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DETERMINATION OF LEAD IN COMMERCIAL MINERAL WATER BY DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMMETRY TECHNIQUE

Dissertation submitted in partial fulfillment for the degree of

Bachelor of Science (Health) in Forensic Science

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CERTIFICATE

This is to certify that dissertation entitled

DETERMINATION OF LEAD IN COMMERCIAL MINERAL WATER BY DIFFERENTIAL PULSE ANODIC STRIPPING VOLTAMMETRY TECHNIQUE

is bonafide record of research work done by

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during period of **December 2005** to **April 2006**
under my supervision

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ABBREVIATIONS

AAS - Atomic Absorption Spectroscopy

ASV - Anodic Stripping Voltammetry

DPASV - Differential Pulse Anodic Stripping Voltammetry

EPA - Environment Protection Agency

FDA - Food and Drugs Administration

GF-AAS - Graphite Furnace Atomic Absorption Spectroscopy

ICP-AES - Inductively Coupled Plasma Atomic Emission Spectroscopy

ICP-MS - Inductively Coupled Plasma Mass Spectroscopy

NAA - Neutron Activation Analysis

ppb - parts per billion

WHO - World Health Organization

ABSTRACT

Voltammetric determination of lead in commercial mineral water using Differential Pulse Anodic Stripping Voltammetry (DPASV) technique is described. The analysis is carried without any pretreatment and using Britton-Robinson buffer as the supporting electrolyte. The electrodes used in this analysis are hanging mercury dropping electrode (HMDE), which act as the working electrode, a platinum electrode as auxiliary electrode and an $Ag/AgKCl_{sat}$ reference electrode, respectively. Optimum voltammetric parameter for the analysis of the samples such as initial potential (E_i), final potential (E_f), deposition potential (E_{acc}), deposition time (t_{acc}) and scan rate (v) are determined prior to sample analysis using lead standard solution. Optimum voltammetric condition of analysis, pH of supporting electrolyte is also determined. The detection of lead is carried out at concentration of 15 parts per billion (ppb). The result shows that the optimum voltammetric parameters for the determination of lead in mineral water were, initial potential, E_i of –0.7 Volt, final potential, E_f of –0.2 Volt, deposition potential, E_{acc} of –0.7 Volt, deposition time, t_{acc} of 140 seconds and scan rate (v) of 0.020 Volt per second was obtained. The pH 3.0 was found out to be the optimum voltammetric condition for the determination of lead in samples. 15 different samples of mineral water were analyzed in this research project. The results show that for all the samples, lead was not detected.

INTRODUCTION

Water is the most important and precious resource. It is a marvelous substance that is flowing, rippling, swirling around obstacles in its path, seeping, dripping, trickling, constantly moving from sea to land and back again. Water can be clear, crystalline, icy green in a mountain stream or black and opaque in a cypress swamp. The shape of a water molecule can be represented roughly by a tetrahedron with oxygen in the center and hydrogen ions at the two corners.

Next to oxygen, water is the most important component for our body. Different organisms need different amounts of water to survive. (Ortleb, *et al.*, 2002). Our body is over 75% water in one form or another. Not only does water form a major component of blood which circulates essential nutrients throughout the body, it also performs innumerable other vital functions. It moistens our lungs to enable respiration, lubricates our joints, keeps the skin and the muscle tone resilient flushes out waste products. It helps the liver in converting fat into energy, keeps the normal body temperature constant and combines with other elements to produce and secrete necessary body fluids. In fact inadequate intake of water can lead to dehydration, the ill effects of which can be severe even fatal. (http://www.naturalmineralwater.com/facts.html). Humans could live for a few weeks without food but only few days without water. (William *et al.*, 2003).

In USA, the Food and Drug Administration (FDA) has categorized bottled water as a food and a minimum standard has been established. FDA classifies the bottled waters as distilled water, fluorinated water, hard water, mineral water, natural water, public water, soft water and spring water which are explained in the Glossary of Water Terms of FDA. However, in Malaysia, bottled waters are only classified into two categories; `natural mineral water' and `packaged drinking water'. As defined in Malaysian Food Act 1983 (anonymous, 1995), natural mineral water shall be ground water which is obtained for human consumption from subterranean water-bearing strata through a spring, well, bore or other exit, with or without the addition of carbon dioxide, while packaged drinking water shall be potable water or treated potable water, other than natural mineral water, that is hermetically sealed in bottles or other packages and is intended for human consumption. (Bahrudin, *et al.*, 1997).

Ground water contains minerals dissolved from the soil through which the water has passed. It also contains some suspended materials. (George, *et al.*, 1994). Mineral water which was derived from this source should be analyzed for its contents to make sure it does not contain excess amount of heavy metals which could harm our body. As stipulated in the WHO's drinking water standards, the standard concentration of lead permitted in drinking water is 0.01 milligram per liter. (http://www.lenntech.com/WHO's-drinking-water-standards.html)

Lead and copper are two of the most useful and common metals in existence. Unfortunately, they have also become environmental hazards in the latter decades of the 20th century. The toxic effects of the two metals, especially lead, have long been recognized. However, lead and copper in drinking water is a relatively new concern, and regulations dealing with the problem are just beginning. (http://www.hhs.state.ne.us/enh/pbcuwatr.htm).

Lead in drinking water is a major global problem. The sources of the lead are from solder, which was used to join copper pipes, and from lead pipes used in older homes and buildings. Over time, lead can leach out and contaminate water.

Acute lead poisoning in children can cause anorexia, vomiting, malaise and convulsions. Permanent brain damage can result. Chronic lead poisoning can cause weightloss, weakness and anemia. (http://www.cypresssystems.com/Experiments/leadtap.html).

According to the U.S. Environmental Protection Agency (EPA), lead dosage that would have little effect on an adult can harm a small child. Lead in drinking water can be a problem for infants whose diet consists of liquids, such as baby formula made with water. Since they are growing, children absorb lead more rapidly than adults. That lead can then impair a child's development, resulting in learning disabilities or stunted growth. (http://www.ces.ncsu.edu/depts/fcs/housing/pubs/fcs395.html).

The EPA has set an "action level" of 0.015 milligrams a liter for lead, meaning that levels higher than that in drinking water could pose a risk to human health. (http://www.hhs.state.ne.us/enh/pbcuwatr.htm).

In this research project, the DPASV was applied to detect the presence of lead in mineral water samples. Anodic Stripping voltammetry (ASV), particularly with the use of pulsed potential waveforms, is one of the most sensitive, convenient, and cost effective analytical method for detection and quantitation of metal contaminants in rivers, lakes, process streams and drinking water. Another advantage is that several metals such as Cu, Pb and Cd can be analyzed simultaneously. ASV has been used for several years to analyze heavy metals such as Cu, Pb, Cd and Zn. (http://www.cypresssystems.com/Experiments/asv.html).

In this experiment, metals, as ions in solution, are plated onto an electrode by applying a negative potential (deposition potential) for a specific period of time (deposition time). The deposition serves to concentrate the metal ions from the solution onto the electrode in the metallic form. If the electrode is Hg, the metals often form an amalgam. After deposition, the potential is scanned toward positive potentials. Current peaks appear at potentials corresponding to the oxidation of metals as they are oxidized (stripped) from the electrode back into the solution. The peak height or area can be correlated with the concentration of the metal ions in the solution.

Differential Pulse Anodic Stripping Voltammetry is used due to their lower detection limits where by for metal ions, it can detect the concentration at sub-ppb concentrations.

(http://www.epsilon-web.net/Ec/manual/Techniques/Stripping/stripping.html).

LITERATURE REVIEW

Stripping analysis has been widely recognized as a powerful tool for trace metal analysis. Its remarkable sensitivity is attributed to the combination of a preconcentration step coupled with differential measurements that generate an extremely favourable signal-to-noise ratio. Mercury electrodes have been traditionally employed for achieving high reproducibility and sensitivity of the stripping technique (Legeai *et al.*, 2006).

According to Dragoe *et al.*, (2005), anodic stripping voltammetry (ASV) is inherently a very sensitive method and its use for trace analysis of heavy metals. Several techniques of anodic stripping voltammetry have been successfully employed for lead detection; most of them involved either hanging mercury drop electrodes, or mercury film electrodes.

Mercury has several advantages as a working electrode. Perhaps its most important advantage is its high overpotential for the reduction of H_3O^+ to H_2 . A species such as Zn^{2+}, which is difficult to reduce at other electrodes without simultaneously reducing H_3O^+, is easily reduced at a mercury-working electrode. Other advantages include the ability of metals to dissolve in the mercury, resulting in the formation of an amalgam, and the ability to easily renew the surface of the electrode by extruding a new drop (Harvey, D., 2000).

Nevertheless, due to obvious toxicity considerations, mercury free analytical systems for lead determination are currently sought. In this respect, the possibility of using disposable screen-printed electrodes has been recently investigated, either for square wave Anodic Stripping Voltammetry, or differential pulse Anodic Stripping Voltammetry (Dragoe *et al.*, 2005).

Shams *et al.*, (2004) also reported that anodic stripping voltammetry that is the most popular stripping voltammetric technique for the determination of trace amounts of metals ions and it is also has always regarded as one of the most sensitive techniques for trace metals analysis (Abdelsalam *et al.*, 2002). Futhermore, these methods, are widely diffused as alternative to spectroscopic techniques in the determination of metals, due to the capability of quantitatively evaluate concentrations up to the trace levels by using a relatively cheap instrumentation. In principle, they allow full or partial metal speciation studies, depending on the complexity of the system (Sannaa *et al.*, 2000).

ASV involves a two-step measurement sequence: (i) electroreducing the ions at a negative potential to form metal deposits on the electrode surface, thereby preconcentrating the analytes, and (ii) selectively electro oxidizing each metal during a slow potential scan toward positive potentials (Sonthalia *et al.*, 2004).

The major advantage of stripping compared with direct voltammetric measurement and other analytical techniques is the pre-concentration factor (Shams *et al.*, 2004). Instead of that, Barbeira *et al.*, (1997) reported that the stripping method has the important advantage over AAS of a lower detection limit.

Sonthalia *et al.*, (2004) in their research states that, anodic stripping voltammetry (ASV) is an established method for trace metal ion analysis in contaminated water samples. Several analytical methods, in addition to ASV, are routinely applied for such measurements: atomic absorption, plasma emission, and X-ray fluorescence spectrometry.

Another advantages of voltammetric techniques is that it require relatively inexpensive instrumentation and are capable of determining elements accurately at trace to ultra-trace levels and have demonstrated ability for multi-element determination (Inam *et al.*, 2000). It becomes the technique of choice, since most of the sensitive and selective and selective methods recently available such as ICP-AES, ICP-MS, GF-AAS and NAA are too expensive to be used in routine analysis. (Shams *et al.*, 2004).

OBJECTIVES

The objectives of this study are ;

i. To determine lead qualitatively in various brands of mineral water.
ii. To determine lead quantitatively in various brands of mineral water.
iii. To develop optimum voltammetric parameters for detection of lead in mineral water using Differential Pulse Anodic Stripping Voltammetry technique.
iv. To develop an optimum voltammetric condition parameter for the detection of lead in mineral water samples using Differential Pulse Anodic Stripping Voltammetry technique.
v. To develop a method for detection of lead in mineral water.

MATERIALS AND METHODS

Chemicals and reagents

The chemicals and reagents used in the preparation of solution such as, boric acid (Merck), glacial acetic acid (Merck), natrium hydroxide (Merck), 32% acid hydrochloric (Merck) and plumbum nitrate ($Pb(NO_3)_2$) stock solution (Merck).

Glassware

Voltammetric cell, volumetric flask 1000 mL, beaker 50 mL, serological pipette 10 mL, pipette filler, analytical pipette 100 μL, pipette tip, bulb pipette and amber bottle.

Sample Collection

15 brands of mineral water were purchased from the supermarket all over the Peninsular Malaysia. The samples were analyzed without any pretreatment using Metrohm 757 VA Computerace Voltammetric Analyser combined with Multimode Electrode (MME) System.

Instrumentation

A Metrohm 757 VA Computrace Voltammetry with three electrode system was used to determine the presence of lead in the mineral water samples. The electrode system consists of a working electrode (mercury electrode), a platinum electrode as the auxiliary electrode and an $Ag/AgCl/KCl_{sat}$ reference electrode. Hanging Mercury Drop Electrode (HMDE) was used as the type of working electrode. The voltammetric parameters such as initial potential (E_i), final potential (E_f), deposition potential (E_{acc}), deposition time (t_{acc}) and scan rate (v) and experimental condition such as a pH of supporting electrolyte were optimized prior to sample analysis. Before starting the analysis, the supporting electrolyte was purged with nitrogen gas for 1200 seconds to remove dissolve oxygen in that solution. A Cyberscan 1000 pH meter had been utilized to check the pH value of the supporting electrolyte in the voltammetric cell prior to any analysis. After gas purging was stopped, the scanning was immediately effective using the pre-conditioned parameters. The peak height (ip) were measured and recorded for each parameter used in optimization procedure. The graph of peak height, ip versus each parameter was plotted.

Experimental

The determination of lead in mineral water is carried out by pursuing the systematic working procedure as below.

Preparation of solution (BRB, 0.04M, NaOH 1M, HCl 1M)

↓

Determination of optimum voltammetric condition (pH)

↓

Determination of optimum voltammetric parameters for sample analysis

1. i. Initial potential, E_i
2. ii. Final potential, E_f
3. iii. Deposition potential, E_{acc}
4. iv. Deposition time, t_{acc}
5. v. Scan rate, ν

↓

Method validation

1. i. Linearity
2. ii. Regression, R^2
3. iii. Sensitivity
4. iv. Limit of detection (L.O.D)

↓

Application for analysis of real samples

Preparation of solutions

Britton-Robinson Buffer (BRB), 0.04 M

BRB with a buffering range from 2.0 to 12 was prepared by dissolving 2.47 g of boric acid (Fluka) in 1000 mL volumetric flask containing distilled water and 2.30 mL glacial acetic acid (Merck) and 2.70 mL orthophosphoric acid (Merck). The solution then diluted to the 1 liter mark of the volumetric flask.

100 mL HCl, 1M

The solution was prepared by adding 9.8 mL of 32% HCl and distilled water up to 100 mL mark of the 100 mL volumetric flask. This solution then was transferred into an amber bottle.

100 mL NaOH, 1M

4 gram of NaOH powder was dissolved into 100 mL of distilled water. The solution was placed in an amber bottle.

Supporting electrolyte

10 mL of BRB, 0.04 M for optimization procedure using lead standard solution.

9 mL of BRB, 0.04 M for sample analysis.

Determination of optimum condition parameter (pH)

The optimum pH of supporting electrolyte for sample analysis is determined. A series of pH were tested. The result was presented in a graph of peak height, ip versus pH.

Determination of optimum voltammetric parameters for sample analysis

All of the analyses were done at selected pH. Triplicate measurements were performed for each selected parameters for each standards. The parameters include, initial and final potential, deposition potential, deposition time and scan rate.

Initial potential, E_i and final potential, E_f

The optimized Initial potential, E_i and final potential, E_f for samples analysis is determined. The optimized initial potential, E_i was the potential that exclude hydrogen potential and the optimized final potential, E_f was the potential before the mercury potential.

Deposition potential, E_{acc}

The optimized deposition potential, E_{acc} is obtained by analyzing a series of selected deposition potential which were, -0.7, -0.6, -0.5, -0.4, -0.3, -0.2, and 0.0 Volt. The findings were as presented in a graph.

Deposition time, t_{acc}

The optimized deposition time, t_{acc} for the determination of the lead in mineral water samples is determined. A series of deposition time (0, 10, 20, 30, 40, 50, 60, 80, 100, 120, 140 and 160 seconds) were tested. The findings were presented in a graph.

Scan rate, v

The optimum scan rate, v for analysis was determined by analyzing lead stock solution with a series of selected scan rate, which were 0.01, 0.015, 0.02, 0.03, 0.040, and 0.050 V/s. The findings for lead standard solution analysis were presented in a graph.

Method validation

A series of different volume (50, 75, 100, 125, 150, 175 and 200 μL) of lead was analyzed against the selected optimum voltammetric parameters and as well as optimum voltammetric condition parameter. Based on the findings, a calibration curve is drawn. The linearity, regression, sensitivity, standard deviation and limit of detection of analysis were calculated.

Analysis of the real samples

9 mL of Britton-Robinson buffer is used as the supporting electrolyte. 1 mL of each sample is added and analyzed at optimum voltammetric condition and optimum voltammetric parameters. In this study, 15 mineral water samples labeled as A, B, C, D, E, F, G, H, I, J, K, L, M, N and O were analyzed. Triplicate measurements were completed for each sample analysis.

Figure 1 : Metrohm 757 VA Computerace Voltammetric Analyser combined with Multimode Electrode (MME) System

Figure 2 : Multimode Electrode (MME) System

Figure 3 : 15 bottles of mineral water sample

RESULTS

All the findings of this study are presented in the form of graphs and tables. It comprises the findings of determination of optimum voltammetric condition (pH), optimum voltammetric parameters (E_i, E_f, E_{acc}, t_{acc} and ν), calibration curve and findings for determination of lead in mineral water samples. The findings are as follows ;

Optimum Voltammetric Condition (pH)

PH value	Peak height, ip (μA)
2	0
3	2.67
4	2.0
5	0
6	0
7	0

Table 4 : Findings for the determination of optimum voltammetric condition (pH of the supporting electrolyte)