EFFECTS OF POLYVINYLPYRROLIDONE ADDITIVE ON THE PERFORMANCE OF HOLLOW FIBER ION EXCHANGER MIXED MATRIX MEMBRANE FOR COPPER REMOVAL

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KELVIN WONG JING ZHI

Thesis submitted in partial fulfilment of the requirements
for the award of the degree of
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JANUARY 2015

SUPERVISOR'S DECLARATION

We hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Bachelor of Chemical Engineering.

Signature :
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STUDENT'S DECLARATION

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

Signature :
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ID Number : KA12001
Date :

Dedication

To my beloved parents for their support

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ABSTRACT

The existence of copper in the environment is a concern due to the acute and long term toxicity. With the advantages of lower capital cost, easy operation process and high copper removal percentage, ion exchange technology offers the best treatment for copper removal but it has a drawback where it will cause a vast drop in pressure. In order to overcome this limitation, an ion exchanger mixed matrix membrane was produced in this study. Amberlite IR 120H cation exchanger was incorporated in the polyethersulfone (PES) based polymer solution. The effect of polyvinylpyrrolidone (PVP) pore forming additive in the PES dope solution was studied in the range of 0 to 10wt%. The hollow fiber membrane was synthesized using dry-wet spinning procedure. The pore structure of the membrane was characterized using Scanning Electron Microscope (SEM) and was found more porous as the concentration of PVP increases. The permeability was also increased as the concentration of PVP increases. The optimum concentration of PVP for the removal of copper is between 3wt% and 5wt%.

ABSTRAK

Kewujudan kuprum dalam alam sekitar adalah kebimbangan disebabkan oleh ketoksikan jangka akut dan panjang. Dengan kelebihan kos modal yang lebih rendah, proses operasi yang mudah dan tembaga tinggi peratusan penyingkiran, teknologi pertukaran ion menawarkan rawatan yang terbaik untuk penyingkiran kuprum tetapi ia mempunyai kelemahan di mana ia akan menyebabkan penurunan besar dalam tekanan. Dalam usaha untuk mengatasi had ini, ion membran penukar matriks bercampur dihasilkan dalam kajian ini. Amberlite IR 120H kation penukar diperbadankan pada polyethersulfone yang (PES) penyelesaian polimer berasaskan. Kesan polyvinylpyrrolidone (PVP) liang membentuk bahan tambahan dalam larutan PES telah dikaji dalam julat 0 hingga 10wt%. Membran gentian geronggang telah disintesis menggunakan prosedur berputar kering-basah. Struktur liang membran dicirikan menggunakan Mikroskop Imbasan Elektron (SEM) dan didapati lebih poros sebagai kepekatan kenaikan PVP. Kebolehtelapan ini juga meningkat kepekatan kenaikan PVP. Kepekatan optimum PVP untuk penyingkiran tembaga adalah antara 3wt% dan 5wt%.

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LIST OF SYMBOLS

Greek

ν_l	kinematic viscosity

Subscripts

g	gas
l	liquid
eff	effective

LIST OF ABBREVIATIONS

AAS	Atomic Absorption Spectrometry
BOD	Biological Oxygen Demand
COD	Chemical Oxygen Demand
$CuSO_4.5H_2O$	Copper Sulphate Pentahydrate
NMP	N-Methyl-2-pyrrolidone
PAM	Polyacrylmide
PAN	Polyacrylite
PEG	Polyethylene glycol
PES	Polyethersulfone
PVDF	Polyvinyllidene fluoride
PVP	Polyvinylpyrrolidone
SEM	Spectrometry Electron Microscope

1 INTRODUCTION

1.1 Motivation and statement of problem

Abundant of heavy metals waste water has been generated worldwide due to the industry activities such as mining, metals plating, electric device manufacturing, surface treatment and raw material for synthesis. Heavy metals such as copper, lead, mercury and chromium are toxic to human as it compromises acute and long term effect to our health(Farooq, et al., 2010).

Copper is vastly used as the major material of electronic industries. It is one of the most common metals be used in industries for the construction of structures as it has a relative high tensile strength (Kuhn & Medlin, 2000)

As a result of application of copper in electronic industries, it generates an environmental problem as the heavy metals are toxic, environment persistent and have the tendency to accumulate in the body tissues (Al-Rashidi, et al., 2013).

Membrane technology in the separation processes have became one of the emerging technologies which experienced a rapid growth of during the past decades. The membrane technology has been widely used in the gas separation where heat is not required or the mixture is an azeotrope (Hillmen, 2000). In the removal of heavy metals, membrane is not widely used as the dead end filtration is prone to fouling and concentration polarization (Zhang & Vecitis, 2014).

Several processes have been practiced for the removal of heavy metals. These methods include chemical precipitation, ion-exchange, membrane filtration, carbon adsorption, co-precipitation/adsorption and electrochemical removal (Babel & Kurniawan, 2003). Ion exchange processes mostly uses selective chelating resins contain anion functional group that have affinity towards the heavy metals ions. Besides that, the ion exchange resins causes a vast drop in pressure as the treated water passes through the ion exchange bed filled with resins (Stremovskii & Klyueva, 1974).

To date, the removal of heavy metals from wastewater using membrane are mostly flat sheet profile (Sato, et al., 2002). Microfiltration and nanofiltration are unique due to the separation mechanism which is working based on size exclusion, charge repulsion and have a higher rejection of multivalent heavy metals ions as compared to UF membranes. (Gherasim, et al., 2013). Recently hollow fiber has become a progress due to the high total surface area as compare to flat sheet (Peng, et al., 2012).

1.2 Objective

The objective of this research is to study the effects of polyvinylpyrrolidone additive concentration on the performance of hollow fiber ion exchanger mixed matrix membrane for copper removal.

1.3 Scope of this research

The following are the scope of this research:

i) To produce ion exchange hollow fiber MMM by incorporating cation resin, Amberlite IR120H into a polymer solution consist of PES, NMP and PVP.

ii) To study the effect of PVP additive concentration in the PES-Amberlite IR120H dope polymer solution from 0-10wt% on the performance of adsorptive MMM for copper removal.

iii) To characterize the MMM in term of pore structure, water permeability and static adsorption properties for copper removal.

iv) To study the effect of pH on the adsorption capacity of the membrane.

1.4 Main contribution of this work

The following are the contributions:

1) To provide an economic alternative for the removal of copper from the wastewater.
2) To provide a more efficient alternative for the removal of copper.
3) To enhance the quality of water in order to reduce the pollution of the river caused by the electronic industries in Malaysia.

1.5 Organisation of this thesis

This thesis was distributed into five chapters. Following the introduction in Chapter 1, Chapter 2 provides a description of the applications and general design features of ion exchanger mixed matrix membrane (MMM). A general description on the hollow fiber membrane, as well as the ion exchange and adsorptive membrane. This chapter also provides a brief discussion of the advanced experimental techniques available for copper removal, mentioning their applications and limitations for permeability and adsorption analysis. A summary of the previous experimental work on copper removal is also presented. A brief discussion on the characterisation methods for Ion Exchanger Mixed Matrix Membrane is also provided.

Chapter 3 is essential as it provides the information on the materials and methods of synthesizing and characterising the Ion Exchanger Mixed Matrix Membrane for Copper Removal. The performance of the Ion Exchanger Mixed Matrix Membrane (MMM) for Copper Removal with different concentration of Polyvinlypyrrolidone (PVP) additive range from 0-10wt% will be explained. The performance of the Ion Exchanger MMM was studied based on the permeability, adsorption and structure. The experimental data were compared to determine the optimum concentration of the PVP. Both static and dynamic adsorptions of the copper by the ion exchanger were studied.

Chapter 4 focused on the major findings of this research with relevant discussion. The first section will be discussing about the characterized membrane developed in this research using SEM and permeability. The effect of pH on the membrane was also discussed. The performance of the membrane is discussed based on the static and dynamic adsorption capacity and elution recovery. The analysis was done based on the data obtained.

Chapter 5 is focused on the conclusion and recommendation of the dissertation based on the results and discussion.

2 LITERATURE REVIEW

2.1 Heavy Metals Pollution

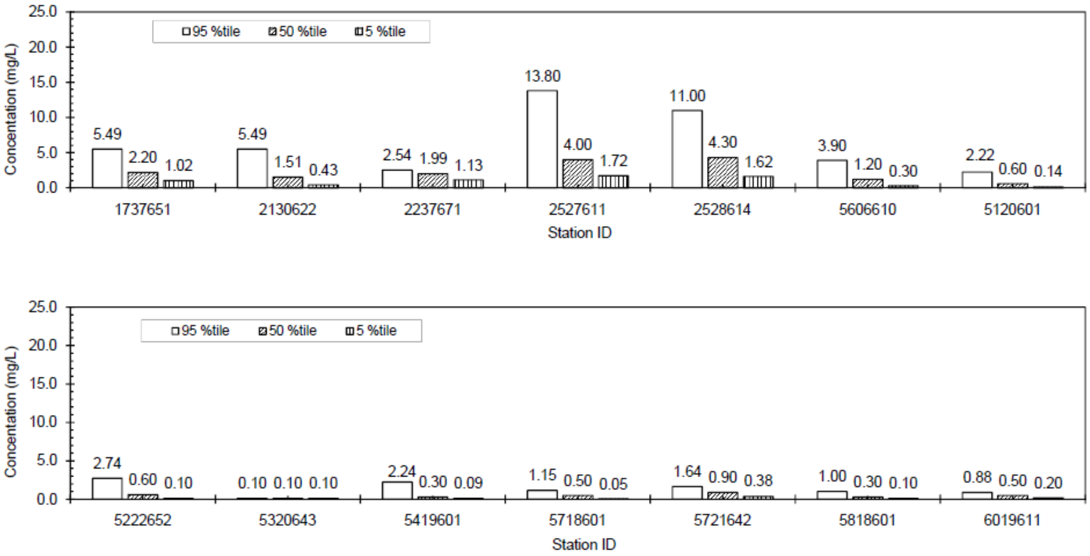
Heavy metals in industrial wastewater effluent are mainly from the heavy industries. Heavy metals are toxic and non-biodegradable and may have the continuity to exist in our water bodies. The release of heavy metal to the environment has effect on both aquatic and land organisms as heavy metals inhibits the activity of most biological body that resulting maybe acute or chronic effect to the health. Furthermore, heavy metals are not easily removed from the body. Hence a strict environmental regulation has been legislated to mitigate the heavy metals contamination especially in the discharge of industrial effluent that contains high concentration of heavy metals. The Table 2.1 shows the limits of Standards A and B that includes the limits for heavy metals. The heavy metal that is chosen to be studied is copper as it is common in our wastewater. The following Figure 2.1 and Figure 2.2 show the concentration of copper in the various sampling stations in Malaysia in year 2009. It is found out that only two of the station readings comply with the acceptable limits of Standard A for copper which are 0.20mg/L and 1.0mg/L. Whereas in compliance of Standard B, there are a few that did not comply with the reading as high 20.60mg/L which is four times the limit of 5.00mg/L of Standard B for Iron acceptance level.

Table 2.1: Parameter Limits of Effluent of Standards A and B **(Department of Enviroment, 2000)**

ACCEPTABLE CONDITIONS FOR DISCHARGE OF INDUSTRIAL EFFLUENT OR MIXED EFFLUENT OF STANDARDS A AND B

	Parameter	Unit	Standard	
			A	B
	(1)	(2)	(3)	(4)
(i)	Temperature	^{o}C	40	40
(ii)	pH Value	-	6.0-9.0	5.5-9.0
(iii)	BOD at 20^{o}C	mg/L	20	50
(iv)	Suspended Solids	mg/L	50	100
(v)	Mercury	mg/L	0.005	0.05
(vi)	Cadmium	mg/L	0.01	0.02
(vii)	Chromium, Hexavalent	mg/L	0.05	0.05
(viii)	Chromium, Trivalent	mg/L	0.20	1.0
(ix)	Arsenic	mg/L	0.05	0.10
(x)	Cyanide	mg/L	0.05	0.10
(xi)	Lead	mg/L	0.10	0.5
(xii)	Copper	mg/L	0.20	1.0
(xiii)	Manganese	mg/L	0.20	1.0
(xiv)	Nickel	mg/L	0.20	1.0
(xv)	Tin	mg/L	0.20	1.0
(xvi)	Zinc	mg/L	2.0	2.0
(xvii)	Boron	mg/L	1.0	4.0
(xviii)	Iron (Fe)	mg/L	1.0	5.0
(xix)	Silver	mg/L	0.1	1.0
(xx)	Aluminium	mg/L	10	15
(xxi)	Selenium	mg/L	0.02	0.5
(xxii)	Barium	mg/L	1.0	2.0
(xxiii)	Fluoride	mg/L	2.0	5.0
(xxiv)	Formaldehyde	mg/L	1.0	2.0
(xxv)	Phenol	mg/L	0.001	1.0
(xxvi)	Free Chlorine	mg/L	1.0	2.0
(xxvii)	Sulphide	mg/L	0.50	0.50
(xxviii)	Oil and Grease	mg/L	1.0	10
(xxix)	Ammoniacal Nitrogen	mg/L	10	20
(xxx)	Colour	ADMI*	100	200

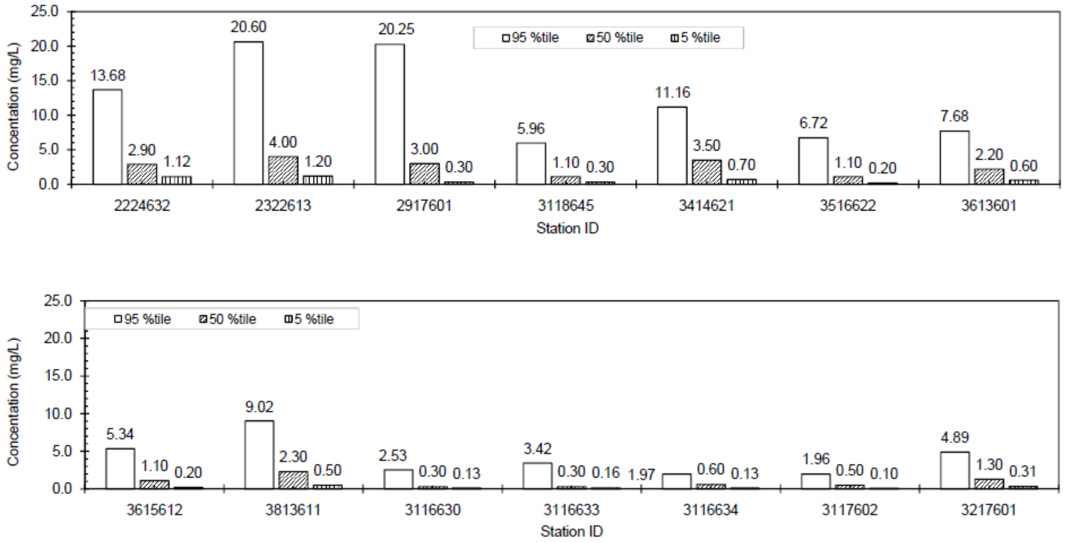
*ADMI-American Dye Manufacturers Institute



National Water Quality Standards (NWQS) and Ministry of Health (MOH) Malaysia Guidelines

Parameter	Unit	Class I	Class IIA	Class IIB	Class III	Class IV	Class V	MOH
Iron	mg/L	-	0.3	-	1	1	-	1

Figure 2.1: Percentile Values of Cu (Copper) at all Sampling Stations **(Department of Irrigation and Drainage, 2009)**



National Water Quality Standards (NWQS) and Ministry of Health (MOH) Malaysia Guidelines

Parameter	Unit	Class I	Class IIA	Class IIB	Class III	Class IV	Class V	MOH
Iron	mg/L	-	0.3	-	1	1	-	1

Figure 2.2: Percentile Values of Cu (Copper) at all Sampling Stations continued

(Department of Irrigation and Drainage, 2009)

2.1.1 Copper

Copper is a ductile metal with a very high electrical and thermal conductivity. It is used as a conductor of electricity and heat, parts of several metal alloys and construction material. It has been used for thousands of years. Copper compromises 50 parts per million in of the earth crust. Copper element can be found in the earth crust naturally and the Cu^{2+} ions are easily combine with sulphur and oxygen containing compounds such as hydroxides, oxides, carbonates and sulphides. Chalcopyrite and Chalcocite are the most common compound of copper found in nature. Copper (as Cu^{2+}) concentrations of 40 µg/litre can be detected by taste in distilled water. In mineralized spring water with total dissolved solids (TSS) content of 500 mg/litre, the taste threshold value was 0.12 mg/litre.

Copper is vital in human nutrition. The estimated of the minimum daily requirement for copper range from about 0.9 to 1.3 mg/day(FAO, 1988). The average lethal dose of copper is 10 mg/kg of body weight. Studies have shown that in excess of copper dosage can cause to tissue injury and disease. The oxidation potential of copper is responsible for some of its toxicity in excess ingestion cases that causes oxidative damage to the human body system that includes peroxidation of lipids and other macromolecules (Bremner, 1998). There's research that shows the significance of the excess of copper in the progression of Alzheimer's disease due to the accumulation of metal homeostasis disturbance that develops in individuals with Alzheimer's disease brains that possibly be damaging by the toxic buildup of amyloid beta in the brain (Bhattacharya, 2003).

2.2 Heavy Metals Removal Techniques

2.2.1 Adsorption

It is recognized as an economic and effective method of removing heavy method as it provides the flexibility of design and operation for the removal of heavy metals. In most cases, it is able to produce high quality treated heavy metals effluent. In addition, it is able to be regenerated through desorption process of the adsorbents. Activated carbon is the most widely used adsorbent to remove heavy metals. It is derived from carbonaceous source of material such as coconut husk, wood, coal and recently from biomass. It is produced through either chemical activation or physical activation. Activated carbon is extensively used in removal of heavy metals as it is highly porous and high surface are per volume. Langmuir and Freundlich are the two isotherms used to describe the application of water treatment. The Langmuir isotherm is

$$q = \frac{q_o c}{K + c}$$

(2.1)

In Langmuir isotherm, only a fixed number of active sites available for adsorption. It is also a reversible and reaches equilibrium.

The Freundlich isotherm is

$$q = Kc^n$$

(2.2)

In Freundlich isotherm, it explained the variation of adsorption with temperature. This isotherm is fails at higher pressure. The mechanism of adsorption is visualized in the Figure 2.3.

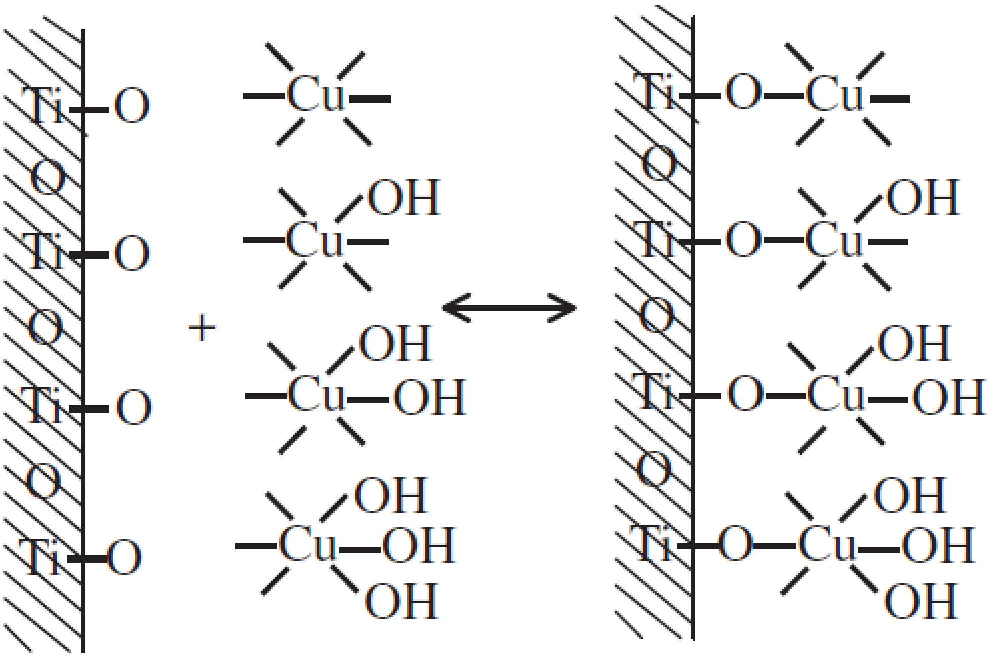


Figure 2.3: The adsorption mechanism of Cu(II) on hydrous TiO_2 **(Barakat, 2005)**

2.2.2 Chemical Precipitation

Chemical Precipitation the most widely used technique as it is inexpensive and relatively simple to operate (Ku & Jung, 2001). The chemicals react with heavy metals to form insoluble precipitates that will be then removed using filtration method. The chemicals widely used for precipitation are such as hydroxides and sulfides. Hydroxides are widely used as the pH control is easy (Huisman, et al., 2006). The range of the hydroxides is pH from 8.0-11.0. The metals hydroxides such as potassium hydroxides and sodium hydroxides can be removed using sedimentation and flocculation. In addition, aluminum oxide and iron salts are being used to boost the removal of the heavy metals. The drawback of hydroxide precipitation is that it produces a large amount of sludge that poses disposal problems (Kongsricharoern & Polprasert, 1995).

Aside from metals hydroxides, sulfide precipitation is also an effective method to remove heavy metals. It is more preferred to be used due to the solubility of most sulfide compounds are less soluble as compare to hydroxides that provides a more effective removal of heavy metals. However, sulfide precipitation process is causing problems due to the hydrogen sulfide toxic fumes with the reaction of acidic conditions. Thus the process should be done in neutral or alkaline condition. Lastly, the sulfide precipitation is prone to form colloidal precipitates that causes problem in filtration and settling process.

Recently, chelating precipitants are used to precipitate heavy metals from the solution. The three widely used chelating precipitants for heavy metals removal are trimercaptotriazin, sodium dimethyl dithiocarbonate and potassium/sodium dimethyldithiocarbonate. Chelating precipitation is a particular method that ions and molecules bind metals ions to form precipitants and removed through filtration(Wang, et al., 2012). Chelating precipitation shows a remarkable result of reducing the concentration of heavy metals with an immediate reduction of the heavy metals but if the precipitate is not removed immediately, it will decompose and form by products such as tetramethylthiuram and thiram which are toxic to aquatic organisms (Atwood & Zaman, 2006). In Figure 2.4, shows the process of a conventional metals precipitation treatment plant.

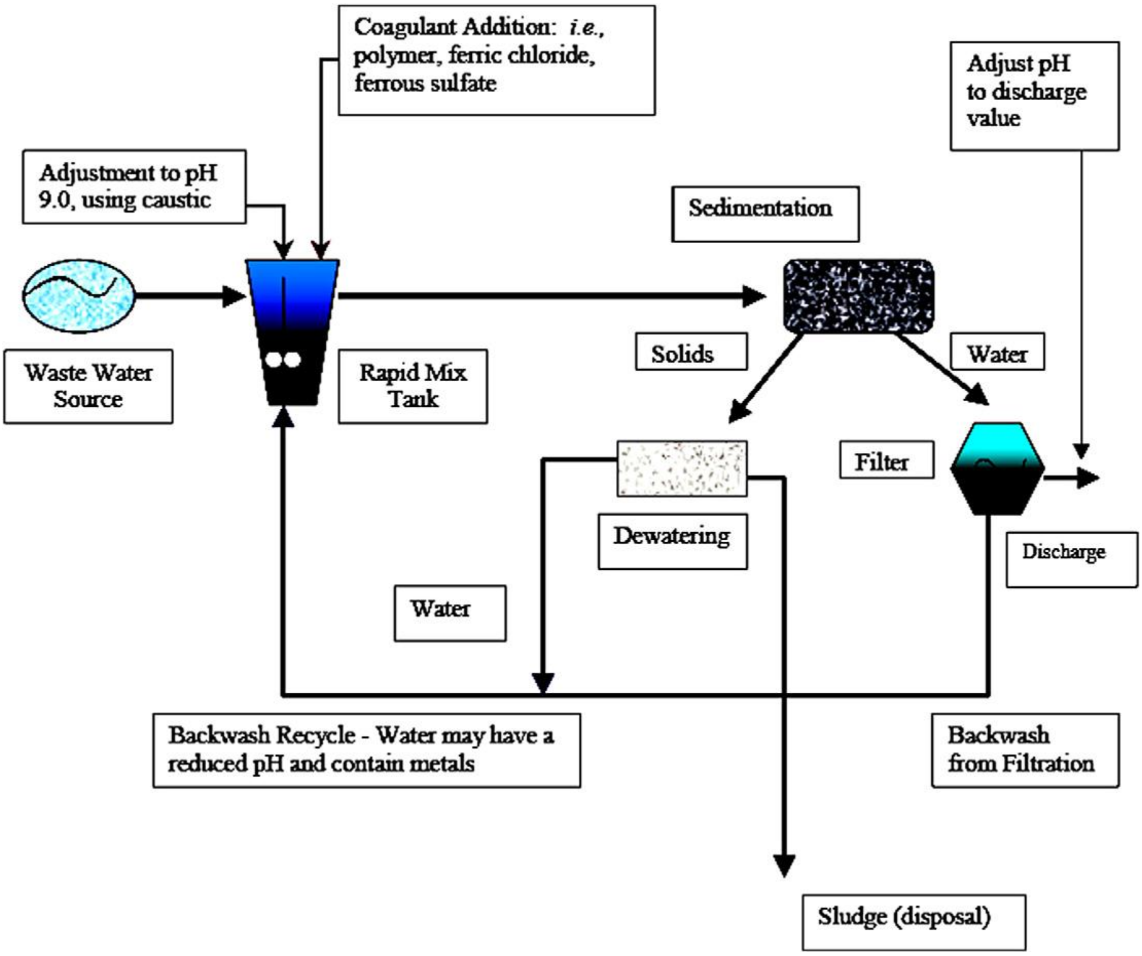


Figure 2.4: Processes of a conventional metals precipitation treatment plant **(Wang, et al., 2005)**.

2.2.3 Coagulation and flocculation

The processes before sedimentation are coagulation and flocculation. Coagulation is the process of destabilising the colloids by neutralising the forces that keep the colloids apart. Aluminium oxide and ferric chloride are the most widely used coagulant in the conventional wastewater treatment processes. Flocculation is the formation of bridges between the flocs and binds to form larger agglomerates. Suspended particles are flocculated into larger particles can be removed by filtration or floatation. Polyferric sulphate (PFS) and polyacrylamide (PAM) are the widely used flocculants. However, most of these flocculants and coagulants are not able to remove heavy metals (Chang & Wang, 2007). These processes require the support of other treatment to fully remove heavy metals. In order to overcome the limitation of coagulation, electrocoagulation technique had been introduced. Electrocoagulation involves the formation of coagulants in situ by dissolving electrically iron or aluminium ions from iron or aluminium electrodes (Chen, 2004). The metals ions are formed at the anodes and hydrogen gas is released from the cathodes. The hydrogen gas that is released assists the floatation of the flocculated particles out of the water. The removal efficiency of heavy metals is able to achieve 99% (Mulligan, 2009). However the electrocoagulation technique requires a huge amount of energy to remove heavy metals (Kim, et al., 2014).

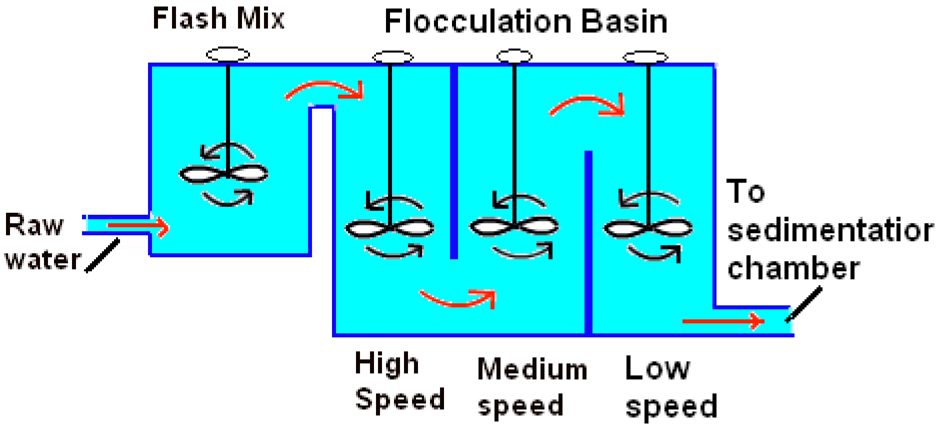


Figure 2.5: Mechanism of Flocculation**(Chemistry.TutorVista.com, 2014)**

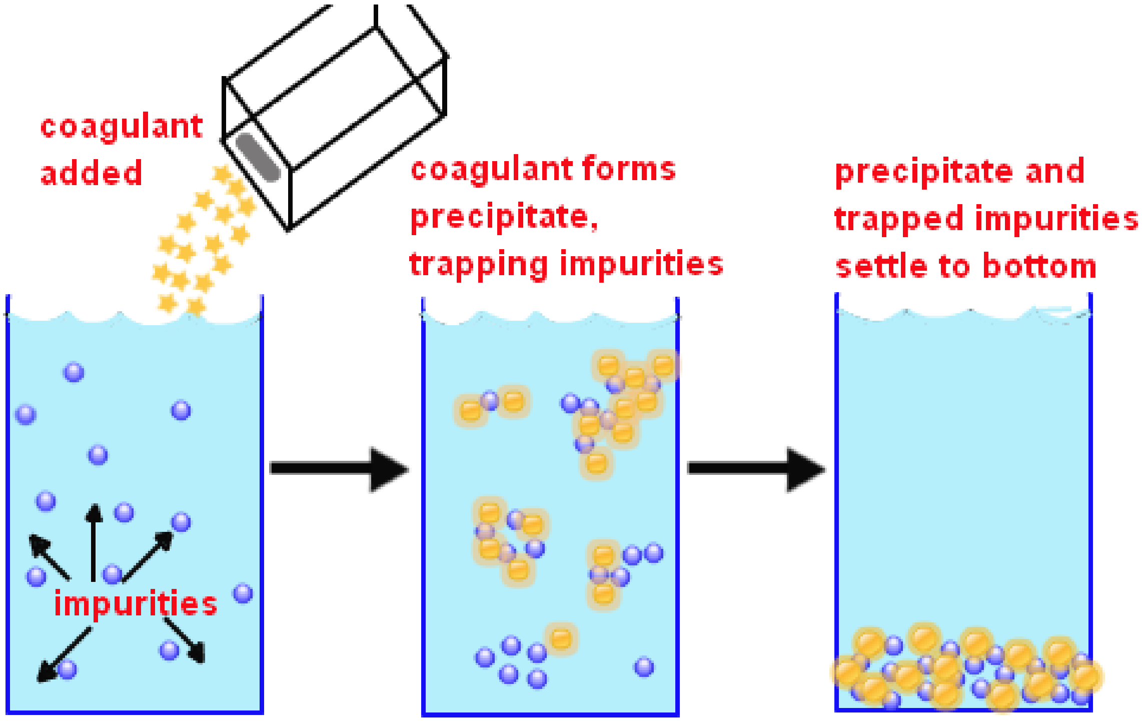


Figure 2.6: Mechanism of Coagulation **(Chemistry.TutorVista.com, 2014)**

Figure 2.7: Coagulation and Flocculation Tank **(Dynamic-des.com, 2014)**

2.2.4 *Membrane*

Membrane is a thin barrier that allows certain constituents and retains other constituents found in the liquid based on the ionic charge and size of the constituents (Cheryan, 1998). The membrane is separated by one bulk phase with higher concentration of certain constituents and another lower concentration of it as shown in Figure 2.8 (Geankoplis, 2003). In terms of pressure or concentration gradient, the driving force initiates from the chemical potential gradient. Industrial membranes separation processes can be categorized into several groups based on the driving force that initiates the flow of the permeate through the membrane (Matsuura, 1994). In Table 2.2 the types of membrane separation process classified based on the driving force. In general membrane is prone to fouling and concentration polarization (Moreno-Villoslada, et al., 2005).

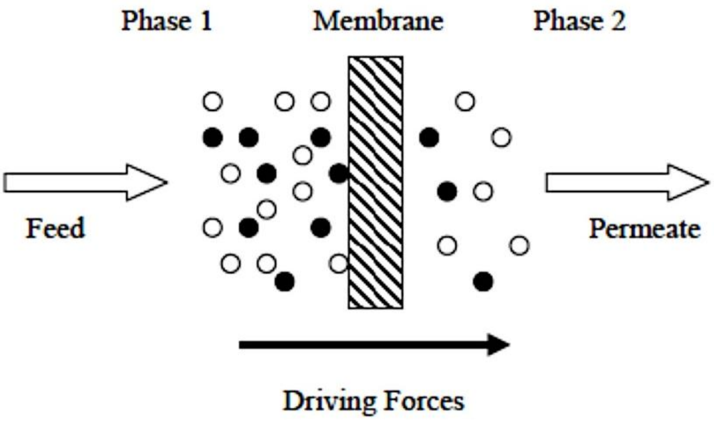
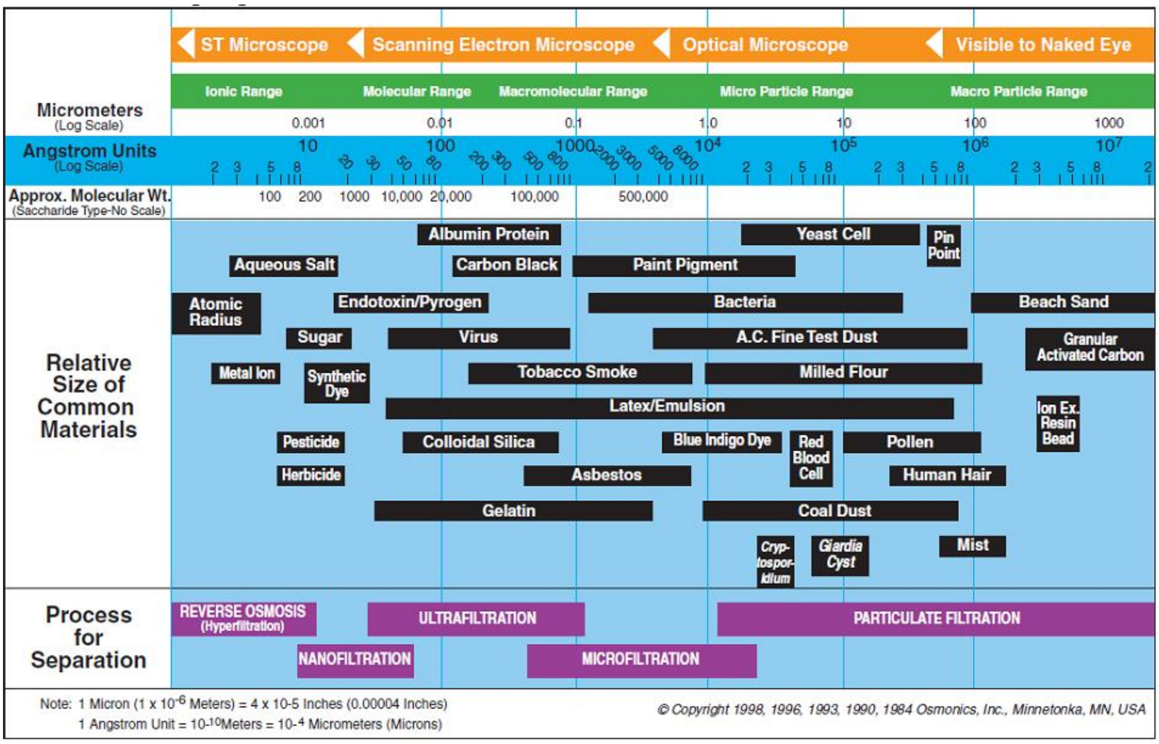


Figure 2.8: Schematic diagram of a two-phase separation system separated by a membrane.**(Tin, 2005)**

Table 2.2: Membrane separation process classified driving force

Type of Driving Force	Separation Process
Pressure difference	▪ Reverse Osmosis ▪ Microfiltration ▪ Ultrafiltration ▪ Pervaporation
Concentration difference	▪ Forward Osmosis ▪ Dialysis
Temperature difference	▪ Membrane Distillation
Electric potential difference	▪ Electrodialysis

The membranes that work on the pressure difference can be divided based on the pore size. The classification of the membranes based on the size exclusion of pressure differences are as the following Figure 2.9.



Note: 1 Micron (1 x 10^{-6} Meters) = 4 x 10-5 Inches (0.00004 Inches)
1 Angstrom Unit = 10^{-10}Meters = 10^{-4} Micrometers (Microns)

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Figure 2.9: Pore Size of Membrane Processes **(Radcliff & Zarnadze, 2004)**

There are a few configurations of membrane which are namely flat sheet, tubular, spiral wound and hollow fiber.

2.2.4.1 Flat Sheet Configuration

Flat sheet membranes are typically synthesized to a filtration system that consists of stacks of modules with a quantity of sheets. Flat sheet has been used in the removal of heavy metals for decades. The cost of running flat sheet membrane will be higher as compared to other conventional techniques as it requires the high pressure application of 20 bars and the module is prone to fouling though it is able to remove heavy metals with the efficiency of more than 96%(Tanninen, et al., 2006). The Figure 2.10 shows the image of flat sheet membrane.

Figure 2.10**:** Flat Sheet Membrane**(EC Plaza, 2013)**

2.2.4.2 Hollow Fiber Configuration

Hollow fiber module membrane has gain rapid progress in the last 12 years in bioseparation, drinking water purification, wastewater treatment and gas phase separation as it has a high separation areas and selectivity compared to the conventional flat sheet module (Feng, et al., 2013). The excellent mass transfer properties of hollow fiber membrane configuration had lead to a number of industrial applications. The Hollow fiber element permits a higher surface area in small volumes that provide the configuration to adapt in the industry by using a minimal space as compared to the flat sheet module. Hollow fiber is able to reduce the fouling as the fluid flows from inside the hollow fiber and passes through the outer of the membrane (Li, et al., 2014). Figure **2.11** shows the structure of hollow fiber membrane.

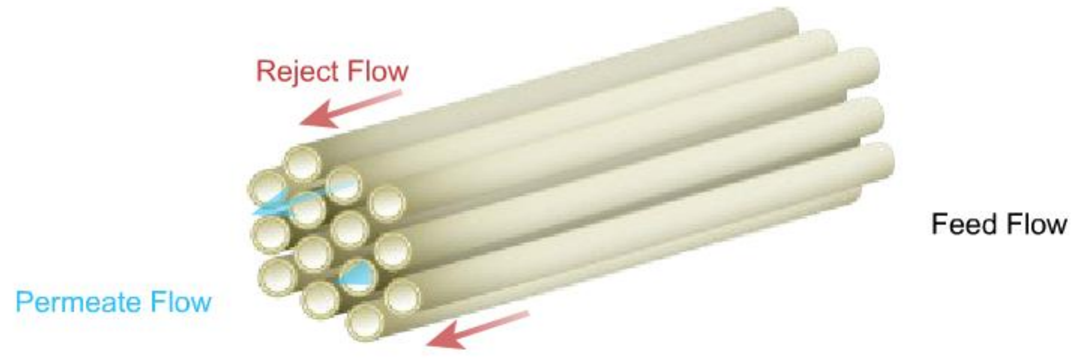

Figure 2.11: Structure of a Hollow Fiber Membrane **(Hyfluxmembranes.com, 2008)**

The excellent mass transfer properties of hollow fiber configuration allows it to be used in various fields such as water desalination and purification, gas separation, azeotropic separation and medical usage.

2.2.5 *Ion Exchange*

Whenever an ion is removed from the aqueous solution and replaced by another ionic species is generally called as ion exchange. Ion exchange is normally used for food & beverages, chemical, petrochemical, semiconductor, water treatment and pharmaceutical industries. Mostly the application of ion exchange is to produce deionized water for such industries. Besides that, it is widely used to soften ground water by exchanging with calcium (Ca^{2+}) and magnesium (Mg^{2+}) ions with H^+ ions. Zeolite, clay and soil hummus are natural ion exchangers. In industry, commercialized ion exchangers are normally synthesized from polystyrene and polyacrylate that are consist of small, porous beads that are insoluble in water and organic solvents (Neunmann, 2009). Each of the monomer units of the polymer, functional groups are attached. Ions are either positively (cations) or negatively (anions) charged. The functional groups are charged that allows the interaction between ions and functional groups is exhibited through electrostatic forces. Positively charged functional groups such as sulfonic-, phosphoric- or carboxylic acid group will interact with cations. Whereas negatively charged groups such as quarternary amine group will interact with anions. The interaction of between the attached ions is relatively loose and can be reversed by another ion passing. This allows the ion exchange resins to be recharged for repetitively used. The mechanism of the ion exchange is visualized in Figure 2.12. The drawback of ion exchanger is that it will cause a vast drop in pressure(Moreno-Villoslada, et al., 2005). Ion exchange technology uses a very low amount of energy as compared to electrolysis process as electrocoagulation consumes very high amount of energy(Abdelwahab, et al., 2009).

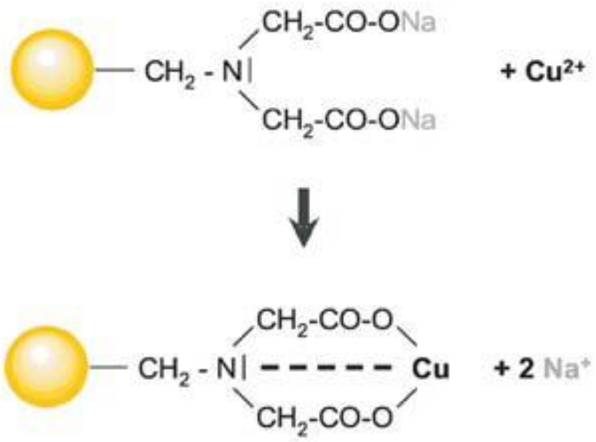

Figure 2.12: Mechanism of Binding of Copper ion to the Functional

2.2.6 Comparison of the Heavy Metals Removal Techniques

In the development of heavy metals removal in the recent years, the following **Error! Not a valid bookmark self-reference.** shows the comparison of the several techniques that are normally used for the removal of heavy metals.

Table 2.3: Comparison of the Heavy Metals Removal Techniques

Heavy Metals Removal Technique	***Descriptions***	***References***
Adsorption	Effective and economic method for the removal of heavy metals	(Anwar, et al., 2009)
	Able to bind metals even from dilute solutions	(Volesky, 1990)
	Vast pressure drop after treatment of water	(Chahbani & Tondeur, 2001)
Chemical Precipitation	High reagent cost	(Javaid, et al., 2011)
	Requires further treatment of the wastewater such as filtration to remove the precipitated heavy metals	(Ku & Jung, 2001)
Coagulation and Flocculation	Removal of Arsenic and Iron through coagulation pH dependent as most reagents are not soluble in condition that is too alkaline or acidic.	(Mohan & Pittman, 2007)
	Disposal problem as it generates a huge amount of sludge	(Lakshmanan, et al., 2010)
	More economical and effective compare to ion exchange and adsorption	(Ghurye, et al., 2004)

	Complex system as it requires the correct continuous dosing amount of reagent dosage and pH correction	(Lakshmanan, et al., 2009)
	Requires the need of other equipment such as filtration to further increase the efficiency of heavy metals removal	(Han, et al., 2002)
Membrane	Fouling is limiting the potential of the membrane that increases the cost of operation	(Shi, et al., 2014)
	High efficiency of heavy metals removal	(Radcliff & Zarnadze, 2004)
	Low retention time	(Wallace, et al., 2006)
	Require small space of operation	(Kurniawan, et al., 2006)
	Concentration polarization but can be decreased with increase of feed flowrate	(Sablani, 2007), (Gherasim & Mikulášek, 2014)
	Hollow fiber geometry reduces the cost of operation with the high surface area and reduction in fouling and concentration polarization	(Di Luccio, et al., 2002)
Ion Exchange	Low cost of operation with regeneration ability	(Cummings, et al., 2007)
	High pressure drop of treated water	(Barragán & Pastuschuk, 2014)
	Achieving low concentration of metals ion	(Burns & Gregory, 1995)
	Able to operate at low level of metals ion in the solution	(Sun, et al., 2012)

2.3 Ion Exchanger Mixed Matrix Membrane

In the advancement of membrane, various types of membranes have been developed for the use of ultrafiltration, reverse osmosis, microfiltration, electrodialysis and pervaporation. Among the membranes developed, Ion Exchange Membranes are one of the most advanced separation membranes as it incorporates both membrane and ion exchange technology in it and it has potential applications as a new generation of membrane for the separation processes. Ion exchange membranes have been recently used in protein, sugar, dye and demineralization processing (Nagarale, et al., 2006). In the removal of heavy metals, not much commercialized membrane was using the ion exchange membrane. Ion exchange mixed matrix membrane is able to overcome the limitations of both ion exchange and membrane technology. Ion exchange mixed matrix membrane is synthesis by adding ion exchange resin into the dope solution and form a mixed matrix structure as shown in Figure 2.13. With the increased of ionic functionality, mixed matrix membrane is able to enhance the selectivity of the membrane for the removal of heavy metals. The introduction of resins into the membrane requires a careful control of the pore size as the functionality of the mixed matrix depends on the porosity of the membrane. The loading capacity of the resin must be monitored to ensure that the mechanical strength of the mixed matrix membrane is not compromised as the introduction of resin reduces its mechanical properties such as tensile strength. Aside from higher performance, Ion Exchanger Mixed Matrix Membrane will also allow the Hollow Fiber module to be regenerated by using strong acid such hydrochloric or sulfuric acids to regenerate the cation part of the resin with H^+ charge. This allows the cost of operation and maintenance of the hollow fiber membrane to be lower as hollow fiber membrane is known for its limited cleaning due to the structure of it.

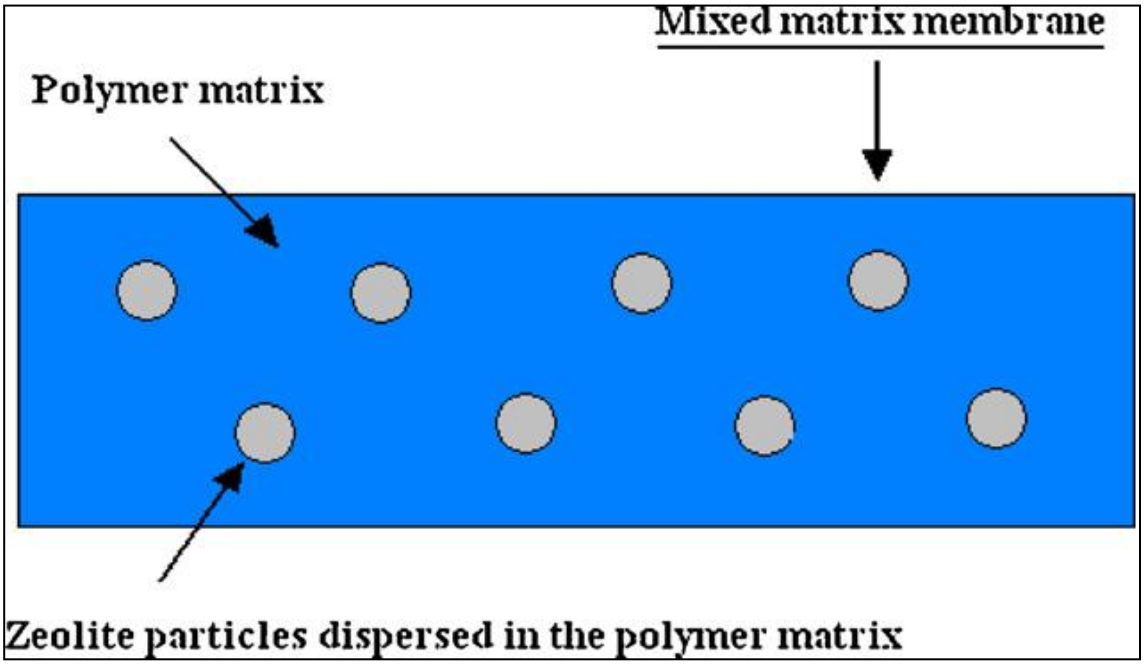

Figure 2.13: Schematic of Mixed Matrix Membrane (MMM)**(Bastani, et al., 2013)**

2.4 Opportunities of Copper Removal Mixed Matrix Ion Exchange Membrane

The current research is based on the greater opportunity of turning the studied product into a potential separation unit in industries. In regards to its energy efficiency, heavy metals removal using mixed matrix ion exchange membrane has its potential as compare to other technologies as being discussed for its high mechanical properties, removal efficiency of heavy metals, low energy consumption, low maintenance since the fouling limitations of membrane can be reduced with introduction of ion exchange in its matrix. According to Malaysian External Trade Development Corporation (MATRADE), Electrical & Electronics industry is one of the leading industries that contributes 24.5 percent of the manufacturing sector in the Malaysia's Gross Domestic Product (GDP)(MATRADE, 2013). About 60% of the copper produced are used in electrical wires and electronic applications.

2.5 Polyethersulfone

Polymeric material such as Polyvinlydenefluoride (PVDF), Polyacrylite (PAN) and Polypropylene (PP) are the most commonly used material for the production of membrane (Michael, et al., 2003). Polyethersulfone is a thermoplastic that is known for its toughness, stability at high temperature and hydrostatic pressure. The disadvantage of PES is that it is hydrophobic and its one of the factor of fouling in membranes (Zhao, et al., 2013). However, by blending the PES with additives such as PVP and PEG can reduce the hydrophobic characteristic of PES (Zhao, et al., 2013).

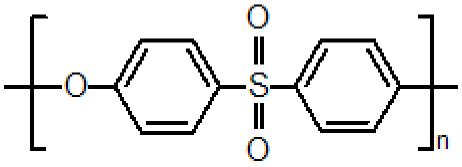

Figure 2.14: Molecular Structure Polyethersulfone (PES)

The introduction of additive into the membrane dope solution also affects the coagulation bath and the formation of the inner and outer surfaces of the hollow fiber membrane. It was demonstrated by Kong and Li that the addition of additive to the dope solution resulted a higher porosity of membrane (Kong & Li, 2001). The permeation flux of the membrane will be increased with the use of additive(Wang, et al., 1999).

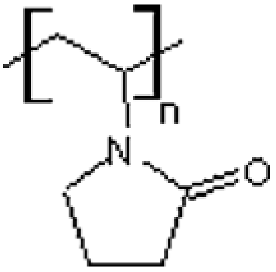

Figure 2.15: Molecular Structure of Polyvinylpyrrolidone (PVP)

2.6 Analysis Methods of Permeability and Adsorption of Membrane

Membrane acts as a filter to separate one or more heavy metals from a feed mixture. In general, there are two characteristics that dictate the membrane performance in the current study, which are permeability and adsorption. Permeability is the flux of a fluid through the membrane. The permeability of the membrane is important as it is needed to allow water to pass through it to ensure that the pressure drop can be minimized(Loh & Wang, 2012). The permeability can be studied using the pure water permeability (PWP) test that will be discussed in the methodology. The relationship between permeability, diffusivity and solubility can be represented by Equation. (3). Adsorption is the adhesion of ions or molecules of gas, liquid or dissolved solids to a surface which is generally solid. The adsorption of the membrane can be explained by the equation developed by Lagmuir in 1916 or Freundlich.

$$P = DS \tag{2.3}$$

Where;

P is the permeability coefficient (cm^3 (STP) cm^{-2} s^{-1} cm Hg^{-1}) or refers to the measure of the flux of membrane.

D is the diffusivity coefficient (cm^2 s^{-1}) or a measure of the mobility of molecules within the membrane and S is the solubility coefficient (cm^3 (STP) cm Hg^{-1})

2.7 Summary

Ion Exchanger Mixed Matrix Membrane has the potential for the removal of copper from wastewater based on the past studies done. Separation of copper from wastewater is crucial as it cause harmful effect to our health. Hollow fiber module is a trend in the removal of heavy metals industry because of the low occurrence of fouling compare to the flat sheet system. Besides that, hollow fiber configuration also can reduce the pressure drop that is posed by the resin technology. The factor that will be studied in this research will be the concentration of the additive on the performance of the membrane in terms of permeability, adsorption capacity and the pore structure. However, other parameters such as the take up speed, air gap height and depth of dope solution are not studied due to the limitation of time given to complete this undergraduate research project

3 METHODOLOGY

3.1 Chemicals

Polyethersulfone Radel@ from Solvay Advance were used as the base membrane polymer. NMP, PVP and copper (II) sulphate pentahydrate and Amberlite IR120H cation resin are purchased from Sigma-Aldrich.

3.2 *Preparation of Dope Polymer Solution*

Amberlite IR120H washed with deionized water to remove any impurities and dried in a conventional oven at 80ºC for 24 hours. The dried resin is grinded with an ultra centrifuge grinder (Retsch Rottor Mill ZM200). The ground resin further sieved using 45µm test sieve.

Figure 3.1: Retsch Rottor Mill ZM200

Different types of dope polymer solution will be prepared according to Table **3**.**1**. The PES was kept constant at 18wt% with the PVP concentration varied from 0 to 10wt%. PES and PVP dissolved in NMP under continuous stirring at 60ºC for six hours at 800rpm as shown in Figure **3**.**2**. Ground Amberlite IR120H mixed into the prepared PES polymer solution at 20wt% cation loading relative to the amount of PES for four hours.

Table 3.1: Dope solution composition of hollow fiber membrane

Dope no.	Dope solution composition		Bore fluid composition
1	PES/NMP	18:82	H_2O
2	PES/NMP/PVP	18:79:3	H_2O
3	PES/NMP/PVP	18:77:5	H_2O
4	PES/NMP/PVP	18:74:8	H_2O
5	PES/NMP/PVP	18:72:10	H_2O

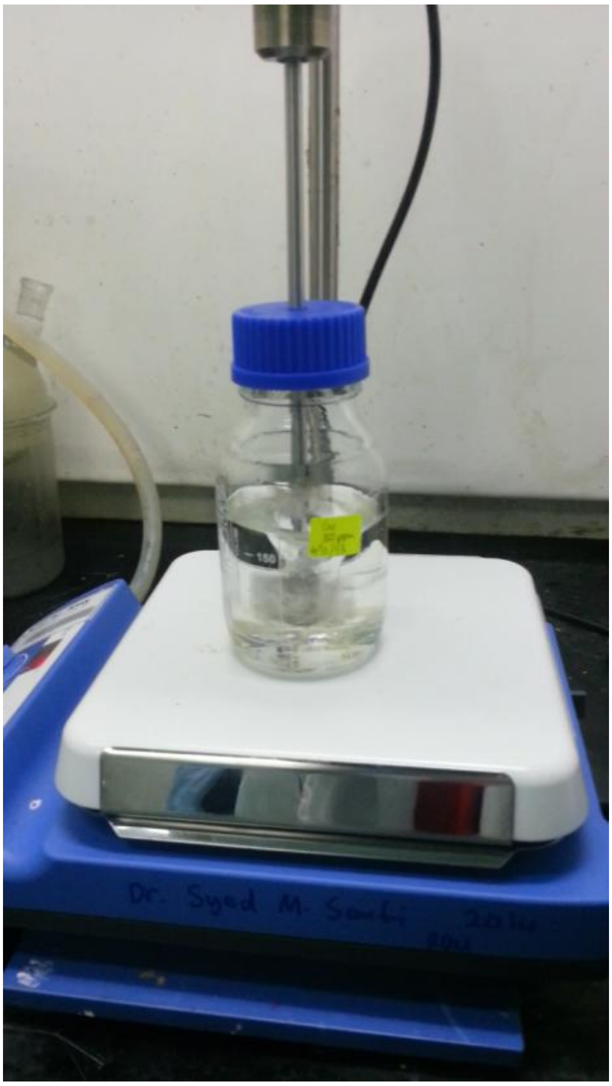

Figure 3.2: Dope Solution Preparation

3.3 *Hollow Fiber Dry-Wet Spinning Process*

The dry-wet spinning technique is used to synthesize the hollow fiber membrane. The other parameters such as weight ratio of the resin, the applied pressure, bore fluid flow rate set at 1 bar pressure and fiber take up speed set at 31 revolutions per minute. The Figure 3.3 shows the preparation of the hollow fiber membrane. The Figure 3.4 shows the hollow fiber membrane produced at the take up drum. The synthesized membrane was dip in water bath as shown in Figure 3.5 to allow the membrane to settle further.

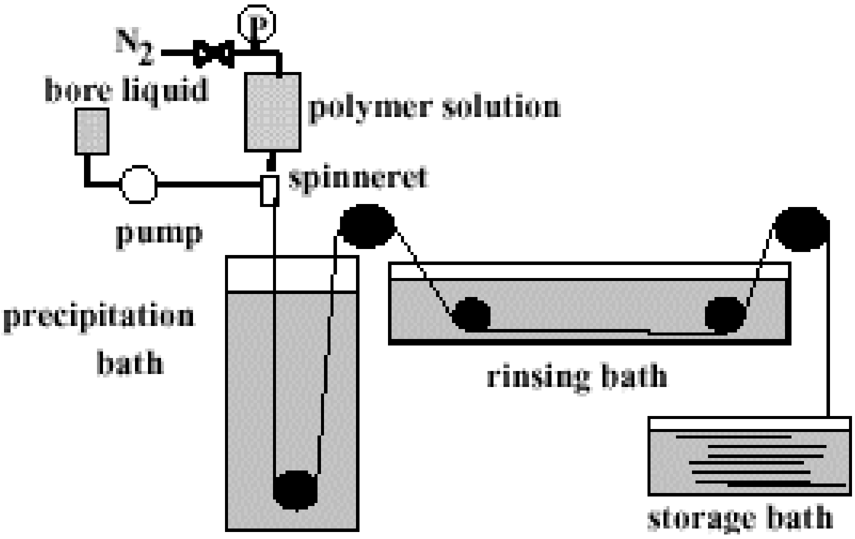

Figure 3.3: Dry-wet Spinning Process

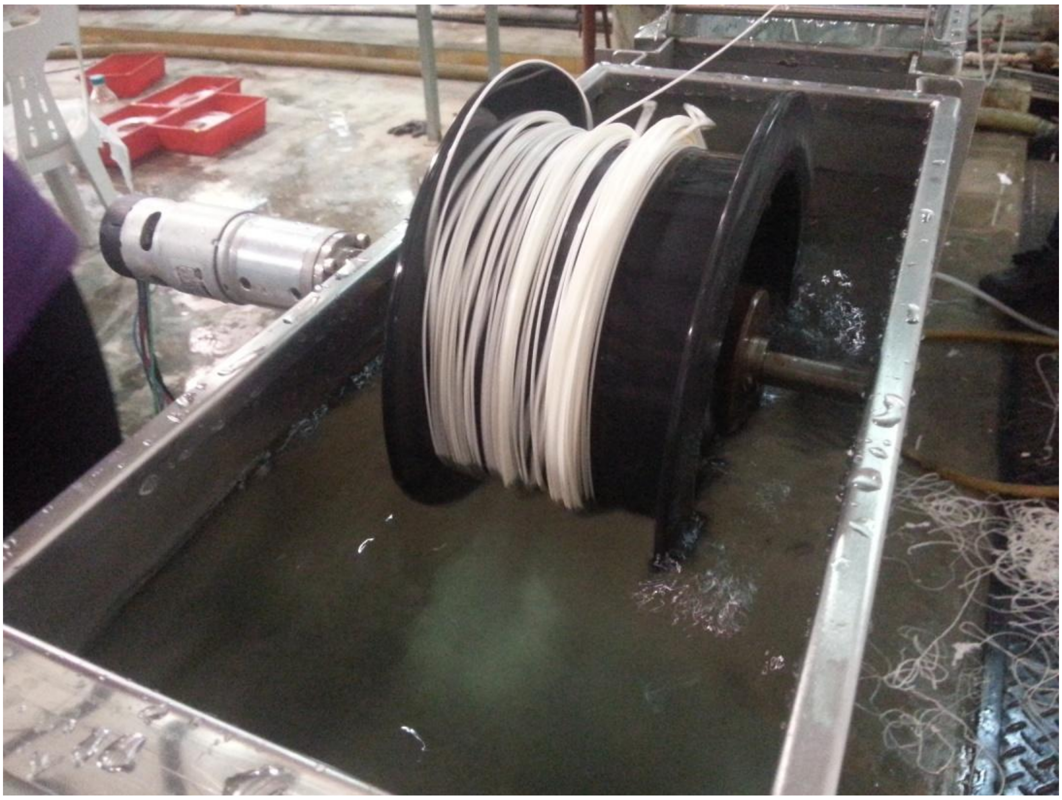

Figure 3.4: Hollow fiber membrane produced at the take up drum

Figure 3.5: Storage bath of the hollow fiber membrane

3.4.3 Membrane Module Fabrication

Module fabrication has constantly been treated as proprietary know-how. Systematic teaching and scientific research on the module fabrication and design are not widely available in the academic journals(Li, et al., 2004). Hollow fiber modules may have different configurations to meet the requirements of various applications. The most general one is the shell-side feeding hollow fiber module and visualised in Figure 3.6. It can be seen that there are two epoxy tube sheets that holds the hollow fiber ends in place. At one end, it is an open end that allows the permeate to flow out, whereas the other end is a dead end and allows the retentate to flow out. The flow pattern inside the module is cross-flow. This type of configuration of membrane is used in the research as the submerged unconfined hollow fiber module is highly recommended for the application of dissolved solid-containing water treatment such as the removal of copper(Fame, et al., 2002).

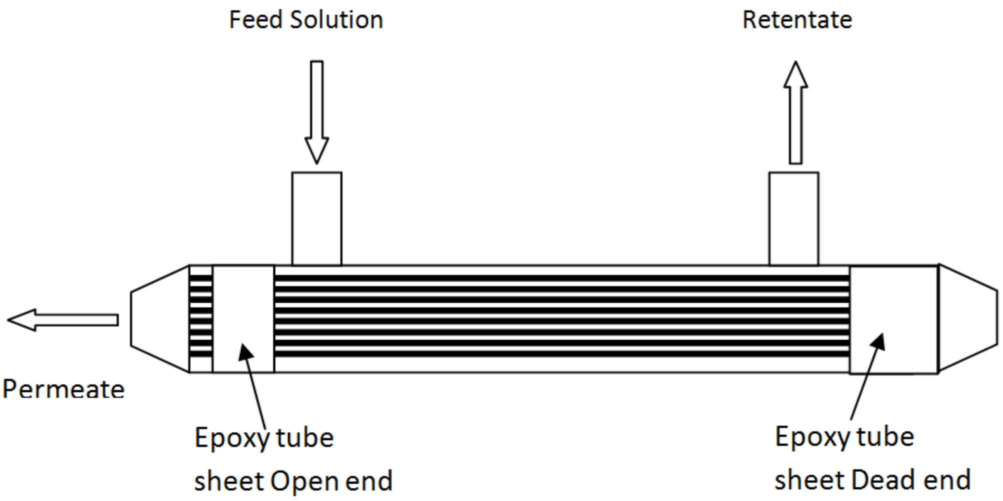

Figure 3.6: Shell-side Hollow Fiber Module

In general, small modules are made of 10-20 pieces of hollow fibers and tested for performance evaluation. The diameter of commercial modules are ranged from 1 to 12 in. with the diameter between 2 to 8 in. as the most common one. For lab-scale modules, a suitable diameter is suggested to be 1/2 to 3/4 in. with the consideration of material and operational cost (Li, et al., 2004).

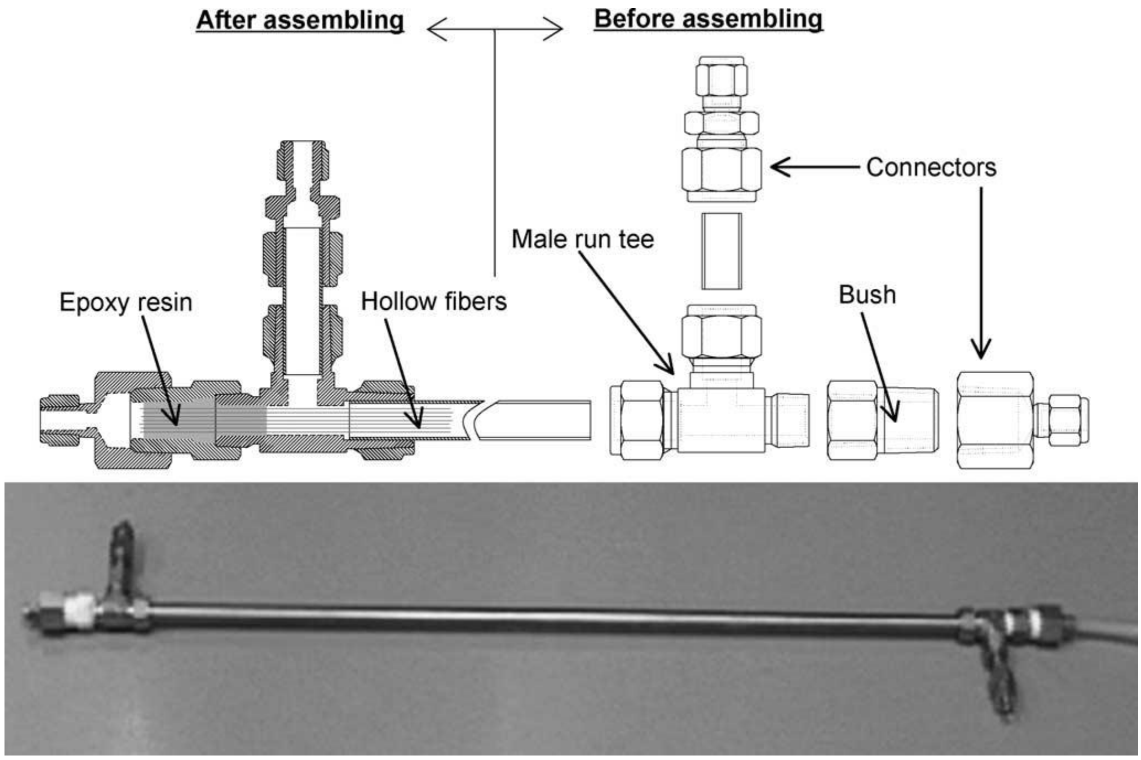

Figure 3.7: Structure of lab-scale modular module **(Li, et al., 2004)**

The module is prepare as the following steps:

a) 15 hollow fiber membranes were selected and it is cut into the desired length and the visibly defective fibers (creases, collapses and uneven thickness) are removed.
b) Parafilm barrier film is used to wrap the bundled membrane as shown in Figure 3.8B to hold the membrane in place. This is done for both ends
c) A small amount of fast curing epoxy resin is used to cure the open end and is left for 20 minutes before placing the bundle into the module.
d) The module shell is vertically placed on a retort stand and membrane is then inserted into the module shell as shown in Figure 3.8E.
e) Both of the ends are inserted with a hose as the mold for the epoxy resin tube sheet casting.
f) The hose mold is then covered with Parafilm to avoid the flowing of the epoxy resin.
g) The curing epoxy is then injected to the mold using a 10mL syringe.
h) The mold is then wrapped with Parafilm again to close the hole caused by the syringe and is left for 24 hours as shown in the Figure 3.9 to allow the epoxy resin to be fully cured.

i) The solidified resin located outside the module tube sheets is removed using a handsaw and cut clean cross-section using blade.

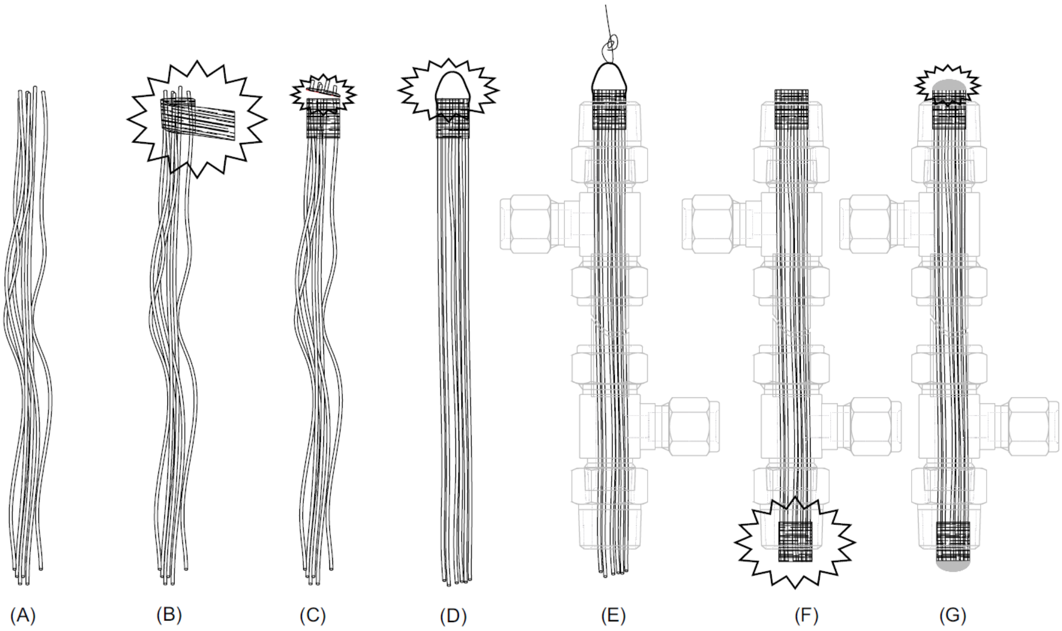

Figure 3.8: Bundle preparation and module assembly**(Li, et al., 2004)**

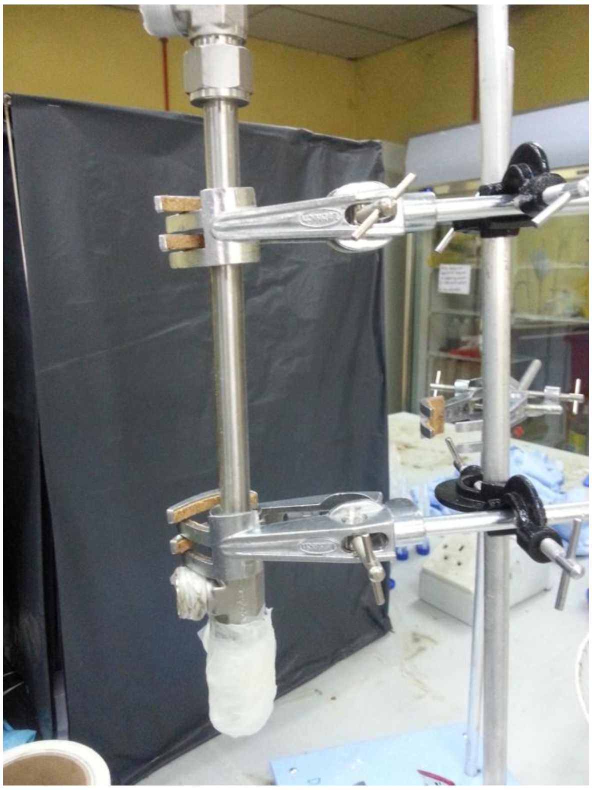

Figure 3.9: Curing of the Epoxy Resin

The constructed membrane module will be setup as shown in Figure 3.10 and Figure 3.11.

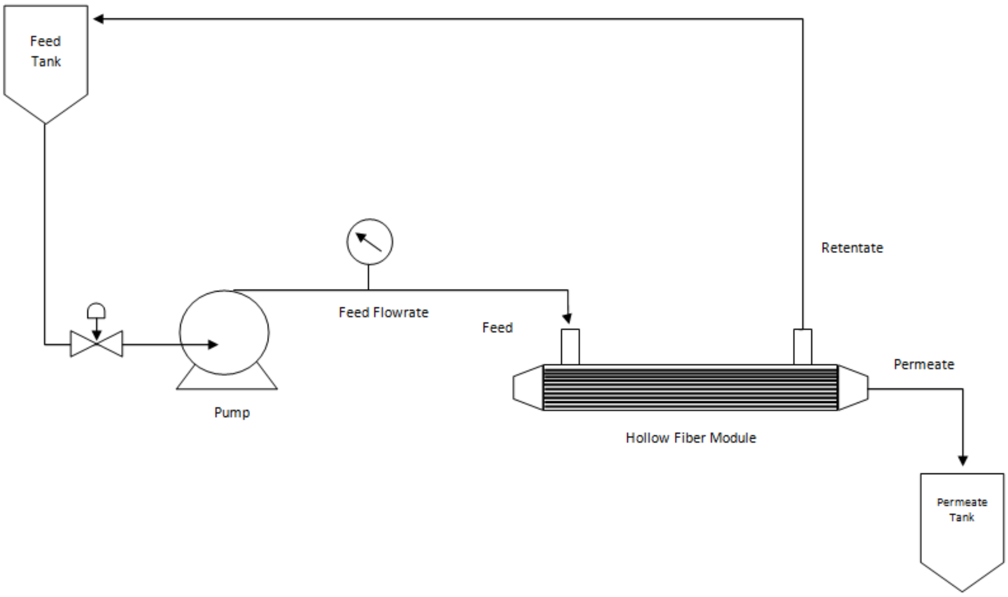

Figure 3.10: Schematic Diagram of Membrane Module Setup

Figure 3.11: The Membrane Module Setup

3.4.4 Scanning Electron Microscope

The structure of hollow fiber is characterized using scanning electron microscope (SEM). Hollow fiber membrane is immersed and fractured in liquid nitrogen for the sample preparation. The samples are then coated with platinum before being observed under SEM. The cross section of the hollow fiber membrane is observed at 40x, 50x 200x, 400x and 1000x magnification. The example of hollow fiber membrane under SEM is shown in Figure 3.12

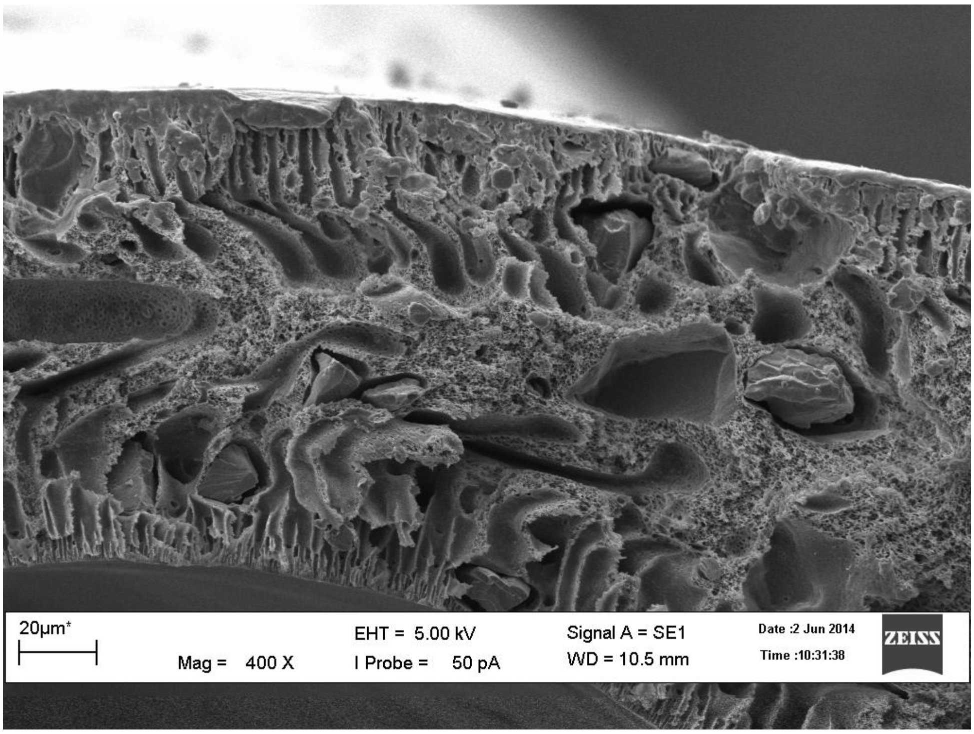

Figure 3.12: Scanning Electron Microscope (SEM) at 400x Magnification

3.4.5 Water Permeability

Each set of the different membranes tested for the permeability of the membrane. The tested membranes are 0, 3, 5, and 8wt% of PVP as the 10wt% PVP membrane has a low mechanical property that caused the fabrication of the module to be difficult. Wang et al., (2011) suggested that the pure water permeability (PWP) tested using the deionised water under a transmembrane of 1 bar and calculated using the following equation (Wang, et al., 2011):

$$PWP = \frac{Q}{A\Delta P} \tag{3.1}$$

Where:
Q is the water volumetric flow rate at the permeate side (L/h)
A is the effective filtration area (m^2)
ΔP is the transmembrane pressure (bar,1bar = 0.1Mpa).

A=πDLn
Where:
D=Diameter of the hollow fiber
L=Length of the hollow fiber
n=Number of Hollow Fiber

3.4.6 Static Adsorption Capacity

A solution of containing 1000ppm copper is prepared using copper sulphate pentahydrate ($CuSO_4.5H_2O$). The calculation of the 1000ppm of Cu solution is done using the equation (3.2) and (3.3).

$$1g\ of\ copper\ = \frac{\frac{249.7g}{mol}CuSO_4.5H_2}{\frac{63.5g}{mol}Cu} = 3.9322gCuSO_4.5H_2O \tag{3.2}$$

$$1000ppm\ Cu\ = \frac{1mg}{L}Cu\ = \frac{1000g}{L}\ Cu \tag{3.3}$$

To prepare 1000ppm of copper ion in a liter, 3.9322g of $CuSO_4.5H_2O$ is required. The preparation of the 1000ppm (1g/L) copper ion solution is done by using the dilution flask. To prepare 500ppm of copper ion in 1L, 1.9661g of $CuSO_4.5H_2O$ is required.

The membrane incubated with a known concentration of copper solution of 500ppm using a centrifugal machine for 24 hours. After binding the remaining copper concentration will be determined using AAS (Perkin AAnalyst 400 Flame Atomic Absorption Spectrometer) as shown in Figure 3.13. A set of standard solution is prepared from 0ppm to 5 ppm of Cu^{2+} in order to obtain the calibration curve. Then a solution with 3ppm of Cu^{2+} is tested to verify the calibration curve. With the calibration curve verified, the treated water concentration is tested to determine the final concentration of the Cu^{2+}. Before being tested, the solution is diluted for 200 times as the maximum detection limit of the AAS is 4ppm. The dilution of the treated copper solution is done by using a micro-pipette with the sensitivity of 1μL and centrifuged container.

Figure 3.13: Perkin AAnalyst 400 Flame Atomic Absorption Spectrometer

The 50 µL (0.05mL) of the treated solution is being extracted using a micro-pipette and being placed into the centrifudge container. Then the container is the added with distilled water up to the 12.00mL limit as it is the required volume for the dilution of 200 times using 50µL of solution. This is

$$\frac{12.00ml}{0.05ml} = 200\ times$$

(3.4)

$$Amount\ of\ Copper\ Bound\ (mg) = \frac{(C_o - C_e)V}{1000}$$

(3.5)

Where

C_0= Initial concentration of copper (ppm)

C_e= Final copper concentration (ppm)

V= Initial Volume of solution (mL)

C_{AAS}= Concentration of Sample by AAS

$$C_e = C_{AAS} \times Dilution\ Factor$$

(3.6)

3.4.7 Effect of pH

The effect of pH is studied by employing the static adsorption technique by introducing a set of different pH of copper solution from pH 2.0 , 2.5, 3.0, 3.5 , 4.0, 5.0, 5.5, 7.0, 12.0 and 13.0 with 10mL of volume. The different pH solution of acidic solutions were prepared by using 1% Hydrochloric acid and tested using the Mettler Toledo Seven Easy pH meter. Whereas the alkaline solutions using 0.1M Sodium Hydroxide and tested using the Mettler Toledo Seven Easy pH Meter. The solutions are incubated with three 5cm of 8wt% PVP membranes for 24 hours using the centrifuge. The 8wt% PVP membrane was used as the amount synthesized is the most. The samples is then diluted 250 times before being analysed under AAS.

3.4.8 Dynamic Copper Removal Test

The dynamic copper removal test is done under the cross-flow configuration setup after the Pure Water Permeability test. The tested membrane are 0, 3, 5 and 8wt% PVP Mixed Matrix Membrane Module. The 10wt% were not tested as the module could not be casted due to the low mechanical strength of the membrane that make the fabrication of the module to be difficult.

In the copper removal test, the copper ion solution used is 1000ppm in concentration and 500mL of volume. The retentate is recycled and the permeate is collected at the permeate tank.

The system is allowed to stabilise and after 30 minutes, the operation of the cross flow is stopped. The permeate and retentate are collected. The collected samples are then diluted 500 times and is tested using the AAS. The procedure is repeated for the replication of the second sample with a different module.

The amount of copper bounded on the membrane were calculated as the following equations:

$$Copper\ Bound\ (mg) = Initial\ amount\ of\ Copper - Permeate\ amount\ of\ Copper - Retentate\ amount\ of\ Copper$$

(3.7)

$$Initial\ amount\ of\ Copper\ (mg) = \frac{C_o V_o}{1000}$$

(3.8)

where;

C_o=1000ppm

V_o=500mL

$$Permeate\ amount\ of\ Copper\ (mg) = \frac{C_P V_P}{1000}$$

(3.9)

where;

C_p= $C_{P\ AAS}D_F$ (mg/L)

$C_{P\ AAS}$= AAS concentration of Permeate

D_F=Dilution Factor (500)

V_P=Permeate volume (mL)

$$Retentate\ amount\ of\ Copper\ (mg) = \frac{C_R V_R}{1000}$$

(3.10)

where;

C_R= $C_{R\ AAS}D_F$ (mg/L)

D_F=Dilution Factor (500)

$C_{R\ AAS}$= AAS concentration of Retentate

V_R=Retentate Volume (mL) = Initial Feed Volume (mL) -Permeate Volume (mL)

The derivation of the above equations forms the below equation:

$$Copper\ Bound\ (mg) = \frac{C_o V_o}{1000} - \frac{C_P V_P}{1000} - \frac{C_R V_R}{1000}$$

(3.11)

3.4.9 Elution Test

After the removal of the copper, the membrane module is being tested for the elution to recover the copper from the membrane. This procedure is the regeneration procedure of the membrane. In the elution process, 10% 250mL of Hydrochloric Acid were used to regenerate the membrane as suggested by Sigma Aldrich that acidic medium should be employ to regenerate the Amberlite IR120H resins. The system is allowed to run for 30 minutes. The eluted permeate and retentate are collected and diluted 500 times for the analysis of AAS to determine the recovery of copper.

The recovery of the copper is calculated as the following equations:

The initial feed volume is 250mL

$$Total\ copper\ eluted\ (mg) = Copper\ eluted\ in\ Permeate + Copper\ eluted\ in\ Retentate$$

(3.12)

$$Copper\ eluted\ in\ Permeate = \frac{C_P V_P}{1000}$$

(3.13)

where;

$C_p = C_{P\ AAS} D_F$ (mg/L)

$C_{P\ AAS}$= AAS concentration of Permeate

D_F=Dilution Factor (500)

V_P=Permeate volume (mL)

$$Copper\ eluted\ in\ Retentate = \frac{C_R V_R}{1000}$$

(3.14)

where;

$C_R = C_{R\ AAS} D_F$ (mg/L)

$C_{R\ AAS}$= AAS concentration of Permeate

D_F=Dilution Factor (500)

V_R=Retentate volume (mL)

The total amount of copper eluted is then used to calculate the recovery percentage of the membrane as shown in

$$Recovery\ Percentage = \frac{Copper\ Bound\ (mg)}{Copper\ eluted\ (mg)} \times 100\%$$

(3.15)

4 RESULTS AND DISCUSSION

4.1 Synthesis of Hollow Fiber Membrane

The synthesis of the fiber membrane were done when the dope solution was prepared. In the first phase of the research, two sets of samples namely 0 and 10 wt% of PVP dope solution were used to prepare the hollow fiber. In the 10wt% of PVP dope solution, it is found out that the structure of the membrane is seen to be more porous as compared to the one without any PVP added into it. The images of the membranes synthesised are shown in Figure 4.1 and Figure 4.2. The occurrence can be due to the effect of PVP that allows the membrane structure to be more porous that eventually will increase the water flux (Lan & Wang, 2012). During the synthesis, the dope solution pressure was set at 2 bars and 4 bars. It is found is found out that the synthesis of the hollow fiber membrane is easier for dope pressure with 4 bars as the size of the fiber diameter produced is higher compared to 2 bars. The suggested pressure for PES hollow fiber membrane is around 3.0 ±0.1bars (Ismail, et al., 2006).

Figure 4.1: Surface of the Membrane for 10wt% PVP dope solution

Figure 4.2: Surface of the Membrane for 0wt% PVP dope solution

The take up speed of the membrane synthesis is found to be optimum around 28-32 rpm. When the take up speed is lower than 28rpm, it is found out that the fiber produced does not form hollow tubing. On the other hand, when the take up speed is higher than 32 rpm, the fiber is easily snapped before it managed to solidify properly and settle.

In addition, it is also found out that the air gap is 14 cm. When the air gap is less than 14cm, it is found that the formation of the membrane to be flat. Whereas when the air gap is more than 14cm, the inner tubular membrane is found to be less in diameter.

In the second phase of the synthesis of membrane, 3, 5 and 8wt% of PVP dope solution were used to prepare the membrane.

The prepared membrane is found to be more porous through the naked eye as the concentration of the PVP of the dope solution used. The introduction of dope solution increases the hold up of water during the phase inversion process of the dry-wet spinning of the membrane that causes the membrane to be more porous(Rahimpour & Madaeni, 2010).

4.2 *Scanning Electron Microscope (SEM)*

After the membrane was synthesized, each of the membrane were sent for Scanning Electron Microscope for the structure analysis.

The scanning of the membrane at different magnifications are as the following figures:

Full Cross Section of the Membrane

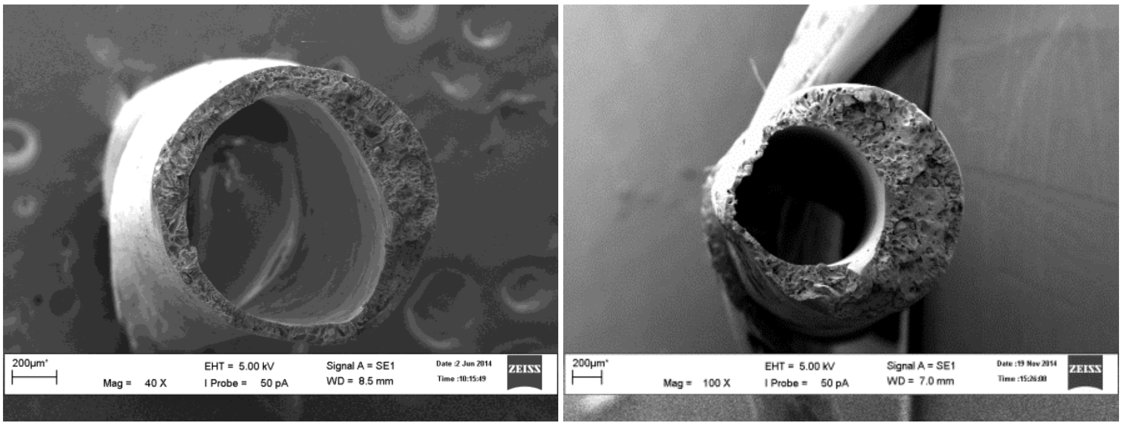

Figure 4.3: Cross Section of 0wt% and 3wt% PVP Membrane

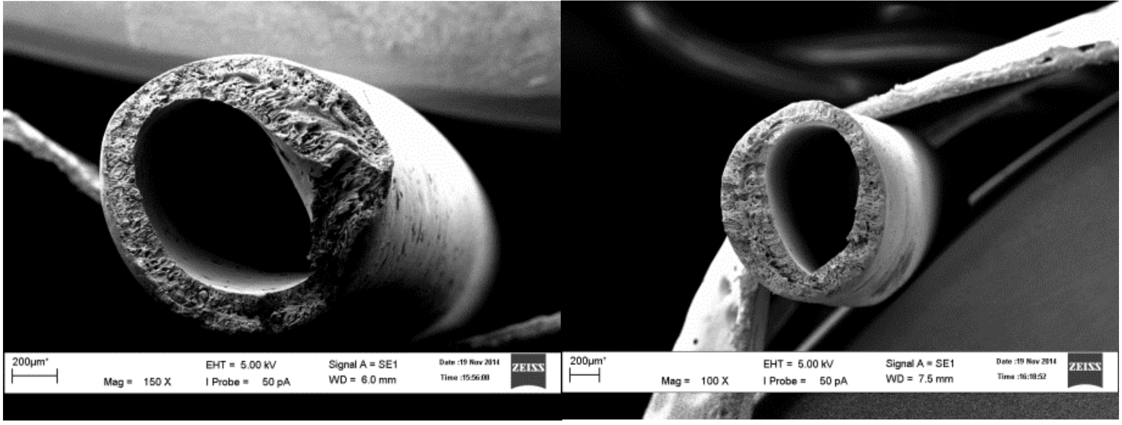

Figure 4.4: Cross Section of 5wt% and 8wt% PVP Membrane

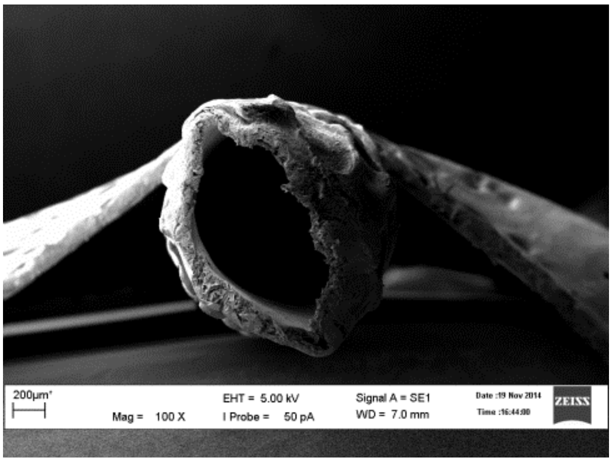

Figure 4.5: Cross Section of 10wt% PVP Membrane

Cross Section of the Membrane at 400x Magnification

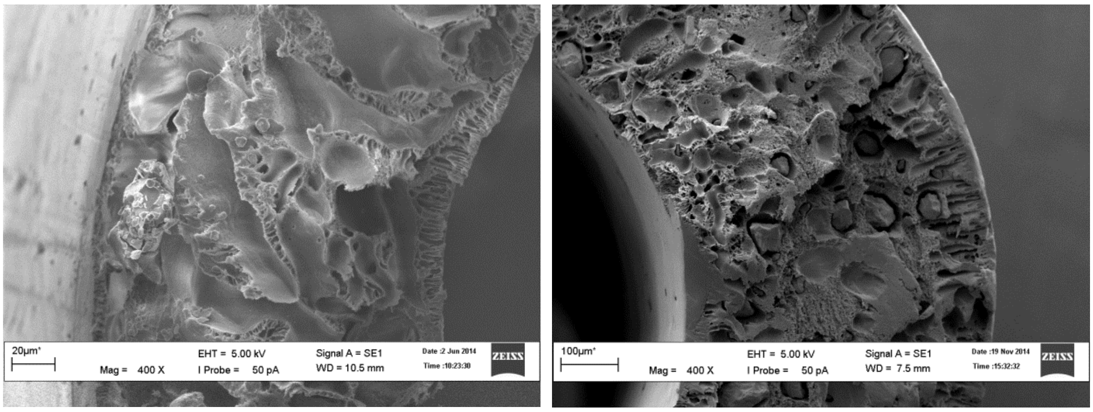

Figure 4.6: Cross Section of 0wt% and 3wt% Membrane at 400x Magnification

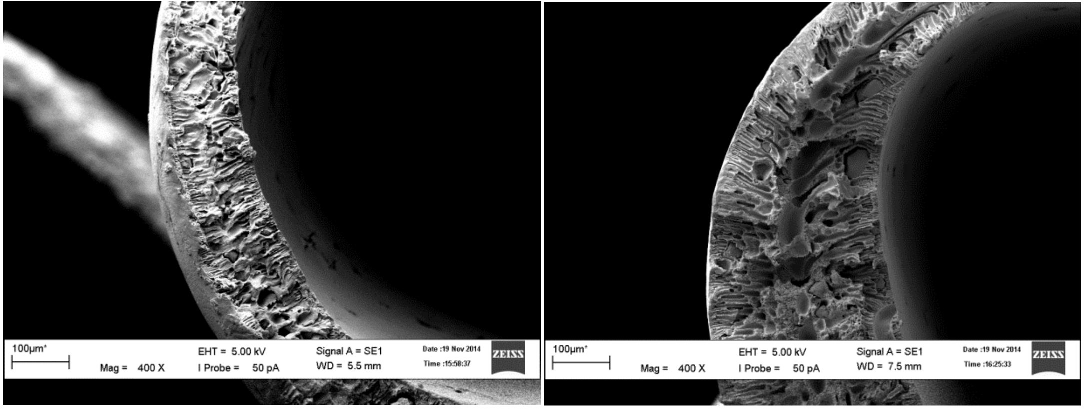

Figure 4.7: Cross Section of 5wt% and 8wt% Membrane at 400x Magnification

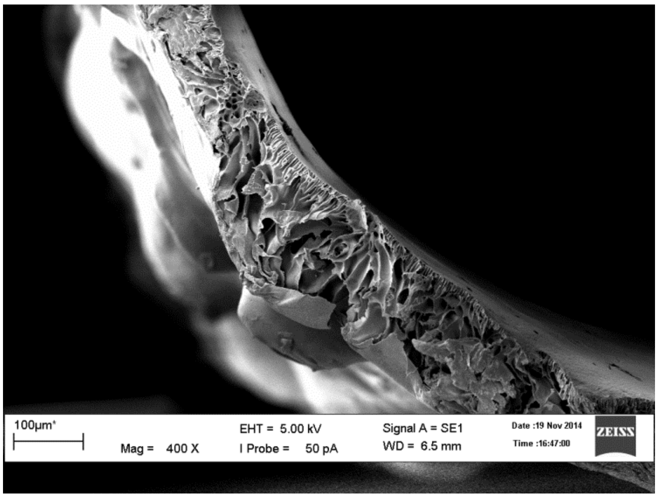

Figure 4.8: Cross Section of 10wt% Membrane at 400x Magnification

Cross Section of the Membrane at 1000x Magnification

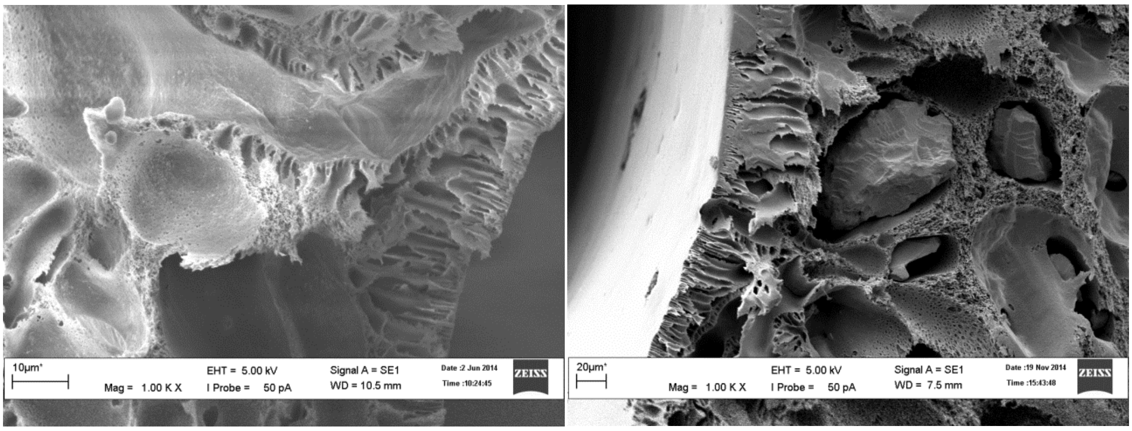

Figure 4.9: Cross Section of 0wt% and 3wt% Membrane at 1000x Magnification

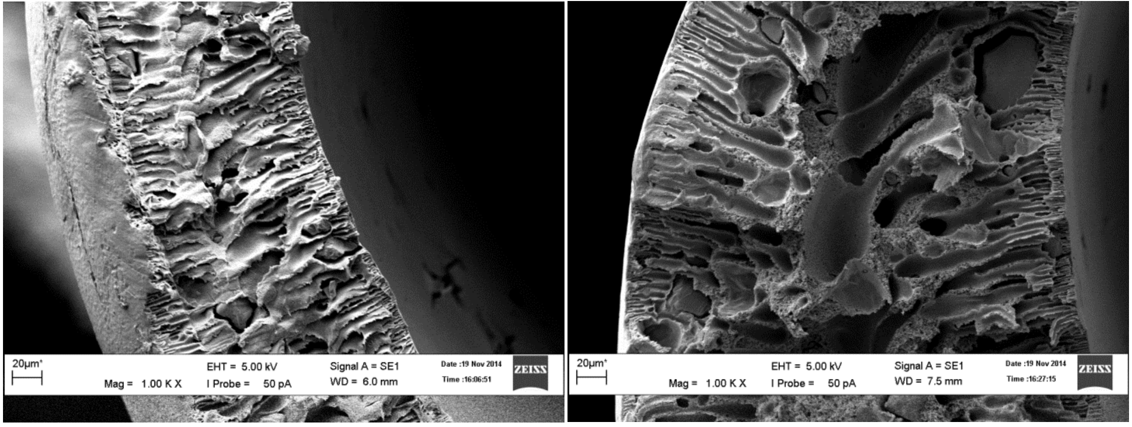

Figure 4.10: Cross Section of 5wt% and 8wt% Membrane at 1000x Magnification

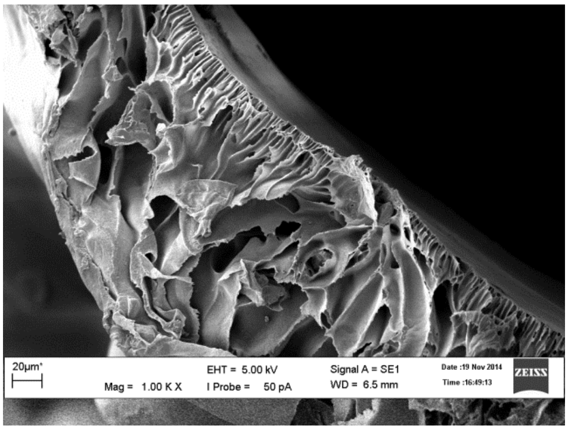

Figure 4.11: Cross Section of 10wt%Membrane at 1000x Magnification

From the images above, it's found out that the structure of the 10wt% is slightly deformed as compared to others. The increase of the concentration of the co-polymer increases the porosity of the membrane that causes the structure to be deformed when the concentration of the co-polymer is high(Tang, et al., 2010). It is also found out that the porosity of the membrane increases as the concentration of the PVP increases. The porosity of the membrane increases as the concentration of PVP increases as PVP is a hygroscopic co-polymer that can holds water up to 40wt% of water and causes the structure of the membrane to be more porous during the dry-wet spinning process(Rahimpour & Madaeni, 2010).

4.3 Static Adsorption Test

In order to test the performance of the Mixed Matrix Membrane, the static adsorption is being carried out. Static adsorption is done by preparing a known concentration of a simulated water containing 500 ppm of copper. Each of the membrane were tested for three replications. The results of the static adsorption test is as the following table:

Table 4.1: Results of the Static Adsorption of Different PVP Concentration Membrane

PVP concentration wt%	Copper Adsorb Sample A (mg)	Copper Adsorb Sample B (mg)	Copper Adsorb Sample C (mg)	Average Copper Adsorb (mg)
0	6.732	6.822	6.723	6.759
3	7.154	7.050	7.113	7.106
5	7.120	7.241	7.056	7.166
8	7.155	7.226	7.244	7.208
10	7.382	7.424	7.397	7.401

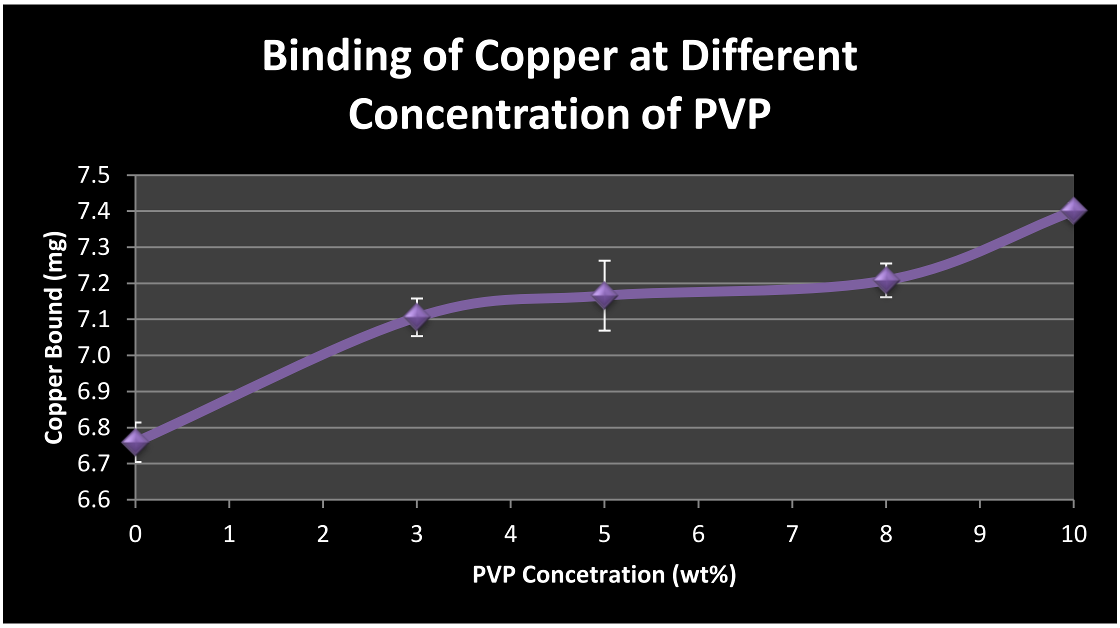

Figure 4.12: Binding of Copper at Different Concentration of Co-polymer

Table 4.2: Statistical Data for Different PVP Concentration

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
PVP 0wt%	3	20.277	6.7590	0.0030
PVP 3wt%	3	21.3165	7.1055	0.0027
PVP 5wt%	3	21.4965	7.1655	0.0094
PVP 8wt%	3	21.624	7.2080	0.0022
PVP 10wt%	3	22.2015	7.4005	0.0005

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.656188	4	0.164047	46.18245	**2.05E-06**	3.47805
Within Groups	0.035522	10	0.003552			
Total	0.691709	14				

From Figure 4.12, it is found that the increase of the concentration of the co-polymer, PVP increases the binding capacity of the membrane. The increase of co-polymer concentration increases the porosity of the membrane that allows the membrane to adsorb more copper ion (Ismail & Hassan, 2007). The statistical data from Table 4.2 suggest that the results are reproducible as the p-value is less than 0.5.

4.4 Effect of pH

The solution is then prepared into a few pH condition to study the effect of pH on the adsorption capacity of the Mixed Matrix Membrane containing Amberlite IR120H resin. As a preliminary to determine the suitable pH for the adsorption of copper by the membrane, the following solutions at different pH is prepared. The membrane used for the preliminary testing to determine the optimum pH for the adsorption of the mixed matrix membrane.

Table 4.3: pH Testing for Optimum pH condition for the Adsorption of the Membrane

pH Testing			
Sample	pH	Length of Membrane (cm)	Number of Membrane
I	2.0	5.0	3
II	3.0	5.0	3
III	3.5	5.0	3
IV	4.0	5.0	3
V	4.5	5.0	3
VI	5.0	5.0	3
VII	5.5	5.0	3
VIII	12.0	5.0	3
IX	13.0	5.0	3

From the initial preparation of the solution at different pH value, it is found out that precipitate is formed when the solution is alkaline which is at pH12 after the incubation is done. This should be due to the double decomposition caused by the sodium hydroxide solution to prepare the base solution which is a blue precipitate but the formed precipitate is black in colour as shown in **Figure 4.13**. This should be due to the formation of copper (II) oxide (Cudennec & Lecerf, 2003). The study of pH at base condition is eliminated as there's precipitation being formed. Besides that, the basic condition of solution will hinder the cation activity of the resin as cation resin works with the presence of hydrogen ions (H^+)(Sigma-Aldrich, 2013).

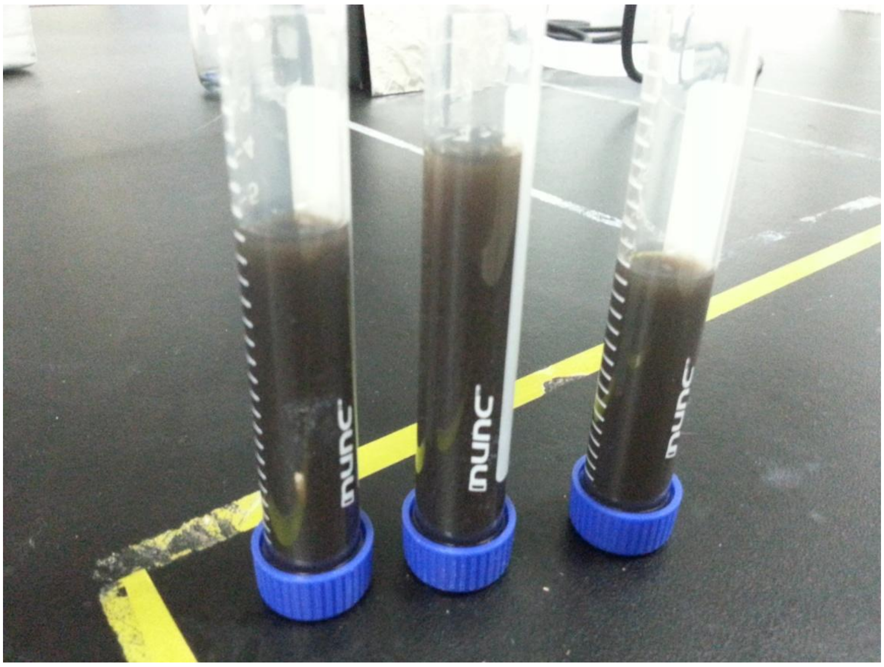

Figure 4.13: Precipitation formed in pH12 and pH13 (Alkaline solution)

As a preparation for the adsorption capacity, the standard copper ions were detected using AAS. A set of standard solutions ranged from 0ppm to 4ppm. The AAS is only able to detect copper ions at the maximum concentration of 4ppm precisely and the maximum detection is 10ppm, thus dilution of the treated water need to be done before using the AAS. The simulated wastewater is prepared at a constant concentration of Cu^{2+} ions of 1000ppm, thus it requires the treated water to be diluted with the factor of 125 parts to enable the AAS to detect the Cu^{2+} ions maximum at 8ppm

The studies of optimum pH was done as the follows:

Table 4.4: Concentration of Copper after Incubation

Sample	pH	Co (ppm)	C AAS (ppm)	Dilution	C (ppm)	Binding (ppm)	Copper Bound(mg)	Initial Copper (mg)
I	2.0	1000	6.8040	125	850.50	149.50	1.4950	10
II	3.0	1000	5.9360	125	742.00	258.00	2.5800	10
III	3.5	1000	3.2940	125	411.75	588.25	5.8825	10
IV	4.0	1000	3.1890	125	398.63	601.38	6.0138	10
V	4.5	1000	3.7250	125	465.63	534.38	5.3438	10
VI	5.0	1000	4.3330	125	541.63	458.38	4.5838	10
VII	5.5	1000	5.5900	125	698.75	301.25	3.0125	10
VIII	12.0	1000	4.6410	125	580.13	419.88	4.1988	10
IX	13.0	1000	0.0253	125	3.16	996.84	9.9684	10

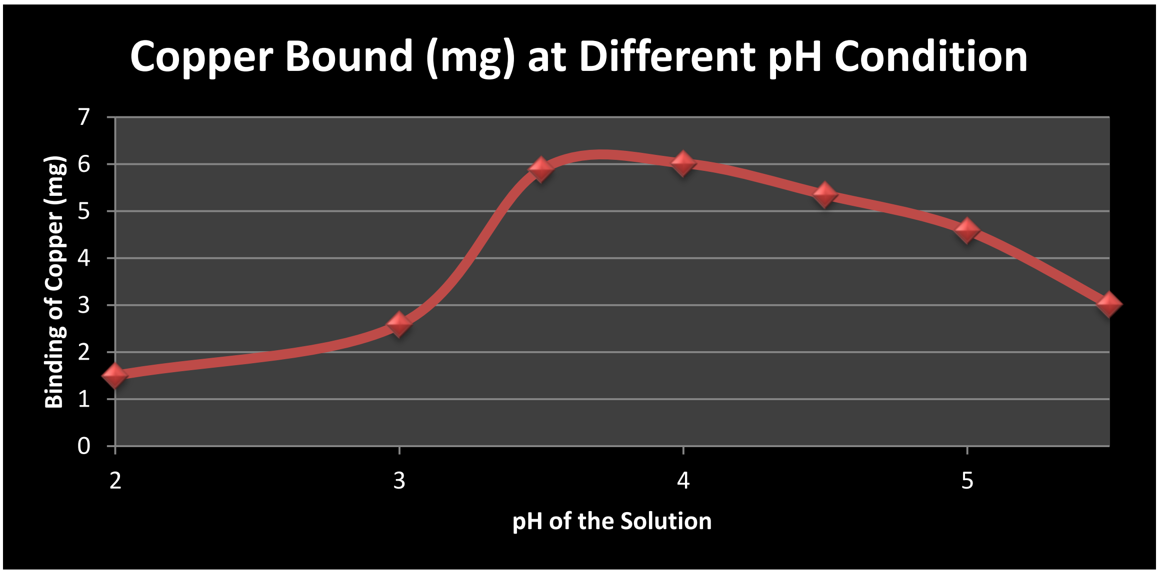

Figure 4.14: Effect of pH on the Binding of Copper

It is found that the optimum pH for the binding of the copper is below pH5.5 as the condition is found to be acidic. The adsorption of copper is at its optimum when the condition of the solution is acidic as the acidic condition allows ions in the Amberlite IR120H resin to be exchanged with the copper ion in the solution but when the pH is too low, the adsorption capacity of the membrane reduces as the membrane need to compete with the hydrogen ions of the acid solution to compete with the copper ion to be exchanged in the Amberlite IR120H resin(Jha, et al., 2009). In order to obtain the optimum pH of the copper binding, the study of the pH has been narrowed down to pH 3.0 , 3.5, 4.0 and 4.5.

The volume of the copper solution used is 10mL and the concentration used is 1000ppm with dilution factor of 250 times.

The results of the narrowed down studies is as the following table:

Table 4.5: Study of the Optimum Acidic pH condition

pH	Copper Bound Sample A (mg)	Copper Bound Sample B (mg)	Copper Bound Sample C (mg)	Average Copper Bound (mg)
3.0	5.773	5.173	5.378	5.441
3.5	6.193	5.273	5.353	5.606
4.0	5.405	5.620	5.398	5.808
4.5	5.095	5.325	5.348	5.256

Table 4.6: Statistical Data of Different pH Static Adsoption

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
pH 3.0	3	16.3225	5.4408	0.0930
pH 3.5	3	16.8175	5.6058	0.2597
pH 4.0	3	17.4225	5.8075	0.2726
pH 4.5	3	15.7675	5.2558	0.0195

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	0.49755	3	0.16585	1.028687	**0.430007**	4.066181
Within Groups	1.2898	8	0.161225			
Total	1.78735	11				

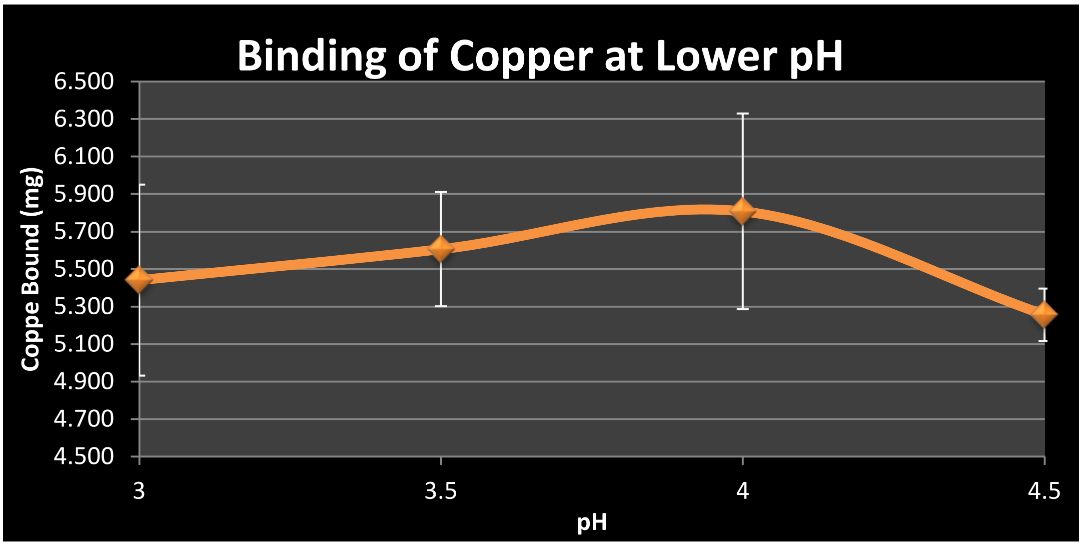

Figure 4.15: Binding of Copper at Low pH

In the study of the binding of copper at low pH , it is found out that pH 4.0 is the optimum pH for the adsorption of the copper at low pH. At pH 4.0, the competition between the copper ions with the hydrogen ions in the acid solution is lesser causes the adsorption capacity of the membrane containing Amberlite IR120H to increase(Nabi, et al., 2005). The statistical data from Table 4.6 suggest that the results are reproducible as the p-value is less than 0.5.

4.5 Water Permeability

The permeability of water were done when the membrane module were fabricated. All membranes were tested for water permeability except for 10wt% as the membrane has a low mechanical property that causes it difficult to be fabricated into the module.

The pure water permeability were calculated based on the Equation (4.1)

$$PWP(\mathrm{L/m^2.h.bar}) = \frac{Q}{PA}$$

(4.1)

Where;
Q = flow rate of the water (L/h)
P = pressure of the trans-membrane, in this case its 1bar
A= Effective filtration area of the module (m^2)

Table 4.7: Pure water permeability of Different PVP Concentration Membrane

PVP wt%	Diameter (m)	Length (m)	Number of membranes	Effective Area (m^2)	Flowrate (mL/min)	Flowrate (L/h)	Pure water Permeability (L/m^2.h.bar)
0	0.0013	0.2	15	0.0123	1.0	0.060	4.895
3	0.0017	0.2	15	0.0160	1.4	0.084	5.264
5	0.0013	0.2	15	0.0128	1.6	0.096	7.542
8	0.0011	0.2	15	0.0105	1.5	0.090	8.591

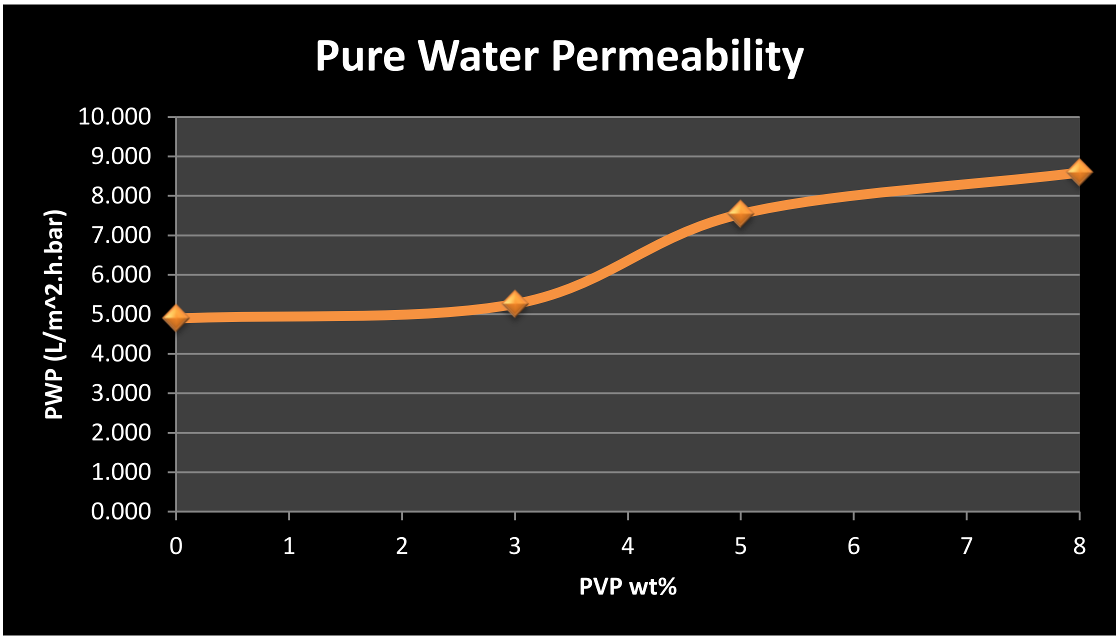

Figure 4.16: Pure Water Permeability at Different PVP Concentration

It is found out that the water permeability increases as the concentration of the PVP. The increase of PVP concentration increases the instantenous demixing that increases the diffusional exchange rate of solvent and non solvent during the phase inversion that eventually increases the permeability of the membrane to certain point(Al Malek, et al., 2012).

4.6 Dynamic Copper Removal Test

The dynamic copper removal test is to test the removal of copper from the solution in a continuous flow of solution. In this research, the cross-flow configuration was being used. The tested membrane were 0, 3, 5 and 8wt% PVP membrane at pH 4.0. Two sets of module were used for each of the membrane category to replicate the data. The data of the experiment carried is shown in the tables below:

Table 4.8: Dynamic Copper Removal Test Run 1

PVP wt%	Feed Volume (mL)	Feed Concentration (mg/L)	Feed Copper Mass (mg)	Permeate Volume (mL)	Permeate Concentration (mg/L)	Permeate Copper Mass (mg)	Retentate Volume (mL)	Retentate Concentration (mg/L)	Retentate Copper Mass (mg)	Copper Bound (mg)
0	500	1000	500	42	375.00	15.750	458	479.50	219.611	264.639
3	500	1000	500	34	476.00	16.184	466	520.00	242.320	241.496
5	500	1000	500	40	285.50	11.420	460	456.50	209.990	278.590
8	500	1000	500	43	425.00	18.275	457	475.00	217.075	264.650

Table 4.9: Dynamic Copper Removal Test Run 2

PVP wt%	Feed Volume (mL)	Feed Concentration (mg/L)	Feed Copper Mass (mg)	Permeate Volume (mL)	Permeate Concentration (mg/L)	Permeate Copper Mass (mg)	Retentate Volume (mL)	Retentate Concentration (mg/L)	Retentate Copper Mass (mg)	Copper Bound (mg)
0	500	1000	500	45	440.50	19.823	455	483.00	219.765	260.412
3	500	1000	500	31	371.00	11.501	469	522.00	244.818	243.681
5	500	1000	500	42	358.50	15.057	458	161.67	161.674	323.269
8	500	1000	500	44	476.00	20.944	456	413.00	188.328	290.728

Table 4.10: Average copper bound and rejection efficiency

PVP wt%	Average Copper Bound (mg)	Average Copper Bound per Area (mg/m^2)	Average Rejection Efficiency (%)
0	262.5275	21,171.75	52.51
3	242.5885	15,230.06	48.52
5	300.9295	25,255.39	60.19
8	277.6890	27,688.38	55.54

Table 4.11: Statistical Data for Cross Flow

Anova: Single Factor

SUMMARY

Groups	*Count*	*Sum*	*Average*	*Variance*
PVP 0wt%	2	525.0515	262.5258	8.931651
PVP 3wt%	2	485.177	242.5885	2.387112
PVP 5wt%	2	601.859	300.9295	998.1065
PVP 8wt%	2	555.378	277.689	340.031

ANOVA

Source of Variation	*SS*	*df*	*MS*	*F*	*P-value*	*F crit*
Between Groups	3639.052	3	1213.017	3.595574	**0.124128**	6.591382
Within Groups	1349.456	4	337.3641			
Total	4988.508	7				

It is found out that the rejection of copper at 1000ppm concentration is the highest when the PVP concentration of the dope solution is 5wt% as the increase of pore size increases the adsorption capacity of the membrane to remove the copper from the solution. The rejection capacity of the membrane reduces when the concentration of PVP is 8wt%. This is due to the effect of PVP that increases the viscosity of the dope solution that causes the membrane to become a sponge-like structure that causes the permeate flow to decrease and eventually decrease the rejection rate(Al Malek, et al., 2012). The statistical data from Table 4.11 suggest that the results are reproducible as the p-value is less than 0.5.

4.7 Elution Test

The elution test is done to determine the recovery rate of the membrane by the treatment of acidic solution. The elution was done using 250mL of 10% Hydrochloric Acid. The data of the elution process is shown in the table below:

Table 4.12: Elution for the Run 1 Membrane

PVP wt%	Permeate Volume (mL)	Permeate Concentration (mg/L)	Permeate Copper Mass (mg)	Retentate Volume (mL)	Retentate Concentration (mg/L)	Retentate Copper Mass (mg)	Copper Eluted (mg)	Recovery (%)
0	75	250.0	18.75	175	184.5	32.29	51.04	19.3
3	60	586.5	35.19	190	214.0	40.66	75.85	31.4
5	61	275.0	16.78	189	60.5	11.43	28.21	10.1
8	53	151.5	8.03	197	85.0	16.75	24.77	9.4

Table 4.13: Elution for the Run 2 Membrane

PVP wt%	Permeate Volume (mL)	Permeate Concentration (mg/L)	Permeate Copper Mass (mg)	Retentate Volume (mL)	Retentate Concentration (mg/L)	Retentate Copper Mass (mg)	Copper Eluted (mg)	Recovery (%)
0	72	411.5	29.63	178	137.0	24.39	54.01	20.7
3	58	561.5	32.57	192	198.5	38.11	70.68	29.0
5	60	255.0	15.30	190	90.5	17.20	32.50	10.1
8	48	439.0	21.07	202	83.0	16.77	37.84	13.0

It is found that the elution recovery of the membrane is the highest at 3wt% PVP and starts to drop at 5wt% PVP. The elution recovery is highest at 3wt% because of the hydrophilic effect of the PVP that causes the elution of copper to increase(Yin, et al., 2012). The elution of copper in higher concentration of PVP decreases the copper recovery due to the blockage of the pores of the membrane due to the increase of the viscosity of the dope solution that causes blockage in the pores though the porosity of the membrane increases causing the recovery to be hindered(Yin, et al., 2012)

5 Conclusions and Recommendation

5.1 *Conclusion*

Currently the removal of copper are mainly done by the application of resin and coagulation. This study was intended to look in the probable alternative removal of copper from the water. This research is a game changer that changes the membrane technology to a new frontier by combining the technology of adsorption and ion exchange with membrane. In general, membrane is known for its tendency to fouling that increases the cost of the operation. In this research, the effect of PVP as the co-polymer for the PES Mixed Matrix Membrane in terms of the adsorption capacity, permeability and elution as PVP is a known co-polymer to reduce the fouling of the membrane.

Phase inversion technique is used by using the dry-wet spinning method to synthesis the hollow fiber membrane. It is found that the porosity of the membrane increases as the concentration of the co-polymer increases as the ability of the PVP to hold water up to 40wt% of its mass that causes the membrane to form pores during the spinning process.

The membranes were tested for the significance of the effect of pH and it is found that the optimum pH for the operation of the membrane is pH 4.0 as at this pH the copper ion does not need to compete with the hydrogen ions in the acid to be exchanged with the resin.

When the solution is basic, the adsorption capacity could not be tested accurately as the formation of precipitate when the solution is added with sodium hydroxide due to the double decomposition reaction that occur. The precipitate formed causes the reading of the AAS to be inaccurate as there's is some possibility that the copper ion is removed by the 0.45μm filter before injecting to the AAS.

In this finding, the permeability of the membrane increases as the concentration of the PVP increases due to the hydrophilic nature of PVP that increases the permeability of the membrane. At the concentration of 8wt% PVP, the permeability is found to be 8.59L/m^2.h.bar as compared to 4.90L/m^2.h.bar of the membrane without PVP added.

In addition to that, the increase of PVP concentration increases the rejection efficiency to a certain point before it drops at 8wt% of PVP. The rejection efficiency of 5wt% PVP is found to be as high as 60.19%.

In terms of elution recovery, the 3wt% PVP membrane perform better than higher concentration of PVP membranes as this might be due to the blockage of the pores due to the increase of PVP concentration that increases the viscosity of the dope solution that causes the membrane to be sponge-like structure that unable to remove the adsorb copper efficiently.

5.2 Recommendations

As this study achieved its objectives, several recommendations were proposed to improve the quality of the work and to generate better results. The recommendations are listed below.

5.2.1 Study on the Static Adsorption

In the study of the static adsorption, the number of membranes that are incubated plays a role in the performance of the adsorption. The increase in the number of the membrane incubated increases the adsorption rate of the copper. In is suggested that in the future, the study should include the number of membrane as one of the parameters in the studies.

5.2.2 Study on the Effect of pH

Effect of the pH has been studied using hydrochloric acid as acidic solution and sodium hydroxide as base solution. It is found that the formation of copper hydroxide when sodium hydroxide is used due to the double decomposition reaction that occur between sodium hydroxide and copper sulphate that causes black precipitate. It is suggested that in the future, the study of the alkaline condition should be done using non metallic base solution such as ammonium hydroxide to ensure that the study of the alkaline condition can be done properly.

5.2.3 Study on the Water Permeability

The pressure of the permeate and the retentate outlets should be take into consideration in the future to obtain a more precise result although in this system, the role of pressure is not significant.

5.2.4 Study on the Dynamic Copper Removal

The study should include the treatment time and the concentration of the feed solution as the adsorption efficiency changes accordingly to the concentration of the solution and the time of treatment.

5.2.5 Study on the Elution Recovery

The study on the concentration of acid used should be included in the future as the concentration of acids plays a role in the elution of copper from the membrane due to the availability of the hydrogen ion to be exchanged with the copper with the resin. Besides that, the type of acid should be studied as different types of acids has different disassociation of hydrogen ions to be exchanged with the resin.

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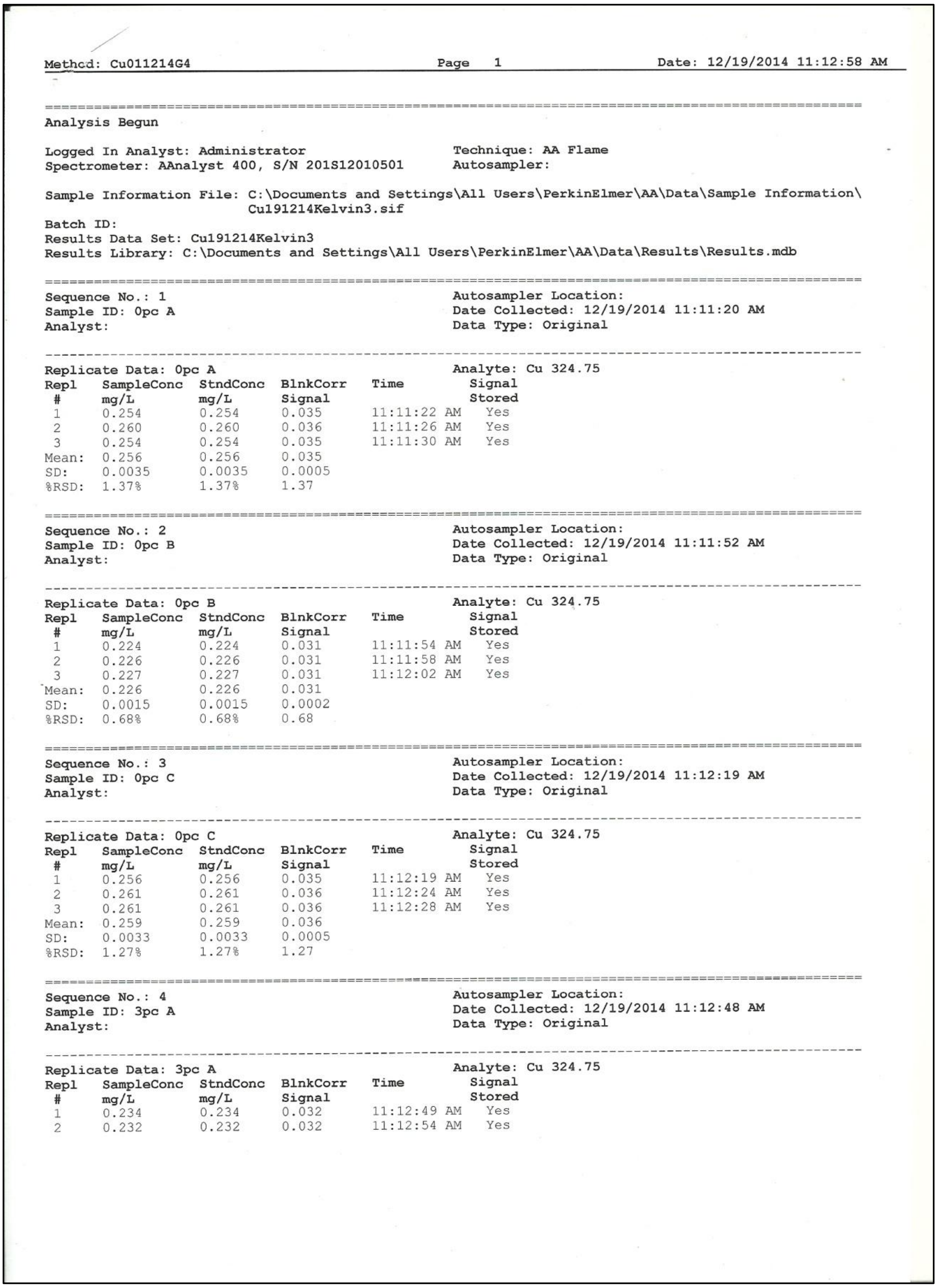
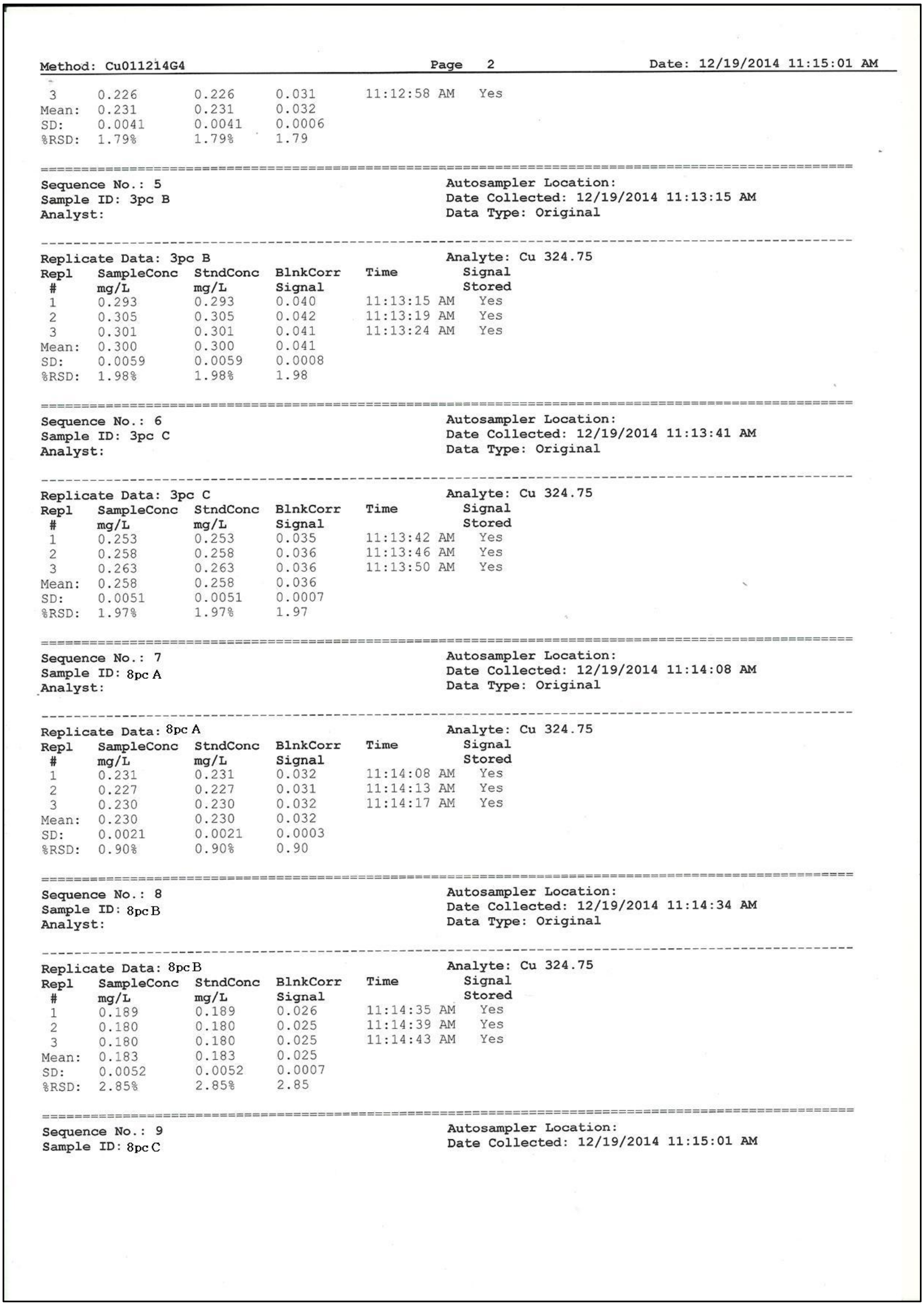
APPENDICES

A.1 Static Adsorption



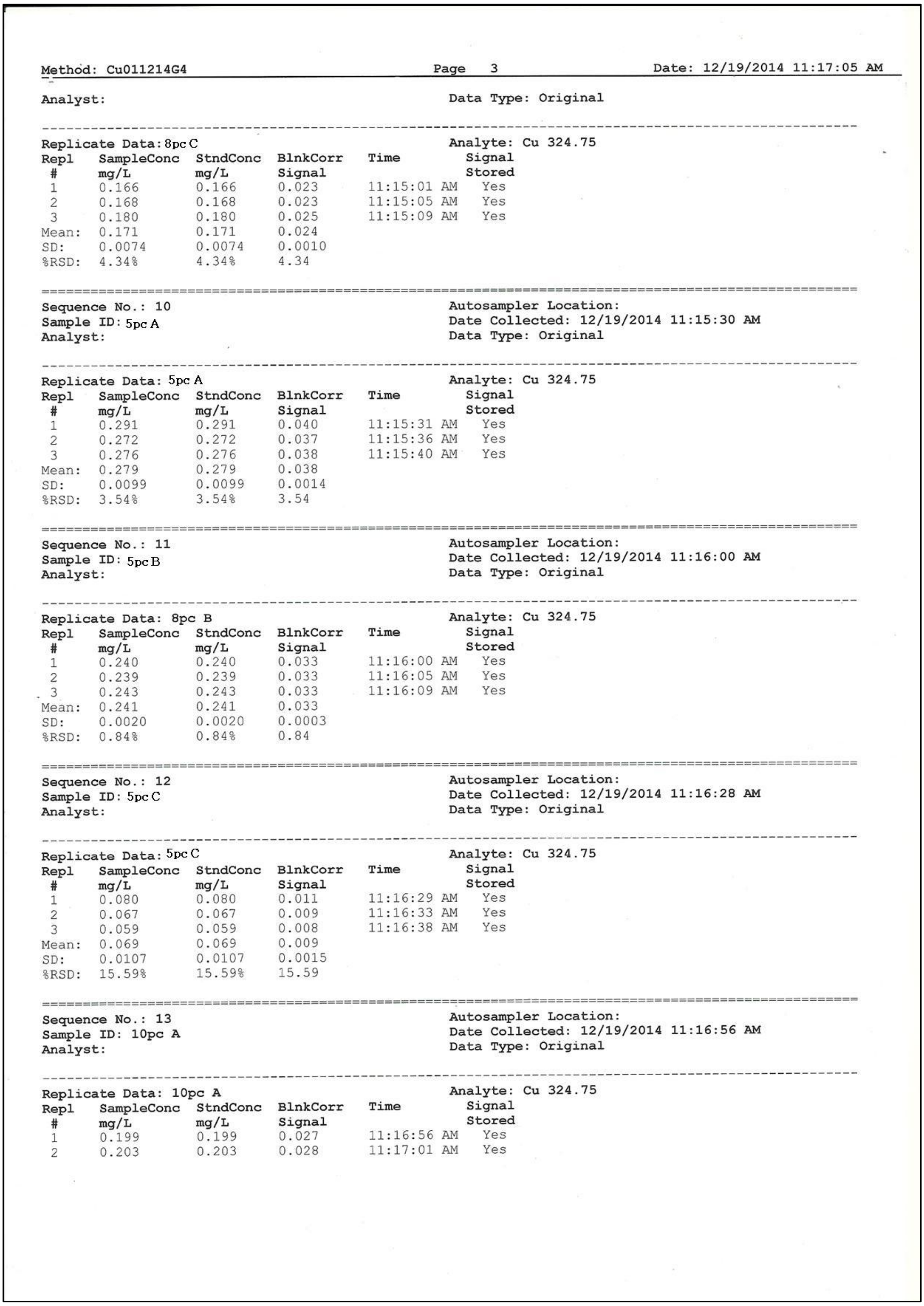
```
Method: Cu011214G4                              Page   1                 Date: 12/19/2014 11:12:58 AM

=====================================================================================================
Analysis Begun

Logged In Analyst: Administrator                       Technique: AA Flame
Spectrometer: AAnalyst 400, S/N 201S12010501           Autosampler:

Sample Information File: C:\Documents and Settings\All Users\PerkinElmer\AA\Data\Sample Information\
                         Cu191214Kelvin3.sif
Batch ID:
Results Data Set: Cu191214Kelvin3
Results Library: C:\Documents and Settings\All Users\PerkinElmer\AA\Data\Results\Results.mdb

=====================================================================================================
Sequence No.: 1                                        Autosampler Location:
Sample ID: 0pc A                                       Date Collected: 12/19/2014 11:11:20 AM
Analyst:                                               Data Type: Original

-----------------------------------------------------------------------------------------------------
Replicate Data: 0pc A                                  Analyte: Cu 324.75
Repl    SampleConc   StndConc   BlnkCorr    Time          Signal
 #      mg/L         mg/L       Signal                    Stored
 1      0.254        0.254      0.035       11:11:22 AM    Yes
 2      0.260        0.260      0.036       11:11:26 AM    Yes
 3      0.254        0.254      0.035       11:11:30 AM    Yes
Mean:   0.256        0.256      0.035
SD:     0.0035       0.0035     0.0005
%RSD:   1.37%        1.37%      1.37

=====================================================================================================
Sequence No.: 2                                        Autosampler Location:
Sample ID: 0pc B                                       Date Collected: 12/19/2014 11:11:52 AM
Analyst:                                               Data Type: Original

-----------------------------------------------------------------------------------------------------
Replicate Data: 0pc B                                  Analyte: Cu 324.75
Repl    SampleConc   StndConc   BlnkCorr    Time          Signal
 #      mg/L         mg/L       Signal                    Stored
 1      0.224        0.224      0.031       11:11:54 AM    Yes
 2      0.226        0.226      0.031       11:11:58 AM    Yes
 3      0.227        0.227      0.031       11:12:02 AM    Yes
Mean:   0.226        0.226      0.031
SD:     0.0015       0.0015     0.0002
%RSD:   0.68%        0.68%      0.68

=====================================================================================================
Sequence No.: 3                                        Autosampler Location:
Sample ID: 0pc C                                       Date Collected: 12/19/2014 11:12:19 AM
Analyst:                                               Data Type: Original

-----------------------------------------------------------------------------------------------------
Replicate Data: 0pc C                                  Analyte: Cu 324.75
Repl    SampleConc   StndConc   BlnkCorr    Time          Signal
 #      mg/L         mg/L       Signal                    Stored
 1      0.256        0.256      0.035       11:12:19 AM    Yes
 2      0.261        0.261      0.036       11:12:24 AM    Yes
 3      0.261        0.261      0.036       11:12:28 AM    Yes
Mean:   0.259        0.259      0.036
SD:     0.0033       0.0033     0.0005
%RSD:   1.27%        1.27%      1.27

=====================================================================================================
Sequence No.: 4                                        Autosampler Location:
Sample ID: 3pc A                                       Date Collected: 12/19/2014 11:12:48 AM
Analyst:                                               Data Type: Original

-----------------------------------------------------------------------------------------------------
Replicate Data: 3pc A                                  Analyte: Cu 324.75
Repl    SampleConc   StndConc   BlnkCorr    Time          Signal
 #      mg/L         mg/L       Signal                    Stored
 1      0.234        0.234      0.032       11:12:49 AM    Yes
 2      0.232        0.232      0.032       11:12:54 AM    Yes
```

Static Adsorption Page 1



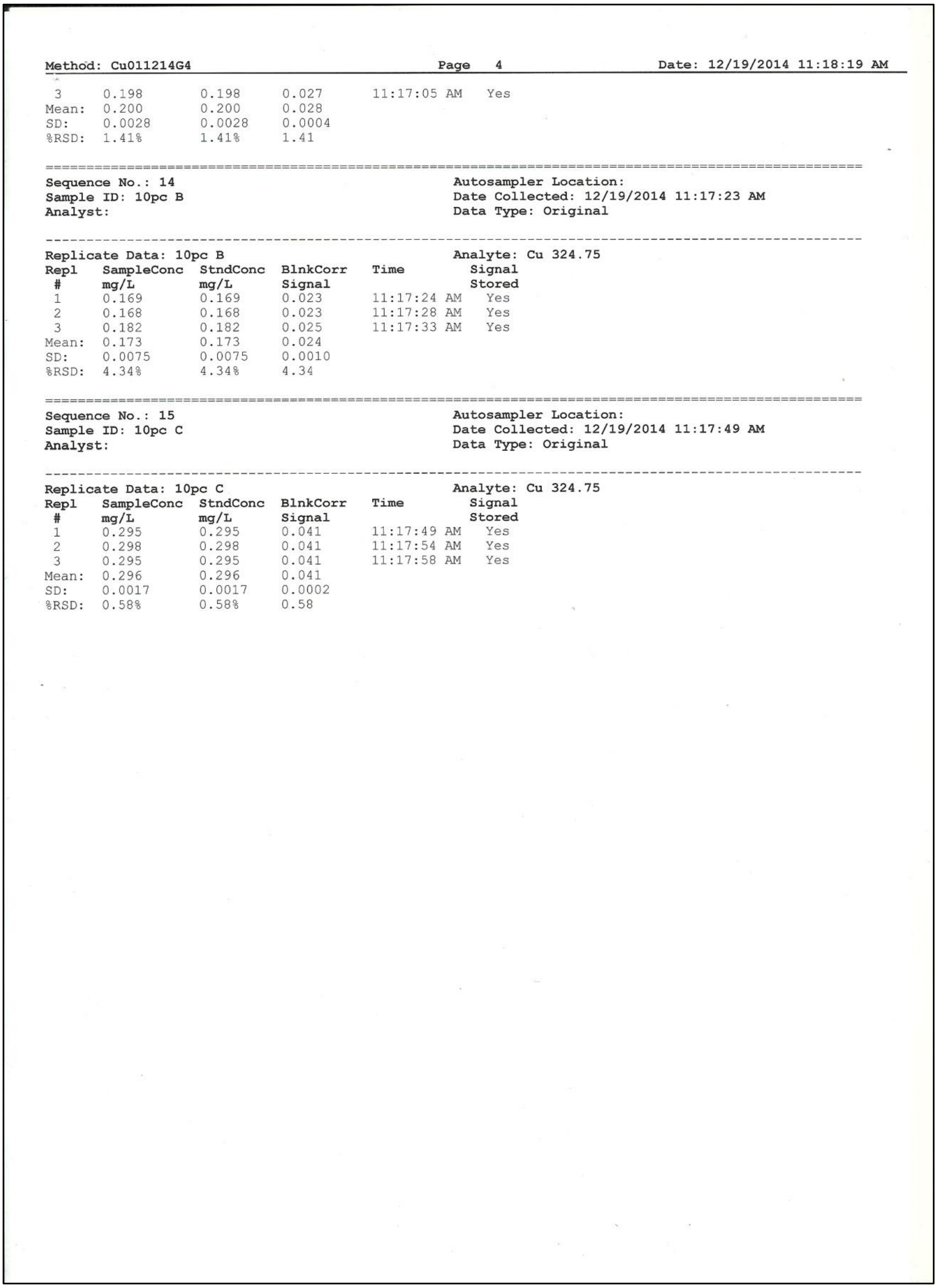
```
Method: Cu011214G4                               Page   2               Date: 12/19/2014 11:15:01 AM
  3     0.226         0.226       0.031        11:12:58 AM   Yes
Mean:   0.231         0.231       0.032
SD:     0.0041        0.0041      0.0006
%RSD:   1.79%         1.79%       1.79

=========================================================================================================
Sequence No.: 5                                               Autosampler Location:
Sample ID: 3pc B                                              Date Collected: 12/19/2014 11:13:15 AM
Analyst:                                                      Data Type: Original

---------------------------------------------------------------------------------------------------------
Replicate Data: 3pc B                                         Analyte: Cu 324.75
Repl    SampleConc    StndConc    BlnkCorr     Time          Signal
 #      mg/L          mg/L        Signal                     Stored
 1      0.293         0.293       0.040        11:13:15 AM   Yes
 2      0.305         0.305       0.042        11:13:19 AM   Yes
 3      0.301         0.301       0.041        11:13:24 AM   Yes
Mean:   0.300         0.300       0.041
SD:     0.0059        0.0059      0.0008
%RSD:   1.98%         1.98%       1.98

=========================================================================================================
Sequence No.: 6                                               Autosampler Location:
Sample ID: 3pc C                                              Date Collected: 12/19/2014 11:13:41 AM
Analyst:                                                      Data Type: Original

---------------------------------------------------------------------------------------------------------
Replicate Data: 3pc C                                         Analyte: Cu 324.75
Repl    SampleConc    StndConc    BlnkCorr     Time          Signal
 #      mg/L          mg/L        Signal                     Stored
 1      0.253         0.253       0.035        11:13:42 AM   Yes
 2      0.258         0.258       0.036        11:13:46 AM   Yes
 3      0.263         0.263       0.036        11:13:50 AM   Yes
Mean:   0.258         0.258       0.036
SD:     0.0051        0.0051      0.0007
%RSD:   1.97%         1.97%       1.97

=========================================================================================================
Sequence No.: 7                                               Autosampler Location:
Sample ID: 8pc A                                              Date Collected: 12/19/2014 11:14:08 AM
Analyst:                                                      Data Type: Original

---------------------------------------------------------------------------------------------------------
Replicate Data: 8pc A                                         Analyte: Cu 324.75
Repl    SampleConc    StndConc    BlnkCorr     Time          Signal
 #      mg/L          mg/L        Signal                     Stored
 1      0.231         0.231       0.032        11:14:08 AM   Yes
 2      0.227         0.227       0.031        11:14:13 AM   Yes
 3      0.230         0.230       0.032        11:14:17 AM   Yes
Mean:   0.230         0.230       0.032
SD:     0.0021        0.0021      0.0003
%RSD:   0.90%         0.90%       0.90

=========================================================================================================
Sequence No.: 8                                               Autosampler Location:
Sample ID: 8pcB                                               Date Collected: 12/19/2014 11:14:34 AM
Analyst:                                                      Data Type: Original

---------------------------------------------------------------------------------------------------------
Replicate Data: 8pcB                                          Analyte: Cu 324.75
Repl    SampleConc    StndConc    BlnkCorr     Time          Signal
 #      mg/L          mg/L        Signal                     Stored
 1      0.189         0.189       0.026        11:14:35 AM   Yes
 2      0.180         0.180       0.025        11:14:39 AM   Yes
 3      0.180         0.180       0.025        11:14:43 AM   Yes
Mean:   0.183         0.183       0.025
SD:     0.0052        0.0052      0.0007
%RSD:   2.85%         2.85%       2.85

=========================================================================================================
Sequence No.: 9                                               Autosampler Location:
Sample ID: 8pcC                                               Date Collected: 12/19/2014 11:15:01 AM
```

Static Adsorption Page 2



```
Method: Cu011214G4                         Page   3               Date: 12/19/2014 11:17:05 AM

Analyst:                                                  Data Type: Original

--------------------------------------------------------------------------------------------
Replicate Data:8pc C                                      Analyte: Cu 324.75
Repl    SampleConc   StndConc   BlnkCorr    Time            Signal
 #      mg/L         mg/L       Signal                      Stored
 1      0.166        0.166      0.023       11:15:01 AM     Yes
 2      0.168        0.168      0.023       11:15:05 AM     Yes
 3      0.180        0.180      0.025       11:15:09 AM     Yes
Mean:   0.171        0.171      0.024
SD:     0.0074       0.0074     0.0010
%RSD:   4.34%        4.34%      4.34

============================================================================================
Sequence No.: 10                                          Autosampler Location:
Sample ID: 5pc A                                          Date Collected: 12/19/2014 11:15:30 AM
Analyst:                                                  Data Type: Original

--------------------------------------------------------------------------------------------
Replicate Data: 5pc A                                     Analyte: Cu 324.75
Repl    SampleConc   StndConc   BlnkCorr    Time            Signal
 #      mg/L         mg/L       Signal                      Stored
 1      0.291        0.291      0.040       11:15:31 AM     Yes
 2      0.272        0.272      0.037       11:15:36 AM     Yes
 3      0.276        0.276      0.038       11:15:40 AM     Yes
Mean:   0.279        0.279      0.038
SD:     0.0099       0.0099     0.0014
%RSD:   3.54%        3.54%      3.54

============================================================================================
Sequence No.: 11                                          Autosampler Location:
Sample ID: 5pc B                                          Date Collected: 12/19/2014 11:16:00 AM
Analyst:                                                  Data Type: Original

--------------------------------------------------------------------------------------------
Replicate Data: 8pc B                                     Analyte: Cu 324.75
Repl    SampleConc   StndConc   BlnkCorr    Time            Signal
 #      mg/L         mg/L       Signal                      Stored
 1      0.240        0.240      0.033       11:16:00 AM     Yes
 2      0.239        0.239      0.033       11:16:05 AM     Yes
 3      0.243        0.243      0.033       11:16:09 AM     Yes
Mean:   0.241        0.241      0.033
SD:     0.0020       0.0020     0.0003
%RSD:   0.84%        0.84%      0.84

============================================================================================
Sequence No.: 12                                          Autosampler Location:
Sample ID: 5pc C                                          Date Collected: 12/19/2014 11:16:28 AM
Analyst:                                                  Data Type: Original

--------------------------------------------------------------------------------------------
Replicate Data: 5pc C                                     Analyte: Cu 324.75
Repl    SampleConc   StndConc   BlnkCorr    Time            Signal
 #      mg/L         mg/L       Signal                      Stored
 1      0.080        0.080      0.011       11:16:29 AM     Yes
 2      0.067        0.067      0.009       11:16:33 AM     Yes
 3      0.059        0.059      0.008       11:16:38 AM     Yes
Mean:   0.069        0.069      0.009
SD:     0.0107       0.0107     0.0015
%RSD:   15.59%       15.59%     15.59

============================================================================================
Sequence No.: 13                                          Autosampler Location:
Sample ID: 10pc A                                         Date Collected: 12/19/2014 11:16:56 AM
Analyst:                                                  Data Type: Original

--------------------------------------------------------------------------------------------
Replicate Data: 10pc A                                    Analyte: Cu 324.75
Repl    SampleConc   StndConc   BlnkCorr    Time            Signal
 #      mg/L         mg/L       Signal                      Stored
 1      0.199        0.199      0.027       11:16:56 AM     Yes
 2      0.203        0.203      0.028       11:17:01 AM     Yes
```

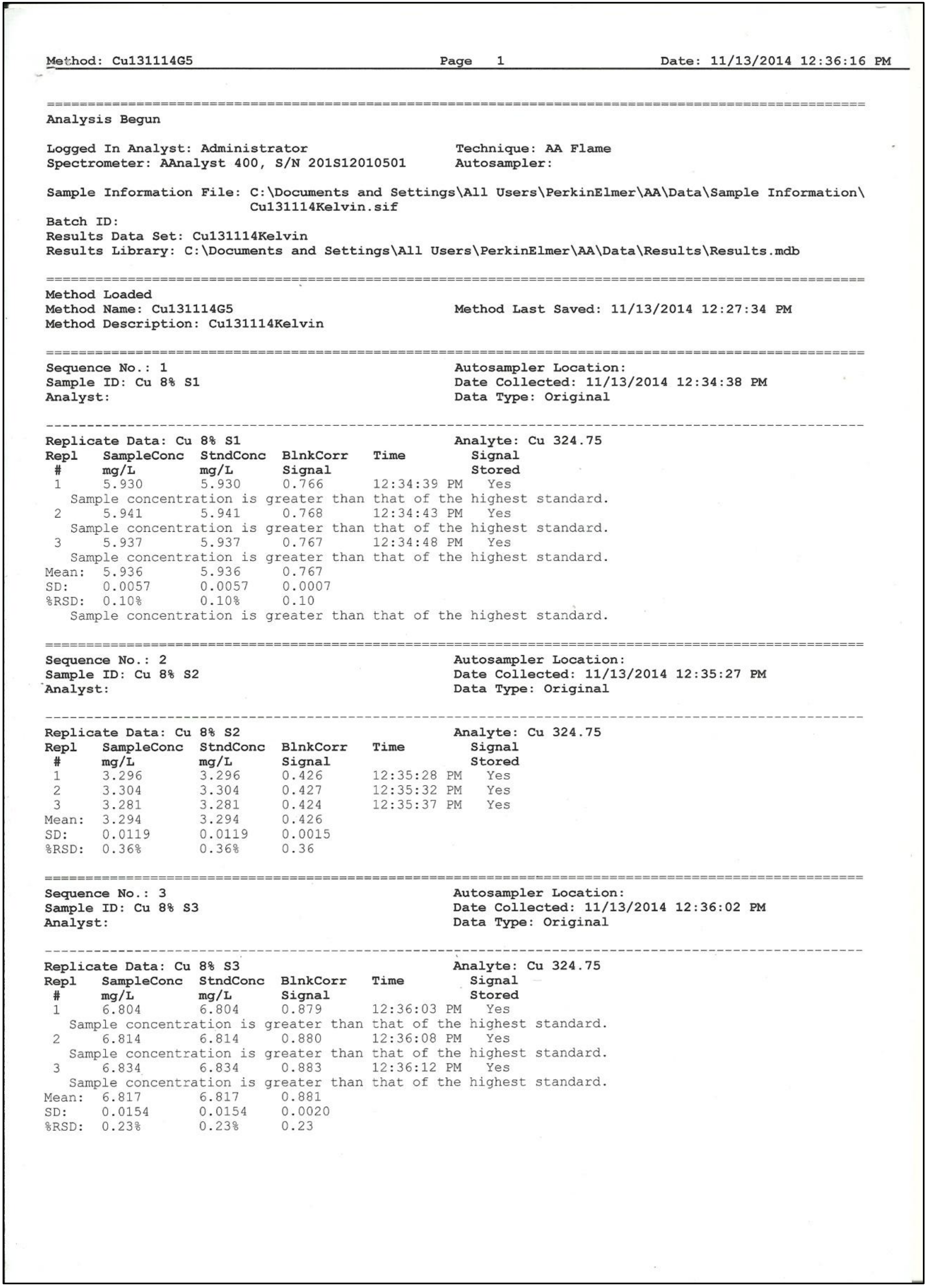
Static Adsorption Page 3



```
Method: Cu011214G4                              Page   4               Date: 12/19/2014 11:18:19 AM
 3      0.198       0.198      0.027      11:17:05 AM   Yes
Mean:  0.200       0.200      0.028
SD:    0.0028      0.0028     0.0004
%RSD:  1.41%       1.41%      1.41

=====================================================================================================
Sequence No.: 14                                    Autosampler Location:
Sample ID: 10pc B                                   Date Collected: 12/19/2014 11:17:23 AM
Analyst:                                            Data Type: Original

-----------------------------------------------------------------------------------------------------
Replicate Data: 10pc B                              Analyte: Cu 324.75
Repl    SampleConc  StndConc   BlnkCorr   Time          Signal
 #      mg/L        mg/L       Signal                   Stored
 1      0.169       0.169      0.023      11:17:24 AM   Yes
 2      0.168       0.168      0.023      11:17:28 AM   Yes
 3      0.182       0.182      0.025      11:17:33 AM   Yes
Mean:  0.173       0.173      0.024
SD:    0.0075      0.0075     0.0010
%RSD:  4.34%       4.34%      4.34

=====================================================================================================
Sequence No.: 15                                    Autosampler Location:
Sample ID: 10pc C                                   Date Collected: 12/19/2014 11:17:49 AM
Analyst:                                            Data Type: Original

-----------------------------------------------------------------------------------------------------
Replicate Data: 10pc C                              Analyte: Cu 324.75
Repl    SampleConc  StndConc   BlnkCorr   Time          Signal
 #      mg/L        mg/L       Signal                   Stored
 1      0.295       0.295      0.041      11:17:49 AM   Yes
 2      0.298       0.298      0.041      11:17:54 AM   Yes
 3      0.295       0.295      0.041      11:17:58 AM   Yes
Mean:  0.296       0.296      0.041
SD:    0.0017      0.0017     0.0002
%RSD:  0.58%       0.58%      0.58
```

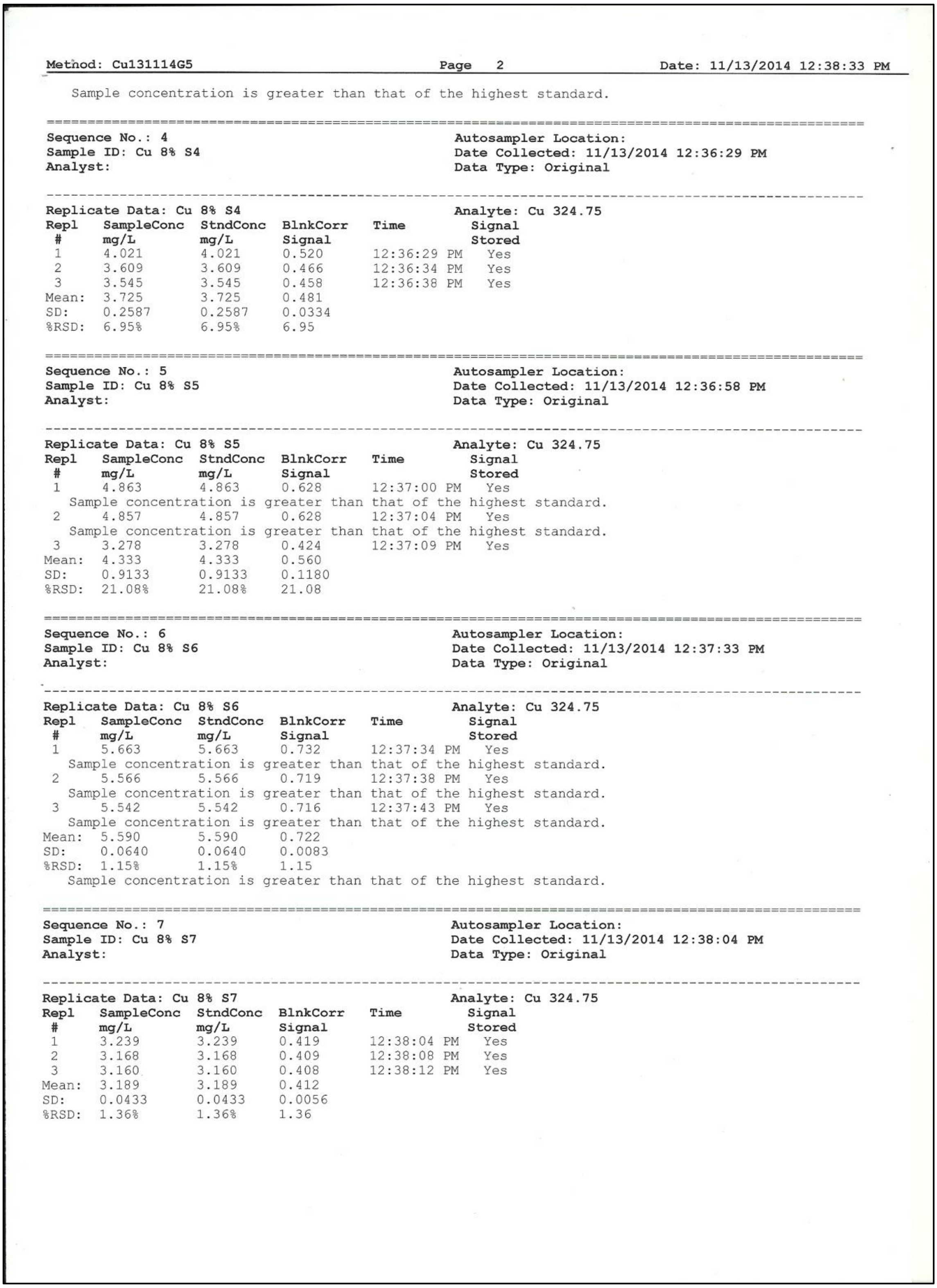
Static Adsorption Page 4

A.2 Effect of pH



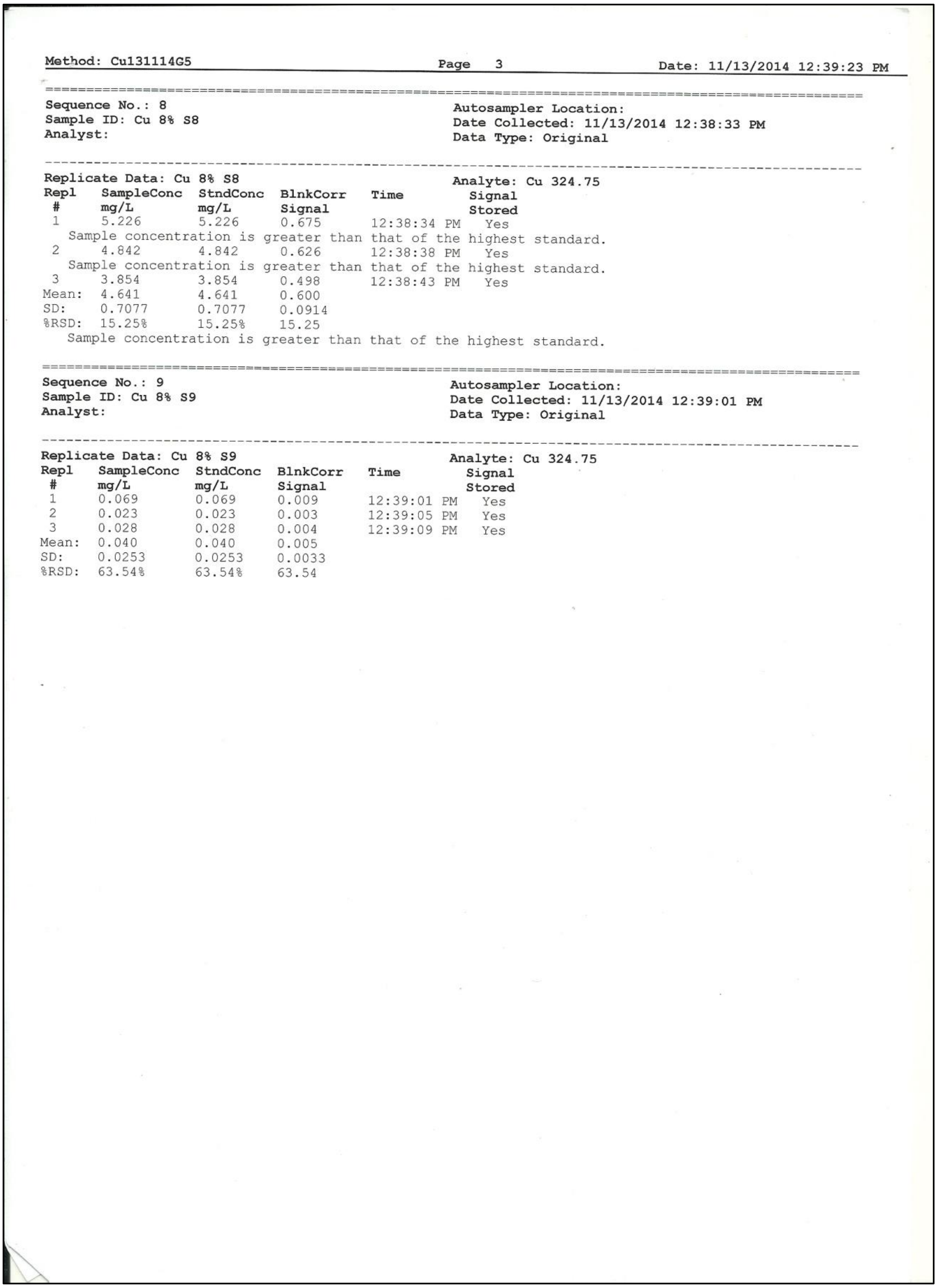
```
Method: Cu131114G5                       Page   1                Date: 11/13/2014 12:36:16 PM

==========================================================================================
Analysis Begun

Logged In Analyst: Administrator                   Technique: AA Flame
Spectrometer: AAnalyst 400, S/N 201S12010501       Autosampler:

Sample Information File: C:\Documents and Settings\All Users\PerkinElmer\AA\Data\Sample Information\
                         Cu131114Kelvin.sif
Batch ID:
Results Data Set: Cu131114Kelvin
Results Library: C:\Documents and Settings\All Users\PerkinElmer\AA\Data\Results\Results.mdb

==========================================================================================
Method Loaded
Method Name: Cu131114G5                            Method Last Saved: 11/13/2014 12:27:34 PM
Method Description: Cu131114Kelvin

==========================================================================================
Sequence No.: 1                                    Autosampler Location:
Sample ID: Cu 8% S1                                Date Collected: 11/13/2014 12:34:38 PM
Analyst:                                           Data Type: Original

------------------------------------------------------------------------------------------
Replicate Data: Cu 8% S1                           Analyte: Cu 324.75
Repl   SampleConc  StndConc  BlnkCorr  Time          Signal
 #     mg/L        mg/L      Signal                  Stored
 1     5.930       5.930     0.766     12:34:39 PM    Yes
   Sample concentration is greater than that of the highest standard.
 2     5.941       5.941     0.768     12:34:43 PM    Yes
   Sample concentration is greater than that of the highest standard.
 3     5.937       5.937     0.767     12:34:48 PM    Yes
   Sample concentration is greater than that of the highest standard.
Mean:  5.936       5.936     0.767
SD:    0.0057      0.0057    0.0007
%RSD:  0.10%       0.10%     0.10
   Sample concentration is greater than that of the highest standard.

==========================================================================================
Sequence No.: 2                                    Autosampler Location:
Sample ID: Cu 8% S2                                Date Collected: 11/13/2014 12:35:27 PM
Analyst:                                           Data Type: Original

------------------------------------------------------------------------------------------
Replicate Data: Cu 8% S2                           Analyte: Cu 324.75
Repl   SampleConc  StndConc  BlnkCorr  Time          Signal
 #     mg/L        mg/L      Signal                  Stored
 1     3.296       3.296     0.426     12:35:28 PM    Yes
 2     3.304       3.304     0.427     12:35:32 PM    Yes
 3     3.281       3.281     0.424     12:35:37 PM    Yes
Mean:  3.294       3.294     0.426
SD:    0.0119      0.0119    0.0015
%RSD:  0.36%       0.36%     0.36

==========================================================================================
Sequence No.: 3                                    Autosampler Location:
Sample ID: Cu 8% S3                                Date Collected: 11/13/2014 12:36:02 PM
Analyst:                                           Data Type: Original

------------------------------------------------------------------------------------------
Replicate Data: Cu 8% S3                           Analyte: Cu 324.75
Repl   SampleConc  StndConc  BlnkCorr  Time          Signal
 #     mg/L        mg/L      Signal                  Stored
 1     6.804       6.804     0.879     12:36:03 PM    Yes
   Sample concentration is greater than that of the highest standard.
 2     6.814       6.814     0.880     12:36:08 PM    Yes
   Sample concentration is greater than that of the highest standard.
 3     6.834       6.834     0.883     12:36:12 PM    Yes
   Sample concentration is greater than that of the highest standard.
Mean:  6.817       6.817     0.881
SD:    0.0154      0.0154    0.0020
%RSD:  0.23%       0.23%     0.23
```

Effect of pH Page 1



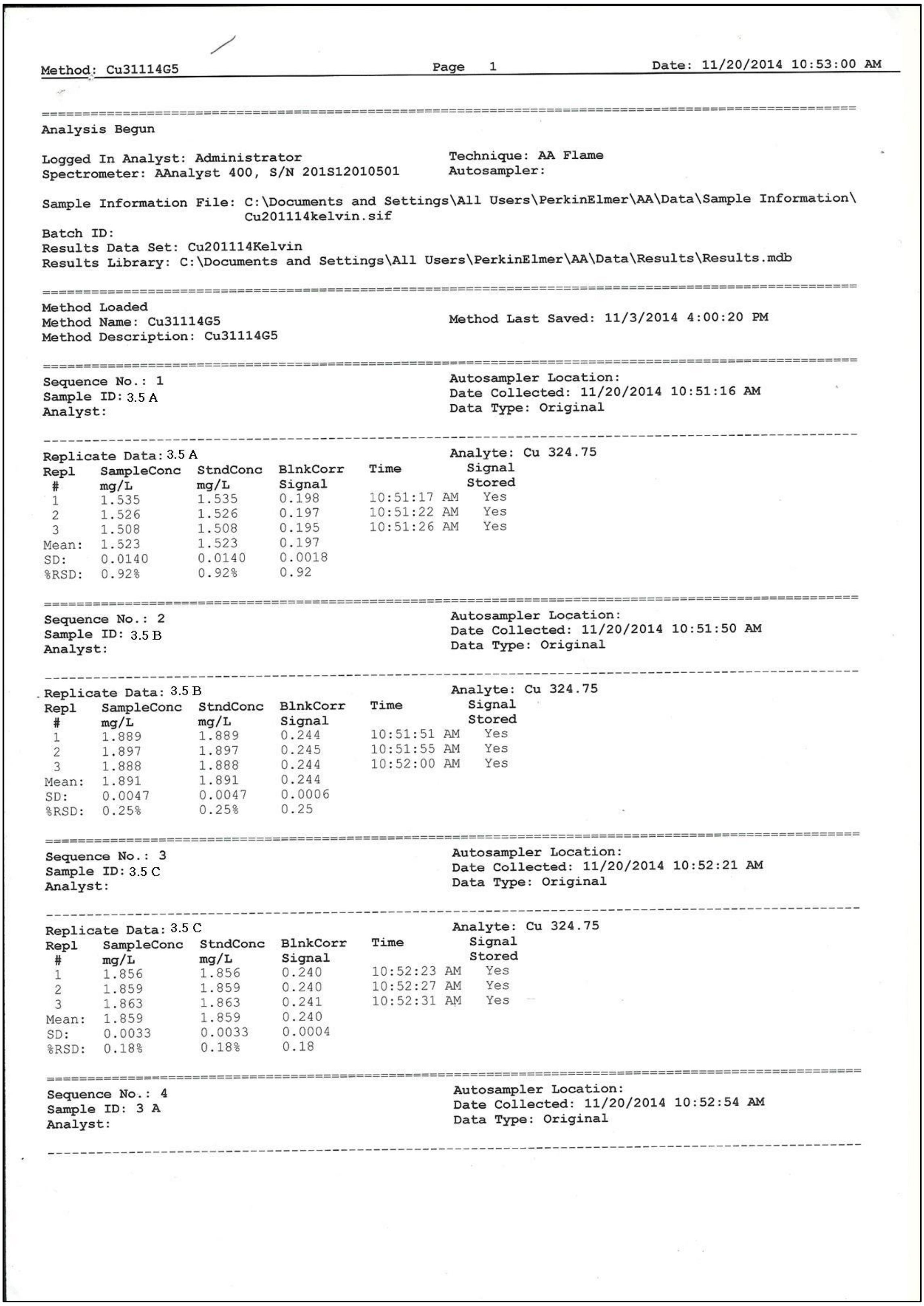
```
Method: Cu131114G5                              Page   2                 Date: 11/13/2014 12:38:33 PM

   Sample concentration is greater than that of the highest standard.

==============================================================================================
Sequence No.: 4                                         Autosampler Location:
Sample ID: Cu 8% S4                                     Date Collected: 11/13/2014 12:36:29 PM
Analyst:                                                Data Type: Original

----------------------------------------------------------------------------------------------
Replicate Data: Cu 8% S4                                Analyte: Cu 324.75
Repl    SampleConc   StndConc   BlnkCorr   Time          Signal
 #      mg/L         mg/L       Signal                   Stored
 1      4.021        4.021      0.520      12:36:29 PM    Yes
 2      3.609        3.609      0.466      12:36:34 PM    Yes
 3      3.545        3.545      0.458      12:36:38 PM    Yes
Mean:   3.725        3.725      0.481
SD:     0.2587       0.2587     0.0334
%RSD:   6.95%        6.95%      6.95

==============================================================================================
Sequence No.: 5                                         Autosampler Location:
Sample ID: Cu 8% S5                                     Date Collected: 11/13/2014 12:36:58 PM
Analyst:                                                Data Type: Original

----------------------------------------------------------------------------------------------
Replicate Data: Cu 8% S5                                Analyte: Cu 324.75
Repl    SampleConc   StndConc   BlnkCorr   Time          Signal
 #      mg/L         mg/L       Signal                   Stored
 1      4.863        4.863      0.628      12:37:00 PM    Yes
   Sample concentration is greater than that of the highest standard.
 2      4.857        4.857      0.628      12:37:04 PM    Yes
   Sample concentration is greater than that of the highest standard.
 3      3.278        3.278      0.424      12:37:09 PM    Yes
Mean:   4.333        4.333      0.560
SD:     0.9133       0.9133     0.1180
%RSD:   21.08%       21.08%     21.08

==============================================================================================
Sequence No.: 6                                         Autosampler Location:
Sample ID: Cu 8% S6                                     Date Collected: 11/13/2014 12:37:33 PM
Analyst:                                                Data Type: Original

----------------------------------------------------------------------------------------------
Replicate Data: Cu 8% S6                                Analyte: Cu 324.75
Repl    SampleConc   StndConc   BlnkCorr   Time          Signal
 #      mg/L         mg/L       Signal                   Stored
 1      5.663        5.663      0.732      12:37:34 PM    Yes
   Sample concentration is greater than that of the highest standard.
 2      5.566        5.566      0.719      12:37:38 PM    Yes
   Sample concentration is greater than that of the highest standard.
 3      5.542        5.542      0.716      12:37:43 PM    Yes
   Sample concentration is greater than that of the highest standard.
Mean:   5.590        5.590      0.722
SD:     0.0640       0.0640     0.0083
%RSD:   1.15%        1.15%      1.15
   Sample concentration is greater than that of the highest standard.

==============================================================================================
Sequence No.: 7                                         Autosampler Location:
Sample ID: Cu 8% S7                                     Date Collected: 11/13/2014 12:38:04 PM
Analyst:                                                Data Type: Original

----------------------------------------------------------------------------------------------
Replicate Data: Cu 8% S7                                Analyte: Cu 324.75
Repl    SampleConc   StndConc   BlnkCorr   Time          Signal
 #      mg/L         mg/L       Signal                   Stored
 1      3.239        3.239      0.419      12:38:04 PM    Yes
 2      3.168        3.168      0.409      12:38:08 PM    Yes
 3      3.160        3.160      0.408      12:38:12 PM    Yes
Mean:   3.189        3.189      0.412
SD:     0.0433       0.0433     0.0056
%RSD:   1.36%        1.36%      1.36
```

Effect of pH Page 2



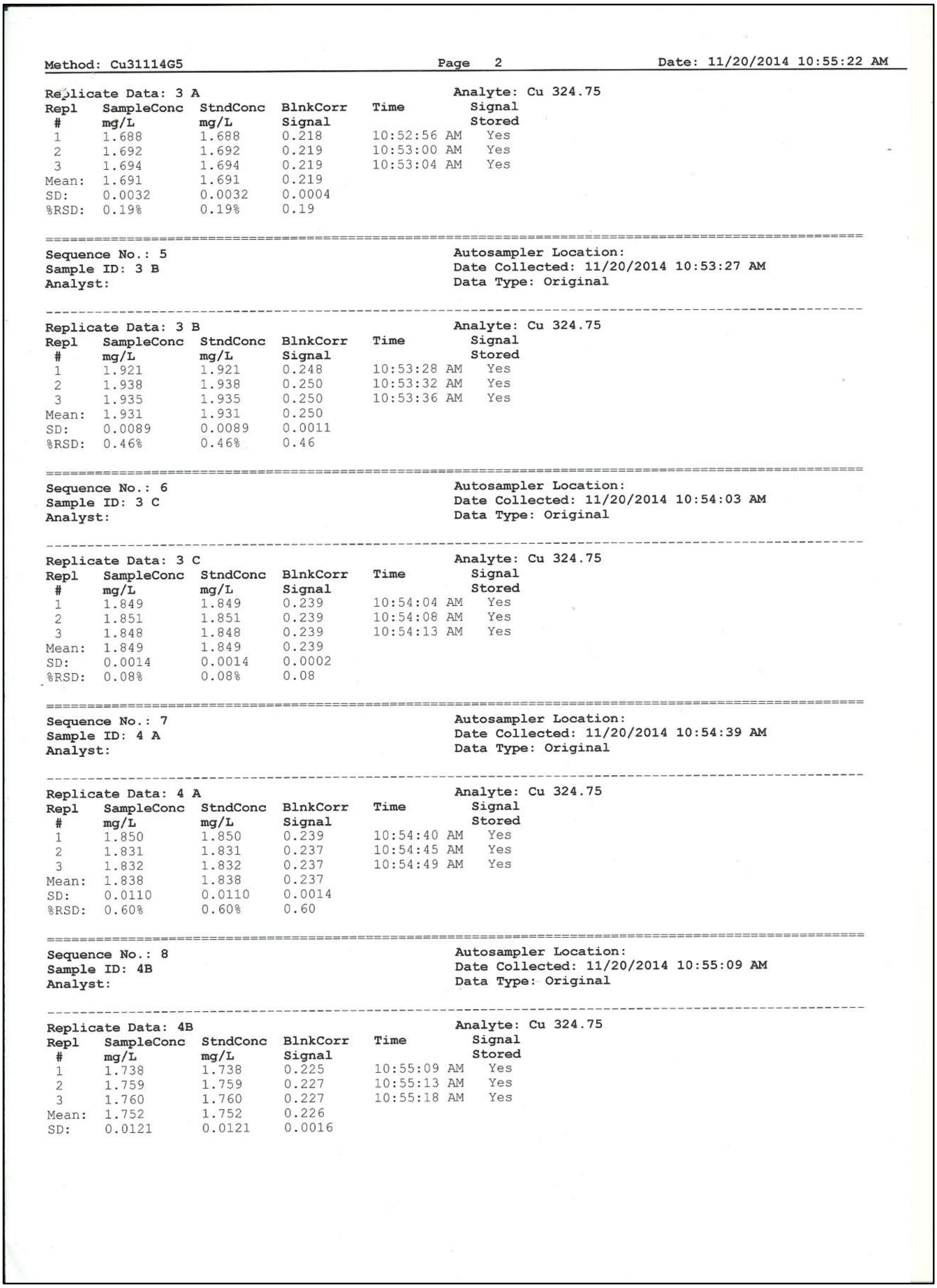
```
Method: Cu131114G5                               Page   3                Date: 11/13/2014 12:39:23 PM
==================================================================================================
Sequence No.: 8                                             Autosampler Location:
Sample ID: Cu 8% S8                                         Date Collected: 11/13/2014 12:38:33 PM
Analyst:                                                    Data Type: Original

--------------------------------------------------------------------------------------------------
Replicate Data: Cu 8% S8                                    Analyte: Cu 324.75
Repl    SampleConc    StndConc    BlnkCorr    Time            Signal
 #      mg/L          mg/L        Signal                      Stored
 1      5.226         5.226       0.675       12:38:34 PM      Yes
   Sample concentration is greater than that of the highest standard.
 2      4.842         4.842       0.626       12:38:38 PM      Yes
   Sample concentration is greater than that of the highest standard.
 3      3.854         3.854       0.498       12:38:43 PM      Yes
Mean:   4.641         4.641       0.600
SD:     0.7077        0.7077      0.0914
%RSD:   15.25%        15.25%      15.25
   Sample concentration is greater than that of the highest standard.

==================================================================================================
Sequence No.: 9                                             Autosampler Location:
Sample ID: Cu 8% S9                                         Date Collected: 11/13/2014 12:39:01 PM
Analyst:                                                    Data Type: Original

--------------------------------------------------------------------------------------------------
Replicate Data: Cu 8% S9                                    Analyte: Cu 324.75
Repl    SampleConc    StndConc    BlnkCorr    Time            Signal
 #      mg/L          mg/L        Signal                      Stored
 1      0.069         0.069       0.009       12:39:01 PM      Yes
 2      0.023         0.023       0.003       12:39:05 PM      Yes
 3      0.028         0.028       0.004       12:39:09 PM      Yes
Mean:   0.040         0.040       0.005
SD:     0.0253        0.0253      0.0033
%RSD:   63.54%        63.54%      63.54
```

Effect of pH Page 3



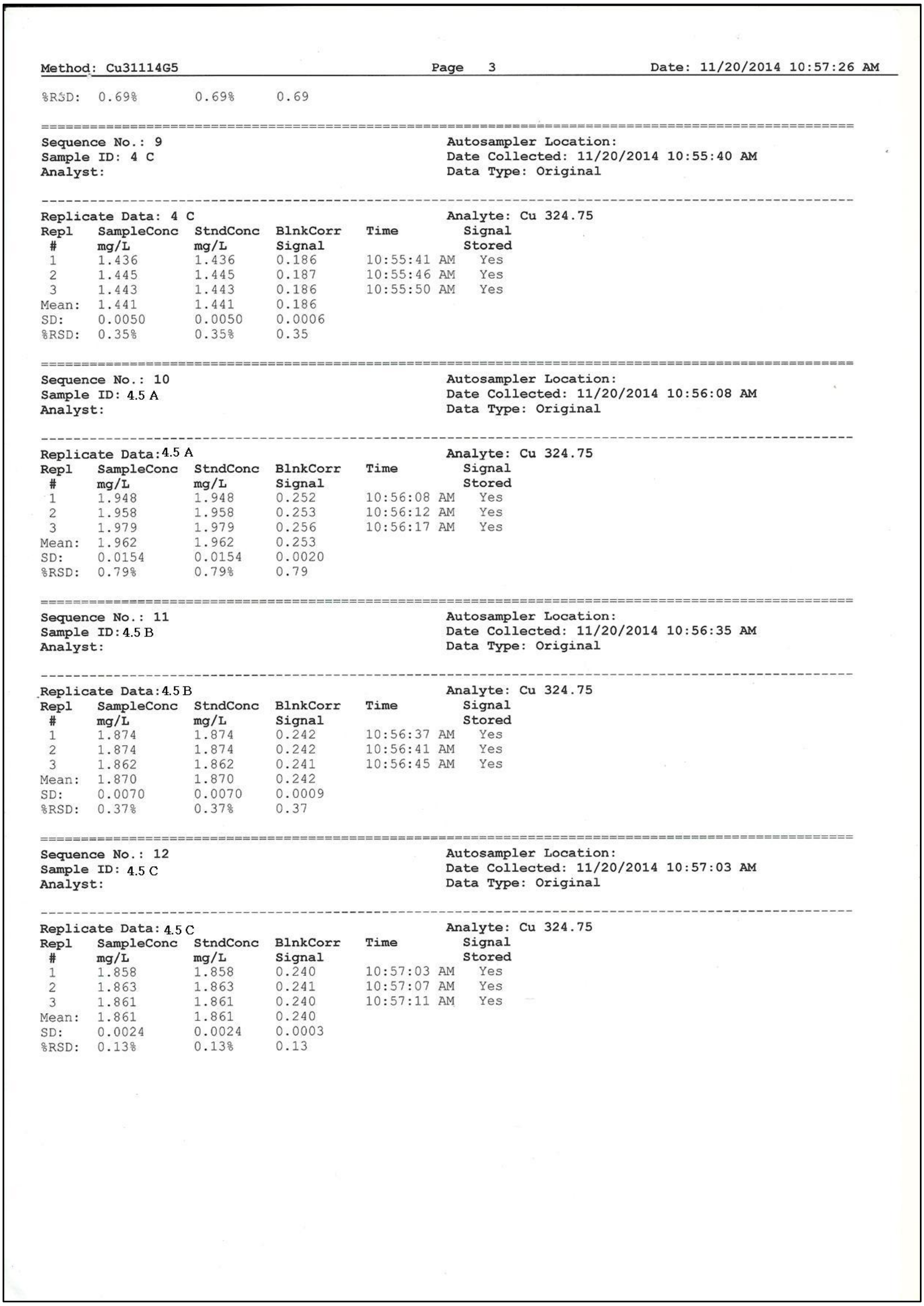
```
Method: Cu31114G5                              Page   1              Date: 11/20/2014 10:53:00 AM

=============================================================================================
Analysis Begun

Logged In Analyst: Administrator                  Technique: AA Flame
Spectrometer: AAnalyst 400, S/N 201S12010501      Autosampler:

Sample Information File: C:\Documents and Settings\All Users\PerkinElmer\AA\Data\Sample Information\
                         Cu201114kelvin.sif

Batch ID:
Results Data Set: Cu201114Kelvin
Results Library: C:\Documents and Settings\All Users\PerkinElmer\AA\Data\Results\Results.mdb

=============================================================================================
Method Loaded
Method Name: Cu31114G5                            Method Last Saved: 11/3/2014 4:00:20 PM
Method Description: Cu31114G5

=============================================================================================
Sequence No.: 1                                   Autosampler Location:
Sample ID: 3.5 A                                  Date Collected: 11/20/2014 10:51:16 AM
Analyst:                                          Data Type: Original

---------------------------------------------------------------------------------------------
Replicate Data: 3.5 A                             Analyte: Cu 324.75
Repl    SampleConc   StndConc   BlnkCorr    Time           Signal
 #      mg/L         mg/L       Signal                     Stored
 1      1.535        1.535      0.198       10:51:17 AM    Yes
 2      1.526        1.526      0.197       10:51:22 AM    Yes
 3      1.508        1.508      0.195       10:51:26 AM    Yes
Mean:   1.523        1.523      0.197
SD:     0.0140       0.0140     0.0018
%RSD:   0.92%        0.92%      0.92

=============================================================================================
Sequence No.: 2                                   Autosampler Location:
Sample ID: 3.5 B                                  Date Collected: 11/20/2014 10:51:50 AM
Analyst:                                          Data Type: Original

---------------------------------------------------------------------------------------------
Replicate Data: 3.5 B                             Analyte: Cu 324.75
Repl    SampleConc   StndConc   BlnkCorr    Time           Signal
 #      mg/L         mg/L       Signal                     Stored
 1      1.889        1.889      0.244       10:51:51 AM    Yes
 2      1.897        1.897      0.245       10:51:55 AM    Yes
 3      1.888        1.888      0.244       10:52:00 AM    Yes
Mean:   1.891        1.891      0.244
SD:     0.0047       0.0047     0.0006
%RSD:   0.25%        0.25%      0.25

=============================================================================================
Sequence No.: 3                                   Autosampler Location:
Sample ID: 3.5 C                                  Date Collected: 11/20/2014 10:52:21 AM
Analyst:                                          Data Type: Original

---------------------------------------------------------------------------------------------
Replicate Data: 3.5 C                             Analyte: Cu 324.75
Repl    SampleConc   StndConc   BlnkCorr    Time           Signal
 #      mg/L         mg/L       Signal                     Stored
 1      1.856        1.856      0.240       10:52:23 AM    Yes
 2      1.859        1.859      0.240       10:52:27 AM    Yes
 3      1.863        1.863      0.241       10:52:31 AM    Yes
Mean:   1.859        1.859      0.240
SD:     0.0033       0.0033     0.0004
%RSD:   0.18%        0.18%      0.18

=============================================================================================
Sequence No.: 4                                   Autosampler Location:
Sample ID: 3 A                                    Date Collected: 11/20/2014 10:52:54 AM
Analyst:                                          Data Type: Original

---------------------------------------------------------------------------------------------
```

Effect of low pH Page 1



```
Method: Cu31114G5                          Page   2                Date: 11/20/2014 10:55:22 AM

Replicate Data: 3 A                                     Analyte: Cu 324.75
Repl    SampleConc   StndConc    BlnkCorr    Time          Signal
 #      mg/L         mg/L        Signal                    Stored
 1      1.688        1.688       0.218       10:52:56 AM     Yes
 2      1.692        1.692       0.219       10:53:00 AM     Yes
 3      1.694        1.694       0.219       10:53:04 AM     Yes
Mean:   1.691        1.691       0.219
SD:     0.0032       0.0032      0.0004
%RSD:   0.19%        0.19%       0.19

==============================================================================================
Sequence No.: 5                                         Autosampler Location:
Sample ID: 3 B                                          Date Collected: 11/20/2014 10:53:27 AM
Analyst:                                                Data Type: Original

----------------------------------------------------------------------------------------------
Replicate Data: 3 B                                     Analyte: Cu 324.75
Repl    SampleConc   StndConc    BlnkCorr    Time          Signal
 #      mg/L         mg/L        Signal                    Stored
 1      1.921        1.921       0.248       10:53:28 AM     Yes
 2      1.938        1.938       0.250       10:53:32 AM     Yes
 3      1.935        1.935       0.250       10:53:36 AM     Yes
Mean:   1.931        1.931       0.250
SD:     0.0089       0.0089      0.0011
%RSD:   0.46%        0.46%       0.46

==============================================================================================
Sequence No.: 6                                         Autosampler Location:
Sample ID: 3 C                                          Date Collected: 11/20/2014 10:54:03 AM
Analyst:                                                Data Type: Original

----------------------------------------------------------------------------------------------
Replicate Data: 3 C                                     Analyte: Cu 324.75
Repl    SampleConc   StndConc    BlnkCorr    Time          Signal
 #      mg/L         mg/L        Signal                    Stored
 1      1.849        1.849       0.239       10:54:04 AM     Yes
 2      1.851        1.851       0.239       10:54:08 AM     Yes
 3      1.848        1.848       0.239       10:54:13 AM     Yes
Mean:   1.849        1.849       0.239
SD:     0.0014       0.0014      0.0002
%RSD:   0.08%        0.08%       0.08

==============================================================================================
Sequence No.: 7                                         Autosampler Location:
Sample ID: 4 A                                          Date Collected: 11/20/2014 10:54:39 AM
Analyst:                                                Data Type: Original

----------------------------------------------------------------------------------------------
Replicate Data: 4 A                                     Analyte: Cu 324.75
Repl    SampleConc   StndConc    BlnkCorr    Time          Signal
 #      mg/L         mg/L        Signal                    Stored
 1      1.850        1.850       0.239       10:54:40 AM     Yes
 2      1.831        1.831       0.237       10:54:45 AM     Yes
 3      1.832        1.832       0.237       10:54:49 AM     Yes
Mean:   1.838        1.838       0.237
SD:     0.0110       0.0110      0.0014
%RSD:   0.60%        0.60%       0.60

==============================================================================================
Sequence No.: 8                                         Autosampler Location:
Sample ID: 4B                                           Date Collected: 11/20/2014 10:55:09 AM
Analyst:                                                Data Type: Original

----------------------------------------------------------------------------------------------
Replicate Data: 4B                                      Analyte: Cu 324.75
Repl    SampleConc   StndConc    BlnkCorr    Time          Signal
 #      mg/L         mg/L        Signal                    Stored
 1      1.738        1.738       0.225       10:55:09 AM     Yes
 2      1.759        1.759       0.227       10:55:13 AM     Yes
 3      1.760        1.760       0.227       10:55:18 AM     Yes
Mean:   1.752        1.752       0.226
SD:     0.0121       0.0121      0.0016
```

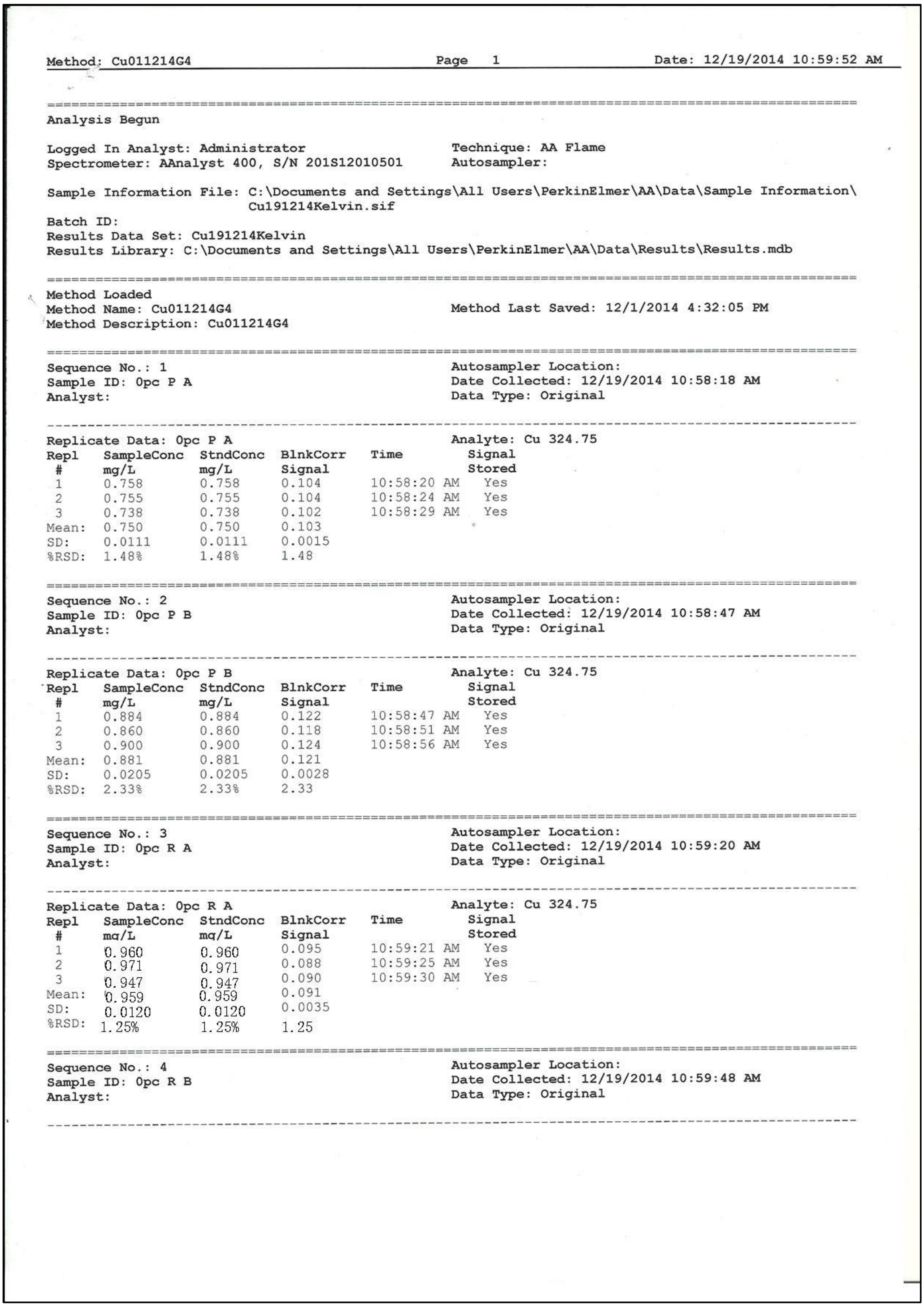
Effect of low pH Page 2



```
Method: Cu31114G5                               Page   3                  Date: 11/20/2014 10:57:26 AM
%RSD:  0.69%        0.69%      0.69

=======================================================================================================
Sequence No.: 9                                           Autosampler Location:
Sample ID: 4 C                                            Date Collected: 11/20/2014 10:55:40 AM
Analyst:                                                  Data Type: Original

-------------------------------------------------------------------------------------------------------
Replicate Data: 4 C                                       Analyte: Cu 324.75
Repl    SampleConc    StndConc   BlnkCorr    Time          Signal
 #      mg/L          mg/L       Signal                    Stored
 1      1.436         1.436      0.186       10:55:41 AM     Yes
 2      1.445         1.445      0.187       10:55:46 AM     Yes
 3      1.443         1.443      0.186       10:55:50 AM     Yes
Mean:   1.441         1.441      0.186
SD:     0.0050        0.0050     0.0006
%RSD:   0.35%         0.35%      0.35

=======================================================================================================
Sequence No.: 10                                          Autosampler Location:
Sample ID: 4.5 A                                          Date Collected: 11/20/2014 10:56:08 AM
Analyst:                                                  Data Type: Original

-------------------------------------------------------------------------------------------------------
Replicate Data:4.5 A                                      Analyte: Cu 324.75
Repl    SampleConc    StndConc   BlnkCorr    Time          Signal
 #      mg/L          mg/L       Signal                    Stored
 1      1.948         1.948      0.252       10:56:08 AM     Yes
 2      1.958         1.958      0.253       10:56:12 AM     Yes
 3      1.979         1.979      0.256       10:56:17 AM     Yes
Mean:   1.962         1.962      0.253
SD:     0.0154        0.0154     0.0020
%RSD:   0.79%         0.79%      0.79

=======================================================================================================
Sequence No.: 11                                          Autosampler Location:
Sample ID:4.5 B                                           Date Collected: 11/20/2014 10:56:35 AM
Analyst:                                                  Data Type: Original

-------------------------------------------------------------------------------------------------------
Replicate Data:4.5 B                                      Analyte: Cu 324.75
Repl    SampleConc    StndConc   BlnkCorr    Time          Signal
 #      mg/L          mg/L       Signal                    Stored
 1      1.874         1.874      0.242       10:56:37 AM     Yes
 2      1.874         1.874      0.242       10:56:41 AM     Yes
 3      1.862         1.862      0.241       10:56:45 AM     Yes
Mean:   1.870         1.870      0.242
SD:     0.0070        0.0070     0.0009
%RSD:   0.37%         0.37%      0.37

=======================================================================================================
Sequence No.: 12                                          Autosampler Location:
Sample ID: 4.5 C                                          Date Collected: 11/20/2014 10:57:03 AM
Analyst:                                                  Data Type: Original

-------------------------------------------------------------------------------------------------------
Replicate Data: 4.5 C                                     Analyte: Cu 324.75
Repl    SampleConc    StndConc   BlnkCorr    Time          Signal
 #      mg/L          mg/L       Signal                    Stored
 1      1.858         1.858      0.240       10:57:03 AM     Yes
 2      1.863         1.863      0.241       10:57:07 AM     Yes
 3      1.861         1.861      0.240       10:57:11 AM     Yes
Mean:   1.861         1.861      0.240
SD:     0.0024        0.0024     0.0003
%RSD:   0.13%         0.13%      0.13
```

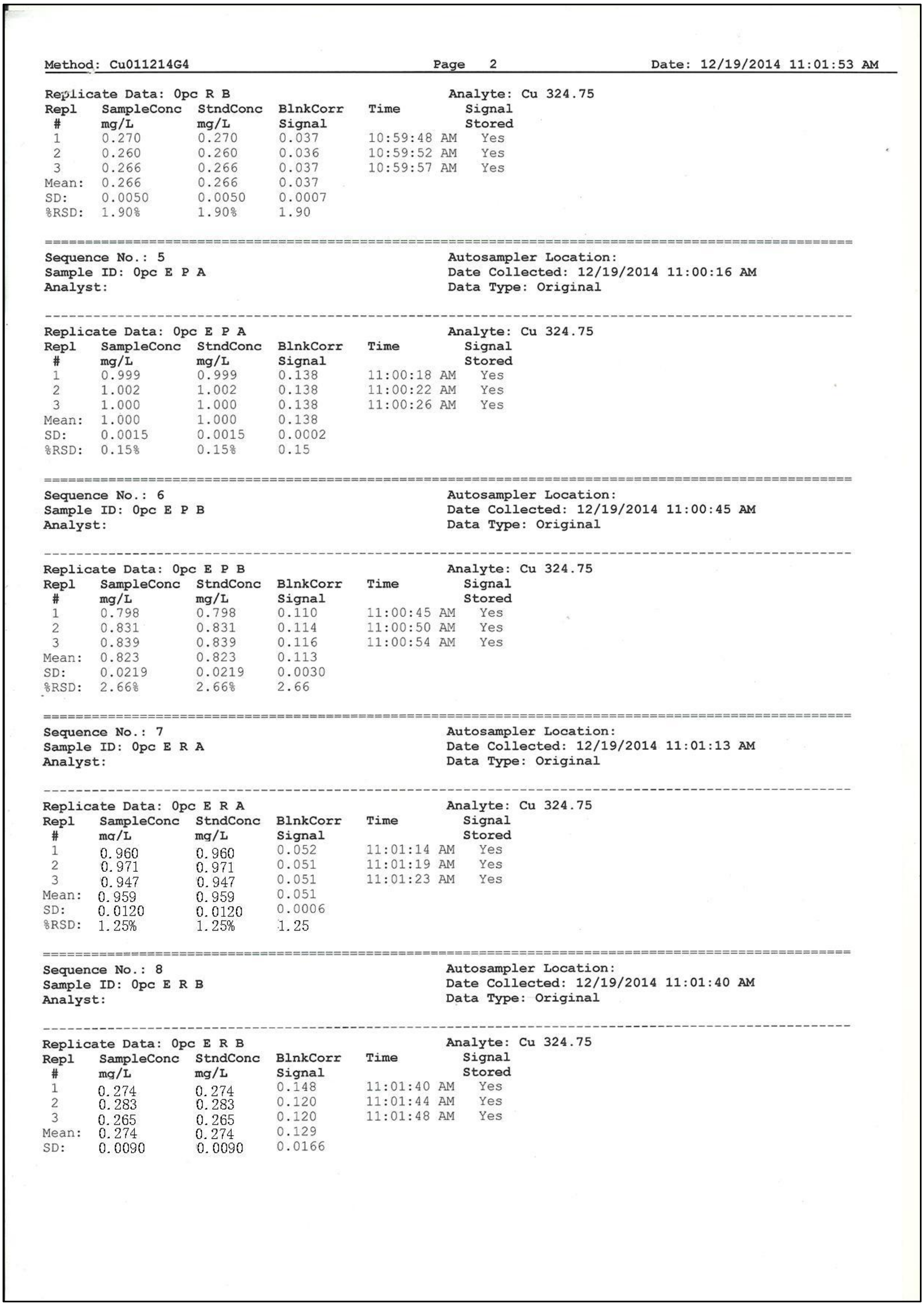
Effect of low pH Page 3

A.3 Cross Flow Data



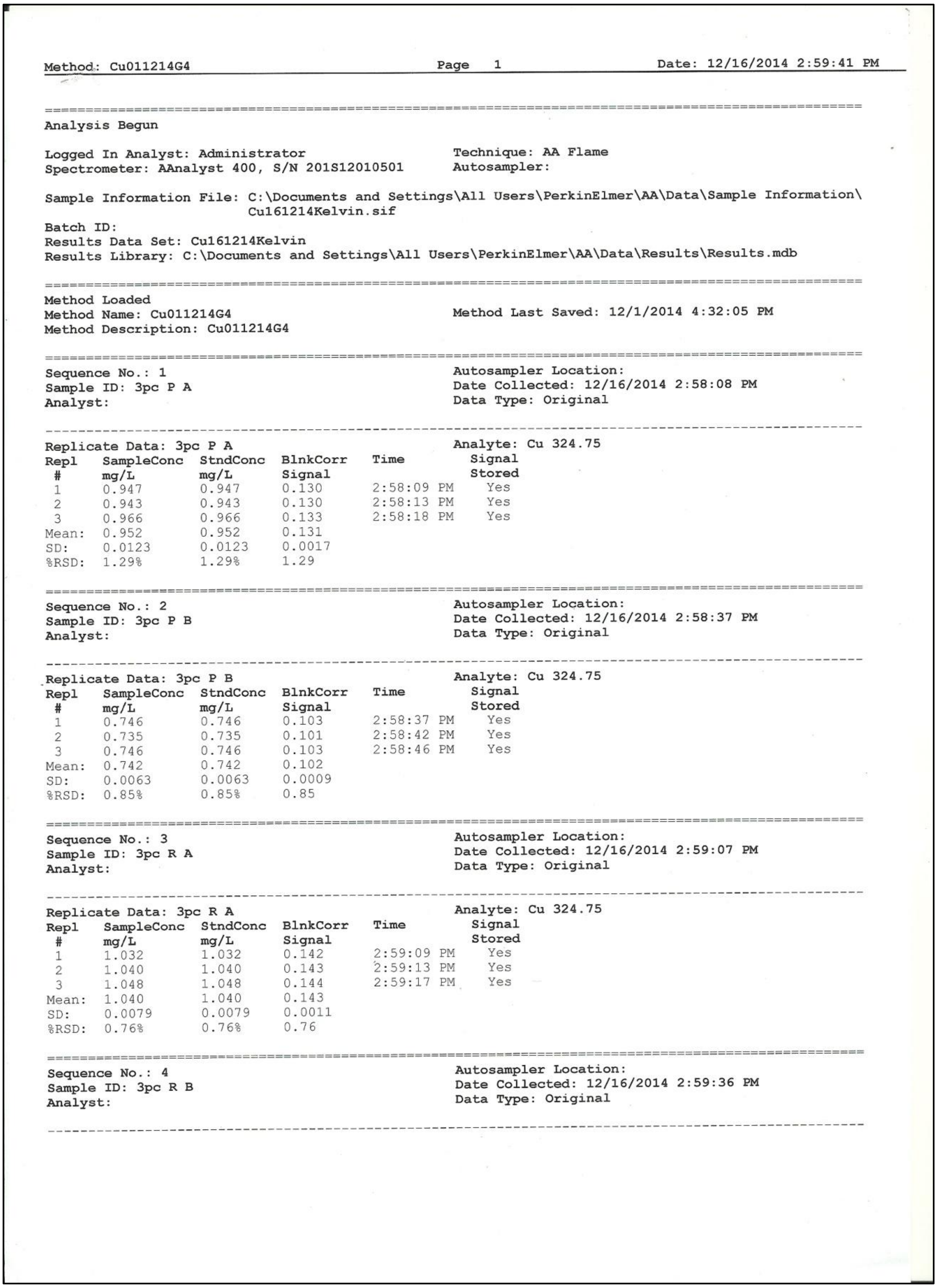
```
Method: Cu011214G4                              Page   1                  Date: 12/19/2014 10:59:52 AM

====================================================================================================
Analysis Begun

Logged In Analyst: Administrator                  Technique: AA Flame
Spectrometer: AAnalyst 400, S/N 201S12010501      Autosampler:

Sample Information File: C:\Documents and Settings\All Users\PerkinElmer\AA\Data\Sample Information\
                         Cu191214Kelvin.sif
Batch ID:
Results Data Set: Cu191214Kelvin
Results Library: C:\Documents and Settings\All Users\PerkinElmer\AA\Data\Results\Results.mdb

====================================================================================================
Method Loaded
Method Name: Cu011214G4                           Method Last Saved: 12/1/2014 4:32:05 PM
Method Description: Cu011214G4

====================================================================================================
Sequence No.: 1                                   Autosampler Location:
Sample ID: 0pc P A                                Date Collected: 12/19/2014 10:58:18 AM
Analyst:                                          Data Type: Original

----------------------------------------------------------------------------------------------------
Replicate Data: 0pc P A                           Analyte: Cu 324.75
Repl   SampleConc  StndConc  BlnkCorr   Time        Signal
 #     mg/L        mg/L      Signal                 Stored
 1     0.758       0.758     0.104      10:58:20 AM   Yes
 2     0.755       0.755     0.104      10:58:24 AM   Yes
 3     0.738       0.738     0.102      10:58:29 AM   Yes
Mean:  0.750       0.750     0.103
SD:    0.0111      0.0111    0.0015
%RSD:  1.48%       1.48%     1.48

====================================================================================================
Sequence No.: 2                                   Autosampler Location:
Sample ID: 0pc P B                                Date Collected: 12/19/2014 10:58:47 AM
Analyst:                                          Data Type: Original

----------------------------------------------------------------------------------------------------
Replicate Data: 0pc P B                           Analyte: Cu 324.75
Repl   SampleConc  StndConc  BlnkCorr   Time        Signal
 #     mg/L        mg/L      Signal                 Stored
 1     0.884       0.884     0.122      10:58:47 AM   Yes
 2     0.860       0.860     0.118      10:58:51 AM   Yes
 3     0.900       0.900     0.124      10:58:56 AM   Yes
Mean:  0.881       0.881     0.121
SD:    0.0205      0.0205    0.0028
%RSD:  2.33%       2.33%     2.33

====================================================================================================
Sequence No.: 3                                   Autosampler Location:
Sample ID: 0pc R A                                Date Collected: 12/19/2014 10:59:20 AM
Analyst:                                          Data Type: Original

----------------------------------------------------------------------------------------------------
Replicate Data: 0pc R A                           Analyte: Cu 324.75
Repl   SampleConc  StndConc  BlnkCorr   Time        Signal
 #     mg/L        mg/L      Signal                 Stored
 1     0.960       0.960     0.095      10:59:21 AM   Yes
 2     0.971       0.971     0.088      10:59:25 AM   Yes
 3     0.947       0.947     0.090      10:59:30 AM   Yes
Mean:  0.959       0.959     0.091
SD:    0.0120      0.0120    0.0035
%RSD:  1.25%       1.25%     1.25

====================================================================================================
Sequence No.: 4                                   Autosampler Location:
Sample ID: 0pc R B                                Date Collected: 12/19/2014 10:59:48 AM
Analyst:                                          Data Type: Original

----------------------------------------------------------------------------------------------------
```

Cross Flow of 0% PVP Page 1



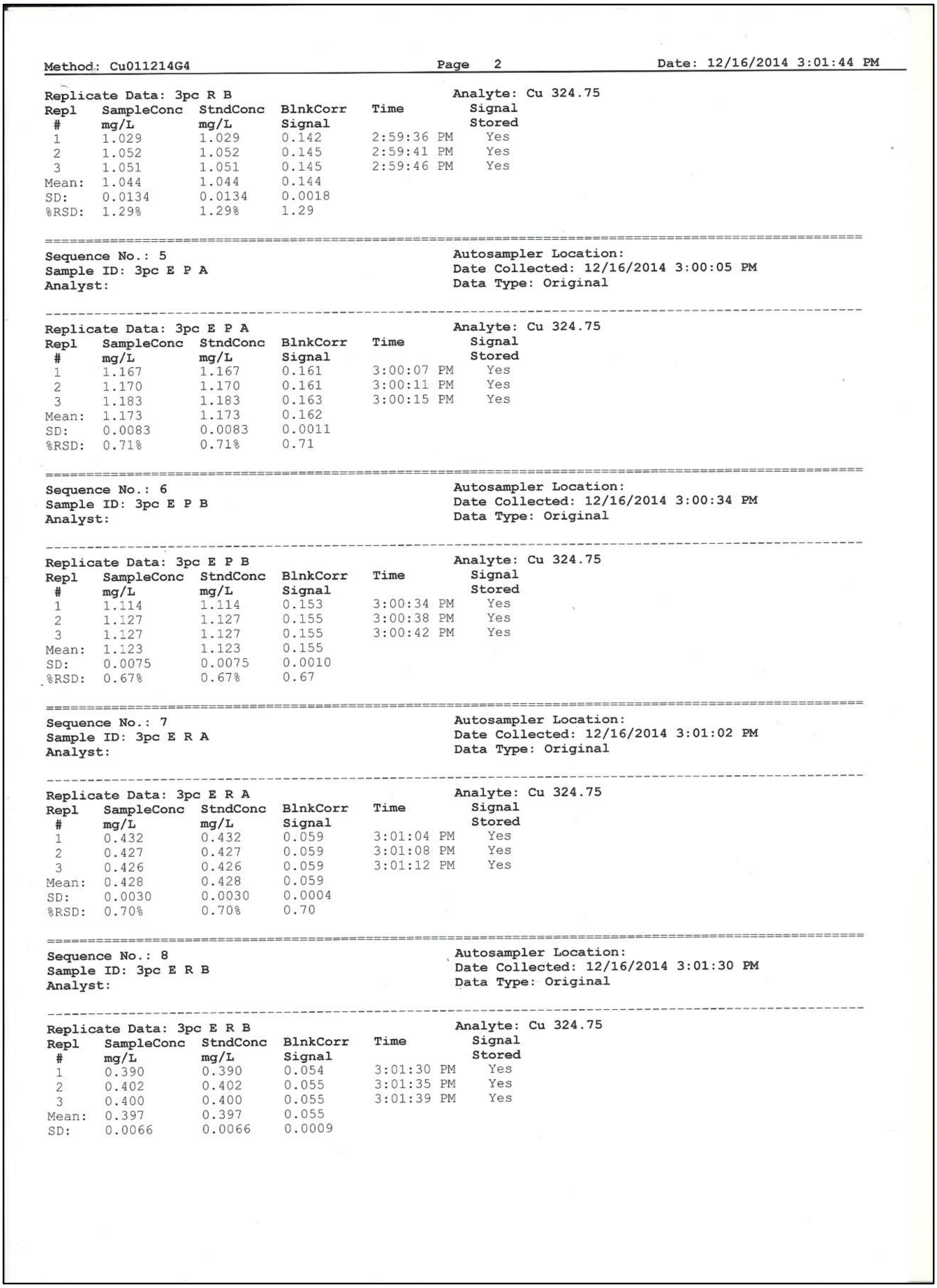
```
Method: Cu011214G4                              Page   2                Date: 12/19/2014 11:01:53 AM

Replicate Data: 0pc R B                                        Analyte: Cu 324.75
Repl    SampleConc   StndConc   BlnkCorr    Time          Signal
 #      mg/L         mg/L       Signal                    Stored
 1      0.270        0.270      0.037       10:59:48 AM    Yes
 2      0.260        0.260      0.036       10:59:52 AM    Yes
 3      0.266        0.266      0.037       10:59:57 AM    Yes
Mean:   0.266        0.266      0.037
SD:     0.0050       0.0050     0.0007
%RSD:   1.90%        1.90%      1.90

==================================================================================================
Sequence No.: 5                                                Autosampler Location:
Sample ID: 0pc E P A                                           Date Collected: 12/19/2014 11:00:16 AM
Analyst:                                                       Data Type: Original

--------------------------------------------------------------------------------------------------
Replicate Data: 0pc E P A                                      Analyte: Cu 324.75
Repl    SampleConc   StndConc   BlnkCorr    Time          Signal
 #      mg/L         mg/L       Signal                    Stored
 1      0.999        0.999      0.138       11:00:18 AM    Yes
 2      1.002        1.002      0.138       11:00:22 AM    Yes
 3      1.000        1.000      0.138       11:00:26 AM    Yes
Mean:   1.000        1.000      0.138
SD:     0.0015       0.0015     0.0002
%RSD:   0.15%        0.15%      0.15

==================================================================================================
Sequence No.: 6                                                Autosampler Location:
Sample ID: 0pc E P B                                           Date Collected: 12/19/2014 11:00:45 AM
Analyst:                                                       Data Type: Original

--------------------------------------------------------------------------------------------------
Replicate Data: 0pc E P B                                      Analyte: Cu 324.75
Repl    SampleConc   StndConc   BlnkCorr    Time          Signal
 #      mg/L         mg/L       Signal                    Stored
 1      0.798        0.798      0.110       11:00:45 AM    Yes
 2      0.831        0.831      0.114       11:00:50 AM    Yes
 3      0.839        0.839      0.116       11:00:54 AM    Yes
Mean:   0.823        0.823      0.113
SD:     0.0219       0.0219     0.0030
%RSD:   2.66%        2.66%      2.66

==================================================================================================
Sequence No.: 7                                                Autosampler Location:
Sample ID: 0pc E R A                                           Date Collected: 12/19/2014 11:01:13 AM
Analyst:                                                       Data Type: Original

--------------------------------------------------------------------------------------------------
Replicate Data: 0pc E R A                                      Analyte: Cu 324.75
Repl    SampleConc   StndConc   BlnkCorr    Time          Signal
 #      mg/L         mg/L       Signal                    Stored
 1      0.960        0.960      0.052       11:01:14 AM    Yes
 2      0.971        0.971      0.051       11:01:19 AM    Yes
 3      0.947        0.947      0.051       11:01:23 AM    Yes
Mean:   0.959        0.959      0.051
SD:     0.0120       0.0120     0.0006
%RSD:   1.25%        1.25%      1.25

==================================================================================================
Sequence No.: 8                                                Autosampler Location:
Sample ID: 0pc E R B                                           Date Collected: 12/19/2014 11:01:40 AM
Analyst:                                                       Data Type: Original

--------------------------------------------------------------------------------------------------
Replicate Data: 0pc E R B                                      Analyte: Cu 324.75
Repl    SampleConc   StndConc   BlnkCorr    Time          Signal
 #      mg/L         mg/L       Signal                    Stored
 1      0.274        0.274      0.148       11:01:40 AM    Yes
 2      0.283        0.283      0.120       11:01:44 AM    Yes
 3      0.265        0.265      0.120       11:01:48 AM    Yes
Mean:   0.274        0.274      0.129
SD:     0.0090       0.0090     0.0166
```

Cross Flow of 0% PVP Page 2



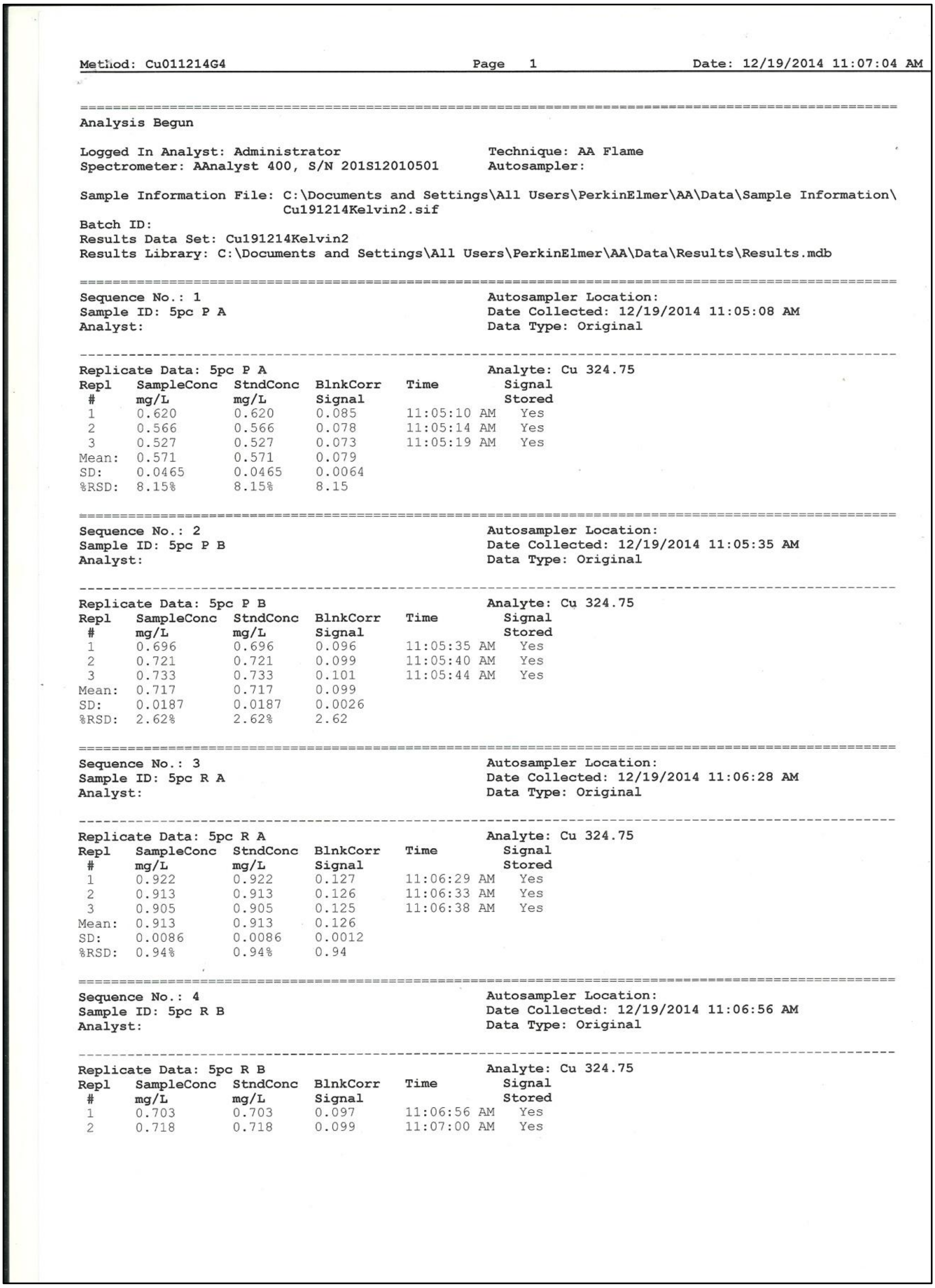
```
Method: Cu011214G4                        Page   1              Date: 12/16/2014 2:59:41 PM

==========================================================================================
Analysis Begun

Logged In Analyst: Administrator                 Technique: AA Flame
Spectrometer: AAnalyst 400, S/N 201S12010501     Autosampler:

Sample Information File: C:\Documents and Settings\All Users\PerkinElmer\AA\Data\Sample Information\
                         Cu161214Kelvin.sif
Batch ID:
Results Data Set: Cu161214Kelvin
Results Library: C:\Documents and Settings\All Users\PerkinElmer\AA\Data\Results\Results.mdb

==========================================================================================
Method Loaded
Method Name: Cu011214G4                          Method Last Saved: 12/1/2014 4:32:05 PM
Method Description: Cu011214G4

==========================================================================================
Sequence No.: 1                                  Autosampler Location:
Sample ID: 3pc P A                               Date Collected: 12/16/2014 2:58:08 PM
Analyst:                                         Data Type: Original

------------------------------------------------------------------------------------------
Replicate Data: 3pc P A                          Analyte: Cu 324.75
Repl    SampleConc    StndConc    BlnkCorr    Time          Signal
 #      mg/L          mg/L        Signal                    Stored
 1      0.947         0.947       0.130       2:58:09 PM      Yes
 2      0.943         0.943       0.130       2:58:13 PM      Yes
 3      0.966         0.966       0.133       2:58:18 PM      Yes
Mean:   0.952         0.952       0.131
SD:     0.0123        0.0123      0.0017
%RSD:   1.29%         1.29%       1.29

==========================================================================================
Sequence No.: 2                                  Autosampler Location:
Sample ID: 3pc P B                               Date Collected: 12/16/2014 2:58:37 PM
Analyst:                                         Data Type: Original

------------------------------------------------------------------------------------------
Replicate Data: 3pc P B                          Analyte: Cu 324.75
Repl    SampleConc    StndConc    BlnkCorr    Time          Signal
 #      mg/L          mg/L        Signal                    Stored
 1      0.746         0.746       0.103       2:58:37 PM      Yes
 2      0.735         0.735       0.101       2:58:42 PM      Yes
 3      0.746         0.746       0.103       2:58:46 PM      Yes
Mean:   0.742         0.742       0.102
SD:     0.0063        0.0063      0.0009
%RSD:   0.85%         0.85%       0.85

==========================================================================================
Sequence No.: 3                                  Autosampler Location:
Sample ID: 3pc R A                               Date Collected: 12/16/2014 2:59:07 PM
Analyst:                                         Data Type: Original

------------------------------------------------------------------------------------------
Replicate Data: 3pc R A                          Analyte: Cu 324.75
Repl    SampleConc    StndConc    BlnkCorr    Time          Signal
 #      mg/L          mg/L        Signal                    Stored
 1      1.032         1.032       0.142       2:59:09 PM      Yes
 2      1.040         1.040       0.143       2:59:13 PM      Yes
 3      1.048         1.048       0.144       2:59:17 PM      Yes
Mean:   1.040         1.040       0.143
SD:     0.0079        0.0079      0.0011
%RSD:   0.76%         0.76%       0.76

==========================================================================================
Sequence No.: 4                                  Autosampler Location:
Sample ID: 3pc R B                               Date Collected: 12/16/2014 2:59:36 PM
Analyst:                                         Data Type: Original
------------------------------------------------------------------------------------------
```

Cross Flow of 3% PVP Page 1



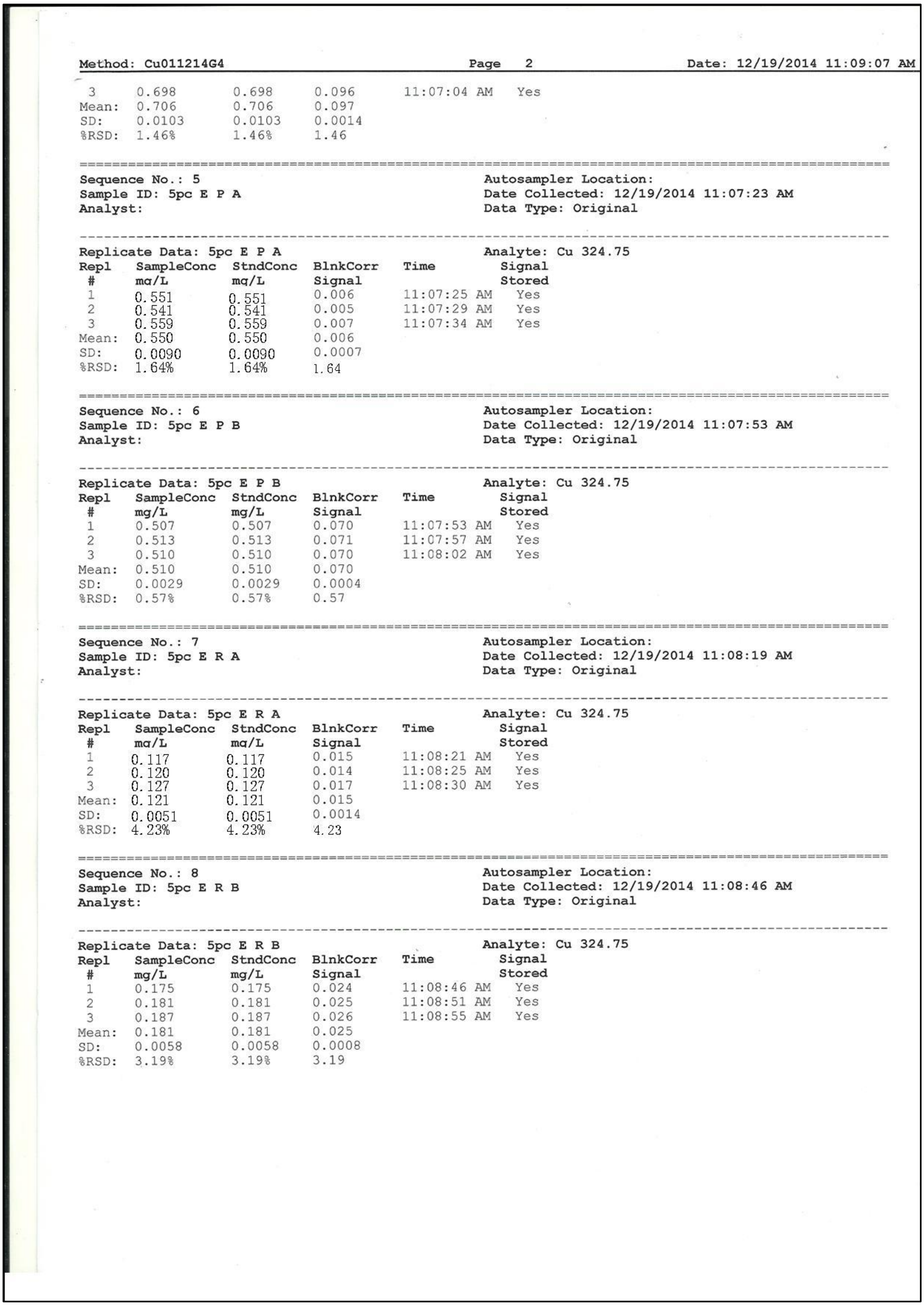
```
Method: Cu011214G4                              Page   2                    Date: 12/16/2014 3:01:44 PM

Replicate Data: 3pc R B                                       Analyte: Cu 324.75
Repl    SampleConc  StndConc  BlnkCorr    Time           Signal
 #      mg/L        mg/L      Signal                     Stored
 1      1.029       1.029     0.142       2:59:36 PM       Yes
 2      1.052       1.052     0.145       2:59:41 PM       Yes
 3      1.051       1.051     0.145       2:59:46 PM       Yes
Mean:   1.044       1.044     0.144
SD:     0.0134      0.0134    0.0018
%RSD:   1.29%       1.29%     1.29

=====================================================================================================
Sequence No.: 5                                               Autosampler Location:
Sample ID: 3pc E P A                                          Date Collected: 12/16/2014 3:00:05 PM
Analyst:                                                      Data Type: Original

-----------------------------------------------------------------------------------------------------
Replicate Data: 3pc E P A                                     Analyte: Cu 324.75
Repl    SampleConc  StndConc  BlnkCorr    Time           Signal
 #      mg/L        mg/L      Signal                     Stored
 1      1.167       1.167     0.161       3:00:07 PM       Yes
 2      1.170       1.170     0.161       3:00:11 PM       Yes
 3      1.183       1.183     0.163       3:00:15 PM       Yes
Mean:   1.173       1.173     0.162
SD:     0.0083      0.0083    0.0011
%RSD:   0.71%       0.71%     0.71

=====================================================================================================
Sequence No.: 6                                               Autosampler Location:
Sample ID: 3pc E P B                                          Date Collected: 12/16/2014 3:00:34 PM
Analyst:                                                      Data Type: Original

-----------------------------------------------------------------------------------------------------
Replicate Data: 3pc E P B                                     Analyte: Cu 324.75
Repl    SampleConc  StndConc  BlnkCorr    Time           Signal
 #      mg/L        mg/L      Signal                     Stored
 1      1.114       1.114     0.153       3:00:34 PM       Yes
 2      1.127       1.127     0.155       3:00:38 PM       Yes
 3      1.127       1.127     0.155       3:00:42 PM       Yes
Mean:   1.123       1.123     0.155
SD:     0.0075      0.0075    0.0010
%RSD:   0.67%       0.67%     0.67

=====================================================================================================
Sequence No.: 7                                               Autosampler Location:
Sample ID: 3pc E R A                                          Date Collected: 12/16/2014 3:01:02 PM
Analyst:                                                      Data Type: Original

-----------------------------------------------------------------------------------------------------
Replicate Data: 3pc E R A                                     Analyte: Cu 324.75
Repl    SampleConc  StndConc  BlnkCorr    Time           Signal
 #      mg/L        mg/L      Signal                     Stored
 1      0.432       0.432     0.059       3:01:04 PM       Yes
 2      0.427       0.427     0.059       3:01:08 PM       Yes
 3      0.426       0.426     0.059       3:01:12 PM       Yes
Mean:   0.428       0.428     0.059
SD:     0.0030      0.0030    0.0004
%RSD:   0.70%       0.70%     0.70

=====================================================================================================
Sequence No.: 8                                               Autosampler Location:
Sample ID: 3pc E R B                                          Date Collected: 12/16/2014 3:01:30 PM
Analyst:                                                      Data Type: Original

-----------------------------------------------------------------------------------------------------
Replicate Data: 3pc E R B                                     Analyte: Cu 324.75
Repl    SampleConc  StndConc  BlnkCorr    Time           Signal
 #      mg/L        mg/L      Signal                     Stored
 1      0.390       0.390     0.054       3:01:30 PM       Yes
 2      0.402       0.402     0.055       3:01:35 PM       Yes
 3      0.400       0.400     0.055       3:01:39 PM       Yes
Mean:   0.397       0.397     0.055
SD:     0.0066      0.0066    0.0009
```

Cross Flow of 3% PVP Page 2



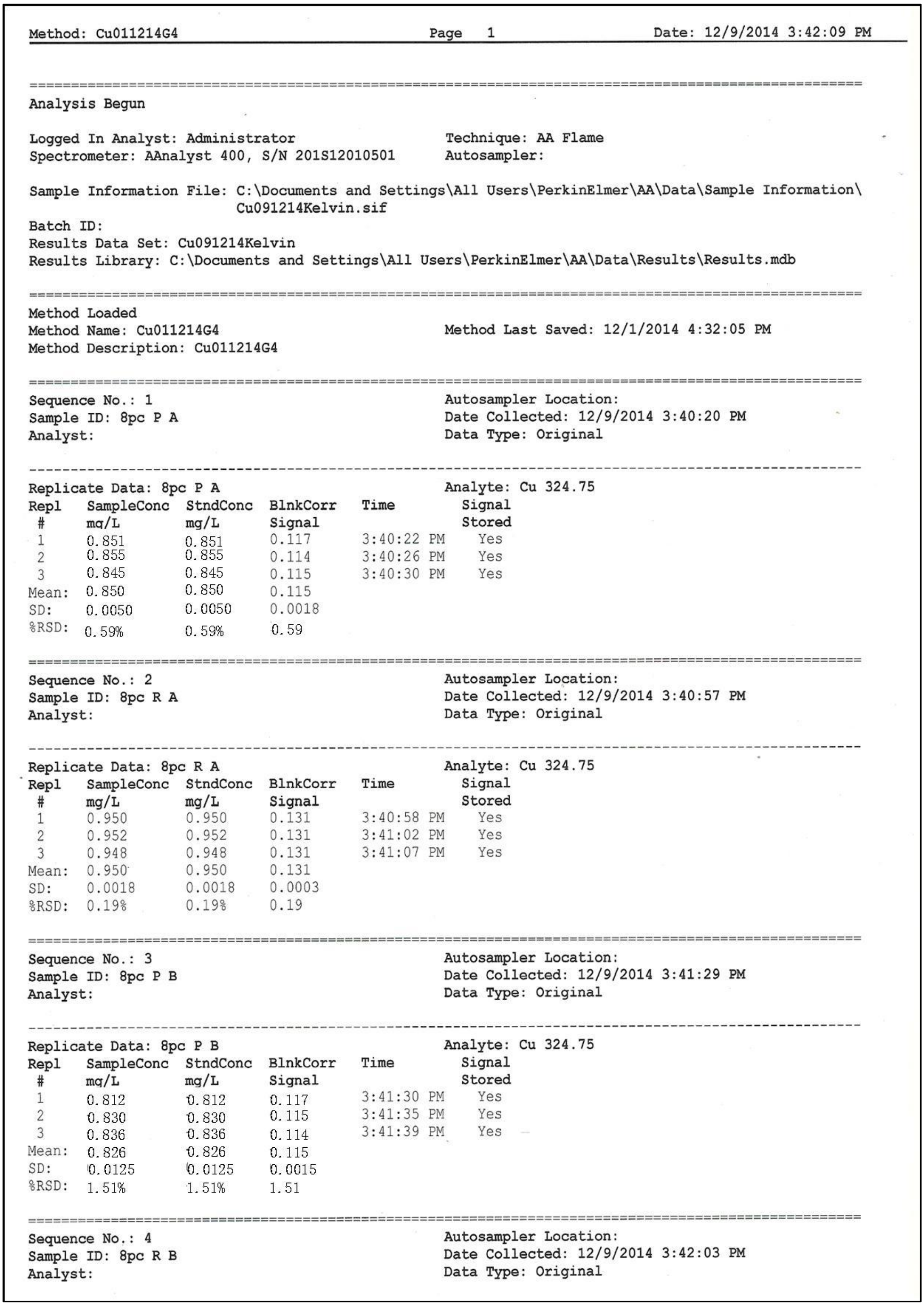
```
Method: Cu011214G4                          Page   1              Date: 12/19/2014 11:07:04 AM

============================================================================================
Analysis Begun

Logged In Analyst: Administrator                   Technique: AA Flame
Spectrometer: AAnalyst 400, S/N 201S12010501       Autosampler:

Sample Information File: C:\Documents and Settings\All Users\PerkinElmer\AA\Data\Sample Information\
                         Cu191214Kelvin2.sif
Batch ID:
Results Data Set: Cu191214Kelvin2
Results Library: C:\Documents and Settings\All Users\PerkinElmer\AA\Data\Results\Results.mdb

============================================================================================
Sequence No.: 1                                    Autosampler Location:
Sample ID: 5pc P A                                 Date Collected: 12/19/2014 11:05:08 AM
Analyst:                                           Data Type: Original

--------------------------------------------------------------------------------------------
Replicate Data: 5pc P A                            Analyte: Cu 324.75
Repl    SampleConc  StndConc  BlnkCorr   Time          Signal
 #      mg/L        mg/L      Signal                   Stored
 1      0.620       0.620     0.085      11:05:10 AM   Yes
 2      0.566       0.566     0.078      11:05:14 AM   Yes
 3      0.527       0.527     0.073      11:05:19 AM   Yes
Mean:   0.571       0.571     0.079
SD:     0.0465      0.0465    0.0064
%RSD:   8.15%       8.15%     8.15

============================================================================================
Sequence No.: 2                                    Autosampler Location:
Sample ID: 5pc P B                                 Date Collected: 12/19/2014 11:05:35 AM
Analyst:                                           Data Type: Original

--------------------------------------------------------------------------------------------
Replicate Data: 5pc P B                            Analyte: Cu 324.75
Repl    SampleConc  StndConc  BlnkCorr   Time          Signal
 #      mg/L        mg/L      Signal                   Stored
 1      0.696       0.696     0.096      11:05:35 AM   Yes
 2      0.721       0.721     0.099      11:05:40 AM   Yes
 3      0.733       0.733     0.101      11:05:44 AM   Yes
Mean:   0.717       0.717     0.099
SD:     0.0187      0.0187    0.0026
%RSD:   2.62%       2.62%     2.62

============================================================================================
Sequence No.: 3                                    Autosampler Location:
Sample ID: 5pc R A                                 Date Collected: 12/19/2014 11:06:28 AM
Analyst:                                           Data Type: Original

--------------------------------------------------------------------------------------------
Replicate Data: 5pc R A                            Analyte: Cu 324.75
Repl    SampleConc  StndConc  BlnkCorr   Time          Signal
 #      mg/L        mg/L      Signal                   Stored
 1      0.922       0.922     0.127      11:06:29 AM   Yes
 2      0.913       0.913     0.126      11:06:33 AM   Yes
 3      0.905       0.905     0.125      11:06:38 AM   Yes
Mean:   0.913       0.913     0.126
SD:     0.0086      0.0086    0.0012
%RSD:   0.94%       0.94%     0.94

============================================================================================
Sequence No.: 4                                    Autosampler Location:
Sample ID: 5pc R B                                 Date Collected: 12/19/2014 11:06:56 AM
Analyst:                                           Data Type: Original

--------------------------------------------------------------------------------------------
Replicate Data: 5pc R B                            Analyte: Cu 324.75
Repl    SampleConc  StndConc  BlnkCorr   Time          Signal
 #      mg/L        mg/L      Signal                   Stored
 1      0.703       0.703     0.097      11:06:56 AM   Yes
 2      0.718       0.718     0.099      11:07:00 AM   Yes
```

Cross Flow of 5% PVP Page 1



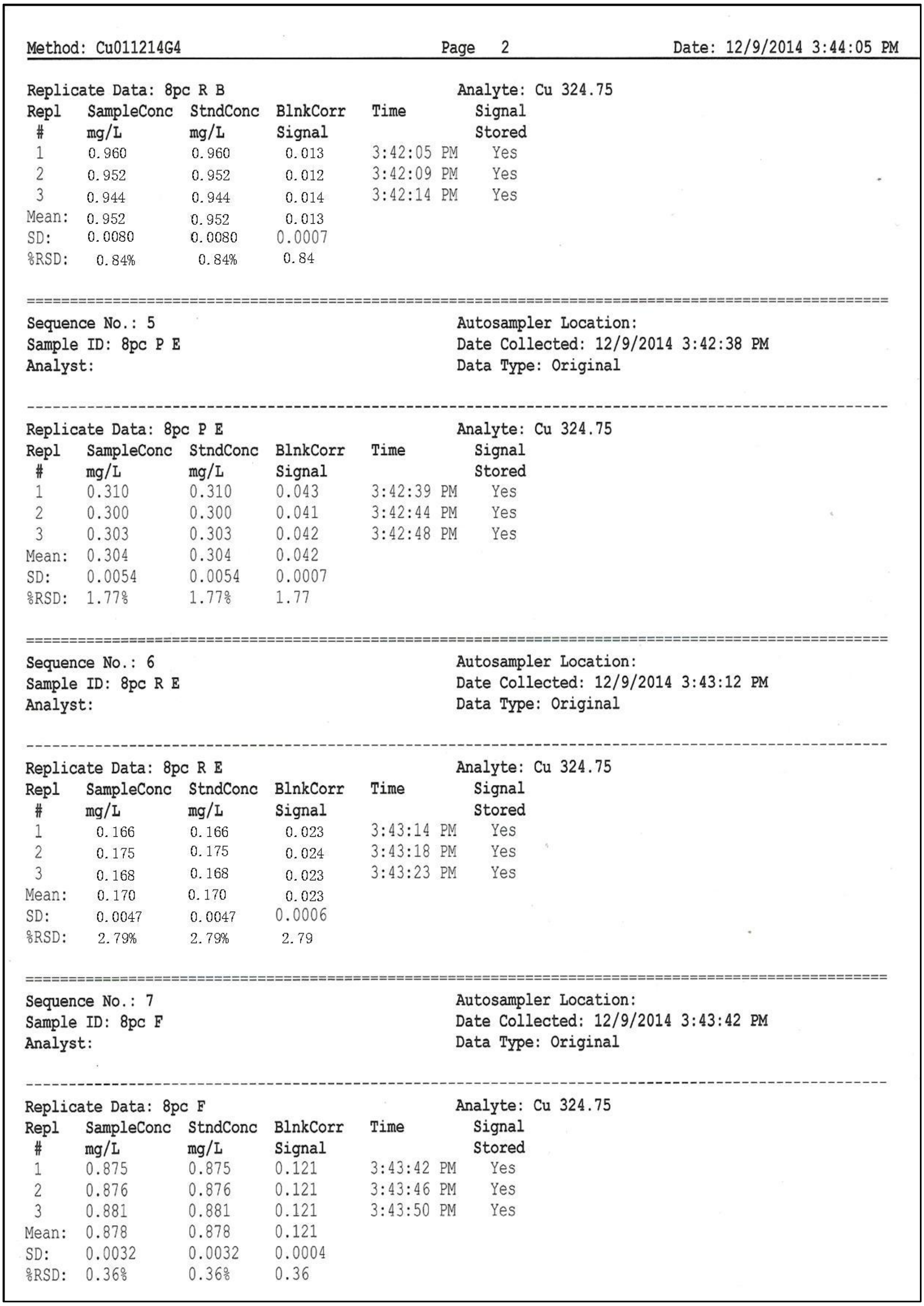
```
Method: Cu011214G4                             Page   2                 Date: 12/19/2014 11:09:07 AM
  3     0.698        0.698       0.096       11:07:04 AM   Yes
Mean:   0.706        0.706       0.097
SD:     0.0103       0.0103      0.0014
%RSD:   1.46%        1.46%       1.46

==================================================================================================
Sequence No.: 5                                        Autosampler Location:
Sample ID: 5pc E P A                                   Date Collected: 12/19/2014 11:07:23 AM
Analyst:                                               Data Type: Original

--------------------------------------------------------------------------------------------------
Replicate Data: 5pc E P A                              Analyte: Cu 324.75
Repl    SampleConc   StndConc    BlnkCorr    Time          Signal
 #      mg/L         mg/L        Signal                    Stored
 1      0.551        0.551       0.006       11:07:25 AM   Yes
 2      0.541        0.541       0.005       11:07:29 AM   Yes
 3      0.559        0.559       0.007       11:07:34 AM   Yes
Mean:   0.550        0.550       0.006
SD:     0.0090       0.0090      0.0007
%RSD:   1.64%        1.64%       1.64

==================================================================================================
Sequence No.: 6                                        Autosampler Location:
Sample ID: 5pc E P B                                   Date Collected: 12/19/2014 11:07:53 AM
Analyst:                                               Data Type: Original

--------------------------------------------------------------------------------------------------
Replicate Data: 5pc E P B                              Analyte: Cu 324.75
Repl    SampleConc   StndConc    BlnkCorr    Time          Signal
 #      mg/L         mg/L        Signal                    Stored
 1      0.507        0.507       0.070       11:07:53 AM   Yes
 2      0.513        0.513       0.071       11:07:57 AM   Yes
 3      0.510        0.510       0.070       11:08:02 AM   Yes
Mean:   0.510        0.510       0.070
SD:     0.0029       0.0029      0.0004
%RSD:   0.57%        0.57%       0.57

==================================================================================================
Sequence No.: 7                                        Autosampler Location:
Sample ID: 5pc E R A                                   Date Collected: 12/19/2014 11:08:19 AM
Analyst:                                               Data Type: Original

--------------------------------------------------------------------------------------------------
Replicate Data: 5pc E R A                              Analyte: Cu 324.75
Repl    SampleConc   StndConc    BlnkCorr    Time          Signal
 #      mg/L         mg/L        Signal                    Stored
 1      0.117        0.117       0.015       11:08:21 AM   Yes
 2      0.120        0.120       0.014       11:08:25 AM   Yes
 3      0.127        0.127       0.017       11:08:30 AM   Yes
Mean:   0.121        0.121       0.015
SD:     0.0051       0.0051      0.0014
%RSD:   4.23%        4.23%       4.23

==================================================================================================
Sequence No.: 8                                        Autosampler Location:
Sample ID: 5pc E R B                                   Date Collected: 12/19/2014 11:08:46 AM
Analyst:                                               Data Type: Original

--------------------------------------------------------------------------------------------------
Replicate Data: 5pc E R B                              Analyte: Cu 324.75
Repl    SampleConc   StndConc    BlnkCorr    Time          Signal
 #      mg/L         mg/L        Signal                    Stored
 1      0.175        0.175       0.024       11:08:46 AM   Yes
 2      0.181        0.181       0.025       11:08:51 AM   Yes
 3      0.187        0.187       0.026       11:08:55 AM   Yes
Mean:   0.181        0.181       0.025
SD:     0.0058       0.0058      0.0008
%RSD:   3.19%        3.19%       3.19
```

Cross Flow of 5% PVP Page 2



```
Method: Cu011214G4                                Page   1                 Date: 12/9/2014 3:42:09 PM

==========================================================================================
Analysis Begun

Logged In Analyst: Administrator                         Technique: AA Flame
Spectrometer: AAnalyst 400, S/N 201S12010501             Autosampler:

Sample Information File: C:\Documents and Settings\All Users\PerkinElmer\AA\Data\Sample Information\
                         Cu091214Kelvin.sif
Batch ID:
Results Data Set: Cu091214Kelvin
Results Library: C:\Documents and Settings\All Users\PerkinElmer\AA\Data\Results\Results.mdb

==========================================================================================
Method Loaded
Method Name: Cu011214G4                                  Method Last Saved: 12/1/2014 4:32:05 PM
Method Description: Cu011214G4

==========================================================================================
Sequence No.: 1                                          Autosampler Location:
Sample ID: 8pc P A                                       Date Collected: 12/9/2014 3:40:20 PM
Analyst:                                                 Data Type: Original

------------------------------------------------------------------------------------------
Replicate Data: 8pc P A                                  Analyte: Cu 324.75
Repl   SampleConc  StndConc  BlnkCorr   Time         Signal
 #     mg/L        mg/L      Signal                  Stored
 1     0.851       0.851     0.117      3:40:22 PM    Yes
 2     0.855       0.855     0.114      3:40:26 PM    Yes
 3     0.845       0.845     0.115      3:40:30 PM    Yes
Mean:  0.850       0.850     0.115
SD:    0.0050      0.0050    0.0018
%RSD:  0.59%       0.59%     0.59

==========================================================================================
Sequence No.: 2                                          Autosampler Location:
Sample ID: 8pc R A                                       Date Collected: 12/9/2014 3:40:57 PM
Analyst:                                                 Data Type: Original

------------------------------------------------------------------------------------------
Replicate Data: 8pc R A                                  Analyte: Cu 324.75
Repl   SampleConc  StndConc  BlnkCorr   Time         Signal
 #     mg/L        mg/L      Signal                  Stored
 1     0.950       0.950     0.131      3:40:58 PM    Yes
 2     0.952       0.952     0.131      3:41:02 PM    Yes
 3     0.948       0.948     0.131      3:41:07 PM    Yes
Mean:  0.950       0.950     0.131
SD:    0.0018      0.0018    0.0003
%RSD:  0.19%       0.19%     0.19

==========================================================================================
Sequence No.: 3                                          Autosampler Location:
Sample ID: 8pc P B                                       Date Collected: 12/9/2014 3:41:29 PM
Analyst:                                                 Data Type: Original

------------------------------------------------------------------------------------------
Replicate Data: 8pc P B                                  Analyte: Cu 324.75
Repl   SampleConc  StndConc  BlnkCorr   Time         Signal
 #     mg/L        mg/L      Signal                  Stored
 1     0.812       0.812     0.117      3:41:30 PM    Yes
 2     0.830       0.830     0.115      3:41:35 PM    Yes
 3     0.836       0.836     0.114      3:41:39 PM    Yes
Mean:  0.826       0.826     0.115
SD:    0.0125      0.0125    0.0015
%RSD:  1.51%       1.51%     1.51

==========================================================================================
Sequence No.: 4                                          Autosampler Location:
Sample ID: 8pc R B                                       Date Collected: 12/9/2014 3:42:03 PM
Analyst:                                                 Data Type: Original
```

Cross Flow of 8% PVP Page 1



```
Method: Cu011214G4                              Page   2              Date: 12/9/2014 3:44:05 PM

Replicate Data: 8pc R B                                Analyte: Cu 324.75
Repl    SampleConc  StndConc  BlnkCorr   Time          Signal
 #      mg/L        mg/L      Signal                   Stored
 1      0.960       0.960     0.013      3:42:05 PM     Yes
 2      0.952       0.952     0.012      3:42:09 PM     Yes
 3      0.944       0.944     0.014      3:42:14 PM     Yes
Mean:   0.952       0.952     0.013
SD:     0.0080      0.0080    0.0007
%RSD:   0.84%       0.84%     0.84

=============================================================================================
Sequence No.: 5                                        Autosampler Location:
Sample ID: 8pc P E                                     Date Collected: 12/9/2014 3:42:38 PM
Analyst:                                               Data Type: Original

---------------------------------------------------------------------------------------------
Replicate Data: 8pc P E                                Analyte: Cu 324.75
Repl    SampleConc  StndConc  BlnkCorr   Time          Signal
 #      mg/L        mg/L      Signal                   Stored
 1      0.310       0.310     0.043      3:42:39 PM     Yes
 2      0.300       0.300     0.041      3:42:44 PM     Yes
 3      0.303       0.303     0.042      3:42:48 PM     Yes
Mean:   0.304       0.304     0.042
SD:     0.0054      0.0054    0.0007
%RSD:   1.77%       1.77%     1.77

=============================================================================================
Sequence No.: 6                                        Autosampler Location:
Sample ID: 8pc R E                                     Date Collected: 12/9/2014 3:43:12 PM
Analyst:                                               Data Type: Original

---------------------------------------------------------------------------------------------
Replicate Data: 8pc R E                                Analyte: Cu 324.75
Repl    SampleConc  StndConc  BlnkCorr   Time          Signal
 #      mg/L        mg/L      Signal                   Stored
 1      0.166       0.166     0.023      3:43:14 PM     Yes
 2      0.175       0.175     0.024      3:43:18 PM     Yes
 3      0.168       0.168     0.023      3:43:23 PM     Yes
Mean:   0.170       0.170     0.023
SD:     0.0047      0.0047    0.0006
%RSD:   2.79%       2.79%     2.79

=============================================================================================
Sequence No.: 7                                        Autosampler Location:
Sample ID: 8pc F                                       Date Collected: 12/9/2014 3:43:42 PM
Analyst:                                               Data Type: Original

---------------------------------------------------------------------------------------------
Replicate Data: 8pc F                                  Analyte: Cu 324.75
Repl    SampleConc  StndConc  BlnkCorr   Time          Signal
 #      mg/L        mg/L      Signal                   Stored
 1      0.875       0.875     0.121      3:43:42 PM     Yes
 2      0.876       0.876     0.121      3:43:46 PM     Yes
 3      0.881       0.881     0.121      3:43:50 PM     Yes
Mean:   0.878       0.878     0.121
SD:     0.0032      0.0032    0.0004
%RSD:   0.36%       0.36%     0.36
```

Cross Flow of 8% PVP Page 2

A.4 Pure Water Permeability

A=πDLn
Diameter is obtained from the SEM images

0wt% PVP

D	0.0013	m
A	0.12257	m
Q	1	mL/min
	0.06	L/h
PWP	4.8591	L/m^2.h.bar

3wt% PVP

D	0.001692	m
A	0.015956	m
Q	1.4	mL/min
	0.084	L/h
PWP	5.2645	L/m^2.h.bar

5wt% PVP

D	0.00135	m
A	0.012729	m
Q	1.6	mL/min
	0.096	L/h
PWP	7.5421	L/m^2.h.bar

8wt% PVP

D	0.001111	m
A	0.010476	m
Q	1.5	mL/min
	0.09	L/h
PWP	8.5909	L/m^2.h.bar

A.5 Cross Flow Processed Data

CROSSFLOW FILTRATION EXPERIMENT	
Feed,	**Run1 Membrane 0wt% PVP**
Vol,ml	500
Conc, mg/L	1000
Mass, mg	500
Retentate	
Vol,ml	458
Dil Factor	500
AAS Conc	0.959
Conc, mg/L	479.5
Mass, mg	219.611
Permeate	
Time, min	29
Vol,ml	42
Dil Factor	500
AAS Conc	0.750
Conc, mg/L	375
Mass, mg	15.75
Copper Bound, mg	**264.639**
Elution	250
Time. Min	30
Permeate Side	
Vol,ml	75
Dil Factor	500
AAS Conc	1
Conc, mg/L	250
Mass, mg	18.75
Retentate Side	
Vol,ml	175
Dil Factor	500
AAS Conc	0.369
Conc, mg/L	184.5
Mass, mg	32.2875
Total Eluted	**51.0375**
Elution Recovery	**19.3%**

CROSSFLOW FILTRATION EXPERIMENT	
Feed,	**Run 2 Membrane 0wt% PVP**
Vol,ml	500
Conc, mg/L	1000
Mass, mg	500
Retentate	
Vol,ml	455
Dil Factor	500
AAS Conc	0.966
Conc, mg/L	483
Mass, mg	219.765
Permeate	
Time, min	30
Vol,ml	45
Dil Factor	500
AAS Conc	0.881
Conc, mg/L	440.5
Mass, mg	19.8225
Copper Bound, mg	**260.4125**
Elution	250
Time. Min	30
Permeate Side	
Vol,ml	72
Dil Factor	500
AAS Conc	0.823
Conc, mg/L	411.5
Mass, mg	29.628
Retentate Side	
Vol,ml	178
Dil Factor	500
AAS Conc	0.274
Conc, mg/L	137
Mass, mg	24.386
Total Eluted	**54.014**
Elution Recovery	**20.7%**

CROSSFLOW FILTRATION EXPERIMENT	
Feed,	**Run 1 Membrane 3wt% PVP**
Vol,ml	500
Conc, mg/L	1000
Mass, mg	500
Retentate	
Vol,ml	466
Dil Factor	500
AAS Conc	1.04
Conc, mg/L	520
Mass, mg	242.32
Permeate	
Time, min	30
Vol,ml	34
Dil Factor	500
AAS Conc	0.952
Conc, mg/L	476
Mass, mg	16.184
Copper Bound, mg	**241.496**
Elution	250
Time. Min	30
Permeate Side	
Vol,ml	60
Dil Factor	500
AAS Conc	1.173
Conc, mg/L	586.5
Mass, mg	35.19
Retentate Side	
Vol,ml	190
Dil Factor	500
AAS Conc	0.428
Conc, mg/L	214
Mass, mg	40.66
Total Eluted	**75.85**
Elution Recovery	**31.4%**
CROSSFLOW FILTRATION	

EXPERIMENT	
Feed,	**Run 2 Membrane 3wt% PVP**
Vol,ml	500
Conc, mg/L	1000
Mass, mg	500
Retentate	
Vol,ml	469
Dil Factor	500
AAS Conc	1.044
Conc, mg/L	522
Mass, mg	244.818
Permeate	
Time, min	30
Vol,ml	31
Dil Factor	500
AAS Conc	0.742
Conc, mg/L	371
Mass, mg	11.501
Copper Bound, mg	**243.681**
Elution	250
Time. Min	30
Permeate Side	
Vol,ml	58
Dil Factor	500
AAS Conc	1.123
Conc, mg/L	561.5
Mass, mg	32.567
Retentate Side	
Vol,ml	192
Dil Factor	500
AAS Conc	0.397
Conc, mg/L	198.5
Mass, mg	38.112
Total Eluted	**70.679**
Elution Recovery	**29.0%**

CROSSFLOW FILTRATION EXPERIMENT	
Feed,	**Run 1 Membrane 5wt% PVP**
Vol,ml	500
Conc, mg/L	1000
Mass, mg	500
Retentate	
Vol,ml	460
Dil Factor	500
AAS Conc	0.913
Conc, mg/L	456.5
Mass, mg	209.99
Permeate	
Time, min	30
Vol,ml	40
Dil Factor	500
AAS Conc	0.571
Conc, mg/L	285.5
Mass, mg	11.42
Copper Bound, mg	**278.59**
Elution	250
Time. Min	30
Permeate Side	
Vol,ml	61
Dil Factor	500
AAS Conc	0.55
Conc, mg/L	275
Mass, mg	16.775
Retentate Side	
Vol,ml	189
Dil Factor	500
AAS Conc	0.121
Conc, mg/L	60.5
Mass, mg	11.4345
Total Eluted	**28.2095**
Elution Recovery	**10.1%**

CROSSFLOW FILTRATION EXPERIMENT

Feed,	**Run 2 Membrane 5wt% PVP**
Vol,ml	500
Conc, mg/L	1000
Mass, mg	500
Retentate	
Vol,ml	458
Dil Factor	500
AAS Conc	0.706
Conc, mg/L	353
Mass, mg	161.674
Permeate	
Time, min	30
Vol,ml	42
Dil Factor	500
AAS Conc	0.717
Conc, mg/L	358.5
Mass, mg	15.057
Copper Bound, mg	**323.269**
Elution	250
Time. Min	30
Permeate Side	
Vol,ml	60
Dil Factor	500
AAS Conc	0.51
Conc, mg/L	255
Mass, mg	15.3
Retentate Side	
Vol,ml	190
Dil Factor	500
AAS Conc	0.181
Conc, mg/L	90.5
Mass, mg	17.195
Total Eluted	**32.495**
Elution Recovery	**10.1%**

CROSSFLOW FILTRATION EXPERIMENT	
Feed,	**Run 1 Membrane 8wt% PVP**
Vol,ml	500
Conc, mg/L	1000
Mass, mg	500
Retentate	
Vol,ml	457
Dil Factor	500
AAS Conc	0.95
Conc, mg/L	475
Mass, mg	217.075
Permeate	
Time, min	30
Vol,ml	43
Dil Factor	500
AAS Conc	0.85
Conc, mg/L	425
Mass, mg	18.275
Copper Bound, mg	**264.65**
Elution	250
Time. Min	30
Permeate Side	
Vol,ml	53
Dil Factor	500
AAS Conc	0.303
Conc, mg/L	151.5
Mass, mg	8.0295
Retentate Side	
Vol,ml	197
Dil Factor	500
AAS Conc	0.17
Conc, mg/L	85
Mass, mg	16.745
Total Eluted	**24.7745**
Elution Recovery	**9.4%**

CROSSFLOW FILTRATION EXPERIMENT	
Feed,	**Run 2 Membrane 8wt% PVP**
Vol,ml	500
Conc, mg/L	1000
Mass, mg	500
Retentante	
Vol,ml	456
Dil Factor	500
AAS Conc	0.826
Conc, mg/L	413
Mass, mg	188.328
Permeate	
Time, min	30
Vol,ml	44
Dil Factor	500
AAS Conc	0.952
Conc, mg/L	476
Mass, mg	20.944
Copper Bound, mg	**290.728**
Elution	250
Time. Min	30
Permeat Side	
Vol,ml	48
Dil Factor	500
AAS Conc	0.878
Conc, mg/L	439
Mass, mg	21.072
Retentate Side	
Vol,ml	202
Dil Factor	500
AAS Conc	0.166
Conc, mg/L	83
Mass, mg	16.766
Total Eluted	**37.838**
Elution Recovery	**13.0%**