

SILVER RECOVERY FROM SPENT IPA USING
SOLID LIQUID EXTRACTION

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SILVER RECOVERY FROM SPENT IPA USING SOLID LIQUID EXTRACTION

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SUPERVISOR'S DECLARATION

I hereby declare that I have checked this project and in my opinion, this project is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering.

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STUDENT'S DECLARATION

I hereby declare that the work in this project is my own except for quotations and summaries which have been duly acknowledged. The project has not been accepted for any degree and is not concurrently submitted for award of other degree.

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ABSTRACT

Perhaps the most challenging field in environmental engineering practice at the present time is the treatment and disposal of industrial and hazardous wastes. Isopropyl alcohol (IPA) is an organic solvent that widely use as a cleaning agent in electronic industry, particularly for solder paste cleaning of defective electronic products. The spent IPA consist of solder paste can cause a serious problem in term of storage and pollution since it contains high concentration of heavy metals. There are few possible alternatives to treat this waste and one of the ways is to recover precious metal such as silver. In this study, a sample of waste IPA is taken from one electronic company in Pahang which consume almost 100kg of IPA every three weeks. This company use IPA as a cleaning agent. Solid-liquid extraction (leaching process) is used in this study to extract the silver because of its simplicity, environmental friendly, lower cost and provides high purity of product. In order to get better understanding in this study, few parameters such as type of leaching agent, concentration of leaching agent and retention time were investigated. Based on the result obtain, it can conclude that all the parameters affect silver leaching. Most of leaching agent that been used in this study show the potential on silver leaching because of the existence of free chloride ions produce by HCl and form silver chloro complexes with Ag^+ ions. The percentage of silver leaching also high which is up to 90% due to the effect of leaching agent concentration. This study is believed to be the first attempt to extract silver from spent IPA.

ABSTRAK

Mungkin bidang yang paling mencabar dalam bidang kejuruteraan alam sekitar pada masa sekarang adalah rawatan dan pelupusan sisa industri dan berbahaya. Isopropil alkohol (IPA) pelarut organik yang digunakan secara meluas sebagai agen pembersihan dalam industri elektronik, terutamanya untuk pembersihan pes pateri cacat produk elektronik. Sisa IPA terdiri daripada pes pateri boleh menyebabkan masalah yang serius dalam jangka penyimpanan dan pencemaran kerana ia mengandungi kepekatan logam yang tinggi. Terdapat beberapa cara alternatif untuk merawat sisa ini dan salah satu cara adalah dengan mendapatkan kembali logam berharga seperti perak. Dalam kajian ini, sampel sisa IPA diambil dari sebuah syarikat elektronik di Pahang yang menggunakan hampir 100kg IPA setiap tiga minggu. Syarikat ini menggunakan IPA sebagai agen pembersihan. Pengekstrakan pepejal-cecair (proses larut lesap) digunakan dalam kajian ini untuk mengekstrak perak kerana kemudahan, mesra alam, kos yang menjimatkan dan penghasilan ketulenan produk yang tinggi. Dalam usaha untuk mendapatkan pemahaman yang lebih baik dalam kajian ini, beberapa parameter seperti jenis ejen larut lesap, kepekatan ejen larut lesap dan masa telah dikaji. Berdasarkan keputusan, boleh disimpulkan bahawa semua parameter mempengaruhi larut lesap perak. Kebanyakan ejen larut lesap yang digunakan dalam kajian ini menunjukkan potensi pada larut lesap perak kerana kewujudan ion klorida bebas yang dihasilkan oleh kompleks perak HCl dalam bentuk chloro dengan Ag^+ ion. Peratusan larut lesap perak juga tinggi iaitu sehingga 90% disebabkan oleh kesan kepekatan ejen larut lesap. Kajian ini dipercayai sebagai percubaan pertama untuk mengekstrak perak dari sisa IPA.

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LIST OF SYMBOLS

AgCl	Argentum Chloride
Cl ⁻	Chloride ion
Ag ⁺	Silver ion
AgCl _n ⁻⁽ⁿ⁻¹⁾	Silver chloro complexes
AgHDz	Silver dithizonate
H ₂ Dz	Dithizone
CuO	Cuprum oxide
Ag ₂ S	Argentite
AgBr	Argentum Bromide
AgNO ₃	Argentum Nitric
K _d	Acid dissociation constant of dithizone
%	Percentage
pH _{eq}	pH at equilibrium
pH _o	Initial pH
pK _a	-log K _a where K _a is acid dissociation constant

LIST OF ABBREVIATIONS

IPA	Isopropyl Alcohol
AAS	Atomic Absorption Spectrophotometer
EDAX	Energy dispersive x-ray analysis
PCB	Printed circuit board
LLE	Liquid-liquid Extraction
FKKSA	Fakulti Kejuruteraan Kimia dan Sumber Asli

CHAPTER 1

INTRODUCTION

1.1 Research Background

Isopropyl alcohol (IPA) is a solvent which is largely use as a cleaning and dehydrating agents in electronic and precision machinery industry. Other than that, in semiconductor manufacturing process, IPA is widely use in multiple and variety stages of water surface washing and cleaning. On that purpose, IPA is used for cleaning Printed Circuit Board (PCB). PCB is a main component in electrical appliances which is consisting of various precious metals like gold, silver and palladium (Young & Derek, 2009). In Malaysia, one of the companies which are use IPA as cleaning agent is Alps Electronic Malaysia Sdn. Bhd. In producing and manufacturing electrical component for variety of uses, the company use IPA to clean the metal plate and the metal mask from the solder paste in order to use it again. The solder paste consists of three percent of silver together with other substance like stanumn, 96.5% and cuprum oxide, CuO, 0.5%. The silver metal possibly introduced into the waste IPA during the cleaning process. Thus due to high concern on valuable metal such silver is wasted, recovery of silver from spent IPA using solid-liquid extraction is conducted. As the development of the technology nowadays, silver consumption also increases. The demand of silver can be describe in three major categories which is in industrial uses, photography and jewelry & silverware. Based on that, silver price had raised rapidly from year to year. The silver price nowadays is US\$1.16 per gram and will be always increase compared to its price during 1970's which was US\$0.07 per gram (The Silver Institute, 2011).

1.2 Problem Statement

Silver consumption nowadays is rapidly increased due to the emphasis and development of the technology. As the result, the main silver source which is at earth's crust is exhausted. Thus, recovery of silver from spent IPA is important in order to introduce a new alternative way of recycling this precious metal. Variety of method had been developed and studies in order to recover silver from different sources such as processing waste and metal scrape. As stated by Mat and Seng (2006) in their study, many potential and most common method for silver recovery like flotation technique, pyrometallurgical process, biological process, electrometallurgical process hydrometallurgical process, liquid-liquid and also solid-liquid extraction process. There were few factors that may affect on the yield and selectivity in solid-liquid extraction process. In this research, in order to get high selectivity of extraction, the effect of leaching agent type, concentration of leaching agent and the retention time of stirring were studied.

1.3 Research Objectives

The objectives of this research are:

- a) To study the effect of effect of leaching agent type on Silver extraction
- b) To investigate the effect of retention time on Silver extraction.
- c) To analyze the effect concentration of leaching agent on Silver extraction

1.4 Research Scope

In order to achieve the objective, some boundary or scope need to be specified. This research covers the recovery of silver using solid-liquid extraction method. The solid-liquid extraction method is chose because of it advantages and simplicity. Firstly, the spent IPA is taken from the Alps Electronic Malaysia Sdn. Bhd. located at Lot 3, Industrial Estate Phase 2, Bandar Pusat Jengka, Pahang. Secondly, this research is run with several experiments using solid-liquid extraction method. Thus, the certain parameter will take place in order to achieve the objective. The parameters consist of:

- a) The type of leaching agents.
- b) The retention time of the silver extraction
- c) Concentration of the leaching agent

1.5 Rationale and Significances

The content of heavy metals in waste is primarily a consequence of the intended use of heavy metals in industrial application. Alps Electronic Malaysia Sdn. Bhd located at Bandar Jengka Pahang consumes almost 100kg of waste (IPA) every three weeks and spent over RM 5000.00 per year in order to manage this schedule waste. There are few possible alternatives to treat this waste and one of the ways is to recover precious metal such as silver. In this study, a sample of waste IPA is take from the electronic industry (Alps Electronic Malaysia Sdn. Bhd) and an attempt to extract the silver is made using solid-liquid extraction.

This research is carried out because of the increasing of silver price out weight the gold price. Silver demand on solar energy, medical and water purification expected to be increase by 400 percent next ten years. On the other hand, in the photographic and jewelry industries, there were also had rising of silver demand up to 7200 this year (M. Pistil 2011). Other than that Silver make our modern life become more efficient. In side switches, silver contact, computer, keyboard, automobile dashboard, washing machine's control panel and many other electrical appliances had silver to operate smoothly. There are many type of separation technique that can be done in order to recover silver from spent IPA. This research is carried out with leaching technique as well known as solid-liquid extraction technique rather than using other separation technique which is consist of precipitate, ion-exchanger, or leaching. The reason using solid-liquid separation technique because it has lot of advantages like simple method, environment friendly, less energy intensive and provide high purity of product (Mat & Seng, 2006).

CHAPTER 2

LITERATURE REVIEW

2.1 IPA

Isopropanol or Isopropyl Alcohol (IPA) is also known as rubbing alcohol. Sometimes, IPA is also called 2-propanol because of its tendency to being an isomer of an inorganic compound known as propanol. IPA is classified as a simple secondary alcohol with chemical formula C_3H_8O . In room temperature, IPA is a clear and flammable liquid with odor resembles that of a mixture of ethanol and acetone. It is also widely used as cleaning and drying agent in manufacture of electronic part, for metals and photographic films, in glass cleaners, detergent, and in aerosol. The characteristic shown that IPA has high concentration over 65% because it is an important waste solvent generated in the semiconductor manufacturing process besides other organic pollutants and strong color (Lin & Wang, 2004).

According to the Chemical Land website, IPA has many other uses include coupling agent, coolant in beer manufacture, dehydrating agent, polymerization modifier in the production of polyvinyl fluoride, foam inhibitor, de-icing agent, preservative and heat-exchange medium. IPA also may harm human body if it is over exposure or not conducted in well condition. It may cause symptoms like nausea, dizziness and fatal whereas a long term can cause defatting of the skin (Said, 2008). Besides that, based on Occupational Safety and Health Guideline for Isopropyl Alcohol, acute exposure to IPA cause eye and mucous irritation and may cause narcosis. Because of the hazardous of IPA the control

measure in order to decrease the possibility to harm human body like personal hygiene procedures, storage and respiration protection should be applied.

Table 2.1: Physical & Chemical Properties of IPA.

Isopropyl alcohol	
General	
Systematic name	Propan-2-ol
Other names	2-propanol, isopropanol, Isopropyl alcohol
Molecular formula	C_3H_8O
Molar mass	60.10 g/mol
Appearance	Colourless liquid
Density and phase	0.785 g/cm ³ , liquid
Solubility in water	Fully miscible
Solubility in brine	Slightly soluble
In ethanol, ether	Fully miscible
In acetone, toluene	Soluble
Melting point	-89 °C (185 K)
Boiling point	82.3 °C (355 K)
Acidity (pKa)	16.5 for H on hydroxyl
Viscosity	2.86 cP at 15 °C 1.77 cP at 30 °C
Dipole moment	1.66 D (gas)

Source: Said, (2008)

2.2 Silver

Mankind has discovered silver a long time ago since the Pre-Historical times and estimated to be found after copper and gold. The word Silver was derived from the Anglo-Saxon, [seolfor], compare Old German silabar. Ag is the symbol for silver and possibly from Latin name, Argentum or [Argyros]. The symbol of circle was gave by the Egyptians to gold because it is a perfect metal and silver was given the symbol of a semi-circle since it was closest to gold in perfection (Refiker 2005). Silver also include in the platinum group metals which is consist of platinum, palladium, rhodium, iridium, osmium and ruthenium together with gold. This group of metal is also well known as precious metal due to their economic value as well as their rare occurrences.

Argentite (Ag_2S) is the main silver mineral which is usually occurs together with other sulfides as cooper and lead sulfide in earth crust. According to The Mineral & Gemstone Kingdom (2011), silver is very malleable, ductile and very easy to work with but silver can't resist to pressure and easily bend. Because of that, to increase its toughness and durability, silver is alloyed with other metal. Table 2.2 below shows the most top 20 countries which is producing silver in year 2009 (The Silver institute, 2011).

Table 2.2: Top 20 Silver Producing Country

Top 20 Silver Producing Countries in 2009 (millions of ounces)					
1	Peru	123.9	7	Canada	19.6
2	Mexico	104.7	8	Argentina	17.1
3	China	89.1	9	Turkey	14
4	Australia	52.6	11	Sweden	8.7
5	Bolivia	42.6	12	Morocco	8.3
6	Russia	42.2	13	Indonesia	7.7

Source: The Silver institute, (2011)

2.2.1 Uses of Silver

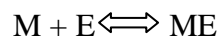
Some uses of silver are as follow:

- a) as sterling silver for jewellery and silverware
- b) in photography (AgBr , AgNO_3),
- c) in dental alloys,
- d) in solder and brazing alloys,
- e) for electrical contacts,
- f) in high capacity silver-zinc and silver-cadmium batteries,
- g) in some paints which are used for making printed circuits,
- h) in mirror production,
- i) as AgI for seeding clouds to produce rain and
- j) as coinage metal

2.3 Liquid-liquid Extraction (LLE)

Liquid-liquid extraction is an important separation technique which is largely use in industry including chemical industry. LLE also play significant role in separation technique due to its lower energy cost and more gentle treatment compared to distillation and other separation techniques (Hashem, 2006).

Based on Geankoplis (2003) in LLE, the separations of two phases are chemically quite different, which is lead to separate the component according to physical and chemical properties. In other word, LLE is a separation process that removes the solutes from the liquid by adding the aqueous solution. The aqueous solution referred to immiscible or partially miscible liquid normally called diluents or solvent. The equilibrium process can simply describe as the following reaction.



The metal M is firstly will transfer from an aqueous phase to the organic phase by the organic solvent or also known as extractant, E. Then it will form as complex ME. After that, because this is an equilibrium process, the reaction will reverse it back which means the metal is transferred from organic phase to an aqueous phase (stripping stage). So, basically the LLE just needs the simple operation that requiring only a shift in the equilibrium process (Mat & Seng, 2006).

2.3.1 LLE of Silver Using Dithizone

There had been several studies carried out to extract silver from much kind of sample and condition such as in chloride solution, from waste water sample and many more. A part of that, the type of extractant use is also various. A comprehensive study of dithizone properties by Irving and Pearson showed that the most suitable extractant for silver is dithizone. Besides that, Thiagarajan and Subbaiyan (1992) stated that dithizone is more stable if it is dilute in chloroform. From aqueous solution, dithizone was employed to form neutral metal-dithizone complexes with heavy metal ions to extract them (Ursula & Anna 2009).

2.3.2 Physical and Chemical Properties of Dithizone

Dithizone is a sulfur organic compound. The IUPAC name for dithizone is (1E) - 3-anilino-1-phenylimino-thiourea and the other name is Diphenylthiocarbazone. The pure dithizone appearance in dark brownish (black) powder having molecular weight of 253.3 gmol^{-1} and the density of 1.35 gml^{-1} . This material is stable under normal temperature and pressure. The condition that must be avoided is excess heat, dust generation and incompatible materials. Dithizone has very high solubility in chlorinated paraffin but very low in water make it suitable for extraction process.

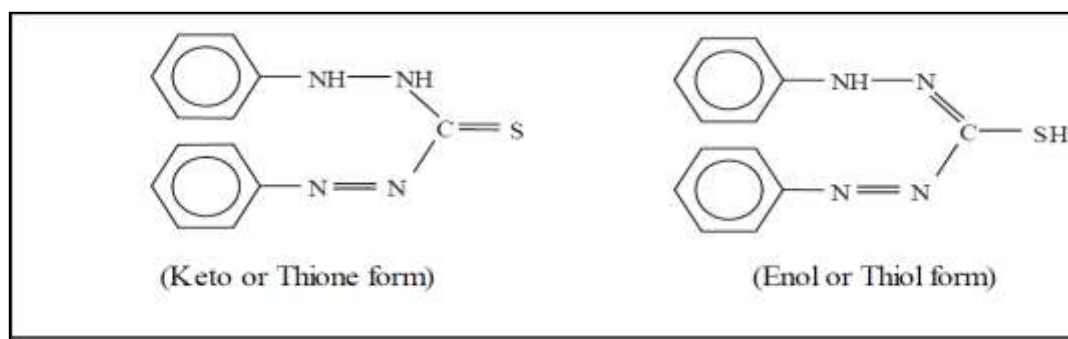


Figure 2.1: Tautoric forms of dithizone

Source: Mat & Seng (2006)

In acidic solution silver will react with dithizone to form the primary dithizonate $\text{Ag}(\text{HDz})$ and will give yellow solution if dissolves in CCl_4 or CHCl_3 (Mat & Seng 2006). But, in neutral or basic medium, the red-violet secondary dithizone (Ag_2Dz) is formed and insoluble in CCl_4 . It has been reported that complexing agents like EDTA may to be added in the aqueous solution in order to prevent the co-extraction of other elements.

2.3.3 Effect of pH on LLE of Silver Using Dithizone

There equilibrium reaction occurs between primary silver and dithizone in LLE can be simplified describe in figure 2.3:

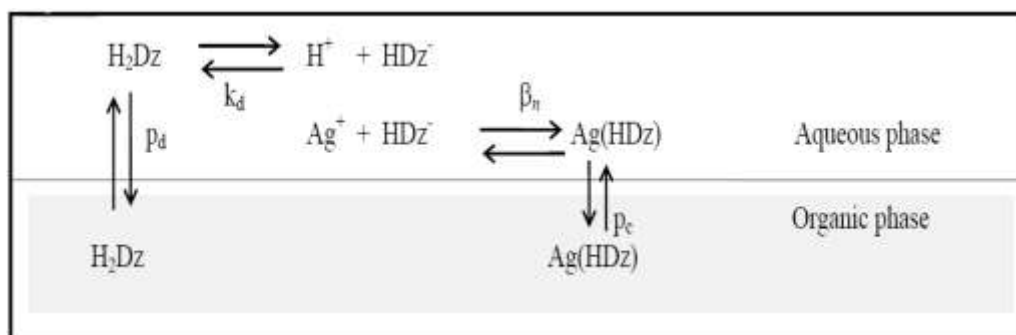
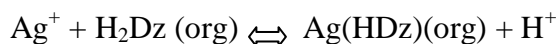


Figure 2.2: Equilibrium reactions involved in the silver extraction using dithizone

Source: Mat & Seng, (2006)

The fundamental equation for silver extraction using dithizone is given by:



$$K_{\text{ex}} = \frac{[\text{Ag(HDz)}]_{\text{o}}[\text{H}^+]}{[\text{Ag}^+][\text{H}_2\text{Dz}]_{\text{o}}} = \frac{p_c k_d}{\beta_n p_d}$$

Based on the equation 2.1, K_{ex} which is the equilibrium constant will be increase as the ionization of the chelae in the aqueous phase is decreasing and will increase the partitioning into the organic phase, increase the ionization of the chelating agent and its increase partitioning into the aqueous phase (Mat & Seng 2006).

2.4 Solid-liquid Extraction (Leaching) Process

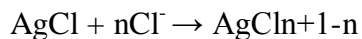
Nowadays, several of studies on the recovery of silver have been done due to increment of silver consumption all over the world. Many technologies can be applied to recover silver from any kind of sources such as ion-exchange, biosorption, liquid membrane, solvent extracting, solid-liquid extraction and many more. In this study, the focus of the research is using solid-liquid extraction or also called leaching process due to the simplicity and environmental friendly. Solid-liquid extraction is a process where the required metal is dissolves into solution from a solid substance.

Technically, the leaching process involves three different steps. Firstly, the solute (metal substance) will change its phase as it dissolves in the solvent. Then, it's diffuse through the solvent in the pores of the solid to the outside of the particles and lastly, the transfer of the solute from the solution in contact with the particles to the main bulk of the solution (Mat and Seng, 2006). Solid-liquid extraction involves similar principal with solvent extraction (liquid-liquid extraction) but differ in technology aspect (Charlesworth, 1981). The solid phase in solid liquid extraction plays the role of solvent in liquid-liquid

extraction process. The mechanism of the system is slightly the same but the solid and liquid phase make it different in term of reactivity and ion formation.

2.4.1 Effect of Leaching Agent Types

There were many type of leaching agent that can be use in the extraction process as reported in the literature. To ensure good solver leaching can be achieved, the selection of leaching agent is very important. As reported in literature, there were several potential leaching agents include thiourea, cynide acids and chloride. These types of leaching agents have their own ability to gain formation with heavy metal ions and give the effect on leaching efficiency. A lot of studies have been accomplished in studying the potential of silver leaching using chloride-leaching agent. These include the studies of the Ag-FeCl₃ / CuCl₂-HCl system (Kolodziej, 1988), Ag₂S-FeCl₃-HCl system (Dutrizac, 1994) and AgCl-FeCl₃-HCl system (Dutrizac, 1994). In this study, the main sources of chloride ions are came from HCl solutions which have been used as one of leaching agents. This free chloride ions that produce by HCL can increase the solubility of AgCl and Ag by forming silver chloro complexes. The reaction of the aggressive formation of silver chloro complexes can be described by following reaction (Mat and Seng, 2006),



Based on previous studies, HCl is the best and strong leaching agent that can provide high leached of silver. However, there might be the limitation on the performance of HCl as leaching agent for silver extraction. Sometimes, HCl will give low percentage of silver leaching due to the limitation of the available free chloride ions contribute by HCl. This occurs because the chloride ions might be reacting with other metal compounds that coexist in the sample. In this study, the chloride ion can be reacting with copper ions to form copper chloro complexes.

2.4.2 Effect of Leaching Agent Concentration

The efficiency of leaching process is very depends on how well the leaching agent can perform and thus give the high result on the silver leached or other heavy metal. One of the factors that would affect the efficiency is the leaching agent concentration. Leaching process involve the reaction between the leaching agent and the heavy metal inside the solid substance. Therefore, when more leaching agent is introduce into the leaching system, it will produce more rapid and effective leaching behavior that can affect the efficiency and the yield of extraction of heavy metal.

Based on previous study by Yuliusman et al (2006), they found that silver leaching increases fairly gradually when the concentration of leaching agent (HCl) is at 2.0 M. they stated that, the increment of silver leach is proportional to the increasing oh HCl concentration. As the concentration of HCl is increase, the existence of chloride ions also increase. The aggressive formation of AgCl ions is the result from above behavior.

2.4.3 Effect of Retention Time

Besides the concentration of leaching agent, the retention time of leaching process also can affect the efficiency of a leaching system. The kinetic behavior of leaching process can be described using the time needed to achieve an equilibrium condition. The reaction of formation between the ions would occur if the system achieves the equilibrium condition. Some system got low equilibrium condition that makes the reaction take some time to occur. If the system can achieve high equilibrium condition, then the reaction would occur so fast and the leaching system will give the leached of silver faster.

In the other hand, based on previous study on waste water system by Mat & Seng (2006), the relation between retention time and the percentage of silver leach is directly proportional to each others. When the mixing time is increased, the percentage of silver leached also increase. It is because the leaching process of silver might be control by the diffusion of some species through the liquid boundary layer adjacent to the surface of the

stirred particles or the diffusion of product species out from the surface. As the result, the rate of silver leaching would be increase.

2.5 Atomic absorption spectrophotometer (AAS)

Atomic absorption spectrophotometer (AAS) is an analytical technique that measures the concentration of heavy metal. AAS is so sensitive that it can measure down to parts per billion of a gram in a sample. The basic principle of AAS is use of the wavelengths of light specifically absorbed by an element. From one energy level to another energy level, the energy needed by the electron is promoted to the much higher energy level (Levinstonson, 2011). It has many uses in different area of chemistry such as in clinical analysis, environmental analysis, pharmaceuticals, industry and mining. In environmental analysis, AAS is used to monitor environment conditions by finding out the levels of various elements in rivers, seawater, drinking water, air, petrol, and so on.

The process of (AAS) requires a liquid sample to be aspirated, aerosolized, and mixed with combustible gases. The example of combustion gasses that have always been used are acetylene and air or acetylene and nitrous oxide. After that, the mixture is ignited in a flame whose temperature ranges from 2100 to 2800 °C.. So, to provide element specific wavelengths, a light beam from a lamp whose cathode is made of the element being determined is passed through the flame. Thus, a device such as a photomultiplier can detect the amount of reduction of the light intensity due to absorption by the analyst, and this can be directly related to the amount of the element in the sample (Ma and Winson, 1997).

In this experiment, a Polarized Zeeman Atomic Absorption Spectrophotometer (Model Z-5000 Series) (Figure 1) will be operating for water/wastewater analysis. The main unit consists of a lamp chamber, burner, graphite atomizer furnace, monochromatic, detector, mechanisms and electrical circuits. In addition, it is provided with a gas controller used to control various gases in flame analysis, power supply for graphite furnace atomization and auto sampler.



Figure 2.3: Polarized Zeeman Atomic Absorption Spectrophotometer (Model Z-5000 Series)

Source: FKKSA Laboratory

CHAPTER 3

METHODOLOGY

3.1 Raw Material and Equipment

The materials and equipment used in this experiment are listed in table below:

Table 3.1: List of Chemical

Chemical	Function
HCl	Leaching agent
NaCl	Leaching agent
NaOH solution	To form basis medium
HCL solution	To form acidic medium
Deionized Water	Dilute NaCH and HCL
Silver Standard Solution	To measure the concentration of Silver

Table 3.2: List of Equipment

Equipment	Function
Centrifugation	Remove precipitate
Mechanical shaker	Shaken the mixture
Atomic Adsorption Spectroscopy, AAS	Measure Silver concentration

3.2 Sample of waste IPA

20 Liters of waste IPA receive from local electronic industry which use IPA as cleaning agent was treated using rotary evaporator to recover the pure IPA and for others studies. The residue that left inside the receiver flask was collected and then left overnight in the oven to get dry sample of waste IPA. The dry sample is used for the leaching experiment. This waste existed as a metal hydroxide sludge is categorized under classification number N151 of the Environmental Quality (Scheduled Waste) Regulation 1989. As stated by Mat &Seng (2006) in their research, excessive oral intake of this kind of waste might result in acute or chronic poisoning. It will also affect the blood, digestive, respiratory, lungs, liver, and kidneys if it is chronic overexposure. By continued excessive contact with the waste might cause dermal irritation.



Figure 3.1 : Collected sample of concentrated residual of waste IPA

3.3 Reagent and Materials

Analytical reagent grade chemicals hydrochloric acid, HCl (37 % purity) Sodium chloride, NaCl (99.5 % purity) obtained from R&M Chemical was used as an additional source of chloride ion in leaching process. All the chemicals were used as received. Distilled and deionized water with 18 MΩcm purity which is available at the FKKSA laboratory was used for all dilution of chemical used to get the desired concentration.

Throughout the experiments, a silver (Ag) solution of 1000 ppm obtained from BDH Limited was used as standard solutions for Atomic Absorption Spectrophotometer (AAS) calibration. To obtain the working curve for silver standard, the standard calibrations were prepared at 0ppm, 1ppm, 2ppm, 4ppm, and 8ppm. All the dilution for AAS standard calibration curve was used the ultra pure water to adjust the concentration.

3.4 Apparatus

Centrifuge (model: Hettich Zentrifuger EBA 12) at 5000 rpm for 30 minutes was used to separate the aqueous solution in the leaching experiment. Silver element concentrations were determined using Polarized Zeeman Atomic Absorption Spectrophotometer (Model Z-5000 Series). Every sample tested using AAS were filtered using the vacuum pump to separate solid particles.

3.5 Leaching Agent

In the leaching experiment, the conventional acid leaching was used. Hydrochloric acid, HCl (37 % purity) and NaCl (99.5 % purity) were used as leaching agent in the experiment. All the leaching agents were prepared and diluted using distilled and deionized water. All chemical obtain from R&M Chemical, MERCK and Fischer Chemical respectively and the chemicals were used as received.

3.6 Solid-liquid Extraction (Leaching) Experiment

Throughout the leaching experiment, few parameter were analyzed which is type of leaching agent, concentration of the leaching agent and the retention time. The retention time was investigated during the mixing process of the sample and the leaching agent. The stirring speed was decided to be constant which at full level of stirring speed at room temperature.

In this experiment, 5 gram of dry sample of waste IPA was added into 50ml beaker that contain leaching agent. Using the magnetic stirrer, the mixture was then stirred on the stirred plate at full level of stirring speed. During the stirring, the retention time were taken started with 5 minutes, 10 minutes, 15 minutes, and 20 minutes using 4molar of leaching agent. Based on the previous studies, the mixing time of 20 minutes was well enough to achieve equilibrium.

Mean while, during the stirring process also 5ml of leaching solution was withdrawn using pipette at selected time intervals. The sample then separated using centrifuge (model: Hettich Zentrifuger EBA 12) at 5000 rpm for 30 minutes which was enough to separate the mixture completely. After that, the complete supernatants sample then used to determine the silver concentration using Polarized Zeeman Atomic Absorption Spectrophotometer (Model Z-5000 Series). Summarize of the experimental condition of different set of leaching agent were showed in table below.

Table 3.3: Experimental conditions of different sets of leaching experiment

Studied parameter	Experimental Condition	
	Varied	Constant
Type of Leaching agent	HCl (4M) NaCl (4M) HCL - NaCl (4M)	Temperature : 30 °C Time: 20 minutes Vigorous stirring speed
HCl concentration	1M, 2M, 3M, and 4M	Temperature : 30 °C Time: 20 minutes Vigorous stirring speed
NaCl concentration	1M, 2M, 3M, and 4M	Temperature : 30 °C Time: 20 minutes Vigorous stirring speed
HCl- NaCl	0.5M, 1M, 1.5M, and 2M	Temperature : 30 °C Time: 20 minutes Vigorous stirring speed
Retention time	5minutes, 10minutes, 15minutes, and 20 minutes.	Temperature : 30 °C Vigorous stirring speed Leaching agent : HCl 4M

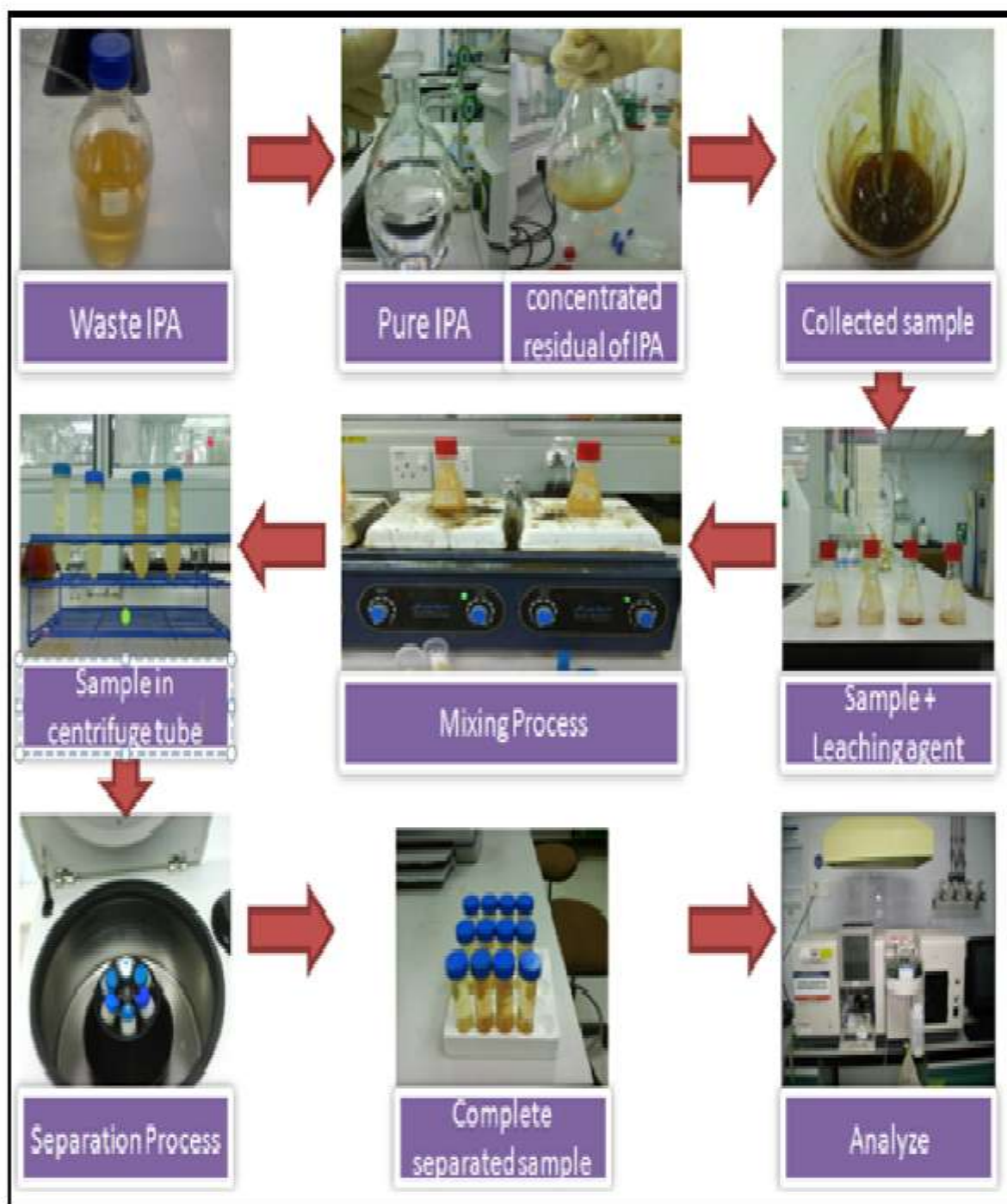


Figure 3.2 : Graphical view of leaching process

CHAPTER 4

RESULT AND DISCUSSION

4.1 Sample Characterization and Observation

Before the experiment was conducted, initial concentration of heavy metal had been detected first in order to analyze the effectiveness of the leaching process. The initial concentration of heavy metal exists in waste IPA was detected using atomic adsorption spectrometry. It was found that in the waste IPA containing silver and cooper metal. The initial concentration of silver metal was 0.32ppm while initial concentration for cooper was 1.87ppm. But, in this study will be focusing for silver leaching because silver is a valuable material. The sample got from the company was initially yellowish in colour. After treated using rotary evaporator, the colour change from yellowish to cristal clear solution. The solution produce was the pure IPA which can use back as cleaning agent. In the other hand, the sample left in the flask was the concentrated residual IPA. the concentrated IPA was golden in colour and it was believe that the heavy metal left insade the residual.

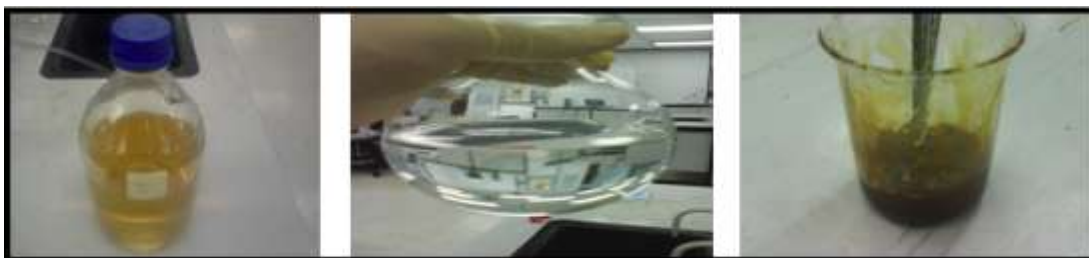


Figure 4.1: Observation the changes on spent IPA

4.2 Effect of Leaching Agent Types

There were many leaching agent that can be used in leaching experiment as reported in literature. To get better understanding on how types of leaching agent will affect silver leaching, three type of leaching agent have been used which is HCL, NaCl and HCl-NaCl. These three types of leaching agent contain Cl^- ions that can combine with silver ion and produce AgCl . A part from that, selective leaching procedure was considered in order to investigate which ones will give higher leached of silver. Figure 4.2 shows the behavior of silver leaching using different types of leaching agent.

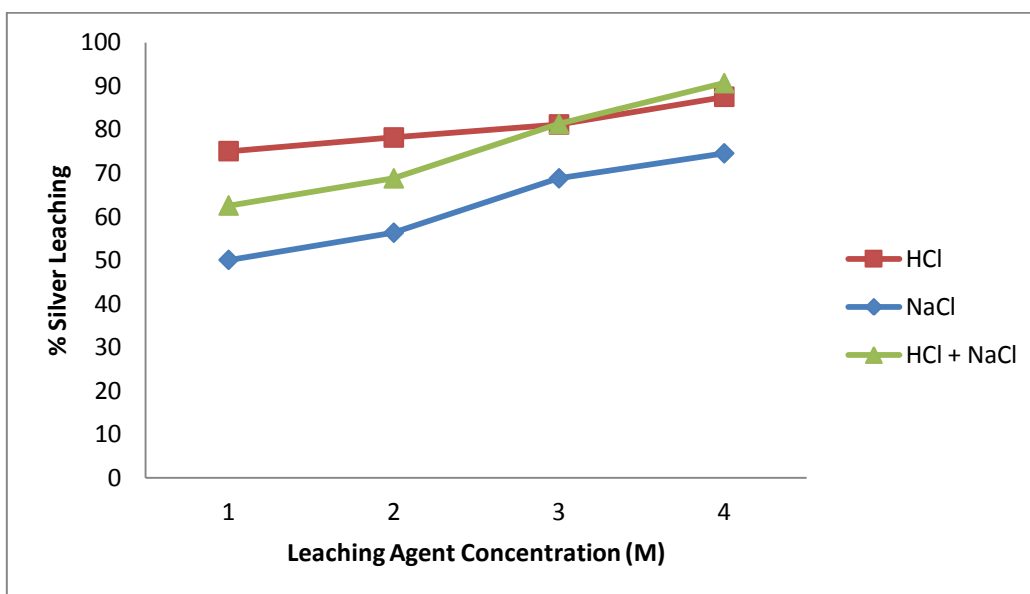


Figure 4.2: Effect of leaching agent types on the extent of silver leaching

By referring to figure 4.2 above, all the leaching agents shows the same trend on the increment of silver leaching. But at low concentration, NaCl give the lower silver leached, followed by HCl-NaCl and then HCl. This low percentage might be due to the limitations of the available of free chloride ions contributed by HCl. In the other hand, at higher concentration, HCl-NaCl leaching agent proved higher silver leached compared with others. This is happen because HCl-NaCl can provide much Cl^- ion and can increase the solubility of AgCl and Ag by forming silver chloro complexes (Yuliusman et. al. 2006)

4.3 Effect of Hydrochloric Acid Concentration

The existence of Cl^- ions is the main factor of the extent silver leaching process and essentially to increase solubility of AgCl . Thus, to get the better understanding on how Cl^- ions affect the silver leaching, experiment on HCl concentration is carried out. Figure 4.3 below shows the result of the increment of silver leached is affected by the increasing of HCl concentration. At lower concentration, amount of silver leached is slightly low and as the HCl concentration increase up to 4M HCl , the percentage is gradually increase more than 80% of leaching result.

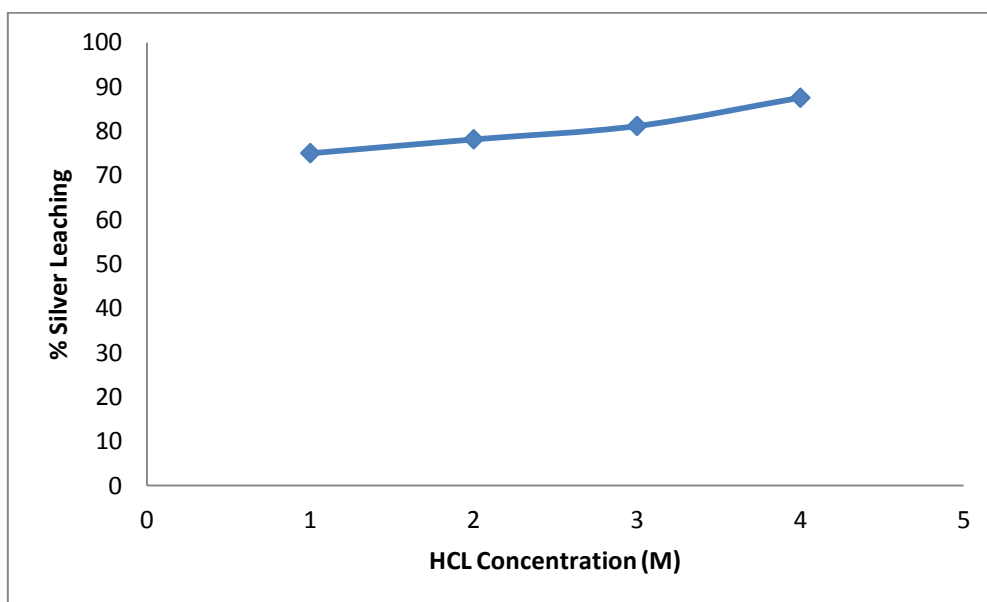


Figure 4.3: Effect of HCl concentration on the extent of silver leaching

The progressive formation of soluble silver chloro complexes is the main factor of the increment of silver leaching (Yuliusman et. al. 2006). On the other hand, this process is occurred at very high equilibrium constant. Thus it was found that at lower concentrated chloride (1M HCl) provide more than 70% silver leached. The reaction forced to generate more soluble silver chloro complexes at high concentration of Cl^- ions which follow the Le Chatelier principles (Mat and Seng, 2006).

4.4 Effect of Sodium Chloride Concentration

Uses of concentrated HCl were not applicable and preferable in industry although it produce high amount of silver leaching. The high concentrated HCl will cause serious corrosion problem to piping system and have to invest a lot of money in order to prevent it happen. Because of that, alternatively, the chloride source was replaced by sodium chloride. With the same purpose and condition, figure 4.4 represents the result of NaCl concentration on silver leaching.

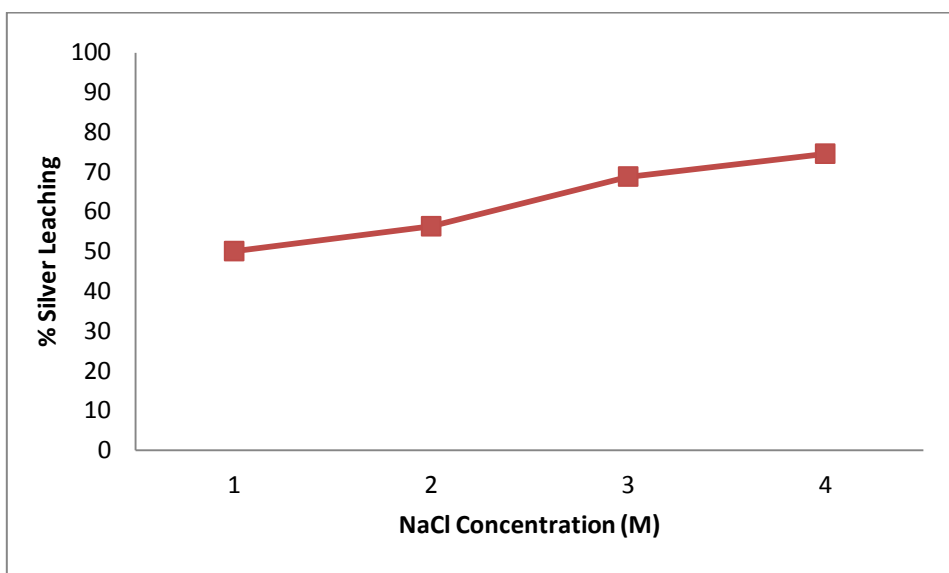


Figure 4.4: Effect of NaCl concentration on the extent of silver leaching

From figure 4.4, it can say that the trend of silver leaching is the same as silver leaching on HCl concentration. The graph shows silver leached increased as the concentration of NaCl increased. This implement that the additional cationic ion from sodium chloride ion were not affect the basic mechanism of the formation of soluble silver chloro complexes and it still can leached a high percentage of silver leaching. But at lower concentration of NaCl, the leached amount is much lower compared to HCl on low concentration. It shows that the effect of NaCl concentration on silver leaching is significantly at higher NaCl concentration (4.0 M NaCl) (Mat and Seng, 2006).

4.5 Effect of Hydrochloric Acid in Sodium Chloride Concentration

The other leaching agent to be investigated in this research is HCl - NaCl solution. Above analysis have been discussed the effect of both medium when the concentration is increased. Then, in this experiment, researcher want to investigate the effect of mixing this two leaching agent to the percentage of silver leaching. The concentration for HCl was fixed at 4M while the concentration of NaCl was decided to be variables. Figure 4.5 illustrate the result on effect of hydrochloric acid in sodium chloride concentration to silver leaching.

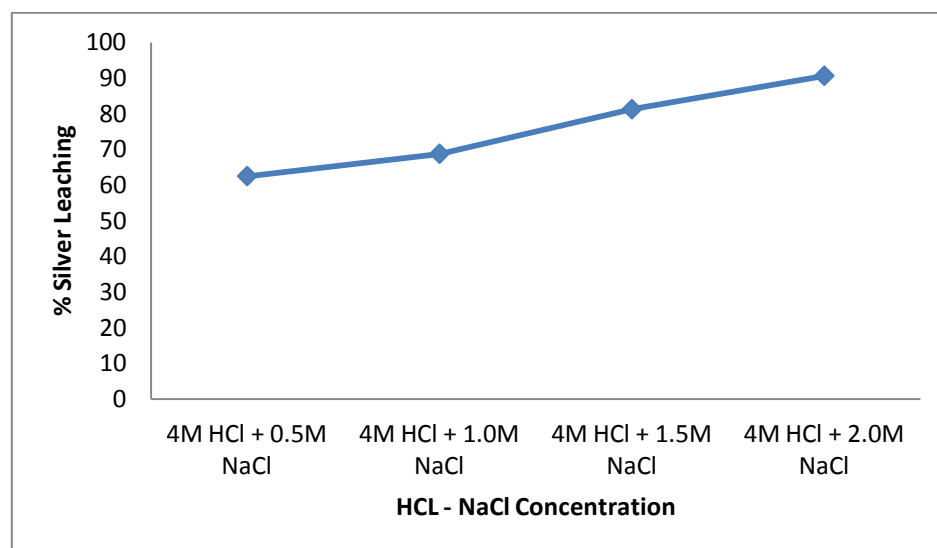


Figure 4.5: Effect of HCl - NaCl concentration on the extent of silver leaching.

Based on figure 4.5, the extent of silver leaching show the increment as well as the concentration of HCl - NaCl concentration was increased. In this experiment, an assumption have made which is HCl and NaCl dissociated completely without involve any chemical reaction between these two electrolytes (Sadikin et. al. 2000). As shown in figure 4.5, the silver leaching rise up to 90% which is the highest percentage compared to others leaching agent. This is because in HCl-NaCl leaching system produced much higher of free Cl⁻ ions and can perform very well due to increment of soluble silver chloro complexes.

4.6 Effect of Retention Time on HCl Leaching System

HCl has shown the ability as best and strong leaching agent that can provide high leached of silver. To study the kinetic behavior of the leaching process, the retention time during the leaching process was investigated. This experiment is very important to know at what time interval the leaching process will produce higher leaching. An assumption had been made which was as the time increase, the percentage of silver leaching also would be increase. Figure 4.6 emphasize the relation between retention time and the silver leaching in HCl leaching system.

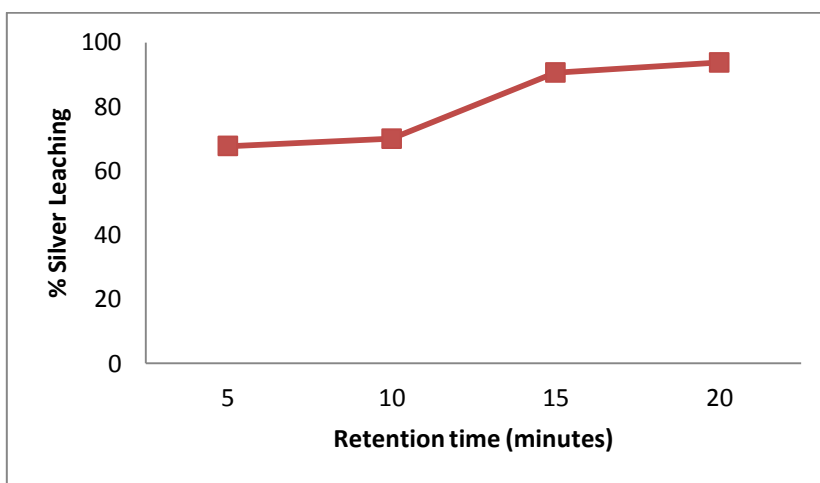


Figure 4.6: Effect of retention time on the extent of silver leaching.

From figure 4.6, it describe that the percentage of silver leaching was increase when the retention time is increase. This trend of increment gives explanation on the kinetic behavior of silver leaching. The leaching process is achieved equilibrium condition as early as 5 minutes. It is suggest that there were some fast reaction to occur in order to allow the Cl^- ions to achieve the equilibrium process with the silver ion and form silver chloro complexes. By referring to figure 4.6, time interval at 20 minutes was enough to attain the optimize result on silver leaching which is over 90%. It is necessary to minimize the leaching time once the equilibrium is achieve because the leaching efficiency will shift toward reprecipitation of silver in leach solution (Anlmore, 2001).

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 Conclusion

Spent IPA collected from local electronic industry contains 0.32ppm of silver existed mostly in the form of Ag and AgCl. This waste then treated to get the dry sample and proceed to leaching process. The result shows the potential of silver recovery from this waste based on the high percentage of silver leaching. Silver leaching is depends on types of leaching agent, concentration of the leaching agent and the retention time of leaching process (HCl as leaching medium). It has been prove that different type of leaching agent will produce different percentage of silver leached. Leaching agent which contains much Cl⁻ ions will give higher silver leached. Besides that, the concentration of leaching agent plays the important role to get higher selectivity of silver leaching. When the concentration of leaching agent is increase, it will cause the percentage of silver leached to be increase. The high concentration of chloride ion will contribute the progressive formation of soluble silver chloro complexes, $\text{AgCl}_n^{-(n-1)}$ from Ag and AgCl.

Other than that, the retention time of leaching process also was taking into account. This study, HCl shows the best leaching agent and the leaching system gain its equilibrium conditions as early as 5 minutes then can leach silver more than 50%. But still the optimum silver leaching obtain after 20 minutes of leaching process because of the complete mixing between the sample and leach solution which produce much formation of soluble silver chloro complexes. Overall, this lab scale silver recovery procedure makes it possible to recover silver selectivity and was successfully attaining higher recovery.

5.2 Recommendation

Throughout the experiment, there were many aspect can be improve so that better silver recovery on spent IPA can be done for further study. For sample characterization, it is not enough to identify existence of silver and other heavy metal by just using AAS. Therefore, other equipment analysis such Energy Dispersive X-ray Spectroscopy (EDAX spectrum) can be use to bet better characterization result.

Other than that, used other types of leaching agent such as HNO_3 or H_2SO_4 to get much understanding on the effect of leaching agent type on silver leaching. Lastly, due to limited sources of sample, this study cannot carry out with multiple testing. So that, to ensure the result obtain is precise and more accurate, the experiment on studied parameters should be done few times.

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APPENDIX A

SAFETY (MSDS) FOR ISOPROPYL ALCOHOL

General

Synonyms: Isopropanol; Dimethylcarbinol; sec-Propyl alcohol; Rubbing alcohol
Molecular formula: C₃H₈O
CAS No: 67-63-0

Physical Data

Appearance: colourless liquid
Melting point: -88 °C
Boiling point: 82 °C
Vapour density: 2.1
Vapour pressure: 33 mm Hg @ 20 deg C
Specific gravity: 0.7850
Flash point: 18 deg C
Explosion limits: 2%
Autoignition temperature: 399°C

Stability

Stable, highly flammable, incompatible with oxidizing agent, reducing agents.

Toxicology

Harmful if inhaled or ingested. May be harmful through skin contact. Eye, respiratory and skin irritant.

Risk Phrases

(The meaning of any risk phrases which appear in this section is given in appendix C)

R 11, R 36, R67

Environmental Information

Very toxic to aquatic organisms may cause long-term damage to the environment.

Transport Information

(The meaning of any UN hazard codes which appear in this section is given in appendix D)

UN No 1219. Hazard class 3.0. Packing group II.

Personal Protection

Safety glasses, good ventilation, keep away from sources of ignition.

Safety Phrases

(The meaning of any safety phrases which appear in this section is given in appendix E)

S16, S24, S26, S7.

APPENDIX B

RISK PHRASES

Chemical data sheets available in many countries now contain codes for certain “ risk phrases”, shown as R23, R45 etc. These risk phrase codes have the following meanings:

- R1: Explosive when dry
- R2: Risk of explosion by shock, friction, fire or other sources of ignition
- R3: Extreme risk of explosion by shock, friction, fire or other sources of ignition
- R4: Forms very sensitive explosive metallic compounds
- R5: Heating may cause an explosion
- R6: Explosive with or without contact with air
- R7: May cause fire
- R8: Contact with combustible material may cause fire
- R9: Explosive when mixed with combustible material
- R10: Flammable
- R11: Highly flammable
- R12: Extremely flammable
- R14: Reacts violently with water
- R15: Contact with water liberates extremely flammable gases
- R16: Explosive when mixed with oxidising substances
- R17: Spontaneously flammable in air
- R18: In use, may form flammable/explosive vapour-air mixture
- R19: May form explosive peroxides
- R20: Harmful by inhalation
- R21: Harmful in contact with skin
- R22: Harmful if swallowed
- R23: Toxic by inhalation
- R24: Toxic in contact with skin
- R25: Toxic if swallowed
- R26: Very toxic by inhalation
- R27: Very toxic in contact with skin
- R28: Very toxic if swallowed
- R29: Contact with water liberates toxic gas.

- R30: Can become highly flammable in use
- R31: Contact with acids liberates toxic gas
- R32: Contact with acids liberates very toxic gas
- R33: Danger of cumulative effects
- R34: Causes burns
- R35: Causes severe burns
- R36: Irritating to eyes
- R37: Irritating to respiratory system
- R38: Irritating to skin
- R39: Danger of very serious irreversible effects
- R40: Limited evidence of a carcinogenic effect
- R41: Risk of serious damage to eyes
- R42: May cause sensitisation by inhalation
- R43: May cause sensitisation by skin contact
- R44: Risk of explosion if heated under confinement
- R45: May cause cancer
- R46: May cause heritable genetic damage
- R48: Danger of serious damage to health by prolonged exposure
- R49: May cause cancer by inhalation
- R50: Very toxic to aquatic organisms
- R51: Toxic to aquatic organisms
- R52: Harmful to aquatic organisms
- R53: May cause long-term adverse effects in the aquatic environment
- R54: Toxic to flora
- R55: Toxic to fauna
- R56: Toxic to soil organisms
- R57: Toxic to bees
- R58: May cause long-term adverse effects in the environment
- R59: Dangerous for the ozone layer
- R60: May impair fertility
- R61: May cause harm to the unborn child
- R62: Possible risk of impaired fertility
- R63: Possible risk of harm to the unborn child

- R64: May cause harm to breast-fed babies
- R65: Harmful: may cause lung damage if swallowed
- R66: Repeated exposure may cause skin dryness or cracking
- R67: Vapours may cause drowsiness and dizziness
- R68: Possible risk of irreversible effects

APPENDIX C UN HAZARD CODES

* **Class 1: Explosive**

- 1.1 Substances with a mass explosion hazard: TNT, dynamite, nitroglycerine.
- 1.2 Substances which present a projection hazard but no mass explosion hazard.
- 1.3 Substances which present both a fire hazard and a minor blast or projection hazard (or both) but not a mass explosion hazard.
- 1.4 No significant hazard.
- 1.5 Very insensitive substances with a mass explosion hazard.
- 1.6 Very insensitive articles with no mass explosion hazard.

* **Class 2: Gas**

- 2.1 Flammable gases: Gases which ignite on contact with an ignition source, such as acetylene and hydrogen.
- 2.2 Non-flammable, non-toxic gases: Gases which are neither flammable nor poisonous. Includes the cryogenic gases/liquids (temperatures of below -100°C) used for cryopreservation and rocket fuels, such as nitrogen and neon
- 2.3 Toxic gases: Gases liable to cause death or serious injury to human health if inhaled, such as fluorine, chlorine, and hydrogen cyanide.

* **Class 3: Flammable liquids**

- Packing group I, if they have an initial boiling point of 35°C or less at an absolute pressure of 101.3 kPa and any flash point such as diethyl ether or carbon disulfide.
- Packing group II, if they have an initial boiling point greater than 35°C at an absolute pressure of 101.3 kPa and a flash point less than 23°C, such as gasoline (petrol) and acetone.

- Packing group III, if the criteria for inclusion in Packing Group I or II are not met, such as kerosene and diesel.

* **Class 4: Flammable solids**

- 4.1 Flammable solids: Solid substances that are easily ignited and readily combustible such as nitrocellulose, magnesium, safety or strike-anywhere matches.
- 4.2 Spontaneously combustible: Solid substances that ignite spontaneously such as aluminium alkyls, white phosphorus.
- 4.3 Dangerous when wet: Solid substances that emit a flammable gas when wet or react violently with water such as sodium, calcium, potassium, calcium carbide.

* **Class 5: Oxidizing substances and organic peroxides**

- 5.1 Oxidizing agents other than organic peroxides: calcium hypochlorite, ammonium nitrate, hydrogen peroxide, potassium permanganate.
- 5.2 Organic peroxides, either in liquid or solid form: benzoyl peroxides, cumene hydroperoxide.

* **Class 6: Toxic and infectious substances**

- 6.1 Toxic substances
- 6.2 Infectious substances

* **Class 7: Radioactive substances and articles: uranium and plutonium.**

* **Class 8: Corrosive substances**

- 8.1 Acids: sulfuric acid, hydrochloric acid.
- 8.2 Alkalis: potassium hydroxide, sodium hydroxide.

- * **Class 9: Miscellaneous dangerous substances: asbestos, air bag inflators, self inflating life rafts, dry ice.**

APPENDIX E

SAFETY PHRASES

Under Ec legislation, data sheets available in the UK now contain codes for certain “safety phrases”, shown as S1, S20 etc. These phrases are also extensively used elsewhere in the world. Safety phrase codes have the following meanings:

- S1: Keep locked up
- S2: Keep out of the reach of children
- S3: Keep in a cool place
- S4: Keep away from living quarters
- S5: Keep contents under ... (appropriate liquid to be specified by the manufacturer)
- S6: Keep under ... (inert gas to be specified by the manufacturer)
- S7: Keep container tightly closed
- S8: Keep container dry
- S9: Keep container in a well-ventilated place
- S10: Keep contents wet
- S11: not specified
- S12: Do not keep the container sealed
- S13: Keep away from food, drink and animal foodstuffs
- S14: Keep away from ... (incompatible materials to be indicated by the manufacturer)
- S15: Keep away from heat
- S16: Keep away from sources of ignition - No smoking
- S17: Keep away from combustible material
- S18: Handle and open container with care
- S20: When using do not eat or drink
- S21: When using do not smoke
- S22: Do not breathe dust
- S23: Do not breathe gas/fumes/vapour/spray (appropriate wording to be specified by the manufacturer)
- S24: Avoid contact with skin
- S25: Avoid contact with eyes
- S26: In case of contact with eyes, rinse immediately with plenty of water and

- seek medical advice
- S27: Take off immediately all contaminated clothing
- S28: After contact with skin, wash immediately with plenty of ... (to be specified by the manufacturer)
- S29: Do not empty into drains
- S30: Never add water to this product
- S33: Take precautionary measures against static discharges
- S35: This material and its container must be disposed of in a safe way
- S36: Wear suitable protective clothing
- S37: Wear suitable gloves
- S38: In case of insufficient ventilation wear suitable respiratory equipment
- S39: Wear eye/face protection
- S40: To clean the floor and all objects contaminated by this material use ... (to be specified by the manufacturer)
- S41: In case of fire and/or explosion do not breathe fumes
- S42: During fumigation/spraying wear suitable respiratory equipment
(appropriate wording to be specified by the manufacturer)
- S43: In case of fire use ... (indicate in the space the precise type of fire-fighting equipment. If water increases the risk add **-Never use water**)
- S45: In case of accident or if you feel unwell seek medical advice immediately
(show the label where possible)
- S46: If swallowed, seek medical advice immediately and show this container or label
- S47: Keep at temperature not exceeding ... °C (to be specified by the manufacturer)
- S48: Keep wet with ... (appropriate material to be specified by the manufacturer)
- S49: Keep only in the original container
- S50: Do not mix with ... (to be specified by the manufacturer)
- S51: Use only in well-ventilated areas
- S52: Not recommended for interior use on large surface areas
- S53: Avoid exposure - obtain special instructions before use
- S56: Dispose of this material and its container at hazardous or special waste collection point
- S57: Use appropriate containment to avoid environmental contamination
- S59: Refer to manufacturer/supplier for information on recovery/recycling

- S60: This material and its container must be disposed of as hazardous waste
- S61: Avoid release to the environment. Refer to special instructions/safety data sheet
- S62: If swallowed, do not induce vomiting: seek medical advice immediately and show this container or label where possible
- S63: In case of accident by inhalation: remove casualty to fresh air and keep at rest
- S64: If swallowed, rinse mouth with water (only if the person is conscious)

APPENDIX F

Table F1: Percentage of Silver Leach on Various Concentration HCl Leaching System

HCL concentration (M)	% Silver leaching
1	75.00
2	78.13
3	81.13
4	87.50

Table F2: Percentage of Silver Leach on Various Concentration NaCl Leaching System

NaCL concentration (M)	% Silver leaching
1	50.00
2	56.25
3	68.75
4	74.50

Table F3: Percentage of Silver Leach on Various Concentration HCl-NaCl Leaching System

HCL + NaCl concentration (M)	% Silver leaching
4M HCL + 0.5M NaCL	62.50
4M HCL + 1.0M NaCL	68.75
4M HCL + 1.5M NaCL	73.20
4M HCL + 2.0M NaCL	82.80

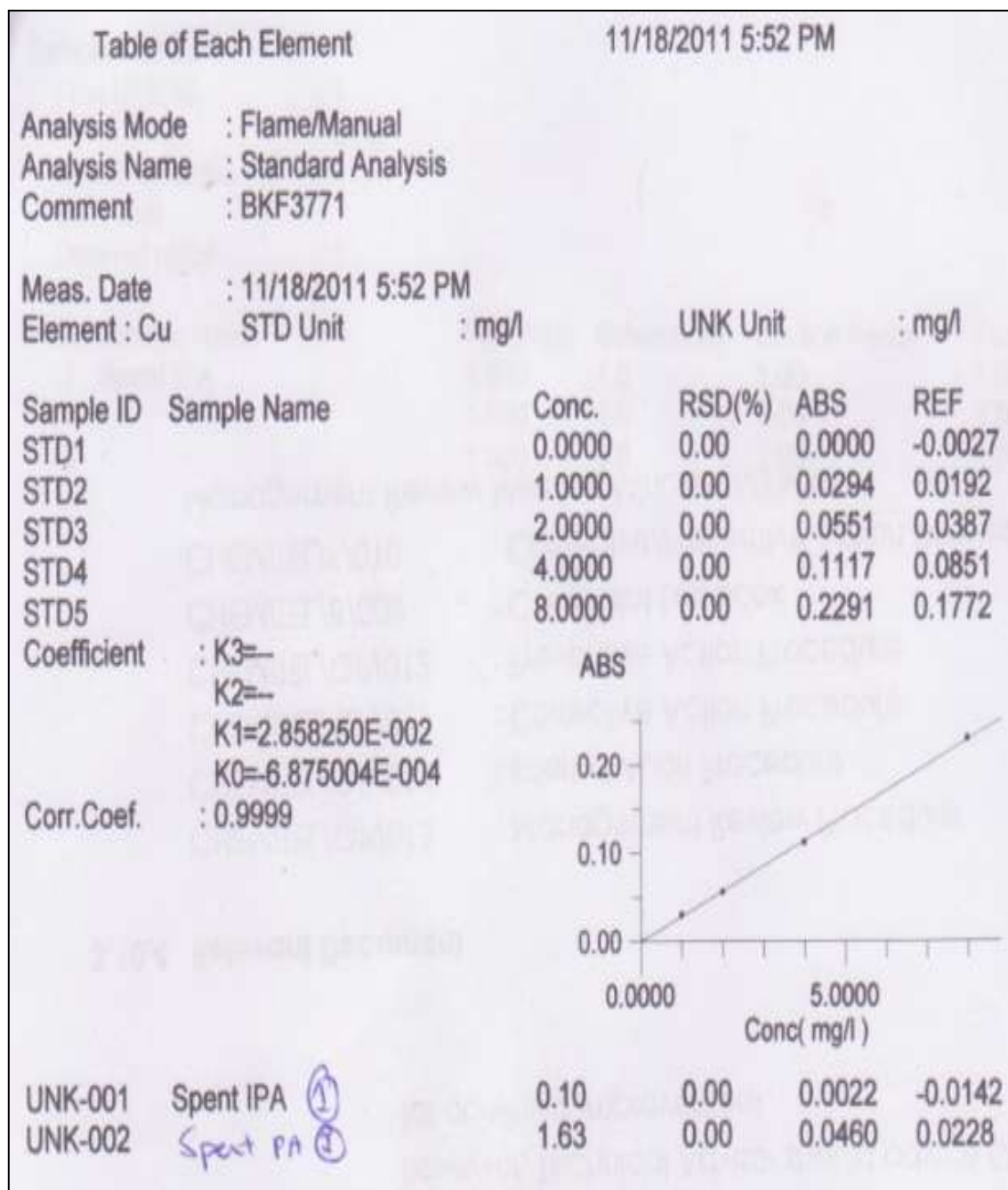
Table F4: Percentage of Silver Leach on Different Retention Time in HCl Leaching System

Retention time (minutes)	% Silver leaching
5	67.75
10	70.00
15	90.63
20	93.75

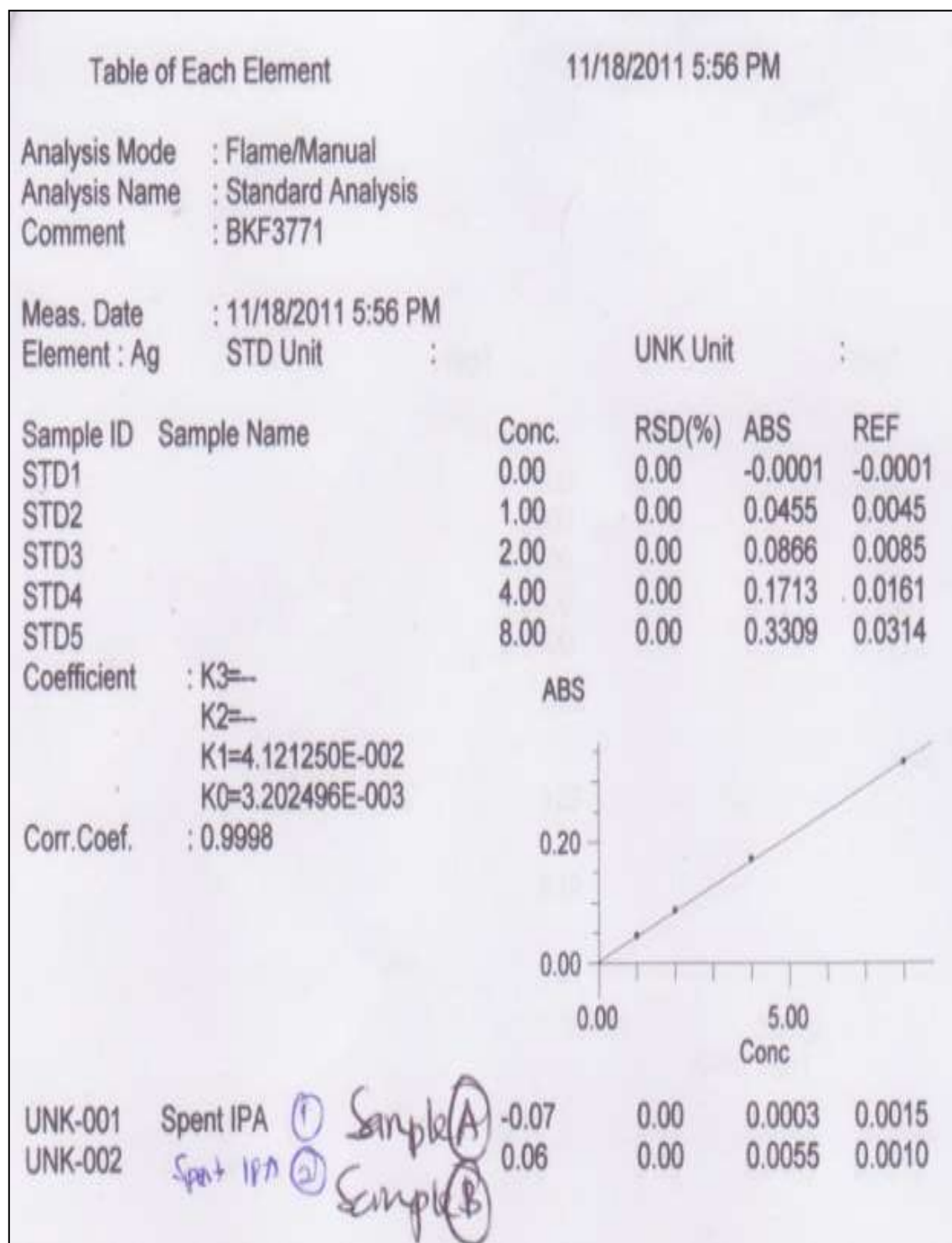
APPENDIX G

AAS RESULT

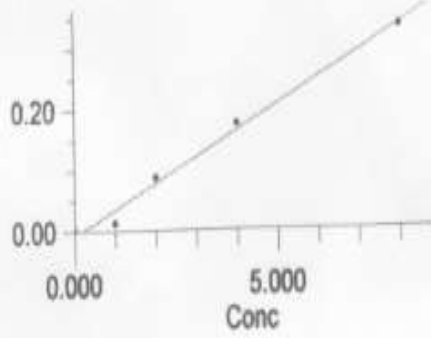
G1: Characterization on Spent IPA (Cu)



G2: Characterization on Spent IPA (Ag)



G3: Sample Analysis

Table of Each Element			12/1/2011 5:32 PM				
Analysis Mode		: Flame/Manual					
Analysis Name		: Standard Analysis					
Comment		: BKF3771					
Meas. Date		: 12/1/2011 5:32 PM					
Element : Ag		STD Unit		UNK Unit			
Sample ID	Sample Name	Conc.	RSD(%)	ABS	REF		
STD1		0.000	25.00	0.0004	0.0005		
STD2		1.000	0.87	0.0115	0.0010		
STD3		2.000	0.46	0.0861	0.0081		
STD4		4.000	1.44	0.1740	0.0163		
STD5		8.000	0.24	0.3317	0.0305		
Coefficient		: K3=					
		K2=					
		K1=4.305500E-002					
		K0=8.425001E-003					
Corr.Coeff.		: 0.9946					
		ABS					
							
		Conc					
UNK-001	A	0.28	0.00	0.0037	0.0081		
UNK-002	B	0.26	0.00	0.0028	0.0066		
UNK-003	C	0.25	0.00	0.0022	0.0040		
UNK-004	D	0.24	0.00	0.0020	0.0017		
UNK-005	E	0.26	0.00	0.0026	-0.0002		
UNK-006	F	0.29	0.00	0.0040	-0.0001		
UNK-007	G	0.22	0.00	0.0012	0.0000		
UNK-008	H	0.20	0.00	0.0004	-0.0004		
UNK-009	I	0.30	0.00	0.0046	0.0001		
UNK-010	J	0.21	0.00	0.0005	-0.0004		
UNK-011	K	0.29	0.00	0.0041	-0.0001		
UNK-012	L	0.22	0.00	0.0012	-0.0009		
UNK-013	M	0.22	0.00	0.0011	-0.0010		
UNK-014	N	0.32	0.00	0.0052	0.0199		