THESIS

ON

SEPARATION OF THORIUM FROM EGYPTIAN MONAZITE BY ANION EXCHANGE METHODS

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SEPARATION OF THORIUM FROM EGYPTIAN MONAZITE BY ANION EXCHANGE METHODS

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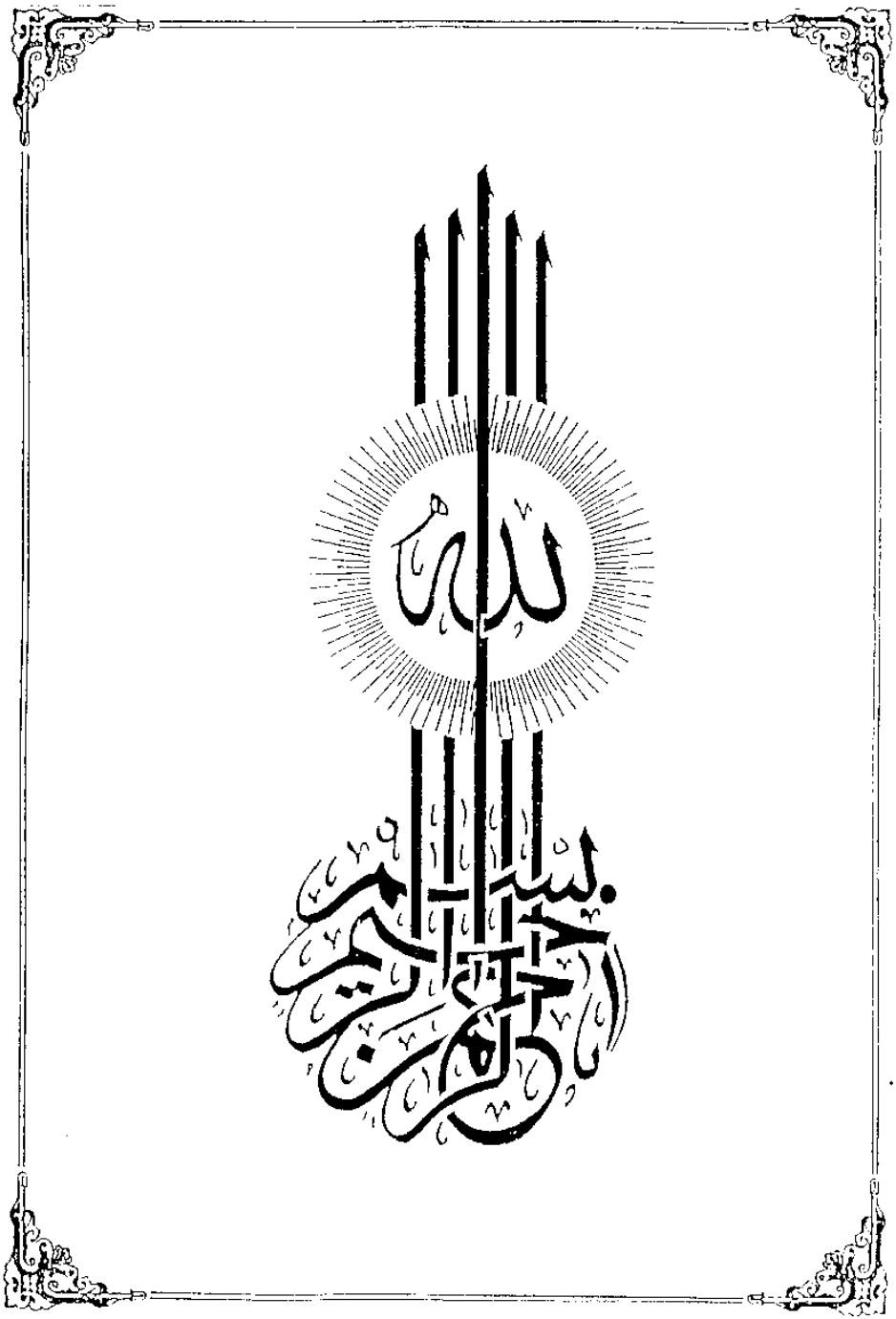

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NOTE

The Candidate has attended postgraduate courses for two yeers in Inorganic and Physical Chemistry covering the following topics:

1- Chemistry of the Solid State.

2- Techniques of Inorganic Chemistry.

3- Structural inorganic chemistry.

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CONTENTS

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PART I

SEPARATION OF THORIUM FROM EGYPTIAN MONAZITE BY ANION EXCHANGE CHROMATOGRAPHY

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CHAPTER I

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Ion exchange resins consist essentially of a cross-linked polymer network to which are attached ionized or ionizable groups. In the case of cation exchange resins these groups are acidic groups (e.g. $-SO_3H$, -COOH, phenolic -OH), while in the anion exchange resins the groups are basic in character (e.g. quaternary ammonium, aliphatic or aromatic amine groups).

Depending on the ionizable groups, the exchange resins may be classified into 4 main types, namely,

1- Strongly acidic cation - exchange resins.

2- Weakly acidic cation - exchange resins.

3- Strongly basic anion - exchange resins.

4- Weakly basic anion - exchange resins.

Anion Exchange Resins:

Anion exchangers may be regarded as polyvalent cations with negatively charged ions or as high molecular-weight insoluble bases or salts of such bases, respectively. The weakly basic anion exchange resins are characterized by that the number of ionized groups, and hence the exchange capacity, depends largely on the pH value of the solution. Resins containing only weakly basic groups, e.g. condensation products of meta-phenylenediamine and formaldehyde, will be highly ionized and may be used for anion exchange

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in acid medium. At higher pH values, the resins will be mostly un-ionized and inert [1]. Anion exchangers of weakly basic type may also be made from cross-linked polystyrene resins (Dowex-3 and Amberlite IR-45). The exchange capacity is further affected by the valence of the anions[2,3,4]. Anion exchangers possess the property of binding coordinately certain cations with a strong tendency for forming amine complexes.

On the other hand, in strongly basic type, the exchange capacity is independent of the pH of the solution. A hydroxyl-ion-saturated resin of this type behaves as a strong base, and the exchanger must be considered completely dissociated[5]. The anion exchanger can thus be used in alkaline solutions, e.g. for liberating bases from neutral salts. The uptake of complex anions, e.g. complex citrates and oxalates, is of particularly great analytical interest. A most important observation is that certain metal ions, e.g. ion (III) and cobalt (II), may be taken up quantitatively from strong HCl acid, e.g. 9N, as chlorocomplex anions.

Factors Affecting Separation:

The variables which determine the separation of exchangeable ions in the elution step may be classified into two groups:

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A) Factors affecting the equilibrium separation.

B) " affecting column separation.

A- Factors affecting the Equilibrium Separation:

From dilute solutions contsining ions of different valence the ions of higher valence are preferentially held by the resin and that the differencies in affinity increase on dilution of the solution. Separation of ions of different valence are, therefore, improved by diluting the solution. Furthermore, the separation of ions, independent of the valence, is better for ion-exchangers with high exchange capacity per unit volume.

On the other hand, Tompkins et al.[6,7,8,9] have shown that separation is most efficient when the amount of the ions to be separated in the resin phase is low. Complexing agents are, therefore, conventiently used as elutriants, since they reduce the fractions of solutes in the exchangeable form[10,11]. Complexing agents are also preferred as elutriants because these agents may be used to shift the ion exchange equilibrium in such a direction that the separation is favoured. In the separation of very similar ions, as rare earths, complexing agents are helpful, because of differencies in dissociation constant of the complexes. The separation effects of the exchanger and the complexing agent supplement each other[8,12].

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For such complexing agents, as citrate, in which the complex equilibrium depends upon the pH of the solution, the course of elution is markedly influenced by the pH[6,7,8,11,12,13]. The choice of pH is, therefore, of utmost importance for a successful separation. The optimal conditions may vary from one resin to another, depending upon the concentration in the resin phase[7-12].

B- Factors affecting Column Efficiency:

1- Particle Size:

It is common practice to use fine particles in ion exchange chromatography. Too small particles will effect too high resistance against flow and must, therefore, be removed by screening or decantation.

2- The Flow Rate:

The flow rate has a great influence. Increasing flow rate means that the ions are carried at a faster rate down the column, so that they have less time to diffuse through the resin particles, and thus are prevented from reaching all exchanging groups[14,15,16]. Too high flow rate will cause a long trailing edge of the elution curves and thus an increased overlap of the curves for the ions to be separated.

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3- Temperature:

High temperature increases the diffusion rates and, therefore, the number of exchanges in a given column. Improved separations were observed by Ketelle and Boyd[12] when working at elevated temperatures.

4- Column Dimensions:

The ions to be separated are lodged in a band near the top of the column. The separation occurs chiefly when the ions move down the column during the elution step. Depending on the differencies in exchange potentials, a longer or shorter resin bed is necessary to effect separation.

With certain limits separation is improved by increasing the length of the resin bed. However, there is a critical bed length beyond which no improvement in separation can be gained.

Separation of Rare Earths:

A number of early attempts were made to separate rare earths, by ion exchange methods, making use of the differencies in chelate stabilities[6,8,12,13,17,18,19]. In these separations, citric acid, buffered with ammonium citrate, was used as the eluant. Complexing agents other

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than citrate have been used to resolve mixtures of rare earths on cation-exchange systems. The list includes the hydroxy acids - glycolic[20,21,22], lactic[20,23-29], α-hydroxyisobutyric[30-35], malic[20,36], and tartaric[36]; the amino- and aminopolyacetic acids - amino-acetic[36], nitriloacetic[37], hydroxyethyliminodiacetic[38,39], O-cyclohexanolamine diacetic[38], and ethylenediamine tetra-acetic[20,21,40], and a few miscellaneous inorganic reagents - ammonium thiocyanate[34,41,42], sodium triphosphate[43], and buffered pyrophosphoric acid. With these eluants, as well as with citrate, the best[28] and most rapid separations have been accomplished at elevated temperatures.

In 1955, Nervik[25] showed that pH-gradient elution could be used to obtain more rapid elution of the more readily separable but tenacious cerium-group elements. The work of Stewart[21] and Nervik[25] led to the separation of rare-earths, by their sorption followed by elution with neutral ammonium lactate. They employed a concentration-gradient technique rather than the pH-gradient technique of Nervik to promote the elution of cerium-group rare earths.

Stewart[35] showed that temperature-gradient elution with ammonium α-hydroxyisobutyrate was comparable to

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