#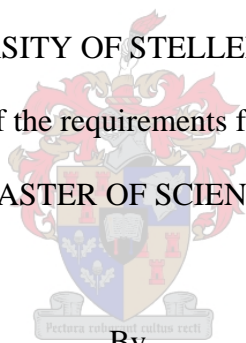 ION EXCHANGE BEHAVIOUR OF 42 SELECTED ELEMENTS ON AG MP-50 CATION EXCHANGE RESIN IN NITRIC ACID AND CITRIC ACID MIXTURES

A thesis submitted to the

UNIVERSITY OF STELLENBOSCH

In fulfilment of the requirements for the degree of

MASTER OF SCIENCE

By

NICHOLAS VAN DER MEULEN

Supervisor: Dr. T. N. van der Walt

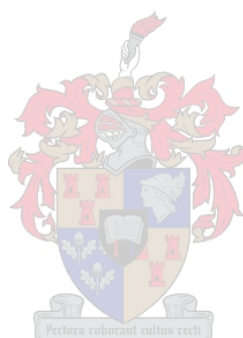Co-Supervisor: Prof. H. G. Raubenheimer

January 2003

DECLARATION

I, the undersigned, hereby declare that the work contained in this thesis is my own original work and has not previously, in its entirety or in part, been submitted at any university for a masters degree in chemistry.

Signature: _____

Date: _____

ACKNOWLEDGEMENTS

I wish to express my gratitude to the following people without whom this study would not have been possible:

- Dr. Nico van der Walt, my promoter, for his encouragement, support and guidance towards this work and giving me the opportunity to further my studies. His guidance in the field of study, including the corrections to this work, was invaluable.

- Prof. Helgard Raubenheimer, my co-promoter, for accepting me as a student at the University of Stellenbosch and for all the help provided in the layout of the study, as well as for his patience.

- Stuart Dolley, Monique van Rhyn and Etienne Vermeulen for their friendship, support and assistance they have provided at some stage during this endeavour.

- My wife, for helping me to believe I can do it.

- My parents, who have provided me with love and support and have always encouraged me in all I do.

- Friends, family and colleagues whom I have not mentioned, but who are in my heart.

- The Lord Jesus Christ, for giving me strength, perseverance and determination when I had none left to give.

This work is dedicated to my father, whom I blame for leading me into the field of chemistry.

ABSTRACT

The equilibrium distribution coefficients of 42 elements [Li(I), Na(I), K(I), Rb(I), Cs(I), Sc(III), Ti(IV), V(IV), V(V), Mn(II), Fe(III), Ni(II), Zn(II), Al(III), Ga(III), As(V), Y(III), Zr(IV), Nb(V), Mo(VI), Cd(II), In(III), Sn(IV), Sb(V), Ta(V), W(VI), Pb(II), Bi(III), La(III), Ce(III), Th(IV), U(VI), Co(II), Ag(I), Ge(IV),Mg(II), Sr(II), Ba(II), Tb(III), Yb(III), Cr(III) and Cu(II)] on Bio Rad AG MP-50 macroporous cation exchange resin in varying citric acid – nitric acid mixtures were successfully determined. The equilibrium distribution coefficients of these selected elements were determined in 0.1 M and 0.25 M citric acid at various concentrations of nitric acid, namely, 0.2 M, 0.5 M, and 1.0M, respectively.

Two component [Mo(VI)-Y(III); Zr(IV)-La(III) and As(V)-Zn(II)] and three component [Nb(V)-Ta(V)-V(V)] elemental separations on a 10 ml AG MP-50 resin column were successfully determined to illustrate how the results of the above equilibrium distribution coefficients can be utilised.

From the equilibrium distribution coefficients obtained for magnesium(II) and sodium(I), a proposal was put forward to modify the current sodium-22 production performed at iThemba LABS. While the results did not predict a possible separation between the two elements, a theory concerning the use of citric acid in the production was proven not to hold under the chosen conditions.

OPSOMMING

Die ewewig verdelingskoëffisiënte van 42 elemente [Li(I), Na(I), K(I), Rb(I), Cs(I), Sc(III), Ti(IV), V(IV), V(V), Mn(II), Fe(III), Ni(II), Zn(II), Al(III), Ga(III), As(V), Y(III), Zr(IV), Nb(V), Mo(VI), Cd(II), In(III), Sn(IV), Sb(V), Ta(V), W(VI), Pb(II), Bi(III), La(III), Ce(III), Th(IV), U(VI), Co(II), Ag(I), Ge(IV),Mg(II), Sr(II), Ba(II), Tb(III), Yb(III), Cr(III) en Cu(II)] is op Bio Rad se AG MP-50 makroporeuse kationiese uitruilerhars in verskillende sitroensuur – salpetersuur mengsels met sukses bepaal. Die verdelingskoëffisiënte is in 0.1 M en 0.25 M sitroensuur met verskillende konsentrasies van salpetersuur (0.2 M, 0.5 M en 1.0 M) bepaal.

Twee-komponent [Mo(VI)-Y(III); Zr(IV)-La(III) en As(V)-Zn(II)] en drie-komponent [Nb(V)-Ta(V)-V(V)] skeidings op 'n 10 ml AG MP-50 harskolom is suksesvol bepaal om te demonstreer hoe die verdelingskoëffisiëntresultate gebruik kan word.

As 'n uitvloeisel van die verdelingskoëffisiëntresultate vir Mg(II) en Na(I), is 'n voorstel ingedien om die huidige natrium-22 produksiemetode, tans in gebruik by iThemba LABS, te modifiseer. Die resultate het nie 'n skeiding tussen die twee elemente voorspel nie, maar het bewys dat 'n teorie oor die gebruik van sitroensuur in die produksie nie heeltemal korrek was onder die huidige toestande nie.

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1. INTRODUCTION AND MOTIVATION FOR PROJECT

iThemba LABS utilises a 66 MeV proton beam for the production of a number of radionuclides for radiopharmaceutical purposes and other applications. Bombarding the appropriate target material, which is sintered, cut or pressed into a disc, produces a radionuclide, which results from a nuclear reaction that takes place within the target. The radionuclide has to be chemically separated from the target material, purified from any contaminants and sterilised before it can be labelled and considered for use as diagnostic medicine.

The chemical separation of the radionuclide from the target material is complicated by the fact that a very small quantity of radionuclide is formed (10^{-9}-10^{-12} g) in comparison with the very large quantity of target material it has to be separated from (1-16 g). What complicates the matter even further is the fact that there may be other radionuclides present which are produced by side reactions in the bombardment or by the decay of some of these radionuclides, as well as the chemical impurities initially present in the target material. Many chemical techniques have been attempted to separate the radionuclide from the non-required elements, namely, solvent extraction, distillation, electro-deposition, precipitation, co-precipitation and ion exchange chromatography.

Ion exchange chromatography has been used in many disciplines in the past and is sometimes regarded as an obsolete application of chemistry for these disciplines, with chemists and engineers using other "more effective" forms of chemistry. Although

ion exchange chromatography is not widely used in industry today, it is still regarded as being the cutting edge of technology in radiochemistry. It is easy to use in a hot cell environment and the removal of impurities in the separation process before eluting the radionuclide of choice, provides a much purer product than any other method used.

Some points have to be considered when planning an ion exchange separation. Due to the fact that the target material in a specific production is generally of a large quantity (gram quantities), while the radionuclide to be produced is found in much smaller quantities (< μg quantities), a large separation factor (α^A_B) is required to separate the radionuclide (A) from the target material (B). It is generally considered that the radionuclide should have a high distribution coefficient ($K_d > 500$), while the target material should have a much lower distribution coefficient ($K_d < 10$). Initially, the separation factor should be greater than 50. It is recommended that equilibrium be reached as quickly as possible; therefore, it is necessary to have a column with good kinetics such that a sharp separation is obtained, with very little "tailing". A relatively small resin column will always be preferred over a larger column, as smaller elution volumes are preferred to elute the sorbed elements. This would also lead to a short chemical separation process and can be an important factor in the final product whose yield is dependent on the half-life of a specific radionuclide. It would also minimise the quantities of waste solutions being generated (which are normally radioactive, should the separation involve radioactivity), which are monitored and, normally, have to be stored for a period of time before being released to waste storage dams on site.

Ion exchange resins are normally categorised into three types, namely, cation exchange resins (for example, Dowex 50 or Bio Rad AG50- and AG MP-50 resins), anion exchange resins (such as Dowex 1 or Bio Rad AG1- and AG MP-1 resins) and chelating ion exchange resins (like Chelex 100 or Purolite S940). There are other types of resins available, including those containing no ion exchange groups (for example, Amberlite XAD-7), but these are not often used for the purposes at iThemba LABS (Samuelson 1956, Reiman and Walton 1970 and Van der Walt, 1993).

The type of resin to be used in a chemical separation depends on the charge of the radionuclide and that of the target material (that is, positive or negative) and the oxidation number of the radionuclide. Should the radionuclide be cationic, or a cationic species is formed by complex formation, then a cation exchange resin is chosen as the resin column of use for the production. Should the target material, however, be anionic, or an anionic species is formed by complex formation, then an anion exchange resin would be chosen to retain the radionuclide. Media that will promote the sorption of the required radionuclide cation, while eluting the target material anion at the same time, has also to be determined.

The radionuclide and the target material are not usually of opposite charge: they are generally found to be of the same charge and a separation with a cation or anion exchange resin can be devised with the aid of distribution coefficients in a specific resin/solution system. In this case the size, charge and valencies of the element ions play a vital role. The element is more strongly sorbed to the resin with an increase in ionic charge, while the other factor playing an important role is that of the nature and type of eluting solution, be it the concentration of the solution, the availability of

coordinating ligands therein, the acidity of the solution and whether the solution is a mixture or not.

Radionuclides have been manufactured in South Africa since 1965. The project began at the CSIR cyclotron in Pretoria and, since its closure in 1988, with the separated-sector cyclotron (SSC) at iThemba LABS supported by a strong research and development programme. The high energy of the Separated-Sector cyclotron and its superior facilities makes it possible to introduce a variety of short-lived radionuclides, such as I-123, Rb-81, Ga-67, F-18, In-111 and Tl-201, as well as longer-lived radionuclides such as Na-22, Ge-68, Sr-82 and Ce-139. The longer-lived radionuclides are usually exported and Na-22 and Ce-139 are manufactured for non-medical use.

1.1 RADIONUCLIDE PRODUCTION AT iTHEMBA LABS
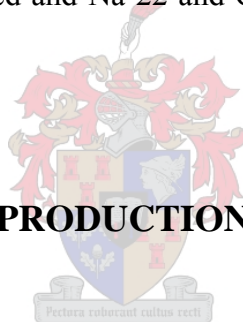
The Radionuclide Production Group at iThemba LABS is heavily relied upon by local hospitals and clinics to produce various radiopharmaceuticals, for medical purposes, and to deliver the required activity to them. The group is the main source of income generated for iThemba LABS and sales of the available radionuclides have increased dramatically over the last few years. As a result, the amount of activity to be despatched has increased, which requires certain facilities for personnel to be able to perform their duties safely.

Each specific radionuclide production has an allocated hot cell in which to perform the production, for two reasons. Firstly, each production has a different method, due

to the target material being used, etc. and, therefore, each production has its own uniquely designed panel (for example, the sodium-22 production panel – see figure below). Secondly, and more importantly, a designated hot cell for a specific production prevents any contamination of the final product.
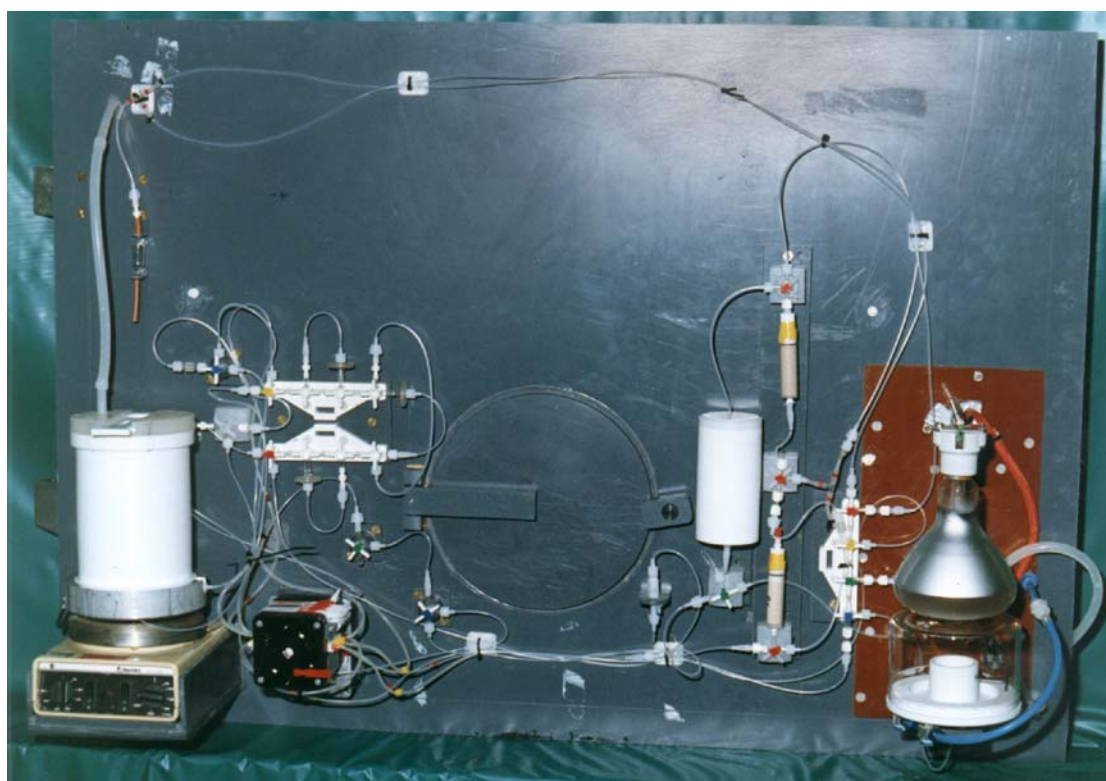
Figure 1.1: Sodium-22 production panel

Once the chemical separation is completed and the desired radiopharmaceutical prepared, it is transported to the dispensing laboratory, where the pharmacist performs the dispensing, according to purchase orders from the hospitals and clinics, in aseptic conditions (Haasbroek *et al.*, 1995). A sample of the final product is taken and quality control procedures are performed on the sample, i.e. the chemical purity, radionuclidic purity etc. is checked, to ensure that it meets with the prescribed specifications as registered with the South African Medical Control Board.

Once the dispensing is taken care of, the vials containing the radiopharmaceutical are sealed and packed into lead pots. The lead pots, in turn, are packed into tins and sealed, before placing them into their respective boxes. The boxes are despatched to the various hospital or clinics that are in need of the product.

1.1.1 Quality control

Various instruments are used in the quality control of radionuclides at iThemba LABS. These include UV/Visible, HPLC, GTA and ICP instruments. The ICP instrument is used for analyses in this work. A brief overview of the ICP instrument is found in Chapter 2.

1.2 MOTIVATION
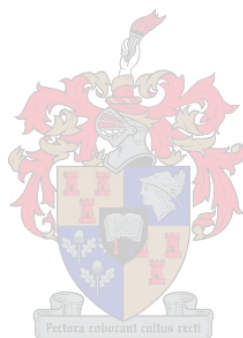
Distribution coefficients of many elements determined on certain cation and anion exchange resins in different media have been reported over the years. The distribution coefficient gives an explanation, to an extent, of the cationic or anionic nature of element ions or complex ions in different media, including the interaction with the active sites on the resin involved. It generally gives an indication of how well an element is retained by the resin (indicating a high distribution coefficient), if at all (indicating a low distribution coefficient).

An increase in the crosslinkage of a resin usually results in an increase in the distribution coefficient of the element. In 1971, Strelow *et al.* proved that, when

using resins with 2% and 4% crosslinkages, the elements tested were not strongly retained and easily eluted and showed this influence of crosslinkage using elements on cation exchange resins purchased from Bio Rad (AG 50W-X2, -X4, -X8, –X12 and –X16). Later, in 1988, van der Walt showed similar effects using elements on anion exchange resins (AG 1-X2, -X4, -X8 and –X10). For elements that are strongly retained by a resin, the particle size of the resin will influence the ability of the element to be eluted. Strelow (1980) and van der Walt *et al.* (1985) proved that it was possible to obtain chemical separations that were sharp, with virtually no "tailing", using 2% and 4% crosslinked resins with a large particle size (100-200 mesh). The characteristics of ion exchange resins are discussed in more detail later in the chapter.

From the explanations concerning the characteristics of ion exchange resins and their use in productions at iThemba LABS, the motivation of this work is simple: *firstly, to carefully obtain distribution coefficients for a number of elements in different concentrations of citric acid/nitric acid media using AG MP-50 cation exchange resin and, secondly, from these results, determine whether it would be possible to perform chemical separations between two or more selected elements for trace analyses of samples, such as geological samples, factory effluent and radionuclide production, to name but a few possibilities.* It is immaterial whether the results show that it may or may not be possible to perform specific separations: the results obtained will always be useful for future experiments performed either at iThemba LABS, or in other laboratories by chemists planning to use the same resin in future.

The work was originally thought of to cater for the sodium-22 production to determine if there was any way of improving the production method, hence, the use of

citric acid (used to dissolve the magnesium target, see chapter 4) with the addition of nitric acid. It was then decided to use this media on other elements in the s-block (the alkali and alkaline earth metals) and expand that to other blocks such as the p-block, the d-block (the transition elements) and the f-block (the lanthanides and actinides). With an expanded view of the elements and their results in this media, using AG MP-50 macroporous cation exchange resin, one could determine whether it would be possible to perform chemical separations of two or more elements, which could also potentially be used for possible future production purposes.

1.3 ION EXCHANGE CHROMATOGRAPHY

1.3.1 A BRIEF HISTORY OF ION EXCHANGE

Surprisingly, recognition of ion-exchange processes antedates the great Swedish chemist Svante Arrhenius, who formulated the ionic theory. In 1850, nine years before Arrhenius was born, separate papers appeared in the *Journal of the Royal Agricultural Society of England* by agriculturist Sir Harry Stephen Meysey Thompson and chemist John Thomas Way, describing the phenomenon of ion exchange as it occurs in soils. They observed that, when a solution of ammonium sulphate was passed through a layer of certain soils, the effluent solution contained calcium sulphate.

In his paper, entitled "On the Power of Soils to Absorb Manure," Way addressed himself to the question of how soluble fertilizers like potassium chloride were retained by soils even after heavy rains. Way took a box with a hole in the bottom,

filled it with soil, and poured onto the soil a solution of potassium chloride, collecting the liquid that flowed out of the bottom. He then washed the soil with rainwater and analyzed the water he had collected, from both the solution and the rainwater. The water turned out to contain all of the chloride that had been originally added but none of the potassium; the potassium had been replaced by chemically equivalent amounts of magnesium and calcium. Way called the process "base exchange" because of the basic (nonacidic) character of the exchanged elements. That term persisted until after 1940, by which time the process had become universally known as ion exchange.

Ion exchange products featured commercially in the early 20th century. In Germany, 1905, Dr. R. Gans made use of a zeolite type soil to remove hardness from water on a commercial scale, while in 1913 The Permutit Company of New York marketed the first American Zeolite, which had a greater capacity for the removal of hardness in water than natural zeolites.
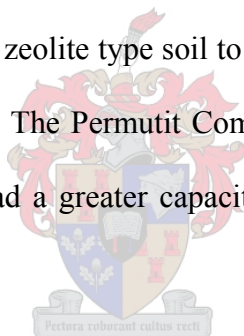
1.3.2   THE THEORY OF ION EXCHANGE

Ion exchange is a reversible chemical reaction wherein an ion (an atom or molecule that has lost or gained an electron and, thus, acquired an electrical charge) from solution is exchanged for a similarly charged ion attached to an immobile solid particle. These solid ion exchange particles are either naturally occurring inorganic zeolites or synthetically produced organic resins. The synthetic organic resins are the predominant type used today because their characteristics can be tailored to specific applications.

In ion exchange chromatography ions are separated according to their charge. The column packing consists of charged functional groups, covalently bound to an insoluble support, and mobile counter ions which associate with the functional groups, because of their opposite charge. When a sample is passed through a column, neutral molecules and ions which bear the same charge as the functional groups are eluted, while the oppositely charged ions compete with the counter ions for binding sites on the functional groups. Ions which are more highly charged than the counter ions are bound to the matrix and are retained on the column. An eluant with the appropriate ionic strength and pH is then used to recover the bound sample.

During practical application of ion exchange chromatography it is important to operate with pH values where the exchangers are mostly ionised and the biopolymers contain an excess of positive or negative charges (for example, they are not near their iso-electric point).
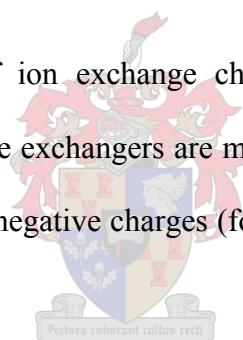
The size of the sample volume in ion exchange chromatography is of secondary meaning, as long as the initial solvent is of low eluting strength, so as not to allow any separation to occur. Under such conditions, the sample components are collected at the top of the column, what might be described as the concentrating step. When the gradient is begun with the addition of stronger eluting mobile phase, then sample components begin their separation. If less than optimal separation is observed, it might be improved by a change in gradient slope.

Ion exchange resins are commonly polymers with attached ionic groups. The attached group is always an electrolyte: one ion which is fixed to the resin while the other, of opposite charge, is mobile. The mobile ion is the ion that is exchanged.

In the case of Bio-Rad AG 50W cation exchange resins, they consist of the resin matrix (styrene divinylbenzene co-polymer) to which $-SO_3^-H^+$ is attached as the functional group. It is the H^+ of this sulphonic group that is mobile and is exchanged for other cations.
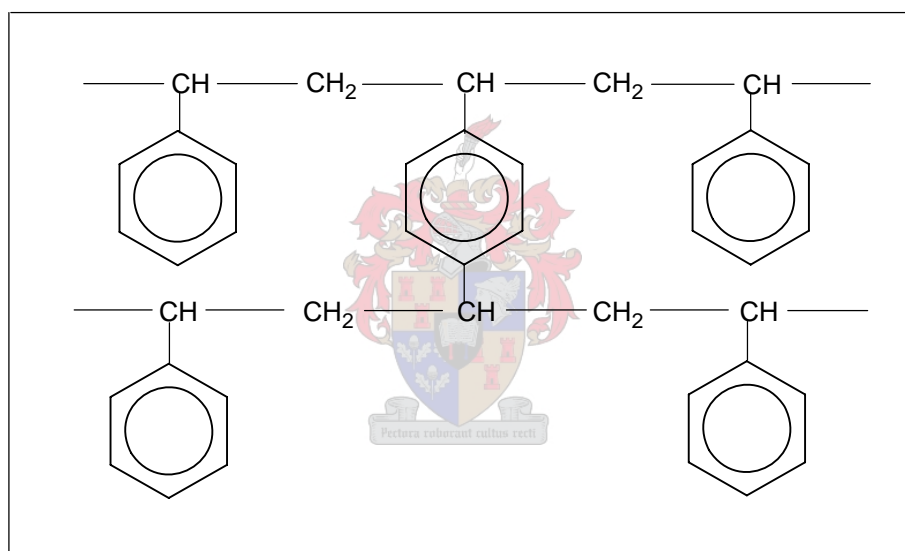
Figure 1.2: An illustration of the styrene-divinylbenzene polymer.

Bio-Rad AG 1 anion exchange resins consist of the resin matrix (styrene divinylbenzene) to which $-N^+(CH_3)_3Cl^-$ is attached. The Cl^- is the mobile exchangeable ion. An anion exchange resin will exchange its mobile ions for other anions present in solution around the resin. The resulting equilibria will be influenced by all the usual equilibria factors, namely, concentration and mobility of each ion and time. The factors of equilibria, as well as the unique characteristics of each resin, will help determine which resin and which particle size is optimum for the separation of

elements. The influence of particle size, flow rate, bed volume, cross-sectional area of the bed, crosslinkage of the resin polymer matrix will all play a role in the choice of ion exchange resin for a specific study.

The chief application of ion exchange today is in the treatment of water, but the principle offers almost unlimited possibilities in other fields. Commercial installations include such processes as the purification of sugar solutions and wines, separation and purification of drugs and fine chemicals, purification of waste effluents and the recovery of valuable wastes, for example, in the metallurgical industries involving the extraction and quantitative separation of elements and metallic complexes which had previously been achieved with great difficulty.

Other examples of their application are the separation by ion exchange of the rare earth elements by making use of their citrate or other complexes, the recovery of chromate from plating liquors and purification of coke oven effluents. Ion exchange resins have found their uses in analytical work in the laboratory, as well as in medical clinical tests.

1.3.3 CLASSIFICATION OF ION EXCHANGERS

Ion exchangers are divided into two main groups, namely, inorganic ion exchangers and organic ion exchangers.

Inorganic ion exchangers are inorganic substances (labelling) with ion exchange properties such as, for example, some minerals, hydrated metal oxides, phosphates,

arsenates, ferrocyanides, aluminium silicates of certain elements. Most of these labellings are synthetically prepared for selective separation of ions. Organic ion exchangers are synthetic resins, which exist as organic polymers with certain percentages of crosslinking occurring.

Synthetic resins are solids, which are insoluble in normal solutions and are used in laboratories. They usually consist of an elastic, three dimensional, porous, hydrocarbon matrix or network, to which functional groups (ionogenic groups) are bound. The matrix is mostly chemically inert (resistant to oxidation, reduction and radiation) with normal use. The functional group consists of a part which is strongly covalently bound to the matrix and forms a certain macro-ion with the matrix; the other part is the mobile ion which is bound to the macro-ion (Hudson, 1986).

Monofunctional or homo-ionic exchangers are ion exchangers which contain only one type of ionogenic group, for example, only sulphonic acid ($-SO_3H$) groups. Resins with more than one ionogenic group are known as polyfunctional ion exchangers. Monofunctional ion exchangers are preferred in analytical chemical separation procedures.

1.3.4 CATION EXCHANGE RESINS

Cation exchange resins have positively charged mobile ions available for exchange. The functional groups of these exchangers determine the chemical behaviour of the resin. These resins are classified as strong or weak cation exchangers.

a) Strong acid cation exchangers with sulphonic acid groups as functional groups:
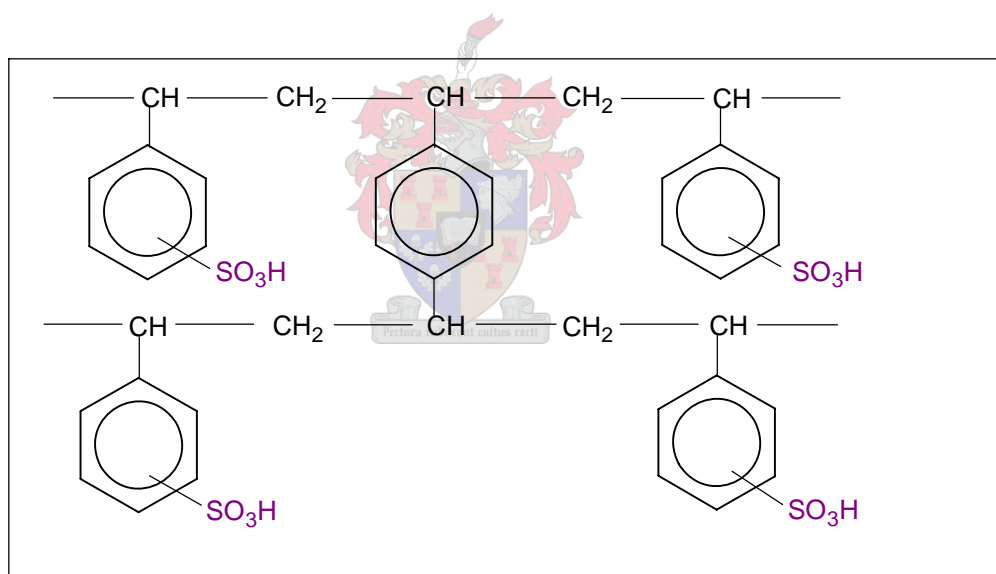
Figure 1.3: An example of a strongly acidic cation exchange resin.

Fixed ion: $-SO_3^-$ Counter ion: H^+

Strong acid resins are so named because their chemical behaviour is similar to that of a strong acid. The resins are highly ionised in both the acid ($R-SO_3H$) and salt ($R-$

SO$_3$Na) form.   They can convert a metal salt to the corresponding acid by the reaction:

$$2(R\text{-}SO_3H) + NiCl_2 => (R\text{-}SO_3)_2Ni + 2HCl$$
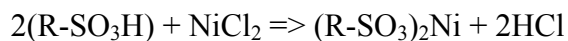
The hydrogen and sodium forms of strong acid resins are highly dissociated and the exchangeable Na$^+$ and H$^+$ are readily available for exchange over the entire pH range. Consequently, the exchange capacity of strong acid resins is independent of solution pH.

b) Mild acid cation exchangers with phosphonic acid groups (-PO(OH)$_2$) or phosphinic acid groups (-HPO(OH)) as functional groups.

c) Weak acid cation exchangers with monofunctional groups (-COOH) and bifunctional groups (-COOH and –OH).
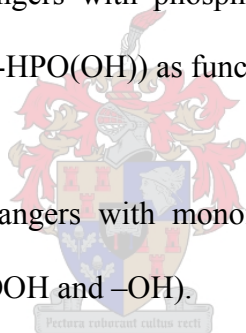
These resins behave similarly to weak organic acids that are weakly dissociated. Weak acid resins exhibit a higher affinity for hydrogen ions than do strong acid resins. The degree of dissociation of a weak acid resin is strongly influenced by the solution pH. Consequently, resin capacity depends in part on solution pH.

1.3.4.1   A brief survey

Systematic studies on the adsorption behaviour of a large number of elements have been performed using the gel-type microporous cation exchange resins, such as Bio

Rad's AG 50W-X8. Studies in different media have been performed, namely, in hydrochloric acid (Strelow, 1960 and Nelson *et al*., 1964), nitric acid (Strelow *et al*., 1965), sulphuric acid (Strelow *et al*., 1965), hydrobromic acid (Nelson and Michelson, 1966 and Strelow *et al*., 1975), perchloric acid (Strelow and Sondrop, 1972), hydrochloric/perchloric acid mixtures (Nelson and Kraus, 1979), hydrochloric acid/ethanol mixtures (Strelow *et al*., 1969), hydrochloric acid/acetone mixtures (Fritz and Rettig, 1962 and Korkisch and Ahluwahla, 1967) and hydrobromic acid/acetone mixtures (Korkisch and Klaki, 1969).

The so-called macroporous, or macroreticular, cation exchange resin, Bio Rad's AG MP-50, which has a rigid, wide, open macroporous structure with a 20 to 25% crosslinkage, combines the advantages in selectivity offered by the high crosslinkage with fast exchange rates. This makes the macroporous resin more suitable for applications in high pressure liquid chromatography procedures for the separation of inorganic ions because of its small change in volume with changes in eluent concentration. Many studies have been performed using this resin in nitric acid media (Marsh *et al*., 1978) hydrochloric acid media (Strelow, 1984) hydrochloric acid/acetone mixtures (Fritz and Story, 1974) and hydrochloric acid/methanol mixtures (Strelow, 1984).

1.3.5   ANION EXCHANGE RESINS

a)   Strong basic anion exchangers with quaternary ammonium groups as functional groups:
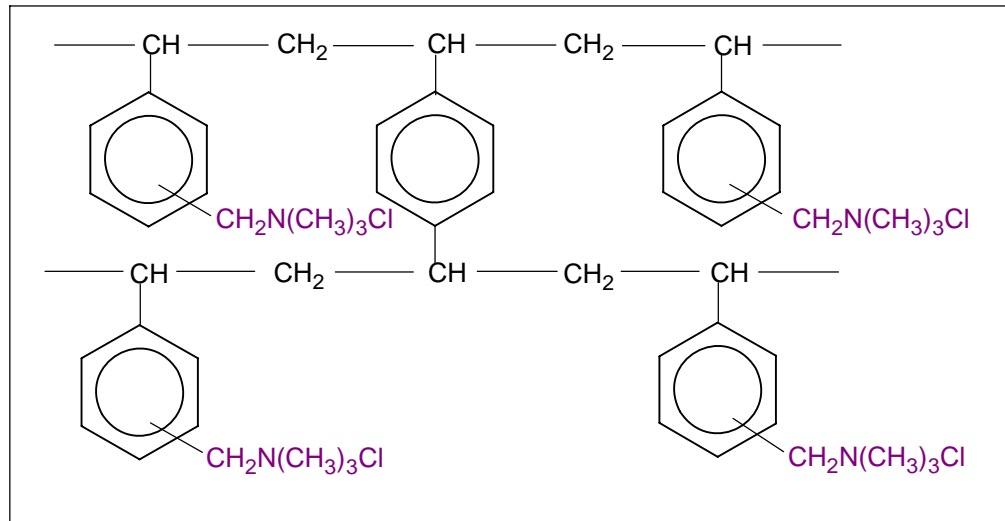
Figure 1.4: An example of a strongly basic anion exchange resin.

Fixed ion: $(CH_3)_3N^+-$ Counter ion: Cl^-

Like strong acid resins, strong base resins are highly ionised and can be used over the entire pH range.

b)   Mild basic anion exchangers with mainly tertiary amine groups as functional groups.

c)   Weak basic anion exchangers contain the following groups, namely, primary or secondary amines ($R-NH_2$ or R_1-NH-R_2).

Weak base resins are like weak acid resins, in that the degree of ionisation is strongly influenced by pH. Consequently, weak base resins exhibit minimum exchange capacity above a pH of 7.0. These resins merely sorb strong acids: they cannot split salts.

1.3.5.1 A brief survey

The separation of inorganic elements using anion exchange resins depends on the ability of the elements to form anionic complexes, which are absorbed.

The first systematic study of anion exchange behaviour of a large number of elements was presented by Kraus and Nelson in 1956. They dissolved the elements in hydrochloric acid and used Dowex 1-X10 resin, a strongly basic quaternary ammonium type resin, with 10% crosslinkage.

Most of the other systematic studies conducted made use of 8% crosslinked resins, such as Bio Rad's AG 1-X8. Studies in different media were performed, namely, in nitric acid (Kraus and Nelson, 1958; Ichikawa, 1961 and Faris and Buchanan, 1964), sulphuric acid (Danielsson, 1965 and Strelow and Bothma, 1967), hydrofluoric acid (Faris, 1960), oxalic acid (de Corte *et al*., 1968), acetic acid (van den Winkel *et al*., 1971) hydrobromic acid (Andersen and Knutsen, 1962 and Marsh *et al*., 1978), hydriodic acid (Marsh *et al*., 1978), phosphoric acid (Polkowska *et al*. 1974), hydrochloric/hydrofluoric acid mixtures (Nelson *et al*. 1960), hydrochloric/oxalic acid mixtures (Strelow *et al*., 1972), hydrobromic/nitric acid mixtures (Strelow, 1978) and inorganic mixtures with organic solvents (Klakl and Korkish, 1969).

Less attention has been paid to the study of anion exchange behaviour of elements using weakly basic anion exchange resins. This may be due to the slow kinetics of the exchange reactions and the limitation of the pH range, should this type of resin be used. Adsorption behaviour of metals with Amberlite CG-4B, a phenol condensation

type of weakly basic anion exchange resin, has, however, been reported. Studies in different media were performed, namely, in sulphuric acid (Strelow and Bothma, 1967 and Kuroda *et al.*, 1972), hydrochloric acid (Kuroda *et al.*,1968) and thiocyanate (Fritz and Kaminski, 1971).

1.3.6   CHELATING ION EXCHANGE RESINS

Other types of ion exchangers are amphoteric ion exchangers, which contain both acidic and basic groups, and the (selective) chelating ion exchangers (Inczedy, 1990), which contain functional groups which react with only a small group of ions, for example, Chelex 100 and Dowex A-1 with the iminodiacetic acid group as the functional group:
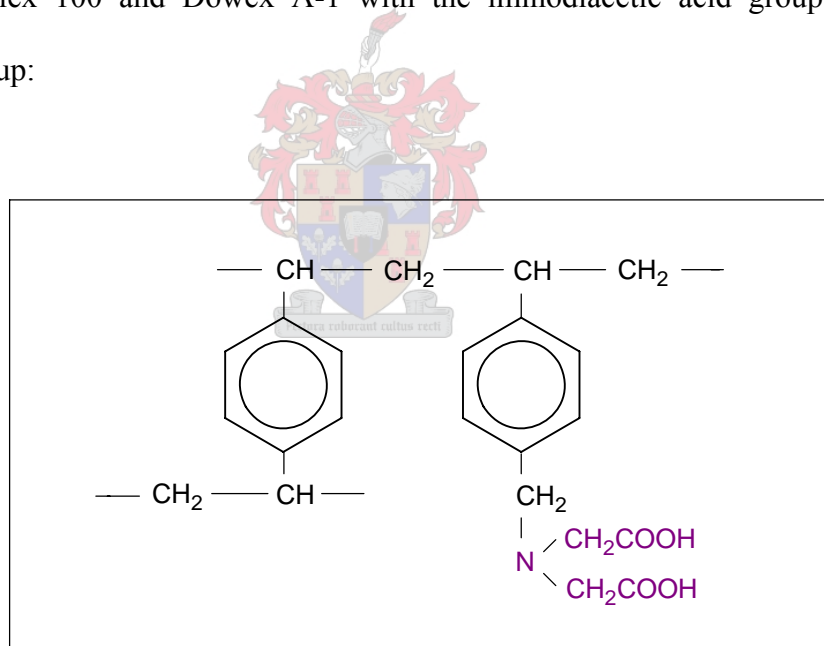
Figure 1.5: The structure of the Chelex 100 ion exchange resin.

Chelex 100, for example, is a chelating resin that shows an unusually high preference for copper, iron and other heavy metals over such cations as sodium, potassium and calcium. In addition, Chelex 100 is much more selective for the alkaline earths than

for the alkali metal cations. The structure of the sodium form is represented here with the "R" indicating the styrene-divinylbenzene copolymer matrix.
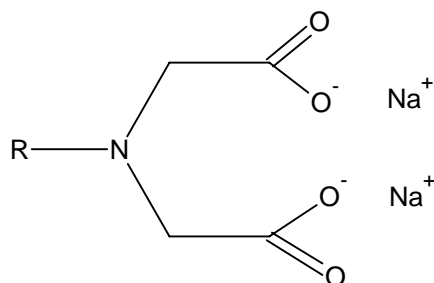
Another type of chelating resin is Purolyte S-940 with the aminophosphonic group as functional group. Other chelation systems from Purolite include the S-920, S-930 and S-950, which all have the same matrix, but have thiouronium, iminodiacetic and aminophosphonic as functional groups, respectively.
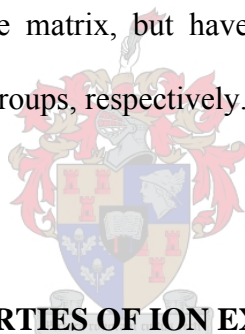
1.3.7   GENERAL PROPERTIES OF ION EXCHANGE RESINS

Ion exchange resins perform efficiently in a variety of applications as a result of their valuable physical and chemical properties. The physical properties of an ion exchange resin include the functional group, the matrix, ionic form, the distribution of particle size, particle shape, swelling and porosity (particularly for macroporous resins) and crosslinkage. The chemical properties include exchange capacity, water retention capacity, thermal and chemical stability, radiation stability, solvent stability and the response to ionic strength.

Ion exchange resins generally have a high effective capacity due to the high permeability and high concentration of functional groups in their chemical structure. Small volumes of resin can retain high molecular amounts of ionic material when used for concentrating substances of interest or for scavenging ions to be eliminated from a solution.

Ion exchange resins also provide high resolution chromatographic separations because many interactions take place per unit of column volume. In addition, the impressive chemical, thermal and radiation stability of ion exchange resins makes them usable with a variety of chromatographic conditions, including high temperature, organic solvents, strong reducing and oxidising agents (albeit only some of them) and a highly radioactive environment. The resin matrix remains chemically unchanged by the ionic interactions that take place at the functional groups and the resins can be regenerated.
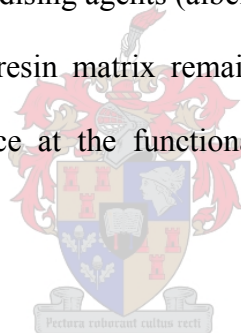
1.3.7.1 Ionic form

Most resins are available in several ionic forms and can be converted from one form to another. In the simplest case the resin is used in an ionic form, with a lower selectivity for the functional group than the sample ions to be sorbed. The sample ions are sorbed when introduced to the resin and can be desorbed by introducing an ion with a high affinity for the resin, or a high concentration of an ion with equivalent or lower affinity. In many cases a high concentration of the original counterion can be used for desorption, thereby regenerating the resin while eluting the sample.

It can be generally accepted that the lower the selectivity of the counterion, the more readily it will exchange for another ion of like charge. The order of selectivity can be used to estimate the effectiveness of different ions as eluants, with the most highly selective being the most efficient. The order of selectivity can also be used to estimate the difficulty to convert the resin from one form to another, therefore, conversion from a highly selective to a less highly selective form would require an excess of the ion to be introduced.

1.3.7.2   Particle Size

Most ion exchange resins are available as spherical, porous beads. The particle size of the resin beads is mostly given as standard mesh size though which the resin can pass. This mesh size, as stated by the U.S. Standard Screen is determined as follows:

Mesh ≈ 16/diameter of resin bead in mm
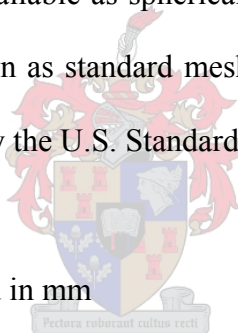
Analytical Grade resin particle size is generally specified as dry mesh: mesh describing the number of openings per inch on the screens used to size the ion exchange resin.

Most Analytical Grade (AG) resins are available in several particle size ranges. The ranges in Analytical Grade resins are more precisely controlled than the commonly used Dowex resins. The flow rate increases with an increase in resin particle size. The attainable resolution, however, increases with a decrease in particle size and with narrow size distribution ranges (less tailing effects). As the particle size of an ion

exchanger decreases the time required to reach equilibrium decreases and, in turn, the flow rate is reduced. The settling rate of the resin is also decreased, while the efficiency of a given volume of resin increases.

In general 200 to 400 mesh and finer resins are used for high-resolution chromatography, while 100 to 200 mesh resins are used for general-purpose ion exchange techniques. The coarser meshed resins, such as 50 to 100 mesh, are used for large scale applications and batch operations, where the resin and sample are slurried together. The larger meshes are also suitable for small-scale applications, such as the removal of a cationic species as an anionic complex in the presence of an uncomplexed cation.

For some elements, which are strongly retained on the resin, the particle size of the resin plays an important role. Resins with small particle size (200 to 400 mesh) often showed less tailing effects, although Van der Walt *et al.* (1985) and Strelow (1980) showed that sharp separations were possible using a 2% and 4% crosslinked resin with a particle size of 100 to 200 mesh.

1.3.7.3   Crosslinking effect and swelling of resin

Ion exchange resins consist of a matrix to which functional groups are attached. The number of individual monomers used in the synthesis of the three dimensional matrix determines the properties of the elastic matrix. These elastic, three-dimensional polymers do not have a determined pore size. The grade of crosslinkage in a polymer exchanger is shown as the fraction divinylbenzene (DVB) contained in the styrene-

divinylbenzene resin beads (between 1 and 25%). The 4% and 8% crosslinkage resins are regarded as ideal for general use.

The use of macroporous resins (20% to 25% crosslinkage) has increased of late as a result of their good exchanging properties and quick exchange kinetics. A disadvantage of these types of resins is that "tailing" occurs when using elements with a distribution coefficient (K_d) between 12 and 40 in a specific eluent. Resins with smaller percentages of crosslinkage have better exchange kinetics and, therefore, ions can be eluted with sharper peaks, even with elements with K_d values as high as 40 (van der Walt, 1993).
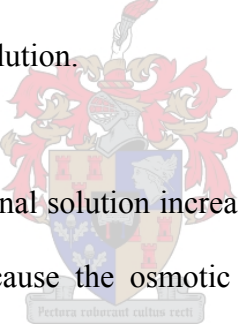
Ion exchange resins have no noticeable porosity, unless it swells in a suitable solution. If dry resin from an ion exchange resin is placed in a solution of water, the water will be absorbed into the resin matrix. The water solvates both ions of the functional groups – the fixed ion and the mobile ion.
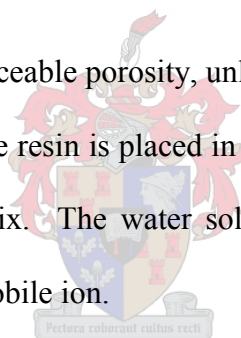
The solvated ionogenic groups can be theoretically regarded as being dissolved in water of hydration and, therefore, forms a very concentrated (electrolytic) solution with the resin bead. As a result of osmotic pressure, more water is pressed into the resin pores to dilute the solution in the pores and to swell the resin beads. The swelling is opposed by the rigidity of the resin matrix. The covalent bonds between the C-atoms of the hydrocarbon chain and the DVB crosslinkings are bent and stretched to accommodate the incoming water. This distortion of the covalent bonds puts pressure on the absorbed water and tries to push the water out of the resin. The resultant effect of these two opposite effects is the intake of a fixed volume of water

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through the resin at equilibrium, which results in a specific amount of swelling of the resin. The swelling can, thus, be regarded as the resultant of the difference in osmotic pressure between the internal solution in the ion exchange resin and the more diluted external solution. This swelling depends on:

1) The grade of crosslinkage of the matrix structure,

2) The characteristic of the surrounding solution and electrolytic concentration

3) The type and concentration of the functional group,

4) The type of counter ion, and

5) The electrolyte concentration in the water if an electrolyte is present in the surrounding solution.
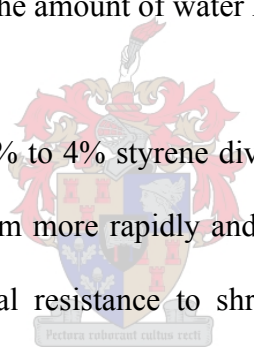
As the concentration of the external solution increases, the amount of water taken up through the resin decreases, because the osmotic pressure difference between the internal and external solution is lower. The swelling is also influenced by the type of electrolyte, as the swelling is a function of ionic form. The greater the radius of the hydrated exchangeable ion, the more the resin swells. Resins with a low grade of crosslinkage swell a lot in aqueous solutions, because it can take in a sizeable quantity of water and swell to a structure, which is soft and gelatinous. Larger ions can move easily through the pores of the exchanger, resulting in fast exchange kinetics. The mechanical strength of the matrix increases with an increase in percentage DVB crosslinkage. Conversely, as crosslinkage increases the hydrocarbon matrix becomes less elastic and the pores of the resin network become smaller. Less water is taken up through the pores and the accessibility for larger ions in the structure decreases. The

styrene divinylbenzene ion exchange resins have a relatively rigid gel type structure. The porosity depends on the hydration of the matrix which, in turn, is controlled by the hydration of the functional groups. Ion exchange resins are most hydrated, or swollen, in water.

Swelling of weak acidic (or weak basic) ion exchange resins in the hydrogen form (or the hydroxide form) is lower as a result of low hydration of their weakly dissociated ionogenic groups. In non-aqueous solutions the swelling of the strong acidic cation exchange resin generally decreases with decreasing hydrophilicity of the solution being used. Anion exchange resins and weak acidic cation exchange resins swell considerably in ethanol, the former also swells in less polar solutions. In a mixture of two solutions one solution will be preferred and absorbed by the resin phase and this leads to different compositions of internal and external solutions. Distribution of the solutions between the resin and the surrounding solution depends on their solvation ability as well as the type and ionic form of the functional groups of the resin. In a mixture of water and a less polar solution (for example, acetone) the solution in the resin can be enriched with water, depending on the type and ionic form of the functional groups of the resin and the grade of crosslinkage. A constant increase in resistance of the polymer network limits the uptake of ions and molecules with increasing size. The selectivity for hydrated ions and the sorption of complexes of trace elements generally increases with an increase in the grade of crosslinkage, e.g. in the case of Bio-Rad anion exchangers AG 1-X2, -X4, -X8 and AG MP-1 the distribution coefficients for Fe(III) in 5 M HCl are 30, 75, 340 and 158, respectively, while for Zn in 5 M HCl the values are 124, 184, 276 and 416, respectively (van der Walt *et al*., 1985). The increase is specific for each element and also depends on the

ligand concentration. Strelow *et al*. (1971) had shown this same influence of crosslinkage on distribution coefficients on the cation exchangers AG 50W-X2, -X4, -X8, -X12 and -X16. The percentage crosslinkage used determines the solubility, swelling, selectivity and other physical and chemical properties for a given type of ion exchanger.

Ion exchange resins swell and shrink with any changes in the ionic strength of the solvent. Resins with high crosslinkage exhibit less volume change with changes in ionic strength than resins with low crosslinkage. These changes are due to osmotic forces: as the concentration of the ions within the resin reaches equilibrium with the ionic media there is a change in the amount of water held by the resin.

Resins with low crosslinkage (2% to 4% styrene divinylbenzene) have a high degree of permeability, reach equilibrium more rapidly and are able to accommodate larger ions. They have lower physical resistance to shrinkage and swelling, thus, they imbibe more water and swell to a larger wet diameter than that of a highly crosslinkaged resin of equivalent dry diameter. The wet capacity is lower, since the functional groups are, in effect, more dilute. The selectivity for certain ions becomes reduced and the physical stability of the resin decreases.

Resins with high crosslinkage (8% to 16% styrene divinylbenzene) exhibit properties opposite to those of resins with low crosslinkage. As the fraction of DVB is increased the crosslinkages occur at closer intervals and the effective pore size, permeability and tendency of the resin to swell in solution are reduced. The ionic groups come into closer proximity with each other, which results in increased sensitivity. The wet

volume capacity increases because highly crosslinked particles swell only slightly and will, therefore, contain more exchange sites per unit volume than that of a resin with low crosslinkage. The rate of equilibrium decreases as a result of ion diffusion through the resin becoming retarded.

When the synthesis of the styrene-DVB matrix takes place in the absence of other materials, a gelatinous matrix is formed during the copolymerisation of both components. The structure of the matrix formed, is created from islands of low porosity in a more porous medium. The size of the pores (given by the distance between the individual polymeric chains) is very small. These resins are called microporous resins. Through additional crosslinking and modification of the porous structure (chloromethylation and crosslinking of these groups) a matrix is created with large enough pores, which is distributed evenly in the matrix. This type of resin is known as isoporous.
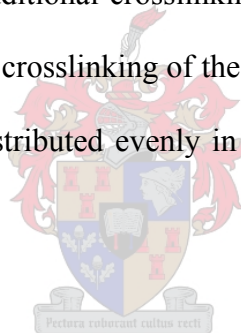
1.3.7.4   Stability of ion exchange resins

The stability of ion exchange resins plays an important role in the choice of a specific resin for the separation of highly active radioisotopes. In this type of separation, radiation stability is the most important requirement. Chemical and thermal stability is also of great interest, as these types of separations take place at relatively drastic chemical conditions and need to be performed at high temperatures. The thermal, chemical, physical and radiation stability of ion exchange resins depend on the type of matrix, its grade of crosslinkage, the type of functional group and counter ion. The methods of synthesis of ion exchange resins also influence the stability. The change

in stability of an ion exchange resin is observed as a decrease of the percentage crosslinks and the volume exchange capacity of the resin, a loss of functional groups as well as the destruction of the resin matrix to a degree.

1.3.7.4.1   Thermal Stability

The thermal stability of an ion exchange is at its lowest when the resin is dry and typical damage is a progressive loss in crosslinkage (Glueckauf, 1955). The trend is for resins with low percentage crosslinkage to be most affected and in practice, if resins have to be dehydrated, the temperature is kept below 60 ˚C. When the resin is in hydrated form a loss of functional groups, rather than crosslinkage, occurs and significant damage has been observed at temperatures above 150 ˚C (Hall, 1963).

High temperatures influence ion exchange resins in two ways, namely, the loss of crosslinks and the loss of functional groups. The extent of these reactions is dependant on temperature, the duration of exposure to heat, the ionic form of the ion exchange resin and the environment in which the resin is used. The thermal stability of an ion exchange resin is strongly influenced by the nature of the ionogenic group, especially that of the counter ion. The salt forms of cation exchange resins are thermally more stable than the hydrogen form of the cation exchange resin, while the salt forms of anion exchange resins are thermally more stable than the hydroxide form of the resin.

Destructive reactions usually occur first in the ionogenic groups as the bonds in these groups are weaker than the bonds in the polymer chains. Cation exchange resins

which contain phosphonic acid groups in the styrene-DVB matrix are thermally more stable than those resins which contain sulphonic acid groups. Anion exchange resins which contain phosphonium or sulphonium ionogenic groups are less stable when heated in air than an ammonium ionogenic group with the same resin matrix. Weak base anion exchange resins are more stable than strongly basic resins; quaternary ammonium groups in hydroxide form dissociate even at room temperature. Anion exchange resins in nitrate form are unstable at temperatures greater than 60°C.

Strong acidic cation exchange resins are relatively stable when heated in water, with the macro net-like resin being more stable than the micro net-like resin. In the presence of concentrated solutions of acids or bases, hydrolysis of ionogenic groups takes place at elevated temperatures. A decrease in ion exchange capacity is also noted if cation exchange resins are heated in non-aqueous solutions. The solutions can react with the ionogenic groups to produce products with high molecular masses.
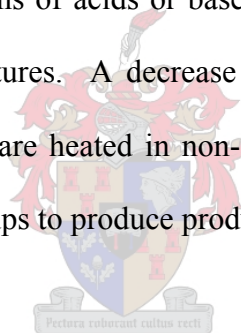
1.3.7.4.2   Chemical Stability

Chemical breakdown of ion exchange resins mainly takes place as a result of oxidation reactions. Oxidation can decrease the grade of crosslinkage of the resin matrix and, in some cases, even dissolve the resin. Resins with low DVB-crosslinkage undergo breakdown more easily as a result of oxidation, especially in the presence of elements, which can behave as catalysts (e.g. Cu and Fe).

Resins with pyridinium as a functional group are more resistant to oxidation than other strongly basic ion exchange resins. Chromate, permanganate and vanadate ions

are reduced by resins when in acid solution. Hydrogen peroxide attacks resins, breaking the crosslinks and reacting with the ionogenic groups of strongly basic anion exchange resins in the hydroxide form. Macroporous, strongly basic anion exchange resins are more stable than microporous anion exchange resins in alkali solutions and, for this reason, AG MP-1 in hydroxide form is usually chosen for use above AG 1-X8 in hydroxide form.

Most ion exchange resins are stable in organic solutions under normal circumstances.

1.3.7.4.3   Radiation Stability

High energy charged α- and β-particles, resulting from radioactive decay, are known as ionising rays, as they transfer energy to the medium through which they move mainly by ionisation and excitation of atoms and molecules occurring in the medium. The energy transfer takes place mainly with the loss of heat, given off due to atomic and molecular vibrations. As a result of the charges from the α- and β-particle, the energy transfer is virtually a continuous process and the ionisation density is very high, while the range is relatively short, e.g. the range for 4 MeV α-particles and 1 MeV β-particles in water is 0.04 mm and 4.3 mm, respectively.

In the case of γ-rays (photons), which is also a result of radioactive decay, ionisation takes place in an indirect way. It is a result of orbital electrons which are kicked out of position by the γ-rays. The ionisation density and energy transfer are, therefore, lower than in the case of α- and β-particles. The γ-rays, however, have a higher penetrative power.

When radioactive material is present in the ion exchange resin, the charged particles of decay (α and β) will deliver the greatest contribution to radiation dose and, therefore, the radiation damage to the resin.

The interaction of ionising radiation with ion exchange resins leads to damage of the resin, especially in the presence of a solvent. Radiation causes a loss of exchange capacity of the resin as a result of the breaking down of the functional groups and the forming of new functional groups. Breaking down of the resin matrix with the destruction of the existing crosslinks or the forming of new crosslinks (especially in resins with few crosslinks) leads to change in swelling. Gaseous products are also formed during the radiolytic breakdown of the resins. Radiolysis of water or hydrogen peroxide, which is present in the resin pores, also damages the resins. The total result of radiation is a change in mechanical, physical and chemical properties (selectivity, capacity, exchange kinetics, etc.). The radiation levels, therefore, influence the choice of resin for a specific separation.

Medium acidic cation exchange resins with phosphonic acid ionogenic groups show a high stability against radiation damage and the exchange capacity remains unchanged up to an internal radiation dose of 10^7 Gy. The strong acid cation exchange resins with sulphonic acid inorganic groups show changes when exposed to radiation doses greater than 10^6 Gy. Weak acid cation exchange resins are more sensitive with respect to radiation in comparison with other types of cation exchange resins (Van der Walt, 1993).

The radiation stability of anion exchange resins also depends on the type of matrix and the character of the functional groups. Anion exchange resins with only aliphatic hydrocarbons in the matrix are less resistant to radiation than the anion exchange resin which contains an aromatic nucleus in its structure. Anion exchange resins with a pyridinium nucleus are rather resistant to radiation up to a radiation dose of 5×10^6 Gy. The exchange capacity of the strong base anion exchange resin decreases considerably to a radiation dose of 10^5 to 10^6 Gy, and can not be used for doses of approximately 10^7 Gy. Monofunctional strong basic resins change to polyfunctional resins with functional groups with different basicities. New functional groups of the –OH and the –COOH type are also formed and the resin changes to a bipolar (amphoteric) ion exchanger. Weak base anion exchange resins are less resistant to radiation and are broken down at a radiation dose of 10^5 Gy (Van der Walt, 1993).

1.3.7.5   Exchange capacity of ion exchangers
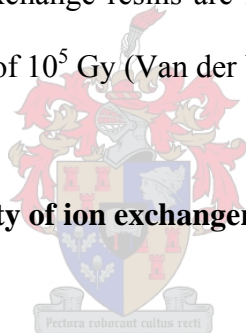
An important property of ion exchangers is the principle of equivalent exchange of ions. The total number of exchangeable counter ions is, therefore, equivalent to the number of fixed ions of the ion exchanger. The capacity of an ion exchanger for counter ions is quantitively described as the number of electrical charges (exchange sites) per unit mass of the exchanger. The capacity is usually shown on a dry mass or wet volume basis. The mass and volume can change when one ionic form is changed to another, but the number of exchange sites in the ion exchanger remains the same and there is the equivalent of one counter ion per exchange site.

The dry mass capacity is the number of exchange sites, expressed in milli-equivalents, per gram of dry ion exchange material (ECD), while the wet volume capacity is the number of exchange sites, expressed in milli-equivalents, per millilitre (or cm^3) of the swollen ion exchanger in water (ECV).

For crosslinked polystyrene resins the ECV for a particular resin type and ionic form increases with crosslinkage, while the ECD is nearly independent of crosslinkage. The ECD for a class of ion exchange resin, for example Bio Rad AG 1 resin, is relatively constant. When all the water is removed from the resin, it will have approximately the same number of functional groups per unit mass of resin, regardless of the degree of crosslinkage.

1.3.7.6 Water retention capacity

The water retention capacity for ion exchange resins is often given as the percentage of water. The water retention capacity varies with crosslinkage and the ionic form of the resin.

The water retention capacity increases with decreasing crosslinkage as a result of the reduced physical strength of the crosslinked lattice. The resin may be more soluble as crosslinkages decrease and, therefore, can absorb more water than resins containing higher crosslinkages. If there were no crosslinkage in the resin, it would be completely soluble in water. The increase in water retention of approximately 8% crosslinkage resins, however, occur where the increasing physical resistance of the

more highly crosslinked resin is balanced by its increasingly hydrophilic character as the concentration of functional groups increases.

1.3.7.7   Rate of ion exchange reactions

The rate of ion exchange reactions has a large influence on the efficiency of column separations and determines the sharpness of the elution peaks and the degree of overlap of peaks in chromatographic column separations.

The exchange process takes place in three steps, namely, film diffusion, resin particle diffusion and chemical exchange (Boyd *et al.*, 1947).

The slowest of the three steps determines the total rate of ion exchange. The actual chemical exchange of one ion with another ion probably takes place instantly. The rate of ion exchange is, therefore, dependent on two rate-determining steps, namely, film diffusion and particle diffusion. The former is concerned with the solution film surrounding the resin bead and the latter has to do with the movement of the ions on the resin bead itself. In very dilute solutions (<1 mM) film diffusion is the rate-determining step, which controls ion exchange reactions. In more concentrated solutions (such as that which occurs in column chromatography) particle diffusion determines the rate of ion exchange reactions.

The rate of ion exchange reactions increases considerably with increasing temperature and with a decrease in particle size of the resin. If film diffusion is the rate determining step, then smaller particles will contribute to a quick exchange reaction

because they have a greater surface area and more diffusion per unit time per unit mass takes place. If particle diffusion is the rate-determining step, the exchange reaction takes place more quickly as the ion involved in the exchange has a shorter path to move through the smaller resin bead.

The degree of swelling of an ion exchange resin also influences the rate of ion exchange reactions. Resins with a low grade of crosslinkage swell more and have a faster exchange rate. Exchange reactions also take place more quickly using macroporous resins. Resins swell very little in non-polar solutions and the resin counter ions dissociate less than in watery solutions and ion exchange takes place more slowly. The oxidation state and size of the hydrated ions also influence the exchange rate of the ions. Larger ions diffuse more slowly than smaller ions through the hydrocarbon chains of the resin matrix (Van der Walt, 1993).

1.3.7.8   The charge and size of the solute
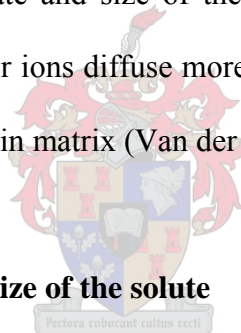
At a given pH a solute may be positively or negatively charged, with the exception of uncomplexed inorganic ions. If the solute is positively charged and it can be made more positively charged by decreasing the pH it will sorb on to a cation exchange resin. The opposite is the case for negatively charged solutes. Sorption occurs because the charge on the resin is opposite to that of the solute. The solute can be desorbed from the resin by changing the pH until the solute has the same charge as that of the resin. It is generally accepted that if the solute is positively charged and the solute is to be sorbed, a cation exchange resin is often used. If the solute is

positively charged and the anionic counterion is to be changed, an anion exchange resin is used.

As the total number of charges increase on a solute the sorption increases, provided that the charges have the same sign at a given condition. Some solutes become so strongly sorbed that, when desorption is attempted, the solute may become denatured. Should this be the case, the choice of ion exchange resin should be limited to those with low crosslinkages or weak functional groups.

As the molecular size of the solute increases it experiences difficulty in penetrating the ion exchange resin. This property is useful for the removal of small ionic contaminants. If sorption and fractionation of large solutes is desired, however, ion exchange gels should be used. Macroporous resins may be used if the total number of charges on the solute is not too great.
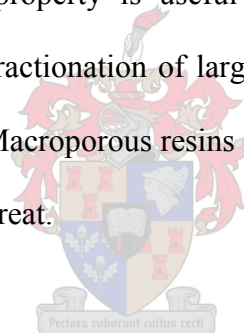
1.3.7.9   Solvent stability

Ion exchange resins are generally stable in the presence of strong bases, strong non-oxidising acids and mild oxidising agents. Substantial structural damage occurs using strong oxidising agents such as permanganate, concentrated nitric acid or hydrogen peroxide. Strongly basic anion exchange resins or strongly acidic cation exchange resins can be used to sorb solutes which can tolerate strong acids or bases, therefore, if a solute is stable in the pH range of 1 to 14 a strong acid or base can be used.

Solutes which are not stable over the entire pH range require the use of a resin which will function over a narrow pH range. The conditions for the use of these resins are mild and, thus, less severe for the solute. The mechanism for sorption and desorption is similar to that of a strong acid or strong basic resin.

Structural similarity between the resin matrix and the solute, for example an aromatic resin and aromatic solute, will determine whether adsorption or ion exchange will take place. The use of high ionic strength solvents or the addition of alcohol to the solvent will reduce the degree of the non-ionic adsorption.

1.3.8   ION EXCHANGE INTERACTIONS

In addition to true ion exchange, other interactions can take place between the solute and the resin, which may either supplement the ion exchange interaction or be used instead of ion exchange to separate ionic or non-ionic species. The following interactions are discussed below.
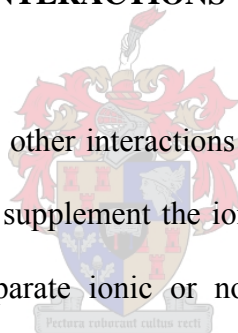
1.3.8.1   Sorption

Aromatic or non-polar interactions between the solute and hydrocarbon matrix of the exchanger have been exploited to separate alcohols, aldehydes and related compounds by using a salt solution as the eluant with either cation or anion exchangers. The salt increases the binding of the non-electrolytes, which are then separated by their degree of attraction for the resin. Adsorption has also been exploited along with other mechanisms to separate ionic species such as aromatic acids. In some cases, however,

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adsorption can interfere with the ion exchange technique and can be reduced by adding organic solvents (for example, methanol or dioxane) to the eluant.

1.3.8.2 Complex formation

A molecule which forms a complex with an ion can be separated by ion exchange chromatography, for example, sugars forming complexes with borates have been separated using anion exchangers in the borate form and complex formation played an important role in this process. The effect of complex formation can be seen by considering a polyvalent ion, A^{n+}, forming a complex with a ligand, L, as shown in the following equation:

$$A^{n+} + mL^- \rightarrow AL_m^{(n-m)+}$$
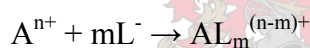
The complexation reaction, in effect, removes a portion of the ion, A, from the exchange process and, therefore, lowers the distribution coefficient. An example of this process would be where cations, such as Ga(III) or Fe(III), which form anionic chloride complexes in hydrochloric acid media show a decrease in distribution coefficients using a cation exchanger as a result of the transformation of the cation to an anion, resulting in an increase in the H^+ concentration. Distribution coefficients increase using an anion exchanger, where the negative charge of the complex ion increases.

Brits and Strelow (1990) proposed the effect of complex formation with respect to Ga(III) in hydrochloric acid and assumed an interaction of $HGaCl_4$ with the organic

skeleton of the resin.   The assumption is similar to solvent extraction, where the HGaCl$_4$ preferred the inside of the resin particles, for thermodynamic reasons, at high acid concentrations.   This extraction-like uptake by the hydrophobic resin matrix leads to higher distribution coefficients compared to those of resins with ion exchange groups (Van der Walt and Strelow, 1983).

1.3.8.3   Partition

Partition chromatography is described as the separation of polar non-electrolytes (for example, sugars) between a stationary polar liquid phase, held by the ionic functional groups of the resin, and a moving non-polar liquid phase used as the eluant.   Sugars separate according to their varying degrees of preference for polar over the non-polar solvent.

1.3.8.4   Ion exclusion

Ionic repulsive forces tend to exclude ions having the same charge as the functional group from the resin at low salt concentrations.   These ions, having an equivalent number of counterions, pass quickly through the column by moving between the beads.   Non-ionic species that move freely in and out of the beads, however, are eluted more slowly.

Ion exclusion has been used, primarily, to separate electrolytes from non-electrolytes, but it can also separate strong electrolytes from weak electrolytes (for example the resolving of organic acids).

1.3.8.5   Ligand exchange

In ligand exchange chromatography a metal which has been bound to a cation exchanger is used, in turn, to bind ligands (such as amino acids or amines) which form co-ordination complexes with the metal.

1.3.8.6   Molecular sieving

The porous matrix of an ion exchange resin acts as a molecular sieve. It excludes molecules that are too large to enter the pores and it retards the migration of the molecules capable of entering the pores, with the larger molecules being eluted first.

Sieving effects may improve the resolution of ions that differ both in size and charge. They also limit the size of the ions that can interact with the functional groups of a given ion exchanger.

1.3.9   EQUILIBRIUM IN ION EXCHANGE

1.3.9.1   Selectivity coefficient

The exchange of ions between a solid ion exchange material and a solution is a typically reversible reaction. Should a solution, containing the cation B^+, be shaken with a solid exchanger AR, containing the cation A^+, the B^+ ions will enter the exchanger, while the A^+ ions will be expelled to the solution. After some time, which

can range from a few minutes to several days depending primarily on the solid exchanger, no further change will be observed and an equilibrium will have been established as follows:

$$AR + B^+ \rightarrow BR + A^+ \tag{1}$$

Should the ions be doubly charged, the equilibrium will then be represented as follows:

$$2AR + B^{2+} \rightarrow BR_2 + 2A^+ \tag{2}$$

A selectivity coefficient is used to represent the final distribution of concentrations, which for the exchanges between ions of equal charge will have the following format:

$$E_A^B = [A^+][BR] / [B^+][AR] \tag{3}$$

The symbols $[A^+]$ and $[B^+]$ indicate the molar or molal concentration in the solution, while $[A]$ and $[B]$ indicate the concentration in the ion exchange resin. It is customary to express E_A^B as a number greater than unity, not mandatory. It is assumed that the B ion is more strongly held by the exchanger than ion A.

In the exchange of ions of equal charge the ratio between the concentrations of A and B does not change with dilution, aside from small effects due to non-ideality. Should the ions be of unequal charge there are two effects to be noted, namely, the ion of higher charge is usually more strongly held by the exchanger and the distribution will

shift with dilution. The more the solution is diluted the more strongly the ion of higher charge is held by the resin and vice versa. This effect is sometimes referred to as "electroselectivity".

1.3.9.2   Thermodynamic equilibrium constant

One should recognise that a proper representation of the ion exchange equilibrium is not ideal in the thermodynamic sense, be it in the external solution or in the ion exchanger. The partial molal free energies are not linear functions of the logarithms of concentrations and this is especially true for the exchange phase, where the ions are much closer together than they would be in the external solution. One can take cognisance of non-ideality by introducing activity coefficients and represent the thermodynamic equilibrium coefficient as follows:

$$K_A^B = (m_A m_B / m_B m_A)(\gamma_A \gamma_B / \gamma_B \gamma_A) \qquad (4)$$

m and γ represent the molality and activity coefficient, respectively.

1.3.9.3   Equilibrium distribution coefficient

The equilibrium state in the system, ion exchange – electrolyte solution, is often described in terms of the distribution coefficient. This measurement is given by the relationship of the equilibrium concentrations of the same ion in the exchanger phase and in the external solution.

The equilibrium distribution coefficient (K_d or D) is defined as:

$$K_d \text{ or } D = \frac{\text{Mass of element per gram dry ion exchanger}}{\text{Mass of element per cm}^3 \text{ solution}}$$

It can be simplified into:

$$D = \frac{\text{Mass of element in resin (g)} \times \text{volume of solution}}{\text{Mass of dry resin (g)} \times \text{mass of element in solution (g)}} \quad (5)$$

The distribution coefficient is, probably, one of the most useful tools in ion exchange chromatography, since it is used to predict the behaviour of ions and, therefore, the elution order from a column (Smith-Jones and Strelow, 1986).

Mayer (1947) proposed one of the fundamental applications of D and it is shown as follows:
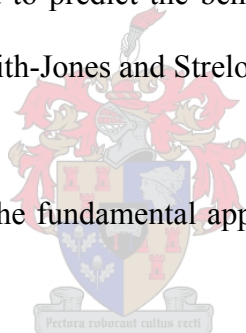
$$V = D.m + V_d$$

V is known as the peak elution volume – the volume of the eluate at which the concentration of the eluted ion reaches its maximum. The symbol m designates the mass of dry resin in the column and V_d is the dead volume of the column.

The K_d is determined using the batch method or the mobile (column) method. In practice the former method is usually preferred, because equilibrium is reached over a period of hours – usually 24 hours (Van der Walt, 1993).

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1.3.9.3.1 The batch process of ion exchange

In the batch process the ion exchanger makes contact with a solution. This is done by creating a slurry, by placing the ion exchanger in the solution and stirring it mechanically. Once equilibrium is reached the ion exchanger is separated from the solution by means of filtering, centrifuging or decantering. The element involved is quantitively determined in both phases (resin and solution) by using an appropriate analytical method.

It is only possible in certain cases to use the full capacity of the resin. In one case the reactions take place virtually completely as a result of a driving force (reaction) such as the production of insoluble products or stable complexes of weak electrolytes (Berg, 1963). In most ion exchange reactions this type of reaction is absent and a small percentage of the total exchange capacity of the ion exchanger is used in batch processes.

Smaller quantities of ion exchanger can be used if the batch process is repeated many times, known as multistep or cascade operation. After each step the separated solution is treated with a new portion of ion exchanger until equilibrium is reached. Although the efficiency of the batch process is increased in this way, this method is time consuming, involves more work and leaves greater margin for error (Van der Walt, 1993).

1.3.9.3.2   The column method of ion exchange

The column method involves pouring a column with the resin and passing the sample through to achieve the separation. Particle size will determine the flow rate, which will affect the separation. The resin should be in the correct ionic form and equilibrated prior to adding the sample.

The column method is incorporated with the elution curve method (Smith-Jones and Strelow, 1986). The solution containing the element to be determined is passed through the resin column and is followed by passing the relevant wash solution through the column. Fractions are taken during each step, usually 10ml, and the fractions are numbered accordingly. The element concerned is then measured in each fraction taken and, as a result, an elution curve can be drawn.
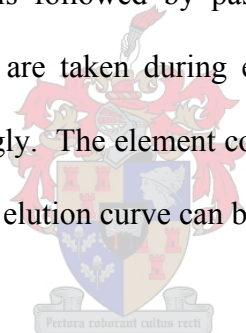
1.3.10   THE SEPARATION FACTOR

The separation of an ion pair, A and B, is determined by the relationship of the distribution coefficients D_A and D_B in a specific experimental environment.   The separation factor is then expressed as:

$$\alpha_A^B = D_B / D_A$$

The greater α_A^B differs from 1 for a given ion pair, the easier the two ions will separate on an ion exchange column.   Should α_A^B have a value greater than 10, then the

separation of the two elements will be effective and, the larger α^B_A the easier it is to separate the two elements.

If the separation factor has a value of less than 10 both elements are regarded as being weakly retained by the resin in question, while if the value is greater than 100 the element in question is well retained by the resin, while the other element flows through the column. Should a separation factor for two specific elements have a value of between 50 and 100, a long column should be used if the element is to be retained by the resin as it moves down the column when elution of another element takes place. A short column can be used for those elements with high separation factors.

1.3.11   AG MP-50: A BACKGROUND

AG MP-50 resin is a macroporous strong acid cation exchange resin, which is useful for single step purification methods, for concentrating cationic solutes and for analytical determinations of various mixed cationic solutes.

These resins are comprised of sulphonic acid functional groups attached to a styrene divinylbenzene copolymer lattice. The amount of resin crosslinking determines the bead pore size. A resin with a lower crosslinkage has a more open structure permeable to higher molecular weight substances than a highly crosslinked resin. It also has a lower physical resistance to shrinkage and swelling, so that it absorbs more water and swells to a larger wet diameter than a highly crosslinked resin of equivalent dry diameter.

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AG MP-50 resin is the macroporous equivalent of AG 50W resins, also available from Bio-Rad laboratories, Richmond, U.S.A. Its effective surface area approximates $35m^2$ per dry gram, or 30 to 35% porosity. It has greater crosslinkage than AG 50W resins and, therefore, elements bind more easily to the resin and the elements elute more easily as well.

The cation exchange resins are thermally stable and resistant to solvents, such as alcohols and hydrocarbons, reducing agents and oxidising agents.

The other reasons for using this resin for this project include the fact that higher flow rates can be used in productions and that less tailing occurs. The distribution coefficients are normally 30 to 60% higher than those from AG 50W resins and, as a result, separations between elements are better.

1.3.11.1 Mechanism
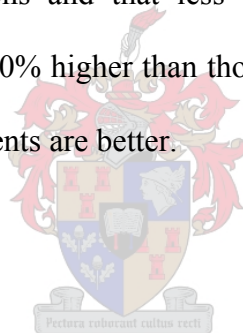
In an ion exchange procedure, the counterions on the resin are replaced by sample ions that have the same charge. In applications involving a cation exchange resin, such as AG MP-50 resin, neutral molecules and anions do not interact with the resin.

AG 50 resins are available with H^+, Na^+ or NH_4^+ counterions. A resin can be converted from one ionic form to another. Usually, the resin is used in an ionic form with a lower selectivity for the functional group than the sample ions to be exchanged. The sample ions are then exchanged when introduced and can be eluted by

introducing an ion with higher affinity for the resin or a high concentration of an ion with equivalent or lower affinity.

In general, the lower the selectivity of the counterion the more readily it exchanges for another ion of like charge. The order of selectivity can also be used to estimate the effectiveness for different ions as eluants, with the most highly selective being the most efficient. The order of selectivity can be used to estimate the difficulty of converting the resin from one form to another. Conversion from a highly selected to a less highly selected form requires an excess of the new ion.

The AG 50 resins are available in several particle size ranges. The flow rate in a chromatographic column increases with increasing particle size. The attainable resolution, however, increases with decreasing particle size and narrower distribution ranges.
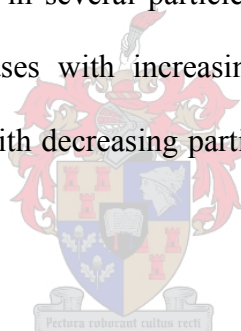
Particle size is given either in mesh size or micron size. Large mesh material (20 to 50, or 850 to 300 μm, and 50 to 100 mesh, or 300 to 150 μm) is used primarily for large preparative applications and batch operations where the resin and sample are slurried together. Medium mesh resin (100 to 200 mesh, or 150 to 75 μm) is used primarily in column chromatography for analytical and laboratory scale preparative applications. Fine mesh material (200 to 400 mesh, or 75 to 38 μm) is used for high resolution analytical separations.

AG MP-50 resins are available in 100 to 200 mesh size in hydrogen form.

1.3.11.2 Resin conversion

Resin conversion is most effectively carried out in the column mode. When choosing a column, however, it must be taken into account that the resin may shrink, or it may swell as much as 100%, depending on the conversion.

To convert the resin to an ionic form with a higher selectivity, the resin should be washed with two to three bed volumes of a 1 M solution of the desired counterion. Should the resin be converted to an ionic form with a lower relative selectivity for the resin, the necessary volume of counterion solution will depend on the difference in selectivity. As a general rule, 1 bed volume of 1 M counterion solution for each unit difference in relative selectivity is used. For example, converting AG 50W-X8 resin from the K^+ form (relative selectivity 2.5) to the H^+ form (relative selectivity 1.0) would require two to three bed volumes of 1 M hydrochloric acid. The conversion is complete when all the K^+ ions are displaced by the H^+ ions.
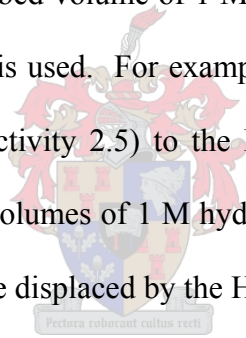
2. APPARATUS AND REAGENTS

This chapter contains a short description of the instrumentation used, volumetric apparatus and reagents used in this work.

2.1 THE ICP IN ANALYSES AND QUALITY CONTROL

Most experimental analyses in South African laboratories are performed using the Atomic Adsorption (AA) concept. The main reason for this is that AA instruments are common and, although they are very expensive, they are considerably cheaper to purchase and maintain than an inductively coupled plasma (ICP) instrument. Most laboratories do not have the budget to purchase an ICP instrument, unless the laboratory is part of a large company. As a result, there are relatively few instruments of this kind in South Africa, should one perform a comparison between the number of AA instruments and ICP instruments in local laboratories.

The main disadvantage of the ICP instrument in comparison to the AA instrument, from an analytical point of view, is the fact that the ICP instrument does not give accurate results when analysing the alkali and alkali earth metals. The JY Ultima, the ICP instrument used for these analyses, overcomes this problem with the use of a sheath gas, also argon, through an independent line. This allows for more sample to travel to the plasma for excitation and transports the alkali elements into the Normal Analytical Zone such that sensitivity is increased substantially. When testing the instrument using sodium (as it would be extremely useful for analyses in our sodium-

22 production) it produced a detection limit of 5 ppb. The drawback of using this method for production purposes, however, is the fact that more sample and, therefore, more activity is required than when using AA or the graphite furnace, which requires $1/1000^{th}$ of the sample size of the ICP instrument.

Many common interferences in atomic spectroscopy are eliminated by using an inductively coupled argon plasma for emission measurements. The plasma is twice as hot as a conventional flame and the residence time of analyte in the flame is about twice as great. Atomisation is more complete than in a flame and the signal is correspondingly enhanced. Reaction of the analyte to form metal oxide molecules is eliminated. The plasma is also remarkably free of background radiation in the region where sample emission is observed (15-35mm above the load coil). The background concentration of electrons, due to plasma formation, is fairly high and uniform. The temperature is so high that most elements are observed, as ions and the concentration of these ions seem insensitive to the presence of potential suppressors.
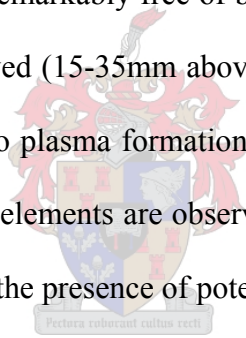
A common problem in flame emission spectroscopy is that there is a lower concentration of electronically excited atoms in the cooler, outer part of the flame than in the warmer, central part of the flame. As a result, emission from the central region is absorbed in the outer region. This self-absorption increases with increasing concentration of analyte and leads to nonlinear calibration curves.

In a plasma the flame temperature is more uniform and self-absorption is not nearly so important. Calibration curves for plasma emission are linear over nearly 5 orders of

magnitude, while conventional flames have a linear range covering about 2 orders of magnitude.

2.1.1   ADVANTAGES AND DISADVANTAGES OF ICP OVER FURNACE AND AA

The use of an ICP instrument for analyses has some advantages over the atomic absorption and graphite furnace instruments. The following points are discussed below.

The ICP instrument generates much higher temperature than the other two instruments mentioned, which allows for good dissociation of a molecular species, thereby limiting matrix effects. Elements are partially ionised, therefore, ionic lines also occur. Some elements have enhanced emission due to ions, for example alkaline earth ions, which behave like alkali elements. This allows for strong emission, higher sensitivity and a low minimum detectable quantity for an element.

As mentioned previously, the ICP has the typical linear dynamic range over at least three orders of magnitude, while the other instruments mentioned has a dynamic range of, at best, two orders of magnitude. This allows for ease of calibration and sample preparation. The ICP instrument can be set up such that it can perform multi elemental analyses.

As with all instruments, the ICP instrument also has its disadvantages. Alkali metals have high excitation energy and, as a result, behave like a noble gas, providing very

weak emissions. It's an expensive machine to purchase and to run and maintenance costs can be high.

2.2   VOLUMETRIC APPARATUS USED

All glassware mentioned and used in this work was of A-grade quality. As the laboratory was air-conditioned, the other apparatus (such as the balances) were not calibrated and was accepted as being correct. Gilsson micropipettes were used for the pipetting of millilitre quantities. The micropipettes used were calibrated at 25°C by weighing the mass of the volume dispensed.

2.3   REAGENTS USED

Analytical grade reagents were used throughout this work and were obtained from Merck (SA) Pty. Ltd or Sigma Aldrich GmbH, which included Sigma, Aldrich, Fluka and Riedel de Haen products. The AG MP-50 macroporous cation exchange resin was obtained from Bio Rad, Richmond, U.S.A.

Wherever water is referred to in the experimental descriptions indicates that de-ionised water was used. This was obtained by de-ionising tap water using a Millipore MilliQ Reagent Grade Water System to a conductivity of greater than 10 megaohm.cm^{-1}.

3. QUANTITATIVE INDICATION OF SEPARATION POSSIBILITIES

The batch method was used to determine equilibrium distribution coefficients, as it was decidedly easier to perform the experiments using this method than the column method.

The column method is not an equilibrium process and is seldom used to determine distribution coefficients.

3.1 APPLICATIONS USING AG MP-50 CATION EXCHANGE RESIN
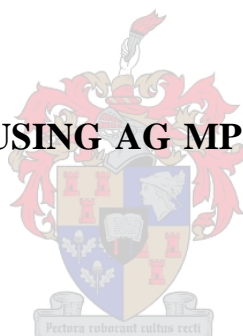
According to the Bio-Rad instruction manual for AG MP-50 cation exchange resin, the only application this resin has been used for is lead separations, by Strelow in 1985. It is known, however, that Strelow also performed distribution coefficients using this resin in various media, namely various concentrations of hydrochloric acid and various percentages of methanol in 0.5 M hydrochloric acid. The resin is used for a number of applications at iThemba LABS, some of which have not been published, but will be described briefly.

One application the resin is used for, but not featured in a publication, is as a radioactive solid food tracer in the alimentary canal in the human body. The

radionuclide used in this method is gallium-67, with a half-life of 78.3 hours and the emission of γ-rays at 184 and 300 keV. The normal dosage to an adult patient is 37 MBq and the resin is taken orally with food or mixed with a Psyllium husk suspension. A dry mass of 0.2 g of the resin is weighed and washed with water, followed by 1 M hydrochloric acid, again with water, ethanol and finally, once again, with water. The gallium-67 solution is added to the resin and the resin is then washed and dried overnight, before being despatched.

Another application using AG MP-50 cation exchange resin was in the separation of iron from $^{111}InCl_3$ solutions. The iron would sometimes appear as a contaminant in the production of indium-111 and the extra separation using the resin would be required. The indium-111 would be dissolved in 0.5 M hydrochloric acid - 60% methanol mixture and pumped through the resin (equilibrated with 0.5 M hydrochloric acid - 60% methanol). The indium-111 would then be eluted with 0.5 M hydrochloric acid - 60% methanol, before being evaporated to an almost dry state. Concentrated nitric acid was added, before the solution was evaporated to dryness. After the addition of acetic acid, the evaporation process was repeated. It was finally taken up in 0.01 M hydrochloric acid, before being despatched.

The most highly regarded application using the resin at iThemba LABS, however, is in the production of sodium-22 (van der Walt and Haasbroek, 1995), which is the main source of income for the Radionuclide Production group. Two resins are used in this production, namely, Chelex 100 and AG MP-50 cation exchange resin. The AG MP-50 resin is not only used in the production, but also in the purification of many of the reagents to be used in the production.

The resin for the production is prepared by being packed in a column and purified by passing 4 M hydrochloric acid through it and rinsing it with water. The resin is removed from the column and converted to the triethanolammonium form by stirring the resin with 1 M triethanolamine (TEA). The resin is left to settle before decanting the TEA solution and washing the resin with water. The resin is, once again, placed into a column and equilibrated with 0.4 M citric acid - 1.2 M TEA - 80% methanol. The current method used, as well as a proposal of another method to separate sodium from magnesium (the crux of the production) is discussed in Chapter 4.

Other applications found using AG MP-50 resin include the purification of collagen obtained from powdered bone in flow cells which is leached in a system to process archaeological bone to purified gelatine for carbon-14 dating (Law and Hedges, 1989) and the elimination of arsenic traces in liquid effluent (Guenegou *et. al.*, 1998).
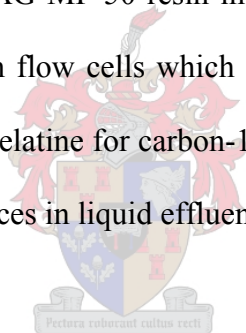
3.2 THE PREPARATION OF THE RESIN

AG MP-50 resin is made available from Bio-Rad Laboratories as dry, free flowing solids. The resin must be thoroughly hydrated with deionised water before applying it to any experiment, whether it is the batch method or the column method. This is done by ensuring that the hydration solution is of the same solvent concentration as a mismatch in solvent concentration will result in poor column packing for column experiments.

The resin was prepared for experiments by performing the following procedure. A quantity of dry resin was slowly added to deionised water (hydration solvent) in a polyethylene bottle, while gently stirring. The resin was allowed to hydrate overnight to ensure that the resin was completely hydrated and free of any entrapped air.

The supernatant was decanted and fresh deionised water added. The resin was left to settle to the bottom of the bottle and the supernatant was, once again, decanted. The supernatant contains all the finer particles of the resin, which could block the column sinters. This process was repeated until all the finer particles were removed.

The resin could be left in hydration solvent for use in the column method of ion exchange, but in the batch process of ion exchange the resin was placed in an oven to dry out, such that a uniform mass could be weighed out for the necessary experiments.

3.3   THE EXPERIMENTAL METHOD

As mentioned above, the resin to be used (AG MP-50 in hydrogen form) in the following determinations is currently used in a number of productions at iThemba LABS, namely, sodium-22, rubidium-81 and it is the resin of choice when distributing gallium-67 resin (generally 1mCi orders). It was decided to use nitric acid and citric acid mixtures, as the sodium-22 production involves the use of citric acid and the gallium-67 is despatched as gallium citrate for local orders.

As a result, 42 elements were chosen for these determinations on AG MP-50 cation exchange resin using six different nitric acid and citric acid mixture concentrations. The mixture concentrations used were as follows:

0.1 M citric acid, 0.2 M nitric acid

0.1 M citric acid, 0.5 M nitric acid

0.1 M citric acid, 1.0 M nitric acid

0.25 M citric acid, 0.2 M nitric acid

0.25 M citric acid, 0.5 M nitric acid

0.25 M citric acid, 1.0 M nitric acid

The elements chosen were taken from all groups of the periodic table, with the exception of the halides and noble gases. The elements to be determined in these experiments were:
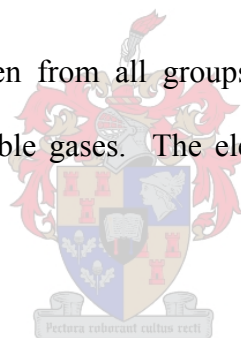
- Lithium(I), sodium(I), potassium(I), rubidium(I), caesium(I).

- Magnesium(II), strontium(II), barium(II).

- Scandium(III), yttrium(III).

- Titanium(IV), zirconium(IV).

- Vanadium(IV), vanadium(V), niobium(V), tantalum(V).

- Chromium(III), molybdenum(VI), tungsten(VI).

- Manganese(II).

- Iron(III).

- Cobalt(II).

- Nickel(II).

- Copper(II), silver(I).

- Zinc(II), cadmium(II).

- Aluminium(III), gallium(III), indium(III).

- Germanium(IV), tin (IV), lead(II).

- Arsenic(V), antimony(V), bismuth (III).

- Lanthanum(III), cerium(III), terbium(III), ytterbium(III).

- Thorium(IV), uranium(VI).

All chemicals were of analytical grade and were purchased from Sigma-Aldrich (Pty) Ltd or Merck SA, as mentioned in Chapter 2. The AG MP-50 cation exchange resin was obtained from Bio-Rad Laboratories, Richmond, U.S.A.

Cobalt, silver, barium, thorium, caesium, zirconium, lead and uranium were dissolved using their nitrates, while the chlorides of sodium, potassium, manganese, nickel, cadmium, tin, lithium, lanthanum, rubidium, magnesium and strontium were dissolved. The oxides of terbium, ytterbium, chromium, scandium, yttrium, arsenic, molybdenum and vanadium (V) were used for the determinations, while aluminium, gallium, indium, titanium, iron, copper, zinc, niobium, tungsten, antimony, tantalum, bismuth and germanium were dissolved in elemental form. Vanadium (IV) was used in the fluoride form.

The Merck Index was consulted to speed up the process of dissolving the elements and, although most of the information gleaned was very helpful, some of the information provided was incorrect and other options had to be used. Vanadium(V) oxide (concentrated acids) and germanium (concentrated nitric acid) had to be

dissolved using hydrogen peroxide, while aluminium (dilute hydrochloric acid or dilute sulphuric acid), titanium (acids on heating, but oxidised by nitric acid), antimony (hot, concentrated hydrochloric acid when finely divided), arsenic trioxide (dilute hydrochloric acid) and molybdenum trioxide (concentrated mineral acids) had to be treated using concentrated hydrochloric acid with the addition of a few drops of hydrogen peroxide.

Tungsten did not dissolve at all and, even when ammonium tungstate(VI) and sodium tungstate(VI) was used to get tungsten into solution, it would only do so with the addition of a certain amount of water: anything less than that amount and the tungsten would precipitate. Once the tungsten did dissolve, it would only precipitate again when 0.1 M nitric acid was added and also did so on the addition of 0.1 M citric acid, 0.2 M nitric acid mixture.
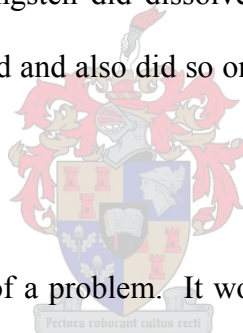
Barium nitrate also posed a bit of a problem. It would dissolve in high quantities of water, but would precipitate after a while. When it was decided to use 0.1 mmol barium per 10 ml solution, however, the barium remained in solution. Antimony, thorium and strontium were made up in a similar way for either the reason stated above, or due to the fact that there was not enough of the chemical in stock.

Vanadium(V) precipitated when any concentration of citric acid/nitric acid mixture was added but, after shaking the solution for approximately 20 hours, the vanadium had gone back into solution and had turned a greenish colour. This indicated that the vanadium had been reduced to the +4 state. This experiment was, nevertheless,

processed as it was felt that it would be interesting to compare the results to that of the actual vanadium(IV) experiment.

1 mmol per 10ml of a specific element was dissolved and evaporated to dryness. The element was then taken up, using 0.1 M nitric acid, and made up in a 100 ml volumetric flask (referred to as the "mother" solution). This was done for each element that was to be determined.

For each element determination, one 250 ml plastic bottle was put aside for each different concentration of acid mixture: six in all. To each plastic bottle, 1 g of dried AG MP-50 resin was added, followed by 10 ml of the "mother" solution of the element to be determined. The solution in each bottle was made up to 100 ml with the addition of different concentrations of acid mixture to give the different concentrations to be used for each determination (see above). The bottle caps were placed on to the bottles and tightened, before placing them on a mechanical shaker for 18 to 24 hours. A reference sample was also prepared, using the same method mentioned in this paragraph, without the addition of the resin and the shaking of the sample. The highest concentration of acid used in these experiments, in this case 0.25 M citric acid/1.0 M nitric acid, was used to make up the reference sample.

Polyethylene columns with an approximate 10 mm diameter were used, with a 70 μm sinter placed at the bottom. The solutions from the bottles were poured through the individual columns, where the sinter kept the resin behind in the column and the solution poured through the column into 250 ml volumetric flasks placed below it. The bottles were then rinsed with 100 ml water and poured through the columns into

the volumetric flasks. The volumetric flasks were then removed and made up to the mark with deionised water. These solutions were referred to as the filtrate solutions.

New volumetric flasks were placed underneath the columns and the columns were eluted using 50 ml 7 M hydrochloric acid. The volumetric flasks were, once again, removed and made up to the mark with deionised water. These solutions were referred to as the eluates.

A few problems occurred in the elution step with thorium, barium and silver when using hydrochloric acid as eluant. In the case of thorium, the results did not correlate with the reference solution and it was later discovered that thorium would be very strongly held to the resin and did not elute easily, but good results were obtained when thorium was eluted using 7 M nitric acid instead.

The results for barium were also not satisfactory and 4 M nitric acid was used to elute this element, as it was thought it would be more effective than using the hydrochloric acid.

Silver posed an interesting problem. It was noted that silver was strongly held onto the resin and, when eluting, the silver would come off the resin without any problems. When diluting the eluate, however, the silver would precipitate. It is necessary to dilute the eluate for measuring purposes and it could not happen here. It was possible to measure the filtrates and compare them to that of the reference, thereby calculating the unknown (the eluate) and the distribution coefficient, but it was eventually

decided to repeat the experiment and elute the silver from the resin using 4 M nitric acid instead.

Both the filtrate and eluate solutions were analysed for the element to be determined using the Jobin Yvon Ultima ICP instrument. These results were then implemented to determine the distribution coefficient for that specific element at that specific concentration of citric acid/nitric acid mixture.
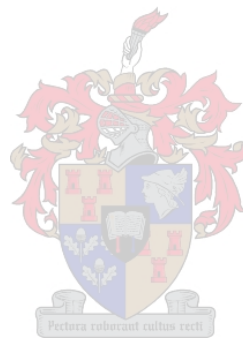
3.4 RESULTS AND DISCUSSION

Table 1: K$_d$ values for elements in citric/nitric acid media on AG MP-50 resin

Element	Citric Nitric	0.1 M 0.2 M	0.1 M 0.5 M	0.1 M 1.0 M	0.25 M 0.2 M	0.25 M 0.5 M	0.25 M 1.0 M
Li		19	10	6	21	10	6
Na		42	23	13	41	22	14
K		126	68	38	<1	<1	<1
Rb		113	63	31	101	55	30
Cs		177	97	50	193	115	55
Sc		144	124	105	151	110	78
Ti(IV)		469	123	33	288	113	33
V(IV)		112	43	19	109	41	17
V(V)*		190	53	20	217	51	30
Mn(II)		261	140	83	378	167	96
Fe(III)		1455	428	160	894	410	149
Ni(II)		277	93	36	299	95	34
Zn		256	87	41	220	88	39
Al		494	165	62	504	174	68
Ga		300	162	63	372	158	63
As(V)		<1	<1	<1	<1	<1	<1
Y		154	119	92	162	125	84
Zr(IV)		52	56	47	18	20	18
Nb(V)		<1	<1	<1	<1	<1	<1
Mo(VI)		<1	<1	<1	<1	<1	<1

Element	Citric Nitric	0.1 M 0.2 M	0.1 M 0.5 M	0.1 M 1.0 M	0.25 M 0.2 M	0.25 M 0.5 M	0.25 M 1.0 M
Cd		478	174	70	478	155	68
In		272	120	56	284	172	84
Sn(IV)		26	7	4	4	4	3.8
Sb(V)[#]		35	34	32	34	34	19
Ta(V)		<1	<1	<1	<1	<1	<1
W(VI)		PPt	PPt	PPt	PPt	PPt	PPt
Pb(II)		664	225	94	591	325	105
Bi(III)		892	326	109	481	217	97
La		4733	970	299	3882	879	307
Ce		65	57	42	65	57	45
Th[#]		$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$
U(VI)		303	104	38	280	91	40
Co		315	94	34	301	110	35
Ag(I)		371	168	82	380	153	129
Ge(IV)		<1	<1	<1	<1	<1	<1
Mg		316	87	31	329	95	31
Sr[#]		868	710	330	918	694	340
Ba[#]		$>10^4$	$>10^4$	1204	$>10^4$	5889	3308
Tb		$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$	$>10^4$
Yb		2984	2361	860	3039	2192	847
Cr(III)		174	103	51	175	112	51
Cu(II)		166	78	36	149	77	40

* reduction took place, resulting in V(IV)   # 0.1 mmol

The results obtained from the experiments conducted are tabulated above. A discussion of these results follows.

Tompkins and Mayer (1947) determined cation exchange separation factors for the promethium-europium lanthanide pair with various complexing agents. Their experiments showed that the factor in tartrate was larger than in citrate, the reagent commonly used for lanthanide separations in those days. As a result, Strelow and van der Walt performed experiments using tartaric acid/nitric acid media on AG 50W-X8, a cation exchange resin (Appendices C and D). Their results will be compared to the results obtained in this work to loosely measure the efficiency of the AG MP-50 cation exchange resin using citric acid/nitric acid media. Strelow's experiments on AG MP-50 resin using different concentrations of hydrochloric acid (Appendix A) and different percentages of methanol in 0.5 M hydrochloric acid (Appendix B) will also be compared to this work.
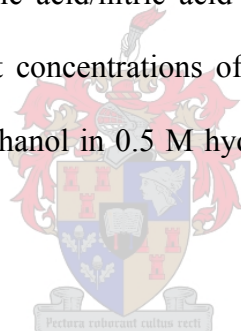
3.4.1 THE ALKALI METALS

Of the alkali metals, lithium, sodium, potassium, rubidium and caesium were used in the experiments.

Strelow and van der Walt's results for these elements in tartaric acid/nitric acid mixture (1982) are the same as those obtained for the elements in pure nitric acid (Strelow *et. al*, 1965).

Lithium and sodium

Interestingly, lithium has similar results with different concentrations of citric acid, which implies that the citric acid does not play a significant role in the ion exchange at these acid concentrations on this specific resin. The same can be said for sodium. Neither of these two elements is held strongly by the resin and their distribution coefficients decrease with an increase in concentration of nitric acid.

Strelow performed experiments on AG MP-50 resin using different concentrations of hydrochloric acid (1984) and different percentages of methanol in 0.5 M hydrochloric acid (1984). His results showed that neither lithium nor sodium was well retained by the resin in various concentrations of hydrochloric acid. The distribution coefficients for lithium increased slightly with an increase of percentage methanol, although having 90% methanol in the initial mixture had a lower distribution coefficient than an 80% mixture. Sodium, on the other hand, was better retained by the resin when the percentage methanol was increased, with a vastly higher distribution coefficient with a 90% methanol mixture than a solution without methanol added to it. This indicates that sodium can be separated from lithium in a 90% methanol mixture, whereas they could not be separated effectively without the addition of methanol. It would appear that methanol, in this case, is more effective when retaining sodium on the resin, than a citric acid/nitric acid mixture.

Strelow and van der Walt's results for lithium were virtually identical to the results obtained in this work, with the exception of the x M citric acid/1.0 M nitric acid distribution coefficient, which was double that obtained by Strelow and van der Walt using tartaric acid/nitric acid media (1982 and 1965). Their results for sodium in

tartaric acid/nitric acid media, however, did differ somewhat from the results obtained in this work. Although the distribution coefficients obtained from both works were low, indicating the low affinity for the element by the resin, the results obtained by Strelow and van der Walt were approximately half that of those obtained in this work. This indicates that the distribution coefficients are higher due to the higher crosslinkage of the macroporous resin, as was expected.

Potassium

Potassium provided different results, being more strongly held to the resin than sodium and lithium when using 0.1 M citric acid mixtures. When the concentration of the citric acid was increased, however, potassium was not held on to the resin at all.

Potassium becomes better retained on to the resin with the addition of methanol, according to Strelow. Like sodium, when in a 90% methanol mixture it is very well held by the resin, more so than sodium. Also, as in the case of sodium, the difference in distribution coefficient between the 90% methanol mixture and the normal hydrochloric acid solution is vast. It shows that, for potassium, methanol mixtures in hydrochloric acid are more effective than citric acid/nitric acid mixtures should one wish to retain potassium on to the AG MP-50 resin.

Strelow and van der Walt's results using tartaric acid/nitric acid media (1982 and 1965) indicate that the distribution coefficients are less than half that obtained in this work using 0.1 M citric acid/x M nitric acid media.

Rubidium

Rubidium is marginally less strongly held by the resin than potassium when using 0.1 M citric acid mixtures, but is still held on to the resin when using 0.25 M citric acid mixtures. Rubidium is marginally less strongly held by the resin when in 0.25 M citric acid mixtures than its 0.1 M citric acid mixture counterparts although, the 0.1 M citric acid/ 1.0 M nitric acid and the 0.25 M citric acid/1.0 M nitric acid results are virtually identical.

Strelow's experiments show that rubidium shows a similar tendency to the addition of methanol in 0.5 M hydrochloric acid as potassium: the distribution coefficient increases dramatically over the original hydrochloric acid solution, even more so than potassium.

As with potassium, Strelow and van der Walt's results obtained for rubidium are less than half that obtained in this work, which indicates that the element in tartaric acid/nitric acid media is not well retained by the resin, whereas in this work the element is better retained by the resin, particularly when in 0.2 M nitric acid and various concentrations of citric acid.

Caesium

Caesium is the most strongly held by the resin of the alkali metals tested and is the only element whose results indicate that it is more strongly held by the resin when the concentration of the citric acid in the mixture is increased.

Caesium, according to Strelow, also has the same tendency as potassium and rubidium and is marginally more strongly retained by the resin when in 90% methanol mixture than rubidium. The same can be said for the results obtained by Strelow and van der Walt (1982) when using various concentrations of tartaric acid/nitric acid mixtures.

All the results for these elements indicate that there is a decrease in distribution coefficient with an increase in the concentration of nitric acid, with the exception of potassium in the 0.25 M citric acid mixtures, which is not held on to the resin at all.

There is a similarity between the experiments performed with different concentrations of hydrochloric acid and those performed with citric acid/nitric acid mixture in this project. It is noted that the distribution coefficients for the alkali metals decrease with an increase in strong acid (i.e. hydrochloric or nitric acid) concentration. Caesium in 0.2 M hydrochloric acid is better retained by the resin than in either concentration of citric acid/0.2 M nitric acid mixture, although less so in 0.25 M citric acid/0.2 M nitric acid mixture. Rubidium in hydrochloric acid has a distribution coefficient which is double that of rubidium in citric acid/nitric acid mixture, whereas potassium in hydrochloric acid is marginally more strongly held by the resin than in 0.1 M citric acid/0.2 M nitric acid mixture. The difference in distribution coefficient, however, is vast in comparison to 0.25 M citric acid/nitric acid mixture, where the potassium in the mixture is not retained by the resin at all. Both sodium and lithium in 0.2 M hydrochloric acid have a distribution coefficient marginally higher than that of their counterparts in citric acid/nitric acid mixtures.

3.4.2   THE ALKALINE EARTH METALS

Magnesium, strontium and barium were the elements in this group that were used in these experiments.

Magnesium

Magnesium is relatively well retained by the AG MP-50 macroporous cation exchange resin when in low concentrations of nitric acid, containing various concentrations of citric acid.   The distribution decreases steadily with an increase in nitric acid concentration, while the results for the element in 0.25 M citric acid/x M nitric acid media indicate that the distribution coefficients are slightly higher than those of the 0.1 M citric acid/x M nitric acid counterparts, with the exception of magnesium in x M citric acid/1.0M nitric acid, where the distribution coefficient is identical.
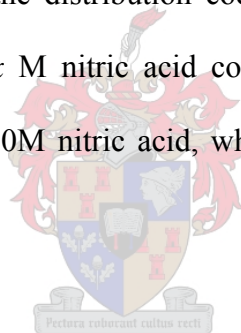
Strelow's experiments with magnesium on AG MP-50 cation exchange resin in various concentrations of hydrochloric acid (1984) indicate a decrease in affinity for the resin as the acid concentration increases.   The distribution coefficients obtained for the element in 0.5 M and 1.0 M hydrochloric acid are similar to the results obtained in 0.5 M and 1.0 M nitric acid, with various concentrations of citric acid, in this work.   The result obtained for the element in 0.2 M hydrochloric acid, however, indicates a greater affinity for the resin than that of magnesium in 0.2 M nitric acid, with various concentrations of citric acid.   When Strelow added various percentages of methanol to the element in 0.5 M hydrochloric acid, the distribution coefficient

increased with an increase in methanol percentage in solution, thereby allowing the element to bind to the resin more effectively.

When comparing the results obtained for magnesium from this work with those obtained by Strelow and van der Walt (1982) using AG 50W-X8 cation exchange resin, the distribution coefficients of the element in 0.1 M citric acid and various concentrations of nitric acid are similar to those obtained in 0.1 M tartaric acid containing various concentrations of nitric acid. The distribution coefficients in this work are slightly higher due to the fact that the AG MP-50 resin is macroporous and, as a result, one can expect slightly higher distribution coefficient results. The same can be said for the results obtained for magnesium in 0.25 M citric acid containing various concentrations of nitric acid in this work and the results Strelow and van der Walt obtained for the element in 0.25 M tartaric acid containing various concentrations of nitric acid which, ironically, are the same as those Strelow obtained for magnesium in pure nitric acid (1965).
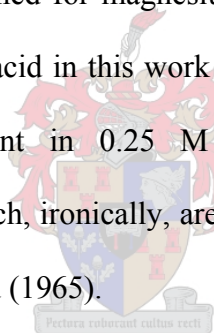
Strelow predicted that citric acid would be a better complexing agent for magnesium than tartaric acid and, as a result, the sodium-22 production was performed using citric acid for dissolving and citric acid-methanol for eluting the magnesium from the column. From these results it can be seen that this is not the case. This will be discussed in more detail in the following chapter.

Strontium

Strontium was well retained by the resin in all concentrations of citric acid/nitric acid media. As for most of the elements determined, the distribution coefficients decrease

with an increase in nitric acid concentration. The distribution coefficient for the element in 0.25 M citric acid/0.2 M nitric acid is greater than that of its 0.1 M citric acid/0.2 M nitric acid counterpart, while the other distribution coefficients for the 0.1 M citric acid/0.5 M nitric acid and 0.1 M citric acid/1.0 M nitric acid are similar to their 0.25 M citric acid/x M nitric acid counterparts.

According to Strelow (1984), strontium in hydrochloric acid is more strongly retained by the resin in 0.2 M and 0.5 M hydrochloric acid than the element in this work. The distribution coefficient decreases sharply with an increase in acid concentration. The addition of methanol to strontium in 0.5 M hydrochloric acid increases the distribution coefficient even further, allowing the element to bind to the resin extremely strongly. The distribution coefficient for the element increases with an increase in methanol percentage of the solution (up to 80% methanol).

With Strelow and van der Walt's experiments with the element in tartaric acid/nitric acid mixtures (1982), it can be seen that the element is well retained in x M tartaric acid/0.2 M nitric acid (a similar figure to those obtained in this work), but the distribution coefficient decreases sharply with an increase in nitric acid concentration. The use of citric acid in this work, it would appear, would be more effective with nitric acid for the element should one wish to retain strontium on the resin, particularly in 0.5 M and 1.0 M nitric acid mixtures.

Barium

Barium has a very strong affinity for the resin in citric acid/nitric acid mixtures. The results indicated high distribution coefficients for the element, with a decrease in

distribution coefficient as the concentration of nitric acid increased. The distribution coefficients for barium in 0.1 M citric acid/x M nitric acid decreased more sharply between 0.5 M nitric acid and 1.0 M nitric acid, while the distribution coefficients for the element in 0.25 M citric acid/x M nitric acid decreased more gradually with an increase in nitric acid concentration.

Strelow's results for the element in different concentrations of hydrochloric acid (1984) indicate that barium is very strongly retained by the resin in 0.2 M hydrochloric acid with distribution coefficients decreasing steadily with an increase in acid concentration, where the element is not well retained at concentrations of 4 M hydrochloric acid or higher. With the addition of methanol to the element in 0.5 M hydrochloric acid, however, the already high distribution coefficient increases with an increase in methanol percentage of solution.

Strelow and van der Walt's experiments with barium using tartaric acid/nitric acid mixtures indicate a decrease in distribution coefficient with an increase in nitric acid concentration. Although the element is well retained by the resin in x M tartaric acid/0.2 M nitric acid, the distribution coefficients are considerably lower than those obtained for citric acid/nitric acid in this work. Barium is poorly retained by the resin when in x M tartaric acid/1.0 M nitric acid mixture, in comparison with the results obtained in this work.

3.4.3　THE TRANSITION ELEMENTS

3.4.3.1　Scandium and Yttrium

Both elements are fairly well held to the resin, with distribution coefficients of over 100 in the lower concentrations of nitric acid. Scandium, however, does have a distribution coefficient of 105 for the 0.1 M citric acid/1.0 M nitric acid mixture.

Scandium's distribution coefficients only decrease marginally with an increase in concentration of nitric acid in the 0.1 M citric acid mixtures, whereas the decrease is more marked in the 0.25 M citric acid mixtures. Scandium in the 0.25 M citric acid/0.2 M nitric acid mixture, is better held by the resin than the 0.1 M citric acid/0.2 M nitric acid mixture. The 0.25 M citric acid/0.5 M nitric acid and 0.25 M citric acid/1.0 M nitric acid mixtures yield results that indicate that scandium is better held on the resin when using the 0.1 M citric acid mixtures.

The results for yttrium indicate that the 0.25 M citric acid mixtures allow the yttrium to be more strongly held by the resin, with the exception of the 0.25 M citric acid/1.0 M nitric acid mixture. This result is marginally less than that of its 0.1 M citric acid counterpart.

Once again, the results show that there is a decrease in distribution coefficient as the concentration of the nitric acid increases, no matter which concentration of citric acid is involved with the mixture.

According to Strelow (1984), both scandium and yttrium are very strongly retained by the resin when experiments were performed in dilute hydrochloric acid. As the concentrations increased, though, the distribution coefficients dropped drastically to a point where they are not well retained by the resin in 6 M hydrochloric acid. In the experiments performed with 0.5 M hydrochloric acid and various percentages of methanol the distribution coefficients increased even more than the very high initial figures. This is in sharp contrast to the experiments performed in citric acid/nitric acid mixtures, as in this paper, where the distribution coefficients are at least 50 times lower and over 100 times lower in the case of scandium. The only similarity between these experiments is that the distribution coefficients decrease with an increase in strong acid concentration. Although it would appear that an increase in citric acid concentration in dilute nitric acid has a slight influence in improving the resin retention of scandium and yttrium, this can only be regarded as slight in comparison of the two elements in dilute hydrochloric acid with an increase in methanol concentration.

Strelow and van der Walt's experiments using tartaric acid/nitric acid mixtures on AG 50W-X8 cation exchange resin indicate that, although the distribution coefficients decrease with an increase in nitric acid, the distribution coefficients for scandium are considerably higher than the results obtained in this work. There is a sharp contrast in distribution coefficient between x M tartaric acid/0.2 M nitric acid and x M tartaric acid/0.5 M nitric acid mixtures. The x M tartaric acid/0.2 M nitric acid indicate a distribution coefficient more than ten times greater than that obtained in this work with x M citric acid/0.2 M nitric acid, although similar results are obtained when in
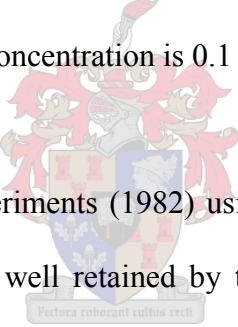
the x M tartaric acid/1.0 M nitric acid and x M citric acid/1.0 M nitric acid region. This would indicate that tartaric acid has a greater effect on the resin's retention of the element at lower nitric acid concentrations than citric acid. The same cannot be said for yttrium, however. Although Strelow and van der Walt only performed experiments using 0.1 M tartaric acid/x M nitric acid mixtures, it can be seen that yttrium is far better retained by the respective resin using tartaric acid than the element in citric acid media. There is a vast difference in distribution coefficient when comparing the element in the two mixtures, particularly 0.1 M tartaric acid/0.2 M nitric acid and 0.1 M tartaric acid/0.5 M nitric acid with their citric acid counterparts. The difference between the distribution coefficient of 0.1 M tartaric acid/1.0 M nitric acid and its citric acid counterpart is not as great.

3.4.3.2   Titanium(IV) and Zirconium(IV)

<u>Titanium(IV)</u>

Titanium could only be dissolved with hydrogen peroxide, so the results must indicate that titanium is in the +4 state. The results indicate that, although the results are similar for the element in the 0.5 M and 1.0 M nitric acid mixtures, the big difference between the two citric acid mixtures is using 0.2 M nitric acid. Titanium is held very strongly by the resin when in the 0.1 M citric acid/0.2 M nitric acid mixture while, although the element is also held strongly to the resin when in the 0.25 M citric acid/0.2 M nitric acid mixture, it is held considerably less strongly than in the 0.1 M citric acid mixture. Once the nitric acid concentration reaches 1.0 M the titanium is weakly held by the cation exchange resin.

According to Strelow (1984), titanium(IV) was retained by the resin better with any increase in methanol concentration in a 0.5 M hydrochloric acid mixture. The distribution coefficient in a 90% methanol mixture was approximately 25 times that of the 0.5 M hydrochloric acid solution. If one has to compare these results with the various concentrations of hydrochloric acid used, it is clear that methanol plays a defining role in the retention of titanium on the resin. As with the results obtained for titanium in this project with citric acid/nitric acid media, the greater the concentration of the strong acid (in this case, hydrochloric acid), the smaller the tendency for the titanium to be retained by the resin. Should one compare the results between 0.2 M hydrochloric acid and x M citric acid/0.2 M nitric acid, it is clear that the citric acid/nitric acid media allows the titanium to be held more strongly on to the resin, particularly when the citric acid concentration is 0.1 M.

Strelow and van der Walt's experiments (1982) using tartaric acid/nitric acid media show that the element is not as well retained by the resin as the element in citric acid/nitric acid media. The distribution coefficients obtained in this work are more than double that of those obtained in tartaric acid/nitric acid media, with the exception of the 0.1 M tartaric acid/0.2 M nitric acid results, although the difference is still vast.

Zirconium(IV)

The results concerning zirconium indicate that the element is not strongly held by the resin at all and the results are similar with a specific concentration of citric acid, no matter what the nitric acid concentration may be. It should be noted that the distribution coefficients of zirconium dropped markedly when mixed with 0.25 M citric acid/x M nitric acid mixtures.

Strelow's results for zirconium indicate that it is extremely strongly held by the resin throughout the percentage range of methanol added although, when zirconium was experimented without methanol and increasing hydrochloric acid concentrations, it was clear that the distribution coefficients decrease with an increase in acid concentration. This is not the case when experiments are performed in citric acid/nitric acid media, but the results differ when different concentrations of citric acid are used. There is a vast difference in distribution coefficient between the strong acids used: zirconium in hydrochloric acid has a distribution coefficient at least 1900 times higher than in nitric acid when in the presence of citric acid.

According to Strelow and van der Walt's results obtained using tartaric acid/nitric acid media (1982), zirconium is not retained by the resin in this environment and, while the results obtained from this work indicate that the element is not very well retained by the resin, the distribution coefficients are still considerably higher in citric acid/nitric acid media.

3.4.3.3 Vanadium(IV), Vanadium(V), Niobium(V) and Tantalum(V)

Vanadium(IV) and (V)

When working with vanadium(V) and mixing it with the various citric acid and nitric acid mixtures, an interesting thing occurred. Precipitation occurred and it was assumed that the vanadium had precipitated. The resin had already been added to the bottle for shaking, so it was decided to continue with the process for the overnight period and check the results the following morning, to determine whether this specific

experiment would work. Upon returning the following morning, the bottles were removed from the shaker and it was observed that the vanadium had gone back into solution, but that the solution colour had turned green. It appeared that the vanadium had been reduced to the +4 state and gone back into solution. The experiment was carried out, nevertheless, to determine whether there was any similarity between this experiment and the vanadium(IV) experiment.

The differences in the results of the two elements are as follows: the marked difference between the two is the results for the 0.2 M nitric acid mixtures. The vanadium(V) experiment has a value almost double that of the original vanadium(IV) experiment, whether mixing it with 0.1 M citric acid or 0.25 M citric acid. The vanadium(V) has slightly higher distribution coefficients for 0.1 M citric acid/0.5 M nitric acid and 0.25 M citric acid/0.5 M nitric acid mixtures than the vanadium(IV) experiment and similar results for the 0.1 M citric acid/1.0 M nitric acid mixture, but it has a distribution coefficient almost double that of the vanadium(IV) experiment for the 0.25 M citric acid/1.0 M nitric acid mixture experiment. It is possible that there was not a total reduction of the vanadium(V) to vanadium(IV) when equilibrium was obtained by means of shaking.

The vanadium(V) is fairly well retained by the resin when in 0.2 M nitric acid/x M citric acid media, but is not well retained in any of the other concentrations of acid tested. The vanadium(IV) is less well retained by the resin in 0.2 M nitric acid/x M citric acid media, with a distribution coefficient of just over 100, while the remaining concentrations of acid do not allow for the vanadium to be well retained by the cation exchange resin.

Strelow (1984) did not perform any experiments using niobium or tantalum (see later), but did perform experiments on vanadium(IV) and vanadium(V). The vanadium (IV) results indicate that the resin better retains the vanadium when the percentage of methanol in solution is increased. When the percentage of methanol in the solution is 60% or higher, the distribution coefficient is greater than that obtained for 0.2 M nitric acid/x M citric acid. When performing the resin in only hydrochloric acid, Strelow found that the lowest concentration of hydrochloric acid tested (0.2 M) had the greatest distribution coefficient, with the distribution coefficient decreasing with an increase in acid concentration. The distribution coefficient was less than 5 for concentrations of 2.0 M hydrochloric acid or higher. Strelow's distribution coefficient calculations for vanadium(V) were all less than 1 in all concentrations of hydrochloric acid, including 0.5 M hydrochloric acid with x % methanol, with the exception of 0.5 M hydrochloric acid containing 80 % and 90 % methanol, respectively. These results yield a distribution coefficient of just over 1, which indicates that vanadium(V) is not retained by the resin.

Strelow and van der Walt's results using AG 50W-X8 cation exchange resin and tartaric/nitric acid mixtures (1982) indicate that vanadium(IV) is better retained by the resin in x M tartaric acid/0.2 M nitric acid than the citric acid/0.2 M nitric acid counterpart. The distribution coefficients for the element in 0.5 M and 1.0 M nitric acid using tartaric acid and citric acid are similar. There is a stark contrast in results between the tartaric acid/nitric acid and citric acid/nitric acid mixtures for vanadium(V), however. The element was far better retained by the resin in x M citric acid/0.2 M nitric acid in this work than the results obtained by Strelow and van der

Walt for the element in x M tartaric acid/0.2 M nitric acid. The results obtained from this work for the element in x M citric acid/0.5 M nitric acid and x M citric acid/1.0 M nitric acid indicate that vanadium(V) is still more strongly retained by the AG MP-50 cation exchange resin than its tartaric acid counterparts on AG 50W-X8 cation exchange resin, although the differences are smaller.

Niobium(V) and Tantalum(V)

The results from the niobium experiment indicate that the niobium passed through the AGMP-50 column with very small amounts of the element being retained by the resin. It appeared that the different concentrations of citric and nitric acid media had no affect on the retention of the element by the resin. The same can be said for tantalum(V), which also yielded distribution coefficients of less than 1.

Niobium(V) precipitated when Strelow and van der Walt performed their experiments using tartaric acid/nitric acid media, with the exception of 0.25 M tartaric acid/0.2 M nitric acid, which yielded a distribution coefficient of less than 0.5, whereas the niobium experiments in this work remained in solution, even though the element was not retained by the resin at all.
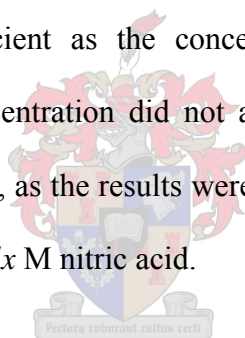
Strelow and van der Walt's experiments with tantalum(V) yielded precipitation when using 0.1 M tartaric acid/x M nitric acid. The resin failed to retain the element in 0.25 M tartaric acid/ x M nitric acid media – similar results to those obtained in citric acid/nitric acid media on AG MP-50 cation exchange resin in this work.

3.4.3.4 Chromium(III), Molybdenum(VI) and Tungsten(VI)

Chromium(III)

Chromium was retained reasonably by the resin, although there was a bit of "tailing". Not all of the chromium was removed from the resin when using 50 ml 7 M hydrochloric acid. The remainder of the element was successfully removed using 4 M hydrochloric acid.

Chromium was better retained by the resin than molybdenum (see below), with a decrease in distribution coefficient as the concentration of the nitric acid was increased. The citric acid concentration did not appear to have any affect on the chromium's affinity for the resin, as the results were similar for 0.1 M citric acid/x M nitric acid and 0.25 M citric acid/x M nitric acid.

Strelow (1984) did not perform experiments on AG MP-50 cation exchange resin in hydrochloric acid and hydrochloric acid-methanol media with chromium.

Strelow and van der Walt's experiments using chromium in tartaric acid/nitric acid mixtures on AG50 W-X8 cation exchange resin show similar results to those obtained using citric acid/nitric acid media in this work. The distribution coefficient determined in x M tartaric acid/0.5 M nitric acid media, however, indicates that the resin slightly less retains the element than the element in its citric acid counterpart using AG MP-50 cation exchange resin.

<u>Molybdenum(VI)</u>

Molybdenum(VI) was not held on to the resin at all, no matter what the concentrations of the citric acid and nitric acids were.

Strelow's (1984) results for molybdenum(VI) in 0.5 M hydrochloric acid and various percentages of methanol are similar to those obtained in this work: his distribution coefficients for this element were also less than 1. This was also the case for the experiments he performed with various concentrations of hydrochloric acid. As a result, one can assume that molybdenum(VI) is not retained by AG MP-50 cation exchange resin, although further tests in other media would be required.

Strelow and van der Walt's results for molybdenum(VI) were similar to those obtained in this work: the resin did not retain the element at all, whether in tartaric acid/nitric acid media or citric acid/nitric acid media.
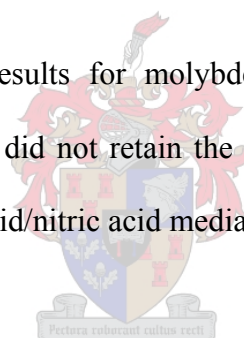
<u>Tungsten(VI)</u>

Tungsten precipitated as soon as it came into contact with nitric acid, whether it was in the presence of citric acid or not and, as a result, the experiment on this element could not be conducted.

Strelow also obtained precipitation of tungsten in his experiments with AG MP-50 cation exchange resin using various concentrations of hydrochloric acid. The results obtained from the remainder of the experiments performed indicate that tungsten is not retained by the resin in hydrochloric acid medium. The experiments performed with the element in various percentages of methanol and 0.5 M hydrochloric acid also

show that tungsten is not retained by the resin, with distribution coefficients of less than 1, except in the case of 0.5 M hydrochloric acid/ 80% methanol, where the distribution coefficient was found to be 1.1.

Strelow and van der Walt were successful in maintaining the tungsten(VI) in solution, but the resin did not retain the element, with distribution coefficients of less than 0.5 throughout.

3.4.3.5   Manganese(II)

Manganese was quite strongly attracted to the resin in both concentrations of citric acid, particularly in the lower concentration of nitric acid (i.e. 0.2 M nitric acid). The 0.25 M citric acid/x M nitric acid mixtures allowed the resin to retain the manganese more strongly than their 0.1 M citric acid/x M nitric acid counterparts.   The distribution coefficients of manganese decrease with an increase in nitric acid for both concentrations of citric acid used.

Strelow's experiments with manganese in hydrochloric acid on AG MP-50 cation exchange resin indicate that the element is strongly retained by the resin in 0.2 M hydrochloric acid. The distribution coefficient decreases drastically when the element is in 0.5 M hydrochloric acid media: manganese is almost 10 times more strongly retained by the resin in 0.2 M hydrochloric acid.   The distribution coefficient continues to decrease with an increase in acid concentration and the element is poorly retained by the resin in hydrochloric acid concentrations over 1.0 M. When adding methanol to 0.5 M hydrochloric acid, however, the distribution coefficient is found to

increase with an increase in percentage methanol in the solution. Manganese is very strongly retained by the resin in solutions containing 60 % methanol or more in 0.5 M hydrochloric acid. The 0.2 M nitric acid/x M citric acid is the only result that can come close to the results Strelow obtained with the addition of methanol, in terms of retention of manganese by the resin.

Strelow and van der Walt's results for manganese were virtually identical using 0.1 M tartaric acid/x M nitric acid, whereas the same could not be said for the results obtained in citric acid/nitric acid media in this work. The results indicate that manganese in 0.1 M citric acid/0.2 M nitric acid is not as well retained by the AG MP-50 cation exchange resin as the element in 0.1 M tartaric acid/nitric acid media using AG 50W-X8 cation exchange resin. The remainder of the results, however, indicate that the element is better retained in citric acid/nitric acid media, with the results in x M citric acid/0.5 M nitric acid and x M citric acid/1.0 M nitric acid almost double that of its tartaric acid counterparts.

3.4.3.6   Iron(III)

Iron(III) was very strongly retained by the resin, particularly at the lower concentration of nitric acid used, that is, 0.2 M nitric acid. One again, the greatest difference between the two concentrations of citric acid used is when they are mixed with 0.2 M nitric acid: the iron(III) in 0.1 M citric acid/0.2 M nitric acid is considerably more strongly held to the resin than the iron(III) in 0.25 M citric acid/0.2 M nitric acid, although it must be said that the latter is still strongly held by the resin. The results for the other two concentrations of 0.1 M citric acid/x M nitric acid

mixtures are similar to those of their counterparts and it should be noted that the weakest that the iron is held in any of these mixtures is still stronger than the strongest of the alkali metals, barring caesium, and scandium.

As with many of the trends for the other elements, the distribution coefficient for iron decreases with an increase in concentration of nitric acid.

Strelow (1984) performed experiments on AG MP-50 resin using iron(III) in various concentrations of hydrochloric acid and methanol and his results indicate that iron(III) is extremely strongly retained by the resin in 0.2 M hydrochloric acid, but less so as the concentration of the acid increases. The distribution coefficient decreases sharply between 0.2 M and 0.5 M hydrochloric and again between 0.5 M and 1.0 M hydrochloric acid, where the element is no longer strongly retained. With the addition of methanol to 0.5 M hydrochloric acid, however, the distribution coefficient increases again, peaking at 60 % methanol and decreasing again with any more methanol added. The retention of iron(III) in this work (0.1 M citric acid/0.2 M nitric acid and 0.25 M citric acid/0.2 M nitric acid) can be compared to the addition of 40 % methanol, in the case of 0.1 M citric acid, and 15 to 20 % methanol, in the case of 0.25 M citric acid.

Strelow and van der Walt's results (1982) for iron(III) were similar in 0.1 M tartaric acid/x M nitric acid and 0.25 M tartaric acid/x M nitric acid media. The distribution coefficient for the element in x M tartaric acid/0.2 M nitric acid was found to be greater than those obtained in x M citric acid/0.2 M nitric acid in this work. The citric acid in 0.5 M and 1.0 M nitric acid, however, proved to be more effective than tartaric

acid in the iron(III)'s binding capacity, as the distribution coefficient proved be greater than their tartaric acid counterparts in each case.

3.4.3.7 Cobalt

Cobalt is fairly well retained by the resin in the lower nitric acid concentration, irrespective of the citric acid concentration. As with most of the other elements determined in this work, the distribution coefficients decreased with an increase in nitric acid concentration. The element was found to be slightly better retained by the resin in 0.2 M nitric acid when in 0.1 M citric acid mixture than its 0.25 M counterpart, while the element had a slightly greater affinity for the resin in 0.5 M nitric acid when in 0.25 M citric acid mixture, instead of 0.1 M citric acid.

Cobalt is strongly bound to the AG MP-50 cation exchange resin when in 0.2 M hydrochloric acid (Strelow, 1984), but the distribution coefficients for the element decrease drastically with an increase in hydrochloric acid concentration, to a degree where cobalt is not retained by the resin at all. The addition of methanol to 0.5 M hydrochloric acid (Strelow, 1984) increases the element's affinity for the resin up to the addition of 80 % methanol in the mixture. Whereas the addition of methanol has increased the distribution coefficient drastically for many elements, it is not the case for cobalt, although it does still become strongly bound to the resin.

Cobalt in 0.1 M tartaric acid mixed with various concentrations of nitric acid (Strelow and van der Walt, 1982) indicates that the distribution coefficients decrease with an increase in nitric acid concentration. The results obtained for the element in 0.2 M,

0.5 M and 1.0 M nitric acid (containing 0.1 M or 0.25 M tartaric acid) are similar to the results obtained using citric acid in this work. The element in x M tartaric acid/0.2 M nitric acid is slightly more strongly retained by the resin than its citric acid counterpart, while cobalt in x M citric acid/0.5 M nitric acid was found to bind the element slightly more strongly to the resin than its tartaric acid counterpart.

3.4.3.8   Nickel(II)

As can be seen from the results, nickel produces similar results whether mixed with 0.1 M citric acid or 0.25 M citric acid. The differences of distribution coefficient with an increase in nitric acid concentration is marked, with the 0.5 M nitric acid result being less than half of that of the 0.2 M nitric acid and the same again when comparing 0.5 M nitric acid and 1.0 M nitric acid.

Strelow's results for nickel in hydrochloric acid media on AG MP-50 resin indicate that the element is well retained by the resin when in 0.2 M hydrochloric acid. It is still fairly well retained when in 0.5 M hydrochloric acid, albeit with a distribution six times lower than that of nickel in 0.2 M hydrochloric acid, and decreases to low distribution coefficients as the concentration of hydrochloric acid increases. With the addition of methanol to the 0.5 M hydrochloric acid, however, increases the affinity of the resin for nickel and, as a result, the distribution coefficients increase, peaking at the addition of 80 % methanol. The lowest distribution coefficient in this work for nickel is still higher than that of nickel in 1.0 M hydrochloric acid and higher.

The results obtained from this work in citric acid/nitric acid media and those obtained by Strelow and van der Walt, using tartaric acid/nitric acid media, were very similar, although the distribution coefficients from nickel in x M tartaric acid/0.2 M nitric acid were slightly higher than those obtained from its citric acid counterparts.

3.4.3.9 Copper(II) and silver(I)

Copper(II)

The results of copper on the AG MP-50 cation exchange resin indicate that there is not much influence from the citric acid in the mixtures, as the results are similar for both 0.1 M and 0.25 M citric acid mixtures. It would appear that it does have a slight influence on the 0.1 M citric acid/0.2 M nitric acid result, as this distribution coefficient is slightly higher than that of its 0.25 M citric acid counterpart. The difference in distribution coefficient between copper in x M citric acid/0.2 M nitric acid and copper in x M citric acid/0.5 M nitric acid is vast: the latter is about half that of the former. The decrease in the resin's affinity for the element is less marked when increasing the concentration of nitric acid from 0.5 M to 1.0 M. As mentioned for many of the elements, the distribution coefficient for copper decreases with an increase in nitric acid concentration.

According to Strelow (1984), copper is strongly retained by the resin in 0.2 M hydrochloric acid, but is far less so when increasing the acid concentration. The resin's affinity for copper is negligible when the copper is in 2.0 M hydrochloric acid or greater. With the addition of methanol to 0.5 M hydrochloric acid, however, the distribution coefficient increases, but not as much as seen in other similar

experiments, performed by Strelow, using other elements. The distribution coefficent reaches a maximum of 265 with the addition of 60 % methanol, but decreases with any further addition of methanol to the hydrochloric acid.

Strelow and van der Walt's experiments using tartaric acid/nitric acid media indicate that copper in x M tartaric acid/0.2 M nitric acid is considerably more strongly retained by the resin than copper in x M citric acid/0.2 M nitric acid. While the distribution coefficients are similar for copper(II) in x M citric acid/0.5 M nitric acid and x M tartaric acid/0.5 M nitric acid, the distribution coefficients for the element in x M citric acid/1.0 M nitric acid is slightly higher than that of the element in x M tartaric acid/1.0 M nitric acid.

Silver(I)

Silver does not form stable complexes with complexing agents such as citrates and tartrates (Korkisch, 1989), so it was expected that the element would be strongly held by the resin.

Silver was found to be more strongly held by the resin than copper throughout. As with the experiments with copper, however, the distribution coefficients for silver at x M citric acid/0.2 M nitric acid was more than double that for the x M citric acid/0.5 M nitric acid counterpart. The distribution coefficients decrease with an increase in nitric acid concentration. The separation factor between copper and silver is a maximum at 0.25 M citric acid/0.5 M nitric acid (3.225), but this is not enough to ensure an effective separation of the two elements.

Strelow's results for silver in various concentrations of hydrochloric acid (1984) indicate a decrease in distribution coefficient with an increase in acid concentration. The element is well retained by the resin in 0.2 M hydrochloric acid (K_d = 581), but it is not well retained by the resin at concentrations of 2.0 M hydrochloric acid or higher. Strelow did not perform any experiments with silver and 0.5 M hydrochloric acid with various percentages of methanol on AG MP-50 cation exchange resin.

When comparing Strelow and van der Walt's results for silver in 0.1 M tartaric acid/x M nitric acid with those done in 0.1 M citric acid/x M nitric acid media in this work, it appeared that the tartaric acid played a role in the distribution coefficient results for the element, as they were about four times lower than the results obtained using citric acid. This implied that the resin better retained silver in citric acid/nitric acid media than its tartaric acid/nitric acid counterparts. Similar results were obtained when using 0.25 M tartaric acid/x M nitric acid with this element.
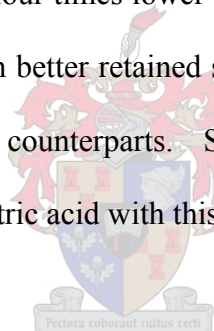
3.4.3.10   Zinc and Cadmium

Zinc

It would appear that there is not a great difference in the distribution coefficients for zinc in the two citric acid concentrations. The only slight difference is with the experiments involving 0.2 M nitric acid, where in the 0.1 M citric acid mixture it is held slightly more strongly on to the resin than for the 0.25 M citric acid mixture. Once again, the distribution coefficients decrease with an increase in nitric acid concentration and the distribution coefficient decreases by more than half from zinc in x M citric acid/0.2 M nitric acid and x M citric acid/0.5 M nitric acid.

Strelow's experiments using zinc and various concentrations of hydrochloric acid on AG MP-50 cation exchange resin indicate that the element is very well retained by the resin in 0.2 M hydrochloric acid, but the distribution coefficient decreases dramatically when the concentration of hydrochloric acid is increased. When adding various percentages of methanol to 0.5 M hydrochloric acid, the resin's affinity for the element increases slightly, peaking with the addition of 20 % methanol. Any further addition of methanol to the hydrochloric acid decreases the distribution coefficient.

The distribution coefficients obtained in this work from citric acid/nitric acid media differed slightly from the results obtained by Strelow and van der Walt (1982) in tartaric acid/ nitric acid mixture. The distribution coefficients of the element in x M tartaric acid/0.2 M nitric acid were higher than those obtained in this work (the citric acid/nitric acid counterparts), but the results obtained in this work for zinc in the other concentrations of citric acid nitric acid media indicated slightly higher distribution coefficients than its tartaric acid/nitric acid counterparts.

Cadmium

As with zinc, the cadmium results are similar for both the 0.1 M and 0.25 M citric acid mixtures. The difference between these results, though, is in the 0.5 M nitric acid mixtures, where the 0.1 M citric acid mixture ensures that the cadmium is held slightly stronger on to the resin than in the case of its 0.25 M counterpart. The distribution coefficients, as before, decrease with an increase in nitric acid concentration. Cadmium is well retained by the resin in the lowest nitric acid concentration, but much less so when in 0.5 M nitric acid.

Strelow's results using cadmium indicates that the element is better retained by the resin when in 0.2 M or 0.5 M nitric acid and x M citric acid, than in hydrochloric acid or hydrochloric acid/methanol mixture. There is, once again, a marked difference in distribution coefficient between the element in 0.2 M hydrochloric acid and 0.5 M hydrochloric acid and the distribution coefficient decreases with an increase in acid concentration. The addition of methanol does not increase the resin's affinity for cadmium. In fact, the distribution coefficient decreases slightly with further addition of methanol to cadmium in 0.5 M hydrochloric acid.

Cadmium is not as well retained by the AG 50W-X8 resin in tartaric acid/nitric acid mixtures (Strelow and van der Walt, 1982) as the element is on AG MP-50 cation exchange resin in citric acid/nitric acid mixtures in this work. The distribution coefficients obtained by Strelow and van der Walt decrease more sharply with an increase in nitric acid concentration than the distribution coefficients obtained in this work, where the values obtained are less than half that obtained in citric acid/nitric acid media when in x M tartaric acid/0.5 M nitric acid and x M tartaric acid/1.0 M nitric acid mixtures.

3.4.4   THE GROUP III ELEMENTS

The elements used in these experiments were aluminium, gallium and indium.

<u>Aluminium</u>

The results for aluminium show that the concentration of citric acid does play a slight role, where the element being retained on the resin is concerned. The results involving the higher concentration of citric acid provide distribution coefficients that are slightly higher than the lower concentration of citric acid. Once again, the distribution coefficients decrease with an increase in nitric acid. It is interesting to note that, in the samples containing 0.2 M nitric acid, the aluminium is substantially better retained on the resin than in the higher concentrations of nitric acid. The difference in distribution coefficient between the 0.5 M nitric acid and 1.0 M nitric acid samples are less marked, however.

Strelow's results for aluminium in hydrochloric acid using the same macroporous resin as in this study (1984) also show a decrease in distribution coefficient with an increase in acid concentration. The decrease in the resin's affinity for aluminium is vast between 0.2 M and 0.5 M hydrochloric acid and again between 0.5 M and 1.0 M hydrochloric acid. The element is extremely strongly retained by the resin when in 0.2 M hydrochloric acid and is still very strongly retained when in 0.5 M hydrochloric acid, but the strength in retention is fairly weak to very poorly retained as the acid concentration increases. The addition of methanol increases the distribution coefficient once again, to a degree where the distribution coefficient is over 10 000 with the addition of 80 % methanol or more. Aluminium is not as well retained in low concentrations of nitric acid in this study.

It would appear that tartaric acid does have some effect in the binding of aluminium to the resin when in the presence of low nitric acid concentrations (Strelow and van der

Walt, 1982). The element is extremely strongly retained by the resin in 0.2 M nitric acid, with a distribution coefficient almost 10 times that of its citric acid counterpart in this work. The decrease in distribution coefficient is marked between 0.2 M nitric acid and 0.5 M nitric acid when mixed with tartaric acid, but less so between x M tartaric acid/0.5 M nitric acid and x M tartaric acid/1.0 M nitric acid. The element in tartaric acid/nitric acid mixtures is more strongly retained by the AG 50W-X8 cation exchange resin than the element in similar concentrations of citric acid/nitric acid using AG MP-50 cation exchange resin in each case.

Gallium

It would appear that citric acid does play a role in the case of gallium and the AG MP-50 cation exchange resin in low concentrations of nitric acid. The results between the two concentrations of citric acid and various concentrations of nitric acid are similar, with the exception of 0.2 M nitric acid where the 0.25 M citric acid/0.2 M nitric acid mixture has a significantly higher distribution coefficient than its 0.1 M citric acid counterpart, which indicates that the gallium is held more strongly on to the resin. The distribution coefficients decrease with an increase in nitric acid concentration.

Strelow's experiments with gallium show that, although extremely strongly retained by the resin in 0.2 M hydrochloric acid with a distribution coefficient greater than 10 000, the resin's affinity for the element decreases vastly with an increase in acid concentration and continues to do so until the element is poorly retained by the resin when in 2.0 M hydrochloric acid or higher. The addition of methanol increases the element's capability of binding to the resin, but peaking at the addition of 60 % methanol. The gallium experiments in this study show that the element does not

decrease its binding ability with the resin so drastically with an increase in nitric acid concentration.

Gallium is extremely strongly retained by AG 50W-X8 cation exchange resin in tartaric acid/nitric acid mixtures, particularly at low concentrations of nitric acid (Strelow and van der Walt, 1982). The distribution coefficients for the elements in xM tartaric acid/0.2M nitric acid and x M tartaric acid/0.5 M nitric acid are over 20 times higher than the distribution coefficients obtained in this work using citric acid/nitric acid mixtures on AG MP-50 cation exchange resin. The distribution coefficients decrease with an increase in nitric acid concentration.

Indium

The concentration of citric acid plays a more significant role in the case of indium. Throughout the concentrations of nitric acid, the results involving the 0.25 M citric acid mixtures have a markedly higher distribution coefficient than its 0.1 M citric acid mixture counterparts. For the lowest concentration of nitric acid used in these experiments, namely, 0.2 M nitric acid, the difference in distribution coefficient between the two citric acid mixtures, however, is slight. Distribution coefficients for this element decrease with an increase in nitric acid concentration.

The experiments with indium using various concentrations of hydrochloric acid on AG MP-50 cation exchange resin (Strelow, 1984) show that the element was fairly well retained by the resin in 0.2 M hydrochloric acid, with a distribution coefficient similar to those obtained in x M citric acid/0.2 M nitric acid in this work. They decrease dramatically with an increase in hydrochloric acid concentration. The

addition of methanol to 0.5 M hydrochloric acid does not manage to increase the resin's affinity for indium. The results obtained from this work show that citric acid and nitric acid increase the element's binding ability to the resin.

Indium is extremely strongly bound to AG 50W-X8 cation exchange resin in tartaric acid mixtures containing low concentrations of nitric acid (Strelow and van der Walt, 1982). Distribution coefficients for the element in x M tartaric acid/0.2 M nitric acid were found to be approximately 50 times higher than those obtained in citric acid/nitric acid media in this work. Indium's affinity for the resin decreases with an increase in nitric acid concentration and its affinity decreases sharply between 0.2 M and 0.5 M nitric acid. It appears that the difference in tartaric acid concentration does not affect the distribution coefficients for indium.

3.4.5   THE GROUP IV ELEMENTS
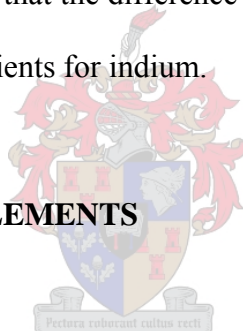
The elements analysed with citric acid/nitric acid media used on AG MP-50 cation exchange resin were germanium(IV), tin(IV) and lead(II).

Germanium(IV)

It was discovered that, when using citric acid and nitric acid media, the resin did not retain the germanium.

Strelow (1984) did not perform experiments on AG MP-50 cation exchange resin with germanium.

No experiments were performed using tartaric acid/nitric acid media using germanium (Strelow and van der Walt, 1982).

Tin(IV)

The tin(IV) experiments with the citric acid/nitric acid media showed that tin was not well held by the resin and, instead, flowed through the column. The only exception to this statement was the tin in 0.1 M citric acid/0.2 M nitric acid media. This had a distribution coefficient of 26, while all the other results indicated a value of less than 10. The tin in 0.1 M citric acid/0.5 M nitric acid media had a marginally higher distribution coefficient than for the rest of the results, which were almost identical to each other. It appears that the citric acid plays a role in the more dilute form, that is, 0.1 M citric acid and the distribution coefficients decrease with an increase in nitric acid concentration. The concentration of nitric acid in the 0.25 M citric acid media plays no role in the distribution coefficients obtained from these experiments.
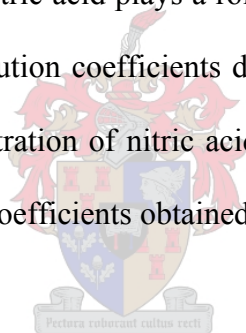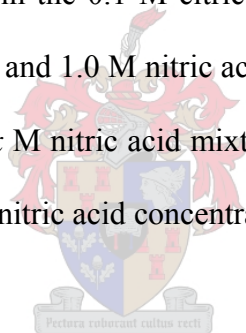
Strelow's results for tin(IV) in hydrochloric acid indicated that the element was not well retained by the resin at all and the tin(IV) hydrolysed in 0.2 M hydrochloric acid. The addition of methanol to 0.5 M hydrochloric acid did not help to increase the distribution coefficient: it decreased slightly whenever a greater percentage methanol was present.

Tin(IV) is not well retained by AG 50W-X8 in tartaric acid/nitric acid mixtures (Strelow and van der Walt, 1982). The results obtained from this work indicated that citric acid/nitric acid media was slightly more effective in the retention of tin(IV) on AG MP-50 cation exchange resin, although this is more likely due to the fact that the

resin used in this work was a macroporous resin. Other than the distribution coefficient of the element in 0.1 M citric acid/0.2 M nitric acid, tin(IV) is not retained by either resin in either of the mixtures.

Lead(II)

The lead(II) was found to be much better retained on the resin that in the case of tin(IV) and, should one wish to separate the two elements, using this type of mixture would prove to be very effective. The distribution coefficients for lead(II) were found to be at least 20 times higher than that of tin(IV) for both concentrations of citric acid used in the citric acid/nitric acid media. Lead(II) is more strongly retained by the resin in 0.2 M nitric acid when in the 0.1 M citric acid mixture than in the 0.25 M citric acid mixture, but for 0.5 M and 1.0 M nitric acid the distribution coefficients are higher in the 0.25 M citric acid/x M nitric acid mixture. The distribution coefficients still decrease with an increase in nitric acid concentration.

Lead(II) was found to be extremely strongly retained by the resin in lower concentrations of hydrochloric acid (Strelow, 1984), but the element was not well retained in concentrations of 1.0 M hydrochloric acid or greater. The distribution coefficient for lead(II) decreased drastically between 0.2 M and 1.0 M hydrochloric acid. The addition of methanol to 0.5 M hydrochloric acid did increase the resin's affinity for the element, but once the solution contained more than 40 % methanol the distribution coefficient would decrease again. The results obtained from this work indicated that the distribution coefficient for lead(II) did not decrease as sharply as for the results Strelow obtained with hydrochloric acid.

Lead(II) is extremely well retained by the AG 50W-X8 cation exchange resin in tartaric acid/nitric acid mixtures at low concentrations of nitric acid (Strelow and van der Walt, 1982). The distribution coefficients indicate that the element is better retained by the resin in 0.1 M tartaric acid/x M nitric acid mixtures than its 0.25 M tartaric acid/x M nitric acid counterpart. The distribution coefficients decrease dramatically between x M tartaric acid/0.2 M nitric acid and x M tartaric acid/0.5 M nitric acid and decreasing more gradually between x M tartaric acid/0.5 M nitric acid and x M tartaric acid/1.0 M nitric acid. While the distribution coefficients for this element in x M tartaric acid/0.2 M nitric acid are considerably higher than those obtained for lead(II) in x M citric acid/0.2 M nitric acid on AG MP-50 cation exchange resin in this work, lead(II) in x M citric acid/0.5 M nitric acid and x M citric acid/1.0 M nitric acid is better retained by the resin than its tartaric acid counterpart.

3.4.6   THE GROUP V ELEMENTS

The elements tested under these conditions were arsenic(V), antimony(V) and bismuth(III).

Arsenic(V)

The resin, when using citric acid and nitric acid media conditions, did not retain arsenic. This result is interesting in that the elements involved in the gallium-67 production at iThemba LABS, namely germanium, arsenic and gallium, only gallium is retained by the resin to a fair degree, which would imply that, theoretically, one could perform a separation in these conditions. The only condition restricting one from using media of this kind is the fact that it will be almost impossible to dissolve

the germanium target using nitric and citric acid. Another problem would be that iron(III) is a possible contaminant and that is retained by the resin far more strongly than gallium, which is the product desired.

Arsenic(V), when experimented with in hydrochloric acid on AG MP-50 resin (Strelow, 1984), was found to have distribution coefficients less than 1, indicating that the resin did not retain the element at all. The element was not tested with hydrochloric acid containing various percentages of methanol.

Strelow and van der Walt (1982) did not perform experiments with tartaric acid/nitric acid mixtures using arsenic(V), but did perform experiments using arsenic(III). The results obtained were similar to those obtained in this work: the resin did not retain the element at all.

Antimony(V)

Antimony showed that it was not very well retained by the resin and the distribution coefficients were very similar throughout with the exception of the 0.25 M citric acid/1.0 M nitric acid media, whose results show a lower distribution coefficient. It would appear that the nitric acid concentration did not play much of a role in these experiments.

Strelow used antimony(III) in various concentrations of hydrochloric acid on AG MP-50 resin and, barring antimony in 1.0 M hydrochloric acid where there may have been hydrolysis, the resin did not retain the element at all. The antimony precipitated in 0.2

M and 0.5 M hydrochloric acid. No tests were performed using various percentages of methanol.

Strelow and van der Walt (1982) also performed experiments using antimony(III) in tartaric acid/nitric acid mixtures, but the element had virtually no affinity for the resin (AG 50W-X8 cation exchange resin), with distribution coefficients of less than 1.

Bismuth(III)

Bismuth(III) was well retained by the resin and, from the results, would be able to be separated from antimony(V) effectively in this media, particularly when using 0.1 M citric acid/0.2 M nitric acid mixtures. The results show that the citric acid concentration does play a role, with the 0.1 M citric acid allowing bismuth to be better retained by the resin. Bismuth in 0.1 M citric acid/0.2 M nitric acid media is more effectively held by the resin than its 0.25 M citric acid counterpart, with a distribution coefficient almost double than that of bismuth in 0.25 M citric acid/0.2 M nitric acid media. In the 0.5 M and 1.0 M nitric acid mixtures the 0.1 M citric acid is less effective but, nevertheless, the difference is still vast, in the case of 0.5 M nitric acid, and only marginal in the case of 1.0 M nitric acid. The distribution coefficient for each concentration of citric acid decreases with an increase of nitric acid concentration in the mixture.

Strelow's experiments involving bismuth(III) show that the element hydrolysed in 0.2 M hydrochloric acid and was not retained by the resin in the remainder of the concentrations of hydrochloric acid used (7.4 decreasing to less than 1). The addition of methanol to 0.5 M hydrochloric acid did not increase the distribution coefficient: it

decreased with an increase in methanol percentage. Bismuth(III) is far better retained by the resin in this work, particularly in 0.1 M citric acid media containing the various concentrations of nitric acid.

Bismuth(III) has a strong affinity for AG 50W-X8 cation exchange resin in tartaric acid/nitric acid mixtures, but only at lower nitric acid concentrations (Strelow and van der Walt, 1982). The distribution coefficients are higher in 0.1 M tartaric acid/x M nitric acid than in 0.25 M tartaric acid/x M nitric acid. When comparing the results with those obtained in this work using AG MP-50 cation exchange resin and citric acid/nitric acid mixtures, it was noted that bismuth(III) in x M tartaric acid/0.2 M nitric acid and x M tartaric acid/0.5 M nitric acid was better retained by the resin than its citric acid counterparts. The element in x M citric acid/1.0 M nitric acid, however, was better retained by the resin than its tartaric acid counterpart. The decrease in distribution coefficient with increase in nitric acid concentration was more gradual in citric acid than tartaric acid.
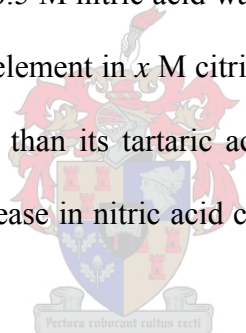
3.4.7   THE LANTHANIDES AND ACTINIDES

The lanthanides and actinides used for these experiments comprised of lanthanum, cerium, terbium, ytterbium, thorium and uranium.

Lanthanum

The results showed that lanthanum is extremely strongly retained by the AG MP-50 cation exchange resin, especially at low concentrations of nitric acid. There is a vast difference between the distribution coefficient of the 0.2 M nitric acid sample and that

of the 0.5 M nitric acid sample. The difference between the 0.5 M and 1.0 M nitric acid samples, although marked, is not as large. It would appear that the citric acid plays a slight role in the retention of lanthanum on the resin: the lower concentration of citric acid allows the element to be better retained, except in the case of the 1.0 M nitric acid sample, where the 0.25 M citric acid solution has a slightly higher distribution coefficient than its 0.1 M counterpart.

In Strelow's experiments with lanthanum on the same macroporous cation exchange resin using hydrochloric acid, the element was extremely strongly retained by the resin for acid concentrations up to 1.0 M hydrochloric acid. It is still strongly retained by the resin using 2.0 M hydrochloric acid, only less so, and the resin's affinity for the element decreases with an increase in acid concentration. The addition of methanol to lanthanum in 0.5 M hydrochloric acid shows that the element still is extremely strongly retained by the resin with distribution coefficients of well over 10 000.
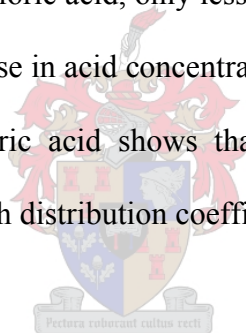
Lanthanum is well retained by AG 50W-X8 cation exchange resin in tartaric acid/nitric acid media, particularly in the lower concentrations of nitric acid (Strelow and van der Walt, 1982). The distribution coefficients for the element in x M tartaric acid/0.2 M nitric acid and x M tartaric acid/0.5 M nitric acid are approximately double that of the distribution coefficients obtained for the element in this work, while the distribution coefficients obtained for lanthanum in x M tartaric acid/1.0 M nitric acid and x M citric acid/1.0 M nitric acid are fairly similar. The decrease in distribution coefficient with an increase in nitric acid concentration is sharper for the element in tartaric acid/nitric acid mixtures than when in citric acid/nitric acid mixtures, as in this work.

Cerium

Cerium is not well retained by the resin and has distribution coefficients lower than 100. The increase in nitric acid concentration does decrease the distribution coefficient slightly, but it would appear that the citric acid has no effect on the retention of this element.

Strelow did not perform experiments using cerium on AG MP-50 resin in hydrochloric acid or hydrochloric acid/methanol media.

Cerium(III) has a very strong affinity for AG 50W-X8 cation exchange resin in tartaric acid/nitric acid mixtures, particularly so when in low nitric acid concentrations. The distribution coefficients decrease with an increase in nitric acid concentration and do so rather sharply throughout the nitric acid concentration range in question, namely, 0.2 M, 0.5 M and 1.0 M nitric acid in tartaric acid mixtures. The tartaric acid concentration does not affect the distribution coefficient values.
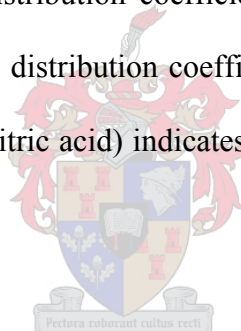
Terbium(III)

Terbium is extremely strongly retained by the resin, yielding distribution coefficients in excess of 10000. Virtually all of the element was retained by the resin and the use of the hydrochloric acid to elute terbium proved to be effective.

Strelow did not perform experiments using terbium on AG MP-50 resin in hydrochloric acid or hydrochloric acid/methanol media.

Terbium was not tested on AG 50W-X8 in various tartaric acid/nitric acid mixtures (Strelow and van der Walt, 1982).

Ytterbium(III)

Ytterbium is also very strongly retained by the cation exchange resin, albeit not as strongly as terbium. The element was not as strongly retained as lanthanum in 0.2 M nitric acid, but is considerably better retained in 0.5 M and 1.0 M nitric acid media. The 0.25 M citric acid plays a role in only the lowest concentration nitric acid sample in this case, as the distribution coefficient of ytterbium is slightly higher than that of its 0.1 M counterpart. The other two results are slightly lower than that of its counterpart. Once again, the distribution coefficient decreases with an increase in nitric acid concentration, but the distribution coefficient of ytterbium in 1.0 M nitric acid (in either concentration of citric acid) indicates that the element is still very well retained by the resin.

Ytterbium is strongly retained by AG MP-50 resin in low concentrations of hydrochloric acid (Strelow, 1984), but is not so strongly retained in concentrations of 2.0 M hydrochloric acid or higher. As with this work, the distribution coefficients decrease with an increase in mineral acid concentration. Ytterbium in 0.2 M and 0.5 M hydrochloric acid is better retained by the resin than ytterbium in the various concentrations of citric acid and nitric acid in this work. The addition of methanol to ytterbium in 0.5 M hydrochloric acid in various percentages increases the element's affinity for the resin.

Ytterbium is very strongly retained by AG 50W-X8 cation exchange resin in tartaric acid/nitric acid mixtures, but less so in the higher nitric acid concentrations. Where the distribution coefficient of the element in x M tartaric acid/0.2 M nitric acid is considerably higher than that obtained for its citric acid counterpart on AG MP-50 resin in this work, the distribution coefficients obtained for ytterbium in x M citric acid/0.5 M nitric acid and x M citric acid/1.0 M nitric acid was found to be considerably higher than its tartaric acid counterpart. Once again, the distribution coefficients for this element in tartaric acid/nitric acid mixtures decrease more sharply than the distribution coefficients in citric acid/nitric acid media in this work.

Thorium

Thorium was extremely strongly retained by the resin and, as a result, required more than 50 ml 7 M nitric acid to remove the element on elution. More of the element was removed when using 4 M nitric acid, but it was discovered that the use of 7 M nitric acid was more effective. Distribution coefficients for this element was found to be greater than 10 000 throughout all of the concentrations of citric acid/nitric acid mixtures tested.

Thorium is well retained by AG MP-50 cation exchange resin in most concentrations of hydrochloric acid (Strelow, 1984), but the distribution coefficients do decrease with an increase in mineral acid concentration. When thorium is in 5 M or 6 M hydrochloric acid, the element is only moderately retained by the resin in comparison with the other concentrations in which the element was tested. When methanol was added to the element in 0.5 M hydrochloric acid (Strelow, 1984), the distribution coefficients remained over 100 000, as it is when no methanol is added.

Thorium has a strong affinity for AG 50W-X8 cation exchange resin in tartaric acid/nitric acid mixtures (Strelow and van der Walt, 1982). The element retention by the resin is slightly more effective in 0.1 M tartaric acid/x M nitric acid mixtures than when in 0.25 M tartaric acid/x M nitric acid mixtures. The distribution coefficients for thorium in this environment decrease with an increase in nitric acid concentration and, although it remains strongly held by the resin, it is considerably more weakly retained by the resin in x M tartaric acid/0.5 M nitric acid and x M tartaric acid/1.0 M nitric acid than thorium in citric acid/nitric acid mixtures on AG MP-50 cation exchange resin, as in this work.

Uranium(VI)

Uranium is fairly well retained by the resin, but the distribution coefficients indicate that quite a lot of uranium flowed through in the filtrate in comparison with terbium, lanthanum and ytterbium. It has a distribution coefficient almost five times that of cerium in the lowest nitric acid concentration, but the distribution coefficients are almost identical when using 1.0 M nitric acid with x M citric acid. The increase in citric acid concentration does not play a significant role in this instance.

Uranium is rather strongly retained by the resin in 0.2 M hydrochloric acid (Strelow, 1984) and the distribution coefficient decreases substantially when the acid concentration is increased to 0.5 M. Once again, the distribution coefficient decreases with an increase in acid concentration. Should various percentages of methanol be added to 0.5 M hydrochloric acid, the resin's affinity for uranium increases, reaching a maximum with the addition of 80 % methanol.

Uranium is fairly well retained by AG 50W-X8 cation exchange resin in x M tartaric acid/0.2 M nitric acid (Strelow and van der Walt, 1982), but becomes less so as the nitric acid concentration increases. The tendency is similar to the results obtained in this work and one can assume that this would be due to the fact that the resin in this work, although very similar to AG 50W-X8, is macroporous. As before, the distribution coefficients decrease with an increase in nitric acid concentration, but more gradually than the likes of thorium and ytterbium. The results indicate that uranium in 0.1 M tartaric acid/nitric acid mixtures is slightly more effective than the element in 0.25 M tartaric acid/nitric acid mixtures as far as affinity for the resin is concerned.

3.5 ELUTION CURVES

From the results obtained in 3.4 elution curves can be created by performing experiments using two or more elements to give an indication of their separation abilities and to determine the separation conditions for quantitative separation experiments. Elements were selected by means of having a high separation coefficient between them (50 or greater). Four experiments were performed in this way and the following separations were attempted:

- Molybdenum(VI) from yttrium

- Zirconium(IV) from lanthanum

- Arsenic(V) from zinc

- Niobium(V) and tantalum(V) from vanadium(V)

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3.5.1   MOLYBDENUM(VI) AND YTTRIUM

100 mg molybdenum and 10 mg yttrium was weighed out and placed into a plastic bottle, before adding 100 ml 0.25 M citric acid/0.2 M nitric acid to the bottle. A 10 ml column was made up, using 100 to 200 mesh AG MP-50 macroporous cation exchange resin. This was connected to a peristaltic pump, to be run at a maximum of 1 ml per minute. The column was equilibrated using 50 ml 0.25 M citric acid/0.2 M nitric acid.

The solution, containing the molybdenum and yttrium, was pumped carefully through the column and 20 ml fractions were taken. This was followed by pumping 150 ml of water through the column, taking 20 ml fractions of the solution (with the exception of the last fraction, which was 10 ml). The column was then eluted using 50 ml 7 M hydrochloric acid, taking 10 ml fractions. All the fractions taken were tested using the ICP instrument.

As can be seen on the figure, which follows the description, the molybdenum was eluted upon loading the column (the initial step), while the yttrium was eluted using the hydrochloric acid. This gives a clear indication of how the results obtained in 3.4 can be interpreted.
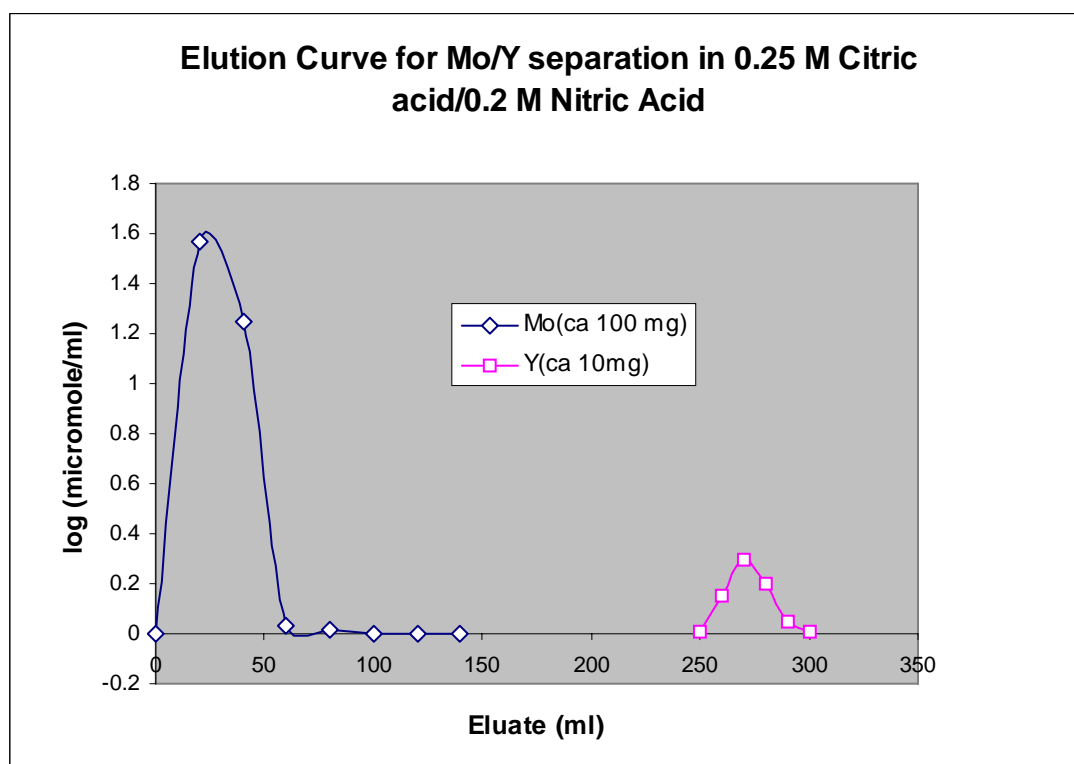
Figure 3.1: Illustration of Mo-Y separation

3.5.2   ZIRCONIUM(IV) AND LANTHANUM

An identical procedure was used for zirconium(IV) and lanthanum, with 100 mg zirconium and 10 mg lanthanum being used in the experiment. The same load solution was used (0.25 M citric acid/0.2 M nitric acid) and similar results were obtained, although molybdenum came out more quickly and the lanthanum had a very slight tailing effect.
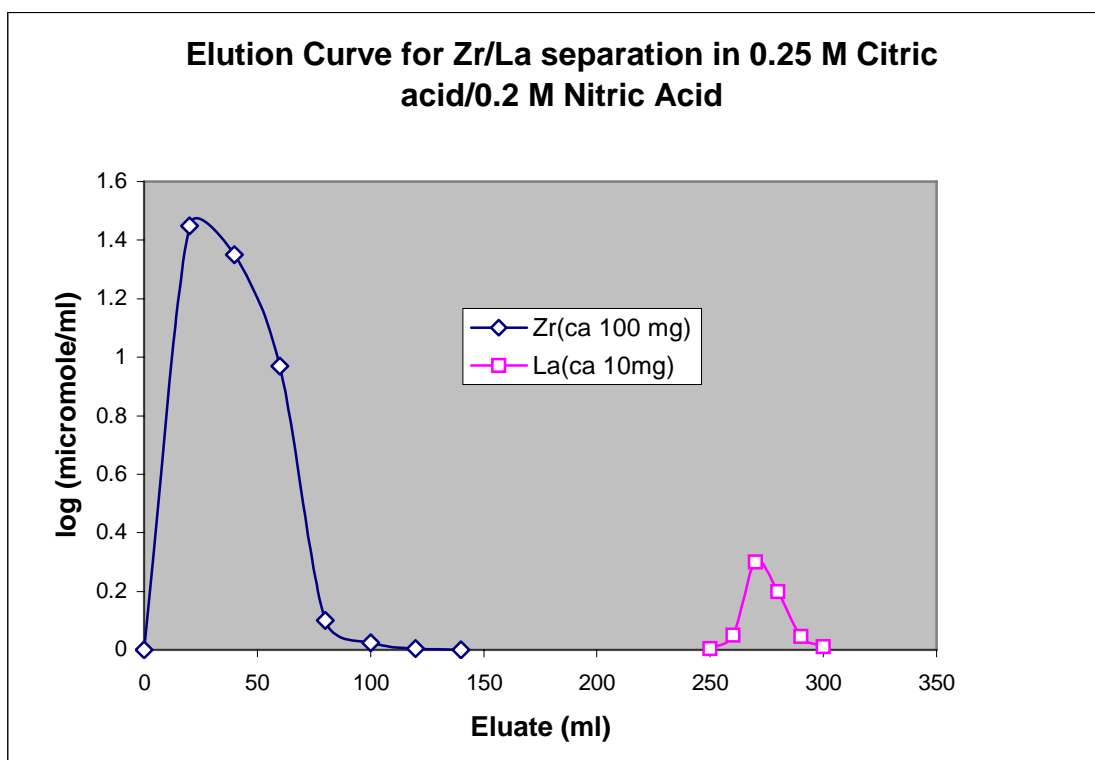
Figure 3.2: Illustration of Zr-La separation

3.5.3   ARSENIC(V) AND ZINC

The identical procedure was used for arsenic and zinc, with 100 mg arsenic and 10 mg zinc being used in the experiment. The same load solution was used (0.25 M citric acid/0.2 M nitric acid). Arsenic came out almost immediately, while zinc was eluted with the hydrochloric acid.

The elution curves for the above experiments are shown over the page. Due to the results obtained and the fact that elution curves could be derived from some of the results, the major objectives for this work described in 1.2 have been achieved.
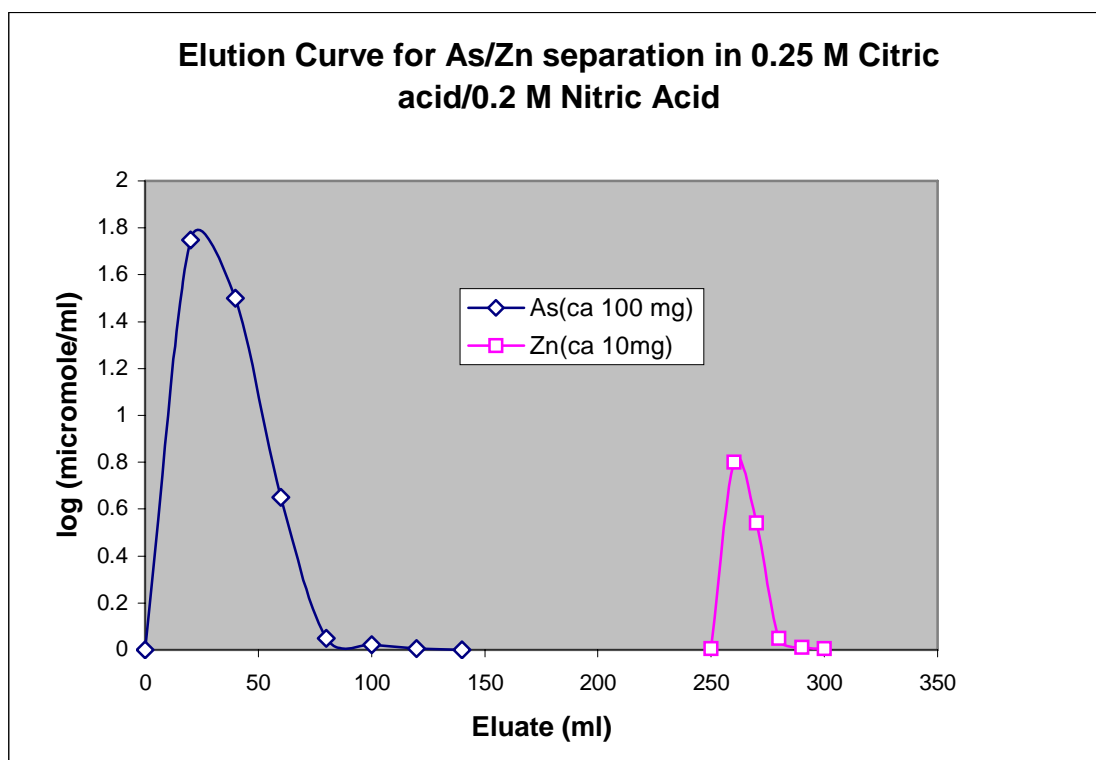
Figure 3.3: Illustration of As-Zn separation

3.5.4   NIOBIUM(V), TANTALUM(V) AND VANADIUM(V)

A similar method was used for this experiment as for the previous three, with 0.1 M citric acid/0.25 M nitric acid used as the load solution and 0.03 % hydrogen peroxide added to the solution containing 100 mg tantalum(V), 100 mg niobium(V) and 50 mg vanadium(V). The peroxide was added to keep the vanadium in the +5 format, while preventing the polymerisation of niobium and tantalum. Similarly, 0.03 % hydrogen peroxide was added to the 7 M hydrochloric acid when eluting the vanadium(V).
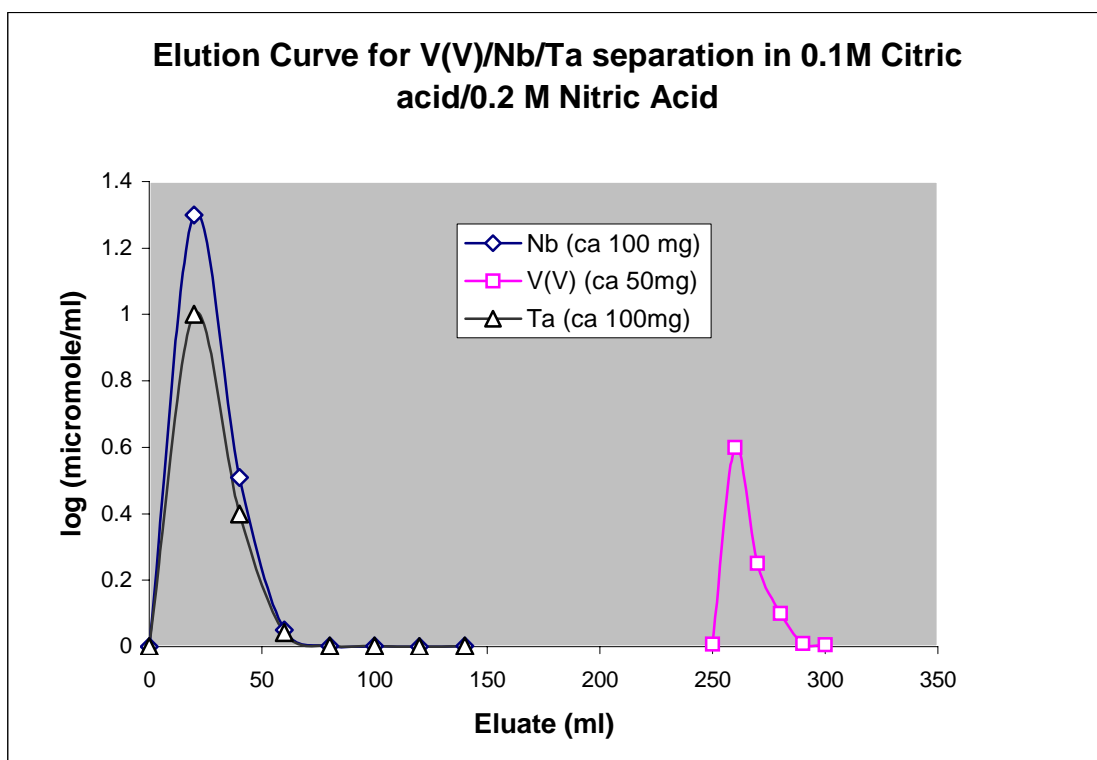
**Figure 3.4: Illustration of Nb-Ta-V(V) separation**

As can be seen in the experiments mentioned above, separations can be effectively performed using the distribution coefficients in 3.4. All of the elution curves show that the initial element(s) to be eluted in the load fraction is done so effectively, while the second element is quantitively eluted with 50 ml 7 M hydrochloric acid.

4. NEW PROPOSED METHOD TO ISOLATE ^{22}Na FROM BOMBARDED MAGNESIUM TARGETS

As mentioned previously, the sodium-22 production involves the use of AG MP-50 cation exchange resin, as well as Chelex 100 resin. The sodium-22 is produced by bombarding a magnesium target encapsulated in an aluminium capsule. The magnesium target is removed from the capsule before the chemical separation and washed with dilute hydrochloric acid, followed by water to remove surface impurities, which may have adhered to the disc. The target is transferred to a polyethylene flask containing 2 M citric acid and dissolved by heating it for six hours. The resultant solution is then cooled, before adding 1 M TEA – 80 % methanol and stirring. The solution is then pumped through a column containing AG MP-50 resin (in tritethanolammonium form) and the magnesium eluted from the column using 0.2 M citric acid - 0.6 M TEA – 80 % methanol, followed by 0.1 M EDTA - 0.6 M TEA – 80 % methanol. The EDTA, methanol and TEA is washed out of the column with water.

The AG MP-50 resin is then converted to the ammonium form by the passage of 1 M ammonium hydroxide – 80 % methanol and the ammonium hydroxide and methanol is washed out of the resin column with water. The sodium-22 is eluted, using 0.5 M ammonium carbonate, and loaded on to a column containing Chelex 100 resin, which is connected to the outlet of the column containing the AG MP-50 resin. The eluate is collected and evaporated to dryness and the sodium-22 dissolved in acetic acid.

The results obtained for magnesium and sodium in citric acid/nitric acid media were not effective enough to warrant a separation between the two elements, as the best separation factor that could be obtained is approximately 8 (in 0.25 M citric acid/0.2 M nitric acid). Using citric acid to dissolve the magnesium target, Strelow suggested that magnesium forms a complex with citric acid, thereby allowing the separation between sodium and magnesium to be more effective, with the sodium being held on to the resin, while the magnesium is eluted. It was initially thought that the use of citric acid to dissolve the target material would simplify the production, as the magnesium would be complexed as early as the dissolving step. The dissolution step would be considerably faster and the length of the production would be shortened a great deal. The results obtained in this work showed that this was not the case: magnesium does not form a complexing agent with citric acid, as the distribution coefficients for the element was found to be considerably higher than that of sodium.
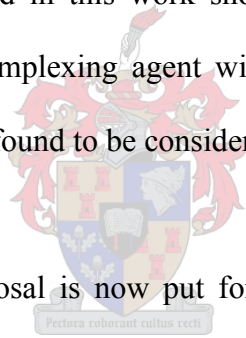
As a result, the following proposal is now put forward to simplify the sodium-22 production and to speed up the production. The magnesium target, containing sodium-22, can still be dissolved in citric acid. NH_3-methanol is added to the solution, so that the citrate complexes the magnesium at a pH of greater than 8, and the resulting solution is then pumped through an AG MP-50 column. The bulk of magnesium is eluted with NH_3-citrate-methanol. NH_3-EDTA-methanol can be used to remove the magnesium completely. The NH_3-EDTA-methanol is washed from the resin column with an NH_3-methanol solution, before eluting the sodium with ammonium carbonate. The eluate is passed through a Chelex 100 column to remove the last traces of magnesium and other elements.

As this proposal falls outside the scope of this work, no attempt was yet made to perform the proposed experiments. This possibility will be investigated in greater detail at a later stage.
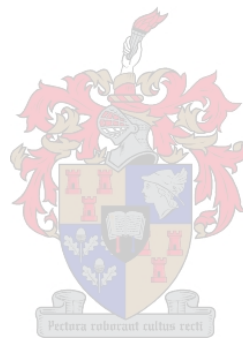
5. CONCLUSION

The major objectives for this work have been achieved, namely, to obtain distribution coefficients for the elements listed above in different concentrations of citric acid/nitric acid media and, from these results, to determine whether chemical separations were possible. Where the work was originally thought of to improve the sodium-22 production, although the results did not provide any useful separation techniques using citric acid/nitric acid media, it did provide a very interesting observation (see Chapter 4).

The outstanding feature of this work is the fact that some of the elements tested in this work, namely, arsenic(V), niobium(V), molybdenum(VI), tantalum(V) and germanium, were very strongly complexed by citrate, even in nitric acid solution, and were not retained by the AG MP-50 macroporous cation exchange resin, while elements like barium, thorium, terbium and even titanium(IV) were retained by the resin in question.

Where the ion exchange of arsenic(V) and the other elements mentioned above were almost entirely dominated by the citrate complex in citric acid/nitric acid media, the other elements behaved differently. Some of them, such as bismuth(III), uranium(VI) and titanium(IV) are affected by the citric acid concentration, especially in low nitric acid concentrations, but many of the other elements are nearly independent of the citric acid concentrations and are almost entirely influenced by the nitric acid concentrations.

Possible separations of elements include gallium and germanium in 0.25 M citric acid/0.2 M nitric acid media, as the citric acid is involved in the complexing of germanium, while also having an effect on the gallium in low nitric acid concentrations. Yttrium can be effectively separated from zirconium (and also molybdenum – see 3.5.1) in the same media as described above, while lanthanum and zirconium can be separated effectively in the same media (see 3.5.2). The same can be said for arsenic(V) and zinc (see 3.5.3). Zirconium can also be effectively separated from niobium and molybdenum (separation factor of over 50 in both cases) in 0.1 M citric acid/0.5 M nitric acid where, once again, the citric acid forms complexes with niobium and molybdenum, while also having some effect on the zirconium. Niobium and tantalum can effectively be separated from vanadium(V) (see 3.5.4), due to a high separation factor in each case.

Lead(II) can be effectively separated from tin(IV) in 0.25 M citric acid/0.2 M nitric acid media, while indium can also be effectively separated from tin(IV) using the same media, a production method for the indium-111 production also effected a similar separation, but using hydrochloric acid-hydrogen peroxide media.

Some of the lanthanides and actinides can be separated from each other as well, such as lanthanum from cerium in 0.1 M citric acid/0.2 M nitric acid, or even cerium from terbium or ytterbium.

Some of the separations mentioned above will be looked at in more detail at a later date.

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