A REAL-TIME MONITORING IONIC LIQUID CHEMICAL SENSOR FOR HEAVY METALS AND TOXIC POLLUTANTS

by

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Dissertation submitted in partial fulfillment of

the requirements for the

Bachelor of Engineering (Hons)

(Chemical Engineering)

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CERTIFICATION OF APPROVAL

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BACHELOR OF ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,

(Assoc. Prof. Dr. Mohd Azmuddin bin Abdullah)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

January 2009

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

YOGENDRAN POONUDURAI

ABSTRACT

Heavy metal and toxic pollutants in water samples cause severe health risks. Current methods used are time consuming, costly, and involve toxic organic solvents. A real-time, ionic liquid monitoring chemical sensor is needed for instantaneous analysis of samples. Ionic liquids, ion compounds with low melting point, have become popular subject of study because of their properties especially non-toxicity, no vapor pressure and electrochemical properties. Recent studies suggest that ionic liquids can be used as solvents, reaction media or electrolyte, substituting volatile organic solvents, for heavy metals and toxic pollutant electrochemical activity. This research focuses on the use of ionic liquid for the development of a chemical sensor to detect and determine toxic analytes especially lead. Lead was chosen as the metal ion for this study due to its effects on children. [HMIM][TFSI] was chosen for this study due to its electrochemical and environmental properties and anodic stripping voltammetry (ASV) was chosen as analysis method due to its sensitivity range, convenience and cost effectiveness. Due to its simplicity and convenience, carbon paste method was chosen to incorporate the ionic liquid into the electrode design. Results show that the ionic liquid modified carbon paste electrodes measure higher current compared to the simple carbon paste electrodes. It is assumed that the modified electrodes are more sensitive to change in measured current compared to the simple ones. However, since [HMIM][TFSI] is a hydrophobic ionic liquid, it alone is not capable of interacting with lead ion since metal ions are always hydrated in a solution. Metal ions were not depositing on the electrode surface and there were no peaks registered in the plot. Through research, it was known that ligands and other types of co-solvents can be used to aid metal ion penetration into the hydrophobic ionic liquid phase. Thus, it is hoped that the project can be expanded by incorporating these ligands into the electrode design in the near future. As a conclusion, the ionic liquid modified carbon paste electrodes shows promising signs to be used as chemical sensors for lead detections due their electrochemical and environmental aspects.

ACKNOWLEDGEMENT

The author would like to convey his gratitude towards Assoc. Prof. Dr. Mohd. Azmuddin bin Abdullah, for being a great supervisor whom has encouraged, enlightened, and educated the author about ionic liquids. The author also would like to convey sincere thanks to Mr. Aamir Amanat Ali Khan who has been of great assistance in guiding the author throughout the whole project. Last but not least, the author wants to thank his fellow group mates, Mohd. Shahrul Amri bin Aminudin, Amir Sharifudin B. Md Surday and Nasirah binti Othman for their support and co-operation.

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CHAPTER ONE
INTRODUCTION

1.1 Background Study

Among industrial hazardous wastes, heavy metal and toxic pollutants such as pesticides have been of primary concern due to their toxicity, resilience and persistence and adverse effect on health (Bloom & Serres, 1996). Lead for example has widespread use in many industrial and chemical processes and the level of lead exposure reported has risen. Food itself may contain lead, especially vegetables and crops that grow in or near the ground and may absorb lead directly from the soil (Barzilay et al., 1999). Traditionally, such trace metal measurements have been carried out in the central laboratory, which involve time-consuming sampling, transportation and storage steps, and bulky atomic spectroscopy instrumentations (Alegret & Merkoçi, 2007). *In-situ* and *on-site* monitoring of trace metals is preferable for most practical situations, since it offers various advantages. However, the determination of heavy metals in samples through continuous monitoring is replete with challenges. To date, there is no sensor that is efficient enough even though many compounds have been synthesized for heavy metal and toxic pollutant detection (Ricco, 1997).

Ionic liquids have intrigued many researchers for its properties such as environmentally-benign, thermal stability, non-flammability, and high ionic conductivity (Kozonoi & Ikeda, 2007). Ionic liquids are compounds that consist of ions and have melting point below 100°C. They are stable at different ranges of temperature, have no measurable vapor pressure unlike volatile organic compounds (VOCs), tunable solubility, non-toxic, recyclable, wide electrochemical potential windows, selective extraction of metals, and can be an excellent electrolyte. Investigations on the solvent extraction of heavy metal ions using ILs have also been carried out (Kozonoi & Ikeda, 2007). Cu, Zn, Pb, and Cd are effectively extracted into [C_4mim][PF6], from aqueous solutions containing dithizone which is an ionic liquid, by controlling pH , (Wei et al., 2003). Thus, ionic liquid has the potential to offer solution for the problems faced by *in-situ* sensor development.

1.2 Problem Statement

The current methods used to test water quality for trace metals and toxic chemicals are usually conducted in a laboratory. These types of tests are normally time consuming, require sampling, transportation and expensive instrumentations. There is a lack of *in-situ* and *on-site* monitoring tools that can provide real-time analysis of samples. Furthermore, in processes such as water quality control, real-time monitoring is indeed needed so that corrective actions and quick decisions can be taken in order to ensure the safety aspect (Alegret & Merkoçi, 2007).

In addition, current methods of analysis largely require the use of volatile organic compounds, (VOCs) and produce wastes that can be hazardous. The solubility of many organic solvents in water is limited. Thus, when such solvent is used on sample with water, interaction between the reactants would be limited, which reduces the performance (Sanghi & Srivastava, 2003). Furthermore, VOCs produce organic vapor that can cause health problems, thermally not stable, and not recyclable.

Selectivity and determination of the amount of analytes present in the system has been a troubling factor. Even though research has been going on to determine lead and other heavy metals in the system for more than a decade, there is still no sensor invented to overcome the problems (Ricco, 1997).

Therefore, this research is focused on developing a chemical sensor that uses ionic liquid to detect heavy metal and toxic chemicals. It is expected that the sensor to be developed is portable, robust, and provide *in-situ*, and real-time monitoring that promotes green technology.

1.3 Objectives and Scope of Study

The objectives of this research were:

- To develop a method of measuring contents of trace metals and toxic chemicals using ionic liquid as solvent, reaction media or electrolyte
- To develop a portable, ionic liquid, economic, real-time monitoring device that incorporates chemical sensor technology for effective heavy metal and toxic chemicals monitoring

The scope of this research would be the study on ionic liquid as the solvent, reaction media or electrolyte in order to develop a chemical sensor for trace metals and toxic chemicals. This would include extensive research on ionic liquid properties, its selectivity over heavy metals, electrochemistry between ionic liquid and analytes, types of electrodes to be used and analytical methods involved in measuring the analytes especially lead.

CHAPTER TWO
LITERATURE REVIEW

2.1 Ionic Liquid as a Sensing Material

There has been a drastic increase in industrial growth past few decades and the impact on the environment is enormous as well. Large amount of industrial wastes were released that eventually pose threat to the people and the environment. In recent studies, heavy metals such as lead in drinking water can have effects on children even at very low amount, as low as 20 ppb (Collin, 2006). Lead is able to travel through groundwater supplies and can climb up the food chain with ease (Hansen, 1994). Children, who are more vulnerable, are subjected to severe health risks including impaired mental development when exposed to lead.

The 11th principle of green chemistry states that there is a "necessity for real-time analysis for prevention of pollution (such as heavy metal and toxic chemicals contamination). In particular, the development of methodologies for real-time, in-process monitoring and control prior to, and in order to avoid, the formation of hazardous substances (Brett, 2007). Environmental Protection Agency, EPA in the United States, has been promoting *in-situ* sensors for monitoring groundwater and treatment systems (EPA, 2002). *In-situ* sensors are needed to detect and determine the concentration of contaminants or to decrease the cost of current trace metal analysis method. It is hoped that ionic liquid can be the answer to these requirements. Ionic liquid is 'a material that is composed of ions, and has a melting point below 100°C (Adams et al., 2004). Ionic liquid, also known as Room Temperature Ionic Liquid, RTIL, is first synthesized by Paul Walden in 1914. Ionic liquids consist cations and anions (as seen in Figure 1) that are linked by H-bonds, dispersive and electrostatic forces. Ionic liquids are mainly imidazolium or pyridium types, but there can be numerous types of RTILs that can be synthesized and tuned as required (Binnemans, 2005).

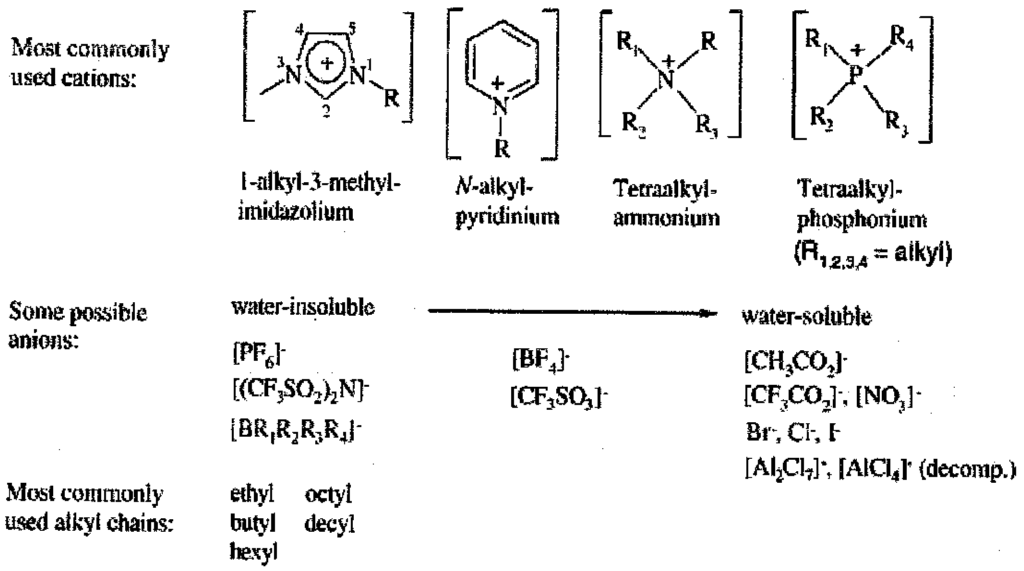


Figure 1: Common cation and anion combinations in ionic liquid synthesis

(Source: (R. Seddon et al., 2000)

The types of ionic liquids for chemical sensor can be designed based on the following wide range of utilities. One can select a specific ionic liquid for a specific pollutant or choose an ionic liquid that is able to interact with variety of pollutants. The main criteria for the selection would be the ability of the ionic liquids to interact with pollutants. Evidence of electrochemical windows, electrochemical potentials, electrodeposition, extraction, solubility and binding ability are assumed to denote the possibility of using such ionic liquid for the development of the chemical sensor. The types of ionic liquids that can be considered for the development of chemical sensor should be task specific.

2.2 Task Specific Ionic Liquids

A task specific ionic liquid, TSIL is the term proposed by Prof. J. H. Davis for heavy metal extracting ionic liquids (Baker et al, 2005). These ionic liquids are sometimes very selective and only interact with a particular metal ion. TSIL are considered as special class of ionic liquids that have functional groups that can be utilized for metal ions extraction from aqueous solutions and capable of acting as both extractants and solvents (Han & Armstrong, 2007). For example, imidazolium cation ionic liquids are capable of interacting and extracting strontium, Sr^{2+} ions due to their high diffusivity coefficient as compared to others (Dai et al, 1999). TSILs are able to extract cations without any ion exchange and some show high selectivity for some metal ions such as mercury, cadmium or actinides (Papaicono et al., 2008). The following sections carry information about some of the ionic liquids and their known metal ion interactions.

2.2.1 [BMIM][PF6]

[BMIM][PF6] is known to be a hydrophobic ionic liquid that is reactive to silver, Ag^{2+}, (He et al., 2004). [BMIM][PF6] also can act as non-task specific ionic liquid and able to interact with many types of metal ions. For example, [BMIM][PF6] added with dithizone, can be used as an alternative solvent to study liquid/liquid extraction of heavy metal ions. Lead, cadmium, mercury, silver, zinc and copper are some of the ions that can be reactive in the above mixture. Cu^{2+} and Ag^{2+} can be extracted effectively at rates up to 97 and 92% respectively (Wei et al., 2003).

2.2.2 [BMIM][Cl]

Co and Co-alloys has electrochemical potentials in 1-butyl-3-methylimidazolium chloride, [BMIM][Cl] (Zell & W.Freyland, 2003).

2.2.3 [BMIM][TFSI]

Copper ions shows high conductivity and extractability in 1-butyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [BMIM][TFSI], (Mekki, et al., 2005).

2.2.4 [BMP][TFSI]

Butylmethylpyrrolidinium bis((trifluoromethyl)sulfonyl)imide, [BMP][TFSI] is a hydrophobic room temperature ionic liquid. Phosphorus chloroxide, $POCl_3$ and Phosphorus trichloride, PCl_3 ions are able to interact with 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, [BMP][TFSI], (Silvester et al., 2006). Tin or Sn ions electrochemical reaction takes place in 1-*n*-butyl-1-methylpyrrolidinium bis((trifluoromethyl)sulfonyl)imide, [BMP][TFSI] at 25 ◦C, (Tachikawa et al., 2008). Palladium and palladium halides are reducible in 1-*n*-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide, [BMP][TFSI] (Bando et al., 2007). Besides that [BMP][TFSI] can be used for electrochemical study of

Manganese ions. It is also acknowledged that the current efficiency of metallic Mn electrodeposition approaches 100% (Deng et al., 2007).

2.2.5 [BMIM][NfO]

1-butyl-3-methylimidazolium nonafluorobutanesulfonate ([BMIM][NfO]) on the other hand, is identified to be interactive with large number of metal ions. The notable ionic reactions would be for the ions such as La (III), Sr (II), Ca (II). Li (I) and Na (I). Electrochemical for other ions using [BMIM][NfO]would be a good study for this project (Kozonoi & Ikeda, 2007).

2.2.6 [DIMCARB]

It was known that lead ions can be reduced in Dimethylamine Carbon Dioxide, DIMCARB (Bhatt et al, 2007). DIMCARB is a recyclable ionic liquid with electrochemical properties that would be ideal to be used in a chemical sensor design.

2.2.7 [EMIM][BF4]

1-ethyl- 3-methylimidazolium tetrafluoroborate [EMIM][BF4] ionic liquid at room temperature also seems to be a good candidate for electrochemical studies for antimony or Sb, tin or Sn ions (Yan et al, 2008).

2.2.8 [EMIM][Cl]

1-ethyl-3 methylimidazolium chloride,[EMIM][Cl] ionic liquid has been previously used for electrochemical study on aluminium ions (Jiang et al, 2006). Mixtures of zinc chloride and 1-ethyl-3-methylimidazolium chloride ($ZnCl2$–[EMIM][Cl]) comprise water-stable ionic liquid systems that are viable alternatives to the aqueous solutions for the electrodeposition of zinc and zinc-containing alloys (Gou & Sun, 2008). The electrodeposition of nickel and nickel–zinc alloys was investigated at polycrystalline tungsten electrode in the $ZnCl2$–[EMIM][Cl] molten salt. The reduction of Ni(II) occurs preferentially than the reduction of Zn(II) in the $ZnCl2$–[EMIM][Cl] molten salt (Gou & Sun, 2008).

2.2.9 [EMICl][BF4]

Antimony, Sb dissolves readily in 1-ethyl-3-methylimidazolium chloride-tetrafluoroborate, [EMICl][BF4] room temperature ionic liquid (Yang & Sun, 2003).

2.2.10 [EMI][DCA]

Besides that, nickel can also be reactive in 1-ethyl-3-methylimidazolium dicyanamide, [EMI][DCA] due to the fact that DCA is a very good ligand anion (Deng et al, 2008).

2.2.11 [OP]

Ionic liquids containing octylpyridinium, [OP] cations are good for extracting mercury ions. When fused with disulfide groups, they are efficient and selective for mercury and copper. Nitrile group on the other hand, are good for silver and palladium (Papaiconomou et al, 2008).

2.2.12 [TMHA][TFSA]

Copper ions are stable in tri-methyl-n-hexylammonium bis((trifluoromethyl)sulfonyl)amide, [TMHA][TFSA] and the current efficiency of cathodic electrodeposition and anodic dissolution can reach almost 100% (Murase et al., 2001), (Katase et al., 2007).

2.3 Ionic Liquids Based On Electrochemical Potential

Ionic liquids with wide electrochemical window also would be ideal to be used for electrochemical studies on many metal ions and toxic pollutants. For example, Tri-butylmethylammonium bis((trifluoromethyl)sulfonyl)imide, [TBMN][TFSI], is able to interact with cesium ions meanwhile (Deng et al, 2007). [Et3NOct][TFSI] ionic liquid has an electrochemical window wide as 5-V (Bhatt et al, 2006). Another example would be Trimethyl-n-hexylammonium bis((trifluoromethyl)sulfonyl)imide ,[TMHA][TFSI] having an electrochemical window of 5.6V at 50°C, and RTIL consisting tetraalkylammonium cations with bistriflimide, Tf2N- anion, and bis(trifluoromethanesulfonyl)imide, TFSI- anion has a wide electrochemical window of about 5V and would be suitable for electrochemical process as well (Murase et al, 2001). Meanwhile, Sun et al. reported that ammonium-imide salts exhibit a large electrochemical window of >4.5V, which is wider than that of alkylimidazolium bis((trifluoromethyl)sulfonyl)amide salts, which can be considered for the development of ionic liquid chemical sensors (J.Sun et al, 1997). [BMP][TFSI] has sufficiently wide electrochemical window comparable to the ammonium-based ionic liquids such as Tri-1-butylmethylammonium bis((trifluoromethyl)sulfonyl)imide, [TBMA][TFSI].

2.4 Ionic Liquids with Ligands as Co-Solvents

Partitioning of metal ions in aqueous solutions is not very effective. Metal ions such as lead ions, have the tendency to remain hydrated. Thus, there will be water molecules attached to the metal ions and this causes problems for metal ion interaction with some ionic liquids. Thus, additional chemicals such as crown ethers (Dai et al., 1993), calixarenes (Luo et al., 2004), ditizone (Wei et al., 2003) and others are added in order to aid the metal ion transfer into the ionic liquid phase. These additives form complexes with metal ions, thus enhancing metal ions partitioning. Thiourea, urea and thioether based ionic liquids have been developed previously in order to extract metal ions effectively, (Visser et al., 2001).

It is also found that some ligands and co-solvents are able to aid ionic liquids in metal ion interaction and extraction. Ligands such as crown ethers are mixed with common ionic liquids to extract metal ions with high efficiency. For example, Dietz et al. found that imidazolium cations with bis((trifluoromethyl)sulfonylimides, [CnMIM][TFSI] in the presence of dicyclohexano-18-crown-6, DCH18C6 crown ether is able to extract strontium and cesium ions from nitrate media with high cationic exchange (Dietz & Stepinski, 2005). DCH18C6 can also be used with 1-alkyl-3- methylimidazolium hexafluorophosphates, to extract K^+, Rb^+, Cs^+, Na^+ and Li^+ (Visser et al, 2000). Some also worked on the use of thioether, thiourea and urea, incorporated in alkyl imidazolium ionic liquids that can be used to extract mercury and cadmium effectively (Visser et al, 2002).

Co-solvents such as Dimethylformamide, DMF are able to increase ionic conductivity in ionic liquids due to their polar properties. The more polar the co-solvent, the higher the ionic conductivity would be (Comminges et al, 2006). (Villagra´na et al, 2004) concluded that ammonia is able to interact in 1-ethyl-3-

methylimidazolium bis(trifluoromethanesulfonylimide) and DMF media and carry out oxidation process in the presence of hydroquinone.

2.5 Chloroaluminate ($Alcl_3^-$) Ionic Liquids as Metal Extractants

Chloroaluminate ionic liquids are ionic liquids that are able to dissolve metal salts, usually chlorides with their Lewis acidity or basicity by changing the composition of $AlCl_3$. Commonly, chloroaluminate ionic liquids have been investigated for electrodeposition of alkaline and alkaline earth metals. Fuller et al. reported that EMI and DMPI chloroaluminate ionic liquids act as solvents for Mg metal ion (Fuller et al, 1998). Electrodeposition of lead ion in an [EMIMCl][$AlCl_3$] ionic liquid has been studies before, by dissolving $PbCl_2$ salt and find that the ion is reduced to metallic Pb (Hussey et al, 1991). The potential of Pb(II)/Pb is reported at 0.4 V.

2.6 Tetrafluoroborate (Bf_4^-) and Hexafluorophosphate (Pf_6^-) Ionic Liquids

Tetrafluoroborate (BF_4^-) and hexafluorophosphate (PF_6^-) are common anions to be used for nonchloroaluminate ionic liquid synthesis. (PF_6^-) is hydrophobic and (BF_4^-) is almost neutral anions. Properties of common anions of ionic liquids are shown in Figure 2. BF_4 ionic liquids are considered to be more moisture stable compared to chloroaluminate ionic liquids. Furthermore, BF_4 anion is not reducible within the potential limits of known organic cations. The reaction between metal ions and BF_4 is not straight forward since the ionic liquid is neutral. However, only small number of metal ions such as antimony and tin (Yan et al, 2008), are able to interact with BF_4 anions. Yan et al (2008) claim that [EMIM][BF4] ionic liquid is a good candidate for electrochemical studies on tin ions. Besides that, [EMIM][BF4] is also able to react with antimony ,Yang et al, (2003).

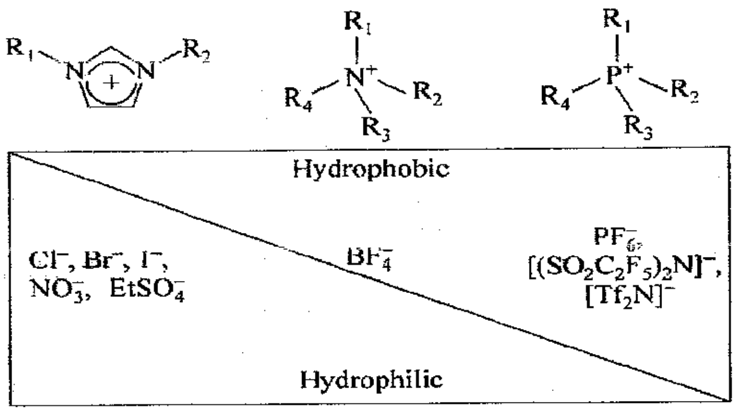


Figure 2: Properties of common anions of ionic liquids

(Source: (Cocalia et al., 2006))

Hexafluorophosphate, PF_6 anions are often used for hydrophobic ionic liquid synthesis. $BMIMPF_6$ is found to be able to interact with silver ions (He et al, 2004), lead, cadmium, mercury, zinc and copper in the presence of dithizone (Wei et al, 2003). However, PF6 is found to be very unstable against moisture and can undergo hydrolysis when it comes in contact with acidic solution. It also forms toxic volatiles such as HF, POF3 and etc when comes into contact with moisture, ad further capable of dissolving glassware and damaging steel (Swatloski et al, 2003). Thus, they are not ideal to be used as sensors in water systems due to environmental and safety issues.

2.7 Other Ionic Liquids

Katayama et al (2005) claim that the cathodic stability of the cations in the ionic liquids alone, is not sufficient for the electrodeposition of metal ions. There are many types of ionic liquids that can be prepared using the combination of quaternary ammonium cations with bis(trifluoromethylsulfonyl)imide,$N(CF_3SO_2)_2^-$, or sometimes called TFSI anion (MacFarlane et al, 2000). These types of ionic liquids are stable against moisture, unlike, chloroaluminate and tetrafluorophosphate ionic liquids. Furthermore, they are benign, water stable, immiscible in water and only a small amount of water dissolves in these ionic liquids. Thus, there won't be any amount of ionic liquid would be lost to the flow if used as a sensor for heavy metal detection in water supplies.

Ionic liquids with TFSI anion are found to be able to interact with wide range of metal ions. Mekki et al (2005) find that copper ions high conductivity and extractability in [BMIM][TFSI]. [BMP][TFSI] has current efficiency of metallic Mn electrodeposition that approaches 100% (Deng et al, 2007). ILs consisting tetra-alkylammonium cations with bistriflimide, [Tf2N] anions, and bis(trifluoromethanesulfonyl)imide, [TFSI] anions have wide electrochemical windows of about 5V and would be suitable for electrochemical process (Murase et al, 2001).

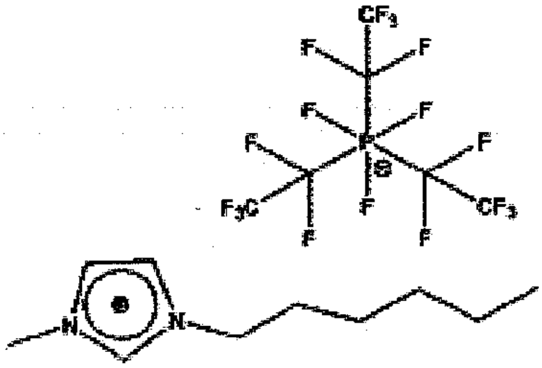
Table 1 : List of ionic liquids and their respective metal ion interactions

Pure Ionic Liquids		
Ionic Liquids	Ions	
[CnMIM]	Sr2+	
Phosphonium	Rare metals, ferrocene	
[BMP][Cl]	PCl3, POCl3	
[BMIM][PF6]	Ag	
[TMHA][TFSA]	Cu	
[CnMIM][Fluorine]	Al	
[EMIM][BF4]	Sn	
[EMIM][Cl]	Zn, Ni	
[EMIM][DCA]	Ni,Al	
[EMI][Cl]+[BF4]	Sb	
DMCARB	Pb	
[BMP][TFSI]	Pd, Pd halides, Mn, PCl3, POCl3, Sn	
[BMIM][Cl]	Co, Co alloys	
[BMIM][NfO]	La, Sr,Ca,Li, Na	
[MBI][Cl]	Ga, Cd, Ni	
Octylpyridinium Disulfide	Hg, Cu	
Octylpyridinium Nitrile	Ag, Pd	
[TBMN][TFSI]	Cs	
[C6MIM][Cl]	Ethanol	
[BMIM][TFSI]	Cu	
[BTMA][Cl]	Al	

Ionic Liquids with ligands mixture		
Ionic Liquids	Ligands	Ions
[CnMIM][TFSI]	DCH18C6	Sr2+, Cs
[CnMIM][PF6]	DCH18C6	K^+, Rb^+, Cs^+, Na^+ and Li^+.
[CnMIM]	thioether, thiourea, urea	Hg, Cd
[EMIM][TFSI]	DMF+ Hydroquinone	NH3
[BMIM][PF6]	dithizone	Pb, Cd, Hg, Ag, Zn, Cu

2.8 1-Hexyl-3-Methyl Imidazolium Bis(Trifluoromethylsulfonyl) Imide

Bis(trifluoromethuylsulfonly)imide or TFSI based ionic liquids have gained large amount of attention and commonly used due to their stability to moisture, air, and high temperature conditions. This anion along with hexyl chained-imidazolium cation has been selected as the standard ionic liquid to be compared with the others (Joanna Achwa, 2006). An ideal electrolyte should have high ionic conductivity, more than 10^{-4} S/cm, large electrochemical windows, fast ion mobility during redox reactions and low volatility. HMIM TFSI has conductivity of $2.6e^{-3}$ S/cm and very low volatile. The TFSI anion has a wide electrochemical window which makes the ionic liquid more stable against oxidation and reduction unlike halide type ionic liquids.



1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide [hmim][Tf2N]

Figure 3: 1-Hexyl-3-Methylimidazolium Bis(trifluoromethylsulfonyl)imide

(*Source* : A. Yokozeki et al., 2008)

Table 2: Comparison of commonly studied ionic liquids with TFSI type ionic liquid

Halide ILs	• Easily oxidized during electrochemical test • Not suitable for electro chemical studies
PF6 ILs	• Unstable against moisture • Undergoes hydrolysis in acidic solution • Creates highly toxic and corrosive volatiles in moist conditions
BF4 ILs	• Metal ion interaction is not straight forward • Not reducible • Only few known metal ion interaction with BF4 type ionic liquid
TFSI ILs	• Electrochemically stable • Medium conductivity • Moisture stable • Benign • Doesn't dissolve in water • Not studied before on lead detection

HMIM TFSI has become the standar ionic liquid to b studied upon due to its green proporties. Its is common now for researchers to make comparison with the ionic liquid they are working on with HMIM TFSI. TFSI type of ionic liquids are considered to be responsive to metal interaction than BF4 type ionic liquids, (Nakashima et al. 2005). It is suspected that cationic exchange of HMIM cation is more prominent than exchange of electrons from the TFSI anions with lead ions. The net electron transfer is explained thorugh the formula below.

$$\mathbf{Pb^{2+} + 2[HMIM][TFSI] \rightarrow Pb[TFSI]_2 + 2[HMIM]^+}$$

Thus, HMIM TFSI was chosen for this study due to its electrochemical and green properties.

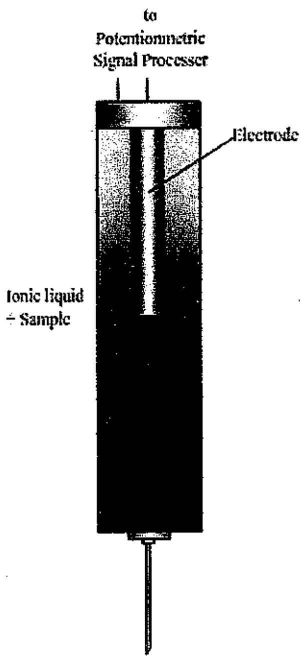
2.9 The Use Of Ionic Liquids In Electrode Development

2.9.1 Liquid Polymer Coated Glassy Carbon Electrodes

Glassy carbon electrodes are isotropic, low porosity, hard, high current conductivity and stable in corrosive media (Tarasevich, 1984). Glassy carbon electrodes are very commonly used for electrochemical studies along with other electrodes such as platinum, silver and etc. The followings are some of the conceptual idea on methods of incorporating ionic liquid into heavy metal detection.

(Sutter et al., 2004) worked on several electrodes such as platinum and silver electrodes, coated with pyrrole conductive polymers for lead ion detection. From their study, it was found that the conductive polymer film able to increase electrodes efficiency in detecting lead ions. Applying the same principle, it is desired to use such surface modified electrode to be used along with ionic liquids that aren't specific to particular metal ions.

Ionic liquids can absorb metal ions into their ionic phase and the lead selective electrode can help to detect only lead ions with the help of the membrane film. Non-specific ionic liquids such as [BMIM][PF6] can be used as to absorb the metal ions into the ionic phase. Furthermore, some ionic liquids can be used to enhance the electrochemical properties of the electrodes (Yu et al., 2005). Thus, in this method, the ionic liquids would act as solvent and electrode enhancer for better metal ion detection.



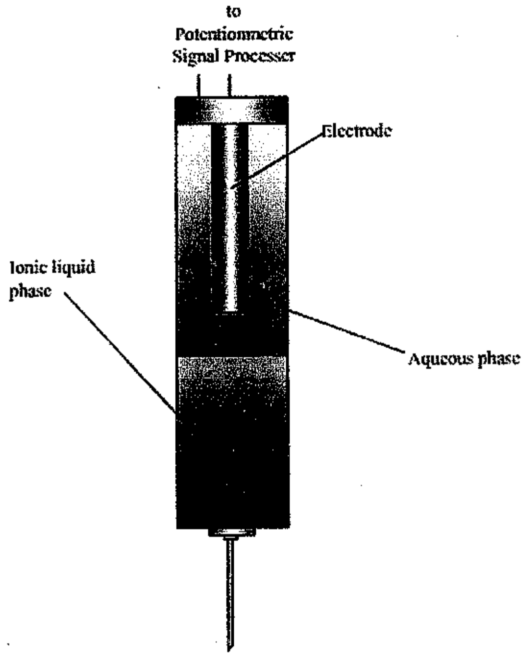


Figure 4 : Single phase system before settling

Figure 5 : Two phase system after settling

2.9.2 Ionic Liquid at Different pH

[BMIM][PF6] is good at extracting ions such as copper and silver into the ionic phase and leave lead in the aqueous phase at lower pH (Wei et al, 2003) found out that. Thus, [BMIM][PF6] can be used to increase the selectivity of the modified glassy carbon electrode by extracting other metal ions and leave behind the lead ions in the aqueous phase at lower pH. Then, the electrode can be used to detect the presence of lead ions in the analyte concentrated aqueous phase.

An ionic liquid with higher density compared to water can be used for this metal ion detection method. A simple syringe setup can be used where the sample is absorbed and mix with the ionic liquid. The ionic liquid would absorb ions such as copper and silver in the ionic phase and leave lead ions in the aqueous phase. Due to density difference, ionic liquid will settle down in the bottom, and the aqueous phase will move to the top. If enough sample is taken, the aqueous face will cover the electrode and measurement can be taken and analyzed.

The ionic liquid to be used for such method needs to be hydrophobic and have different viscosity compared to water. Hydrophobic ionic liquids (Cocalia et al, 2006) are not miscible in water and thus are not lost during sample. The waste can later on further be treated to recover back the ionic liquid. This is a requirement for this to be considered as a green technology. The difference in density will aid the separation of ions into two phases. In this method, the ionic liquid helps to increase the selectivity and increase the analyte concentration in the aqueous phase. Thus, it would be easier to detect and quantify the analytes for the electrode and interference from other analytes can be reduced.

2.9.3 Ionic Liquid with Colorimetric Reagent

The idea is to use ionic liquid along with addtives such as colorometric agents for metal ion detection. Some agents such as Dithizone, exhibit different wavelength absoption level if a particular metal ion is present in the media (Wei et al, 2003). Thus, an optical sensor an be used to detect the change in color similar to a spectrophotometer but at a portable size. The ionic liquid – colorimetric agent mixture to be used needs to exhibit drastic change in color within a short period of time for efficient detection.

2.9.4 Ionic Liquid Modified Carbon Paste Electrodes

There are studies done on modified carbon paste electrode which showed increase in electrode performance (Stozhko et al, 2008). Impurities are added into the graphite structure which changes its properties. In a similar manner, ionic liquids can be added into the graphite electode to increase its selectivity and electrochemical properties. Ionic liquid modified carbon paste electrode has been developed before to detect Dopamine (Sun et al, 2007). Three grams of graphite powder mixed along with 1gram of [BP][PF6] in a mortar and heated at 80°C to obtain a homogeneous carbon paste. The paste is then filled into a 3.8 mm diameter glass tube with a copper wire through it as shown in Figure 6.

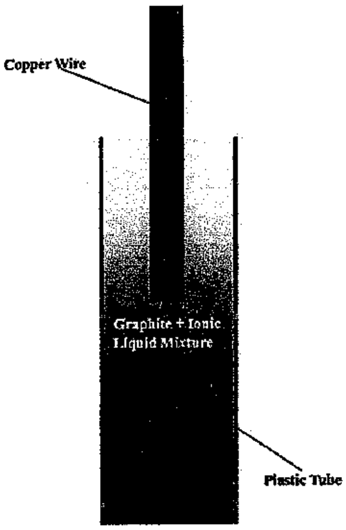


Figure 6 : Ionic Liquid - Carbon Paste Electrode (IL-CPE)

In a similar manner, lead specific ionic liquids can be used to be incorporated into the electrode structure. Not only will it increase the selectivity of the electrode, ionic liquid will also increase the electrochemical properties as stated before. For example, dimethylamine carbon dioxide, DIMCARB, is a lead specific ionic liquid (Bhatt et al, 2007). DIMCARB can be incorporated into the carbon paste electrode both as a binder and enhancer. However, other ionic liquids can be used as well. The modified graphite electrode can be used along with other electrodes for better metal ion analysis since each electrode responds differently to the analytes.

2.10 Proposed Prototype

It is expected that at the end of this study, a proper protoype would be developed based on the design proposed as below.

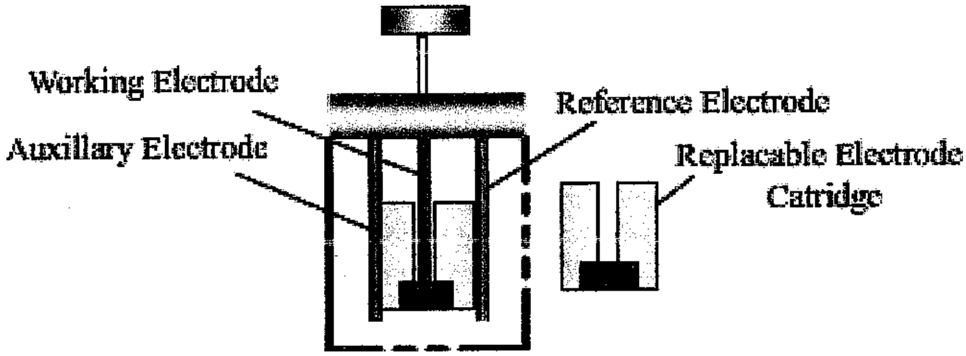


Figure 7: Proposed reloadable ionic liquid heavy metal sensor

It is expected that the carbon paste can be immobilized into the cavity on the teflon tube surface. At this moment, the electrode is to be considered as replacable catridge used along with a detector with exisiting referene and auxilary electrode. After the electrode is placed into the detector, the catridge would be connected with any conductive material and later will be connected to a portable potentiostat.

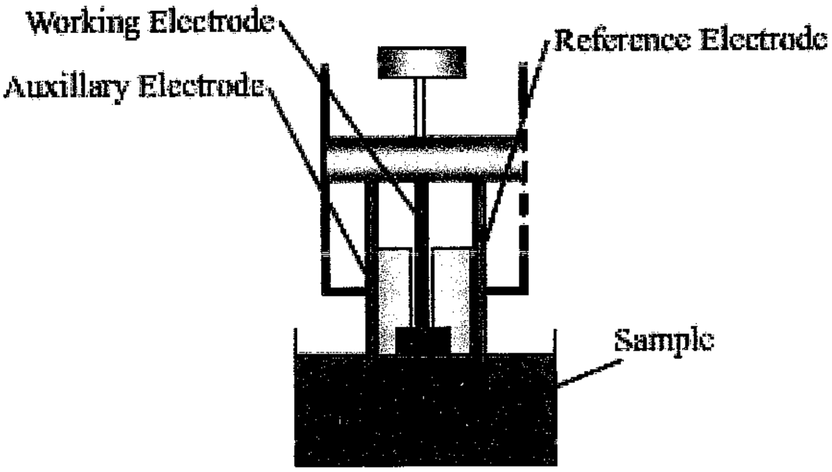


Figure 8: Proposed detection method

Once the electrode is loaded into the detector, the probe is then placed into a sample and measurement is taken using a portable potentiostat.

2.11 Anodic Striping Voltammetry (ASV)

ASV is one of the most sensitive, convenient, and cost effective analytical methods for detection and determination of metal ion contaminants, such as lead, in water whether from rivers, lakes, process streams or drinking sources. With ASV, it is possible to analyze simultaneously very low levels of several metals such as Pb, Cu, Cd and Zn. ASV can detect levels in the range of part-per-million (ppm) or even part-per-billion (ppb) (i.e., ~10^{-10} M).

ASV involves a deposition step (often called pre-concentration) at an applied negative potential for a specified period of time. The metals, as ions in solution, are concentrated by plating them onto the electrode in their metallic form. Then the electrode is scanned linearly toward positive potentials so that the metals, one at a time, is stripped from the electrode and re-oxidized at a potential characteristic of each metal. The resulting current-voltage peaks can be compared with those in a calibration curve done with standard solutions of known quantities of metal ions. Besides determining which metals are present, the quantity of each metal can be correlated to the peak height of the current or the integrated charge under the peak. Thus, this method is ideal to be used for detecting lead particles using the carbon paste electrodes that were to be developed.

The output of the test would be a current versus potential plot. There are normally four notable regions in the graph (Protti, 2001).

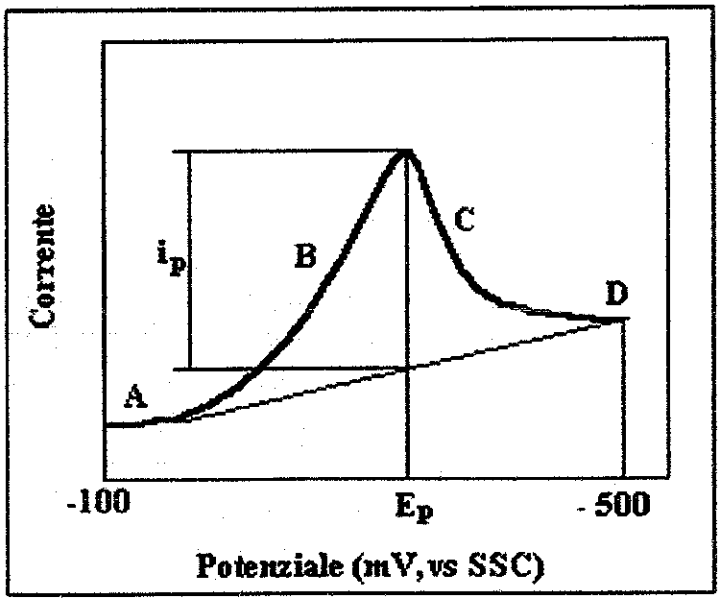


Figure 9 : Current versus potential plot

Background Current (Part A in Figure 8)

At this stage, the potential supplied by the potentiostat is not sufficient enough to discharge any pre-deposited metal ions on the surface of the working electrode. The measured background current can be due to initial resistance of the cell, discharge of oxygen in the solution, the capacitive current, electronic noise of the potentiostat and etc.

Ascending part of the peak (Part B in Figure 8)

The measured current through the working electrode will go up if it's nearing the discharge potential (a point where the ions are discharged from the electrode surface). The lead ions are discharged into the bulk solution and more ions will try to deposit back at the surface.

Descending part of the peak (Part C in Figure 8)

The concentration of lead ions near the electrode surface nears zero. The current starts to decrease as the lead ions won't be able to reach the electrode surface. At this moment, all the lead ions are reduced almost instantaneously before they even have the chance to near the electrode surface. The current trends then diminish as seen in Part D in Figure 8.

Peak Potential (E_p)

The highest point of the graph is denoted at the E_p. This potential peak is than becomes the analytical parameter for qualitative analysis for the lead ions.

Peak current height (i_p)

The peak is considered to be proportional to the concentration of the metal ions in the sample. This parameter is used for the quantitative analysis of the metal ions present.

ASV analysis was carried out with an in-lab potentiostat for prelimnary analysis. Ashwini et al have previously worked on a portable potentiostat and was able to develop a potentiostat with the dimensions of 13x3cm (Ashwini et al., 2005). The potentiostat is portable enough to be carried to sites and cost USD 50 to fabricate.

CHAPTER THREE
METHODOLOGY

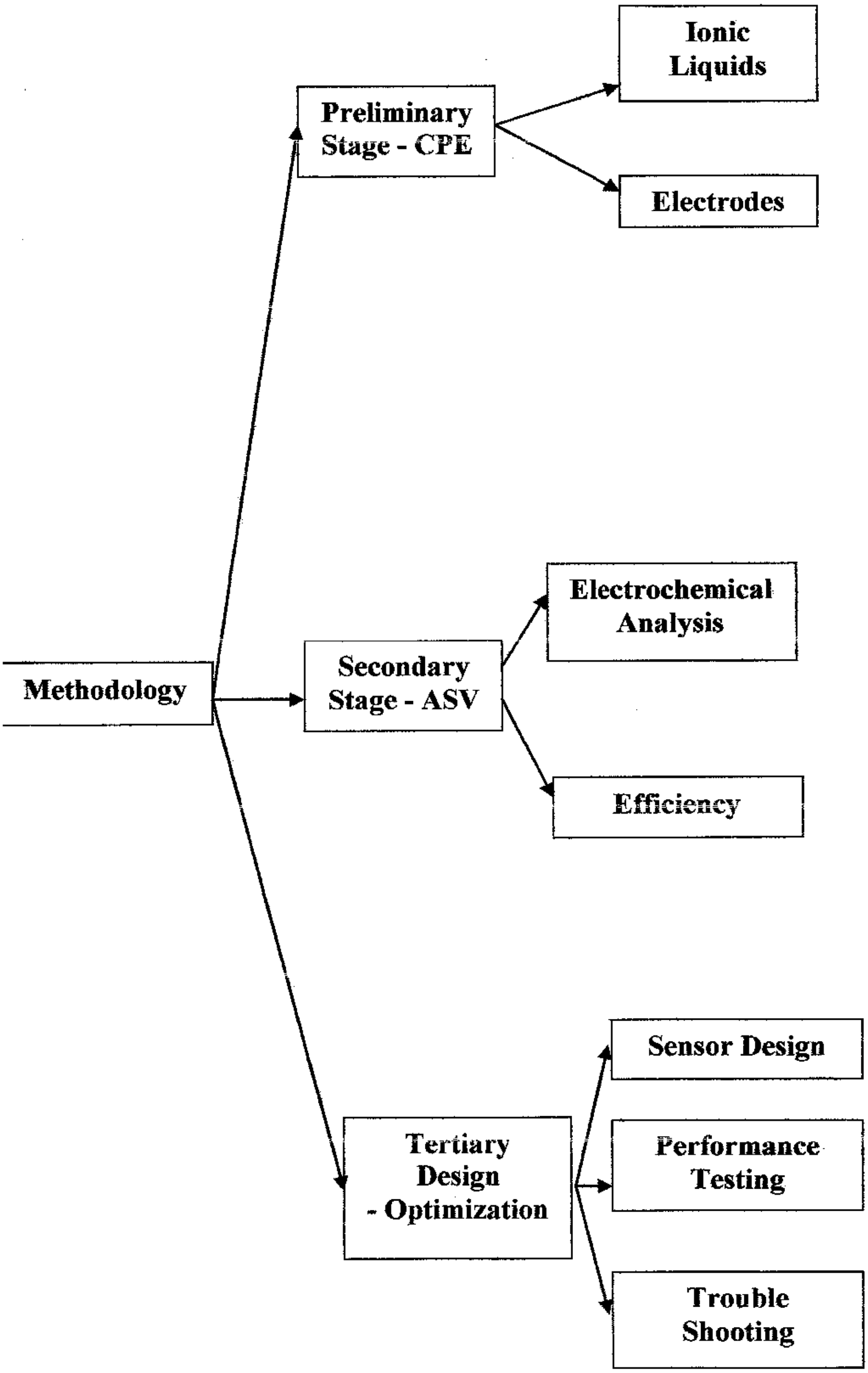


Figure 10: Process Flow of Experimental Design

3.1 Experimental Design

a) Preliminary stage – Preparation of Carbon Paste Electrode (CPE)

For the preliminary stage, the right ionic liquid was chosen. Then, the carbon paste electrode was developed. At first a blank electrode was prepared. 1.0 g graphite powder and 0.5 mL paraffin oil was mixed into a thick paste. The homogeneous paste was packed into a cavity (5mm diameter) at one end of a tube and a copper wire is inserted half way through the other end. Copper wire was added as electrical contact between the paste and measuring device.

The preparation process of the IL-CPE was similar to that of the blank CPE but a replacement of paraffin oil with the chosen IL. Three grams of graphite powder and one gram of IL were mixed thoroughly in a mortar to form a homogeneous carbon paste and further heated at 80 °C for about 1 h. A portion of the carbon paste was filled into one end of a plastic tube and a copper wire was inserted through the opposite end to establish an electrical contact. Prior to use, the surface of the well prepared CPE is smoothed with a sand paper.

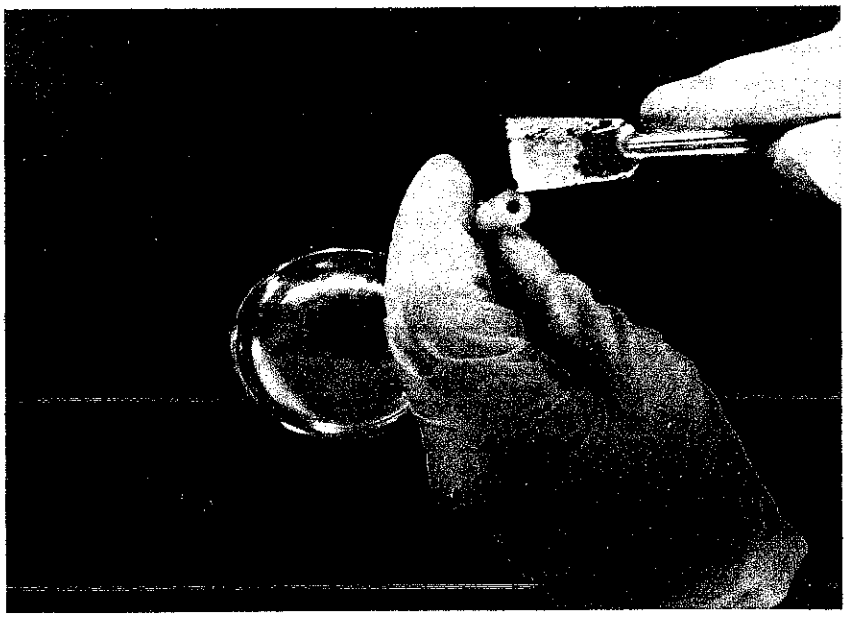


Figure 11 : ionic liquid modified carbon paste is being packed into the Teflon tube cavity

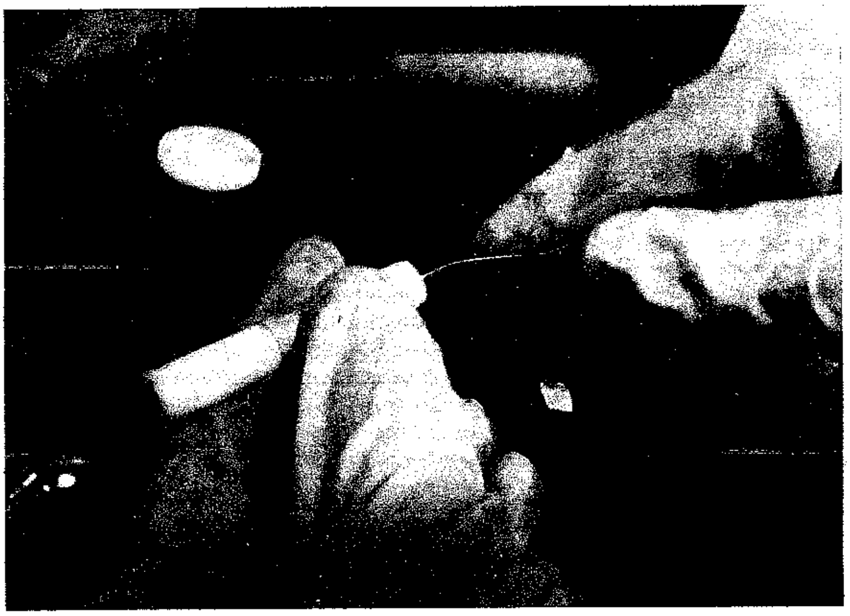


Figure 12 : Copper wire was inserted through the other end of the electrode

b) Secondary stage – Anodic Stripping Analysis

At this stage, the electrode is used in an Anodic Stripping Analysis. First, fresh solutions of Pb^{2+} and Cd^{2+}, 10^{-4} M and 500ml each were prepared. De-ionized water was obtained from the tap and 10ml of 1M HNO_3 was added into each liter in order to preserve its freshness. Then, the electrochemical cell is prepared for analysis. The de-ionized water, doped with HNO_3 was filled into the cell and 5.00 ml of 10mM HCl and 0.05 ml of one of the 10^{-4} M fresh prepared solutions of the metal was introduced into the cell using a pipette. An anodic-stripping analysis under the following conditions was performed using a potentiostat:

Table 3: Anodic Stripping Voltammetry test procedure

Method – Voltammetric analysis: SW	
Deaeration step (bubbling N_2)	t = 120 s
Preconcentration step (Deposition):	E = -800 mV t = 60 s
Rest step (Equilibration):	t = 15 s
Anodic dissolution step:	Potential scan = from -800to 200 mV step duration = 0.1 s step amplitude = 5 mV pulse amplitude = 25 mV
Stirring rate	800 m

Reproducibility

The test was repeated for several times in the same solution for reproducibility. The average and the standard deviation was then reported. Then, the process was repeated with different electrolysis times: from 30 to 120 minutes to see the effect of electrolysis time.

Calibration curve

A calibration curve for the analyzed metal was constructed for two reasons:

(a) To enable rough estimation of the concentration of the metal in the unknowns by comparing peak heights, and

(b) To test if linearity between analytical signal and concentration was obtained in the concentration range of interest.

First, five ml of the 10mM HCl was added into the electrochemical cell. Then, a stripping curve of the blank was recorded. The experiment was repeated with five subsequent additions of 0.05 ml of the 10^{-4} M Pb^{2+} solution. Finally, the calibration curve was plotted using the values obtained.

c) Tertiary Stage - Optimization

At this stage, the values obtained from the analysis were analyzed. Further optimization measures in order to improve the performance of the sensor were also taken into consideration.

3.2 Tools and Equipments

3.2.1 TOOLS

- An analog or computer-controlled potentiostat with appropriate data acquisition equipment
- Electrochemical cell and electrodes
- Graphite powder
- Paraffin oil or silicon oil
- Ionic Liquid – Carbon Paste Electrode
- Pt/ Graphite bar auxiliary electrode
- Ag/AgCl reference electrode

- Sand paper
- A magnetic stirrer and a small bar inside the cell
- 500 ml and 250 ml volumetric flask

3.2.2 CHEMICALS

1. $1.00 \cdot 10^{-4}$ M $Pb(NO_3)_2$ in 10 mM HCl

2. $1.00 \cdot 10^{-4}$ M $CdCl_2$ in 10 mM HCl

3. 10 mM HCl – supporting electrolyte

4. 1 M HNO_3

CHAPTER FOUR
RESULTS AND DISCUSSIONS

4.1 Results

A preliminary scanning electrode microscopy, SEM was done for ionic liquid modified carbon paste of two compositions. SEM was done in order to observe the surface structure of the paste.

Sample No : 1 (1 gram graphite with 250µl [HMIM][TFSI])
Spectrum processing :
No peaks omitted

Processing option : All elements analyzed (Normalised)
Number of iterations = 7
Standard :
C CaCO3 1-Jun-1999 12:00 AM
O SiO2 1-Jun-1999 12:00 AM
F MgF2 1-Jun-1999 12:00 AM
Al Al2O3 1-Jun-1999 12:00 AM
Si SiO2 1-Jun-1999 12:00 AM
S FeS2 1-Jun-1999 12:00 AM
K MAD-10 Feldspar 1-Jun-1999 12:00 AM

Table 4 : Composition of sample 1

Element	Weight%	Atomic%	
C K	70.84	79.31	
O K	10.54	8.86	
F K	13.68	9.69	
Al K	0.45	0.22	
Si K	0.95	0.46	
S K	3.32	1.39	
K K	0.22	0.07	
Totals	100.00		

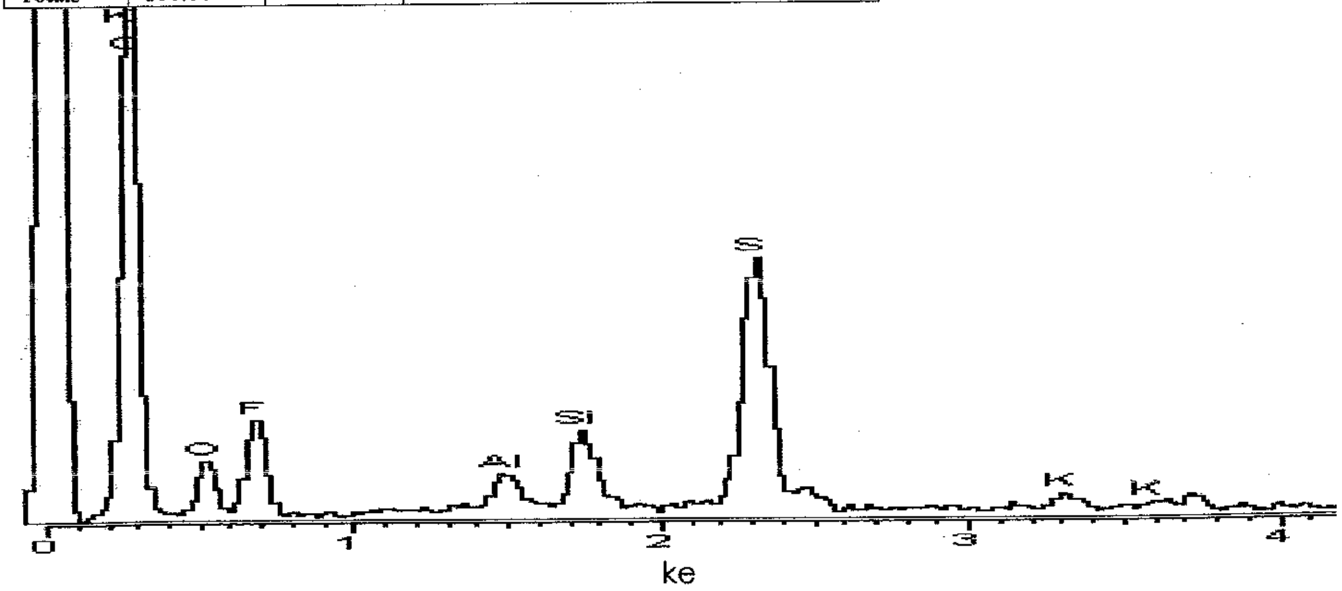


Figure 13: Composition analysis of sample 1

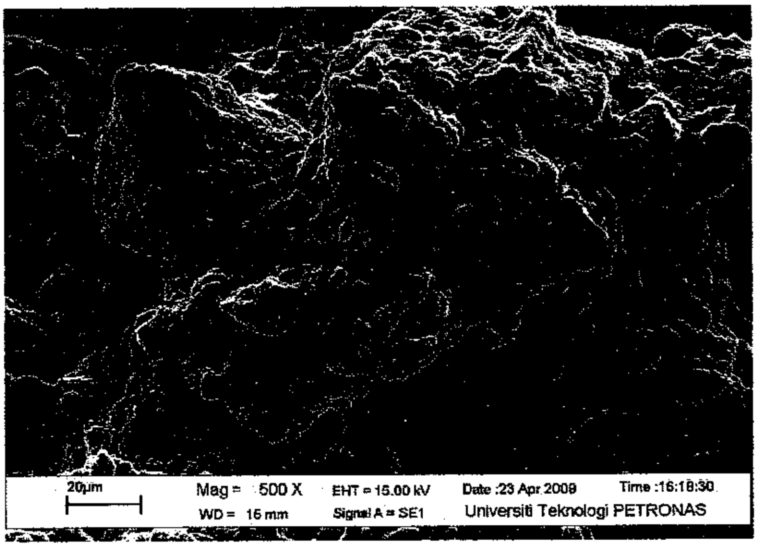


Figure 14 : Sample 1 at 500X magnification

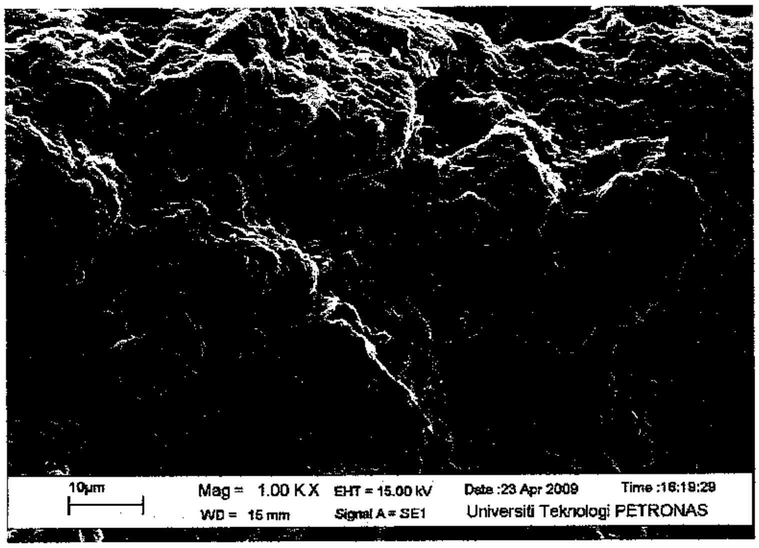


Figure 15 : Sample 1 at 1000X magnification

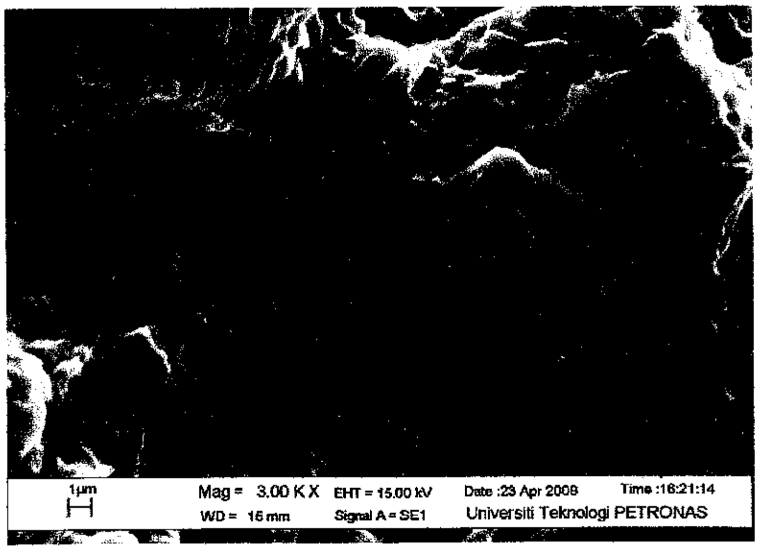


Figure 16 : Sample 1 at 3000X magnification

Sample No : 2 (0.75 gram graphite with 250μl [HMIM][TFSI])
Spectrum processing :
Peak possibly omitted : 9.720 keV

Processing option : All elements analyzed (Normalised)
Number of iterations = 6

Standard :
C CaCO3 1-Jun-1999 12:00 AM
O SiO2 1-Jun-1999 12:00 AM
F MgF2 1-Jun-1999 12:00 AM
Al Al2O3 1-Jun-1999 12:00 AM
Si SiO2 1-Jun-1999 12:00 AM
S FeS2 1-Jun-1999 12:00 AM
K MAD-10 Feldspar 1-Jun-1999 12:00 AM
Ca Wollastonite 1-Jun-1999 12:00 AM
Fe Fe 1-Jun-1999 12:00 AM

Table 5 : Composition of sample 2

Element	Weight%	Atomic%	
C K	63.58	73.14	
O K	19.51	16.85	
F K	8.49	6.17	
Al K	1.04	0.53	
Si K	4.30	2.12	
S K	2.09	0.90	
K K	0.29	0.10	
Ca K	0.19	0.07	
Fe K	0.52	0.13	
Totals	100.00		

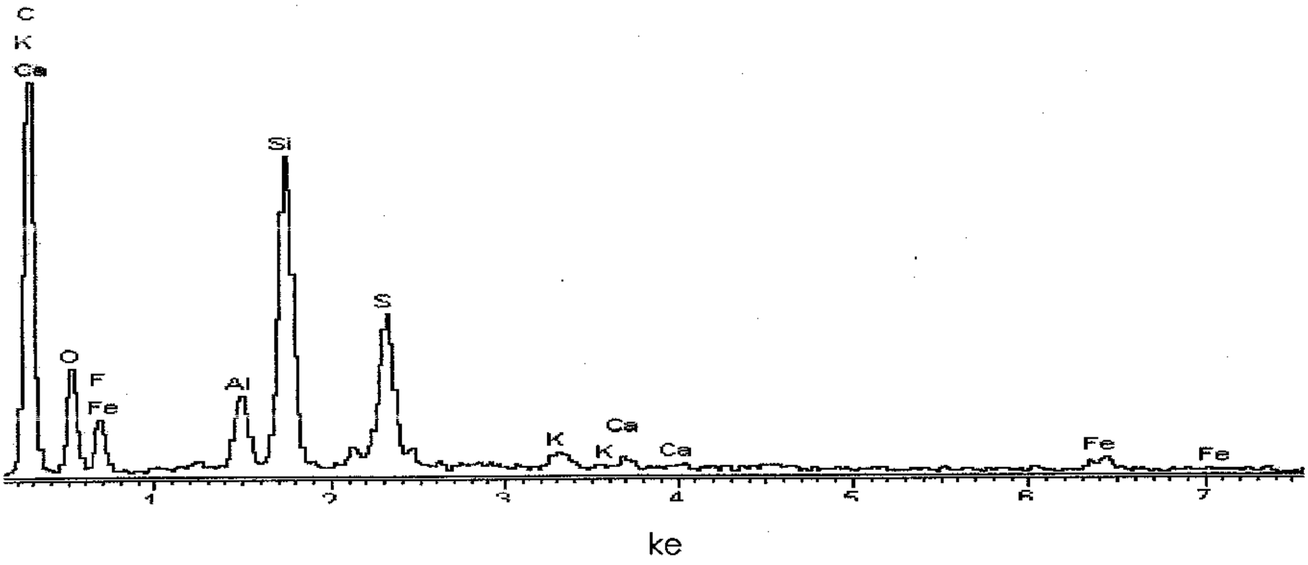


Figure 17: Composition analysis of sample 2

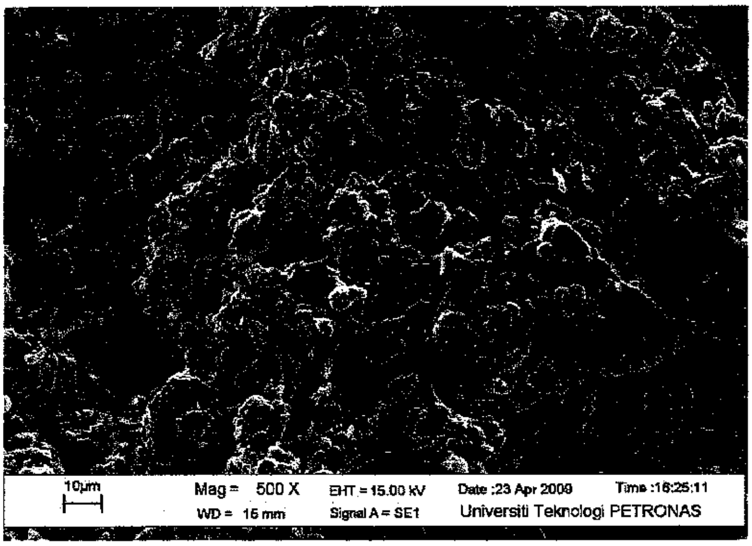


Figure 18 : Sample 2 at 500X magnification

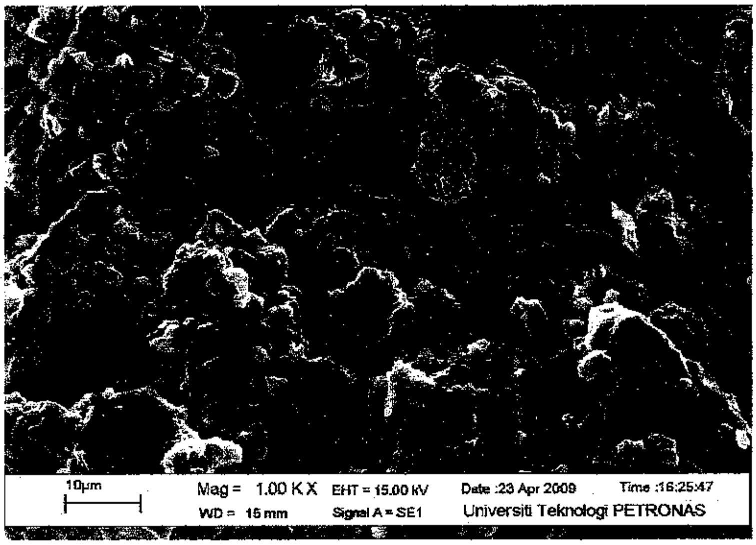


Figure 19 : Sample 2 at 1000X magnification

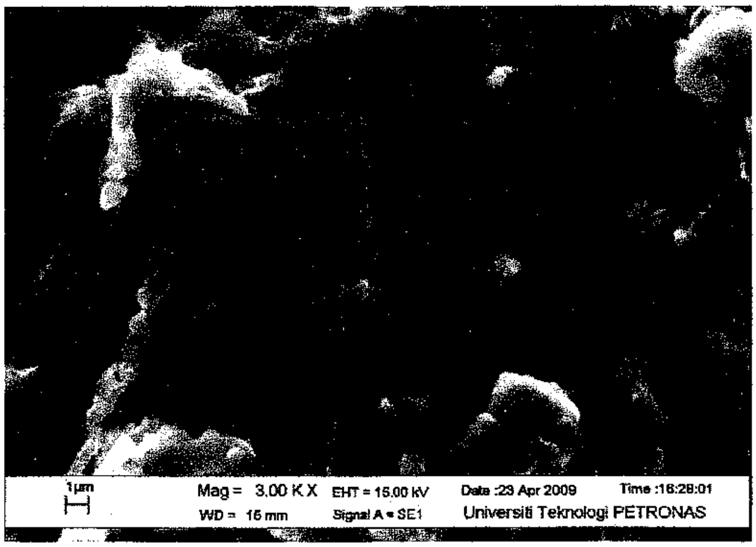


Figure 20 : Sample 2 at 3000X magnification

Some square wave tests were carried using AUT71531 potentiostat, analyzing the performance of simple carbon paste electrodes and ionic liquid modified electrodes. The tests were carried out based on the following parameters:

Reference electrode : Potassium Chloride in Silver/Silver Chloride KCl|Ag|AgCl
Counter electrode : Graphite electrode
Working : Simple carbon paste electrode, ionic liquid modified carbon paste electrodes
Electrolyte solution : 100ml 10mM of Hydrochloric Acid
Analyte solution : 10ml $1x10^{-6}$ M $Pb(NO_3)_2$

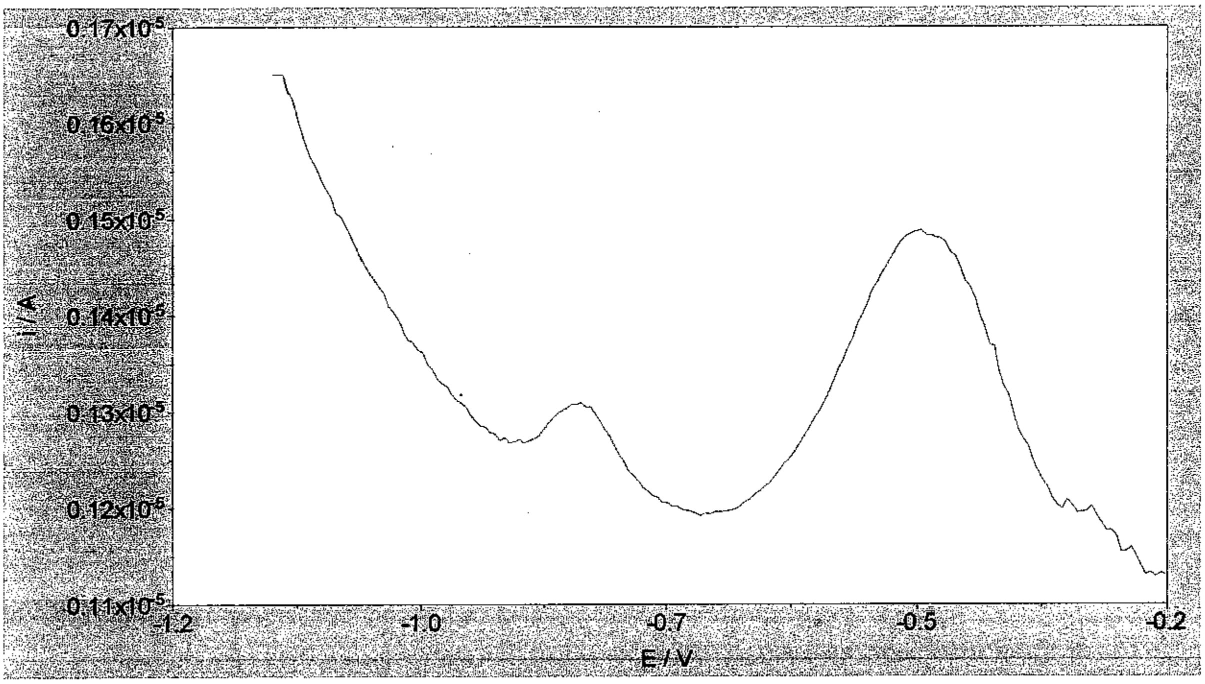


Figure 21 : Current vs Potential plot for simple carbon paste electrode in 10mM KCl

The figure above shows the plot of current versus potential for simple unmodified graphite electrode which was obtained from the analyzer. There are two peaks visible in the plot, present within the potential range of -1.1 to 0.2V. It is assumed that the analytes are emitting certain amount of charge when they are being stripped away from the electrode surface. The current passes through the electrode and later measured by the equipment. Thus, a peak is registered when there is any current is emitted by the analytes.

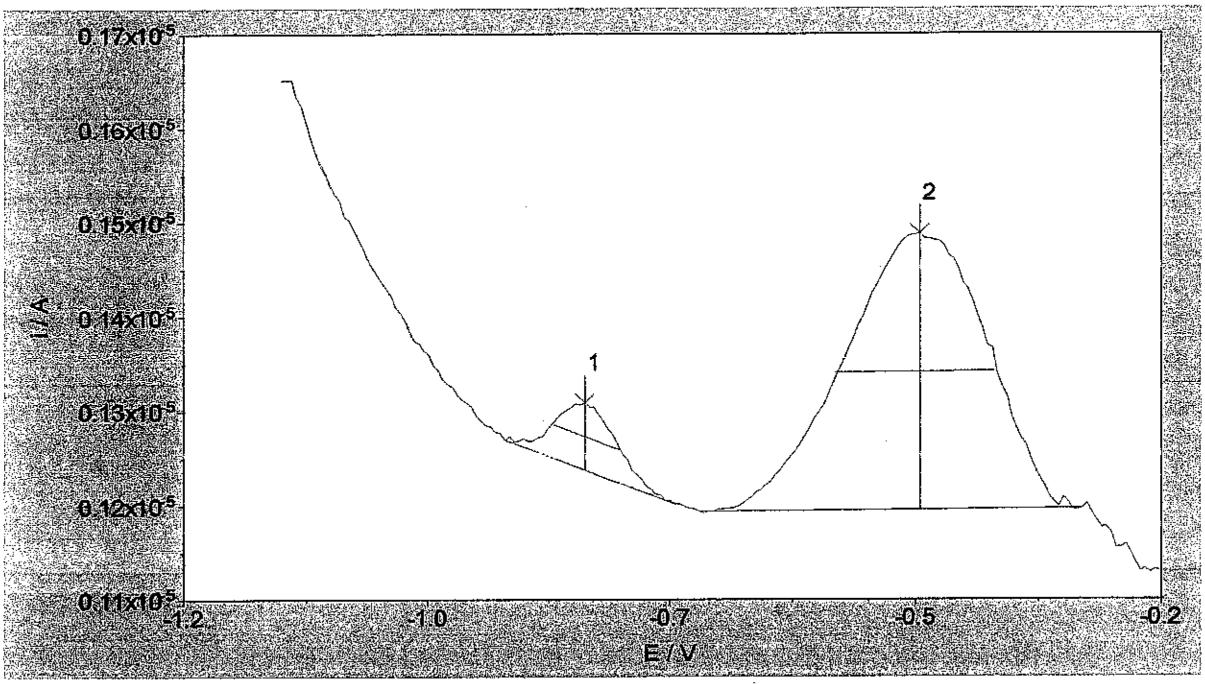


Figure 22: Peak search analysis for simple carbon paste electrode plot in 10mM KCl

Table 6: Data of peak search analysis for simple carbon paste electrode in 10mM KCl

No. of Peaks	Position	Height	Area	Width (1/2)	Derivative
01	-0.788	7.134e-8	5.310e-9	0.068	2.725e-6
02	-0.446	2.929e-7	4.896e-8	0.161	5.506e-6

A peak search analysis was carried out and the data are presented in the table above. The first peak is registered at -0.788 V, with a height of 5.308e-9 A and area of 7.13e-8. The second peak is at -0.446 V, with a height of 2.929e-7 A and area of 4.896e-8. The highest value of the current registered is proportional to the concentration of the analyte at the surface of the sensor. Thus, the potential registered would be the qualitative parameter and the current height would be the quantitative parameter for the lead ion detection.

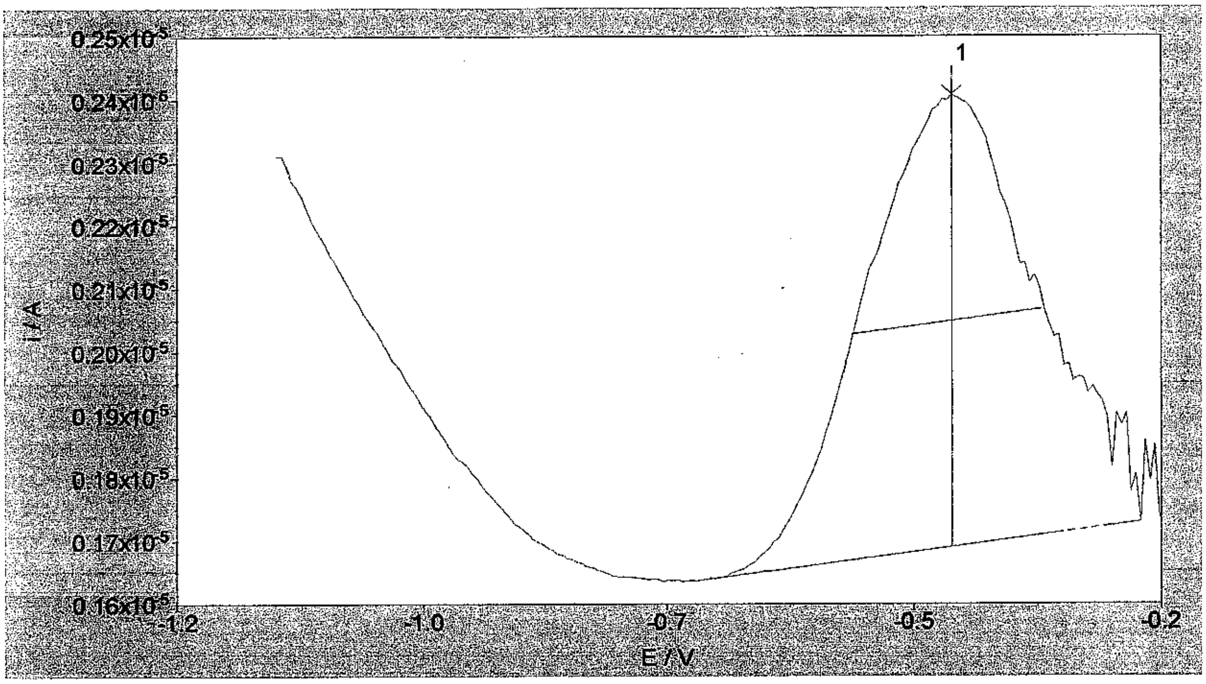


Figure 23: Peak search analysis for simple carbon paste electrode plot in 10mM KCl + 10ml 1µM $Pb(NO_3)_2$

Table 7: Data of peak search analysis for simple carbon paste electrode in 10mM KCl + 10ml 1µM $Pb(NO_3)_2$

No. of Peaks	Position	Height	Area	Width (1/2)	Derivative
01	-0.412	7.168e-7	1.445e-7	0.190	1.162e-5

A peak search analysis for simple carbon paste electrode in 10mM KCl + 10ml 1µM $Pb(NO_3)_2$ was carried out and the data are presented in the table above. The peak is refisted at -0.412 V with a height of 7.16e-7 A and area of 1.445e-7. Compared to the results above, the sensor registered a current difference of 4e-7A. Since the height of the peak has changed, it can be assumed that there were more ions discharged from the surface at -0.4V.

The plot should be registered around -0.13V, since lead ion has half electrode potential of -0.13V. The higher the peaks, more the quantity of lead ions discharge themselves from the electrode surface. Ideally, only one peak needs to be registered at the potential of -0.13V for lead ions in order to consider the sensor is exact.

Few tests were carried on the ionic liquid modified carbon paste electrodes and the results are presented below.

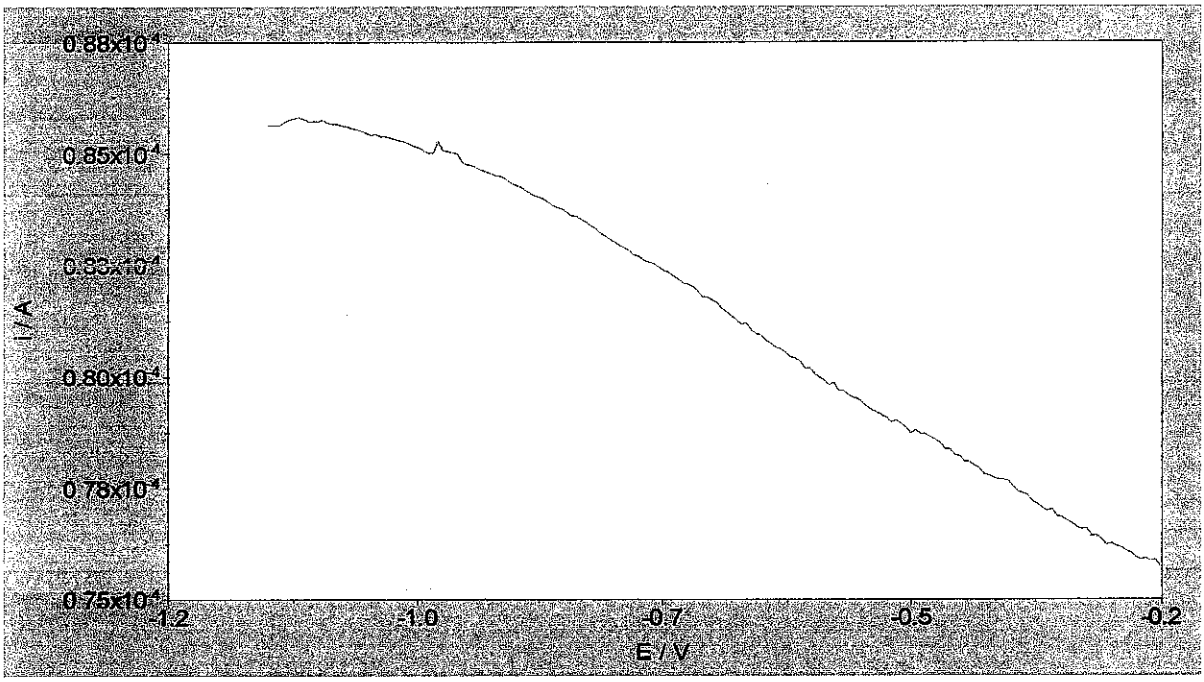


Figure 24 : Current vs Potential plot for 100μl Hmim TFSI carbon paste electrode plot in 10mM KCl

100μl Hmim TFSI ionic liquid was added to 1 gram of graphite powder without any paraffin oil. This was to test the effect of ionic liquid on the conductivity and the ability to bind with the graphite powder without the help of paraffin oil. The electrode recorded current in the 0.75-0.88x10^{-4}A range. As seen in the graph, there are no noticeable peaks in the plot as there are no lead ions. The graph moves downward meaning that there are no ions present anywhere close to the electrode. The current decreases because the potential scanning velocity is so high that the analyte is not able to reach the electrode early. It is assumed that all the ions arriving near the electrode are reduced immediately.

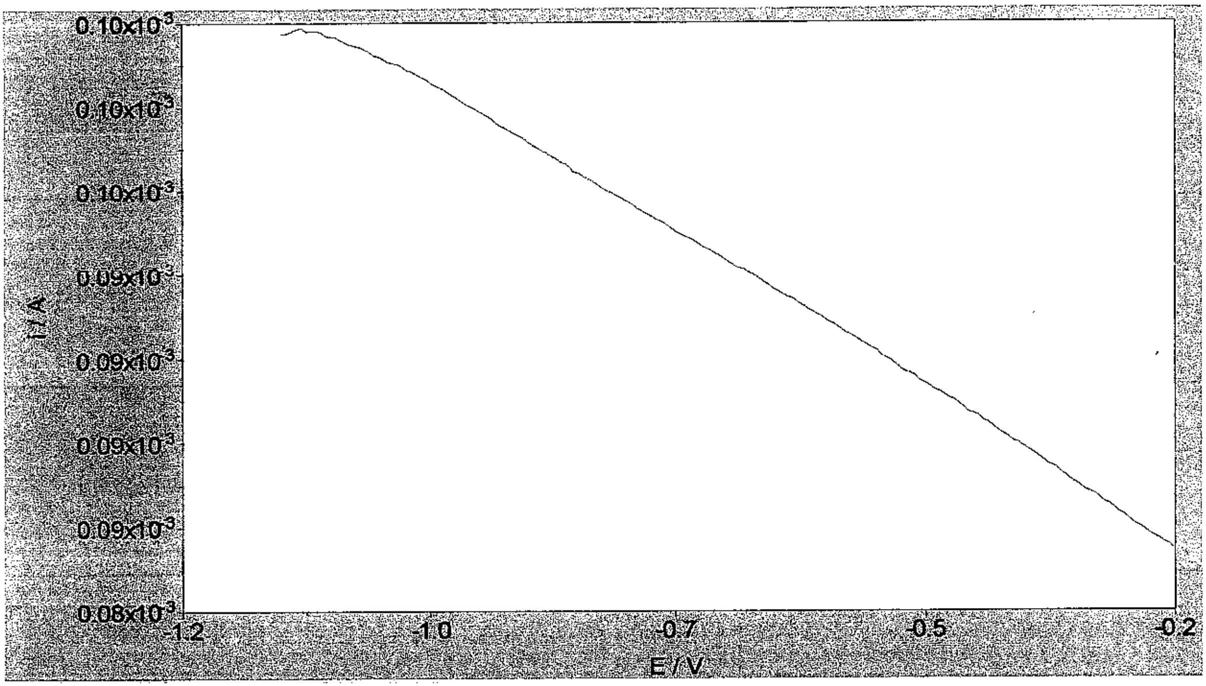


Figure 25: Current vs Potential plot for 100μl Hmim TFSI carbon paste electrode plot in 10mM KCl + 10ml 1μM $Pb(NO_3)_2$

Same as before, the plot did not register any peak within the given potential range. The electrode measured current at 0.08-0.10x10^{-3} A range. The graph also takes a downward path, showing evidence that there are no ions present on near the electrode surface even though lead ions were added to the solution. It is possible that the ionic liquid is not reacting with the lead ions in the solution due to the stability of TFSI anion.

Figure 26 : Current vs Potential plot for 250μl Hmim TFSI carbon paste electrode plot in 10mM KCl

Another electrode was prepared using 250μl of HMIM TFSI and 1g graphite powder and without any paraffin oil. This electrode was prepared to see any effects on the behavior of the modified electrode if the concentration of the ionic liquid was changed. The electrode recorded background current in the 0.55-0.58x10^{-4} A range. Compared to the 100μl ionic liquid modified carbon paste electrode, the current registered is lesser. Similar to the graphs before, there are no noticeable peaks in the plot as there are no lead ions.

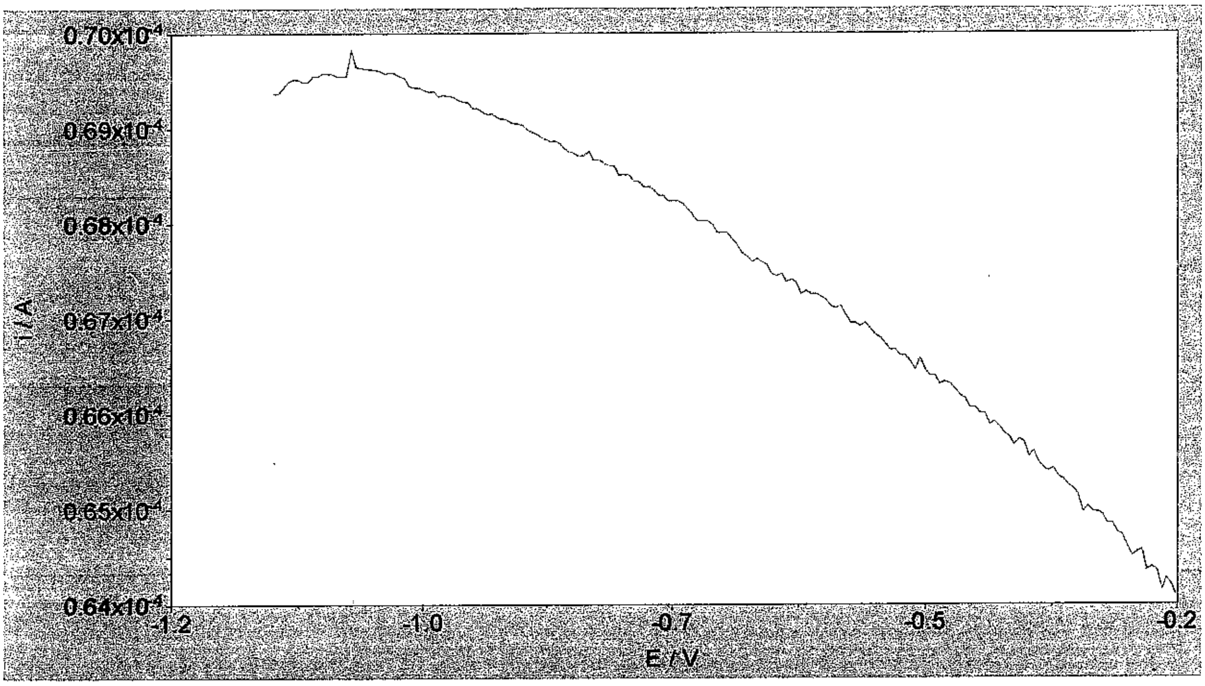


Figure 27: Current vs Potential plot for 250µl Hmim TFSI carbon paste electrode plot in 10mM KCl + 10ml 1µM $Pb(NO_3)_2$

The 250µl Hmim TFSI carbon paste electrode was then tested in 10mM KCl + 10ml 1µM $Pb(NO_3)_2$ solution .The electrode recorded background current in the $0.64\text{-}0.70\text{x}10^{-4}$ A range and is lesser compared to the 100µl electrode. Similar to the graphs before, there are no noticeable peaks in the plot as there are no lead ions. From this graph, it can be concluded that there are no noticeable changes in the detection even if the concentration of the ionic liquid was changed.

4.2 Discussion

As seen from the results, the ionic liquid modified carbon paste electrodes are showing increase in current measured. The current measured by ionic liquid electrodes are within the range of 10^{-4} A, which is more compared to the simple carbon paste electrodes. According to Ohm's law, V – IR. As the current, I, increases, the resistance, R decreases for a fixed potential, V. Since the ionic liquid modified carbon electrodes measure higher current within the range of 10^{-3} and 10^{-4}, compared to the simple carbon electrode, it is assumed that the modified ones are more conductive and less resistive. So, it can be assumed that the modified electrodes are more sensitive to change in current compared to the simple electrodes. Yet, further studies need to be carried for confirmation.

4.3 Issues and Challenges

There are no visible peaks registered in the modified electrode graphs. As previously stated, metal ions tends to remain hydrated in the solution. Since [HMIM][TFSI] is a moisture stable and hydrophobic ionic liquid, it is deduced that the metal ions are being repelled by the ionic liquid molecules. It is possible that the ionic liquid along with the carbon paste forms an impenetrable film at the surface of the modified electrodes, preventing lead ions to deposit. If there are no metal ions deposited, there won't be any current registered during the actual test.

As a solution for this problem, ligands and other types of co-solvents need to be used in order to aid the metal ions to penetrate the hydrophobic film and deposit onto the modified electrode surface. Many have previously worked on additives such as crown ethers along with ionic liquid for metal extraction. It is expected that the additives can be incorporated into the ionic liquid modified carbon paste sensor design for selectivity and efficiency.

4.4 Recommendations

The following section contains some of the recommendations and ideas that should be implemented in order to solve the problems faced in this study and for the development of more efficient, selective, and greener metal ion sensor.

Since the use of [HMIM][TFSI] alone is not practicable, polar additives such as crown ethers should be added along with the ionic liquid and carbon paste in order assure efficient metal partitioning in sample. It is expected that by this mean, the sensor would be able to interact with lead ions and register a peak in the graph.

Lead ion specific ionic liquids such as DIMCARB, can be used in order increase the sensor's selectivity towards lead ions. Furthermore, membranes can be used to coat the surface of the working electrode in order immobilized the carbon paste from moving out. This is to ensure that the sample will not be contaminated by the paste if it were to be used for lead detection in drinking water system. Furthermore, the use of membrane can increase the electrode selectivity by blocking other contaminants from damaging electrode surface and interfering with the results.

The total cost for the fabrication of 10 ionic liquid modified carbon paste electrodes is expected to be RM 50, considering material, labor, transportation, and production and packaging costs. A portable potentiostat can be fabricated at the cost of RM 200 (Ashwini et al, 2005). Thus, the total cost of the product would be RM 250. At the moment, the modified electrodes are not considered for re-usability and it is still economic. Yet, a method of recycling the electrodes, paste and ionic liquid should be devised for economical and environmental advantages.

This ionic liquid carbon paste electrode concept can be further expanded in detection of other metal ions such as mercury, tin, silver or even other contaminants such as phenol and etc.

CHAPTER FIVE
CONCLUSION

Ionic liquids have great potential to be developed as part of methodologies for real-time, *in-situ* monitoring and control of the formation of hazardous substances. The objective of this project was to develop a sensor that is portable, robust, and inexpensive and promotes green technology. Though carbon paste added with [HMIM][TFSI] alone, is not practicable to be used as lead ion sensor, it shows promising sign to be used for chemical sensor design due to its electrochemical and environmental aspects.

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