VOLTAMMETRIC DETERMINATION OF LEAD IN GUNSHOT RESIDUE SAMPLES

by

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LIST OF ABBREVIATIONS

AAS : Atomic absorption spectroscopy

ASV : Anodic stripping voltammetry

DME : Dropping mercury electrode

DPASV : Differential pulse anodic stripping voltammetry

DPV : Differential pulse voltammetry

ETAAS : electro thermal atomic absorption spectrometry

FAAS : Flame atomic absorption spectroscopy

GSR : Gunshot residue

HMDE : Hanging mercury drop electrode

ICP-MS : Inductive Coupled Plasma- Mass Spectrometry

NaAc : Sodium acetate

NaOH : Sodium hydroxide

SCE : saturated calomel electrode

SMDE : Static mercury drop electrode

SME : Syarikat Malaysia Explosives

LIST OF SYMBOLS

% : Percent

V : Volt

V/s : Volt per second

mV : milli Volt

mVs^{-1} : milli Volt per second

mM : milli Molar

M : Molar

μL : micro Liter

mL : milli Liter

s : Second

R^2 : Correlation coefficient

Ω cm : Ohm centimeter

ppb : Parts per billion

ppm : Parts per million

ABSTRAK

Sisa Tembakan (GSR) yang dihasilkan dari pencucuhan dan pembakaran campuran bahan-bahan mudah terbakar dalam peluru yang terdiri daripada tiga elemen utama iaitu plumbum (Pb), antimoni (Sb) dan barium (Ba). Ia boleh dianalisis dengan menggunakan pelbagai teknik seperti *Gas Chromatography Mass* spektrometri (GC-MS), dan dalam kajian ini, teknik pelucutan anodik voltammetri telah berjaya digunakan untuk mengesan kepekatan Pb dalam sampel dengan penggunaan tenaga elektrik. Parameter voltammetrik yang digunakan untuk menganalisis sampel termasuk kelajuan pengacau pada 2000 rpm, masa keseimbangan pada 5 min, nadi amplitud pada 50 mV, potensi mula pada -1500 mV, voltan langkah masa pada 0.6 s, imbasan pada 10 mV / s, di bawah mod nadi berbeza. Kepekatan Pb pada sasaran kain dan kartrij dianalisis dengan menggunakan voltammetri. Hasil kajian menunjukkan bahawa kepekatan Pb ditemui di lokasi yang berbeza daripada sasaran dalam julat 2.677 ± 0.106 ppb hingga 34.09 ± 0,114 ppb manakala 66.010 ± 0.229 ppb hingga 376.700 ± 2.435 ppb dalam sampel kartrij. Kepekatan Pb dalam (GSR) pada sasaran kain telah dibandingkan antara teknik voltammetri dan teknik spektroskopi penyerapan atom (AAS), menunjukkan bahawa kepekatan Pb diperolehi dengan menggunakan teknik pertama adalah lebih tinggi daripada kedua.

ABSTRACT

Gunshot residue (GSR) produced from the ignition and combustion of mixture of combustible materials in an ammunition mainly consists of three major elements namely lead (Pb), antimony (Sb) and barium (Ba). It can be analyzed using various techniques such as Gas Chromatography Mass Spectrometry (GC-MS), and in this work, anodic stripping voltammetric technique was successfully used to detect the concentration of Pb in the sample by application of an electrical potential. The voltammetric parameters used to analyse the sample include stirrer speed at 2000 rpm, equilibrium time at 5 min, pulse amplitude at 50 mV, start potential at -1500 mV, voltage step time at 0.6 s, sweep rate at 10 mV/s, under differential pulse mode. Concentrations of Pb on the cloth targets and cartridge were analysed using voltammetry. The results showed that concentrations of Pb found at the different locations of the targets with a range of 2.677 ± 0.106 ppb to 34.09 ± 0.114 ppb whereas 66.010 ± 0.229 ppb to 376.700 ± 2.435 ppb in cartridge samples. The concentration of Pb in (GSR) on the cloth target was compared between voltammetric techniques and atomic absorption spectroscopy (AAS) technique, showed that the concentration of Pb obtained using former technique is higher than latter.

CHAPTER 1.0 INTRODUCTION

1.1 Gunshot Residue (GSR).

During the investigation of gunshot cases, it is crucial for an investigator to determine if a firearm has been used to shoot on a target. During firing process, firing pin of a firearm strikes the base of cartridge which chemically flares up very sensitive primer mixture and consequently burns the propellant inside the cartridge (Wallace, 2008). As the pressure resulting from combustion of propellant increases gradually, it pushes the bullet out from the chamber through the barrel of that firearm. Upon that mechanism, the heat and pressure will vapourise the metal elements from primer mixture and exits from the cartridge casing either from the muzzle of firearm or from the ejector port (Siegel & Houck, 2010). Thus the vapourised metal elements will be found near the fired gun, or basically found on the hands of shooter as well as at the vicinity of target (Trimpe, 2011).

Components of the primer mixture consist of fuel, oxidiser and sensitisers contributing to the elements such as antimony (Sb), lead (Pb), and barium (Ba). Other compounds that could also be found are binder such as Arabic gum, glue, and others. These components make up a primer which ignites due to sensitiveness to shock, pressure or impact (Heard, 2008). Investigation on gunshot cases regarding the presence of three elements can be concluded in three ways, namely positive identification with particles containing Pb, Ba and Sb, indication or characteristics of GSR with combination of Pb/Sb, Pb/Ba, or Ba/Sb and also inconclusive result containing only Pb, Ba, or Sb (Heard, 2008).

Gunshot residue is also known as trace evidence because it cannot be seen by the naked eyes and need helps of instrumental technique to assist in determining the firer (Schwoeble & Exline, 2000).

When a bullet moves out from barrel, some of the particles follow the direction of the bullet towards the target, involving gases, flame, and particles from the primer mixture (Bardale, 2011). Following shooting, the closer the muzzle of a firearm, the greater the amount of deposited solid particles on the target and vice versa (Lyle, 2008). Pattern of firearm discharge on a target could aid an investigator to predict the distance range of the shot from a muzzle to a target (Taupin & Cwiklik, 2011).

1.2 Lead

Lead is one of the heavy metal listed in the periodic table with an atomic mass 207.2 g/mol, atomic number 82, melting point of 327°C, boiling point 1755°C and appears as bluish-gray metal. The combinations of lead with other metals form an alloy which can be used in pipes, shots, weights, storage batteries, cable covers, sheets covering from radiation and also the powder charge in ammunition such as lead styphnate. It occurs naturally which can be transferred to the surrounding by process of lead mining. Lead could increase the risk of an individual health where lead toxicity could target on human nervous system, hematological, urological and cardiovascular system (Anon, 2007).

1.3 Voltammetry

Voltammetry is an electroanalytical method that measures the analyte both qualitative and quantitatively through the application current flow. A current flow in an electrode immersed in solution containing compounds that responds with the current (Protti, 2001). Current is measured under condition where the oxidation or reduction rate of an analyte is limited by mass transfer rate of an analyte to the electrode surface which is known as a complete concentration polarisation. This technique enables the analysis of both organic and inorganic compounds, and also metals. Voltammetric technique can be applied to study redox reactions under condition changes, the process of adsorption towards the surface, and also mechanisms of electron transfer at a chemically modified surface of the electrode (Skoog, *et al*., 2004).

Components that are commonly used in a typical voltammetric system are potentiostat, computer and electrochemical cell (Kounaves & Samuel, 1997). Potentiostat is connected with working electrode to keep it in an optimised potential. Current flows from the working electrode towards an auxiliary electrode which can select suitable potential to generate the current equal in absolute value of opposite sign of original at the working electrode earlier (Kaifer & Kaifer, 2011). The cell composed of a material such as glass, Teflon, or polyethylene is used to provide the place of sample analysis. Electrochemical cell of the system is composed of working electrode, auxiliary electrode, and reference electrode to connect the transfer of charge. The oxidation and reduction process occur at the working electrode, causes a mass transport of element to the surface of electrode, and thus generates the current (Kounaves & Samuel, 1997).

Working electrode could be varied in its material including platinum, gold, silver, carbon, and commonly used mercury. Selection of materials depends on electrochemical inertness and ability to produce material into many forms. Based on the liquid nature of mercury, it hangs on the working electrode, and also can be known as hanging mercury drop electrode (HMDE). The mercury is dropped by rotation of a micrometer screw and pushing it out from the reservoir passes through a capillary tube (Harvey, 2000). Advantage of using mercury as working electrode is ability of metal to dissolve in mercury to form amalgam during reduction process. Amalgam is crucial for stripping techniques and able to produce well-defined voltammetric curves (Mikkelsen & Schroder, 2003).

Another type of mercury electrode is dropping mercury electrode (DME) which operates following the law of gravity. Mercury is dropped continuously from the reservoir through capillary tube with finite lifetime of several seconds. The mercury at the end of the lifetime can be removed both manually or self-dislodged and replaced with the new one. Static mercury drop electrode (SMDE) functions using plunger that was generated by a solenoid to manage the flow of mercury. The plunger is then lifted to allow the flow of mercury through capillary tube and form a hanging mercury drop. Activation of solenoid continuously results in sequence of mercury drop which performs either HMDE or DME. The other type of electrode is the mercury film electrode, in which a solid electrode is placed in a solution containing mercury ion and subjects it to reduction process. A thin mercury film is then formed on the surface of electrode (Harvey, 2000).

Another electrode that involved in voltammetric system is the reference electrode. It serves as standard for working electrode in every voltammetric experiment by controlling the potential of working electrode (Kelly, 2009). Basically, measuring potential requires a reference point to generate individual potential by comparing to reference point. Reference electrode is placed in the solution containing the analyte and the potential of analytes is measured by energy difference of the two electrodes. Types of electrode that are commonly used are saturated calomel electrode (SCE).

Other electrode used as a standard reference point is Silver/Silver Chloride electrode (Ag/AgCl). It can be reversible converted to chloride ion Cl^- during voltammetry process. The method is used due to its low solubility of silver halides. Advantages of using this electrode are its application in any orientation, small and compact, and also rarely contaminate the samples during analysis. (Newman & Thomas-Alyea, 2012).

System consists of reference and working electrode are the classic examples of electrochemical cell. The addition of another electrode into the system called auxiliary electrode completes the circuit. Auxiliary electrode or counter electrode allows the passes of current between working electrode and auxiliary electrode. It acts as cathode whereas working electrode as an anode or vice versa (Fuchigami, *et al.*, 2014).

1.3.1 Principle of Analysis

Generally, Protti on his study in (2001), the current that passes the electrode consists of faradaic current and charging current which is also known as capacitive current. Faradaic current follows Faraday laws where it occurs by discharge of electro-active compound whereas capacitive current is due to generation of current at the double layer region of the interfacial region of electrode/electrolyte. Total amount of current at the electrode is measure of the collection of both capacitive current and faradaic current. However, capacitive current acts as non-specific background interference for faradaic current to be measured and needs to be avoided through different voltammetric techniques.

In voltammetric technique, the potential varies accordingly to induce either reduction or oxidation of electroactive species. Thus, current measured from redox reaction is corresponding to the concentration of specific species. During immersion of electrode into the electrolyte, a potential started between the electrode surface and the electrolyte. The phases could be consisting of solid such as metal, or liquid in the form of ions or gases. The potential difference occurs due to charge transfer across the interface that involves an electron transfer. A surface-active group in an ionisable media or dipoles orientation also led to potential difference (Srinivasan, 2006). During analysis, reactant is brought to the surface of electrode by three different means, namely migration, mass transfer and convection (Skoog, *et al.*, 2004). Figure 1.1 shows the orientation at the electrode/electrolyte interface based on different theoretical models. The double layer consists of a compact layer in which the potential changes linearly with distance of electrode surface representing Helmholtz layer, whereas the broader area where the potential changes exponentially represented by Gouy-Chapman layer (Corrosion Consulting, 2016).

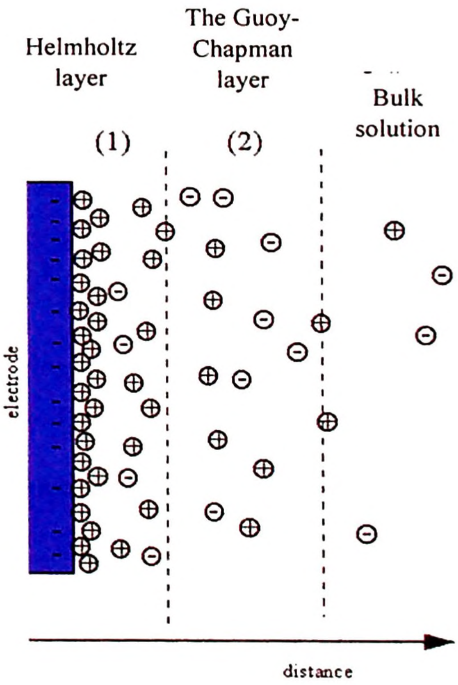


Figure 1.1: Theoretical model of elctrode/electrolyte interface. 1) Helmholtz layer 2) The Guoy-Chapman layer.

Differential Pulse Voltammetry (DPV) involves overlapping of periodical constant pulse of potential with a linear scanning. Measuring of current difference before and after pulse is useful to reduce the elements of capacitive current. The sensitivity of detection ranges between 10-100 μg/L (Protti, 2001). Figure 1.2 shows a potential waveform of different techniques in voltammetry, where A indicates differential pulse, B indicates normal pulse and C indicates square wave voltammetry (Kounaves & Samuel, 1997).

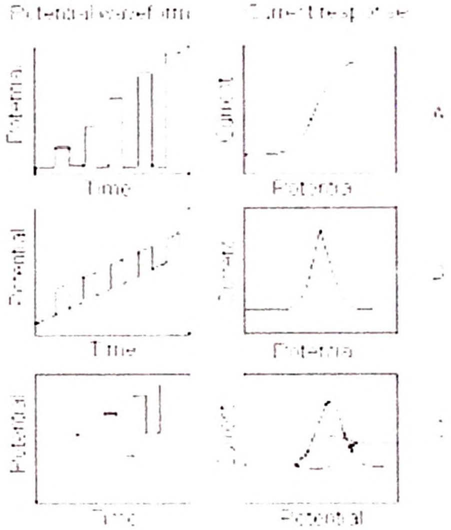


Figure 1.2: The potential waveform of techniques in voltammetry. A) differential pulse; B) normal pulse; C) square-wave voltammetry.

According to International Union of Pure and Applied Chemistry (IUPAC) definition for limit of detection is expressed as concentration obtained at minimum that was detected with reasonable certainty for specific analytical procedure. Stripping voltammetry is known as very sensitive technique as mentioned by Harvey (2000) which able to detect as minimum as 10^{-10} M to 10^{-12} M compared with differential pulse, staircase, square wave that has detection limit of range 10^{-7} M and 10^{-9} M (Mocak, *et al.*, 1997).

CHAPTER 2.0 LITERATURE REVIEW

2.1 Analysis of Lead Determination

The presence of harmful heavy metals in the surroundings such as food, drinking water, water bath, and grounds is unavoidable due to their natural occurrence. Examples heavy metals include arsenic (As), barium (Ba), mercury (Hg), cadmium (Cd), silver (Ag), selenium (Se), lead (Pb), and chromium (Cr). Heavy metals could be exposed into the environment through human activities such as land mining resulting in bioaccumulation in plants, animals and human (Martin & Griswold, 2009). Thus, to avoid elements to be exposed to living things, primary detection of the sources is necessary to generate safety precaution when handling. Voltammetric technique was renowned with the capability to analyse this heavy metals at trace level through the application of electroanalytical system. The detection of heavy metal in bottled water was performed by Chuanuwatanakul, (2008) that suggested a linear relationship between on-line preconcentration and simultaneous determination of Pb(II), Cd(II) and Zn(II) using anodic stripping voltammetry.

In forensic application, the analytical methods used in the investigation of shooting cases involve the detection of elements in Gunshot Residue (GSR). Generally, the presence of Ba, Sb and Pb indicate positive identification of GSR. To enhance the capability of detection, the uses of these methods is necessary to help in investigation. Previously, application of voltammetric technique to detect GSR was performed involving simultaneously detect Pb and Sb by using anodic stripping voltammetry (Brihaye, *et al.*, 1982). Later, the application of differential pulse anodic stripping voltammetry (DPASV) for the detection of GSR was used, showing a successful determination of Pb below the threshold level of 220 ng (Woolever, *et al.*, 1999) and demonstrating a reproducible result performed by Brihaye (1982).

Determination of trace Pb by Flame Atomic Absorption Spectroscopy (FAAS) was performed by applying a pre-concentration and separation techniques, but this technique could not directly detect the sample due to low concentration or the interference of matrices (Bakirciog˘lu , *et al.*, 2003). Other researches also applied these methods due to its fast and easy application (Liu, *et al.*, 2007). Approximately 95% restoration of Cd, Co, and Cu at pH 8.0 and recovery of Cr, Pb, and Fe quantitatively by the operation of model solution buffered with NH_3/NH_4Cl without reagent (Tokalioglu, *et al.*, 2002). Analysis of GSR to rule out the Sb using electro thermal atomic absorption spectrometry (ETAAS) was performed by Fidan & Izgi, (2009) which found that boric acid 5% (m/v) was satisfactory to perform as modifiers for Sb to prevent interference of the analysis GSR determination in biological samples using Zeeman atomic absorption spectrometry based on certain shooting length which measured Pb content of 50 m and 60 m can be differentiated (Lichtenberg, 1987).

2.2 Voltammetric Techniques for GSR Analysis

Many studies about the determination of GSR elements using voltammetry were performed previously by Brihaye, *et. al.* (1982),Woolever, *et al.*, (1999), Woolever, (2001), Rodrigues, *et al.*, (2009), and Salles, *et al.*, (2012) with varying perspective. Brihaye *et. al.* (1982) was one of the pioneer of GSR research using voltammetry which focused on GSR before and after shooting using differential pulse anodic stripping voltammetry (DPASV). Sample collected on the hands of shooter immediately after administration of pistol could be detected by the technique. However, the values obtained could be differed, most probably due to method of sample analysis. DPASV was also used to analyse GSR samples by Woolever (1999) to detect the presence of Pb and Sb which was reproducible compared with previous research (Brihaye, *et al.*, 1982). The limitation of being unable to detect barium was overcome by adjusting the sample preparation method (Woolever & Dewald, 2001). Previous studies of several researcher (Brihaye, *et al.*, 1982; Erden, *et al.*, 2013), suggested the reproducibility of lead on GSR samples by dissolving the sample gathered by cotton swab into nitric acid, HNO_3 to dislodge the metals originated from primer mixture and propellant.

Previous analyses on GSR sample mostly aimed to detect the presence of GSR on the area of suspect's hand and associated weapons (Brihaye, *et al.* 1982; Woolever, *et al.* 1999; Woolever & Dewald, 2001; Rodrigues, *et al.*, 2009; Erden, *et al.*, 2013). A research examines GSR samples on target was performed by Udey *et al.* (2011) using porcine tissue samples and was analysed using Inductive Coupled Plasma-Mass Spectrometry (ICP-MS). There was lacking of study about the distribution of GSR on shooting target. The review about voltammetric technique by Bott (1995) discussed about the sensitiveness of analytical technique for analysis on trace metal element. He also discussed the advantage of the voltammetric method where it was able to distinguish between any chemical forms of metal or metalloid ions.

CHAPTER 3.0 OBJECTIVE

3.1 General Objectives

To determine lead in gunshot residue from the cloth and cartridge samples using anodic stripping voltammetry technique

3.2 Specific Objectives

1. To apply the voltammetric technique for the determination of Pb in gunshot residue sample on the cloth target and cartridge.
2. To study a pattern distribution of Pb in gunshot residue on the cloth target at the point blank (0 m)
3. To build a mapping of the distribution of Pb in gunshot residue based on the concentration of Pb on the cloth target using voltammetric technique.

CHAPTER 4.0 METHODOLOGY

4.1 Materials

4.1.1 Samples

Spent cartridge samples A, B, C, D, E, and F were collected from Kelantan Police authority. There were shot in a closed shooting area in *Ibu Pejabat Daerah* (IPD), Kota Bahru. The cartridge was manufactured by Syarikat Malaysia Explosives (SME), 9 mm, batch 5-04. The cloth target was shot at point blank, (0") using Walther® P99 semi-automatic pistol. Figure 4.1 shows the base of the cartridge labeled "SME", 9 mm, and 5-04. Side view of cartridges A, B, C, D, E, F is illustrated in Figure 4.2 where as the base of cartridge A, B, C, D E, F is illustrated in Figure 4.3. Figure 4.4 shows the cloth target with grid lined at the center of shooting penetration.

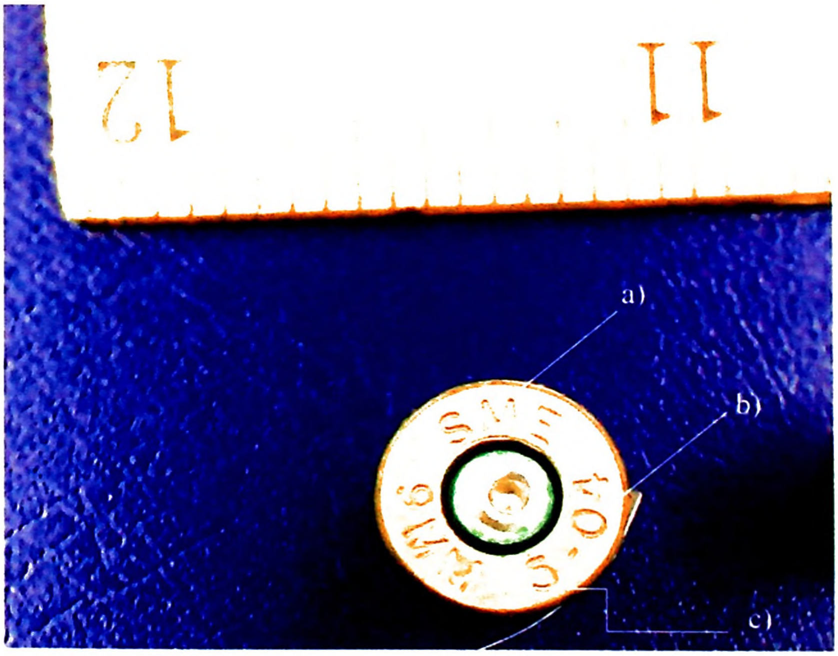


Figure 4.1: Cartridge base. a) Manufacturer; b) Batch number; c) Caliber of cartridge.

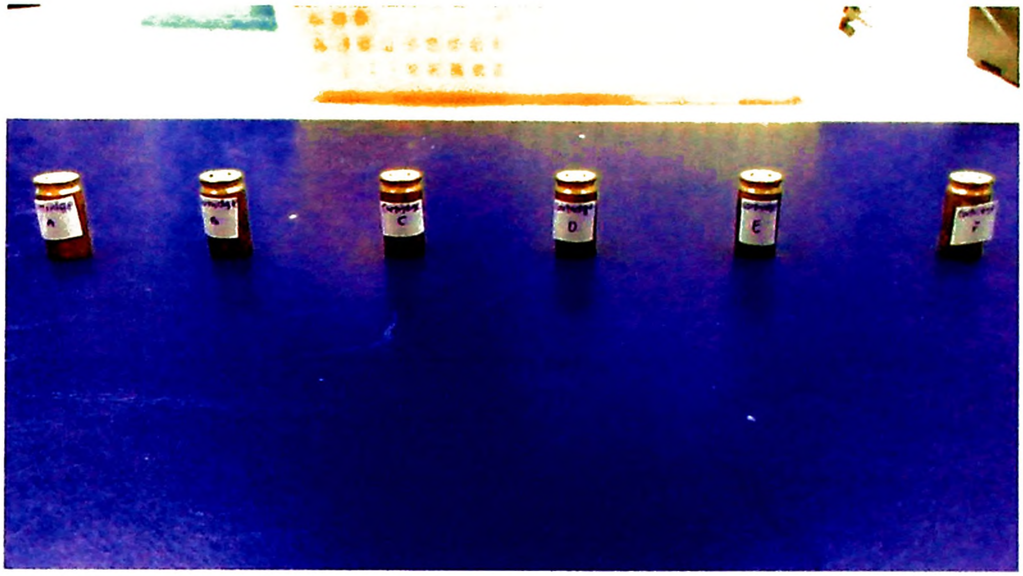


Figure 4.2: Catridges A, B, C, D, E, and F on side view.

Figure 4.3: Bases of the cartridges A, B, C, D, E, and F.

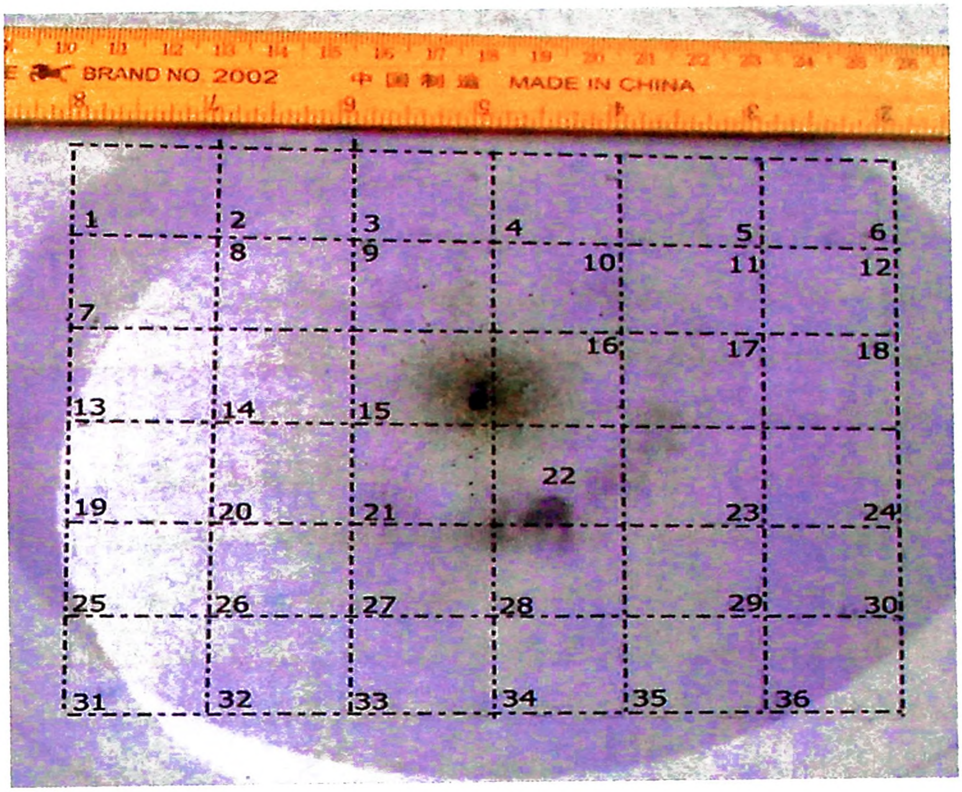


Figure 4.4: The cloth target drawn with grid box.

4.1.2 Chemicals

i. Lead standard solution (Merck, Darmstadt, Germany)

ii. Sodium Acetate

iii. Deionized water

iv. Nitric acid (Fisher Scientific, New Jersey, Canada)

v. Potassium Chloride (Metrohm, Hersiau, Switzerland)

4.1.3 Apparatus

i. Micropipette

ii. Volumetric flask

iii. Micropipette tip

iv. Sterile cotton swab

v. Beaker

4.1.4 Equipment

i. Hannan Instruments pH 211 Microprocessor pH meter

ii. Erla EMS-HP-7000 hot plate and magnetic stirrer

4.1.5 Instrument

Figure 4.5 shows voltammetry of model 797 VA Computrace from Metrohm, Hersiau, Switzerland.

Figure 4.5: 797 VA Computrace. a) monitor; b) voltage supply; c) voltammetric cell d) CPU.

The instrument used in this study was voltammety equipped with monitor, voltage supply and computer processing unit (CPU) from Metrohm, Hersiau, Switzerland as in Figure 4.5. The voltammetry system comprises of three electrodes, namely reference electrode, working electrode, and auxiliary electrode.

4.2 Method

4.2.1 Reagent Preparation

4.2.1.1 Acetate Buffer (pH: 4.64)

In a beaker, 8.26 g of sodium acetate was dissolved with distilled water. After the solid acetate particle dissolved, 6 mL of glacial acetic acid was added and stir it well. The solution was transferred into 100 mL volumetric flask and distilled water was added to mark up to the volume.

4.2.1.2 Lead Standard (0.5 ppm)

Lead standard solution of 0.5 ppm was used in the experiment. 0.005 ml lead standard solution (1000 ppm) was transferred into 10 mL volumetric flask. The deionised water was added to mark up the volume.

4.2.2 Sample Preparation

4.2.2.1 Spent Cartridge

GSR sample in spent cartridge was collected using moist sterile cotton swab by swabbing the internal component of the cartridge. The swab was then transferred into a small beaker and dissolved in deionised water. The solvent was then put into 100 mL volumetric flask and deionised water was added to mark up the volume.

4.2.2.2 The Cloth Target

Grid line was drawn on the cloth target with measurement of 1’× 1’ with total of 36 grid boxes as previously shown in Figure 4.4. Each square was cut and dissolved in 50 mL of deionised water and stirred using magnetic stirrer. The sample in the beaker was then placed on hot plate to dislodge GSR from the cloth target for 10 min. The solution on the beaker was transferred into 100 ml volumetric flask and deionised water was added to mark up the volume.

4.2.2.3 Stripping Voltammetric Analysis

Analysis of samples was performed using Metrohm 797 VA Computrace voltammetry instrument, utilising HMDE. The instrument comprises of three electrodes which were reference electrode using a silver platinum rod, auxiliary electrode by Ag/AgCl solution and working electrode by HMDE. Sample solution was placed into a container to hold three electrodes analysed.

Table 4.1: The parameters used during analysis.

No	Parameters	Value
1	Stirrer Speed	2000 rpm
2	Equilibrium time	5 min
3	Pulse amplitude	50 mV
4	Start potential	-1500 mV
5	Final potential	200 mV
6	Voltage step time	0.6 s
7	Sweep rate	10 mv/s
8	Mode	Differential pulse

Ten mL of sample was placed into electrochemical cell along with 1 mL acetate buffer. The nitrogen gas was purged into the sample to remove all dissolved oxygen.

After equilibrium time, the standard of 0.1 mL was added into the sample as an internal standard and standard addition was repeated for three times linear graph was automatically generated the showing results of Pb concentration. For samples went dilution, the values obtained from the analysis were multiplied with dilution factor to obtain the final concentration of Pb in the sample.

CHAPTER 5.0 RESULTS

5.1 Cartridge samples

Table 5.1shows the concentration of Pb in cartridges A, B, C, D, E and F analysed using voltammetry.

Table 5.1: Pb concentration in cartridge samples.

Samples	**Concentration (ppb)**	**Dilution Factor**	**Actual Concentration (ppb)**	**(Mean ± Standard Deviation) (ppb) n=3**
A	6.601	10×	66.010	66.010 ± 0.029
B	13.329	10×	133.290	133.290 ± 0.260
C	6.657	10×	66.570	66.570 ± 0.081
D	6.189	10×	61.890	61.890 ± 0.136
E	3.341	100×	334.100	334.100 ± 0.086
F	3.767	100×	376.700	376.700 ± 2.435

*n= the number of standard addition

From the results, all the samples from the cartridge were diluted 10× for analysis of sample in a dilute form to detect a trace amount of Pb. Sample cartridge E and F underwent second time dilution of 100×, where at 10× the analysis cannot detect the trace amount of Pb.

Figure 5.1 shows a voltammogram of Pb in cartridge B following the addition of Pb standard. Figure 5.2 shows a plot of current vs concentration.

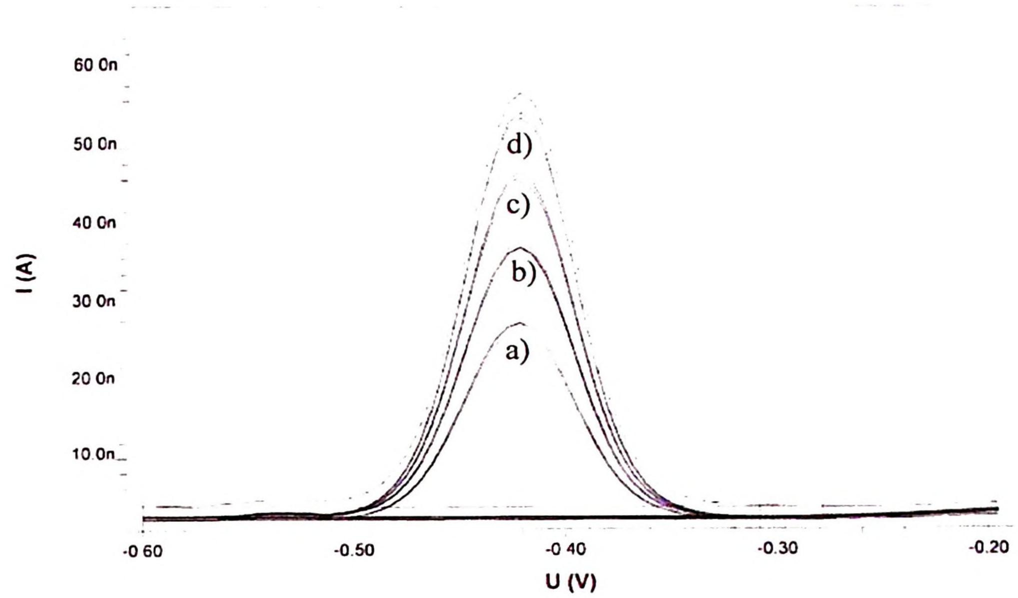


Figure 5.1: Voltammogram of Pb in cartridge B. a) sample; b) standard addition 1 (0.5 ppm); c) standard addition 2 (1.0 ppm; d) standard addition 3 (1.5 ppm).

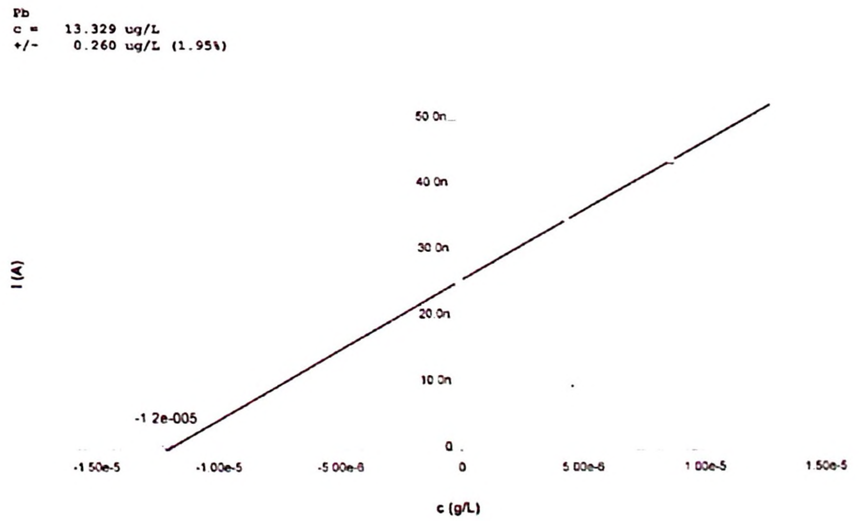


Figure 5.2: Internal standard addition calibration curve of Pb in Cartridge B.

Figure 5.3 shows a voltammogram of Pb in cartridge D following the addition of Pb standard. Figure 5.4 shows a plot of current vs concentration.

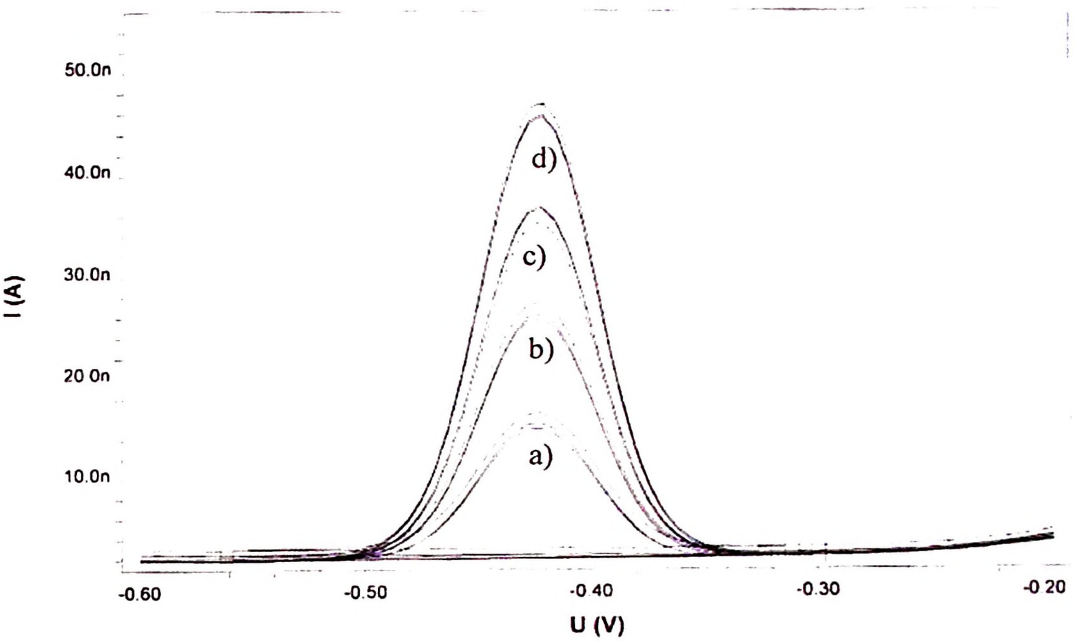
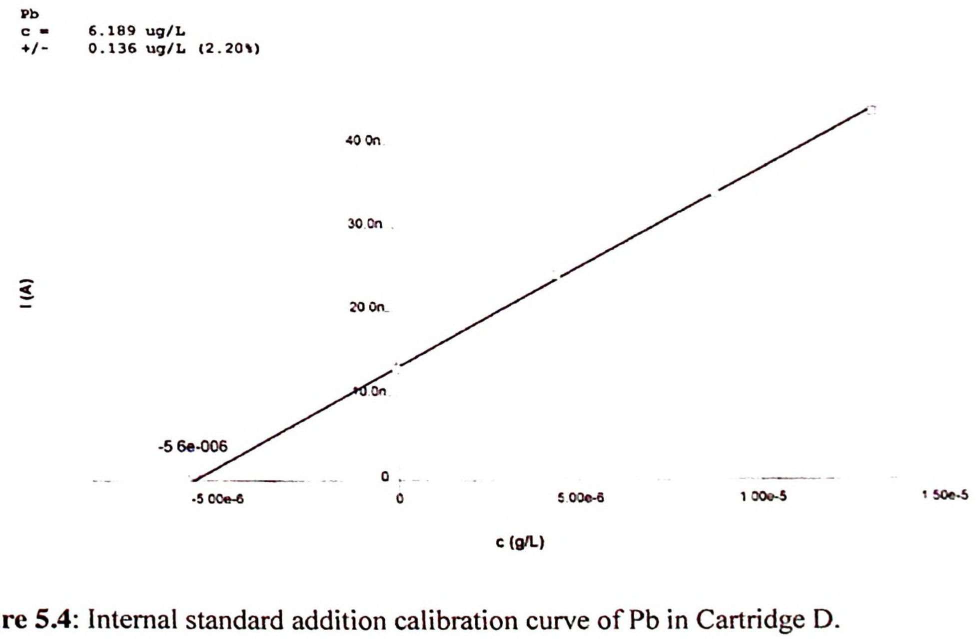


Figure 5.3: Voltammogram of Pb in cartridge D. a)sample; b) standard addition 1 (0.5 ppm); c) standard addition 2 (1.0 ppm); d) standard addition 3 (1.5 ppm).



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Pb
c =     6.189 ug/L
+/-     0.136 ug/L (2.20%)
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Figure 5.4: Internal standard addition calibration curve of Pb in Cartridge D.

Figure 5.5 shows a voltammogram of Pb in cartridge F following the addition of Pb standard. Figure 5.6 shows a plot of current vs concentration.

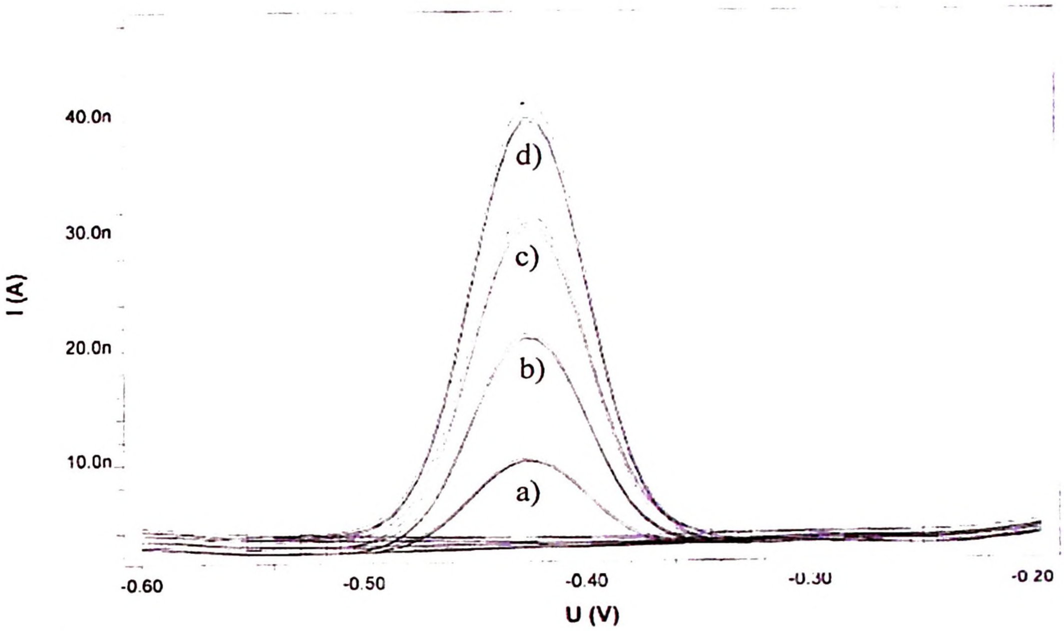
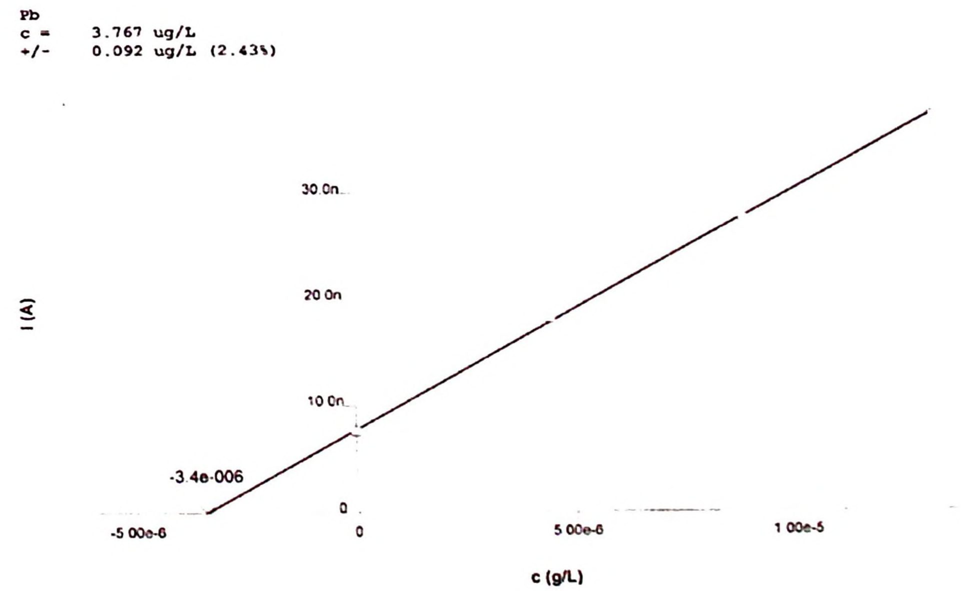


Figure 5.5: Voltammogram of Pb in cartridge F. a)sample; b) standard addition 1 (0.5 ppm); c) standard addition 2 (1.0 ppm); d) standard addition 3 (1.5 ppm).



```
Pb
c =    3.767 ug/L
+/-    0.092 ug/L (2.43%)
```

Figure 5.6: Internal standard addition calibration curve of Pb in Cartridge F.

5.2 Cloth Samples

Table 5.2: Pb concentratration in cloth target the concentration of Pb with 36 pieces of target cloth samples analyzed using voltammetry without dilution due to detection of Pb in trace.

Samples	(Mean ± Standard Deviation) (ppb) n=3	Samples	(Mean ± Standard Deviation) (ppb) n=3
1	4.812 ± 0.178	**18**	2.677 ± 0.106
2	4.675 ± 0.202	**19**	4.456 ± 0.119
3	5.659 ± 0.263	**20**	7.196 ± 0.201
4	3.435 ± 0.098	**21**	24.112 ± 1.258
5	5.423 ± 0.145	**22**	5.063 ± 0.105
6	5.086 ± 0.120	**23**	8.218 ± 0.175
7	6.870 ± 0.196	**24**	8.080 ± 0.706
8	6.974 ± 0.146	**25**	10.806 ± 0.188
9	4.927 ± 0.305	**26**	9.966 ± 0.188
10	6.163 ± 0.166	**27**	12.958 ± 0.343
11	5.056 ± 0.227	**28**	8.724 ± 0.151
12	4.914 ± 0.083	**29**	9.917 ± 0.196
13	6.619 ± 0.350	**30**	6.579 ± 0.212
14	7.034 ± 0.144	**31**	5.719 ± 0.184
15	8.975 ± 0.174	**19**	4.456 ± 0.119
16	8.269 ± 0.118	**20**	7.196 ± 0.201
17	3.047 ± 0.775	**21**	24.112 ± 1.258

Table 5.3: Pb concentration in cloth target sample with dilution. All cloth samples 32, 33, 34, 35, and 36 underwent dilution to allow voltammetry for analysing the trace amount of Pb.

Samples	**Concentration (ppb)**	**Dilution Factor**	**Actual Concentration (ppb)**	**(Mean ± Standard Deviation) (ppb) n= 3**
32	2.211	10x	22.110	22.110 ± 0.223
33	3.369	10x	33.690	33.690 ± 0.094
34	3.409	10x	34.090	34.090 ± 0.114
35	2.653	10x	26.530	26.530 ± 0.149
36	2.443	10x	24.430	24.430 ± 0.164

1 **4.812**	**2** **4.675**	**3** **5.659**	**4** **3.435**	**5** **5.423**	**6** **5.086**
7 **6.870**	**8** **6.974**	**9** **4.927**	**10** **6.163**	**11** **5.056**	**12** **4.914**
13 **6.619**	**14** **7.034**	**15** **8.975**	**16** **8.269**	**17** **3.047**	**18** **2.677**
19 **4.456**	**20** **7.196**	**21** **24.112**	**22** **5.063**	**23** **8.218**	**24** **8.080**
25 **10.806**	**26** **9.966**	**27** **12.958**	**28** **8.724**	**29** **9.917**	**30** **6.579**
31 **5.719**	**32** **22.110**	**33** **33.690**	**34** **34.090**	**35** **26.530**	**36** **24.430**

Figure 5.7: The grid boxes with the concentration of Pb in ppb, which were analysed using voltammetry.

The grid boxes indicated the position of GSR on cloth target and concentrations of Pb detected on each box were stated on target and from that the distribution pattern of Pb in GSR was analysed.