Cape Peninsula
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THE BEHAVIOUR OF SELECTED ELEMENTS ON THE CATION EXCHANGE RESIN DOWEX 50W-X4 IN NITRIC ACID MEDIUM

by

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DECLARATION

I, ZANOXOLO MABUWA, declare that the contents of this thesis denote my own work, and that the thesis has not previously been submitted for academic examination towards any qualification. Moreover, it represents my own opinions and not those of the Cape Peninsula University of Technology.

Signed ______________________ Date : September 2022

ABSTRACT

Ion exchange chromatography is an important technique for the separation and isolation of elemental ions in a solution. Studying the distribution coefficients of individual elements provides important information regarding the separation and isolation of the element from a matrix. This study was carried out to determine the distribution coefficient for the selected monovalent elements: Li, Na, K, Rb and Ag; divalent elements: Mg, Ca, Ba Sr, Zn, Cu, Co, Mn, Cd and Pb; together with Al(III) and Fe(III). The strong acid cation exchange resin, Dowex 50W-X4, was used to determine the distribution coefficients of the elements in various nitric acid concentrations using the batch method.

The distribution coefficients of individual elements provide vital information for possible separation and isolation of the elements from the matrix, and from each other. Concentrated HCl (5.0 M) is strong enough to elute the elements from the resin. The solution containing the cation exchange resin and the specific element, in the appropriate nitric acid concentration (0.1 M, 0.2 M, 0.5 M, 1.0 M, 2.0 M, 3.0 M, or 4.0 M) was shaken for 24 hours at 25 ºC. The phases were separated, and the concentration of the element determined by ICP-OES. The distribution coefficient for the element was then calculated from the values obtained. The distribution coefficients of the elements studied on DOWEX 50W-X4 were compatible with the distribution coefficients of the elements on AG50W-X8.

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GLOSSARY OF TERMS

HNO_3	Nitric acid
ICP-OES	Inductively coupled plasma-optical emission spectrometry
SEM/ EDS	Scanning Electron Microscope – Energy Dispersive Spectroscopy
FTIR-ATR	Fourier Transform Infrared - Attenuated total Reflectance
Kd	Distribution coefficient
cm	Centimetre
mL	Millilitre
mmole	milimoles
mg/L	Milligrams per litre
α	Separation factor
KeV	Kilo electron Volts
Amp	Ammeter
L/min	Litres per minute
mbar	millibar
V	Volts
W	Watts

APPENDICES

CHAPTER 1

1 INTRODUCTION

1.1 Background

Pollutants in the environment such as heavy metals pose a great risk due to the toxicological and physiological effects they can have on the environment as well as public health. Wastewater from different industries comprising pollutants like heavy metals, untreated or partially treated, enter rivers and oceans and lead to contamination. The treatment of contaminated waters and effluent is pertinent to the removal of heavy metals before they enter water streams. Ion exchange chromatography or materials have been used to solve these industrial and environmental concerns. Ion exchange chromatographic techniques offer the best value for money for the separation and isolation of elemental ions in solution due to their simplicity and because they require fewer steps of analytical procedure. The distribution coefficients of individual elements provide important information about possible separation and isolation of the elements from the matrix and from each other.

The term *chromatography* was first used by a Russian chemist named Twett. Derived from the Greek word for 'colour' (Chroma) and 'write' (ein), it was used in the work on the separation of coloured plant pigments into bands of chalk (Fritz, 2004). In the 1930s, chromatographic techniques such as ion-exchange chromatography and thin layer chromatography grew in frequent use (Fritz, 2004). In the 1940s, chromatography was developed into gas chromatography, followed by partition chromatography in the 1950s. In the 1960s, with a swift growth in the use of chromatographic techniques universally, the process was then applied within various disciplines such as chemistry, biology and medicine. It became a production process because it is sensitive enough for trace analyses (Fritz, 2004; Moustafa & Morsi, 2013). Recognition of these chromatographic techniques came in the 20th century, although chromatographic-like separation processes already occur in nature (migration of solutions through soils [osmosis], clays and porous rocks).

The *chromatographic method* was then defined as combined components, separated on an adsorbent, packed on a column in a flowing system. IUPAC later formulated the definition as follows: the separation of components of a sample matrix, constituents are scattered in two phases (mobile phase and stationary phase) of which one is occupying sites on the stationary phase and thus, the opposite one is taken by the mobile phase (Fritz, 2004).

1.2 Problem statement

Finding more cost-effective techniques for the separation and isolation of metal ions from aqueous solutions are continuously researched. Because of the ongoing climate change, there is not enough rain throughout the rainy season. It's important to discuss amicably sea water desalination methods, which include the isolation and separation of metals found in sea water. Metals are frequently used in manufacturing sectors and can enter the environment as trash, which can have an impact on human lives. Both in their elemental and compound forms, they can be hazardous to the environment. The elements (Li, Na, K, Rb, Cs and Ag), divalent elements (Mg, Ca, Sr, Ba, Mn, Co, Ni, Cu, Zn, Cd and Pb) and trivalent elements (Al[III] and Fe[III]) used in this research are widely used, they easily exist in the environment and pose a great risk to human life and ecosystems. The establishment of isolation and separation methods for these metals, which are frequently found in environmental pollution, is required. There is limited data and minimal literature concerning the distribution coefficients of elements on strong acid cation exchange resin Dowex 50W-X4 for the separation of metal ions. Dowex resins are more cost-effective than commonly used Bio-Rad resins. Dowex resins could therefore serve as an alternative if their performance is proven to be comparable.

1.3 Research objectives

The main objective of this study was to ascertain the distribution coefficients (K_d) of 17 elements on Dowex 50W-X4, using various nitric acid medium concentrations.

The sub-objectives of this study were as follows:

- Characterization of resin chemical components by SEM/EDX and the FTIR.
- The K_d values obtained were used to perform elution curve experiments for various elements to determine the conditions for their possible separations.
- The obtained results were compared to those determined on AG 50W-X8 on nitric acid media as determined by Strelow *et al.* (1965).

1.4 Research design and methodology

The concentration range of 0.10 to 4.0 M nitric acid was used for sorption of the selected monovalent elements, divalent elements and trivalent elements on cation exchange resin Dowex 50W-X4 (hydrogen form and 100-200 mesh particle size), categorised as strong acid resin. The Inductively Coupled Plasma instrument was used for quantitative analysis of the element concentration after it was eluted from the resin. The instrument ICP-OES was considered due to its lower inter-element interference because of higher temperatures. Multi-element analysis can be undertaken for minute samples as well as to determine the low concentrations of elements that are highly resistant to decomposition. The distribution coefficient values were determined, and elution curve experiments were then performed for certain elements.

1.5 Delimitation of the research

Only the selected monovalent elements (Li, Na, K, Rb, Cs and Ag), divalent elements (Mg, Ca, Sr, Ba, Mn, Co, Ni, Cu, Zn, Cd and Pb) and trivalent elements (Al[III] and Fe[III]) will be investigated, based on the availability of chemicals. The scope of this work will focus solely on the strong acid cation exchange resin, Dowex 50W-X4. Nitric acid will be the only media that will be used at various concentrations.

2 CHAPTER 2

2.1 Literature review

Ion exchange is a method in which a solution containing ions in an experimental setup is reacted with either a cation exchange or anion exchange resin and active ions on the resin are exchanged by ionic species of similar charge from the analyte solution. An equilibration process is represented by the following reaction (Braithwaite & Smith, 2012):

$$n(R^{-}H^{+}) + M^{n+} \leftrightarrow (R^{-})_nM^{n+} + nH^{+} \qquad \textbf{Eq. 2-1}$$

Ion exchange resins are produced by a chemical reaction that is based on cross-linked polystyrene divinylbenzene copolymers containing ion exchanging functional groups. The cation exchange resins are functionalised by anionic functional groups with positively charged mobile ions. The ion exchanger favours high charge ions and ions that interact strongly with the functional groups of the exchanger (Alyüz & Veli, 2009; Barbaro & Liguori, 2009). Regarding the cation exchange process, a cation exchanger is one which involves the exchange of cations (positively charged ions) on the functional group attached onto the polymer resin. Tertiary or quaternary ammonium groups, such as $–CH_2\text{-}NR_2$ or $–CH_2\text{-}N+R_3$, are the polar groups in anion exchangers and they function in a comparable way. The anion exchangers are typically supplied in a chloride form rather than in a hydroxide form because the chloride form has greater stability (Braithwaite & Smith, 2012).

Factors such as mass-to-charge ratio (m/z), ionic radius of the metal ion and distribution coefficient are key to the separation of individual metal ions from the matrix. It is imperative to determine the distribution coefficient of the elements at different acid concentrations to establish the possibility of metal separation. Thus, the two chemical reactions taking place during ion exchange chromatography are adsorption and desorption on the resin surface (Dudas, 2011).

2.2 Different types of resin

Resins are categorised and illustrated as strong and weak acid and strong base and weak base resins. Strong acid resins get their names based on the chemical behaviour they exhibit, which is similar to that of a strong acid (Braithwaite & Smith, 2012). These resins are available in both the acid ($R\text{-}SO_3H$) and salt ($R\text{-}SO_3Na$) form of the sulfonic acid group, active ions being H^+ and Na^+ respectively.

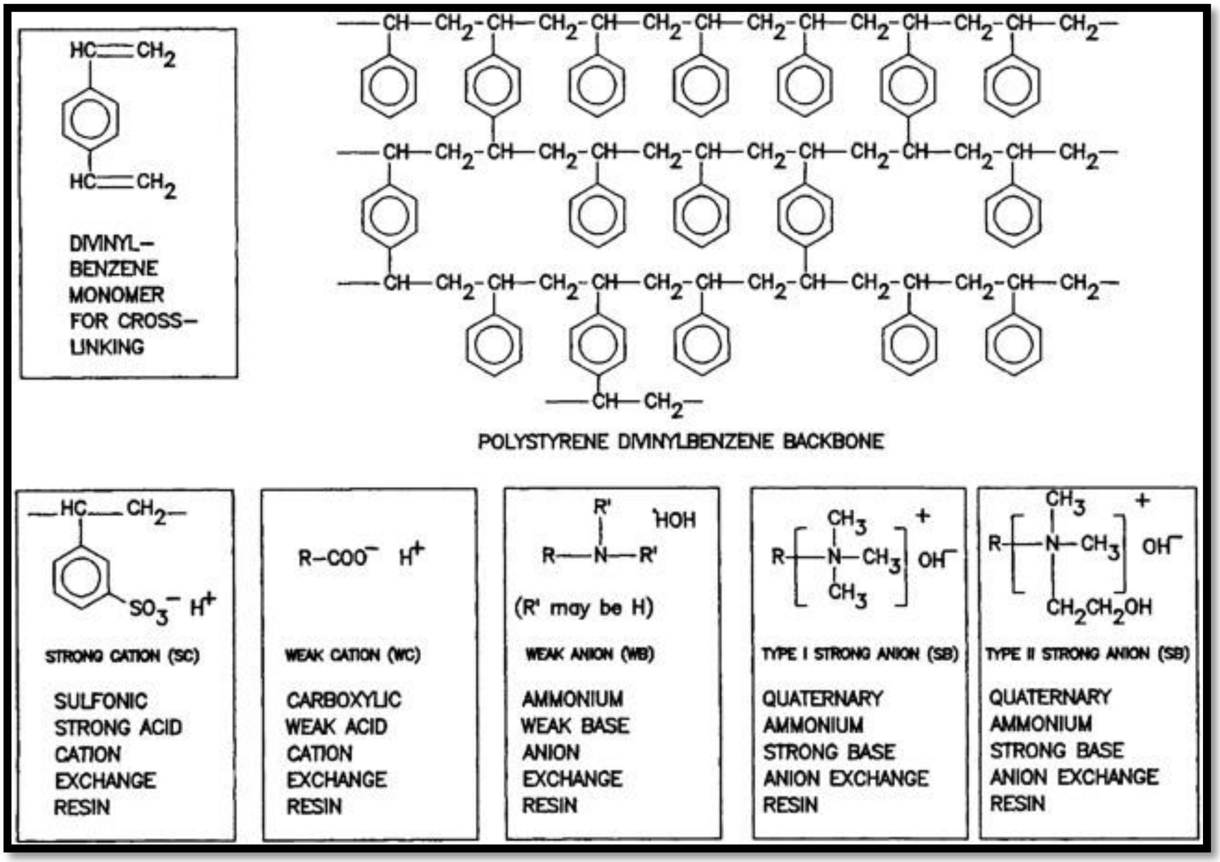

Figure 2-0-1: Categorised structural representation of the polymer ion exchange resins (Bajpai, 2018)

These resins in the hydrogen form are useful for complete deionization, whereas sodium form resins are used for water softening applications (calcium and magnesium removal). To reuse the resin, it is converted back to the hydrogen form (regenerated) by contact with a strong acid solution, or the resin can be converted to the sodium form with a sodium chloride solution (Braithwaite & Smith, 2012).

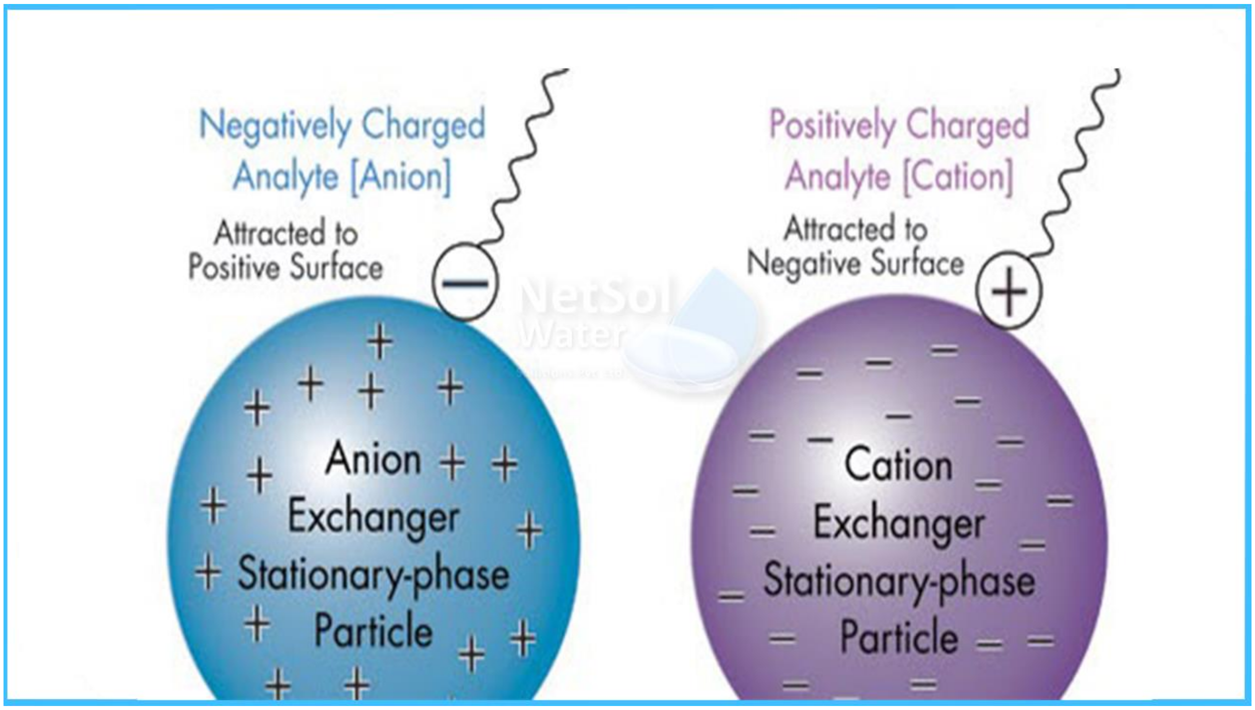

Figure 2-0-2: General classification of ion exchange of resins (Taiyuan Lanlang Technology Industrial Corp., n.d.)

The strong acid resins (hydrogen and sodium form) will exhibit a high separation factor. Strong acid resins are flexible because their separation experiments are not pH dependent and their exchangeable Na^+ and H^+ ions are readily available for exchange over the entire pH range. The strong acid and strong base resins are widely used compared to the weak varieties due to the wide pH range that the strong acid and base resins accommodate. In acidic or alkaline media, the resins can maintain their properties. In contrast, both weak acid and weak base resins are pH dependent. Weak acid resins are somewhat selective towards certain divalent ions, and resin selectivity can be measured experimentally (Braithwaite & Smith, 2012). In this study, as a strong cation exchange resin will be used, pH will not be the considered in the parameters.

2.2.1 Anion exchange resins

Anion exchange resins have positively charged surfaces that are able to attract negative ions in order to be separated. Anion exchange resins can be either strong or weak base. Strong basic anion resins maintain their positive charge across a good pH range, whereas weak basic anions are neutralised at higher pH levels. This can be defined by the following reaction:

$R\text{-}NH_3OH + HNO_3 \leftrightarrow R\text{-}NH_3NO_3 + H_2O$ **Eq. 2-2**

Where R- stands for the polymer group.

Anion exchange resins are predominantly applied within the purification of materials and metals (Braithwaite *et al.*, 1985). Metal ions can be separated on anionic resin on the bases of the metal ion forming a complex ion with the anion of the acid used in the separation. In the study of the isolation of uranium and its radioactive daughters such as thorium (Th^{4+}) and radium (Ra^{2+}) on anionic, resin did not form chloride complexes and were not retained on strongly anionic exchange resins (Monroy-Guzman, 2016). An anion exchange chromatography was the proposed method in the determination of the platinum group elements by using Dowex 1-X10 on the ICP-AES. The study was conducted on a wide variety of biological and environmental matrices (Petya *et al.*, 2002). The determination of Pt and Pd was possible with the use of anion exchange resin (Dowex 1-X10) with thiourea as an eluting agent (Petya *et al.*, 2002).

Nuclear waste is known to contain many beta emitters such as ^{3}H, ^{14}C, ^{60}Co, ^{90}Sr and ^{137}Cs as pollutants. Therefore, a highly effective chemical separation method is required to separate ^{55}Fe and ^{63}Ni from all other radionuclides. Isolation of ^{55}Fe and ^{63}Ni from the waste matrix was achieved with the hydroxide precipitation method. Anion exchange chromatography was used to separate ^{55}Fe and ^{63}Ni from each other, as well as from interfering radionuclides by Dowex 1x4 anionic resin (Morimoto *et al.*, 2011).

Weak basic anion resins do not maintain their charge at high pH levels, owing to their deprotonation. They have impressive character in maintaining excellent mechanical and chemical stability. Anion exchange resin regeneration involves the treatment of the resin with a strongly basic solution, typically NaOH, referred to as caustic soda. When these anion exchange resins are regenerated, the basic solution can flow through the resin packed in a column. Therefore, the negative ions that are trapped are then flushed out to renew the resin exchange capacity. The typical reaction that takes place is as follows:

$$N(R)_4\text{-}OH + HCl \leftrightarrow N(R)_4Cl + H_2O. \qquad \textbf{Eq. 2-3}$$

The weak acid and the weak base resins are only ionized in salt form, and thus their operation is pH dependent (Braithwaite *et al.*, 1985). Both weak acid and weak base resins may show a greater selectivity in certain circumstances.

2.2.2 Chelating resins

Chelating resins are ion exchange resins with ligands attached that can bond with metal cations. Chelating resins are generally cation exchange resins in relation to their chelation properties. Chelating functionality, demonstrated by the Lewis base activity, are selective due to factors such as ionic charge (divalent ions are preferred), hydrated ionic radius and ligand bonding according to the Lewis acid base theory (2022). The chelating resins (LewatitTP 214, Purolite S 920, Chelite S and Duolite GT 73) were used in the palladium (II) complexes recovery 0.1–2.0 M HCl–1.0 M NaCl and 0.1–2.0 M HCl–2.0 M NaCl system (Hubicki & Wołowicz, 2009).

Complexing agents form stable complexes with metals and are remarkably stable with transition metals. The chelating agent such as EDTA forms stable complexes with magnesium and calcium and is used in water softening processes to form complexes of these metals. EDTA-metal complex stability is pH dependent; hence, when studying distribution coefficients of metals using a chelating agent as an eluent, pH needs to be considered. It was determined that manipulating the pH of the EDTA-metal complex produced marked differences in K_d values which is valuable for separation and purification in ion exchange chromatography (Farha *et al.*, 2010).

The masking agent is the reagent that is typically used in chemical analysis, where it selectively reacts with chemical species in the sample matrix to enhance analysis results. In ion exchange chromatography, masking reagents can be used in the separation and purification of metals. Mutual separation of alkaline earth metals was previously studied on strong cationic resin and was achieved by employing cryptands as the masking reagents media. Magnesium was successfully separated from strontium and calcium in cryptand 221 on Amberlist 200CT, whereas strontium was successfully separated from magnesium and calcium in cryptand 222 on Amberlist 200CT (Turubou *et al.*, 2012).

Cation chelating resins such as Lewatit TP was used with sodium dithionite to recover metals like cobalt, nickel copper, zinc and chromium. The pH for the solution was manipulated for these metals where maximum recovery for copper was at pH 2.50, while nickel and cobalt were at pH 3.50 alongside zinc and chromium respectively (Junior *et al.*, 2019)**.**

2.2.3 Cation exchange resin

In cationic exchange chromatography, the polymer resin will possess negatively charged groups, which in turn will attract positively charged cations. These ionic exchange resins can be referred to as acidic ion exchange resins, due to their negative charge result from the ionization of acidic group. Cation exchangers can be subdivided into weak acid cation exchangers that are based on their carboxylic acid group and strong acid cation exchange resins based on the sulphonic acid group, as shown in Figure 2-1.

The resin known as strong cation exchange can be applied to the separation and purification of metals by employing a mixture of two solvents. Kuroda and Hosoi (1984) studied the behaviour of 16 metals on cation exchange resin AG 50W-X8, investigating their distribution coefficients in a nitric acid-oxalic acid mixture. The technique was applied on manganese nodules that could possibly contain some metals that would be of economic value. Manganese nodules are comprised of concentric layers of iron and manganese hydroxide. The technique showed success on the determination of major constituents' iron. The manganese minor elements such as copper, nickel, zinc and cobalt were also determined.

Cation exchange chromatography was applied to enhance the separation and purification of chromium (Cr) from the geological constituents. The variations within the stable isotope ratios of Cr made it challenging to trace and quantify Cr(VI) contamination from both anthropogenic sources and natural attenuation from redox reactions of Cr from mineral constituents. This concern was addressed by studying the K_d values of 38 elements using BioRad AG50-X8 cation exchange resin in various concentrations of HNO_3 (Davies, 2012).

The Dowex 50W-X4 cation exchange resin based on sulphonic acid group was used for this study. The synthesis reaction is illustrated in Figure 2-3 below.

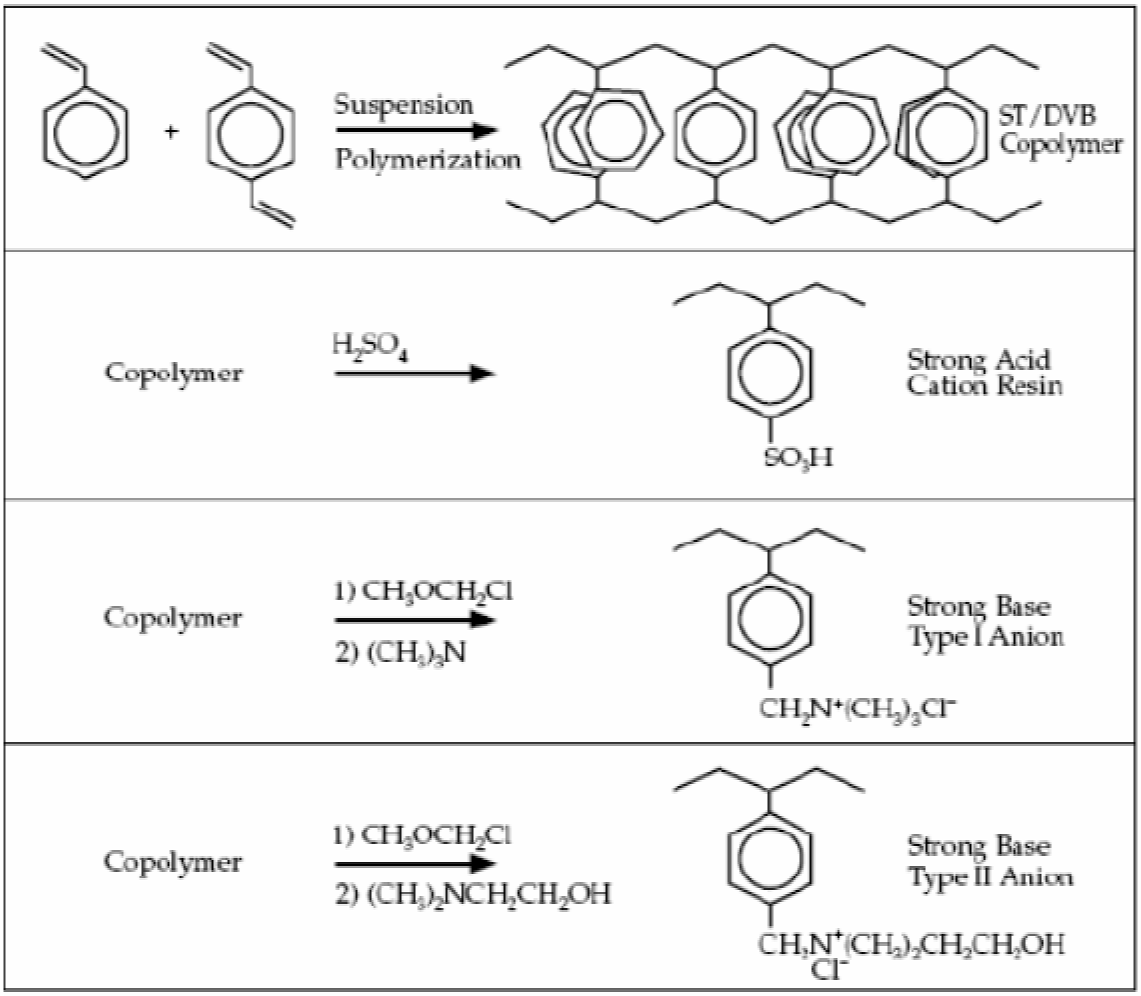

Figure 2-0-3: Synthesis of Dowex ion exchange resin (www.lenntech.com, n.d.)

The cationic exchange will take place when the resin comes into contact in equilibrium with the ionic solution containing the ionic analyte. The exchange will be with the hydrogen ion.

2.3 Properties of Dowex 50W-X4 cation exchange resin

2.3.1 Physical properties of the Dowex 50W-X4

The Dowex 50W-X4 resin is prepared in the form of spherical beads with a 0.5-1.0 mm diameter. When viewed under the microscope they appear solid, but on a molecular level they are open, meaning that they have pores. Dowex 50W-X4 exhibits features such as enhanced ion exchange capacity, maximised exchange speed and good mechanical strength (Sheng Dong Technology Co. Ltd, 2008). After the Dowex 50W-X4 resin has been synthesised and prepared, it has a brownish colour and appears at different particle sizes for various applications (see Figure 2-4 below).

Figure 2-0-4 Physical appearance of Dowex 50W-X4 ready to be used (Made-in-China.com, n.d.)

During the operation of the resin, the colour might change for various reasons. The shape of the resin is spherical. When the resin is placed in water, it swells and the swelling is related to the degree of crosslinking, the exchange capacity of the active group, the density of the electrolyte in the water and the nature of the exchangeable ions. The resin will expand and contract during the exchange and regeneration process. Generally, ion exchange resins are insoluble and heat resistant (Braithwaite & Smith, 2012). Table 2.2 contains summarised information on the properties of the resin.

Table 2.0: Properties of the Dowex 50W-X4 resin

Polymer type	Styrene divinylbenzene
Mobile ion	H^+
Total capacity	1.2 meq/ml
Standard mesh size	16-50 mesh
Moisture retention	66-67%

2.3.2 Particle size and porosity

Resins, having small particle size, will cause reasonable contact time between the fluid and the resin, thereby enabling time for ions to exchange with ions in the resin. A slow flow rate promotes better interaction (Ismail, 2016). The particle size of the resin and porosity of the matrix particles are the main factors affecting the flow characteristics and chromatographic resolution. Small particles offer the advantage of better chromatographic resolution. Stationary phases with particles of uniform size are advantageous to heterogeneous materials in relation to resolution and attainable flow rates. The pore size of ion exchange beads directly impacts its binding capacity (Acikara, 2013). When resin bead size decreases, the surface area per unit volume increases; consequently, the resin provides numerous exchange sites and give better separations on smaller resin particle size (Dudas 2011).

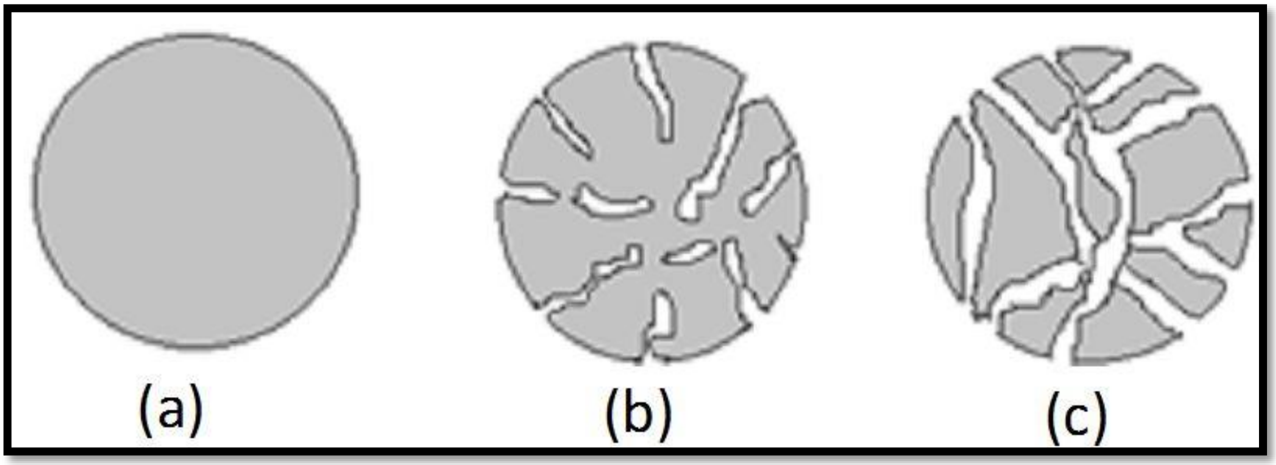

Figure 2-0-5: Schematic representation of different resin types: (a) non-porous bead, (b) microporous bead and (c) macro-porous or macro reticular resin (Acikara 2013)

Dowex 50W-X4 is a macroporous polymer resin. Macro-porous polymer resins are prepared by suspension polymerization technique which produces a macro-porous polymer network in the form of beads with a diameter range of 0.1mm-1.5mm. The copolymerization and crosslinking reactions are formed in the monomer–diluent droplets that result in beads having a glassy, opaque or milky form. A suitable solvent is then used to extract soluble polymers (purification) and the diluent from the network. Water-insoluble monomers have been used primarily in the synthesis of macro-porous copolymers, in addition to the widely used S–DVB co-monomers. The classical suspension polymerization technique is ideal in which an aqueous phase containing additives is utilised as the continuous phase of the reaction (Fathy *et al.,* 2014). When macro-porous resins were developed, proteins were purified on mesh size resins of 400-1000 since the microporous structure permits adequate surface area for sorption irrespective of particle size. The total exchange capacity was determined by titrating the resin with a solution of acid or base to a specific end point (Dechow, 1989).

2.3.3 Cross linking of the resin

Resins with a high degree of cross-linkage (small pore size) become selective for small ions and the larger ions become excluded from the resin (Dudas, 2011). Alterations of cross-linkage degree and resin pore size render the resin selective for particular ions. Accessibility depends on the degree of cross-linkage of the polymer chain. Small crosslinking gives advantage to fast equilibration because of enhanced shell of hydration of the resin particles for the rapid diffusion of ions. The particles of the ion exchange resin used for the water treatment are preferably 20-40 mesh. If the water content of the resin is large, the resin will be more porous and the degree of crosslinking will be smaller.

2.4 Chemical properties of Dowex 50W-X4 cation exchange resins

2.4.1 Ionic strength

Ion exchange resins have different abilities to absorb various ions and selective exchange capacity will indicate how much these resins exchange ions (Braithwaite & Smith 2012). There are two main factors in an ion exchange chromatographic mechanism: ionic charge and the ionic radius of the element. The combination of these factors in the ionic potential gives the relative electrostatic bond strength. The simplicity of the mechanism is on the charge that the metal is carrying, which means the higher the ionic charge the smaller the ionic radius and that metal will strongly bind on to the resin. The metal ion with low charge and bigger ionic radius will have low binding strength onto the resin. Therefore, ions can be separated by manipulating the chemistry of the solution based on the bond strength (Dudas, 2011).

The separation and purification of various metal elements by ion exchange chromatography takes advantage of the variation of the electrostatic bond energies of ions in solution. Several studies have contributed to the explanation of the separation mechanisms of ion exchange. Separation of Cs and/or Sr from fission products was achieved on sulphonic acid resins in nitric acid solutions of 1 to 3 M concentration. The separation mechanism was based on the charge that Sr(II) was retained more by the resin as compared to Cs(I) which eluted first because of its weak interaction with the resin (Bond *et al.,* 2019). Metal ions would sometimes exhibit similar chemical properties, such as alkaline earth metal ions. In most cases, the chemistry of the metals is dominated by the formation and properties of double charged ions which are stabilised by interaction with a solvent like water. The strength of binding in the case of alkaline earth metals varies inversely was the ionic hydration. The best separation of alkaline and alkaline earth ions is achieved by employing a masking agent or complexing agent (Amira, 2022).

2.4.2 Ion exchange resin capacity

Ion exchange resin capacity, the total number of sites available for exchangeable ions, can be determined after resin conversion via chemical regeneration to a given ionic form. The ability of resin particles to take water in the hydration cell is called water swelling of an ion exchanger and is primarily a hydration of the fixed ionic groups. It increases as the capacity increases to the limits imposed by the polymer network. Differing degrees of hydration of ionic species will influence resin volume; consequently, with regards to cation exchanger, there is a hydration volume change with the monovalent ionic species following this trend: $Li^+ > Na^+ > K^+ > Cs^+ > Ag^+$. With polyvalent ions, hydration is reduced by the cross-linking action; therefore, $Na^+ > Ca^{2+} > Al^{3+}$. In more concentrated solutions, less water is taken up owing to greater osmotic pressure (Taiyuan, 2022).

2.4.3 Kinetics of ion exchange resin

The rate at which ion exchange occurs is called reaction-solution kinetics. Diffusion through a solution layer in close contact with the resins and diffusion within the resin particle are both part of the ion exchange process. At low concentrations, film diffusion is a rate-controlling factor, while particle diffusion is rate-controlling at high concentrations. Whether the rate-controlling mechanism is film diffusion or particle diffusion, the resin particle size is likewise a determining factor. Generally, ion exchange reactions are fast. No electron-pair bonds need to be broken, and the rate of the process is limited only by the rate at which ions can diffuse in and out of the exchanger structure, depending on the physical properties of the resin-like particle size of the resin.

2.4.4 Effect of eluent

The use of suitable eluents is to achieve the desired separation of ions. Eluents are required to enhance metal ion attraction towards the resin that has opposite charged ions. The concentration of competing ion in the eluent influences the equilibrium position for ion-exchange process. When the concentration of the competing ion in the eluent is high, it will effectively displace the solute ions from the stationary phase, resulting in rapid elution of the solute from the column. In addition, elution of the solute from the column is also influenced by the eluent flowrate and the temperature. Faster flow rates contribute to lower elution volumes due to less interaction of solute ions to the fixed ions (Acikara 2013).

2.4.5 Effect of pH

The strong acid resins are flexible because their separation experiment is not pH dependent. In the case of weak acid or weak base resins, pH is an important parameter in the separation processes using a buffer solution to control the pH. The concentration of H^+ and the buffering component will influence the ability of the ions to bind to the stationary phase. Thus, knowing the working pH range where the sample is stable is imperative.

The influence of pH on the metal adsorption was studied by evaluating the distribution coefficients of Cu, Zn and Pb in a tartrate concentration range of 0.1 M to 1.0 M and pH range between pH3 – pH6. The distribution coefficient of the elements increased as the pH increased (Gharbi *et al.,* 2014). The pH of the solution also plays a vital role in coordination reactions and electrostatic interactions in physical adsorption processes. Metal ion adsorption was studied by altering the solution pH with dilute HCl and NaOH, resulting in a positive linear relation with the adsorption of Pb and Co ions (Jiang *et al.,* 2015a; Jiang *et al.,* 2015b). The pH in this study is not a considered factor because Dowex 50W-X4 is a strong acid cation exchanger that is not dependent on pH.

2.5.1 Ion exchange equilibrium

The separation of elements in ion exchange chromatography can be planned according to the information based on the distribution coefficient of metal ions measured (Van der Meulen 2003). The distribution coefficient of elements can be experimentally measured on a column containing ion exchange resin. Experimental data of distribution coefficients are important guidelines from which ion exchange separations can be planned. It generally gives an indication of the ability of the resin to retain elements. Higher distribution coefficient of the element means the element is strongly retained by the resin, and low distribution coefficient means that the element is not strongly retained by the resin. It also provides information of how elements can be separated from each other (Van der Meulen, 2003).

The distribution coefficients on cation exchange resins are strongly influenced by the degree of cross linkage of the resin depending on the size of the hydration shell of the cation exchanger. Distribution coefficient is the mathematical value obtained by the following equation:

$$\mathrm{K_d}\ or\ D = \frac{Mass\ of\ element\ per\ gram\ dry\ ion\ exchanger}{Mass\ of\ element\ per\ mL\ solution} \text{ x } 100 \qquad \textbf{Eq. 2-4}$$

Macro-porous resins are resins with rigid sponge-like material with large discrete pores. Their high cross-linkage can show significant differences in element distribution coefficients as opposed to the gel-type of low cross-linkage resins which makes them suitable for separation of elements that are relatively larger (Strelow, 1984). Strelow *et al.* (1971) proved that when using resins with cross-linkages of with 2% and 4%, the elements tested were not strongly retained by the resins purchased from Bio Rad (AG 50W-X2, -X4, -X8, –X12 and –X16). Van der Walt and Coetzee (1989) demonstrated similar effects using elements on anion exchange resins (AG 1-X2, -X4, -X8 and –X10).

2.5.2 Separation factor

Another ‘quantity’ often used to illustrate ion exchange equilibrium relationships is the separation factor, α, defined by the equation below:

$$\alpha \frac{B}{A} = \frac{D^{\mathrm{B}}}{D^{\mathrm{A}}} \qquad \textbf{Eq. 2-5}$$

The separation factor, $\alpha\frac{B}{A}$, is the ratio of the distribution coefficients of two different elements that were determined under specific experimental conditions, given by the ratio of the distribution coefficients of two different elements. The ratio determines the efficiency of the separation of two elements via ion exchange. If $\alpha > 1$ when comparing the distribution coefficients of certain elements that must be separated, then the separation will occur. During the separation of Zr and Hf on cation exchanger resin Dowex 50W-X8 on nitric acid media, the separation factor was calculated by employing the ratio of the concentration indices of Zr and Hf in the resin and in the liquid phase. Thus, the Zr is preferred by the ion exchanger on the basis of the value of $\alpha > 1$ (Hubicki, 1988).

2.5.3 Selectivity coefficient

The reactions of ion exchange are reversible.

A resin can be completely converted to the appropriate salt form by contacting it with an excess of electrolyte (Y^+ in the following reaction):

$RX^+ + Y^+ \rightarrow RY^+ + X^+$ **Eq. 2-6**

With a little amount of ionic species Y^+ in batch contact, however, equilibrium is produced that relies on the quantities of X^+ and Y^+ as well as the resin's selectivity. For this reaction, the selectivity coefficient, K_Y, is represented by the following equation:

$K_Y = m_Y / m_X \ . \ m_x / m_y$ **Eq. 2-7**

Where m_y and m_x refer to concentration of the ions in the resin and in the solution respectively.

Resin selectivity coefficients for a variety of ionic species have been determined and are related to H^+ for cations and OH^- for anions, both of which have selectivity values of 1.00 (Amira, 2022).

Dowex 50W-X4 was studied for its sorption properties towards copper, zinc, nickel, cadmium and lead metal ions. Selectivity increased in this order: Pb > Cd > Cu > Zn > Ni. It has been perceived that selectivity of the $-SO_3H$ group of the resin increases with atomic number, valence and degree of ionization of the exchanged metals. The equilibrium ion exchange capacity of resin for metal ions was measured and explored by using Freundlich and Langmuir isotherms (Pehlivan & Altun, 2006).

2.6 Preparation of ion exchange resin

Ion-exchange resins are organic compounds synthesized polymers and have positively or negatively charged sites at the end of the polymer chain (known as functional groups) that can attract an ion of opposite charge from a surrounding solution. These organic compounds are inert and stable at wide temperature ranges. The exchange reaction only occurs at the functional group under general experimental conditions desired for such experimental objectives. When the functional groups are added to the styrene polymer chain, the resins become characterised and provide the polymer resins reaction sites. The polymer unit acts as if they were individual ions suspended to the water matrix. The individual units are bound by DVB which makes the beads insoluble but swollen in water. The representation is shown in Figure 2-0-6 below.

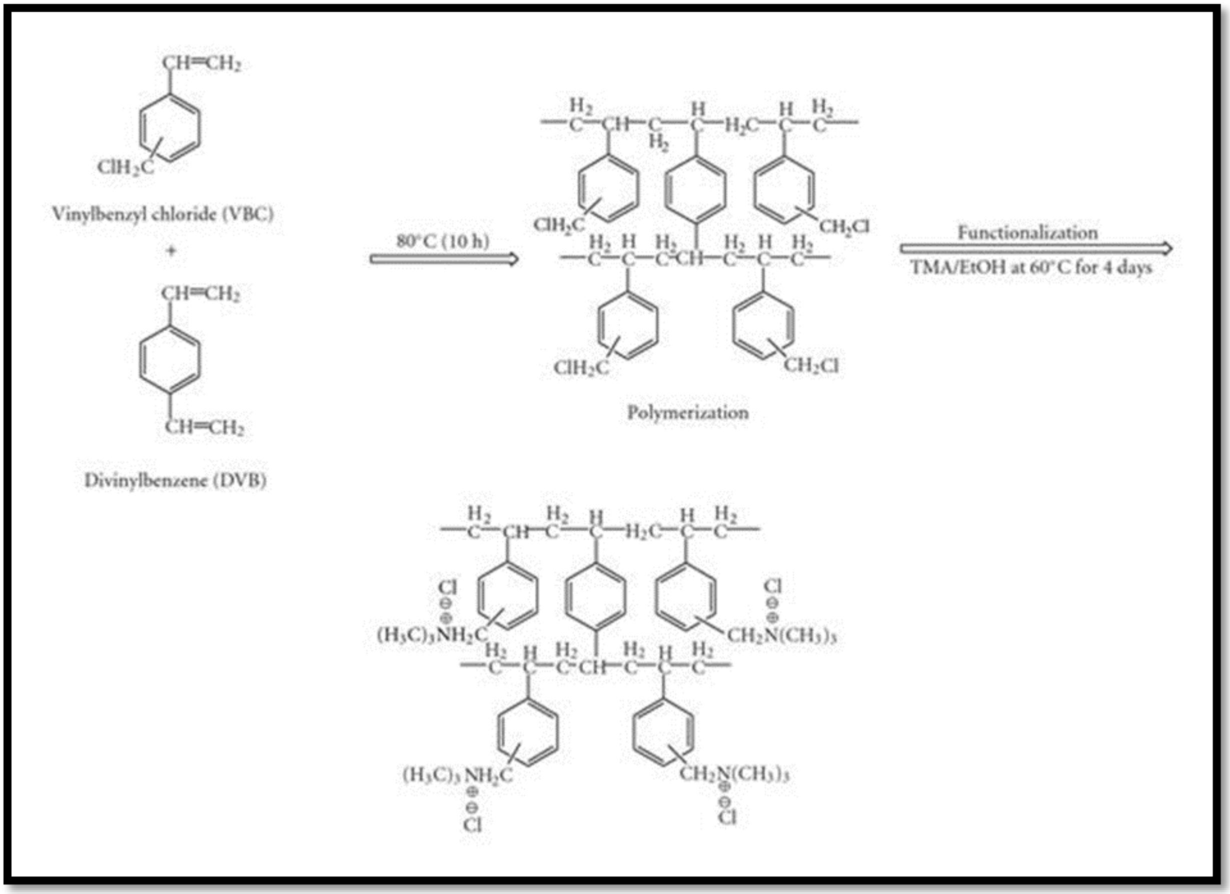

Figure 2-0-6: Reaction mechanism and characterisation of the polymer resin (Ezzeldin et al., 2010*)*

Subsequently, the final product of the synthesis of the polymer resin can be confirmed by FTIR to monitor the transmittance bands to establish the identity of the resin, as shown in Figure 2-0-6.

2.7 Ion exchange resin regeneration

Ion exchange resins have exchange sites that are readily available to the ions introduced by the eluent. When these exchange sites become saturated, the resin needs to be regenerated. Resin regeneration involves pollutant desorption from the media by employing processes that remove the pollutants from the resin without destroying the resin. Thermal and chemical processes can be used to regenerate the resin; however, thermal processes can lead to incomplete regeneration and destroy the polymer resin (Bashir *et al.* 2012). Chemical regeneration of the resin is preferred over thermal regeneration, where a solution of a high concentration containing the original ions is equilibrated with the resin to restore the resin to its original ionic form.

Sulphuric acid solution was used to regenerate a strong cationic resin and a solution of sodium chloride was used to evaluate the resin recovery efficiency. The results show that sulphuric acid was preferred for regeneration of H^+ form resin over Na^+ form in the removal of NH_3-N (Bashir *et al.,* 2012).

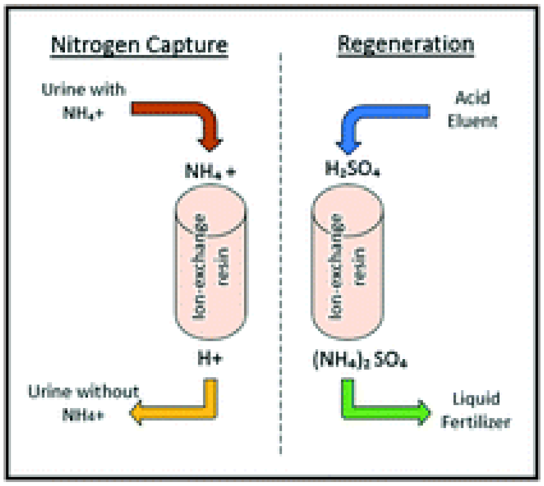

Figure 2-0-7: Resin regeneration flow chart (Tarpeh et al., 2018).

Salts can be used to regenerate resins based on the affinity of the resin generated. The salts like NaCl and $KHCO_3$ were used to regenerate cation exchange resin in the Ca form. Strong cation exchange resin, Amberjet 1200Na, was used to investigate the recovery of Cr(III) and Cr(VI) ions. The resin was regenerated successfully with a solution of H_2O_2 and NaOH was used for the alkalinity of the resin to avoid precipitate formation (Cetin *et al.,* 2013).

Resin selectivity plays a vital role in the regeneration processes. For instance, a resin that prefers Na will take up sodium until it reaches equilibrium. To remove the preferred ion, a solution containing counter ion needs to be run in abundance to reverse equilibrium. The resin that prefers Na can be regenerated by using excess hydrochloric acid to reverse the equilibrium. In cases where concentrated brine is the contaminant in resins for water desalination, a concentrated base such as KOH is necessary. Resin regeneration offers the opportunity for the resin to be re-used and save on frequent purchase of the resin. The strong cation exchanger resin that is investigated in this study, Dowex 50W-X4, can be regenerated by excess HCl depending on the use of the resin (Bashir *et al.,* 2012).

2.8 Applications of cation exchange resins

Macro-porous or macro-reticular, cation exchange resin, Bio-Rad's AG MP-50, which has an inelastic, wide, open macro-porous structure with a 20 to 25% cross-linkage, combines the advantages in selectivity presented by the high cross-linkage with fast exchange rates (Van der Meulen, 2003). This renders the macro-porous resin more suitable when employed in high pressure liquid chromatography procedures with respect to the separation of inorganic ions. This application is preferred because of its small change in volume with changes in eluent concentration. Numerous studies have been performed using this resin in nitric acid media (Marsh *et al.*, 1978), hydrochloric acid media (Strelow, 1984) and hydrochloric acid/methanol mixtures (Strelow, 1984).

The normal gel-type resin of 8% cross AG 50W-X4 was studied and compared with AG 50W-X8. The macro-porous resin showed some remarkable differences offering possibilities of much improved separation of some elements. The separation factors were considerably enlarged. Typically, elements with a small ionic diameter, a relatively high charge density and that are surrounded by a more rigidly held and more strongly ordered larger hydration cloud, show very little differences in their distribution coefficients when comparing the two resins (Strelow, 1984).

The behaviour of polyvalent cations including iron(III), vanadium(V), tin(IV),titanium(IV) and zirconium(IV) exhibited no sorption behaviour in a nitric acid concentration range of 0.1 M - 3.0 M that was studied. The bivalent cations were strongly sorbed from the lower concentration range of oxalic acid nitric acid media. It was determined that the behaviour of these elements contrasts their exhibited behaviour in pure nitric acid media, polyvalent elements such as iron(III), titanium(IV) and zirconium(IV) are strongly sorbed or have a high distribution coefficient in 0.1 M pure nitric acid. However, the distribution coefficients of bivalent elements are lower in the acid mixture media. The oxalic acid-nitric acid cation exchange system deemed suitable for the separation of a certain group of bivalent elements from some common trivalent and tetravalent elements but for multicomponent separation is not feasible. A strong cation exchange resin, Dowex MAC 3, was used in the recovery of nutrients in fertiliser. The resin showed high adsorption density and recovery efficiency. Mineral acids, HCl, HNO_3 and H_2SO_4, exhibited excellent recovery efficiencies compared to NaCl. Due to the health risks they represent to human life, heavy metals have a negative impact on the environment.

It is crucial to analyse the heavy metal content levels in soil samples and ground water since this can reveal how much risk people are exposed to. When these harmful substances are together, understanding their distribution coefficients can help determine whether it's possible to isolate and separate them (Chen and Lu, 2021).

2.9 Application of Dowex 50W-X4 resin

The sorption behaviour of Th and U was investigated using Dowex 50W resins in nitric acid media by both batch and column techniques. The cation salts involved in the sorption were UO_2^{2+} and Th^{4+} onto Dowex 50W-X8 and Dowex 50W-X4 resins (50-100 mesh size), respectively. The batch data yielded a separation factor (Kd of Th/Kd of U) value >100 for the cation-exchanger Dowex 50W-X4 at 1-2 M HNO3. Separation experiment of uranium from thorium was also carried out by the column method in the medium of nitric acid using the cation exchanger Dowex 50W-X4 as well as Dowex 50W-X8. Uranium was eluted using 1.0 M HNO3 while Th could only be eluted at a higher concentration of nitric acid (>6 M) (Bhattacharyya *et al.,* 2006).

CHAPTER 3

3 METHODOLOGY

This chapter outlines the materials and chemicals, apparatus, analytical instrumentation and methods used in this study. The experimental procedures and parameters are linked to the results in Chapter 4.

3.1 Reagents and solutions

3.1.1 Materials and chemicals

The acid and chemicals used in this study was of analytical grade. The 65% HNO_3 were purchased from Sigma Aldrich. Dowex 50W-X4 resin of particle size 100-200 mesh was purchased from BioRad SA. All the metal salts used for the experimental work was in the nitrate form and was purchased from Merck and Sigma Aldrich. The metal ion solutions were prepared from the respective salts. All stock solutions had a concentration of 1000 mg/L and were prepared in 250 mL volumetric flasks. The 1000 mg/L ICP standard solutions were used to prepare the respective metal calibrations standards.

3.2 Apparatus

3.2.1 Mechanical shaker

An automatic mechanical shaker (Labotec model 262) with speed control was used for all the batch adsorption experiments.

3.2.2 Peristaltic pump

A Gilson MINIPULS Evolution peristaltic pump was used in all column experiments.

3.2.3 Analytical Instrumentation

3.2.3.1 Scanning Electron Microscope (SEM)

The scanning electron microscope (SEM) is a type of electron microscope used for directly examining the surfaces of solid objects in this case the cation exchange polymer resin Dowex50W-X4. It works by scanning a beam of focused electrons across the specimen on a regular basis. Similar to those described for the transmission electron microscope, the beam is created and focused by an electron source and electromagnetic lenses (TEM).High-energy backscattered electrons and low-energy secondary electrons are stimulated to emit from the specimen's surface by the action of the electron beam (Tarpeh et al., 2018).

Under the specified experimental conditions, the morphology and elemental content of the metal ions bonding to Dowex 50WX8 resin were examined using scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM/EDS). The working conditions of the

SEM/EDS supplied by AURIGA Field Emission High Resolution Scanning Electron Microscope supplied by Zeiss (Germany) using a software SmartSEM and the AZTEC as EDS Software. The operating conditions were as follows: KV for images is 5 KeV, KV used for EDS was 20 KeV, gun vacuum was $7.7X10^{-10}$ mbar, system vacuum was $7.3X10^{-7}$ mbar and the filament current was 2.359 amps.

3.2.3.2 Fourier Transform Infrared Spectroscopy (FTIR)

The chemical components of organic molecules can be quickly and affordably identified using FTIR spectroscopy, as can the functional groups responsible for the sorption of particular ions. Using Fourier transform infrared (FT-IR) spectroscopy, the functional groups present in the utilized adsorbent were examined in the scanning range of 4000-400 cm1 (Masry et al., 2022). The FTIR ATR ALPHA model was used equipped with LASER CLASS 1 operating at 24 V and 2.0 A.

3.2.3.3 ICP-OES background

A Spectro ARCOS ICP-OES spectrometer was used for the analysis of all metal ion concentrations. The operating parameters are listed in Table 3-1.

Table 3-1: Operating parameters of the ICP-OES spectrophotometer

RF Power	1400W
Argon Flow	12 L/min
Auxiliary Flow	1.0 L/min
Nebuliser Flow	0.8 L/min
Peristaltic Pump Speed	63 rpm

ICP-OES (inductively coupled plasma-optical emission spectrometry) is an analytical technique based on atomic emission spectroscopy that can determine more than 70 elements. ICP is used for liquid samples. The technique has been commercially available since 1974 and due to its reliability, multi-element options and high throughput, it has become widely applied in both routine research as well as for specific analysis purposes. A method for the determination of ^{237}Np and Pu isotopes in large soil samples has been established. The method provided enhanced uranium removal measured on inductively coupled plasma mass spectrometry (ICP-MS) as a method of detection. This process permitted rapid pre-concentration and separation of plutonium and neptunium in large soil samples for the measurement of ^{237}Np and Pu isotopes by ICP-MS. ^{238}U can interfere with ^{239}Pu measurement by ICP-MS as ^{238}UH^{+} mass overlap and ^{237}Np via ^{238}U peak tailing. The method delivered significant removal of uranium by separating Pu and Np initially on TEVA Resin, then transferring Pu to DGA resin for additional purification (Maxwell *et al.,* 2010).

3.3 Experimental procedure

3.3.1 Preparation of resin

The resin was washed with deionized water filtered by gravity filtration and dried at 60 °C in a vacuum oven for 24 hours and cooled in a desiccator.

3.3.2 Preparation of stock metal ion solutions

Each of the stock solutions for the respective metals were prepared from the nitrate salt using 1 M HNO_3 to contain 1mmol for monovalent cations, 0.5 mmol of the divalent cations and 0.33 mmol of the trivalent cations. The elements used in this study have different charged strengths. The distribution of differently charged ions, depends on the total concentration of the solution. The more diluted the solution, the greater the tendency for higher charged ions to accumulate in the exchanger. A doubly charged ion entering the exchanger sends two singly charged ions back into solution. The more dilute the solution, the greater the chance of this exchange. For alkali and alkaline earth metal ions, the bond strength changes inversely with ion hydration. Therefore, the most hydrated alkali metal ion, the lithium ion, is the weakest retained by the resin, followed by sodium, potassium, rubidium and finally cesium to form the strongest bond with the resin. For the alkaline earths, the ascending order is most strongly expressed from beryllium through magnesium, calcium, strontium, barium and radium (Harold F. Walton, 1999).

3.3.3 Equilibration distribution coefficient determination

The equilibrium distribution coefficients were determined by equilibrating 0.50 g of the dry resin, in hydrogen form, with 50 ml of varying HNO_3 concentration solutions by shaking for 24 hours on a mechanical orbital shaker at room temperature. The concentrations of the nitric acid solutions used are shown in Table 3-2.

Table 3-2: HNO_3 solutions for metal ion batch experiments

No.	M HNO_3	Volume of stock solution (mL)	mL 5.0 M HNO_3	Volume water (mL)
1	0.10	5.0	0.0	45.0
2	0.20	5.0	1.0	44.0
3	0.50	5.0	5.0	40.0
4	1.0	5.0	10.0	35.0
5	2.0	5.0	20.0	25.0
6	3.0	5.0	30.0	15.0
7	4.0	5.0	40.0	5.0

After equilibration, the resin was separated from the aqueous phase by filtration. The filtrates were then evaporated to incipient dryness. The residues were dissolved in 10.0 mL 5.0 M HNO_3 and the solutions quantitatively transferred into respective 100 mL volumetric flasks and filled to the mark with deionized water. Four reference standards were prepared for each of the experiments by pipetting 10 mL of the stock solution into a 200 mL volumetric flask and diluting to the mark with water. The amount of metal ions was determined in both the reference standards and the aqueous phases (solutions) by ICP-OES.

The equilibrium distribution coefficients for the metal ions in solutions were calculated according to the following equations.

$$K_{\mathrm{d}} = \frac{Aver.of\ reference\ standards - mass\ of\ element\ in\ solution}{mass\ of\ element\ in\ solution} \qquad \textbf{Eq. 3-1}$$

The equilibrium distribution coefficients for the metal ions on the resin were calculated according to the following equation.

$$K_{\mathrm{d}} = \frac{[\text{mass of element sorbed on the resin}]\text{X}\ [100]}{[(\text{average mass of RS}) - (\text{mass of element sorbed on the resin}]\ \text{X}\ [0.500]} \qquad \textbf{Eq. 3-2}$$

Where [mass of element sorbed on the resin] represents the concentration of the element sorbed on the resin determined by the ICP-OES, RS is the reference standard and the 0.500 is the mass of the resin.

3.3.4 Elemental separation (elution curves): determination of elution curve for Na and Mg

In the ion exchange resin, particularly Dowex 50W-X4, the hard ions like magnesium ions are exchanged with the sodium, and the sodium diffuses into the bulk water solution. The hardness-free water, referred to as soft water, can then be used for low to medium pressure boiler feed water, reverse osmosis system makeup, some chemical processes, and commercial applications such as laundries (Suezwatertechnologies.com, 2019). The separation of magnesium and sodium were chosen because this can provide useful information in water analyses and because ion exchange chromatography is cost-effective and the experimental setup simple.

A slurry of Dowex 50W-X4 resin was prepared with deionized water and transferred to a 20 mL polypropylene column, with a sintered filter at the bottom. A 15 mL column was prepared. The resin was equilibrated with 50 mL 0.2 M HNO_3 solution. The Na^+ solution was passed through the column at a flow-rate of 0.5 mL /min. The Na was eluted with 10 mL fractions of 0.5 M HNO_3. Each of the fractions collected was transferred to a 100 mL volumetric flask and diluted to the mark with 0.5 M HNO_3. The concentration of Na in each fraction was determined on ICP-OES spectrometry and subsequently the elution curve for sodium was established.

The same procedure was applied for Mg determination.

CHAPTER 4

4 Method validation

This chapter is based on the fundamentals of the method performance that include parameters such as selectivity, accuracy, precision and sensitivity that will be judged on the performance of the ICP-OES instrument. Such parameters include preparing a good calibration curve for each element. The acceptance of the calibration curve will be based on the value of the linear regression (R^2) which is supposed to be 0.999.

4.1 Batch acceptance criteria

Batch acceptance criterion was based on linear regression obtained by performing calibration curve of the standards. The calibration curve is a straight line produced by the instrument in relation to the concentrations of the elements prepared by dilutions from the 1000 ppm by dilution formula. A linear fit of the unknown element concentration was accommodated on the straight line represented by $y = mx+c$ where y is the intensity of the instrument, m is the slope of the curve, and x is the concentration on the plot x axis.

Accuracy is the extent to which a given measurement agrees with the standard value of that measurement. In this case, accuracy is measured by comparing the theoretical value of the concentration calculated against the same standard measured by the instrument. The control sample was used which was the maximum standard solution to monitor the trend of the analytical runs to determine the accuracy of the instrument and reliability of the data. This control sample was run randomly in between the runs.

Precision is the assessment of analytical data generated which presents the closeness of the repeated runs. The precision of the measurements refers to the spread of the measured values. Method precision was determined by measuring reference standards that were of the same concentration for each element. Reference standards were also used to validate the method in order to assess element activity on the resin.

Selectivity refers to the extent to which a method can determine particular analytes in mixtures or matrices without interferences from other components.

4.2 Summary of the validation results

4.2.1 Sample Calibration curve

The calibration curve was generated for each element covered on this study by analysing a range of standards as shown on the calibration tables below starting from 0ppm to 200ppm. The instrument response (signal intensity) was plotted against the concentration of the element. The linearity between concentration and signal intensity was monitored: the linear regression value R^2 and the accepted value of R^2 was 0.99.

Table 4-1: Li calibration standards

Conc. Li (ppm)	Intensity (CPS)
0	12436
10	29420
50	87611
100	158483
150	228072
200	298973

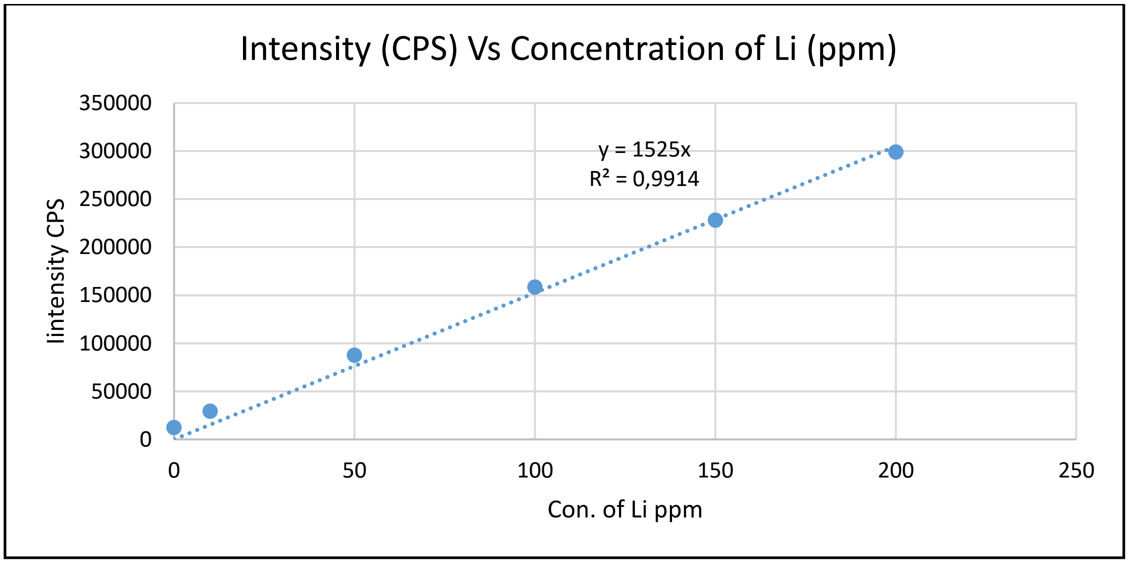

Figure 4-1: Li calibration curve

4.3 Batch criteria

The correlation coefficients for all the calibration curves were around 0.99. This indicates that all calibrations of the ICP for each of the elements are acceptable (see Table 4-19).

Table 4-2: Correlation coefficients for metal ions

Element	Correlation coefficients
Li	0.9999
Na	0.9967
K	0.9973
Rb	0.9997
Mg	0.9963
Ca	0.9967
Sr	0.9995
Ba	0.9945
Al	1.0000
Mn	0.9937
Fe(III)	1.0000
Co	1.0000
Ni	1.0000
Cu	0.9999
Zn	0.9996
Ag	0.9992
Cd	0.9984
Pb	1.0000

4.3.1 Method precision

The precision was determined by measurement of four prepared reference standards. The mean value of the reference standards was used to calculate the percentage relative standard deviation. The table below presents the reference standards measured on the ICP-OES. The method shows very good performance for all the elements as the relative standard deviation (%RDS) is significantly less than 10%.

Table 4.20: Reference standards for the elements analysed obtained from the ICP-OES

Element	REF. 1	REF. 2	REF. 3	REF. 4	MEAN	%RSD
Li	71.38	71.64	72.02	72.98	72.01	0.49
Na	228.90	231.10	232.20	233.10	231.33	0.78
K	402.50	403.50	404.50	406.30	404.20	0.40
Rb	431.10	440.00	435.50	432.70	434.83	0.90
Mg	131.10	135.50	129.00	126.00	130.40	3.06
Ca	213.10	211.00	209.10	218.10	212.83	1.82
Sr	343.40	341.10	350.30	339.60	343.60	1.38
Ba	343.30	345.10	340.90	341.70	342.75	0.54
Al	90.12	91.11	90.96	91.42	90.90	0.61
Mn	290.10	290.50	289.10	289.70	289.85	0.21
Fe(III)	187.10	187.90	186.70	186.30	187.00	0.37
Co	296.00	295.40	296.30	295.70	295.85	0.13
Ni	291.10	293.90	294.10	292.50	292.90	0.48
Cu	321.10	319.70	318.80	319.40	319.75	0.30
Zn	330.00	328.40	329.00	330.40	329.45	0.28
Ag	269.70	270.30	271.60	268.80	270.10	0.43
Cd	563.30	564.00	563.70	564.60	563.90	0.10
Pb	260.10	260.80	259.60	259.30	259.95	0.25

4.3.2 Method accuracy

During the separation of magnesium and sodium, a QC (quality control) sample was analysed for both elements which was 200 ppm. In the table below, calculated values of the parameters such %RE and %RSD are presented. The method showed a good performance based on the percentage relative error and percentage relative standard deviation calculated (see table below). The accepted values of the %RE and %RSD are both significantly less than 10% which shows that accuracy was significantly achieved by the method.

Table 4.21: Quality control sample represented by the highest standard 200ppm for the 2 elements Mg and Na

Element	QC 1	QC 2	QC 3	%RE	%RSD
Na	192.82	195.53	196.11	2.59	1.58
Mg	205.82	203.43	204.26	0.00	0.59

4.3.3 Method selectivity

The selectivity of the method was evaluated by creating a method grouped Na, K and Mg and the concentration of the Mg was determined. The instrument gave a strong signal to magnesium as shown in the table below.

Table 4.22: the data showing method selectivity, Mg sample ran where three (3) elements were included in the method (cocktail method).

Na	K	Mg
0.00 ppm	0.00 ppm	139.77 ppm
0.00 ppm	0.00 ppm	141.11 ppm
0.00 ppm	0.38 ppm	144.56 ppm

The parameters measured and demonstrated on this chapter are based on method validation which shows a very good performance of the method and the instrument. The data presented in this study was determined as reliable.

CHAPTER 5

5 RESULTS AND DISCUSSION

This chapter presents the results obtained for the characterization of the of cation exchange resin (Dowex50W-X4), the batch experimental Kd results for the 18 elements studied and the elemental separation (elution curves) for Na and Mg.

5.1 Characterisation of Dowex 50W-X4 using SEM/EDX

SEM/EDX scanning of the resin particles revealed the chemical make-up of Dowex50W-X4 resin, a cation exchange resin. Results from SEM/EDX revealed the resin's potential qualities but were unable to fully describe the resin's structural makeup since hydrogen elements cannot be read by SEM/EDX. Based on percentage composition, it gave a significant signal for carbon (70.38% of the total atoms), sulphur (10.64%), and oxygen (18.98%). It was considered that the sodium and nitrogen signals were below the detection threshold. Because hydrogen element could not be detected, the SEM/EDX results could not be used to determine the chemical composition of the resin.

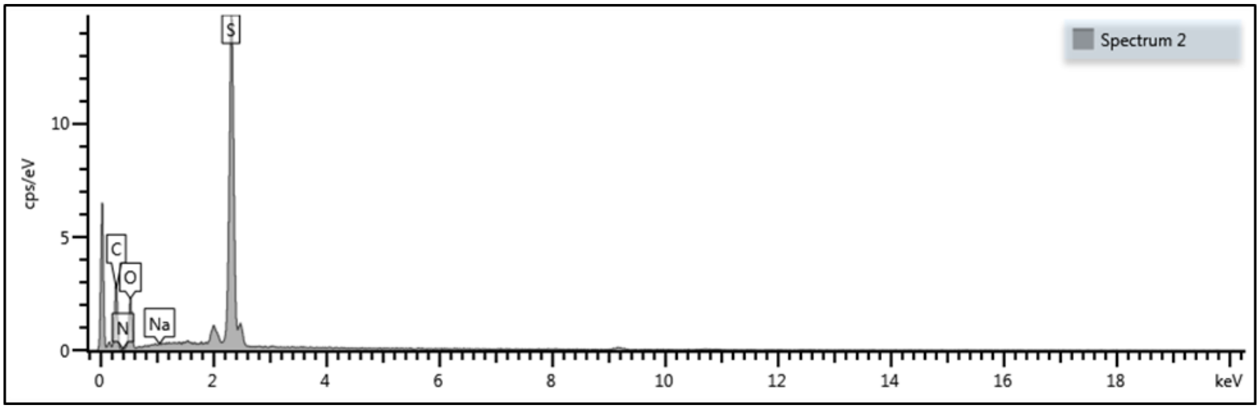

Figure 5-1: SEM/EDX Spectra of the Dowex 50W-X4 resin

Table 3.1: SEM/EDX results of DOWEX 50W-X4resin

Element	Atomic %
C	70.38
N	0
O	18.98
Na	0
S	10.64
Total:	100

5.2 Characterisation of Dowex 50W-X4 on FTIR

Dowex 50W-X4 (a cation exchange resin) was scanned on an FTIR to look at the structural elements, including functional groups.

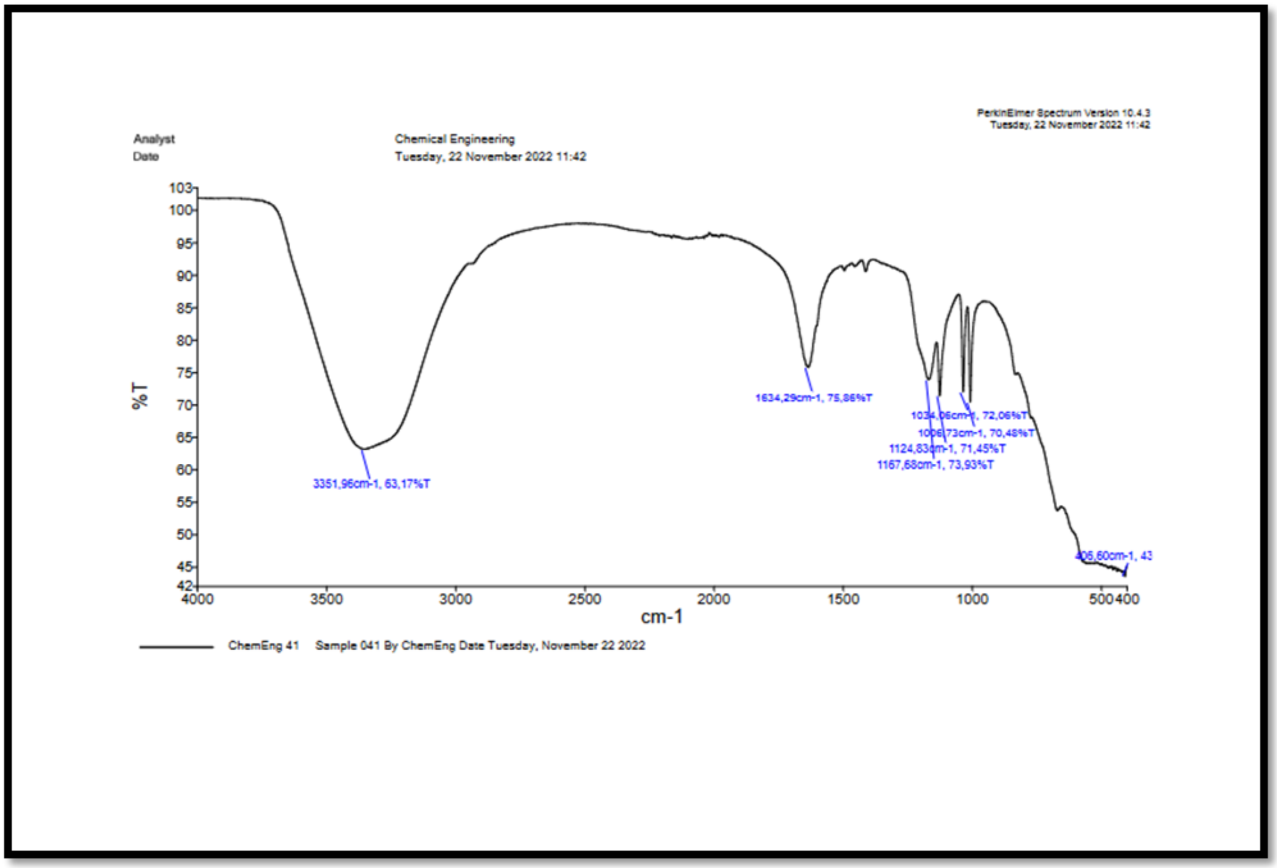

Figure 5-2: FTIR Spectra for Dowex 50W-X4 resin

The IR bands of the resin are shown in th the FTIR spectrum below (**Figure *5-2***).The stretching band at 1634.29 cm^{-1} indicates the presence of alkenes C=C, and in reference to the correlation chart is an indication of the sulphonic acid R-SO_3-H which is consistent with the theoretical knowledge of the resin as it contains sulphonic acid group. The stretching at 3351.96 cm^{-1} is attributed to O-H stretch for alcohols including phenols. A stretch of substituted aromatic rings, which may be aromatic ethers, makes up the 1634.29 cm^{-1}. According to the spectral peaks at 1167.68 cm^{-1}, 1124.83 cm^{-1}, 1067 cm^{-1}, and 1034.06 cm^{-1}, the band stretching between 1200 and 1000 cm-1 is the band of the epoxy ring, which is the characteristic of the polymer resin. Finally, 406.60 cm^{-1} is attributed to the alkane group (Holler et al., 2014).

5.3 Distribution coefficients

The equilibrium distribution coefficients (Kd) of 18 elements on Dowex 50W-X4 resin in varying nitric acid concentration solutions were determined. A summary of the results are presented in Table 5.1 The R and S on the results presented in Table 5.1 is an indication of the concentration of the element on the resin and the concentration of the element in the solution respectively.

Table 5-4:Experimental values of distribution coefficients (Kd) in mL/g of mono, di and trivalent elements from batch experiment on Dowex 50W- X4 in different nitric acid concentration

HNO_3	0.1M R	0.1M S	0.2M R	0.2M S	0.5M R	0.5M S	1.0M R	1.0M S	2.0M R	2.0M S	3.0M R	3.0M S	4.0M R	4.0M S
Li	27.4	27.0	15.3	15.4	7.1	7.0	4.0	3.9	2.4	2.6	1.8	2.0	1.5	1.3
Na	46.7	46.9	26.8	26.6	13.1	13.0	6.3	6.5	4.0	4.1	2.5	2.7	2.0	1.8
K	91	93	57	57	27.7	27.5	13.5	13.6	7.9	7.7	5.1	5.1	3.6	3.4
Rb	101	99	62	65	30.3	29.9	14.8	14.6	6.9	7.3	4.6	4.8	3.6	3.2
Mg	677	673	265	267	65	68	22.1	21.9	8.7	8.6	5.7	5.6	4.1	4.0
Ca	1235	1230	430	434	107	105	33.8	34.0	9.4	9.5	4.0	4.2	1.8	1.8
Sr	2632	2640	702	698	139	136	42.4	42.0	33.8	34.0	9.4	9.4	4.1	4.1
Ba	4251	4249	1402	1398	258	254	66	64	12.6	12.6	4.6	4.4	1.4	1.4
Al	$>10^4$	$> 10^4$	3504	3500	370	366	78	74	16.1	15.9	8.0	8.0	5.2	5.1
Mn	1056	1052	349	351	83	85	27.3	27.3	11.1	10.9	6.8	6.8	3.1	2.9
Fe	$> 10^4$	$> 10^4$	3696	3690	342	338	72	70	13.8	14.0	6.2	6.0	2.9	2.7
Co	1073	1067	352	350	87	83	27.7	27.5	10.1	9.9	6.1	5.9	4.5	4.5
Ni	972	968	346	344	88	84	27.1	27.0	10.1	9.9	8.5	8.3	6.1	5.9
Cu	921	915	318	322	80	78	25.8	25.6	8.3	8.3	4.8	4.6	2.4	2.6
Zn	869	865	315	319	79	77	24.0	24.4	6.5	6.7	4.5	4.5	2.5	2.5
Ag	135	129	76	72	33.1	32.7	21.4	24.4	7.6	7.6	5.4	5.0	4.0	3.8
Cd	1273	1277	354	352	84	88	31.7	31.3	10.6	10.4	6.6	6.5	3.3	3.3
Pb	$>10^4$	$> 10^4$	1280	1276	170	174	34.2	34.4	7.4	7.2	5.1	4.9	4.4	4.4

The K_d values decrease with increasing nitric acid concentration for each element. At higher nitric acid concentration, the elements could possibly form nitrate complexes or ion association tendencies which makes the ion to remain in solution (Strelow, *et. al* 1965). Ion hydration, which influences hydration size, will be impacted by this complex formation as well. Another contributing aspect might be the functional group of Dowex 50W-X4 resin having the ability to be protonated, which would change the cation characteristics to anionic. However, this would necessitate nitrato complexes of the type $M(NO_3)_5$. ("This is an open-access article distributed under the terms of the

Creative Commons Attribution License, which permits unrestricted use, distribution, and reproduction in any medium," 2018)

5.4 Monovalent elements

Table 5-5: Distribution coefficient of the monovalent elements from batch experiments

HNO_3	0.1 M	0.2 M	0.5 M	1.0 M	2.0 M	3.0 M	4.0 M
Li	27.2	15.4	7.0	3.9	2.5	1.9	1.4
Na	46.8	26.7	13.0	6.4	4.0	2.6	1.9
K	90	57	27.6	13.6	7.8	5.1	3.5
Rb	100	64	30.1	14.7	7.1	4.7	3.4
Ag	132	74	32.9	21.4	7.6	5.2	3.9

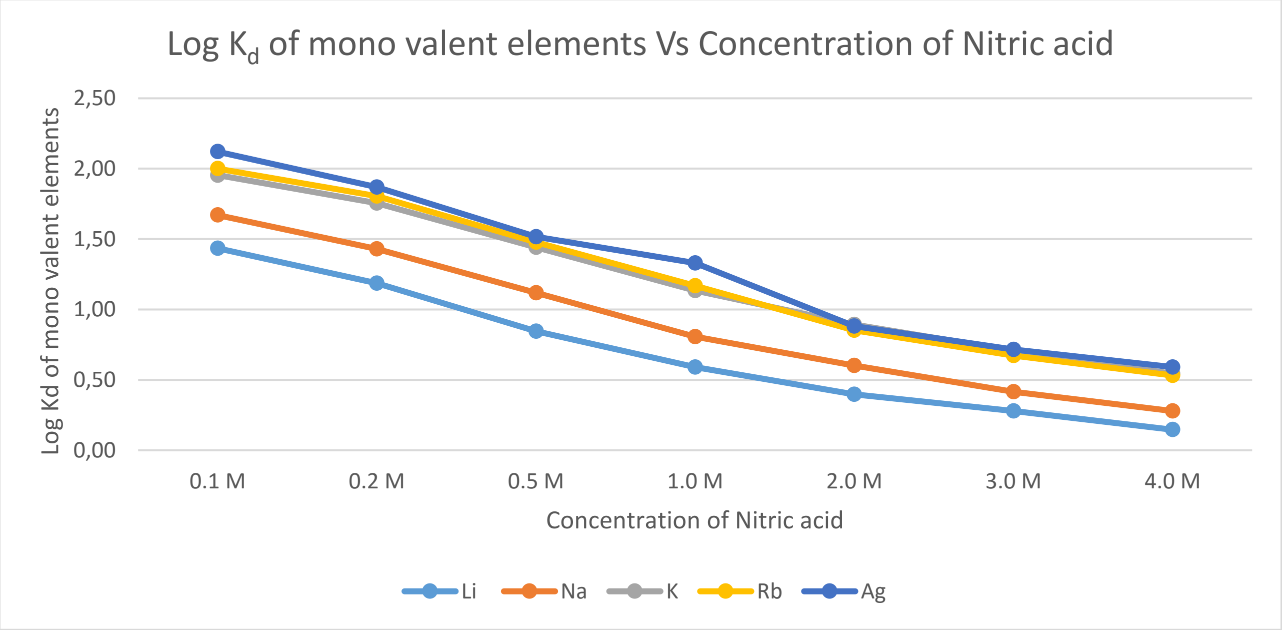

Figure 5-3-1: Log K_d values of monovalent elements Vs concentration of the eluate

To create a linear relationship between the distribution coefficient (dependent variable) and nitric acid concentration, the log K_d values were plotted against the concentration of the nitric acid used as the eluent (independent variable). The usage of logs provides helpful information about how the dependent variable behaves in relation to the independent variable across a specific range. The distribution coefficient of each element on the monovalent group studied decreases as the concentration of nitric acid increases, which is attributed by the protonation of the acid on to the resin. The resin affinity is following this trend – $Li^+<Na^+<K^+<Rb^+<Ag^+$ – which shows that Rb is

more strongly adsorbed by the resin than Li. The elements form nitrate complexes at higher nitric acid concentrations which result in the element not being adsorbed onto the cation exchange resin (Strelow, *et. al* 1965).

5.5 Divalent elements: selected alkaline earth metals distribution coefficients

Table 5-6: Distribution coefficients (mL/g) of divalent elements from batch experiments

HNO_3	0.1 M	0.2 M	0.5 M	1.0 M	2.0 M	3.0 M	4.0 M
Mg	675	266	67	22	8.7	5.7	4
Ca	1232	432	106	33.9	9.4	4.1	1.8
Sr	2635	700	137	42.2	8.5	6	4.5
Ba	4250	1400	255	65	12.6	4.5	3.4
Mn	1054	350	84	27.3	11	6.8	3
Co	1070	351	85	27.6	9.8	6	4.5
Ni	970	345	86	27	10	8.4	6
Cu	918	320	79	25.7	8.3	4.7	2.5
Zn	867	317	78	24.2	6.3	4.5	3.3
Cd	1275	353	86	31.5	10.5	6.6	3.3
Pb	>10^4	1278	172	34.3	7.3	5	4.4

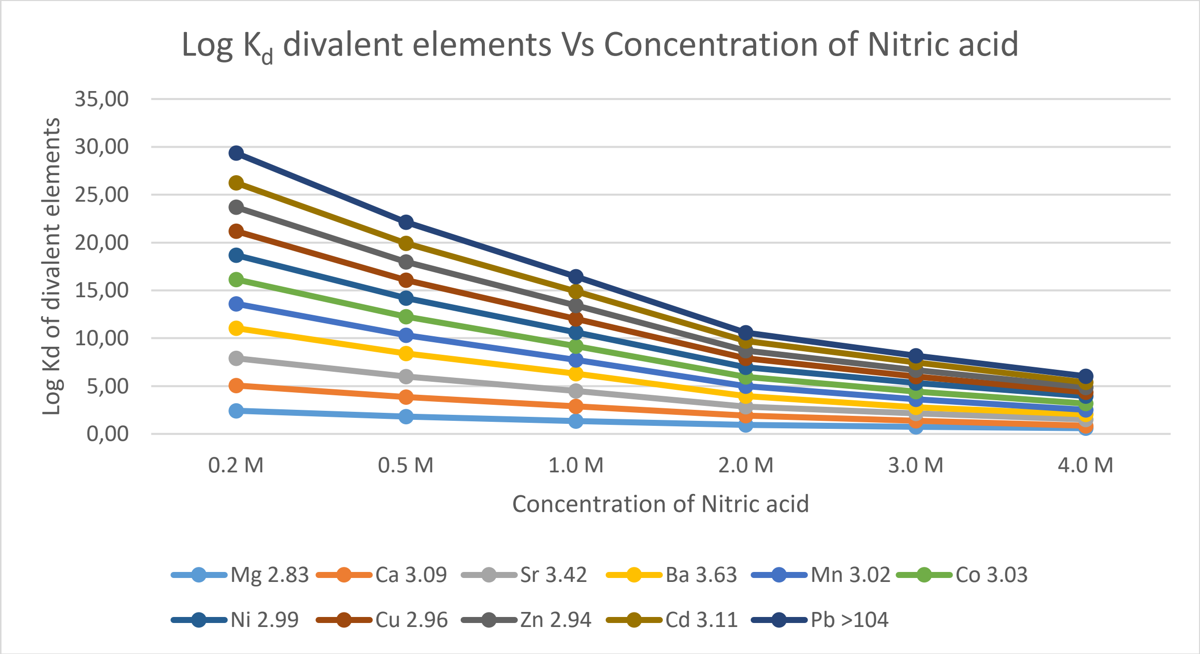

Figure 5-2: Log K_d values of divalent elements plotted against the concentration eluate

The distribution coefficients of each the divalent elements studied on different nitric acid concentrations decrease with an increase in the acid strength (as shown in Figure 5-2). At higher nitric acid concentration, the elements could possibly form nitrate complexes or ion association tendencies which makes the ion to remain in solution (Strelow, et. al 1965). Another contributing aspect could be the functional groups of the Dowex 50W-X4 resin, which have the ability to protonate to change cationic character to anionic. However, for this it needs a nitrate complex of the $M(NO_3)_5$ type. Ion hydration, which influences hydration size, will be impacted by this complex formation as well (Bond et al., 2019)

The distribution of the combined divalent elements studied show a positive trend down the group of the periodic table from 0.1M nitric acid to 1.0 M nitric acid. The resin used in this study, which is Dowex 50W-X4 resin, demonstrates greater affinity for Ba in comparison to Mg and takes the following trend: $Mg^{2+}<Ca^{2+}<Sr^{2+}<Ba^{2+}$. At lower nitric acid, the resin retains the elements more strongly. At higher nitric acid concentrations, the elements are in the solution. The resin shows it is more selective for Mn, Co and Cd which is evidenced by their higher distribution coefficient values at 0.1M nitric acid as compared to Ni, Cu and Zn.

5.6 Trivalent elements distribution coefficients

Table 5-7: Distribution coefficients (mL/g) of trivalent elements from batch experiment

HNO_3	0.1 M	0.2 M	0.5 M	1.0 M	2.0 M	3.0 M	4.0 M
Al(III)	$>10^4$	3502	368	76	16.0	8.0	5.2
Fe(III)	10^4	3693	340	71	13.9	6.1	2.7

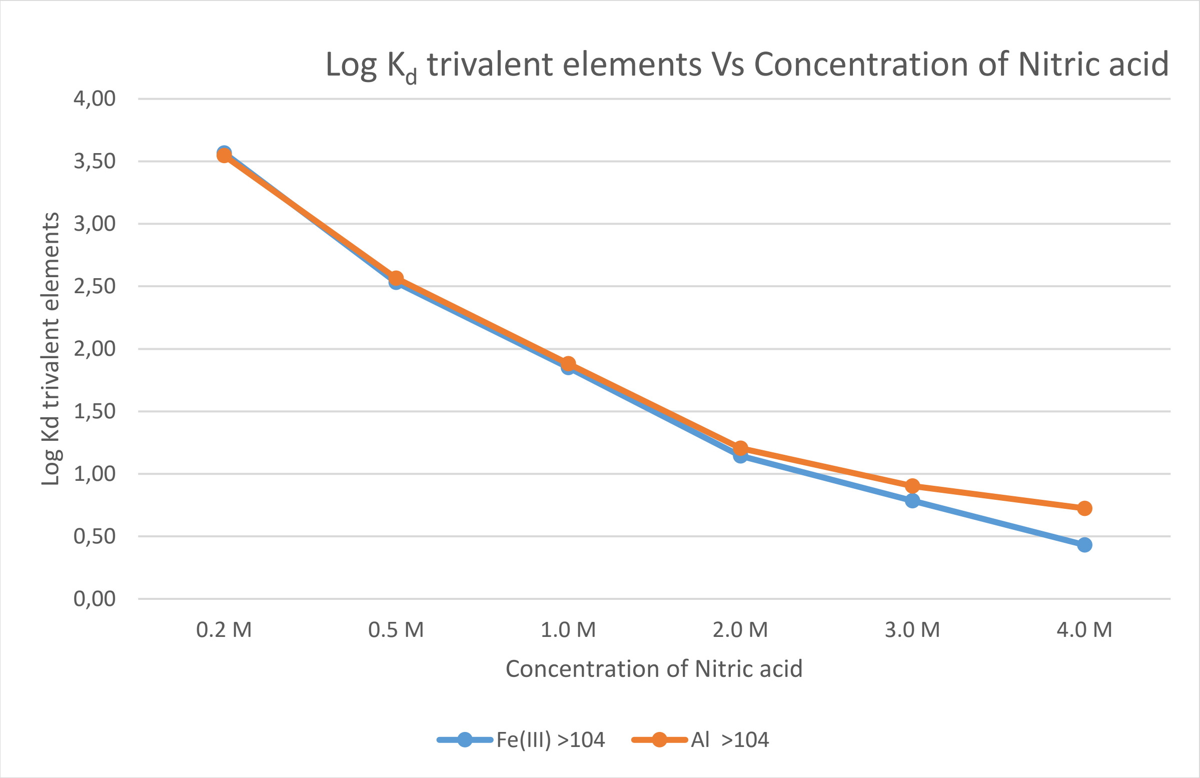

Figure 5-3: Log K_d values of trivalent elements plotted against the concentration eluate

The distribution coefficient is significantly high at 0.1M nitric acid for Al(III) and Fe(III), which shows that the elements are strongly retained by the resin at low acid strength. All the elements in this group have low distribution coefficient at high acid strength due to elements forming nitrate complexes (Abbasian, *et. al* 2011)

Table 5-5: Distribution coefficient (mL/g) results obtained on BioRad 50W-X8 on nitric acid media

Element	0.1M HNO_3	0.2M HNO_3	0.5M HNO_3	1 M HNO_3	2 M HNO_3	3 M HNO_3	4 M HNO_3
Al(III)	$>10^4$	3900	392	79	16.5	8	5.4
Fe(III)	$>10^4$	4100	362	74	14.3	6.3	3.1
Ba(II)	5000	1560	271	68	13	6	3.6
Sr(II)	3100	775	146	39.2	8.8	6.1	4.7
Pb(II)	$>10^4$	1420	183	35.7	8.5	5.5	4.5
Ca(II)	1450	480	113	35.3	9.7	4.3	1.8
Cd(II)	1500	392	91	32.8	10.5	6.8	3.4
Co(II)	1260	392	91	28.8	10.1	6.1	4.7
Mn(II)	1240	389	89	28.4	11.4	7.1	3
Ni(II)	1140	384	91	28.1	10.3	8.6	7.3
Cu(II)	1080	356	84	26.8	8.6	4.8	3.1
Zn(II)	1020	352	53	25.2	7.5	4.6	3.6
Mg(II)	794	295	71	22.9	9.1	5.8	4.1
Ag(I)	156	86	36	18	7.9	5.4	4
K(I)	99	59	26.2	11.4	5.7	3.5	2.6
Na(I)	54	29.4	12.7	6.3	3.4	2	1.3
Li(I)	33.1	18.6	8	3.9	2.6	1.7	1.1

Table 5-6 above presents the distribution coefficient results obtained on BioRad 50W-X8 on nitric acid media (Strelow, Rethemeyer & Bothma, 1965). The results of the Kd values obtained on Dowex 50W-X4 resin are similar to those for Strelow for all 17 elements studied.

5.7 Elution curves of Na and Mg using Dowex 50W-X4

The separation factor in the column separation experiment provides important information on the possibility of separating certain elements; that information is deduced from the distribution coefficient of the elements to be separated, termed as a separation factor. The separation factor given by the symbol α and can be calculated using Eq 2-5. The separation factor for magnesium and sodium at 0.5M nitric acid was found to be 14.4 which is α >1, meaning that sodium can be separated from magnesium on Dowex 50W-x4 cation exchange resin.

The results presented in Figure 5-2 show that magnesium was not eluted from the column using 0.5 M nitric acid. Magnesium was, however, completely eluted using 2.0 M nitric acid.

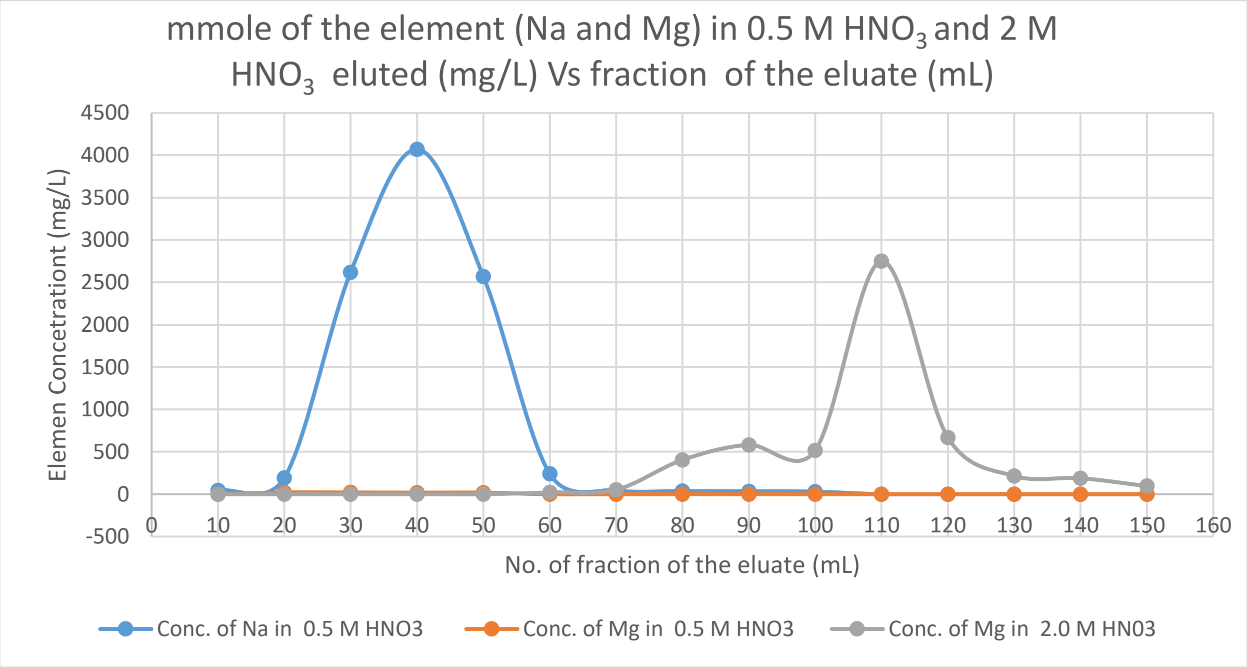

Figure 5-4: Elution curve for Na and Mg separation

During the separation studies, the concentration of the eluent was kept constant for each column experiment. For each separation, 15 fractions of 10 mL were collected. The first five fractions for magnesium were collected using 50 mL of 0.5 M nitric acid, and the remaining fractions were collected using 100 mL of 2.0 M nitric acid. The graph of the element concentration versus number of eluate fractions shows that sodium eluted at the fifth fraction using the 0.5 M HNO_3. The magnesium elution curve shows elution at the sixth fraction using the 2.0 M nitric acid. This indicates Mg and Na can be separated on Dowex 50W-X4. The resin has a stronger affinity for

Mg than for Na. Magnesium could only come out at 2.0 M nitric acid as shown on the elution curves above. This is an indication that it is possible to separate sodium and magnesium on column separation using Dowex 50W-X4 cation exchange resin in nitric acid media on varying acid concentrations.

CHAPTER 6

6 CONCLUSION AND RECOMMENDATIONS

6.1 Conclusion

The research study was based on the determination of the behaviour of some elements on the strong cation exchange resin Dowex 50W-X4 in nitric acid media at different concentrations. The distribution coefficient of each element in each nitric acid concentration was determined using the batch method and samples analysed using the ICP-OES instrument. The results were used to calculate the distribution coefficient. The results indicate that the distribution coefficients of the elements was found to decrease as acid concentration increases.

The distribution coefficients for the elements shown in Tables 5.2, 5.3, 5.4 and 5.5 compare well with the distribution coefficients for the same elements on BioRad AG 50W-X8 as determined by Strelow *et al.* (1965), as shown in Table 5-7 above. These two resins have similar specifications; hence, a good correlation between the results was anticipated. The results from this study confirmed this hypothesis within experimental uncertainties.

6.2 Recommendation

- Further research may include work on the following:
  - Influence of the hydrochloric acid and sulphuric acid concentration on the sorption of the elements on the Dowex 50W-X4 strong acid cation exchange resin.
  - Separation mechanism of monovalent, trivalent metal ions on the Dowex 50W-X4 strong acid cation exchange resin and their separation response to Dowex 50W-X4 strong acid cation exchange resin.

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8 APPENDICES

Appendix A1: Mass calculations for each respective metal from nitrate salts were prepared using 1 M HNO_3 to contain 1 mmol of monovalent cations, 0.5 mmol of the divalent cations and 0.334 mmol of the trivalent cations. The masses used for respective solution are shown below.

CALCULATIONS FOR MONOVALENT ELEMENTS

Li: = 1 mmol x 6.94 g/mol
= 6.94 mg/100 mL
= 69.4 mg/L

Mass of Li $= \frac{69.4 \times 68.946}{6.94}$
= 689.46 mg $LiNO_3$

Na: = 1 mmol x 22.99 g/mol
= 229.9 mg/L
Mass of Na = $\frac{229.9 \times 84.9947}{22.99}$
= 849.95 mg of $NaNO_3$ 100 mL of 1 M HNO_3

K: = 1 mmol x 39.09 g/mol
=39.09 mg/100 mL
=390.9 mg/L

Mass of K = $\frac{390.9 \times 101.1}{39.1}$
= 1010.1 mg of KNO_3 1 M HNO_3

Rb: = 1 mmol x 85.47 g/mol
= 85.47 mg/100 mL
= 854.7 mg/L
Mass of Rb = $\frac{854.7 \times 147.473}{85.467}$
= 1474.62 mg $RbNO_3$ in 1 M HNO_3
Ag: = 1 mmol x 107.858 g/mol
= 107.858 mg /100 mL
= 1078.58 mg/L

Mass of Ag^+ = $\frac{1078, 58 \times 143.32}{107.858}$
= 1433.2 mg of AgCl in 100ml of 1 M HNO_3.

CALCULATIONS FOR DIVALENT ELEMENTS

0.5mmol of the divalent elements in 50ml of the acid but the filtrate was diluted in 100ml
Mg: = 0.5 mmol x 24.305 g/mol
= 12.153 mg/100 mL
= 121.53 mg/L

Mass of Mg^{2+} = $\frac{121.5 \times 148.3}{24.304}$
= 741.5 mg of $Mg(NO_3)_2.6H_2O$ in 100 mL of 1 M HNO_3

Ca: =0.5 mmol x 40.078 g/mol
=20.04 mg/100 mL
=200.39 mg/L

Mass of Ca^{2+} $= \frac{200.39 \text{ mg} \times 236.15}{40.078}$
= 1180.75 mg of $Ca(NO_3)_2.4H_2O$ in 100 mL of 1 M HNO_3

Sr: = 0.5 mmol x 87.62 g/mol
=43.81 mg/100 mL
= 438.10 mg/L

Mass of Sr^{2+} $= \frac{438.10 \times 211.63}{87.62}$
= 1058.15 mg of $Sr(NO_3)_2$ in 100 mL of 1 M HNO_3

Ba: =0.5 mmol x137.32 g/mol
=68.66 mg/100 mL
= 686.60 mg/L

Mass of Ba^{2+} $= \frac{686.60 \times 261.337}{137.32}$
= 1306.69 mg of $Ba(NO_3)_2$ in 100 mL of 1 M HNO_3

Mn: =0.5 mmol x 54.94 g/mol
=27.47 mg/100 mL
=274.50 mg/L

Mass of Mn^{2+} $= \frac{274.50 \times 178.95}{54.94}$
= 894.10 mg of $Mn(NO_3). 4H_2O$ in 100 ml of 1 M HNO_3

Co: =0.5 mmol x 58.93 g/mol
=29.47 g/100 mL
=294.65 g/L

Mass of Co^{2+} $= \underline{294.65 \times 291.04}$

58.93

= 1455.2 mg of $Co(NO_3)_2$. $6H_2O$ in 100 mL of 1 M HNO_3

Ni: =0.5 mmol x 58.69 g/mol

=29.34 g/100 mL

=293.45 mg/L

Mass of Ni^{2+} $= \frac{239.45 \times 290.8}{58.69}$

= 1186.44 mg of $Ni(NO_3)_2$. $6H_2O$ in 100 mL of 1 M HNO_3

Cu: =0.5 mmol x 63.55 g/mol

=31.77 mg/100 mL

=317.7 mg/L

Mass of Cu^{2+} $= \frac{317.7 \times 170.5}{63.55}$

= 852.37 mg $CuCl_2.2H_2O$ in 100 mL of 1 M HNO_3

Zn =0.5 mmol x 65.39 g/mol

=32.70 mg/100 mL

=326.95 mg/L

Mass of Zn^{2+} $= \frac{326.95 \times 81.38}{65.38}$

= 406.96 mg of ZnO in 100 ml of 1 M HNO_3

Cd: = 0.5 mmol x 112.41 g/mol

= 56.2 mg/100 mL

= 562.1 mg/L

Mass of Cd^{2+} $= \frac{562.05 \times 308.49}{112.41}$

= 1542.45 mg of $Cd(NO_3)_2$. $4H_2O$ in 100 mL of 1 M HNO_3

Pb: =0.5 mmol x 207.2 g/mol

=103.6 mg/100 mL

=1.036 mg/L

Mass of Pb^{2+} $= \frac{1.036 \times 331.2}{207.2}$

= 1.656 mg of $Pb(NO_3)_2$ in 100 mL of 1 M HNO_3

Calculations for trivalent elements

0.334mmol of the trivalent elements in 100 ml of HNO_3

Al: = 0.334 mmol x 26.98 g/mol
=9.01mg/100 mL
=0.90 mg/L

Mass of Al^{3+} $= \frac{0.90 \times 375.13}{26.98}$

= 12.51 mg of $Al(NO_3)_3 . 9H_2O$ in 100 mL of 1 M HNO_3

Fe (III): =0.334 mmol x 55.845 g/mol
= 18.65 mg/100 mL
=186.52 mg/L

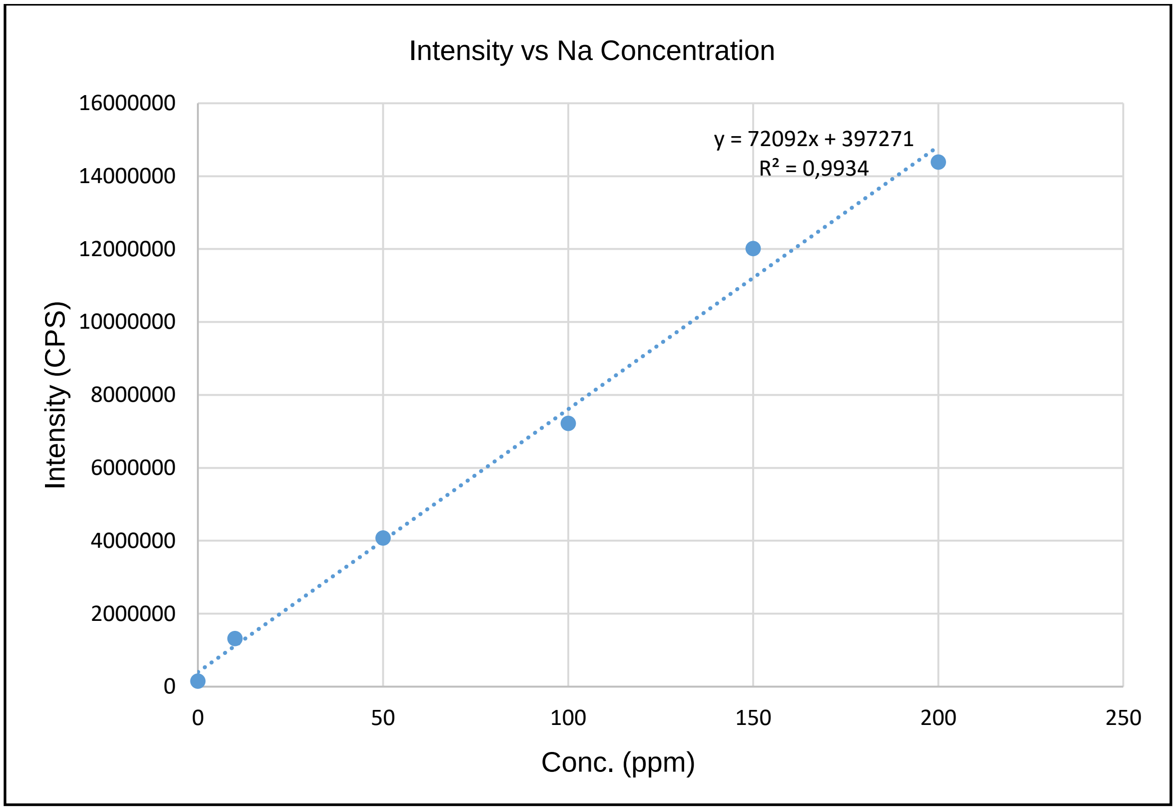
Mass of Fe^{3+} $= \frac{186.52 \times 241.86}{55.845}$

= 807.8 mg of $Fe(NO_3)_3$ in 100 mL of deionized water

Appendix A2: Calibration standards for element measured on the ICP-OES diluted from 1000 ppm to produce a calibration curve

Na calibration standards

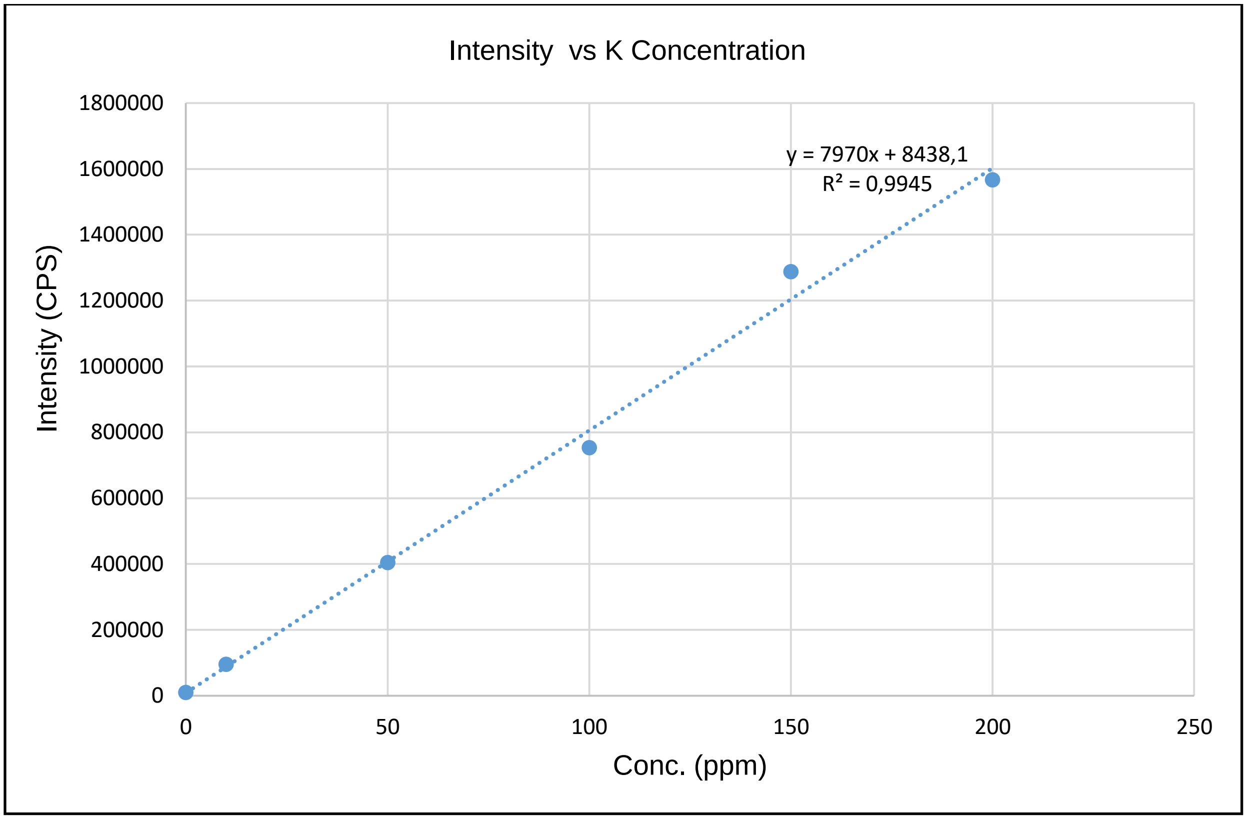
Conc. Na (ppm)	Intensity (CPS)
0	151598
10	1314150
50	4075530
100	7213810
150	12013300
200	14382000



Na calibration curve

K calibration standards

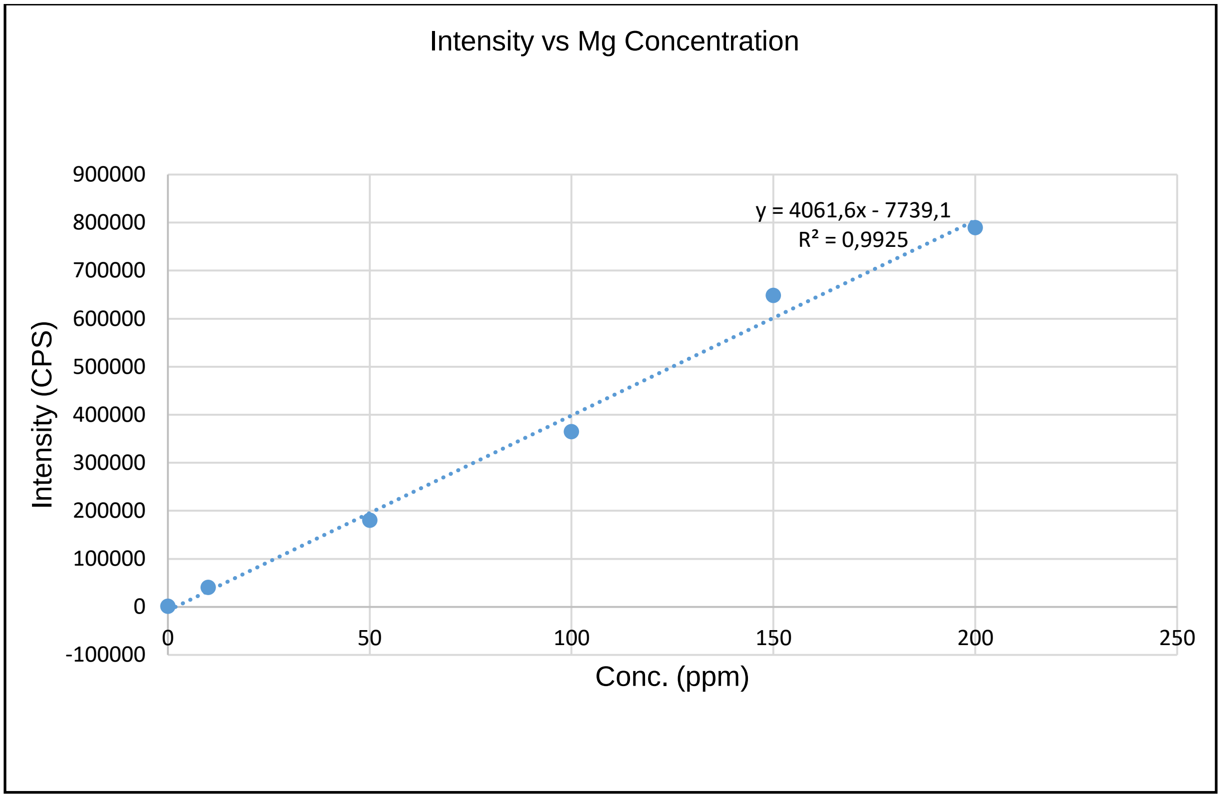
Conc. K (ppm)	Intensity (CPS)
0	9260
10	94773
50	404604
100	752994
150	1287320
200	1566370



K calibration curve

Mg calibration standards

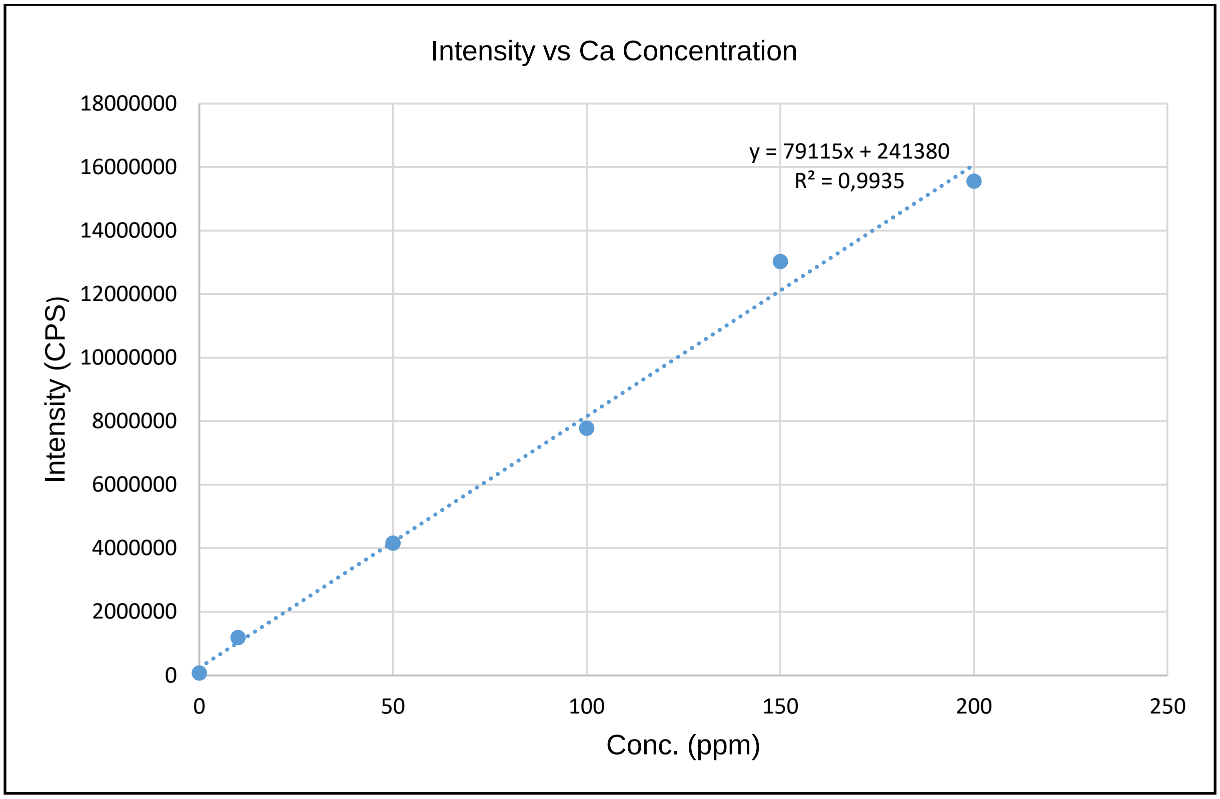
Conc. Mg (ppm)	Intensity (CPS)
0	1247
10	40669
50	180202
100	364839
150	648533
200	789497



Mg calibration curve

Ca calibration standards

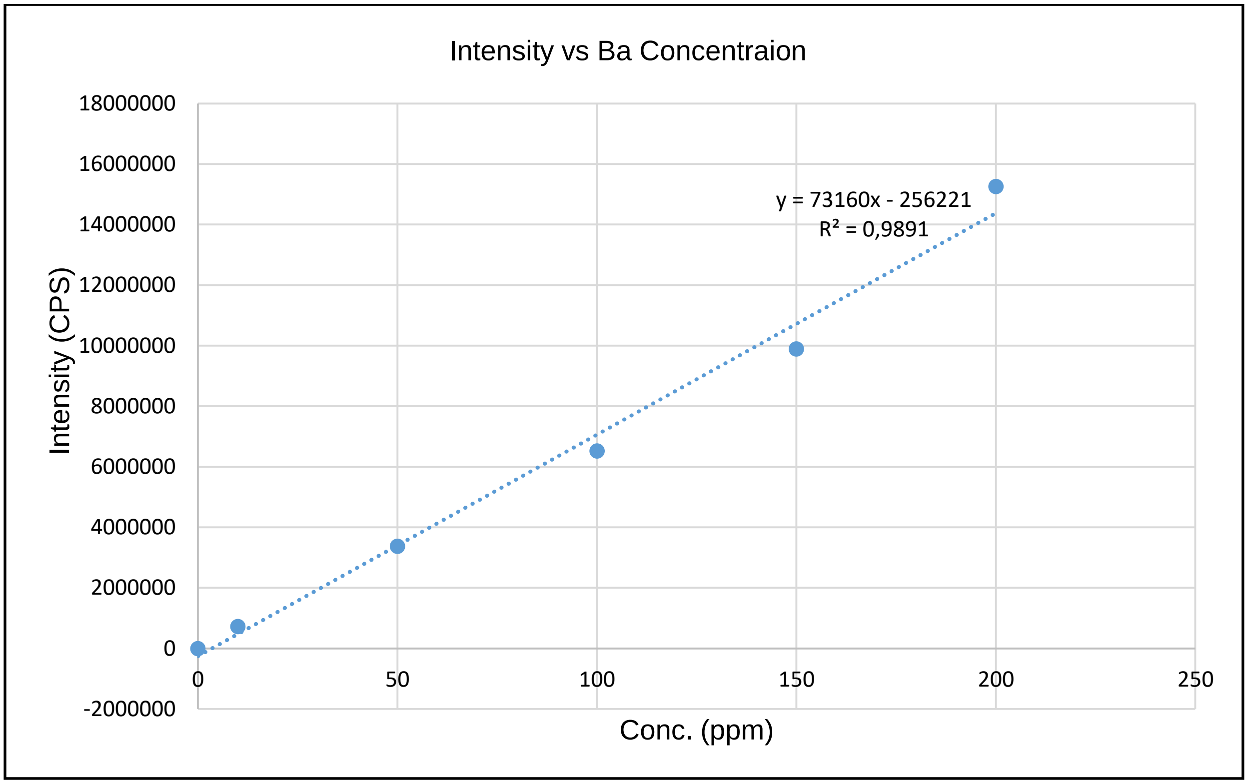
Conc. Ca (ppm)	Intensity (CPS)
0	71974
10	1192510
50	4161100
100	7779030
150	13034100
200	15558200



Ca calibration curve

Ba calibration standards

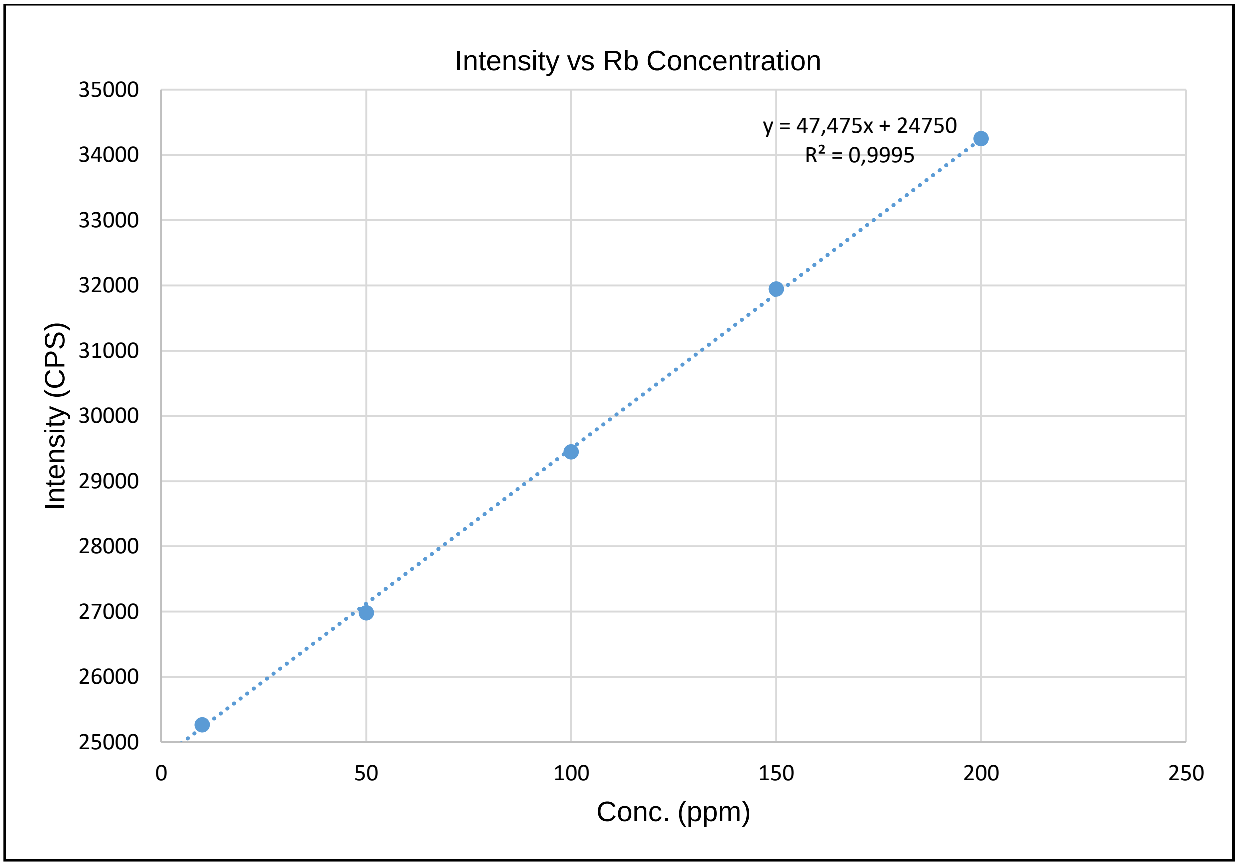
Conc. Ba (ppm)	Intensity (CPS)
0	2822
10	722133
50	3374790
100	6526830
150	9891040
200	15256881



Ba calibration curve

Rb calibration standards

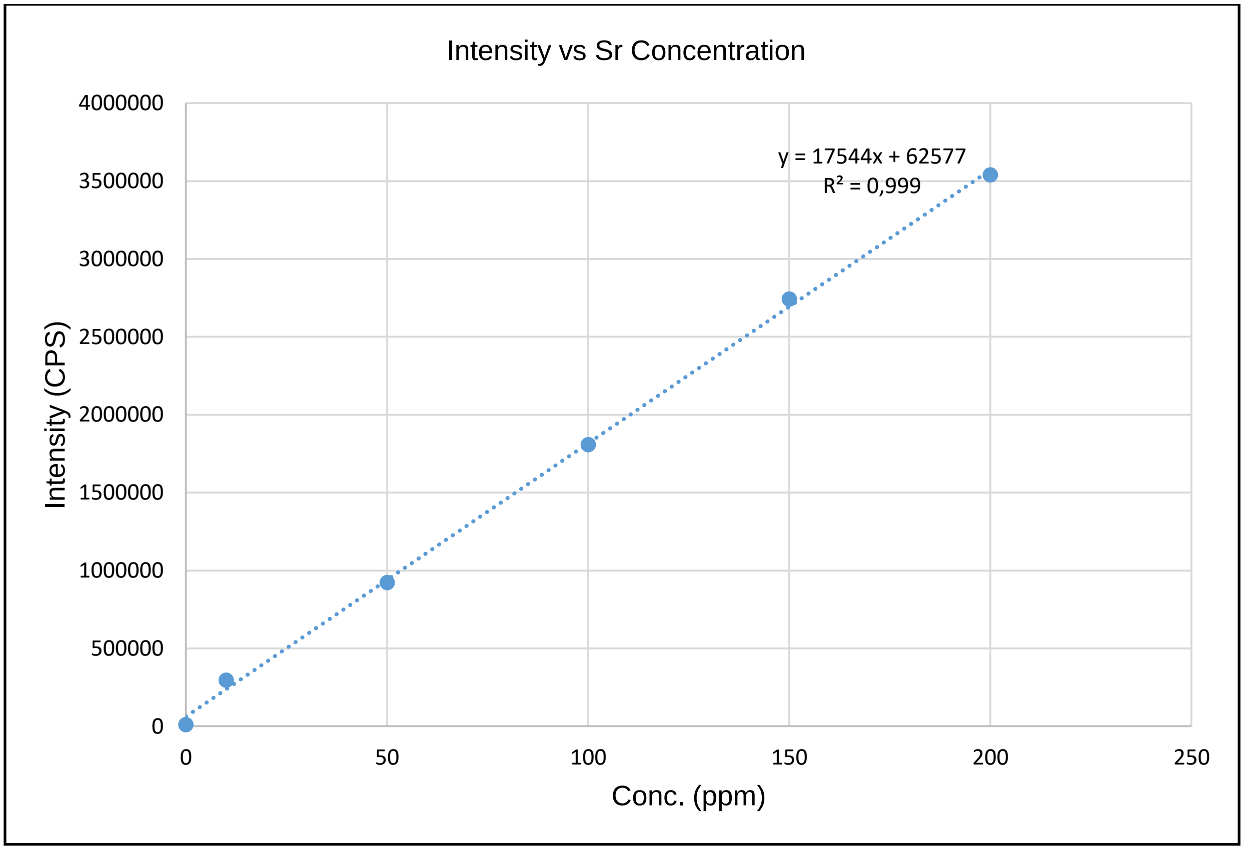
Conc. Rb (ppm)	Intensity (CPS)
0	24829
10	25263
50	26980
100	29447
150	31944
200	34250



Rb calibration curve

Sr calibration standards

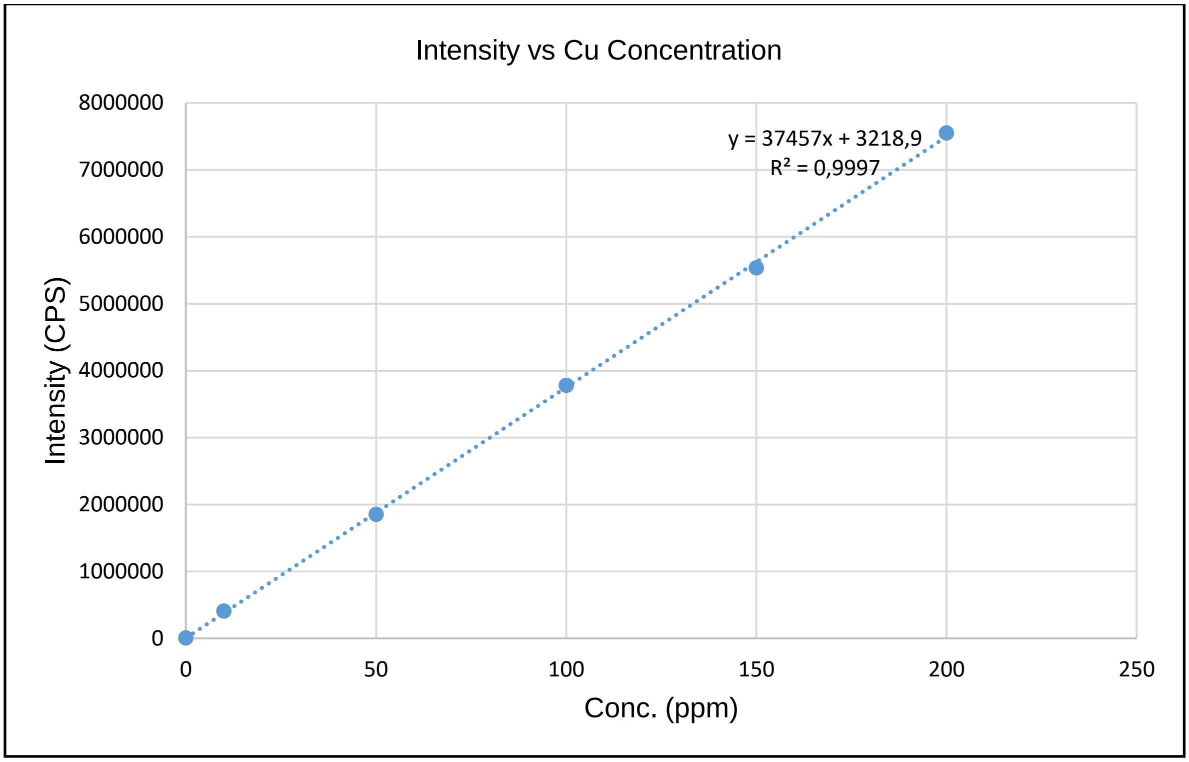
Conc. Sr (ppm)	Intensity (CPS)
0	11685
10	296828
50	922774
100	1808350
150	2742480
200	3540740



Sr calibration curve

Cu calibration standards

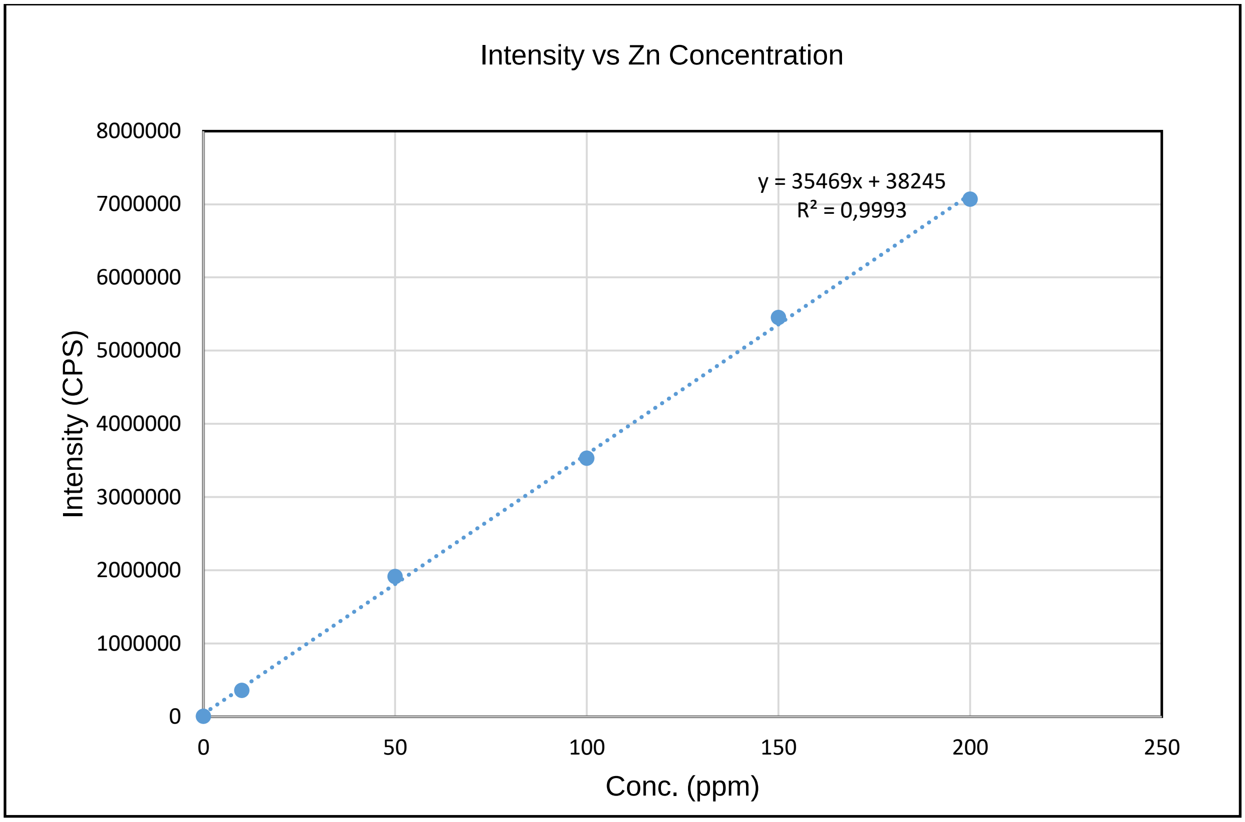
Conc. Cu (ppm)	Intensity (CPS)
0	3568
10	403686
50	1851210
100	3779050
150	5536310
200	7548590



Cu calibration curve

Zn calibration standards

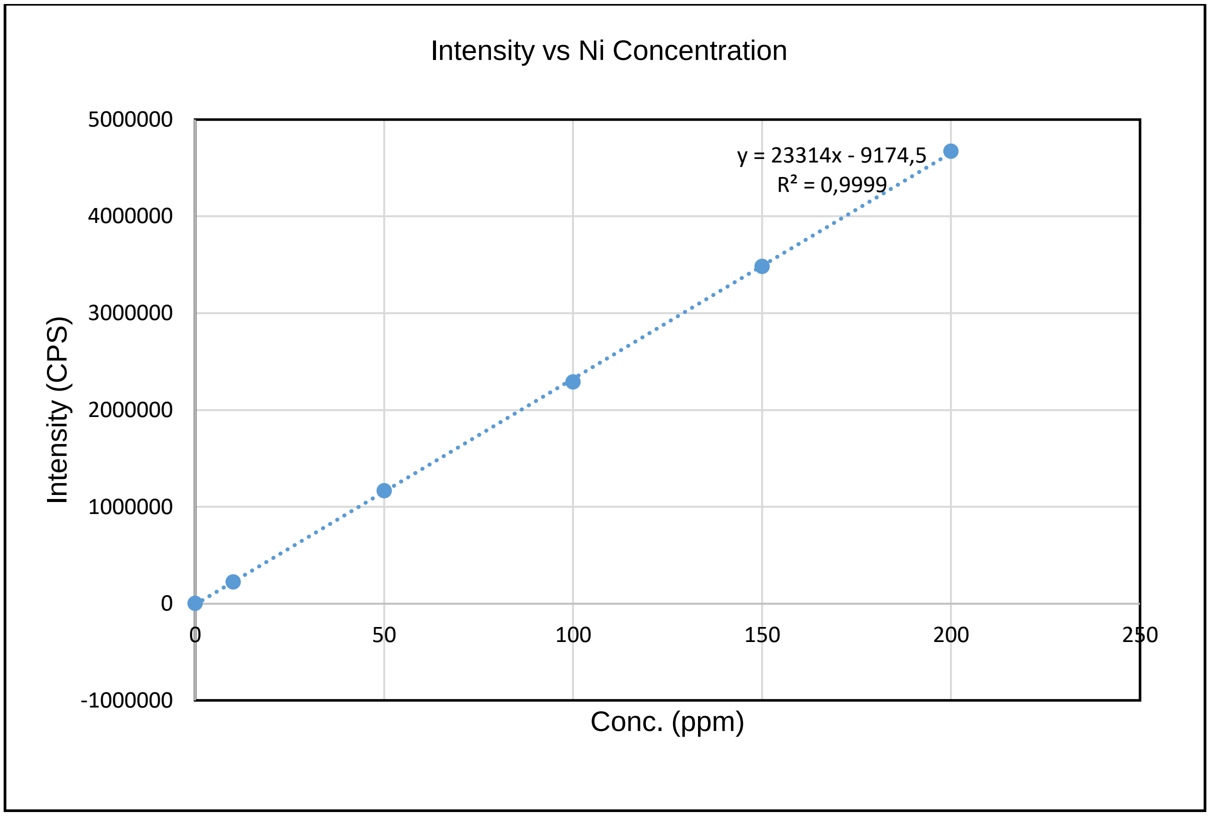
Conc. Zn (ppm)	Intensity (CPS)
0	1844
10	355432
50	1913850
100	3528920
150	5452730
200	7065920



Zn calibration curve

Ni calibration standards

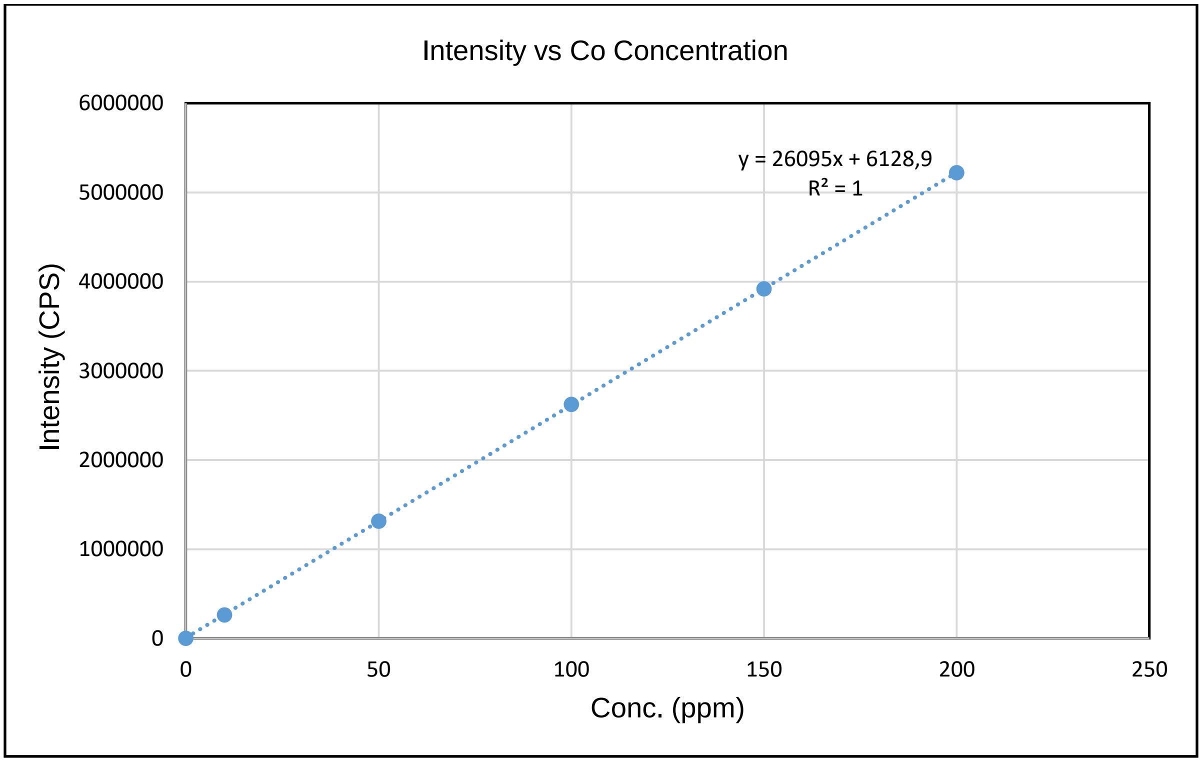
Conc. Ni (ppm)	Intensity (CPS)
0	2176
10	223209
50	1165830
100	2289110
150	3483570
200	4671060



Ni calibration curve

Co calibration standards

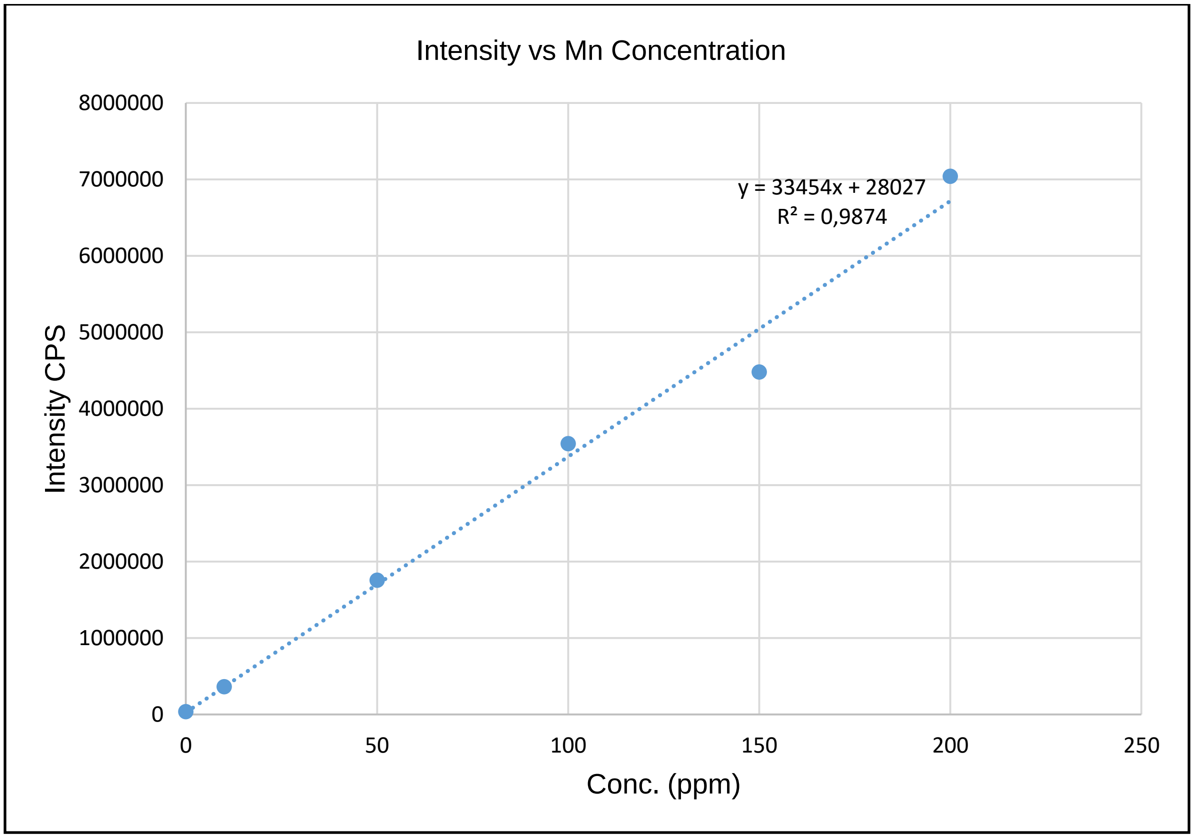
Conc. Co (ppm)	Intensity (CPS)
0	2762
10	262947
50	1314670
100	2625690
150	3918280
200	5221090



Co calibration curve

Mn calibration standards

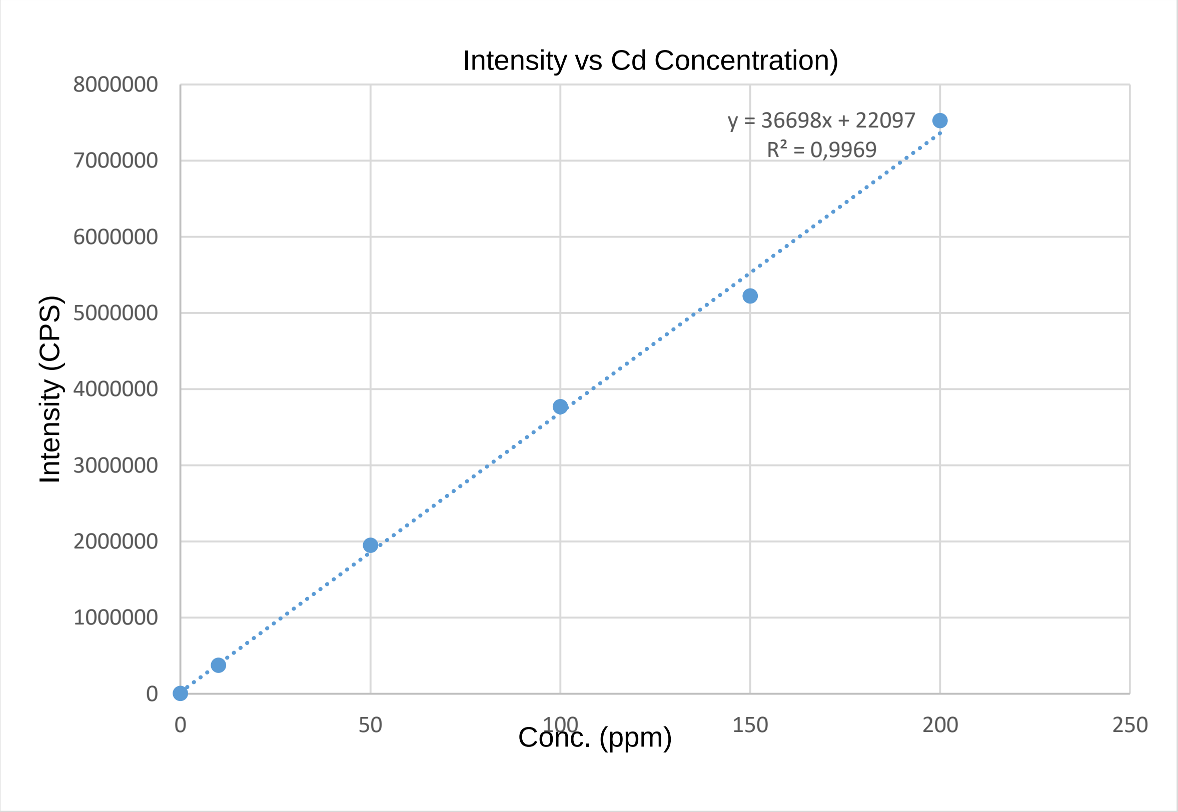
Conc. Mn (ppm)	Intensity (CPS)
0	39027
10	365063
50	1756780
100	3544510
150	4482380
200	7042000



Mn calibration curve

Cd calibration standards

Conc. Cd (ppm)	Intensity (CPS)
0	3203
10	374577
50	1948260
100	3771170
150	5224891
200	7526230



Cd calibration curve

Fe(III) calibration standards

Conc. Fe(III) (ppm)	Intensity (CPS)
0	3752
10	557994
50	2830400
100	5500940
150	8296790
200	10950600

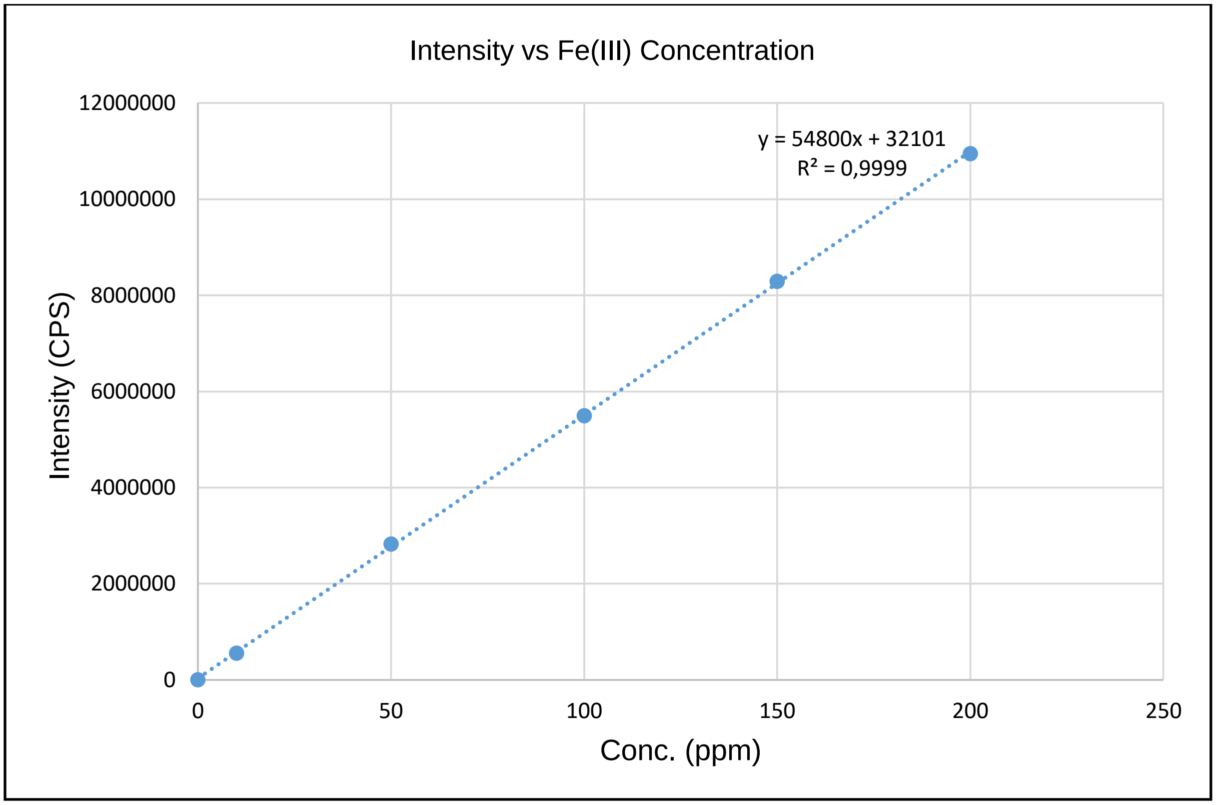


Figure 8-1: Fe(III) calibration curve

Al calibration standards

Conc. Al (ppm)	Intensity (CPS)
0	9429
10	268750
50	1181900
100	2375760
150	3554740
200	4746400

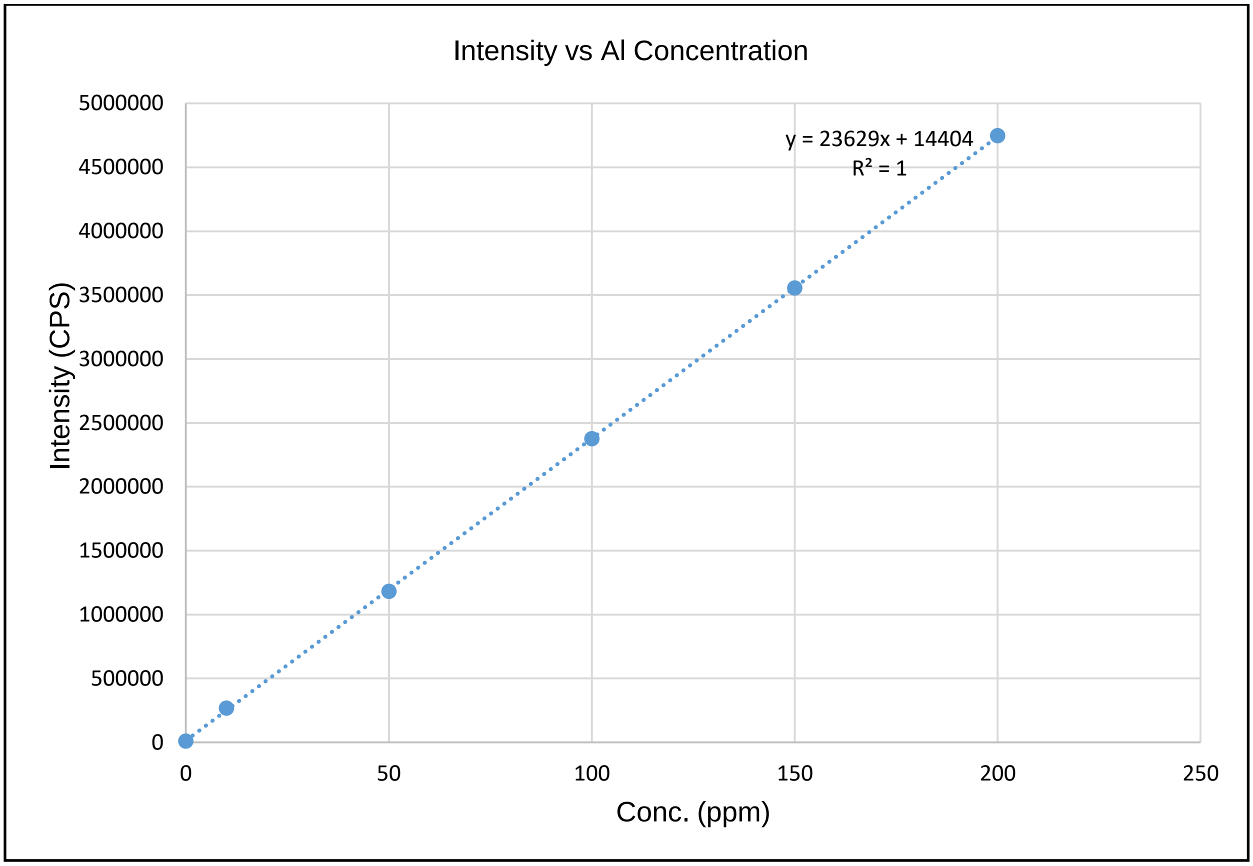


Figure 8-2: Al calibration curve

Pb calibration standards

Conc. Pb (ppm)	Intensity (CPS)
0	2280
10	53850
50	238561
100	465396
150	702392
200	935376

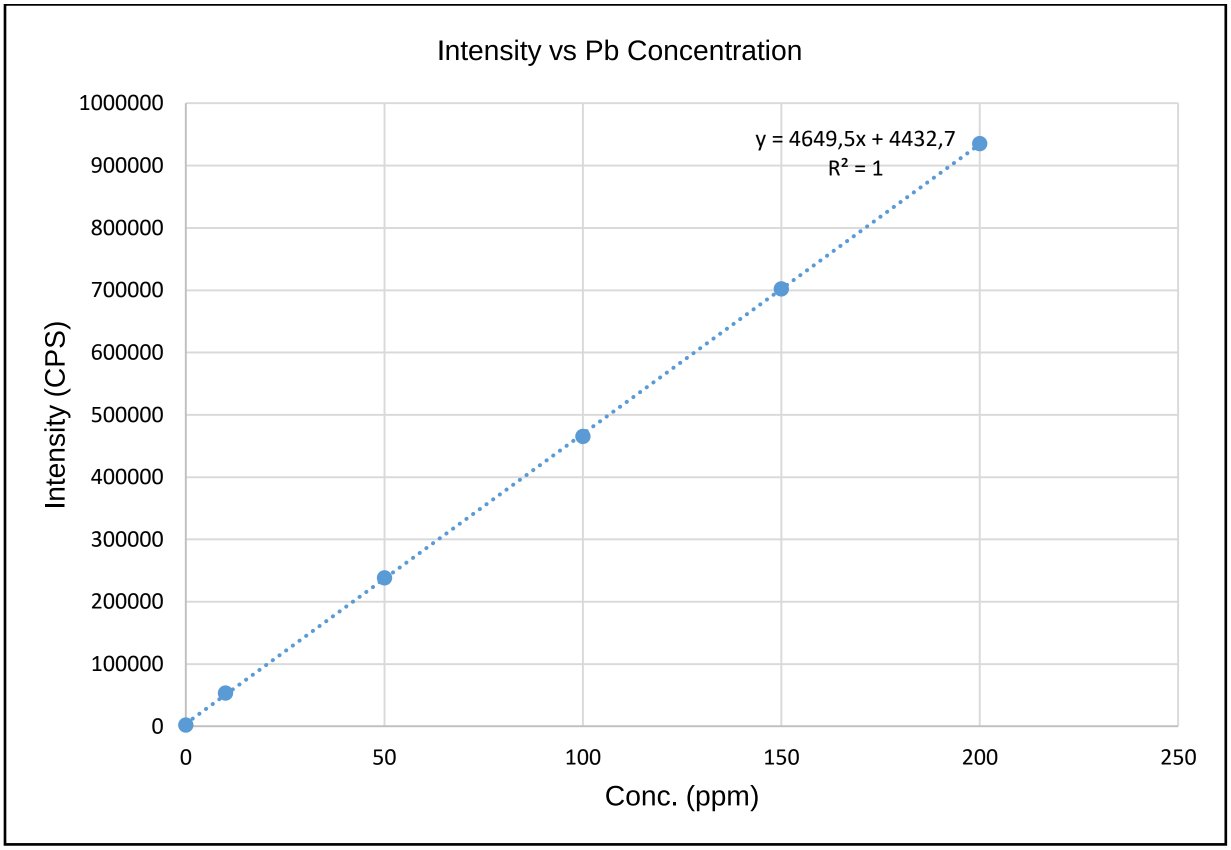
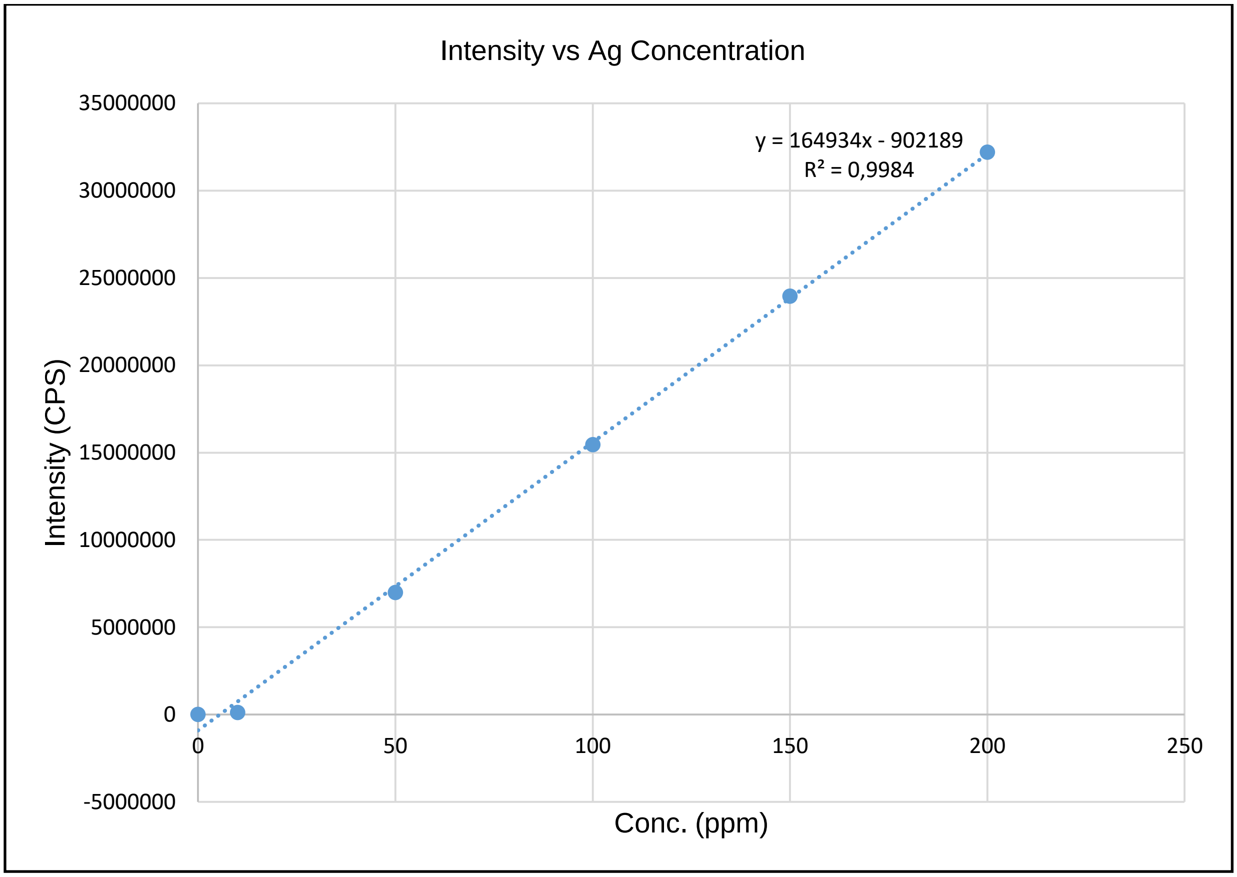


Figure 8-3: Pb calibration curve

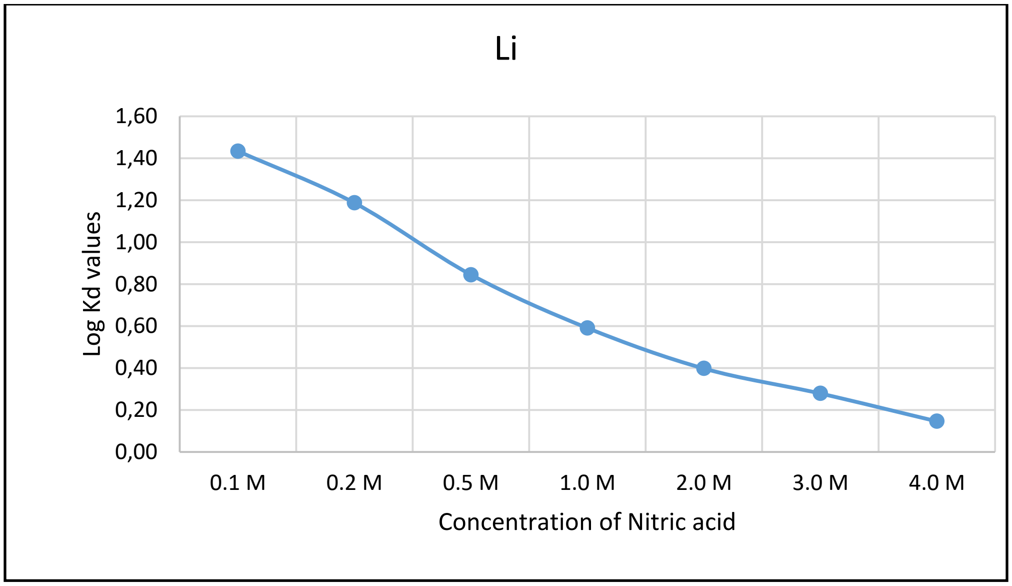
Ag calibration standards

Conc. Ag (ppm)	Intensity (CPS)
0	13438
10	115960
50	6985180
100	15446600
150	23940900
200	32200900

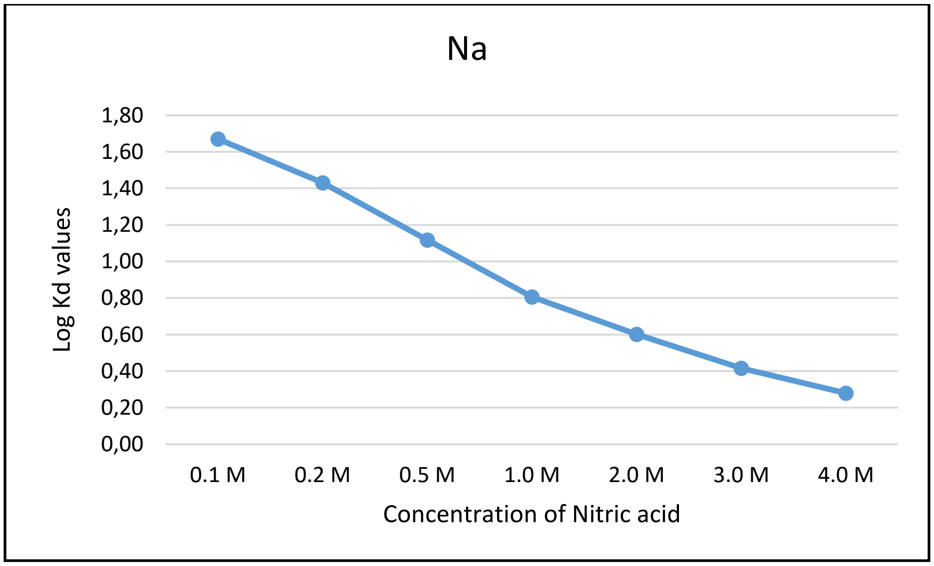


Ag calibration curve

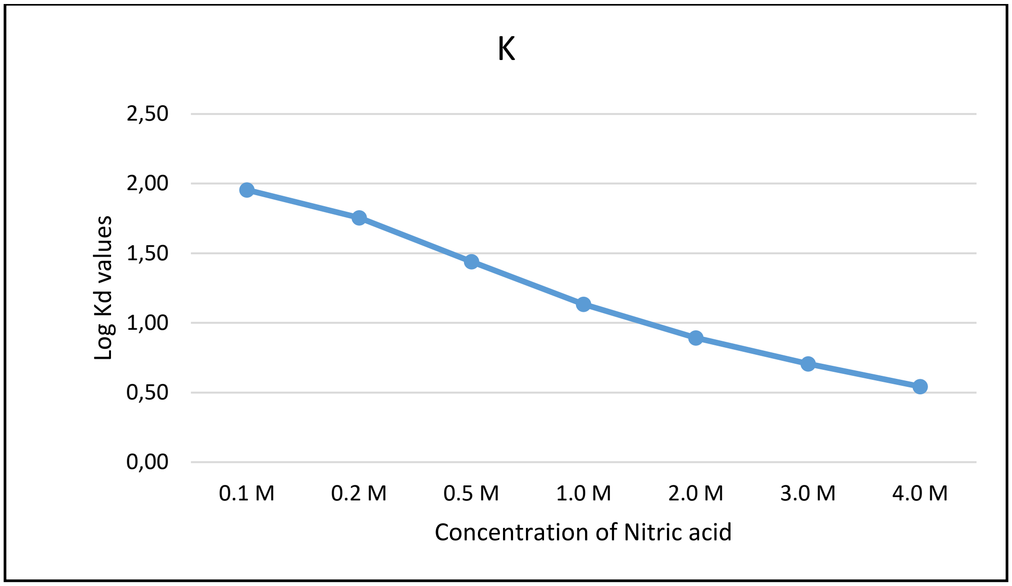
APPENDIX B: Log K_d values of each element studied plotted against the concentration eluate



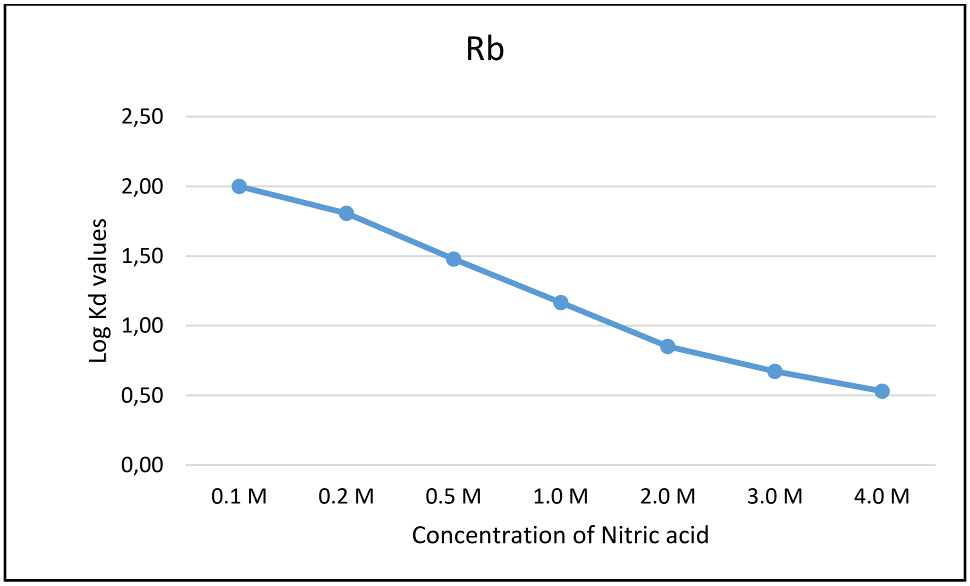
Log Kd values Na plotted against the concentration eluate



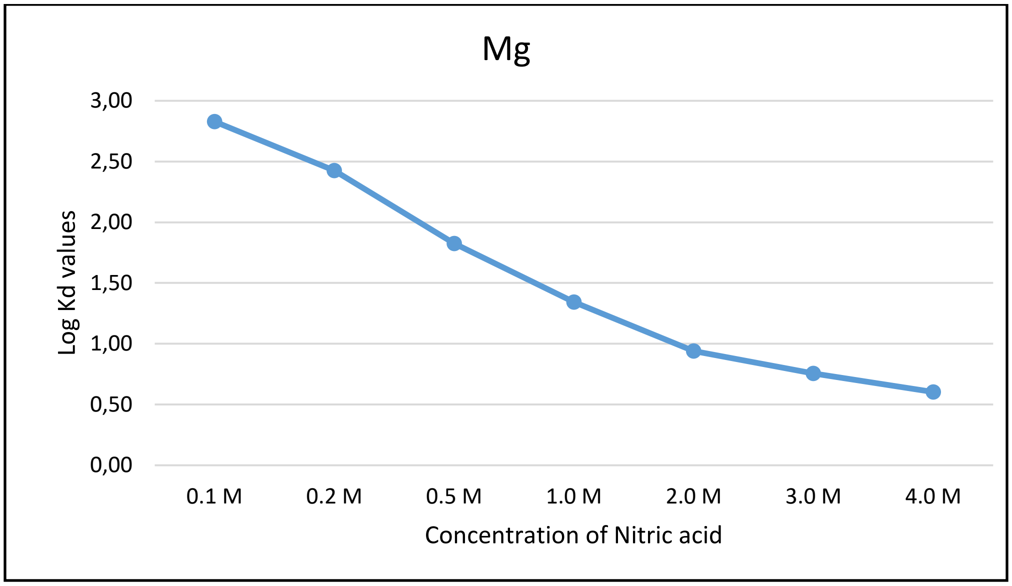
Log Kd values of K plotted against the concentration eluate



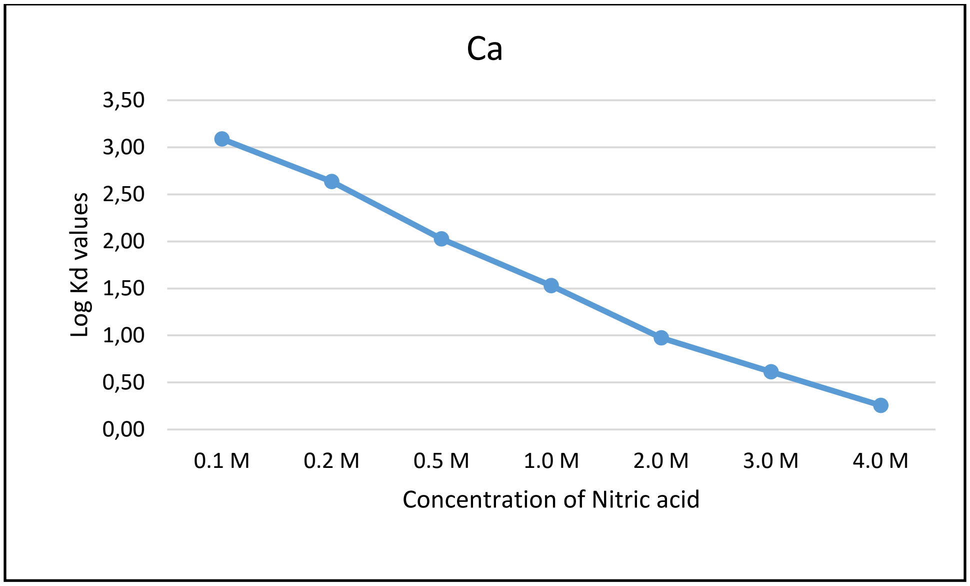
Log Kd values of Rb plotted against the concentration eluate



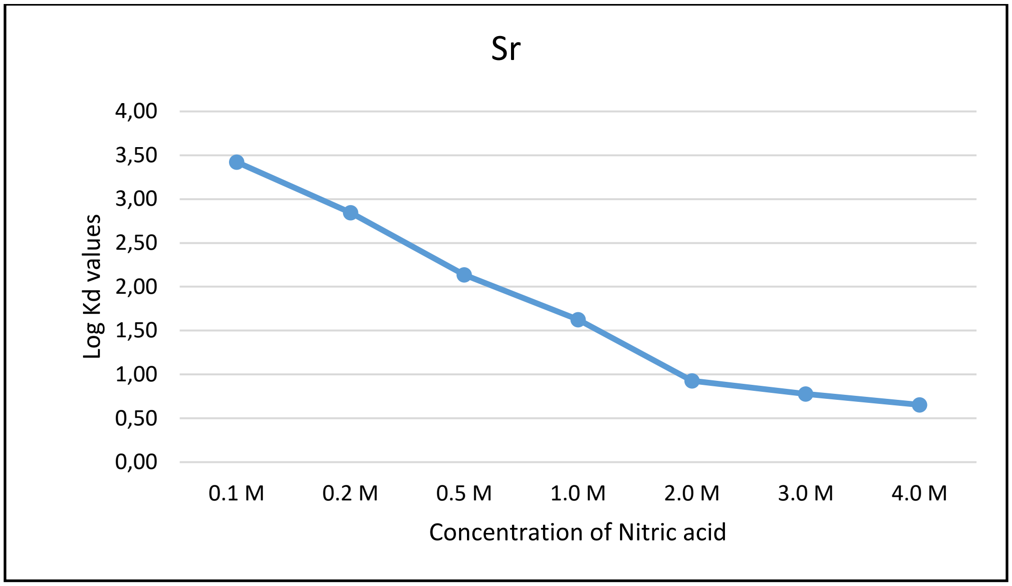
Log Kd values of Mg plotted against the concentration eluate



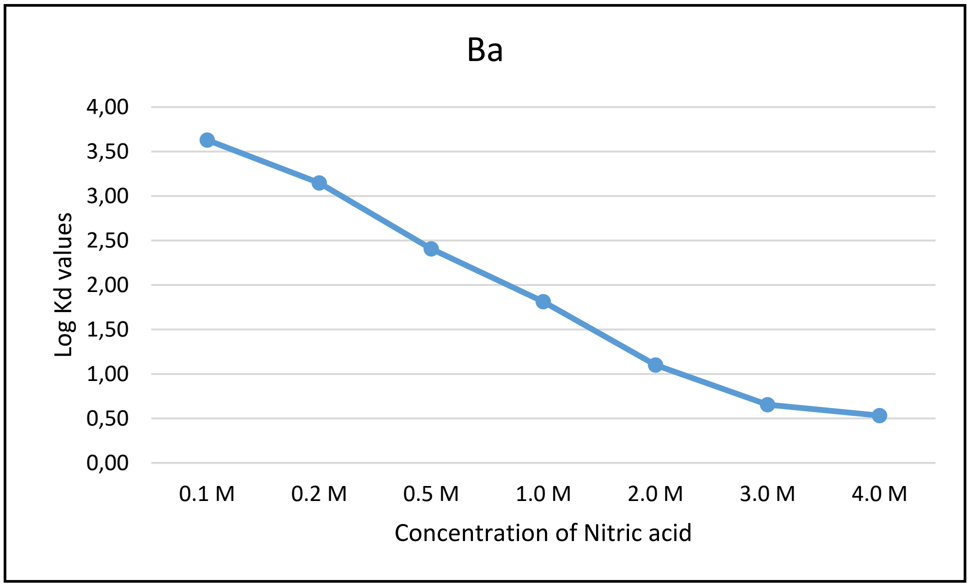
Log Kd values of Ca plotted against the concentration eluate



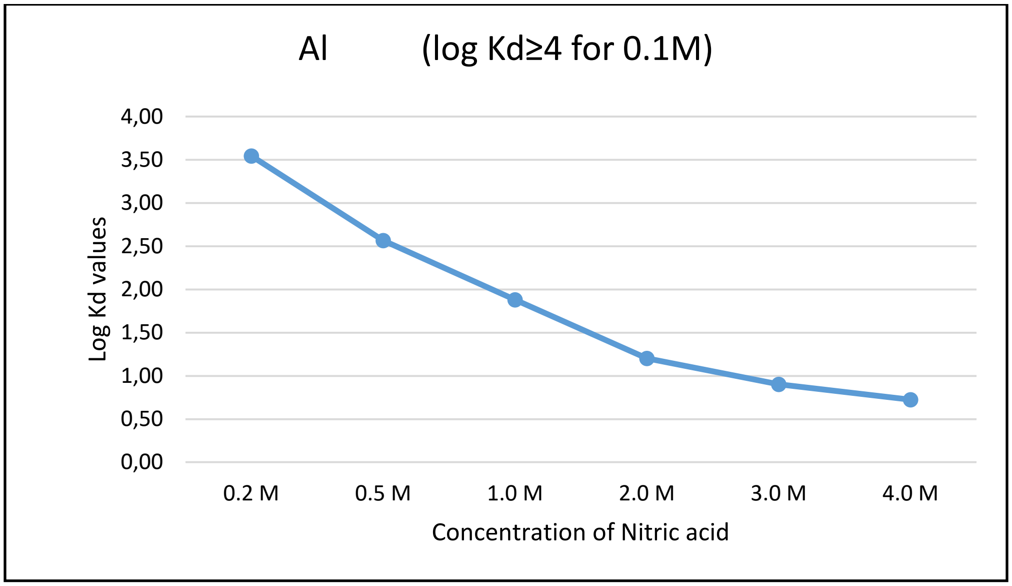
Log Kd values of Sr plotted against the concentration eluate



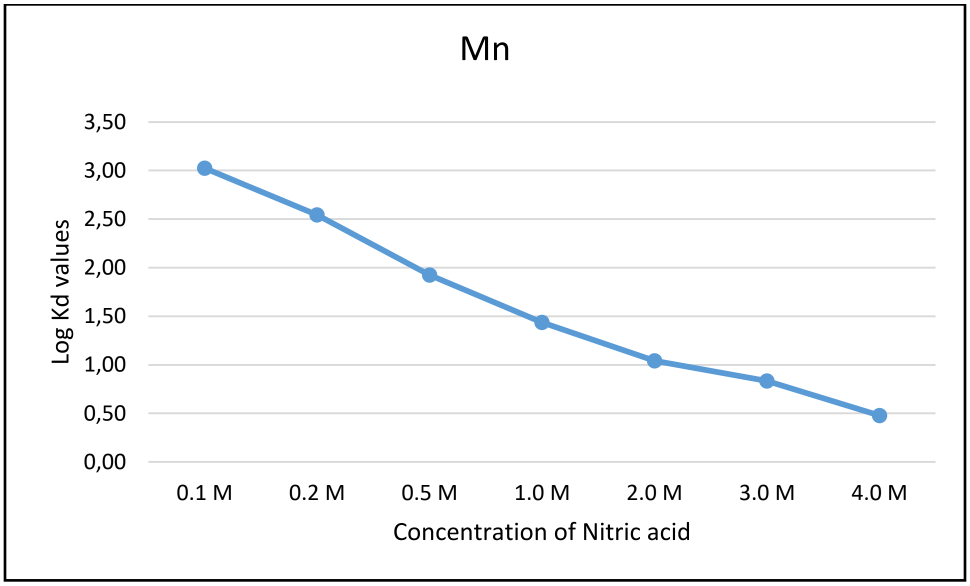
Log Kd values of Ba plotted against the concentration eluate



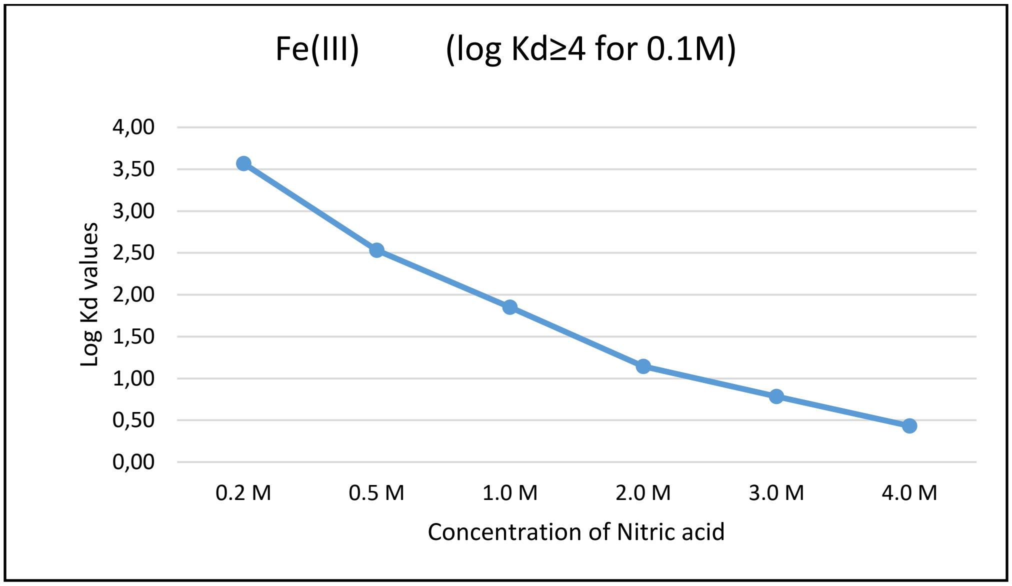
Log Kd values of Al plotted against the concentration eluate



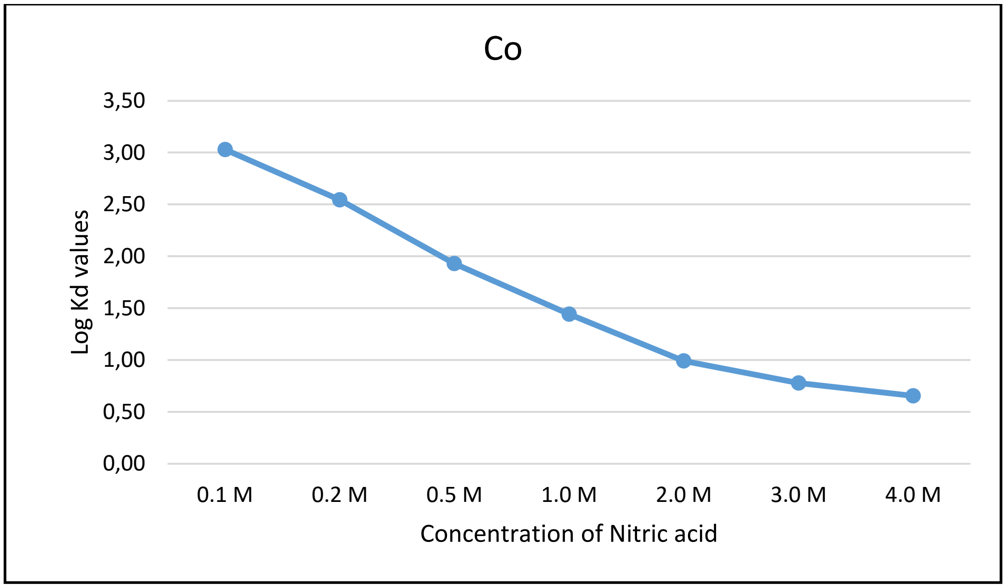
Log Kd values of Mn plotted against the concentration eluate



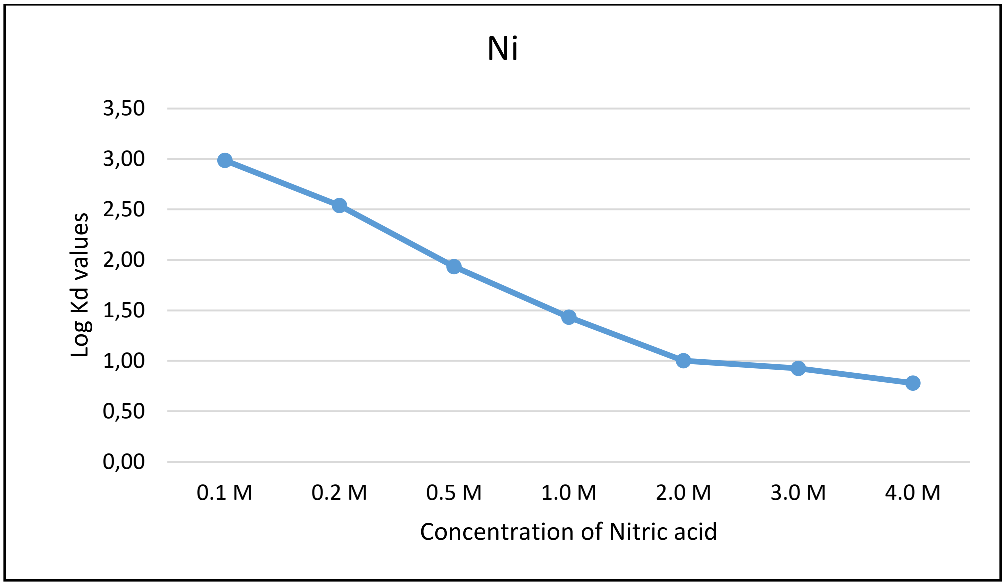
Log Kd values of Fe plotted against the concentration eluate



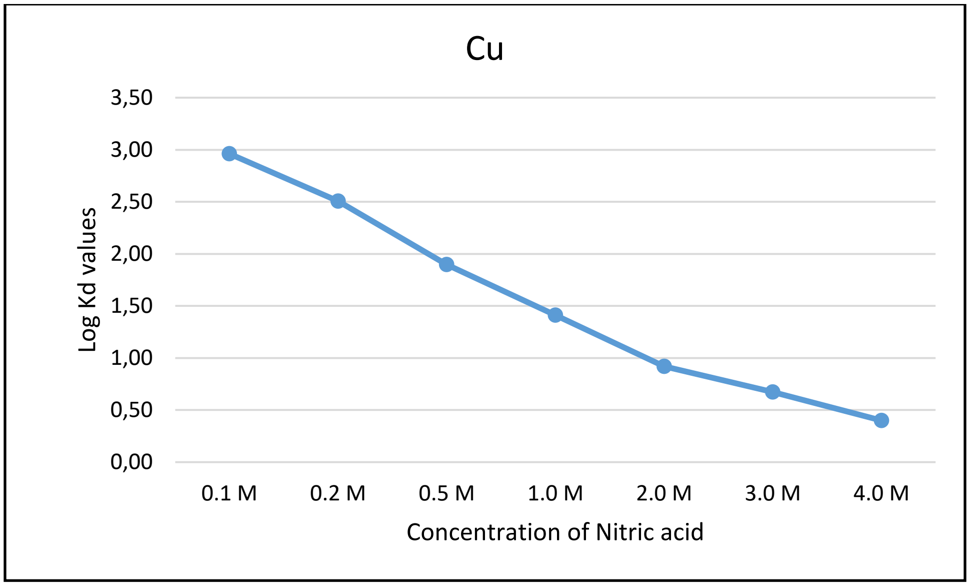
Log Kd values of Co plotted against the concentration eluate



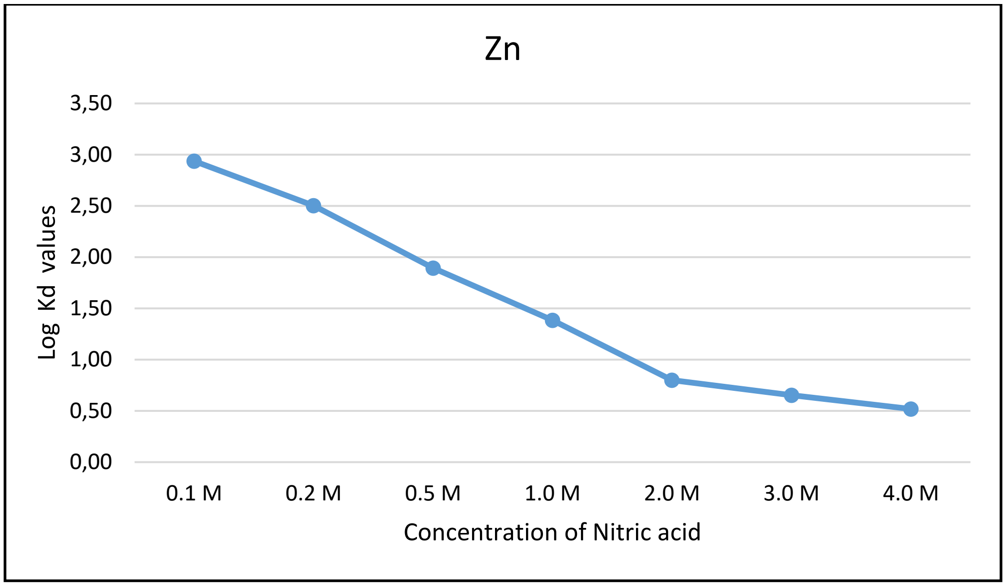
Log Kd values of Ni plotted against the concentration eluate



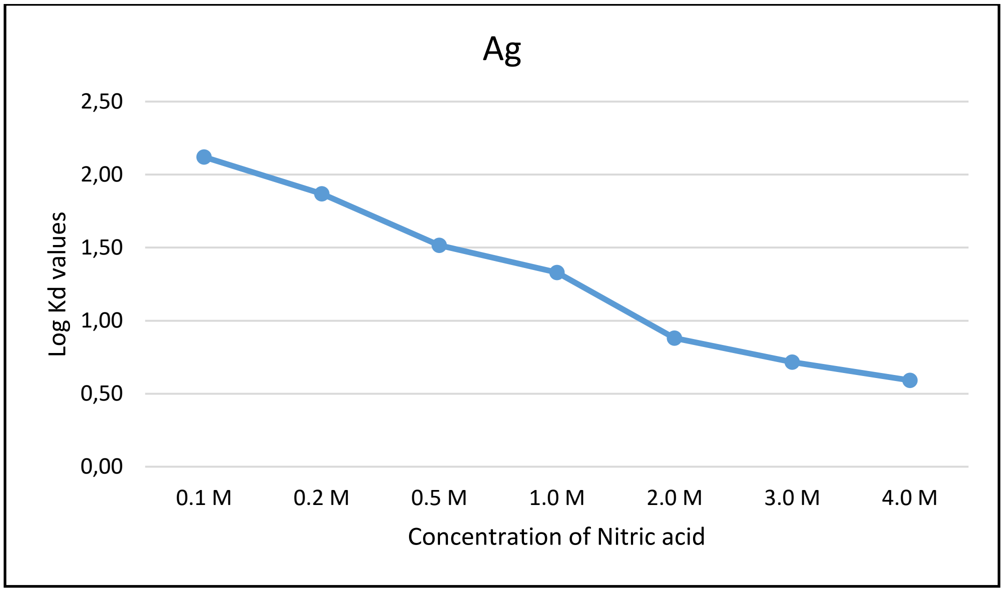
Log Kd values of Cu plotted against the concentration eluate



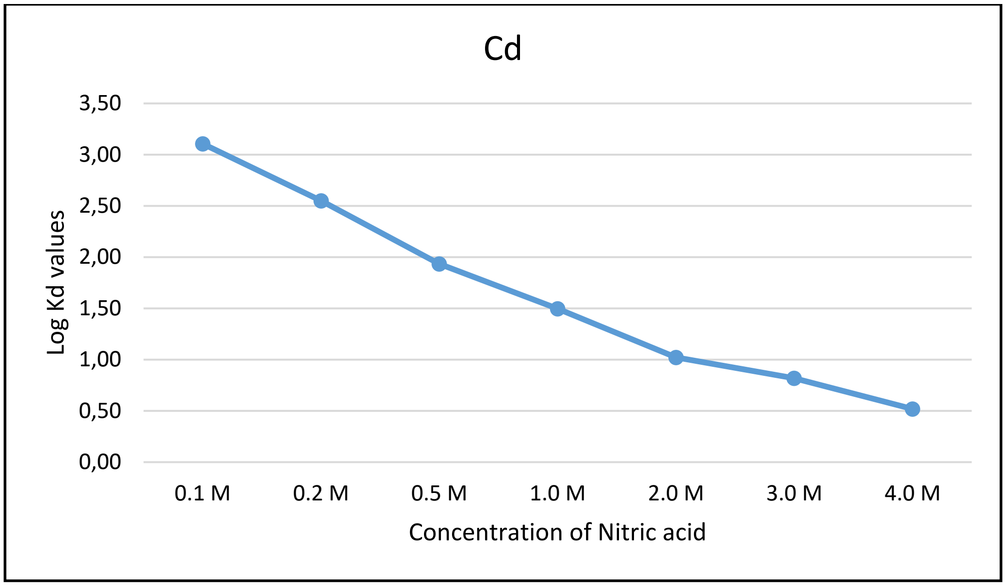
Log Kd values of Zn plotted against the concentration eluate



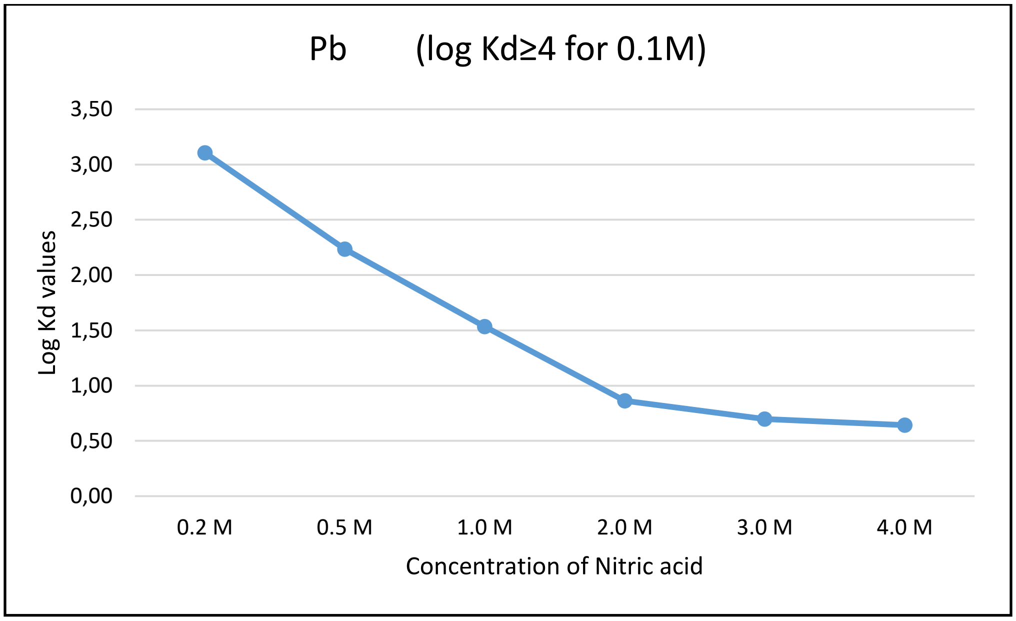
Log Kd values of Ag plotted against the concentration eluate



Log Kd values of Cd plotted against the concentration eluate



Log Kd values of Pb plotted against the concentration eluate



APPENDIX C: Table 5-6: Results of elution of Mg and Na concentrations as it was eluted from the resin and the solution analysed on the ICP-OES

Vol of eluate	Conc. of Na in	Conc. of Mg in	Conc. of Mg in
	0.5 M HNO_3	0.5 M HNO_3	2.0 M $HN0_3$
10	45	0	0
20	192	0	0
30	2620	0	0
40	4070	0	0
50	2570	0	0
60	241	0	21
70	45	0	53
80	38	0	405
90	34	0	583
100	30	0	516
110	0	0	2751
120	0	0	669
130	0	0	216
140	0	0	189
150	0	0	96

APPENDIX D: Table 8-1:ICP-OES results of both Mg and Na after elution

Vol of eluent solution	Mg after eluted	Na after eluted
10	0	3.2
20	0	4.4
30	0	3
40	0	3.2
50	0	5.2

Appendix E: SEM/EDS particle scan