very recent further example developed in the Chemistry Department Institute, Germany laboratory is the analytical procedure for the voltammetric determination of Ni in the routine analysis of waters, biological materials and food. In this study, the peak due to the reduction of Ni(II) appears depending on the composition of the analyte between - 0.90 V and - 1.00 V vs. Ag/AgCl. Usually a linear DC-potential ramp is applied. This has the advantage that a rather fast scan of 20 mV/s can be applied and thus less than 1 min is required to record the voltammogram. Based on the knowledge and optimization of all significant parameters the determination limit could be lowered for Ni(II) in natural waters or in aqueous analytes by more than three orders of magnitude down to 1 ng/L (Iyer, Valenta, & Nurnberg, 1979).

The voltammetric approach has provided due to its inherent properties for the trace analysis of these toxic metals. Nickel one of the most attractive routes of determination and has turned out to be generally in terms of reliability, sensitivity and cost requirements one of the most