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The determination of Distribution Coefficient for some elements on the macroporous cation exchanger Amberlyst 15 using nitric acid – methanol mixtures

by

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DECLARATION

I, Elizabeth Nontombi Mabakane, declare that the contents of this dissertation/thesis represent my own unaided work, and that the dissertation/thesis has not previously been submitted for academic examination towards any qualification. Furthermore, it represents my own opinions and not necessarily those of the Cape Peninsula University of Technology.

01 December 2015

Signed   **Date**

ABSTRACT

The main purpose of this study is to understand the application of ion exchange chromatography on separation of charged ions of elements. Ion exchange chromatography is an analytical method, which is used for the separation of elements, quantitation and qualitation. The use of Amberlyst 15 resin as a source of separation for metal ions has been investigated and studies in various academic disciplines such as chemistry and material science. In this research study, Amberlyst 15 resin was investigated in order to understand the separation of positively charged divalent elements ions (Zn^{2+}, Cu^{2+}, Co^{2+} and Ni^{2+}). The use of nitric acid and methanol mixture enhanced separation of these metal ions by ensuring that nitric acid is constant and varying methanol concentration. In this study, it was found that the resin has a high affinity for the metal ions at high methanol concentration, hence the distribution coefficient values increase but decreases at low methanol concentrations.

The complexities of molecular structure of the salts of the elements provide the more understanding of the metal ion interaction with the resin particle. Furthermore, the role and strength of nitric acid to break the structural bonds and release the metal ions to get sorbed on the resin remains the most essential factor of understanding distribution coefficient values. Method validation parameters such as linearity, precision and accuracy of the method were determined. The method precision and accuracy were determined from the QC samples which is expressed as relative error (%RE) with the total coefficient of variation (%CV's) were < 20%.

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GLOSSARY

Abbreviations	Definition
HNO_3	Nitric Acid
ICP-OES	Inductively Coupled Plasma - Optical Emission Spectrometry
K_d	Distribution coefficient
Ni	Nickel
Cu	Copper
Zn	Zinc
Co	Cobalt
HPIC	High Performance Ion Chromatography
H^+	Hydrogen Ion
g	Grams
mL	Millilitre
M	Moles
PC	Personal Computer
SO_3^-	Sulphite ion
^0C	Degrees Celsius
pH	-log[hydrogen]
mg/L	Milligrams per litre
mL/g	Millilitre per gram
CV	Coefficient of variation
N\A	Not applicable
Zn^{2+}	Zinc ion
Cu^{2+}	Copper ion
Co^{2+}	Cobalt ion
Ni^{2+}	Nickel ion
HPLC	High Pressure Liquid Chromatography
$Cu(NO_3)_2.3H_2O$	Copper (ll) nitrate trihydrate
$Zn(NO_3)_2.6H_2O$	Zinc Nitrate Hexahydrate
$Co(NO_3)_2.6H_2O$	Cobalt (ll) nitrate hexahydrate
$Ni(NO_3)_3.6H_20$	Nickel (ll) nitrate hexahydrate
ppm	parts per million
RSD	Relative standard deviation
Soln	Solution
No	Number
W	Watt
L/mL	Litre/millilitre
RE	Relative error
%	Percentage
nm	Nanometre
µL	Microlitre
QC	Quality Control

CHAPTER 1: INTRODUCTION

1.1 Introduction

The study is based on the determination of equilibrium distribution coefficients for some elements using classic ion exchange chromatography. Classic ion exchange chromatography is the process used to separate ions. The ions separate on the resin, which contains a stationary phase, which allows separation of ions to take place. The separation of ions on the resin depends on the counter-ion of the resin, the pH of the aqueous solution, the concentration of the counterion and selectivity of the resin for different ions. Counterions form part of the functional groups that are on the resin, to provide ionic sites. The ionic sites include cation and anion types (Haddad & Jackson, 1990:4-150).

Resin containing cationic sites exchanges anions and is referred to as anion exchange chromatography. Resin with anionic sites exchange with cations and this process is referred to as cation exchange chromatography (Haddad & Jackson, 1990:4-150). The functional group, which provides counter-ions, differ according to their acid/base strengths. These groups are categorised as weak and strong functional groups exchangers. The weak exchangers can be used over the pH range greater than six and strong exchangers can be used over the pH range less than eight and in strong acid concentrations (Haddad & Jackson, 1990:4-150).

Ion exchange chromatography principle focuses on the interaction between charged ionic groups in the sample molecule and the functional molecules on the resin, which have the opposite charge. Separation is caused by different charged sample particles that require different concentrations of separating solution to displace them from the resin (Haddad & Jackson, 1990:4-150).

Ion exchange chromatography is applied in various areas, for example; mineral processing is the dominating area for application of ion exchange chromatography or separation of elements in mining ores and nuclear institutions (Dyer et al., 1993:442: Harland, 1994). Heavy metals arising from mining wastes and industrial discharges contaminate natural waters. The exposure to the contaminants can be harmful to human health (Badaway et al., 2009).

1.2 Problem Statement

Previous studies have shown distribution coefficients for a number of elements that were presented as curves that allow only an approximate estimation of the actual values of the distribution coefficients (Strelow & Van der Walt, 1982). Actual values of distribution coefficient were determined by Strelow and Van der Walt and these values are more useful to determine the separation factor, showing whether a separation of certain elements is possible under certain conditions (Strelow & Van der Walt, 1982).

Less research on the determination of distribution coefficients with Amberlyst 15 cation exchanger has been conducted in the field of ion exchange chromatography. Amberlyst 15 is an organic cation exchange resin that has good stability in strong acids and organic solvents, as well as in a high radioactive environment (Dumont and Fritz; 1995). More research work on the macroporous Amberlyst 15 needs to be conducted in order to explore the usefulness of the cation exchanger.

1.3 Objectives

The objective of the study is to experimentally determine the distribution coefficients values of transition elements. The separation behaviour of representative elements will be studied on the macroporous Amberlyst 15 cation exchanger. The chemical structure of Amberlyst 15 has sulfonic acid functional groups that are bound to the styrene

divinylbenzene copolymer matrix, commonly referred to as a strong acid cation exchanger. Amberlyst 15 resin has proved to be highly versatile and selective for separation of elements, giving reproducible results (Kunin et al., 1962).

The main aim of the study is to focus on the behaviour of the elements in various nitric acid concentrations (0.1, 0.2, 0.5, 1.0, 2.0, 3.0 and 4.0 M nitric acid) and different methanol concentrations (10, 20, etc. % methanol) using the macroporous Amberlyst 15 cation exchanger.

The new study will be compared to the studies conducted by Strelow (Strelow, 1960).

1.4 Research Design

Ion exchange chromatographic principles will be used for the separation of elements, which will be selected, from the transition metal group of the periodic table. The aqueous mixture of the elements will then be separated using a column containing Amberlyst 15 cation exchange resin. The eluent solution will be applied at different nitric acid and methanol concentrations for the separation of the elements.

1.5 Research Methodology

Nitric acid and methanol mixtures will be used as eluents for separation of metal ions on Amberlyst 15 cation exchange resin. Quality control samples and standards will be freshly prepared for different elements and will be separated on the resin. The eluent strength depends on the acidity, pH or alkalinity to allow sorption or desorption of the elements on the resin, within this the reagent acidity, pH or alkalinity is adjusted to improve sorption and desorption of elements that are retained. The cation exchange resin attraction towards metallic ions can be modified by solution reagent pH, acidity, and alkalinity. (Haddad & Jackson, 1990:4-150).

The Inductively Coupled Plasma instrument will quantitatively determine the elements concentration. The instrument have several benefits, which include lower inter-element interference due to the use of higher temperatures. Multi-element analysis can be done for very small samples and the determination of low concentrations of elements that are highly resistant to decomposition by lower heat temperatures (Yin et al., 2005). The method results will be validated to ensure results integrity by using analytical validation parameters.

The distribution coefficient values will be determined and elution curve experiments will be done for the elements eluted on the macroporous Amberlyst 15 resin. The curves will give experimental conditions for the separation of the elements. Distribution coefficients are determined by using the formula below (Strelow, 1984).

K_d = [mass (g) of the element sorbed on the resin] X [the volume (mL) of the solution]
      [Mass (g) of the element dissolved in the solution) X [mass (g) of the resin]

Equation 1:1 (Adapted from Strelow, 1984)

Elution curves of metal ions will be constructed for different experimental conditions to outline the separation of the element ions in a mixture. The distribution coefficient that is the fundamental base in ion exchange separation will be determined and the values will determine how well the metal ions are retained by the ion exchanger or whether it is not retained by the ion exchanger (Van der Walt & Coetzee: 1996).

Improvement of metal ion separation and chemical modification of the functional group will also be considered. Within this, sorption of elements on the cation exchanger and exchange potential of different ions with respect to the resin will be studied. Statistical method validation will be used to assess whether the method chosen is reproducible and accurate. Figure 1.1 shows a summary of experimental procedure.

Purification of Amberlyst 15 cation exchange resin

↓

Preparation of chemical reagents and samples.solutions.

↓

Sorption and elution behaviour of metal ions on the ion exchange column.

↓

Determination of metal ions concentrations by ICP-OES.

↓

Calculation, validation and interpretation of results
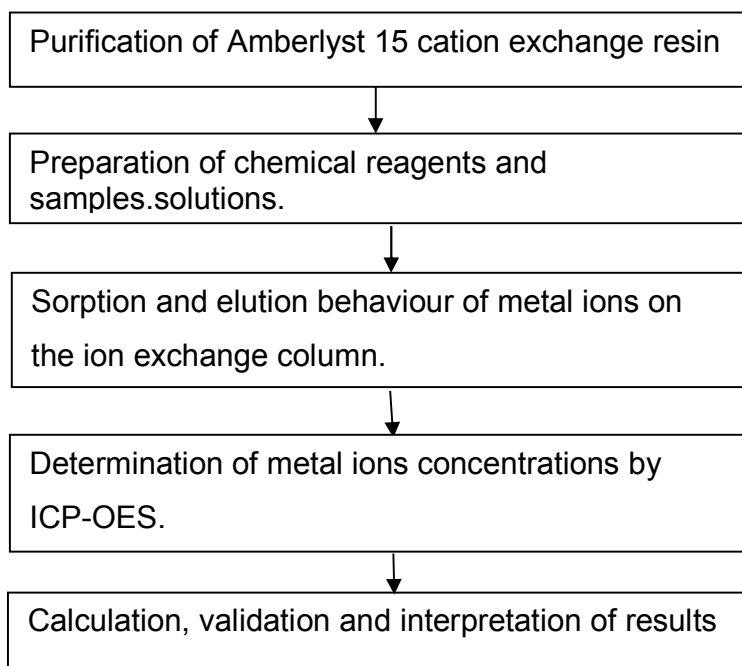
Figure 1.1: Steps to be followed during experimental work

CHAPTER 2: BACKGROUND

The chapter presents the application of ion exchange chromatography in different fields, the types of resins used for separation of metal ions, the separation process of metal ions, the influence of separation solution on metal ions and the resin, the evolution of inductively coupled plasma and the role of distribution coefficients in ion exchange chromatography.

2.1 Application of ion exchange chromatography

The development of ion exchange chromatography has benefitted many different industries. The technique has shown to be a suitable method for separation of radioactive alkali metals and alkali earth metals from liquid streams in nuclear institutions (Chakraborty and Chattopadhyay, 2012; Van der Walt and Coetzee, 1996). Factors such as stability and separation selectivity contributed to the success of ion exchange chromatography (Bader, 2001).The development of high performance ion chromatography (HPIC) made it possible for the separation of transition metal ions from nuclear fuels (Gautier et al., 2011). Quantitative recovery and separation of actinide radionuclides from radioactive waste was achievable by using ion exchange resins (Thakur and Mulholland, 2012).

Ion exchange chromatography has gained major application in the field of water treatment processes. Different studies have recognized its applicability, which includes water softening and wastewater treatment (Alexandratos, 2009). Combination of ion chromatography with membrane technology has created an improvement of the reverse osmosis process for water purification. Ion exchange showed good removal for salts, brine and removal of anions such as sulfate and nitrate, which contributed in production of fresh water (Barakat and Ismat-Shan, 2010).

The combustion of fossil fuels, mining excavations and urban habitation create atmospheric contamination. Application of ion exchange chromatography made it possible for separation of pollutants due to its high stable technique (Shaw and Haddad, 2004). Metal contamination in seawater can be bio-accumulated and bio-magnified through the food chain and finally reach humans who are fish consumers resulting in health risks. Ion chromatography seems to be the best method for metal ion removal due to the high rate of sorption (Wei et al., 2010).

Purification of proteins in the pharmaceutical industry has been a challenging task over the years due to similarities between the impurities and desired proteins. Ion exchange chromatography has overcome the challenge by using separation solutions with different concentration strengths for sorption and separate the proteins from interferences of impurities (Guelat et al., 2010).

In recent years ion exchange chromatography has gained popularity in the food industry, specifically in food production mainly for protein purification, decolourizationn of sugar and sugar solutions, the softening of whey, pectin and gelatine solutions.The desalination of sorbitol, hydrolysed starch and citric acid for production of food colorants as well as for the stabilization of liquid foods such as fruit juice, wine and beer by removing compounds which may cause haze formation upon storage (Kammerer et al., 2010; Omana et al., 2010).

In the agricultural industry ion exchange chromatography, in the form of ion exchange membrane chromatography, is used to purify and concentrate insect viruses that are used in vaccine clinical development. The membrane allows efficient interaction between the virus and charged ionic group on membrane surface, the interaction creates enough virus purification and concentration (Grein et al., 2012).

2.2 Ion Exchange Resins

2.2.1 Background

In ion exchange chromatography, the separation of ions takes place on the resin that contains a charged functional group. The resin is a synthetic organic polymer that has a bead shape. Most ion exchange resins are prepared by chemical reaction that is based on cross linked polystyrene divinylbenzene copolymers containing ion exchanging functional groups. These cross linked resins have a macroporous structure as shown in Figure 2.1. A macroporous refers to the reaction between the styrene and divinylbenzene in the presence of water. Resins with higher cross linkage are referred to as macroreticular resins. The porosity affects some of resin properties such as swelling, capacity, selectivity and equilibrium rate. The pores allows solution reagent to pass through. Resin classification contains two main groups, which is cation exchange and anion exchange resin as shown in Figure 2.2 and Figure 2.3. Each differ by a functional group, X and ionic charge present, Y (Toteja, 1997; Barbaro and Liguori, 2009; Corain et al., 2010).
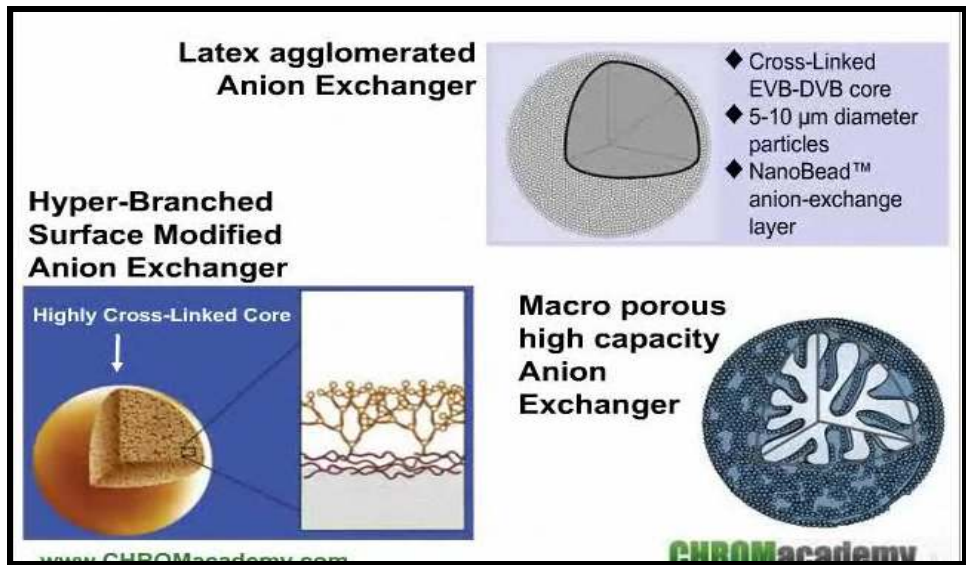
Figure 2.1: Spectroscopic structure of different resins (Taylor and Cook, 2012)

X   Y

SO_3^- H^+
CO_2^- Na^+
NR_3^+ Cl^-
NH_3^+ OH^-
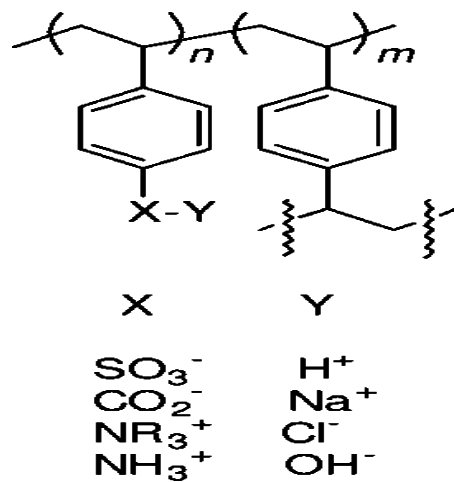
Figure 2.2: Structure of divinybenzene with different functional groups and ionic charges. (Toteja, 1997; Barbaro and Liguori, 2009; Corain et al., 2010).

[1]

Figure 2.3: Different functional groups detected in ion chromatography resins, (Taylor and Cook, 2012)

2.2.2. Cation exchange resins

Cation exchange resins have anionic functional groups and positively charged mobile ions. The resin is classified as strong acid exchanger when it contains functional groups such as the sulfonic acid group as shown in Figure 2.2 and weak acid exchanger when it contains functional groups such as the carboxylic acid group. The exchanger prefers ions of high charge and ions that interacts strongly with the functional groups of the exchanger (Alyuz and Veli, 2009; Barbaro and Liguori, 2009; Chang et al., 2012).

[2]

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[2] For more information visit: www.chromacademy.com

Moreinformationcabe found: http://www.chromacademy.com/Ion_Chromatography.html?tpm=1_1

For more information about ion chromatography: http://www.chromacademy.com/hplc-training.html

A strongly acidic sulphonated polystyrene cation exchange resin

Figure 2.4: Strong cation exchange resin (Alyuz and Veli, 2009; Barbaro and Liguori, 2009; Cheng et al., 2012)

2.2.3 Separation on cation exchange resin

The Cation Exchange Mechanism

Stationary Phase

Mobile Phase

Negatively-Charged Polymeric Particle

Eluent

H^+ from HNO_3, HCl, H_2SO_4, Methanesulfonic acid, tartaric acid, etc.
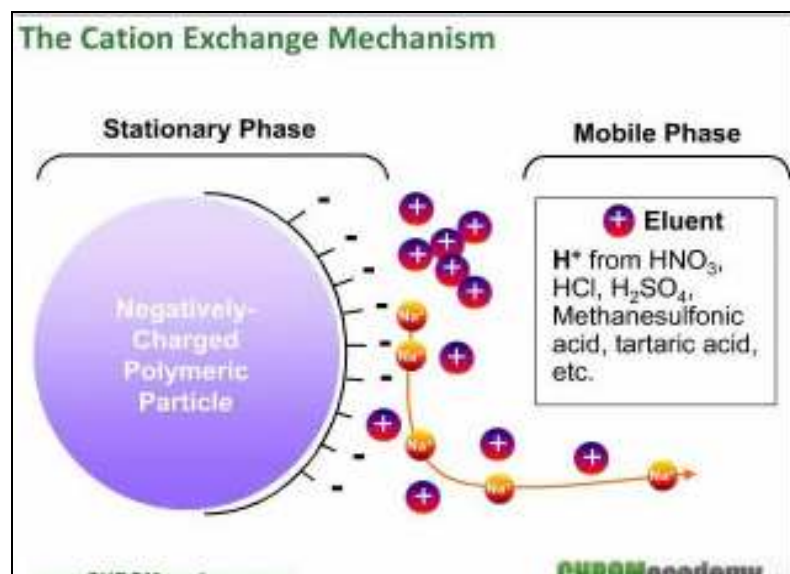
Figure 2.5: Cation exchange mechanism, (Taylor and Cook, 2012)

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[3] For more information visit: www.chromacademy.com

More information can be found: http://www.chromacademy.com/Ion_Chromatography.html?tpm=1_1

For more information about ion chromatography: http://www.chromacademy.com/hplc-training.html

Acidic eluents such as nitric acid, hydrochloric acid, sulphuric acid etc., are used to remove metal ions that are bound to the cation exchange resin. During separation, the positive charged metal ions that are bound to the resin are replaced by the positive charged hydrogen ions, from the acid solution, which replace the element ions and the separation is achieved as shown in Figure 2.5.

2.2.4 Achievements of ion exchange resins

The structural modification of macroporous resins has allowed the resin to be used as a catalyst in industrial reactions (Malshe and Sujatla, 2000). The improvement of the resin properties has allowed the development of new resins with more improved physical stability and improved separation of ions. Resin coating has been performed to allow maximum selectivity of a specific ion during the separation process (Dietz and Horwitz, 2000). Several studies on resin coating have found that coating reagents may be held on the surface of the resin permanently making it very difficult to be removed, which also causes damage on the resin. Preferable coating reagents are those that are easily washed from the resin (Guo and Ding, 2002).

Coated resins were replaced by use of special beads as resins. The flexibility of the beads was based on bead type, size, pore size, porosity and functional group. This type of resin has shown good reproducibility that is sometimes problematic with the coated resins (He *et al.,* 2004). The chelating resins were later developed to overcome challenges, which included the separation of ions at low levels and to overcome ion interference during separations. Chelating resins are formed by use of chelating reagents which are tightly held on the solid support of the resin prior to ion separation (Talwalkar et al., 2006). The resin contains a specific chelating agent as functional group bound to the organic matrix. Continuous improvement of chelating resins resulted in the development of composite chelating resins. Benefits of this type of resin include strong chelating properties, strong thermal and chemical stability (Gao, 2010).

The improvement in the particle shape and porous structure of the resin has led to the development of weak cation exchange resins. The beneficial properties of a weak cation exchange resin include excellent stability over the whole pH range, thermal stability, absence of shrinking or swelling in different water solutions and organic solvents. Within these properties the separation of ions is dependent on repelling of solution by the resin, which is a key factor for separation of ions (Nesterenko et al., 2007). Alexandratos studied the properties of weak cation exchange resins by comparing strong cation exchange resins and weak cation exchange resins. The study showed that strong cation exchange resins have low selectivity while weak cation exchange resins are more selective for divalent alkaline earth ions (Alexandratos, 2009).

Babic and his team showed that by combining the extractive reagents in a porous particle of the resin produces an impregnated resin. This combination forms an insoluble complex in the resin. The separation of ions is based on a diffusion of ions on the resin surface (Babic et al., 2008).

The cross linkage of the polymer resin structure in combination with the chemistry of the covalent bond have gained large application in ion exchange chromatography. Studies have shown that ions are electrostatically bound on the surface of the resin that is made of an insoluble phase (Alexandratos, 2009).

Porous resins beads, which were major microporosity of polymer resins was the major achievement in ion exchange resins, they have high sorption rate and outperforms the conventional resin and have increased the stability of the resins (Alexandratos, 2009).

Impregnated resin were developed with a carbon nanotubes by Mokhodoeva et al. The resin have different ionic liquids and are developed by impregnation of carbon nanotubes and polymeric supports with ionic liquids and ligands. Nano technology is

growing in the field of science and these types of resins can be used for future studies. (Mokhodoeva et al., 2011).

2.3 Metal ion separation mechanism

The science of kinetics has contributed to the understanding of different ion separation processes in ion chromatography. The combination of physics and chemistry have made it possible to explain separation and interaction mechanisms of metal ions on the resin. Several studies have contributed to the explanation of separation mechanisms in ion exchange chromatography (Poole, 2011; Buszewski and Noga, 2012; Small, 2013).

The theory of ion exchange was originally based on the development of the crystal structure which contained a number of ions with opposite charges, a contact with a polar media, an attraction of the ions with the ions of the opposite charge occurred. The theory was a foundation to understand possible mechanism and reaction pathways in ion exchange chromatography (Kunin, 1962: Lopano et al., 2011).

The equilibrium was discovered to be the driving force in the mechanism controlling the sorption of metal ions on the resin surface. Two types of reactions are involved in ion exchange, the forward reaction that involves the sorption of metal ions on the resin and reverse reaction, which is the regeneration of the resin. In both reactions, equilibrium is achieved. (Ketelle and Boyd, 1947; Al-Othman et al., 2011).

Lee discovered that another factor, which contributes to metal ion separation mechanisms, was based on biomass, which is also referred to as size exclusion. Different metal ions molecular weight in the solution will have different equilibration rates this causes metal ions to reach equilibrium at different rates (Lee, 2002). Lopano et al. discovered that smaller ions diffuse more quickly into the macroporous resin than larger ions because of the limited pore size of the resin particle (Lopano et al., 2011).

The effect of an electric field on ion charges during ion exchange was visualized by Tae (Tae, 2002). During the interaction an electric field is generated which contributes to ion transfer. The electric field from one charge points towards the opposite charge, which creates attraction of the charges. The electric field is the mechanism that drives analyte ions to the counter ions on the resin and creates ion distribution (Tae, 2002: Shibukawa et al., 2009).

Particle pore size of the macroporous resin is the contributing factor in the ion separation mechanism. The rate of exchange increases when particle pore size decrease, this was seen as a controlling step during metal ion separation. The macroporous resin properties such as permeability contribute to ion selectivity and separation efficiency (Tae, 2002: Bruzzoniti et al., 2011).

According to Gorka et al. ion exchange kinetics consists of transport of ions from liquid to ion exchange sites by interparticle and intraparticle diffusion (Gorka et al., 2008), The study outlined that the rate-controlling step of the overall process is intraparticle and interparticle diffusion. The inter diffusion is the spreading of exchanging counter ions within the resin and intra diffusion is the spreading of analyte ions on the surface of the resin (Gorka et al., 2008: Al-Othman et al., 2011).

Timsit studied the state of the metal ion before contact with the ions on the resin. The study showed that, ions in a liquid separates from their original structure and generate electric charge that has forces surrounding the ions which pulls them to any direction and creates the movement of ions from one point to another. This creates the spreading of ions on the resin. When the electron wind movement shields the metal ion, it allows the metal ion to be attracted towards the opposite charge. This explains a situation into which metal ions are not diffusing due to a degree of metal ion shielding (Timsit, 2010).

According Mustafa et al. and Rae et al. the mechanism of ion intake on the surface of the resin is dependent on the ion size and the charge of the counter ion initially present inside the resin, separation is controlled by ion interaction with the charged ions on the stationary phase of the resin (Mustafa et al., 2010: Rea et al., 2011).

Liu and his team studied equilibrium mechanisms. They discovered that when metal ions contacts the resin, the sorption time of the metal ion on the resin is quite fast and slowly decreases. This is due to the occupation of sorption sites on the resin and slowly creates fewer available sites for sorption, within this equilibrium is achieved which explains maximum intake of ions on the resin surface (Liu et al., 2011).

2.4 Effect of the eluent

Ion exchange chromatography requires the use of eluents to achieve the desired separation of ions. The use of eluents in ion exchange chromatography is to enhance metal ion attraction towards the resin that has opposite charged ions. Another role of eluent is to drive ions from the liquid phase to the stationary phase. Eluent properties such as pH, affect separation efficiency and separation strength of the resin (Navratil, 1971; Pourjavid et al., 2010; Lammerhofer et al., 2011).

Strelow and Van der Walt used a complexing agent as eluent. The idea was to complex interfering metal ions and to prevent hydrolysis of metal ions in low acidic eluent concentration. The outcome of the study showed that certain metal ions are best separated by use of high acid concentration (Strelow and Van der Walt, 1982; 1983). Acidic eluents favour lower oxidation states of metal ions and basic eluent promotes the stability of the higher oxidation states, which means higher oxidation states gain stability as the pH increases, (Nash and Choppin, 1995:1-177; Cocalia et al., 2006).

A mixture of solvents such as a strong acid and an organic solvent has shown to be suitable eluents for separation of metal ions. The mixtures contribute to the distribution of ions based on the selective sorption of one of the solvent components to the exchanger. This contributes to the separation mechanism as mentioned in 2.3. (Korkisch and Orlandini, 1968; Dorofeyera, 2004; Shibukawa et al., 2009).

The use of complexing agents as eluents was limited as they were only suitable to alkaline earth cations and to a few transition metal ions. On the other hand, complexing eluents made it possible to form stable metal complexes on the surface of the resin with low solubility. Mingyu et al introduced weak acid as the eluent, which provides both the anionic eluent ion and the cationic eluent ion as well its complexing ability. The eluent was suitable to alkaline, earth alkaline and transition metal ion group (Mingyu et al., 1997: Ohta et al, 1997: Dias et al., 2012).

The comparison of strong acid eluents with the weak acid eluents has shown that, strong acid eluents have hydrophobic characteristic and weak acid eluents have hydrophilic characteristics. Selection of eluent is dependent on the type of resin used, such as the use of an acidic eluent with an acidic cation exchange resin (Tanaka et al, 2000; Mori, 2006).

The pH effect in the eluent was shown to play an important role for effective separation of metal ions. Low pH eluents such as acidic eluents create competition between metal ions for biding sites on the resin (Badawy et al., 2009). Selection of eluent pH creates metal ion separation possibility. Micropourouse resins can withstand p H range of more than eight, which makes them to be more effective and stable (Rafati et al., 2010).

Separation of metal ions can be achieved by the selectivity of the resin counter ion, which depends on the acidity, alkalinity or the pH of the eluent. On the other hand, the use of modifiers in the separation eluent was investigated. The role of modifiers is to improve the selectivity of the resin as shown in Figure 2.6. (Holstein et al., 2011; Maruo and Obata, 2011).
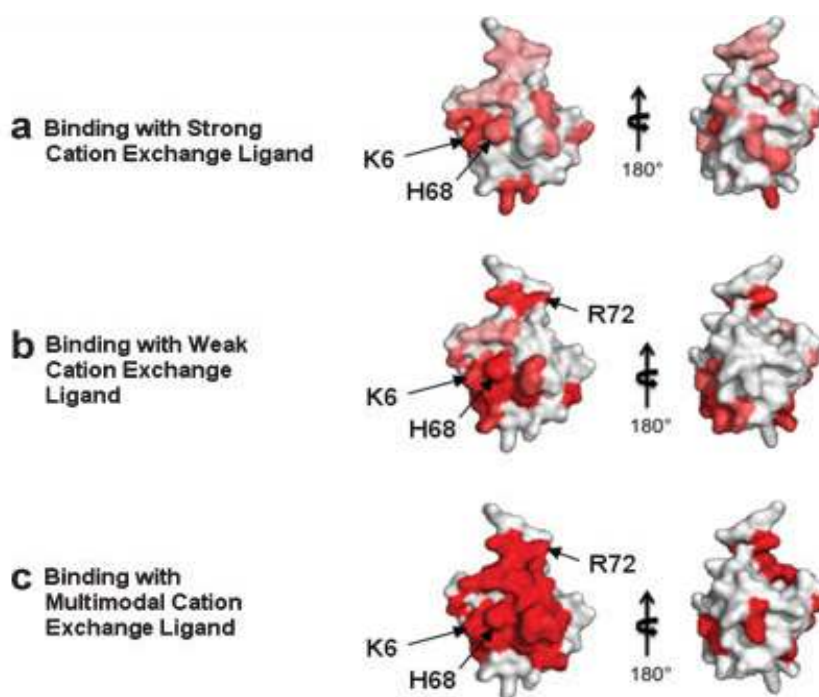
Figure 2.6: Evaluation of modifier with three different resins (Holstein et al., 2011)

2.5 The Inductively Coupled Plasma

Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) determines multi element analysis for measuring trace elements in various sample matrix. The instrument provides reliable consistency data. The application of ICP-OES includes but not limited to pharmaceutical, environmental industrials and food and beverage analysis. Samples are introduced as liquids on the instrument. The liquid sample is converted into a fine spray mist by a gas. (Marechal and Albarede, 2002: Sohrin and Bruland, 2011).

The construction of the ICP-OES instrument consist of the nebulizer, spray chamber and a torch. Each of these instrument parts play an important role. The nebulizer handles the sample solution and mixeses the sample with the argon gas. Spray chamber removes droplets that are bigger from the nebulizer and generates fine mist droplets. The torch allows the sample to collides with electrons and charged ions in the plasma and giving off radiation at selected wavelength of the specific element (Gilon et al., 2011; Naozuka et al., 2011 and Agilent, 2012).
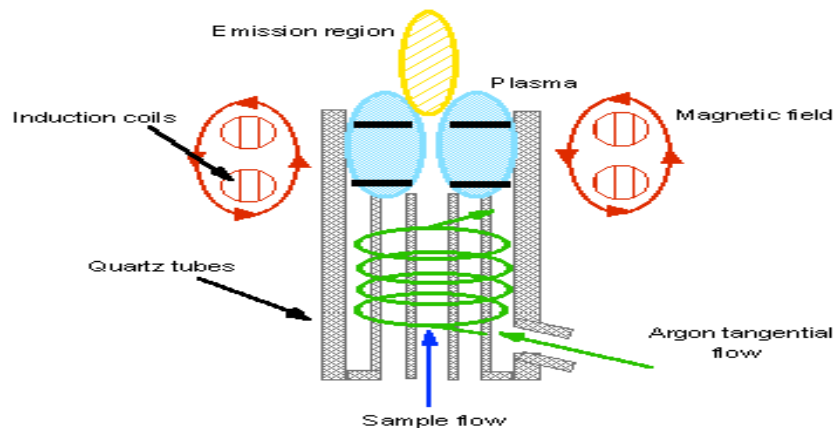
Figure 2.7: Schematic diagram of plasma source inside inductively coupled plasma (Gilon et al., 2011; Naozuka et al., 2011)
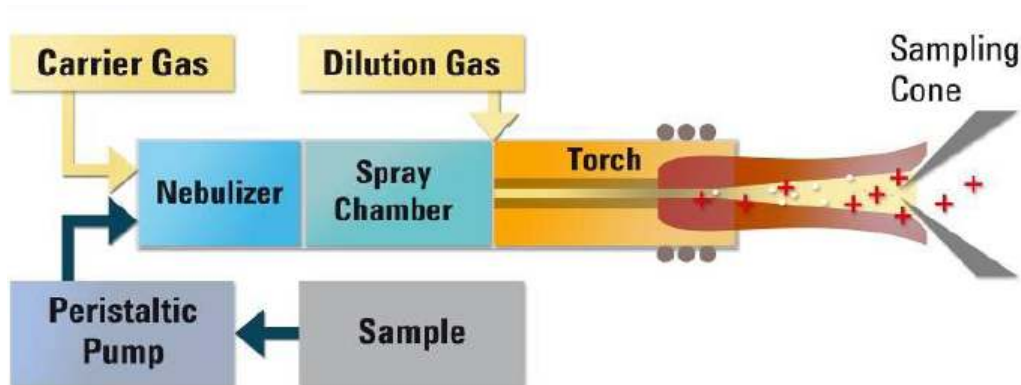
Figure 2.8: Sample flow diagram (Agilent, 2012)

The elements on the periodic table have different wavelengths. Each element will absorb light energy at different wavelength and generates different emission energy. This allows analysis of more than two elements, which is commonly known as multielement analysis. The emission energy is quantified and is proportional to the metal ion concentration in the sample (Karbasi et al., 2009; Escudero et al., 2010).

There has been new instrument developments on ICP-OES. The developments were based on improving sensitivity, reduction of metal ion interferences and determination of targeted metal ions. ICP-MS (inductively coupled plasma mass spectrometry) is the latest instrument in the mark. The instrument has fragmentation technique and is able to determine very low metal ion concentrations. The instrument is more sensitive compared to ICP-OES (Ciu et al., 2011; Cheng et al., 2012; Krachler et al., 2012).

2.6 The distribution coefficient

Ion exchange chromatography separation involves the exchange of ions that takes place in the resin pores. The exchange of ions depends on the ions in the solution to displace counter ions on the resin. The distribution coefficient, simply determines the exchange of two ions between two solutions.. Batch equilibration experiments are mostly use to

experimentally determine distribution coefficient values as shown in Figure 2.11 (Strelow, 1960: Pourmand and Dauphas, 2010).
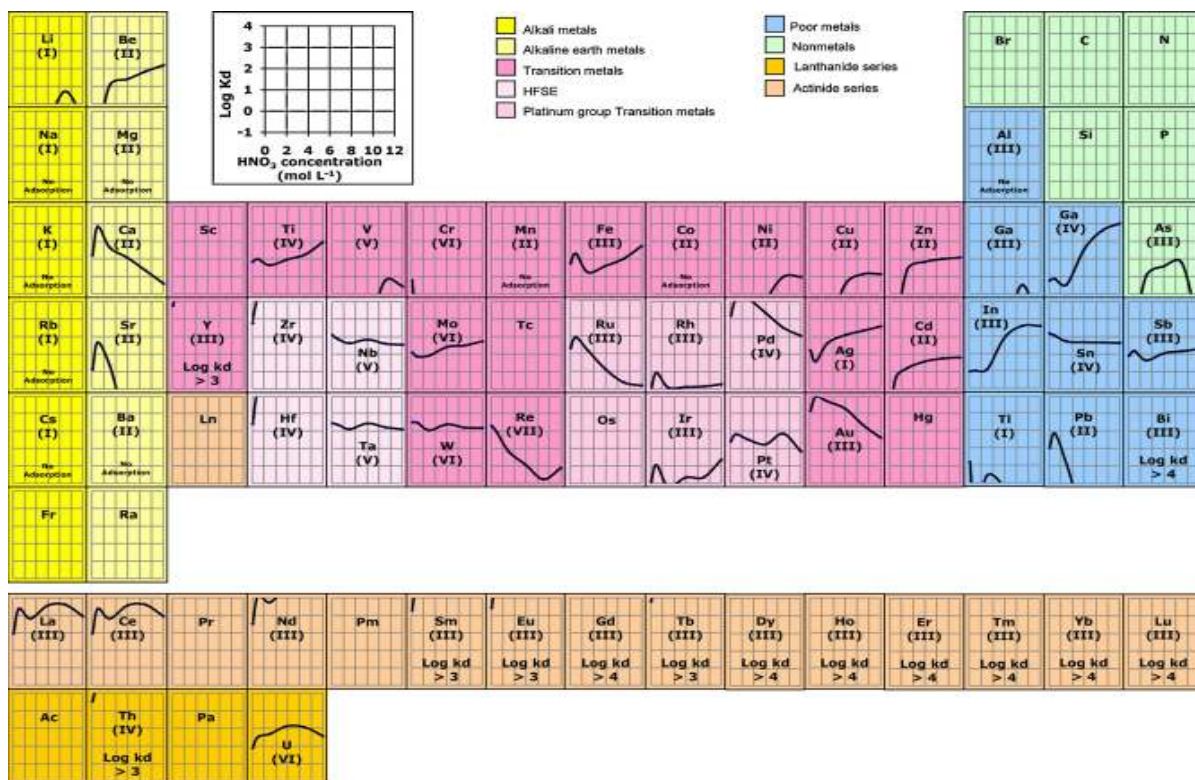
Figure 2.9: Distribution coefficients (Kd) of 60 elements on TODGA resin in logarithmic scale as a function of HNO3 molarity (measured at 0.1, 1, 3, 6, 9 and 12 mol L−1). The six data points used to establish each curve are the geometric averages of two replicate (Pourmand and Dauphas, 2010)

The use of acid-organic eluents specifically for separation of transition metal ions improved distribution coefficient values. The study showed that, the decrease in the value of the distribution coefficient is due to high concentration of acid and organic solvent. At high concentrations of acid, the exchange rate is slower and at low concentrations the exchange rate is fast hence the distribution coefficient values increase (Strelow et al., 1971: Kenaway et al., 2000).

Previous studies have stated that distribution coefficients depend on the type of resin use and the concentration of the solution. Two types of resin were compared to further validate resin impact on distribution coefficient. The macroporous resin and the normal gel type resin were compared to one another. The outcome of the study provided the evidence that macroporous resin offers high values of distribution coefficient due to the structure of the resin that contains a cross linkage and the structure is independent of eluent concentration (Van der Walt and Coetzee, 1996). (Strelow, 1960; 1984).

Harinarayan et al reported a new interpretation of the distribution coefficient. The interpretation was based on the pore size of the resin and the size of the metal ion. The study confirmed that, the pore size influences ion accessibility that affects the distribution coefficient value. Values, which are greater than zero shows that exchange between ions is effective. However, it must be noted that the ions are not only retained in the pores but also on the functional groups on the surface of the resin beads. It was noted that the pH is the driving force for accessibility of ions to the resin pores, but the study does not explain the influence of the pH (Harinarayan et al., 2006).

Nabi and Khan observed the effect of the drying temperature in the oven of the resin and dielectric constant of the solvent on distribution coefficient values. The study revealed that, the distribution coefficient remains unchanged with the increase in oven temperature at low temperatures, but above 45 degrees Celsius a change was observed, which showed the best temperature that allows metal ions uptake by the resin is between 30 and 50 °C, as indicated in Figure 2.12. The use of a solvent that can generate an electric force was noted to have no impact on distribution coefficients for double charged metal ions, however a decrease in distribution coefficient was noted on trivalent and tetravalent charged metal ions as shown in Figure 2.13 (Nabi and Khan, 2006).
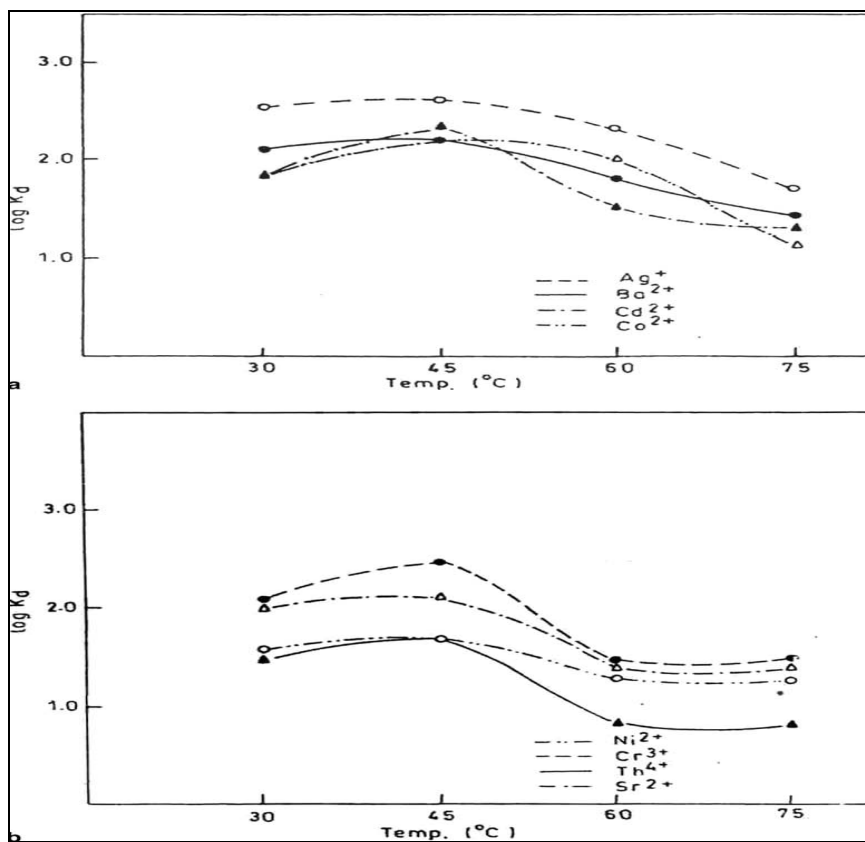
Figure 2.10: Effect of temperature on distribution coeffient of metal ions (Nabi and Khan, 2006)
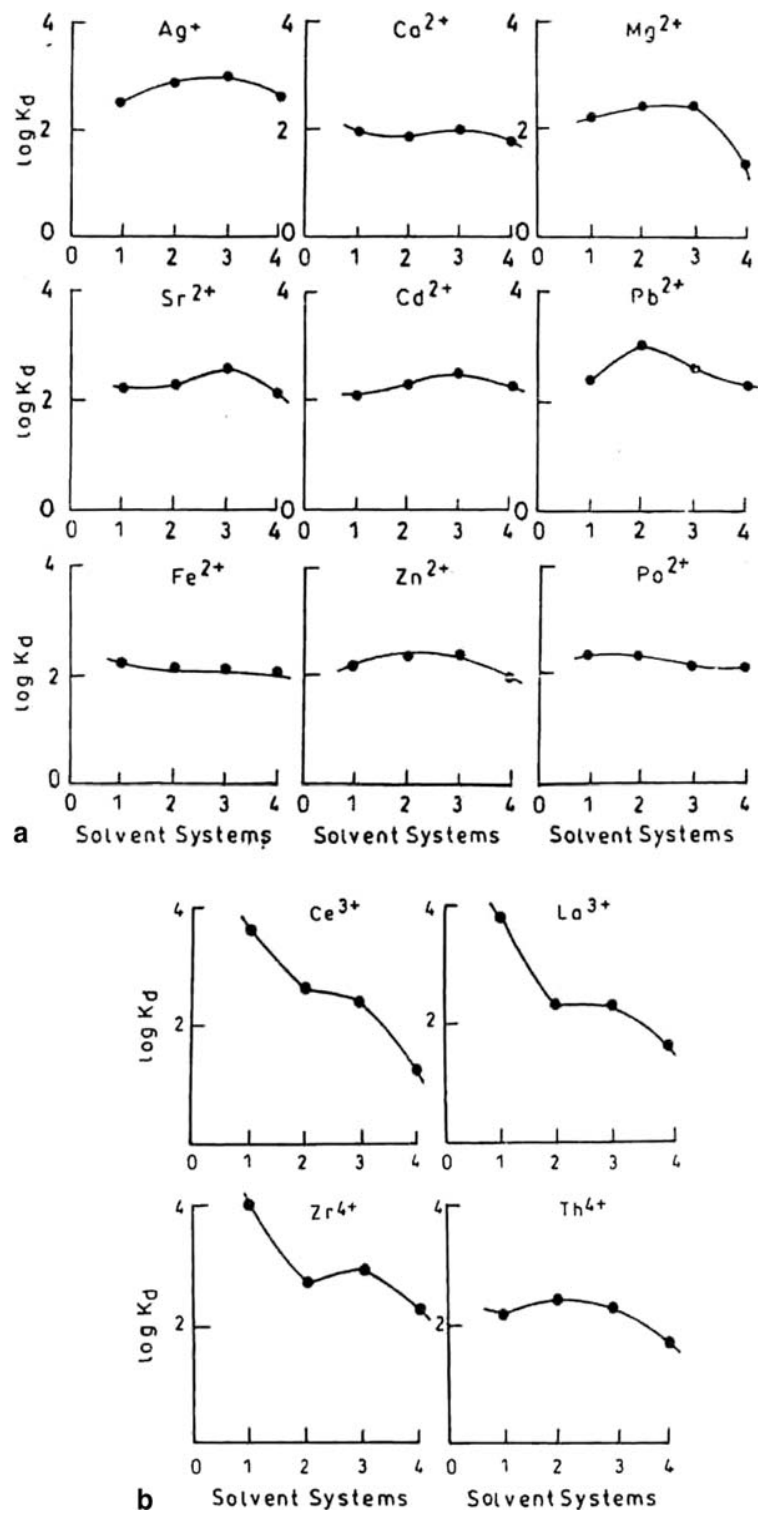
Figure 2.11: Variation of K_d value with dielectric constants of solvents. The solvent systems are arranged in increasing order of dielectric constants: 1, trichloroacetic acid; 2, acetic acid; 3, dimethylsulfoxide; 4, formic acid (Nabi and Khan, 2006)

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The continuous use of different resins has led to the determination of distribution coefficients using impregnated resin for separation of rare earth metals. The study declared that a high value of the distribution coefficient indicate that a metal ion is easily sorbed on the resin and low distribution coefficient value show that a metal ion is not well retained by the resin. The retention rate of anion by the resin contributes to high values of distribution coefficient, which creates sufficient metal ion separation (Lee et al., 2009).

Previous studies have stated that, high values of distribution coefficients show that metal ions have been kept by the resin and low values indicate that metal ions remains in the solution. Badawy and the team provided more evidence by investigating the impact of strong acid and the weak base on distribution coeffient values. The outcome of the study showed that, a decrease in the acid concentration increase distribution coefficient value due to anionic complex formation. On the other hand, an increase in weak base concentration decreases the distribution coefficient value. Interesting part of weak base was the formation of metal ion complex, which influences the intake of metal ion (Badawy et al., 2009).

Determination of distribution coefficients using liquid membranes was measured for metal ion separation. The values of distribution coefficients were determined over a range of metal ions concentration. An increase in distribution coeffient was due to an increase in the solution concentration as illustrated in Figure 2.14. (Singh et al., 2011).
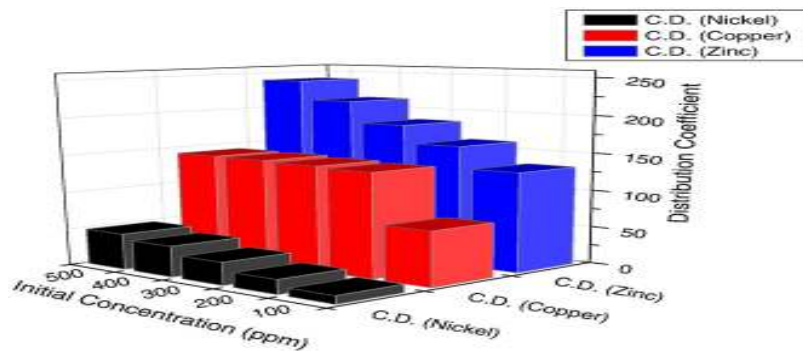
Figure 2.12: Membrane/aqueous distribution coefficients vs initial source phase concentration (Singh et al., 2011)

Jeppu and Clement introduced Modified Langmuir-Freundich (ML-F) isotherm to model the sorption of metal ions. Studied have showed that, pH varies linearly with distribution coefficient which means (ML-F) isotherm can be used as an alternative approach which can be linked with the distribution coefficient to determine sorption of metal ions (Jeppu and Clement, 2012).

2.7 Summary

The chapter presented the background and the current literature on the application of ion exchange chromatography, separation resins, separation mechanism, separation eluents, and inductively coupled plasma together with distribution coefficient.

CHAPTER 3: EXPERIMENTAL PROCEDURE

This chapter presents the characteristics of Amberlyst 15 cation exchange resin and the method procedure employed during experimental work to obtain the distribution coefficient values. The performance of the resin depends on its selectivity and stability under specified chemical conditions as discussed in Chapter 2.2. The separation of metal ions by the resin need to be reproducible.

3.1 Characterization of Amberlyst 15
3.1.1 Background

Amberlyst 15 cation exchanger was discovered through polymerization technique, which provided the ion exchanger with a cross linked polymer structure. The conversion of the polymer by a sulphonation technique generated sulfonated styrene-divinely-benzene copolymer with a macroreticular structure. The cation resin is classified as a macroreticular ion exchange resin based on its structure, which contains pores. Macroreticular resins have a gel phase, where the exchange ion groups are located and which consists of large pores to absorb more solvent (Kunin et al., 1962: Harmer and Sun, 2001: Frija and Afonso, 2012).

3.1.2 Functional group

Amberlyst 15 cation exchange resin has a sulphonic acid group ($SO_3^- H^+$) as a functional group as shown in Figure 3.1, hence it is classified as a strong acid cation exchange resin. In the study, the cation exchange resin is in the H^+ form. The hydrogen ions are competing ions with the metal ions in the solution as discussed in Chapter 1 and Chapter 2. The sulfonic acid group enhances phase separation with a distinguishable hydrophobic phase to limit water uptake and swelling of the sulfonated hydrophilic phase where the metal ion transport takes place (Wu et al., 1997: Jutemar and Jannasch, 2010).
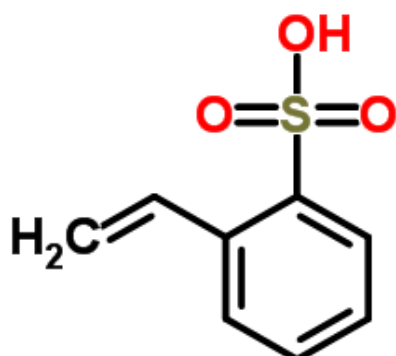
Figure 3.1: Chemical structure of Amberlyst 15 cation exchanger

Adapted from http://www.chemspider.com/Chemical-Structure

3.1.3 Separation mechanism

The sorption of metal ion on Amberlyst 15 cation exchanger involves few processes. First process is the spreading of metal ions through the solution onto the adsorbent particles, the spreading of metal ions through the adsorbent particles, chemical exchange between H^+ and charged metal ion in the interior of the resin particles, the spreading of the displaced cation (H^+) through the solution away from the resin particles which is the reverse of the first process and the spreading of cation (H^+) out of the inside of the resin exchanger which is the reverse of the second process (Mustafa et al., 2010: 2011).

3.2 Material and method

3.2.1 Material

Chemicals and reagents were purchased from Merck, Fluka Analytical and Kimix (South Africa). The chemicals and solvents were of analytical grade

3.2.2 Method

3.2.2.1 Preparation of metal ion stock solution

Metal ion salts of $Cu(NO_3)_2.3H_2O$, $Zn(NO_3)_2.6H_2O$, $Co(NO_3)_2.6H_2O$ and $NiO_6.6H_2O$ were all weighed according to Table 3.1 and were prepared with 0.5 M HNO_3 in 100 ml volumetric flask. Reagents and metal ion salts were purchased from different suppliers of chemicals as listed in Table 3.2.

Table 3.1: Masses of salts of elements weighed

Metal ion	Mass weighed (g)
Cu^{2+}	12.0800
Zn^{2+}	14.8730
Co^{2+}	14.5516
Ni^{2+}	14.5396

Table 3.2: Reagents suppliers list

Reagents	Supplier	Product number
2.5 L, 65% HNO_3	Merck	K 42193143114
Zn 1000 ppm Standard	Merck	HC 962775
Ni 1000 ppm Standard	Merck	HC 127141
Co 1000 ppm Standard	Fluka Analytics	BCBC 8450
Cu 1000 ppm Standard	Merck	HC 114735
Ion Exchanger Amberlyst 15	Merck	K41524635038

3.2.2.2 Preparation of reference standards

For each element, four reference standards were prepared as follows: 1000 µL of the element stock solution was added to a 100 mL volumetric flask, 10 mL 5.0 M HNO_3 added and diluted to the mark with deionized water and well mixed. The concentration of the element was determined by ICP-OES and the average of the four standards was used for the calculation of the distribution coefficients according to Equation 3.1

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3.2.2.3 Preparation of the resin

Amberlyst 15 cation exchange resin was dried in an oven at 60^0C overnight and then storied in a capped container in a desiccator.

3.2.2.4 Sample preparation and experimental work

A batch technique was use for the equilibrium distribution coefficient determination. The technique was carried out to achieve better sorption and contact time between the resin and metal ion solution to obtain intraparticle diffusion. The intraparticle diffusion refers to a sorption of a metal ion within the resin solid particle. (Pandey et al., 2009: Alagumuthu et al., 2010: Gong et al., 2012).

 1000 µL of the element stock solution was added to a 50 mL plastic container containing 0.500 g of resin. Nitric acid, methanol and water were added according to the appropriate table (Table 3.3 – Table 3.9). The mixture was shaken overnight at room temperature at the speed of 170 rpm on a Lasec (South Africa) shaker to allow the ion exchange process to reach equilibrium. The solution was then transferred into a 20 mL polypropylene column with a sinter at the bottom to filter off the resin. The solution was collected in a 250 mL beaker (Beaker A). The bottle and the inside of the column was washed with a jet of water and the washings also collected in Beaker A (Filtrate solution). The element retained on the resin was eluted with small portions of 5.0 M

HNO$_3$ (10 mL in total) and the eluent was collected in a 250 mL beaker (Beaker B). The resin and inside of the column was washed with a jet of water and the washings was also collected in Beaker B (Eluate solution). The solutions in the two beakers were evaporated to incipient dryness on a water bath. The salts in each beaker were respectively dissolved in 10.0 mL 2.5 M HNO$_3$, transferred into a 100 mL volumetric flask, diluted to the mark with water and shaken. The concentration of the element in each flask was determined by ICP-OES and the distribution coefficients calculated with Equation 3.1.

3.2.2.5 Assessment of the method

The method cannot be automated; the experimental conditions were manual as it was necessary to monitor the speed of the droplets coming from the column because both the accuracy and precision had to be maintained at all time. A slow rate had to be maintained as well when transferring the filtrate and the eluent, as this can have an impact on both the accuracy and precision. Care was taken not to lose drops when the solutions were transferred from one container to another one to prevent loss of analyte.

Preparation of batch samples at different nitric acid concentration and methanol was done according to the tables below, Table 3.3 to Table 3.9. All tables resemble each other, the column ''M HNO$_3$'' represents nitric acid concentration in mole units, the column ''% methanol'' represents varying methanol concentration, column ''mL stock solution'' shows the volume of metal solution pipetted out of element stock solution, the column ''mL 5.0 M HNO$_3$'' shows the volume of 5.0 M nitric acid concentration, the column ''mL methanol'' represents the volume of methanol added during sample preparation and the column ''mL water'' represents the volume of water added to each 50 mL plastic container.

Table 3.3: 0.1 M HNO$_3$ + methanol

M HNO$_3$	% methanol	mL stock solution	mL 5.0 M HNO$_3$	mL methanol	mL water
0.1	0	1.000	1.0	0	48.0
0.1	10	1.000	1.0	5.0	43.0
0.1	20	1.000	1.0	10.0	38.0
0.1	40	1.000	1.0	20.0	28.0
0.1	60	1.000	1.0	30.0	18.0
0.1	80	1.000	1.0	40.0	8.0
0.1	90	1.000	1.0	45.0	3.0

Table 3.4: 0.2 M HNO$_3$ + methanol

M HNO$_3$	% methanol	mL stock solution	mL 5.0 M HNO$_3$	mL methanol	mL water
0.2	0	1.000	2.0	0	47.0
0.2	10	1.000	2.0	5.0	42.0
0.2	20	1.000	2.0	10.0	37.0
0.2	40	1.000	2.0	20.0	27.0
0.2	60	1.000	2.0	30.0	17.0
0.2	80	1.000	2.0	40.0	7.0
0.2	90	1.000	2.0	45.0	2.0

Table 3.5: 0.5 M HNO₃ + methanol

M HNO₃	% methanol	mL stock solution	mL 5.0 M HNO₃	mL methanol	mL water
0.5	0	1.000	5.0	0	44.0
0.5	10	1.000	5.0	5.0	39.0
0.5	20	1.000	5.0	10.0	34.0
0.5	40	1.000	5.0	20.0	24.0
0.5	60	1.000	5.0	30.0	14.0
0.5	80	1.000	5.0	40.0	4.0
0.5	90	1.000	2.5 mL 10.0 M HNO₃	45.0	1.5

Table 3.6: 1.0 M HNO₃ + methanol

M HNO₃	% methanol	mL stock solution	mL 10.0 M HNO₃	mL methanol	mL water
1.0	0	1.000	5.0	0	44.0
1.0	10	1.000	5.0	5.0	39.0
1.0	20	1.000	5.0	10.0	34.0
1.0	40	1.000	5.0	20.0	24.0
1.0	60	1.000	5.0	30.0	14.0
1.0	80	1.000	5.0	40.0	4.0

Table 3.7: 2.0 M HNO₃ + methanol

M HNO₃	% methanol	mL stock solution	mL 10.0 M HNO₃	mL methanol	mL water
2.0	0	1.000	10.0	0	39.0
2.0	10	1.000	10.0	5.0	34.0
2.0	20	1.000	10.0	10.0	29.0
2.0	40	1.000	10.0	20.0	19.0
2.0	60	1.000	10.0	30.0	9.0
2.0	70	1.000	10.0	35.0	4.0

Table 3.8: 3.0 M HNO₃ + methanol

M HNO₃	% methanol	mL stock solution	mL 10.0 M HNO₃	mL methanol	mL water
3.0	0	1.000	15.0	0	34.0
3.0	10	1.000	15.0	5.0	29.0
3.0	20	1.000	15.0	10.0	24.0
3.0	40	1.000	15.0	20.0	14.0
3.0	60	1.000	15.0	30.0	4.0

Table 3.9: 4.0 M HNO₃ + methanol

M HNO₃	% methanol	mL stock solution	mL 10.0 M HNO₃	mL methanol	mL water
4.0	0	1.000	20.0	0	29.0
4.0	10	1.000	20.0	5.0	24.0
4.0	20	1.000	20.0	10.0	19.0
4.0	40	1.000	20.0	20.0	9.0
4.0	50	1.000	20.0	25.0	4.0

3.2.2.6 Quantitative determination of the concentration of elements with ICP-OES

The metal ion analysis and quantification were performed with ICP-OES from SPECTRO-ARCOS series. Standard solutions of metal ions were prepared by dissolving appropriate amounts in deionised water to give the desired concentration as shown in Table 3.10; this was done for all the metal ions. The standards were prepared from the highest standard concentration, which is 400 ppm to minimize dilution errors. Analysis of the elements was done at different wavelengths using the parameters as shown in Table 3.11 and Table 3.12.

Table 3.10: Preparation of Cu, Zn, Co and Ni solution standards for ICP-OES analysis

Volume of standard added (mL) from Stock Standard of 1000 ppm	Standard Concentration (ppm)	Volume of distilled water added in a 25 mL volumetric flask
5.0	1.0	20.0
12.5	5.0	12.5
12.5	10	12.5
10.0	20	10.0
12.5	50	12.5
12.5	100	12.5
5.0	200	20.0
10.0	400	15.0

Table 3.11: Element wavelengths selected for ICP-OES analysis

Element	Wavelength selected for analysis (nm)
Cu	324.754
Zn	213.856
Co	228.616
Ni	231.604

Table 3.12: ICP-OES analysis parameters

Auxiliary flow	1.00 L/min)
Coolant flow	13.00 (L/min)
Nebulizer flow	0.80 (L/min)
Plasma	1400 (W)

3.2.2.7 SPECTRO-ARCOS Software Control

The Spectro-Arcos ICP consists of three components, which are the chiller, ICP, auto sampler and a PC (Personal Computer) for results processing. The chiller contains water to cool down the system during analysis. The auto sampler is used to handle samples. The performance of the components is controlled and operated with Spectro-Arcos software in the PC.

Once the method had been created and saved in the control software, the samples were placed on the rack of the auto sampler and the sample data entered in the sample data table, and then the instrument was started. With the flexible control system, the samples can be analyzed manually or automatically.

3.3 The distribution coefficient calculation

The distribution coefficient values were calculated from the values obtained from ICP-OES that are represented as concentration. The values use to calculate distribution coefficient were obtained from both the filtrates and eluent concentrations obtained. The unit of distribution coefficient K_d is ml/g. The distribution coefficient values for the filtrate solutions were determined by the equation below, Equation 3.1.

K_d = {[amount of the element in the reference standard (gram)] – [amount of the element in the solution (gram)] x [volume of the solution (mL)]} ÷ {[amount of the element in the solution (gram)] X [mass of the resin (gram)]}
..........Equation 3.1

3.4 Summary

This chapter described the Amberlyst 15 cation exchanger and its properties and the method used to achieve equilibration, which is a batch technique to yield good sorption of metal ion on the resin surface. In order to obtain good separation, ion chromatography method was use for separation of metal ions on the resin.

The following chapter focuses on the integrity of the method used to generate results and the method validation parameters applied.

CHAPTER 4: VALIDATION OF RESULTS

This chapter presents the fundamentals of the method performance that include parameters such as selectivity, accuracy, precision, sensitivity and reproducibility. The acceptability of analytical data corresponds directly to the criteria used to validate the method. In this chapter, analytical results obtained are evaluated and assessed for its reliability.

4.1 Results

4.1.1 Batch acceptance criteria

A batch acceptance criterion was based on correlation coefficient, which is obtained from the calibration curves, accuracy, precision, and recovery as it was highlighted in Chapter1 under research methodology for results validation. The correlation coefficient, which measure the relationship between two variables and presented as R^2, should be ≥ 0.98. For all the metal ion calibration curves, linear fit was use which presents a straight line by the equation of, y= mx + c. In the equation, m presents the slope and c presents the intercept. The concentrations of the unknown samples were calculated from the calibration curves.

Accuracy is the assessment of the closeness of the determined values by ICP-OES to the true concentration of the analyte, this is determined by a QC (quality control) sample, which is run inbetween the samples to help for evaluating any trends during the run and to assess method robustness. For QC samples, the mean accuracy generated during method validation was less than 20%. A QC sample at concentration level of 25ppm was included and analysed (Voica et al., 2012: Hernandez-Mendoza et al., 2013: Senila et al., 2014).

Precision assesses the closeness of individual repeated injections and this determines whether the method is reproducible. For method validation, one sample was injected two times for each metal ion batch. The sample was QC at concentration of 25 ppm. The average mean of the results was less than 20% (Voica et al., 2012: Hernandez-Mendoza et al., 2013: Senila et al., 2014).

Method selectivity is the performance of the method for a specific analyte in the presence of other interferences such as impurities or a matrix, which does not contain the analyte of intrest. In the validation, a set of blank samples were analysed for each metal ion batch, the mean results showed very low instrument response. (Voica et al., 2012: Hernandez-Mendoza et al., 2013: Senila et al., 2014).

4.1.2 Metal ion validation summary results

4.1.2.1 Zn, Ni, Co and Cu correlation coefficients

The correlation coefficients results for Zn, Ni, Co and Cu were generated from instrument response presented as intensity versus metal ion concentration as shown in Table 4.1. According to the validation guidelines in paragraph 4.1.1, all values were acceptable. The linearity between the two variables is shown in Figure 4.1, 4.2, 4.3 and Figure 4.4.

Table 4.1: Summary of metal ion correlation coefficient

Metal Ion	R^2 Correlation Coefficients	Status
Zn	0.9988	Accepted
Ni	0.9996	Accepted
Co	0.9994	Accepted
Cu	0.9994	Accepted

4.1.2.1 Metal ion representative calibration curves

For each metal ion, eight levels of the calibration standard concentrations were analysed to assess the linearity between the metal ion concentration and instrument intensity. The calibration range was set from 1 ppm to 400 ppm. Table 4.2 and Figure 4.1 present Zn response, Table 4.3 and Figure 4.2 present Ni response, Table 4.4 and Figure 4.3 present Co response. In all the tables intensity increases with the increase in metal ion concentration.

Table 4.2: Zn ion concentration and instrument response

Std	Concentration (ppm)	Intensity (Cnt)
1	1	56295.7
2	5	279519
3	10	571754
4	20	1150300
5	50	2906050
6	100	5851200
7	200	11487300
8	400	21562800
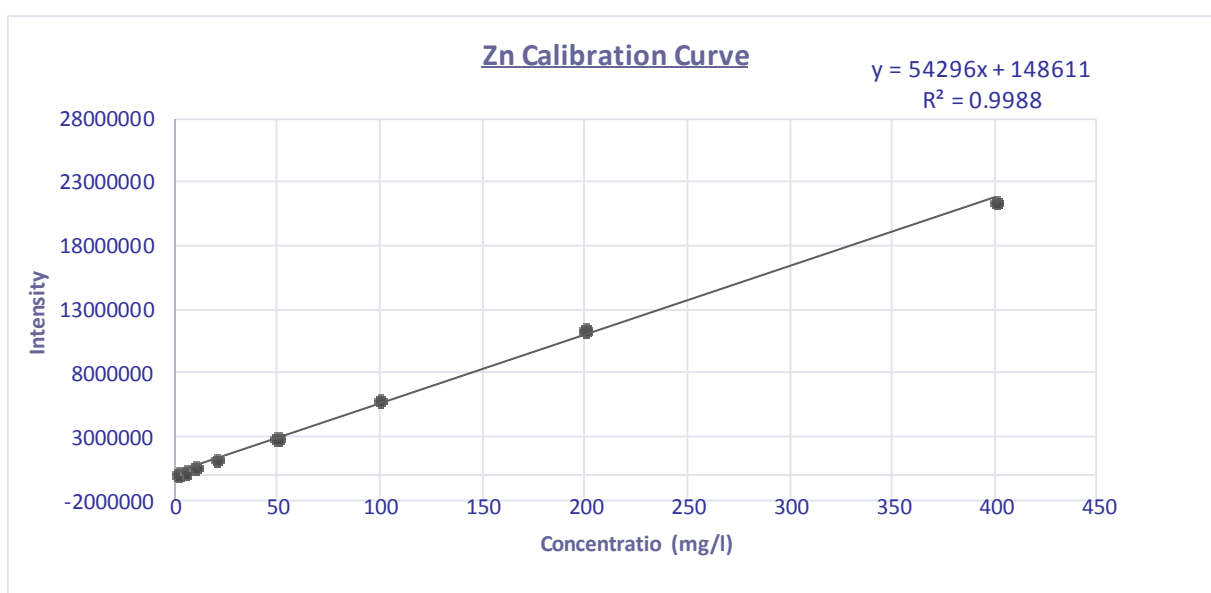
Figure 4.1: Zn Calibration curve

Table 4.3: Ni ion concentration and instrument response

Std	Concentration (ppm)	Intensity (Cnt)
1	1	51262.7
2	5	230424
3	10	457032
4	20	870363
5	50	2177670
6	100	4411520
7	200	8661970
8	400	16660400
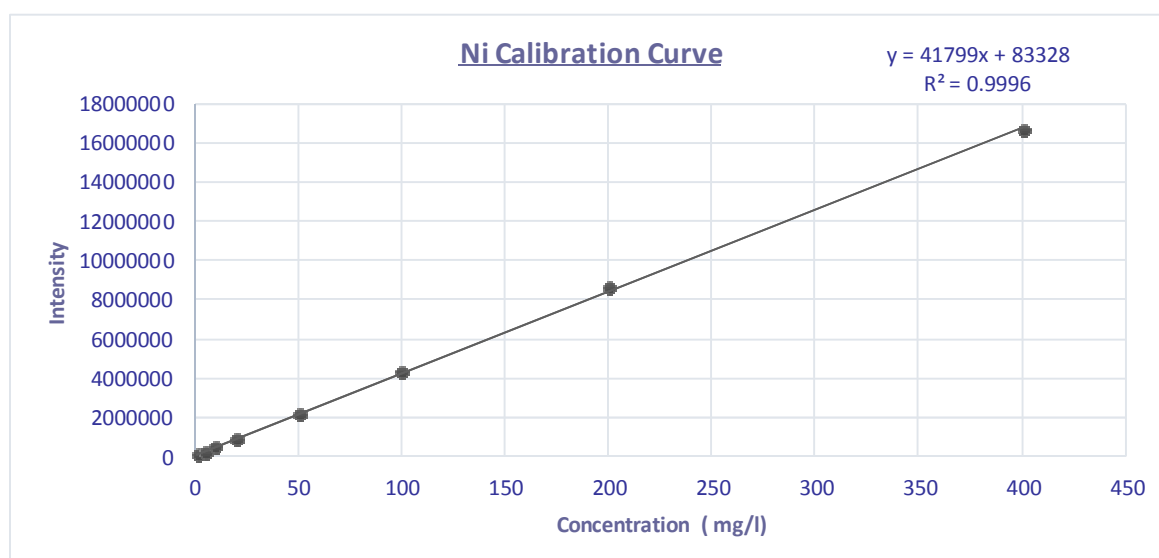
Figure 4.2: Ni Calibration curve

Table 4.4: Co ion concentration and instrument response

Std	Concentration (ppm)	Intensity (Cnt)
1	1	29383.1
2	5	140815
3	10	254296
4	20	513200
5	50	1328740
6	100	2657650
7	200	5348540
8	400	10163600
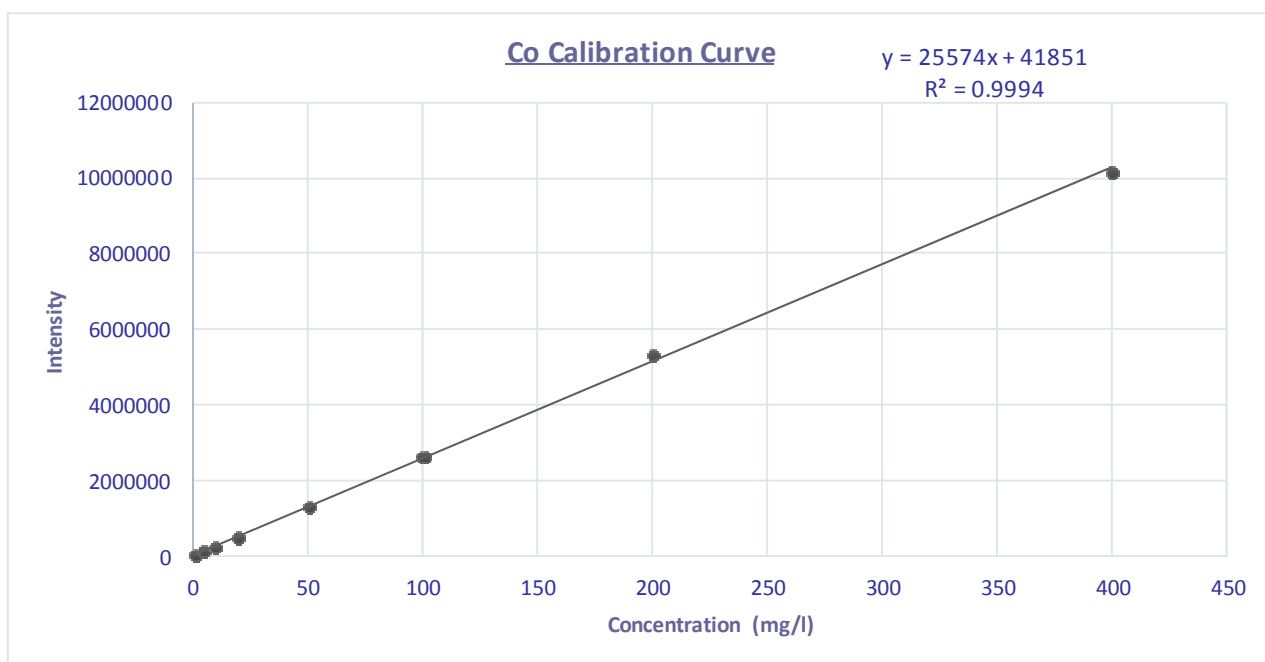
Figure 4.3: Co Calibration curve

Table 4.5: Cu ion concentration and instrument response

Std	Concentration (ppm)	Intensity (Cnt)
1	1	215366
2	5	1042540
3	10	2062900
4	20	4140820
5	50	9728330
6	100	19348700
7	200	37068500
8	400	71140800
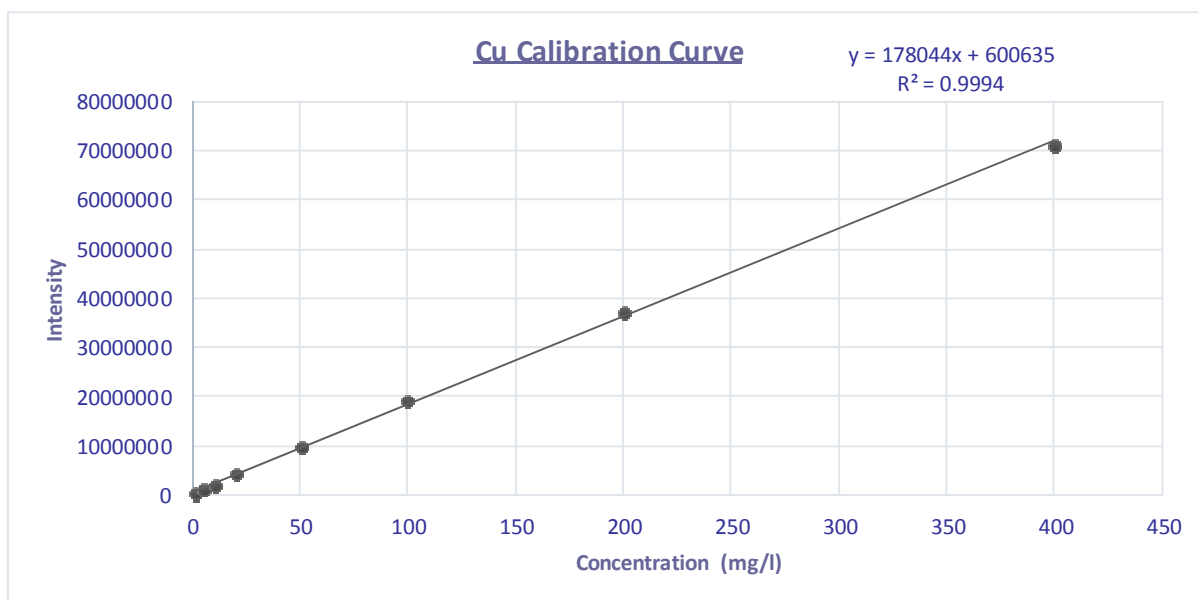
Figure 4.4: Cu Calibration curve

4.1.2.2 Zn, Ni, Co and Cu reference standards summary

The reference standards for each metal ion batch were analysed. For each metal ion, four samples of the same concentration were analysed on ICP-OES. In Table 4.6, the mean precision of the values is less than 20% presented under the RSD colunm. RSD, which is a relative standard deviation, measures the variability between the results.

Table 4.6: Reference Standards Summary

Metal Ion	Std 1	Std 2	Std 3	Std 4	Average	RSD
Zn	364.4	359.7	357.9	357.7	360.0	2.7
Ni	241.5	241.7	243.1	242.6	242.2	0.6
Co	336.9	344.0	332.4	322.4	332.9	7.8
Cu	332.4	334.5	334.9	333.8	333.9	1.0

4.1.3 Method accuracy

The accuracy of the method was assessed by analyzing a QC sample. Three sets of QC samples were analysed inbetween sample batches at the concentration of 25 ppm. In Table 4.7, calculated values of RSD, %CV and %RE were less than 20% .The relative error (RE) is the summary of the calculated deviation from the actual value. A quality control sample for Ni metal ion was lost during sample preparation and is indicated by a star sign in the table.

Table 4.7: Accuracy assessment between samples

Metal Ion	QC1 25ppm	QC2 25ppm	QC3 25ppm
Zn	29.6	27.2	28.4
Ni	24.2	23.6	*
Co	25.1	26.5	26.9
Cu	24.4	24.2	24.4
Average	25.8	25.4	26.5
RSD	2.2	1.5	1.7
%CV	8.6	5.9	6.2
%RE	3.3	1.5	6.1

*(Lost in the process)

4.1.4 Method precision

The precision of the method was determined by analyzing two QC samples at the level of 25 ppm. The second injection of Co metal ion QC sample could not be performed due to sample spillage during sample preparation.

Table 4.8: Assessment of repeatable injections

QC 25ppm				
Metal Ion	**Zn**	**Ni**	**Co**	**Cu**
Injection 1	26.4	24.2	25.1	24.2
Injection 2	25.2	23.6	*	24.4
Average	25.8	23.9	25.1	24.3
RSD	0.6	0.3	0.0	0.1
%CV	2.3	1.2	0.0	0.4
%RE	3.1	-4.3	0.4	-3.0

*(Lost in the process)

4.1.5 Method selectivity

The selectivity of the method was assessed by populating all the intensity values generated by the instrument response, as shown in Table 4.9. 0.04 M HNO_3 solution was used as blank sample. From the table the values are very low, lower than the lowest concentration of the analyte, only one blank sample which showed cobalt metal ion detection, this could be due to sample contamination.

Table 4.9: Assessment of method selectivity

No of Blanks	Zn Intensity (Cnt)	Cu Intensity (Cnt)	Co Intensity (Cnt)	Ni Intensity (Cnt)
1	-2.1	-2.6	9.2	-1.5
2	-2.1	-2.6	-1.3	-1.5
3	-2.1	-2.4	-1.3	-1.5
4	-2.1	-2.5	-1.2	-1.4
5	-2.1	-2.5	-2.3	-1.5
6	-2.1	-2.5	-0.3	-1.5
Average	-2.1	-2.5	0.5	-1.5

4.2 Summary

This chapter demonstrated validation of results according to the guidelines set for validation of heavy metal criteria and assessed the integrity of the method as well the instrument performance. Results reliability is the reflection of the method performance. The data presented is an additional proof that the method is acceptable.

CHAPTER 5: RESULTS AND DISCUSSION

The presented distribution coefficient values were calculated for the different nitric acid concentrations with varying methanol concentration values. Details of the results are given in tables below for each element. Appendice B represents the graphs of the tables specifically the relationship between the distribution coefficient and the concentration of the methanol present in the nitric acid.

Results and Discussion

5.1 Zn distribution coefficients in the presence of nitric acid with different methanol concentrations

The distribution coefficients values for Zn^{2+} were evaluated at different nitric acid concentrations containing varying methanol concentrations as shown in Table 5.1 to Table 5.7. High K_d values were found in 0.1 M and 0.2 M HNO_3, which decrease rapidly at higher concentrations of nitric acid because the excess of hydrogen ions of the acid prevents the sorption of the zinc ions on the resin. A correlation between the K_d values and the methanol concentrations was also noted; at low methanol concentration K_d values are lower and increases with the increase in methanol concentration.

Table 5.1: The effect of methanol on K_d values of Zn^{2+} in 0.1 M HNO_3

HNO_3 (M)	% methanol	Filtrate/ Solution(mg/l)	Resin/Calculated	Solution K_d value (mL/g)
0.1	0	128.6	232.0	180
0.1	10	116.1	244.5	210
0.1	20	112.6	248.1	220
0.1	40	102.4	258.2	251
0.1	60	94.9	265.7	279
0.1	80	85.9	274.7	319
0.1	90	75.0	285.6	380

In Table 5.1 the nitric acid concentration of 0.1 M was kept constant during sample preparation while the methanol concentration varies in all samples. The Zn values of the filtrate/solution were determined with the ICP-OES instrument. The resin values were calculated based on the difference between reference standards and filtrate/solution

values to obtain the exact amount of metal ions retained by the resin. The distribution coefficient values were calculated based on solution/filtrate values using Equation 3.1 in Chapter 3. All tables presented resemble each other, the layout of the tables is the same. In the table, keeping nitric acid concentration constant at 0.1 M and gradually increases methanol concentration from 0 to 90%, the distribution coefficient values increased with increase in methanol concentration.

Table 5.2: The effect of methanol on K_d values of Zn^{2+} in 0.2 M HNO_3

HNO_3 (M)	% methanol	Filtrate/ Solution(mg/l)	Resin/Calculated	Solution K_d value (mL/g)
0.2	0	181.6	179.1	99
0.2	10	178.1	182.5	102
0.2	20	168.6	192.0	114
0.2	40	130.3	230.4	177
0.2	60	77.4	283.2	366
0.2	80	71.8	288.8	402
0.2	90	65.5	295.1	450

Table 5.2, resembles Table 5.1, the difference is the nitric acid concentration of 0.2 M. The distribution coefficient values increase with the increasing methanol concentration.

Table 5.3: The effect of methanol on K_d values of Zn^{2+} in 0.5 M HNO_3

HNO_3 (M)	% methanol	Filtrate/ Solution(mg/l)	Resin/Calculated	Solution K_d value (mL/g)
0.5	0	232.3	128.3	55
0.5	10	212.5	148.1	69
0.5	20	195.1	165.5	84
0.5	40	183.9	176.8	96
0.5	60	164.5	196.1	119
0.5	80	146.0	214.6	147
0.5	90	134.9	225.7	167

Table 5.3 shows the distribution coefficients in 0.5 M HNO_3. The distribution coefficient values increase with increasing methanol concentration, however there is a drop in K_d values compared to Table 5.1 and Table 5.2.

Table 5.4: The effect of methanol on K_d values of Zn^{2+} in 1.0 M HNO_3

HNO_3 (M)	% methanol	Filtrate/ Solution(mg/l)	Resin/Calculated	Solution K_d value (mL/g)
1.0	0	272.9	87.7	32.1
1.0	10	269.7	90.9	33.7
1.0	20	251.9	108.7	43.2
1.0	40	240.2	120.4	50.1
1.0	60	214.0	146.6	69
1.0	80	193.8	166.8	86

In Table 5.4 shows that in 1.0 M HNO_3 the distribution coefficients are lower and the distribution coefficient values increase when the methanol concentration increases. The effect is more noticeable in Table 5.5 to Table 5.7 when the nitric acid concentration increases to 2.0 M, 3.0 M and 4.0 M. The gradual increase in nitric acid concentration lowers the distribution coefficient values, which indicate less metal ions, were sorbed on the resin.

Table 5.5: The effect of methanol on K_d values of Zn^{2+} in 2.0 M HNO_3

HNO_3 (M)	% methanol	Filtrate/ Solution(mg/l)	Resin/Calculated	Solution K_d value (mL/g)
2.0	0	302.2	58.5	19.3
2.0	10	294.5	66.2	22.5
2.0	20	282.0	78.6	27.9
2.0	40	261.1	99.6	38.1
2.0	60	238.8	121.9	51
2.0	80	224.0	136.6	61

Table 5.6: The effect of methanol on K_d values of Zn^{2+} in 3.0 M HNO_3

HNO_3 (M)	% methanol	Filtrate/ Solution(mg/l)	Resin/Calculated	Solution K_d value (mL/g)
3.0	0	309.4	51.2	16.5
3.0	10	303.4	57.2	18.9
3.0	20	300.7	59.9	19.9
3.0	40	282.5	78.1	27.6
3.0	60	264.7	96.0	36.3

Table 5.7: The effect of methanol on K_d values of Zn^{2+} in 4.0 M HNO_3

HNO_3 (M)	% methanol	Filtrate/ Solution(mg/l)	Resin/Calculated	Solution K_d value (mL/g)
4.0	0	336.7	23.9	7.1
4.0	10	322.7	37.9	11.7
4.0	20	317.1	43.5	13.7
4.0	40	313.9	46.7	14.9
4.0	50	301.2	59.4	19.7

5.2 Co distribution coefficients in the presents of nitric acid with different methanol concentrations

The Co results show a similar trend resembling Zn, presented below from Table 5.8 to Table 5.14. High K_d values were obtained in 0.1 to 0.5 M HNO_3 (Table 5.8 – 5.10) but the K_d values for Co are much higher than that obtained for Zn in the low acid concentrations. Tables 5.10 and 5.11 shows a decrease in K_d values and a sharp decrease is observed in Tables 5.12 – 5.14.

Table 5.8: The effect of methanol on K_d values of Co^{2+} in 0.1 M HNO_3

HNO_3 (M)	% methanol	Filtrate/ Solution(mg/l)	Resin/Calculated	Solution K_d value (mL/g)
0.1	0	39.1	293.8	751
0.1	10	36.1	296.8	822
0.1	20	28.1	304.8	1085
0.1	40	22.4	310.5	1386
0.1	60	7.2	325.7	4524
0.1	80	3.7	329.2	8897
0.1	90	3.2	329.7	>10e3

Table 5.9: The effect of methanol on K_d values of Co^{2+} in 0.2 M HNO_3

HNO_3 (M)	% methanol	Filtrate/ Solution(mg/l)	Resin/Calculated	Solution K_d value (mL/g)
0.2	0	93.7	239.2	255
0.2	10	71.5	261.4	365
0.2	20	60.2	272.7	453
0.2	40	37.4	295.5	790
0.2	60	21.6	311.3	1442
0.2	80	10.7	322.2	3006
0.2	90	7.5	325.4	4367

Tables 5.8 and 5.9 show that the distribution coefficients values increase rapidly with increasing methanol concentration but in 0.5 M HNO_3 the increase is much slower, as shown in Table 5.10 below.

Table 5.10: The effect of methanol on K_d values of Co^{2+} in 0.5 M HNO_3

HNO_3 (M)	% methanol	Filtrate/ Solution(mg/l)	Resin/Calculated	Solution K_d value (mL/g)
0.5	0	148.5	184.4	124
0.5	10	143.4	189.5	132
0.5	20	141.5	191.4	135
0.5	40	109.7	223.2	204
0.5	60	59.2	273.7	462
0.5	80	43.1	289.8	673
0.5	90	36.9	296.0	802

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Tables 5.11 to Table 5.14 show that an increase in nitric acid concentration greater 0.5 M give distribution coefficient values which are substantial lower than that obtained in 0.5 M HNO_3, containing methanol or no methanol.

Table 5.11: The effect of methanol on K_d values of Co^{2+} in 1.0 M HNO_3

HNO_3 (M)	% methanol	Filtrate/ Solution(mg/l)	Resin/Calculated	Solution K_d value (mL/g)
1.0	0	225.9	107.0	47.4
1.0	10	216.0	116.9	54
1.0	20	199.9	133.0	66
1.0	40	182.7	150.2	82
1.0	60	154.1	178.8	116
1.0	80	126.5	206.4	163

Table 5.12: The effect of methanol on K_d values of Co^{2+} in 2.0 M HNO_3

HNO_3 (M)	% methanol	Filtrate/ Solution(mg/l)	Resin/Calculated	Solution K_d value (mL/g)
2.0	0	252.9	80.0	31.6
2.0	10	241.9	91.0	37.6
2.0	20	235.8	97.1	41.2
2.0	40	214.4	118.5	55
2.0	60	183.2	149.7	82
2.0	80	145.5	187.4	129

Table 5.13: The effect of methanol on K_d values of Co^{2+} in 3.0 M HNO_3

HNO_3 (M)	% methanol	Filtrate/ Solution(mg/l)	Resin/Calculated	Solution K_d value (mL/g)
3.0	0	293.8	39.1	13.3
3.0	10	287.1	45.8	15.9
3.0	20	273.9	59.0	21.5
3.0	40	262.5	70.4	26.8
3.0	60	218.6	114.3	52

Table 5.14: The effect of methanol on K_d values of Co^{2+} in 4.0 M HNO_3

HNO_3 (M)	% methanol	Filtrate/ Solution(mg/l)	Resin/Calculated	Solution K_d value (mL/g)
4.0	0	312.6	20.3	6.5
4.0	10	304.1	28.8	9.5
4.0	20	302.6	30.3	10.0
4.0	40	280.8	52.1	18.6
4.0	50	263.9	69.0	26.1

5.3 Cu distribution coefficients in the presents of nitric acid with different methanol concentrations

Table 5.15: The effect of methanol on K_d values of Cu^{2+} in 0.1 M HNO_3

HNO_3 (M)	% methanol	Filtrate/ Solution(mg/l)	Resin/Calculated	Solution K_d value (mL/g)
0.1	0	37.4	296.6	793
0.1	10	34.1	299.8	880
0.1	20	26.1	307.8	1178
0.1	40	16.7	317.3	1904
0.1	60	8.3	325.6	3916
0.1	80	2.3	331.6	>10e3
0.1	90	2.1	331.8	>10e3

Tables 5.15 – 5.21 show that the distribution coefficients for Cu resembles that of Co. In 0.1 and 0.2 M HNO_3, containing methanol or no methanol. The K_d values increase rapidly to values > 1000 mL/g. The K_d values are relatively high in 0.5 M HNO_3, with or without methanol but decrease rapidly in higher acid concentrations.

Table 5.16: The effect of methanol on K_d values of Cu^{2+} in 0.2 M HNO_3

HNO_3 (M)	% methanol	Filtrate/ Solution(mg/l)	Resin/Calculated	Solution K_d value (mL/g)
0.2	0	79.9	254.1	318
0.2	10	71.9	262.0	364
0.2	20	65.9	268.0	407
0.2	40	47.0	287.0	611
0.2	60	25.3	308.6	1221
0.2	80	17.0	316.9	1865
0.2	90	14.4	319.6	2224

Table 5.17: The effect of methanol on K_d values of Cu^{2+} in 0.5 M HNO_3

HNO_3 (M)	% methanol	Filtrate/ Solution(mg/l)	Resin/Calculated	Solution K_d value (mL/g)
0.5	0	155.7	178.2	114
0.5	10	142.3	191.6	135
0.5	20	139.6	194.4	139
0.5	40	98.6	235.4	239
0.5	60	67.4	266.5	395
0.5	80	55.7	278.2	499
0.5	90	48.4	285.5	590

Table 5.18: The effect of methanol on K_d values of Cu^{2+} in 1.0 M HNO_3

HNO_3 (M)	% methanol	Filtrate/ Solution(mg/l)	Resin/Calculated	Solution K_d value (mL/g)
1.0	0	235.8	98.1	41.6
1.0	10	226.1	107.9	47.7
1.0	20	219.2	114.7	52
1.0	40	178.3	155.6	87
1.0	60	133.0	200.9	151
1.0	80	99.1	234.9	237

Table 5.19: The effect of methanol on K_d values of Cu^{2+} in 2.0 M HNO_3

HNO_3 (M)	% methanol	Filtrate/ Solution(mg/l)	Resin/Calculated	Solution K_d value (mL/g)
2.0	0	287.9	46.0	16.0
2.0	10	283.2	50.8	17.9
2.0	20	272.5	61.4	22.5
2.0	40	240.7	93.2	38.7
2.0	60	224.9	109.0	48.5
2.0	80	202.5	131.4	65

Table 5.20: The effect of methanol on K_d values of Cu^{2+} in 3.0 M HNO_3

HNO_3 (M)	% methanol	Filtrate/ Solution(mg/l)	Resin/Calculated	Solution K_d value (mL/g)
3.0	0	300.0	34.0	11.3
3.0	10	292.7	41.2	14.1
3.0	20	286.0	47.9	16.8
3.0	40	279.1	54.8	19.6
3.0	60	273.0	61.0	22.3

Table 5.21: The effect of methanol on K_d values of Cu^{2+} in 4.0 M HNO_3

HNO_3 (M)	% methanol	Filtrate/ Solution(mg/l)	Resin/Calculated	Solution K_d value (mL/g)
4.0	0	319.8	14.1	4.4
4.0	10	314.9	19.0	6.0
4.0	0	314.3	19.6	6.2
4.0	40	302.3	31.6	10.5
4.0	50	290.2	43.7	15.1

5.4 Ni distribution coefficients in the presents of nitric acid with different methanol concentrations

The distribution coefficients for Ni resemble that of Zn; relatively high values were obtained in 0.1 and 0.2 M HNO_3, containing methanol or no methanol, but the distribution coefficient values decrease with increasing acid concentrations.

Table 5.22: The effect of methanol on K_d values of Ni^{2+} in 0.1 M HNO_3

HNO_3 (M)	% methanol	Filtrate/Solution(mg/l)	Resin/Calculated	Solution K_d value (mL/g)
0.1	0	99.7	142.5	143
0.1	10	92.7	149.6	161
0.1	20	90.4	151.8	168
0.1	40	75.8	166.5	220
0.1	60	62.9	179.4	285
0.1	80	61.4	180.9	295
0.1	90	56.1	186.1	331

Tables 5.22 – 5.28 show that the distribution coefficient values increase with increasing methanol concentrations.

Table 5.23: The effect of methanol on K_d values of Ni^{2+} in 0.2 M HNO_3

HNO_3 (M)	% methanol	Filtrate/Solution(mg/l)	Resin/Calculated	Solution K_d value (mL/g)
0.2	0	118.1	124.1	105
0.2	10	111.8	130.4	117
0.2	20	102.0	140.3	138
0.2	40	83.5	158.8	190
0.2	60	48.3	193.9	402
0.2	80	47.1	195.1	414
0.2	90	51.8	190.4	367

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Table 5.24: The effect of methanol on K_d values of Ni^{2+} in 0.5 M HNO_3

HNO_3 (M)	% methanol	Filtrate/Solution(mg/l)	Resin/Calculated	Solution K_d value (mL/g)
0.5	0	154.7	87.6	57
0.5	10	144.2	98.0	68
0.5	20	134.6	107.7	80
0.5	40	129.7	112.5	87
0.5	60	112.2	130.0	116
0.5	80	106.2	136.0	128
0.5	90	120.8	121.4	100

Tables 5.24, 5.25, 5.26, 5.27 and 5.28 show that the K_d values are lower compared to the K_d high values obtained in 0.1 and 0.2 M HNO_3 and decrease with increasing acid concentration. The distribution coefficient values increase from low values to high values with the increase in methanol concentration.

Table 5.25: The effect of methanol on Kd values of Ni^{2+} in 1.0 M HNO$_3$

HNO$_3$ (M)	% methanol	Filtrate/ Solution(mg/l)	Resin/Calculated	Solution K$_d$ value (mL/g)
1.0	0	181.3	60.9	33.6
1.0	10	178.5	63.7	35.7
1.0	20	171.0	71.3	41.7
1.0	40	139.8	102.4	73
1.0	60	129.2	113.0	88
1.0	80	118.4	123.9	105

Table 5.26: The effect of methanol on Kd values of Ni^{2+} in 2.0 M HNO$_3$

HNO$_3$ (M)	% methanol	Filtrate/ Solution(mg/l)	Resin/Calculated	Solution K$_d$ value (mL/g)
2.0	0	208.7	33.5	16.1
2.0	10	210.6	31.6	15.0
2.0	20	202.2	40.0	19.8
2.0	40	190.0	52.2	27.5
2.0	60	174.4	67.8	38.9
2.0	80	157.0	85.2	54

Table 5.27: The effect of methanol on Kd values of Ni^{2+} in 3.0 M HNO$_3$

HNO$_3$ (M)	% methanol	Filtrate/ Solution(mg/l)	Resin/Calculated	Solution K$_d$ value (mL/g)
3.0	0	223.6	18.6	8.3
3.0	10	216.6	25.7	11.8
3.0	20	216.5	25.7	11.9
3.0	40	202.5	39.8	19.6
3.0	60	194.8	47.5	24.4

Table 5.28: The effect of methanol on Kd values of Ni^{2+} in 4.0 M HNO$_3$

HNO$_3$ (M)	% methanol	Filtrate/ Solution(mg/l)	Resin/Calculated	Solution K$_d$ value (mL/g)
4.0	0	237.0	5.3	2.2
4.0	10	232.7	9.6	4.1
4.0	20	223.9	18.4	8.2
4.0	40	220.1	22.2	10.1
4.0	50	215.3	27.0	12.5

CHAPTER SIX: CONCLUSION

6.1 Conclusion

The research study is based on the determination of distribution coefficients for the elements in nitric acid and methanol mixtures on the Amberlyst 15 cation exchange resin. The results show that the distribution coefficients for Zn, Cu, Co and Ni decrease with increasing nitric acid concentration. Methanol has an impact on the distribution coefficient values; at low methanol concentrations, the distribution coefficient values were low but the values increase with increasing methanol concentrations.

The distribution coefficients show that the elements cannot be separated easily on a column containing Amberlyst 15 resin unless a long resin column is used to separate Co from Zn, Cu and Ni. Co will be sorbed on the resin from 3.0 M HNO_3 – 60% methanol. Zn, Cu and Ni should pass slowly through the column and can be eluted with 3.0 M HNO_3 – 50% methanol followed by 4.0 M HNO_3 – 50% methanol. Finally, Co can be eluted by 4.0 M HNO_3.

6.2 Recommendation

Further research may include work on the following:

- Influence of the nitric acid concentration on the sorption of the elements on the Amberlyst 15 resin.
- Separation mechanism of monovalent, trivalent metal ions on Amberlyst 15 resin and their separation response to Amberlyst 15 resin.
- Separation of metal ions in a small scale using HPLC and ion exchange chromatography column containing Amberlyst 15 stationary phase.

6.3 Delineation and Limitations

- The study only focused on a few elements of the transition group of the periodic table.
- Nitric acid and methanol were the only chemical reagents utilised for the separation of the elements.
- Amberlyst 15 cation exchange resin was the only resin used in the study.
- ICP-OES instrument breakdown caused the study not to be completed on time.

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APPENDICES

Appendix A

Appendix A.1: Preparation of Metal ion salts

Stock solution of 0.10 m moles of monovalent element in distilled water

$N_2NiO_6.6H_20$: Ni^{2+} = $\underline{290.79g/mol}$
     58.69g/mol   = 4.9547

     $\underline{58.69g/mol \times 50ml}$
      1000   = 2.9345 g
            = 14.5396 g (weigh 14.5396g in 50 ml volumetric

flask)

Stock solution of 0.05 m moles of divalent elements in distilled water

Cu(NO3)$_2$.3H$_2$O : Cu^{2+} = $\underline{241.60g/mol}$
        63.55g/mol   = 3.8017 salt = 1g Cu

       $\underline{63.55 \times 50}$
        1000   = 3.1775 g Cu

      3.8017 = 1g
       X   = 3.17775g
       Xg = 12.0800g (weigh 12.0800g in 50 ml volumetric flask)

 Zn (NO3)$_2$.6H$_2$O : Zn^{2+} = $\underline{297.46g/mol}$
         65.38g/mol = 4.5497 = 1g Zn

     = $\underline{65.38 \times 50}$
       1000
     = 3.2690g Zn
     Xg = 14.8730g (weigh 14.8730g in 50 ml volumetric flask)

Co (NO3)$_2$.6H$_2$O : Co $^{2+}$ = $\underline{291.03g/mol}$
         58.93g/mol   = 4.9386 = 1g Co

    $\underline{58.93 \times 50}$
     1000   = 2.9465
        Xg = 14.5516g (weigh 14.5516 g in 50 ml volumetric flask)

Appendix A.2: Preparation of Nitric Acid reagents

10 M HNO_3 in 2000 ml volumetric flask: Add 686.047 ml of 65% HNO_3 and make up to 2000ml with distilled water.

5.0 M HNO_3 in 2000ml volumetric flask: Double dilute 10 M HNO_3 with distilled water.

0.04 M HNO_3 for preparation of reference standards: Add 100 ml of 0.4M HNO_3 and make up to 1000ml with distilled water.

0.4M HNO_3 for reconstitution: Add 80 ml of 5.0M HNO_3 into 920 ml of distilled water (make up in 1000 ml)

Appendix A.3: Sample calculation for QC sample at 25 ppm from standard stock of 50 ppm

$\underline{50\ ppm}$

2   = 25 ppm (in 100ml volumetric flask)

The stock standard was double diluted with 0.4 M HNO_3

Appendix A.4: Sample calculations for Zn $^{2+}$ at 0.1M HNO_3

Zn $^{2+}$ Resin (calculated) = Average reference standards – filtrate/ solution

$$= 360.6 – 128.6$$
$$= 232.0$$

K_d (Solution) = [Ref.Std mg/l] – [Solution mg/l] x volume of the solution (ml)

Mass of the resin (g) x [solution (mg/l)]

$$= \frac{360.0 – 128.6 \times 50ml}{0.5g \times 128.6}$$

$$= 179.9\ ml/g$$

$$= 180.0\ ml/g$$

Appendix B

Appendix B.1: Graphical representation between Methanol and Kd values of Zn^{2+} at different nitric acid concentrations.

The effect of methanol on (Kd) values of Zn2+ at 0.1M HNO3

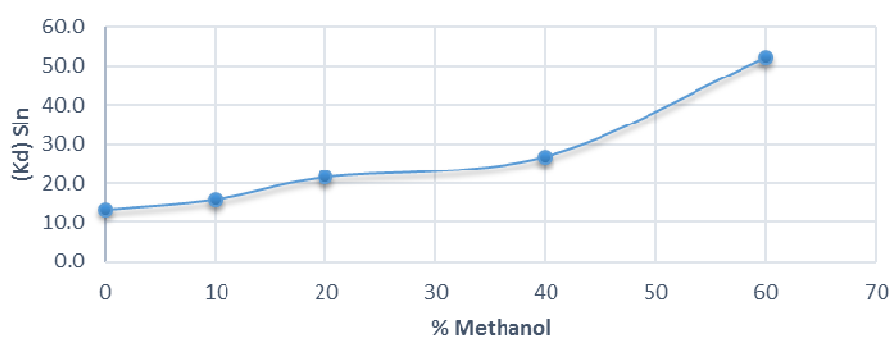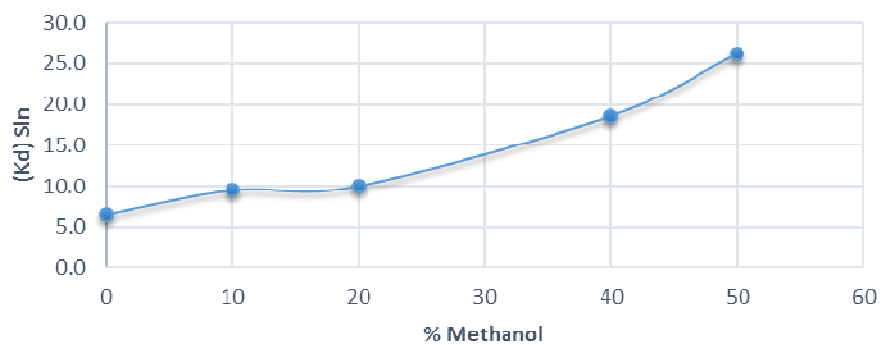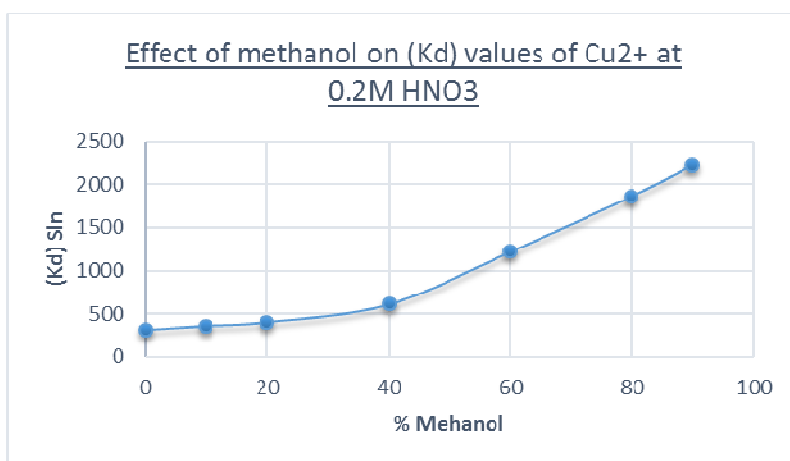The effect of methanol on (Kd) values of Zn2+ at 0.2M HNO3

The effect of methanol on (Kd) values of Zn2+ at 0.5M HNO3
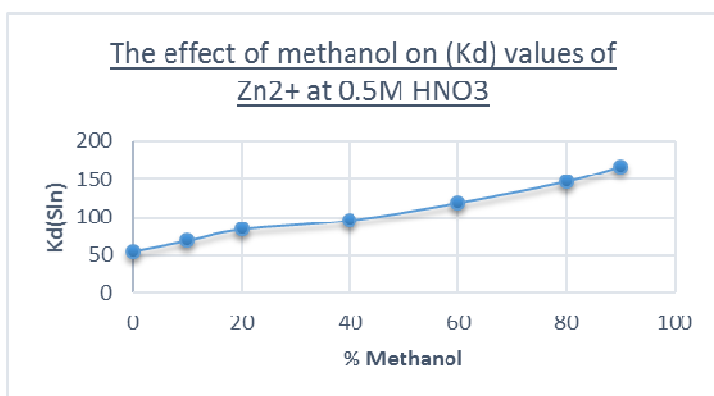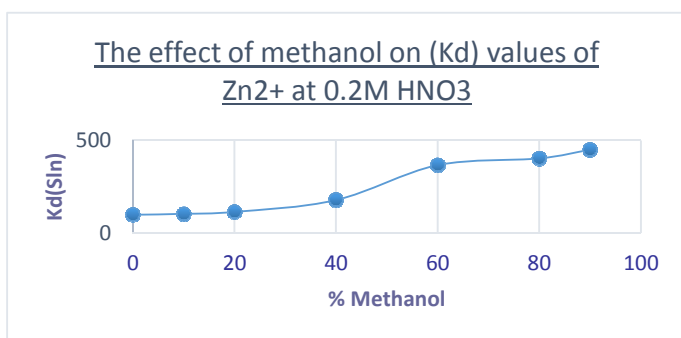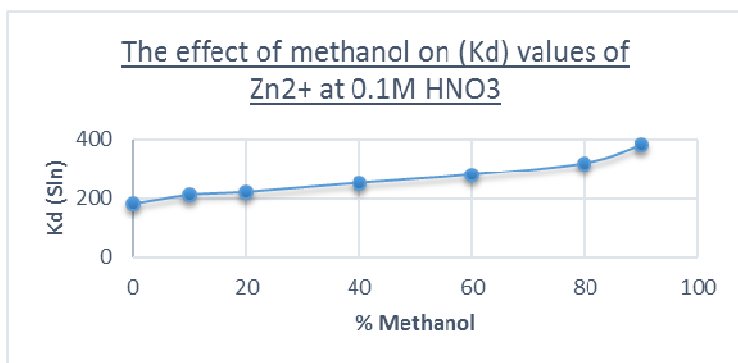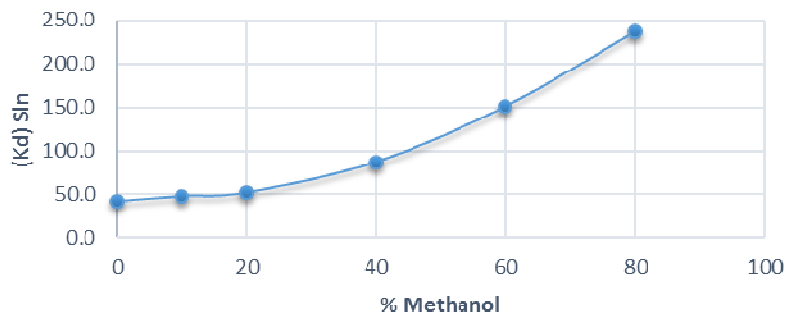
The effect of methanol on (Kd) values of Zn2+ at 1.0M HNO3
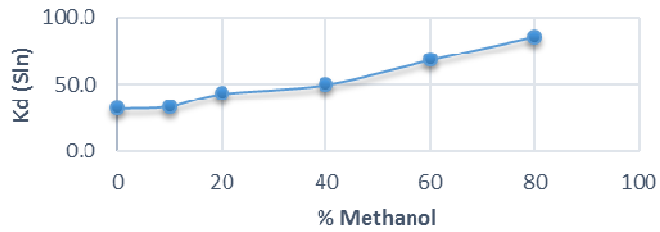
The effct of methanol on (Kd) values of Zn2+ at 2.0M HNO3
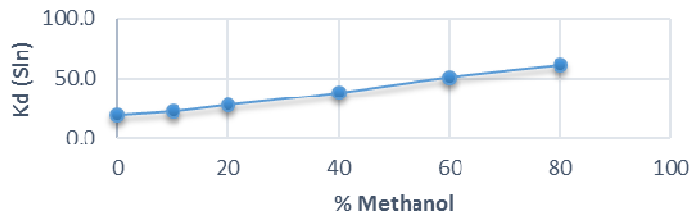
The effect of methanol on (Kd) values of Zn2+ at 3.0M HNO3
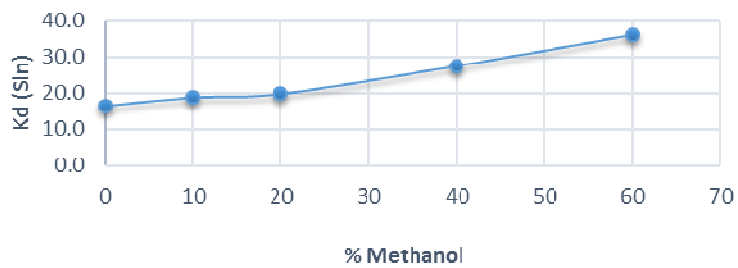
The effect of methanol on (Kd) values of Zn2+ at 4.0M HN03
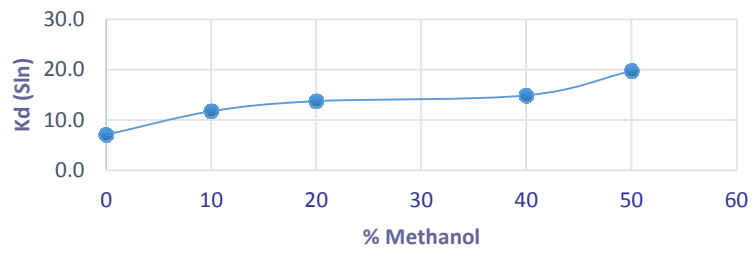
Appendix B.2: Graphical representation between Methanol and Kd values of Co^{2+} at different nitric acid concentrations.
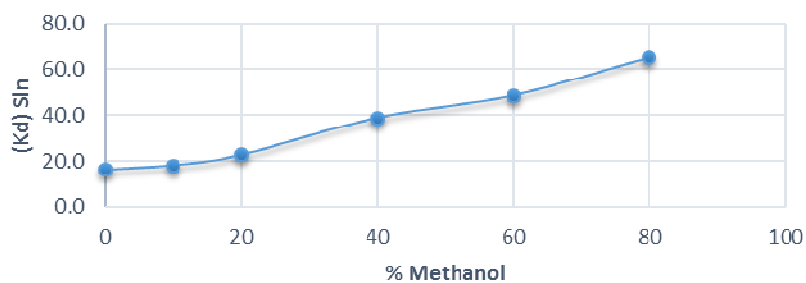

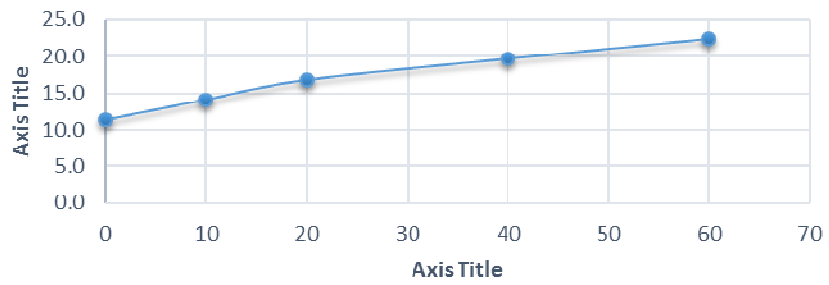Effect of methanol on (Kd) values of Co2+ at 0.1M HNO$_3$

Effect of methanol on (Kd) values of Co2+ at 0.2M HNO3

Effect of methanol on (Kd) values of Co2+ at 0.5M HNO3
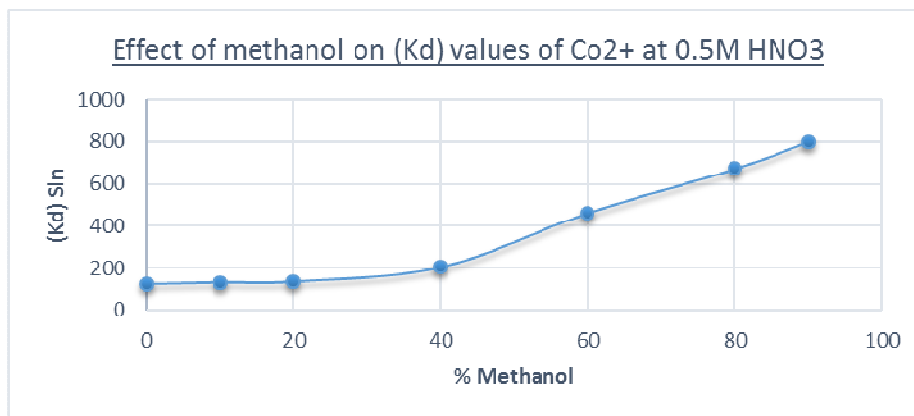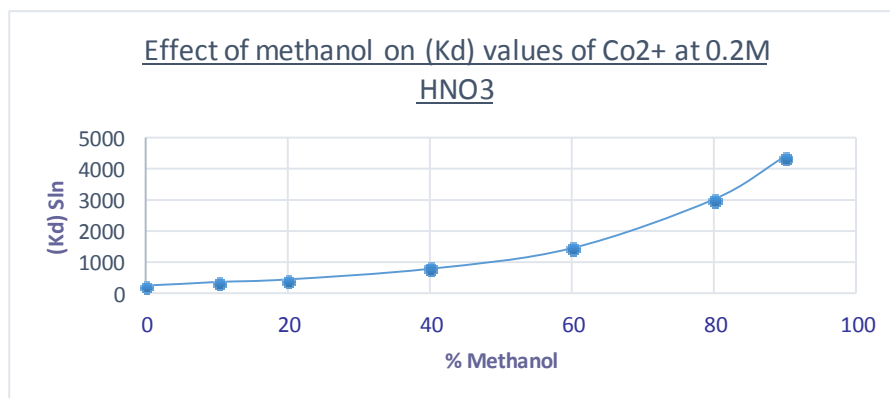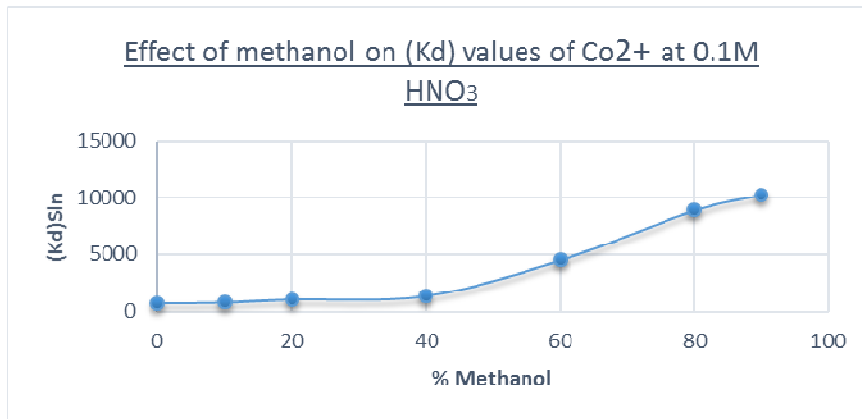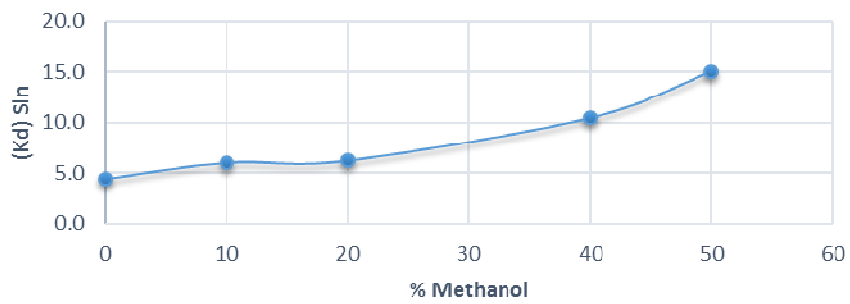
Effect of methanol on (Kd) values of Co2+ at 1.0M HNO3
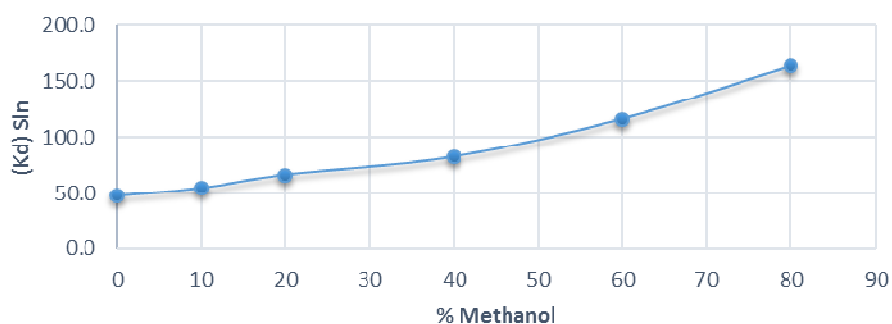
Effect of methanol on (Kd) values of Co2+ at 2.0M HNO3
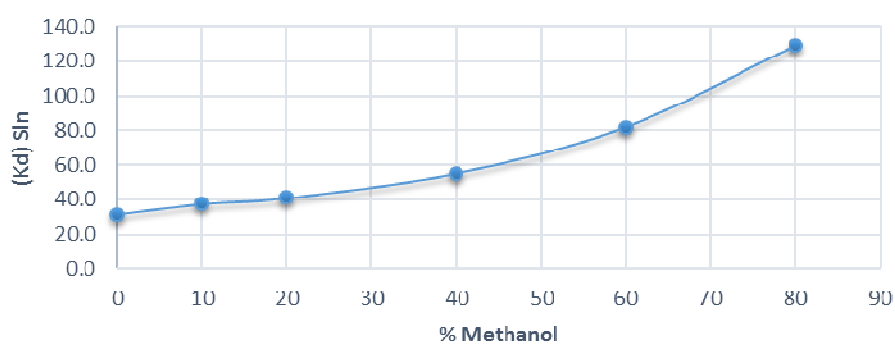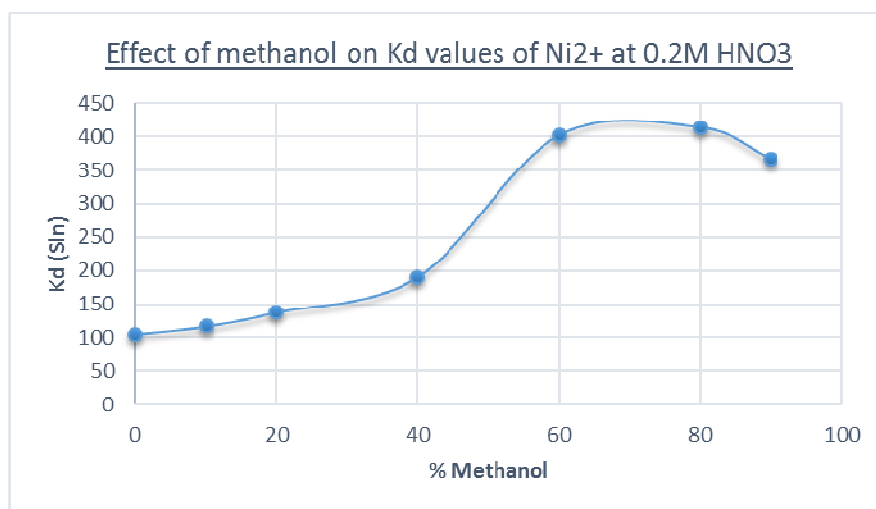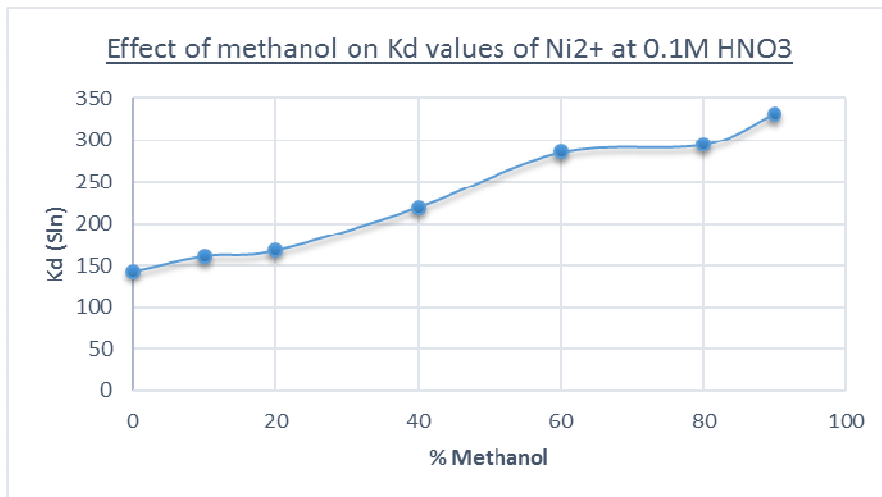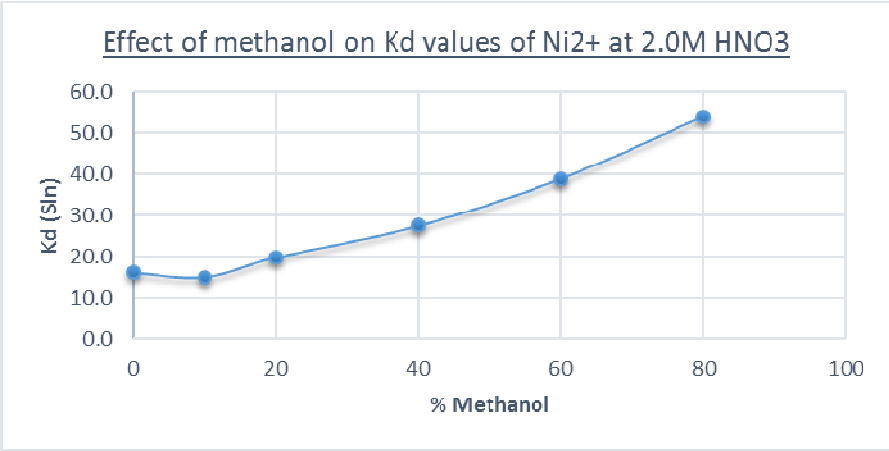

Effect of methanol on (Kd) values of Co2+ at 3.0M HNO3

Effect of methanol on (Kd) values of Co2+ at 4.0M HNO3

Appendix B.3: Graphical representation between Methanol and Kd values of Cu^{2+} at different nitric acid concentrations.

Effect of methanol on (Kd) values of Cu2+ at 0.1M HNO3

Effect of methanol on (Kd) values of Cu2+ at 0.2M HNO3
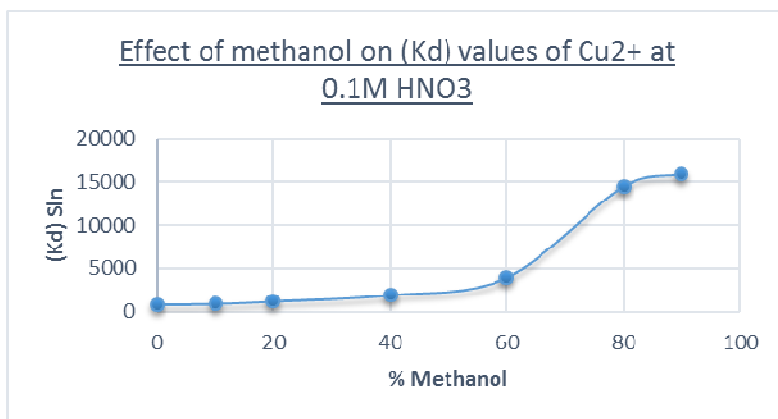
Effect of methanol on (Kd) values of Cu2+ at 0.5M HNO3
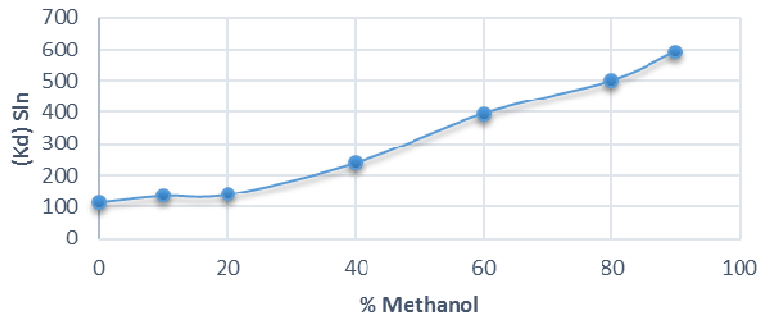
Effect of methanol on (Kd) values of Cu2+ at 1.0M HNO3

Effect of methanol on (Kd) values of Cu2+ at 2.0M HNO3

Effect of methanol on (Kd) values of Cu2+ at 3.0M HNO3
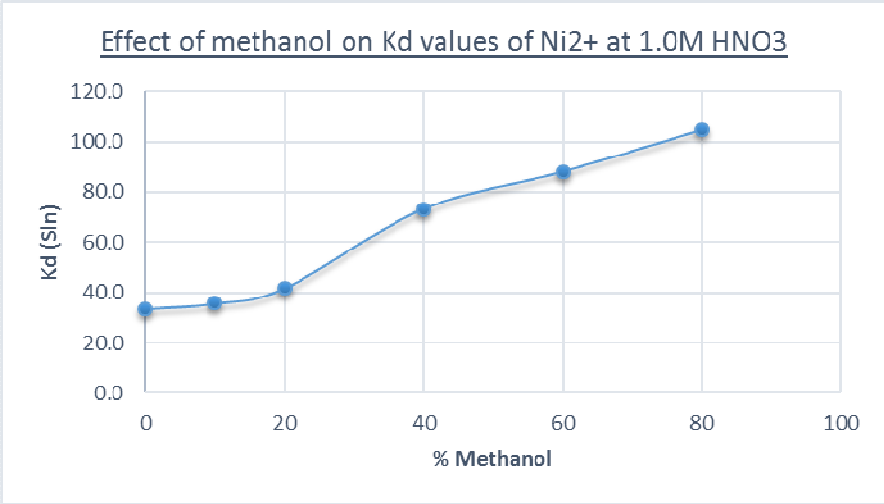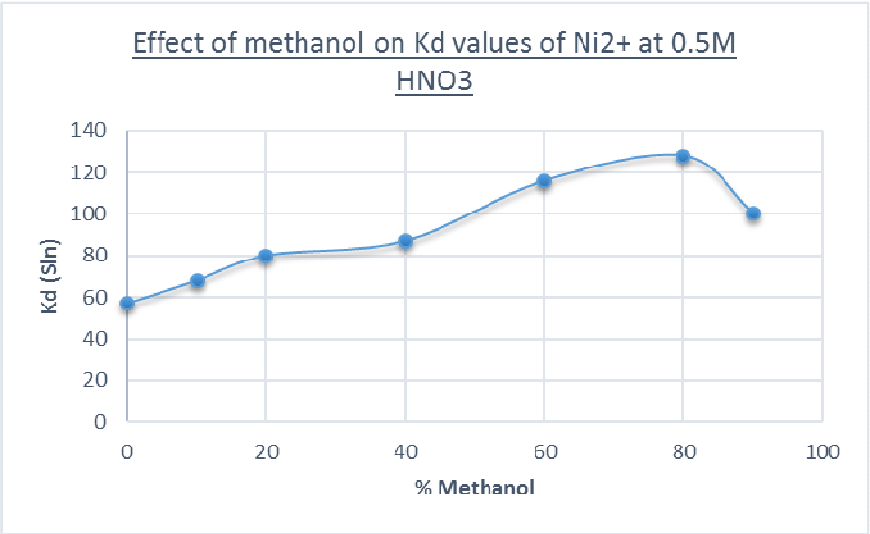

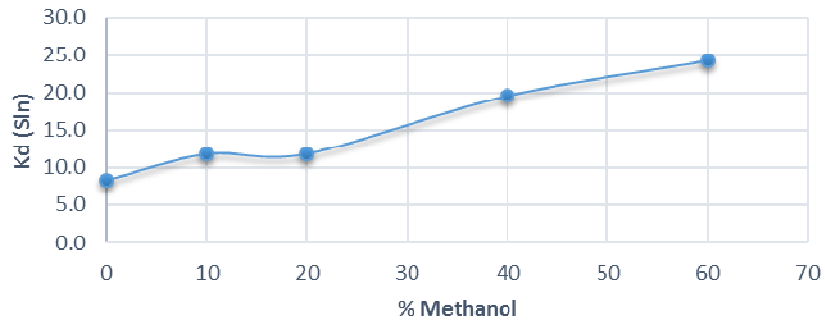Effect of methanol on (Kd) values of Cu2+ at 4.0M HNO3

Appendix B.4: Graphical representation between Methanol and Kd values of Ni^{2+} at different nitric acid concentrations.

Effect of methanol on Kd values of Ni2+ at 0.1M HNO3

Effect of methanol on Kd values of Ni2+ at 0.2M HNO3

Effect of methanol on Kd values of Ni2+ at 0.5M HNO3

Effect of methanol on Kd values of Ni2+ at 1.0M HNO3

Effect of methanol on Kd values of Ni2+ at 2.0M HNO3

Effect of methanol on Kd values of Ni2+ at 3.0M HNO3

Effect of methanol on Kd values of Ni2+ at 4.0M HNO3