



STUDY ON THE USE OF MACROPOROUS CATION EXCHANGE RESINS  
FOR THE SEPARATION AND PURIFICATION OF URANIUM FROM THORIUM

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R. K. Rastogi, M. A. Mahajan and N. K. Chaudhuri  
Fuel Chemistry Division

GOVERNMENT OF INDIA  
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BHABHA ATOMIC RESEARCH CENTRE  
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60 Abstract : The possibility of using macroporous cation exchange resins for the purification of uranium from thorium relevant to the final purification of uranium after reprocessing thorium breeder fuel was explored. Two macroporous cation exchange resins were studied and compared with a commonly used gel type resin. Batch experiments and column experiments were performed to generate equilibrium data and to optimise the procedure for the separation of U from Th under process condition. Under the same condition Tulsion T-42 gave product U containing 0.1% of Th, while Amberlyst-15 gave the product U containing 1% of Th. Loading and washing rates were much higher (120 ml/hr) than those used for gel type resins (40 ml/hr). Though the volume of wash required for >90% recovery of U is more than that required with the gel type resin the disadvantage due to that is more than compensated by the use of high flow rates of loading and washing to give higher throughput. Thus there is a definite advantage of U purification with macroporous resins as compared to usual gel type resins.

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70 Keywords/Descriptors : RESINS; ION EXCHANGE; THORIUM; URANIUM; ISOTOPIIC EXCHANGE; THORIUM NITRATES; URANIUM OXIDES U3O8; QUANTITATIVE CHEMICAL ANALYSIS; SPECTROPHOTOMETRY; DISTRIBUTION FUNCTIONS; DECONTAMINATION; EFFICIENCY; PURIFICATION

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R.K.Rastogi, M.A.Mahajan and N.K.Chaudhuri  
Fuel Chemistry Division  
Bhabha Atomic Research Centre  
Trombay, Bombay 400085,  
India.

1. INTRODUCTION

Methods for the separation of actinides using ion exchangers have been reviewed by several authors<sup>(1-3)</sup>. Synthetic organic ion exchangers used earlier and most even at present are of gel type. These organic exchangers are not so stable towards chemical and radiation effects and therefore not used at initial stage of reprocessing. They are, however, used at later stages of reprocessing like (i) concentrating and further decontaminating the plutonium product stream from solvent extraction processes, (ii) refining of Np and (iii) separation of  $^{233}\text{U}$  from Th at the tail end of reprocessing. Uranium, is separated in tonne quantities from sulphuric acid leach solutions of the ores employing this method.  $^{233}\text{U}$  present in the bulk of thorium, after irradiation of the later, is separated by extracting  $^{233}\text{U}$  into 5% Tri-Butyl-Phosphate (TBP) in kerosene type of solvent<sup>(4)</sup>. Uranium fraction stripped from TBP still contains considerable amount of thorium. Final purification of uranium is done by anion exchange in 8M HCl. This method of purification involves the conversion of the medium from dilute nitric acid to 8M HCl via ammonia precipitation. In spite of excellent decontamination, the method has certain disadvantages like corrosion of equipment and gassing in the ion exchange column<sup>(5)</sup>. Various attempts made to overcome

this problem include, an anion exchange separation in acetic acid medium<sup>(6)</sup>, a cation exchange procedure<sup>(7)</sup> and a sequential precipitation of Th and U<sup>(8)</sup>.

The beginning of a new era in ion exchange was marked<sup>(9)</sup> with the commercial introduction of macroporous (MR type) ion exchange resin Amberlite 200 in 1959. General methods of their manufacture are described in a number of publications<sup>(10-13)</sup> and the large variety of resins manufactured by leading manufacturers have been listed along with many useful data in recent publications<sup>(14,15)</sup>. Lee et al<sup>(16)</sup> have outlined (Fig.1) the difference in synthesis of gel type and macroporous ion exchange resins. In conventional polymerisation technique, a gel type structure is obtained with pores of 10 Å<sup>0</sup> and smaller. On the other hand by using a special medium, a porous or macroreticular texture can be obtained. The macroporous resins have much more complex morphology and texture. Typically, small nuclei (50-200 Å<sup>0</sup>) are tightly grouped into microspheres (1000-2000 Å<sup>0</sup>) which form agglomerates. This texture leads to the presence of two families of pores, small pores of some 10 to 100 Å<sup>0</sup> together with large pores varying from 100 to 10,000 Å<sup>0</sup>. Surface area can be as large as 800 m<sup>2</sup>/g. These characteristics increase greatly the chemical accessibility and the mass transfer of ions and large molecules<sup>(16)</sup> with macroporous resins. These resins have been the subject of investigation by various authors for the actinide separation processes<sup>(17)</sup>. Available data suggest that macroporous resins are superior to gel type in certain respect. Therefore, it was considered worthwhile to generate distribution data to explore the possibility of using some of the macroporous resins

for the purification of U from Th. Accordingly two cation exchange resins, namely Amberlyst-15 (made in France) and Tulsion T-42 (made in India) resins, were taken for studies along with Dowex 50 x 8, a gel type resin. This report presents the ion exchange studies carried out in this regard and includes:

(a) distribution ratio data for the Th(IV) as well as for U(VI) at varying acidity and metal concentrations, (b) determination of breakthrough capacity of the exchangers for Th(IV), (c) column operation at various Th(IV) to U(VI) ratios and their decontamination factor and (d) procedure for obtaining U with as little Th contamination as possible.

## 2. REAGENTS AND CHEMICALS

### (a) Ion exchange resins:

Amberlyst-15, a macroporous cation exchange resin, in hydrogen form and of 16-50 mesh size was obtained from M/s Rohm and Haas, France. Tulsion T-42, a macroporous cation exchange resin in hydrogen form and of 15-50 mesh size was obtained from M/s THERMAX, Pune, India. Dowex 50 x 8, a gel type resin in hydrogen form and of 100 - 200 mesh size was obtained from M/s J.T. Baker Chemical, USA. Dowex 1 x 4 (50-100 mesh) in chloride form was obtained from M/s Dow Chemical Company, USA and used for the separation of Th(IV) from U(VI) for the determination of Th as Th-Arsenazo(III) by spectrophotometry<sup>(18)</sup>.

### (b) Acid Stock Solutions

Nitric acid and hydrochloric acid were of GR grade supplied by M/S Polychemicals, Bombay. Concentrated HCl was diluted with distilled water in the ratio 1:1 to obtain ~ 6 M HCl and was used

for loading preferentially<sup>(19)</sup> anionic chloro complex of U(VI) on Dowex 1x4 from the aliquots containing U(VI) and Th(IV).

(c) Sulphamic Acid Stock Solution

1M sulphamic acid solution was prepared by dissolving about 24.3g of sulphamic acid (B.D.H., reagent grade) in 250 ml of water.

(d) Thorium Stock Solution

A known weight of nuclear grade  $\text{Th}(\text{NO}_3)_4 \cdot 6\text{H}_2\text{O}$ , obtained from M/s Indian Rare Earths, Bombay, was dissolved in distilled water. The concentration of this stock was determined<sup>(20)</sup> by EDTA titration and was found to be 254.4 mg/ml. Dilute solutions containing required concentration of Th(IV) were prepared by taking a known volume from this stock solution, evaporating to dryness under infrared lamp and subsequently dissolving in the desired quantity of nitric acid.

(e) Uranium Stock Solution

Nuclear grade  $\text{U}_3\text{O}_8$  obtained from Uranium Metal Plant, BARC, was dissolved in 1:1  $\text{HNO}_3$  and made up to 500 ml with dilute  $\text{HNO}_3$ . Uranium concentration in this stock solution determined by redox titrimetry using Davies and Gray method<sup>(21)</sup> was found to be 102.7 mg/ml. Dilute solutions containing required concentration of U(VI) were prepared by evaporating a known volume of the stock solution to dryness under infrared lamp and subsequent dissolution in the desired quantity of nitric acid.

(f) Stock Solution Containing Mixture of Th(IV) and U(VI)

Synthetic mixtures of Th(IV) and U(VI) were prepared by



evaporating known volumes of Th(IV) and U(VI) stock solutions (from (d) and (e)) to dryness and subsequently dissolving in the desired quantity of dilute nitric acid.

(g) EDTA Stock Solution

Concentrated and dilute solutions of EDTA were prepared by dissolving disodium salt of EDTA (AR grade) obtained from E. Merck and standardised against a standard solution of  $ZnCl_2$  using Erichrome Black T as indicator<sup>(22)</sup>.

(h) Arsenazo (III) Solution

About ~ 2 mg/ml Arsenazo(III) (E.Merck) was dissolved in 0.01M NaOH solution and filtered.

Chemicals required for uranium analysis<sup>(23)</sup> were all of AR or GR grade.

3 INSTRUMENT AND APPARATUS

(a) Mechanical Shaker

A rotating mechanical shaker in a thermostatic bath maintained at  $23.0 \pm 0.1^\circ C$  was used for equilibration of aqueous solutions and resins for measuring distribution ratio of U(VI) or Th(IV).

(b) Spectrophotometer

A microprocessor based spectrophotometer, Beckman DU-7, from Beckman Instruments Inc., USA, was used for the spectrophotometric determination of Th(IV) at  $\mu g$  level.

(c) Uranium Analysis set up

A digital volt meter from M/s Arun Electronics, India, a

calomel reference electrode from M/s Toshniwal Brothers, India, and a Pt electrode were used for uranium analysis employing Davies and Gray method<sup>(21)</sup>.

(d) Class Columns

Three columns made from Corning glass tube (9.5 mm ID and 12 mm OD) with cups of ~100 ml capacity at the top were used for column experiments.

4 DETERMINATION OF URANIUM AND THORIUM

(a) Uranium : Uranium was determined by redox titrimetry, on weight basis using potentiometry by Davies and Gray<sup>(21)</sup> method and a potentiometric end point detection. The procedure adopted was the same as used in routine analysis<sup>(23)</sup>.

(b) Thorium : In the absence of uranium, mg amounts of Th(IV) were analysed<sup>(20)</sup> by EDTA titration using Xylenol orange as indicator.

During the column breakthrough studies, column operation etc. in which aliquot to be analysed contained Th(IV) in  $\mu\text{g}$  range, Th(IV)-Arsenazo(III) spectrophotometry<sup>(18)</sup> was used for Th analysis. Separation of Th from U was necessary before colour development for the aliquots which contained U along with Th, as U interferes in this spectrophotometric method. In such cases a suitable aliquot (1-5 ml) was taken, evaporated to dryness, dissolved in 1-2 ml of 6 M HCl and then passed through Dowex 1x4 (50-100 mesh) resin. The column was washed with 10 column volumes of 6 M HCl. Uranium was retained by the resin as its anionic chloro complex. Effluent plus washings containing Th were made up (usually 50 ml). A suitable aliquot from this (0.5 to 20 ml) was

taken, evaporated to dryness and transferred into a 10 ml standard flask using 0.5M HNO<sub>3</sub>. 1 ml of sulphamic acid, 3.5 ml of concentrated (~15.5M) nitric acid (so as to make the final acidity 6M) and 1 ml of Arsenazo(III) solution were added and made up to volume with dilute nitric acid. After about 20 minutes the absorbance at 662.5 nm was measured against a reagent blank.

### 5 DETERMINATION OF TIME OF EQUILIBRATION AND DISTRIBUTION COEFFICIENTS

Distribution coefficients of Thorium(IV) and Uranium(VI) were determined by shaking known weights of Resins (~100 mg) with 20 ml of the solution (containing Th or U) for 5 hrs. In a separate set of experiments times of equilibration for Amberlyst and Tulsion were found to be 3 hrs and 4 hrs respectively. However, for all distribution studies an uniform time of 5 hrs was used. From the initial and the equilibrium concentrations of uranium and thorium in the aqueous phase, the distribution coefficient (Kd) as given by eq. (1) was calculated.

$$K_d = \frac{\text{Equilibrium Conc. of the metal ion in the resin (mg/g)}}{\text{Equilibrium Conc. of the metal ion in the soln. (mg/ml)}}$$

$$= \frac{[M]_i - [M]_e}{[M]_e} \times \frac{V}{W} \quad (1)$$

where,

[M]<sub>i</sub> = Initial aqueous concentration of M (mg/ml)

[M]<sub>e</sub> = Equilibrium aqueous concentration of M (mg/ml)

V = Volume of the aqueous phase taken for equilibration (ml)

W = Wt. of the dry resin taken for equilibration (g)

M = Th(IV) or U(VI).

## 6 DETERMINATION OF COLUMN BREAKTHROUGH CAPACITY FOR THORIUM

For studying breakthrough capacity and column operation a glass column as shown in Fig. 2 was used. For all operations 10 ml of the resin was used. Resin was conditioned with 10 bed volumes of 0.5 M HNO<sub>3</sub>. To maintain flow rate almost constant, the head pressure of the column as well as of the reservoir bottle were maintained constant by air locking the system. 0.5 M nitric acid medium was used for all breakthrough studies for thorium as well as for thorium-uranium mixture.

## 7 DETERMINATION OF DECONTAMINATION FACTOR FOR URANIUM FROM THORIUM

Breakthrough data indicated 1% breakthrough of Th at around 55 bed volume. Therefore, for decontamination factor (DF) studies effluent upto ~10 bed volumes less than that was collected in one lot and thereafter effluent of 5-10 bed volumes collected in separate lots. Decontamination factor was obtained on dividing the ratio of Th to U concentrations in the feed by the ratio of Th to U concentrations in the effluent.

## 8 COLUMN EXPERIMENTS

Having obtained breakthrough capacity data and DF data for guidance, a number of column runs were carried out to arrive at the conditions whereby >90% uranium could be separated from Th with least contamination of Th. For all the exploratory work the resin Amberlyst-15 was used. Only those column runs which were found optimum with Amberlyst-15 were repeated with Tulsion T-42.

The following column runs were carried out with resin Amberlyst-15. All operations were carried out under the following conditions unless stated otherwise :

Feed composition - 1 mg/ml Th and 1 mg/ml U; Flow rate-5 min/bed volume; Resin vol.-10 ml; Medium-0.5 M HNO<sub>3</sub>.

Run 1 : 55 bed volumes of feed were passed through three identical columns. First, second and third column were washed with 10 bed volumes of 0.5 M, 1.0 M and 2.0 M HNO<sub>3</sub> respectively.

Run 2 : In this run, after passing 55 and 45 bed volumes of feed through two separate columns, washings of the resin bed with 0.5 M HNO<sub>3</sub> was continued till > 90% U reported in the effluent plus wash. Each time the wash solution of 10 bed volumes was collected separately and analysed for U and Th.

Run 3 : In order to arrest ~ 1% Th, coming out along with wash, a capsule of 1 ml of Dowex 50 x 8 resin was attached to two columns containing Amberlyst-15 resin. One column was washed with 50 bed volumes of 0.5 M HNO<sub>3</sub> whereas the other one was washed with 30 bed volumes of 1.0 M HNO<sub>3</sub>. Feed volumes passed in both the cases were 55 bed volumes.

Run 4 : In this run loading and washing rates were increased from 5 min/bed volumes to 2 min/bed volume. Feed and wash volume passed were 55 and 50 bed volumes respectively.

Run 5 : Column operation with Tulsion T-42 resin : Loading and washing of the Tulsion T-42 resin were done with 55 bed volumes (feed) and 50 bed volumes respectively using 0.5 M HNO<sub>3</sub> (wash). Volume of additional 0.5 M HNO<sub>3</sub> wash required to recover remaining U was also found out by washing with more bed volumes using 0.5 M HNO<sub>3</sub>. These washings were collected separately and

analysed for U and Th.

Elution of the bulk of Th from the resin was done by washing it with 10-12 bed volumes of 6-7 M HNO<sub>3</sub>. Remaining Th was then removed by using 2:1, 3 M Ammonium acetate - 1.5 M acetic acid mixture (pH 5.5) as described for Dowex 50x8 work<sup>(7)</sup>. The column was finally washed with water and reused after conditioning.

## 9 RESULTS AND DISCUSSION

Batch distribution data for Th and U with resin Amberlyst-15 are given in Tables 1 and 2. The data for these metal ions obtained for Tulsion T-42 are given in Tables 3 and 4. These batch distribution data show that the K<sub>d</sub> values of U(VI) and Th(IV) decrease with an increase in the molarity of nitric acid as well as with increase in the concentration of U and Th. The decrease in K<sub>d</sub> values with acidity is expected. The effect of the concentration of H<sup>+</sup> on K<sub>d</sub> values can be deduced by writing down the equilibria between resin phase and aqueous phase and applying law of mass action i.e.



where Th<sup>4+</sup> and H<sup>+</sup> are the cations in the solution phase and ThR<sub>4</sub> and HR are those in the resin phase. The equilibrium constant K is given by

$$\begin{aligned} K &= \frac{[\text{ThR}_4] [\text{H}^+]^4}{[\text{Th}^{4+}] [\text{HR}]^4} \\ &= K_d \frac{[\text{H}^+]^4}{[\text{HR}]^4} \end{aligned}$$

$$K_d \propto \frac{1}{[H^+]^4} \quad (2)$$

Equation 2 envisages fourth power dependence of  $K_d$  on  $H^+$  concentration. However, such a drastic decrease in  $K_d$  values is not observed from Tables 1-4. This is primarily due to not taking into account the (i) nitrate complexing of Th in the aqueous phase, (ii) changes in the activity coefficient and (iii) partial saturation of the resin due to the loading of metal ion. A decrease in  $K_d$  with increase in the concentration of the metal ion is observed. This is due to the partial saturation of the resin by the metal ion and thereby reducing proportionately the effective quantity of resin available for the metal ion.  $K_d$  values for Th(IV) were higher than that of U(VI) for both the resins. These  $K_d$  values and  $\beta$  [defined as  $(K_{dTh})/(K_{dU})$ ] values of 4 and 6.1 for Amberlyst-15 and Tulsion T-42 respectively at a concentration level of 1 mg/ml of Th(IV) and U(VI) level (Tables 1-4) indicated the feasibility of separating U from Th using these resins.

The breakthrough curves for Th(IV) are shown in Fig.3. It is clear from the figure that the change in breakthrough capacity for feed with and without U(VI) is negligible. However, a decrease in breakthrough capacity of Amberlyst-15 is observed when Th:U ratio is 2:1. The same trend is anticipated for Tulsion T-42 resin for the Th:U ratio 2:1. Breakthrough is sharp for Amberlyst-15 and Dowex 50x8 as compared to Tulsion T-42. Results of breakthrough runs at 10% breakthrough capacity are summarised in Table 5.

Breakthrough capacity of Tulsion is slightly higher than

that of Amberlyst-15, while both of them have much lower capacities than Dowex 50x8. It is seen from Tables 6-8 that uranium starts appearing in the effluent much earlier than Th and the ratio of the concentration of U in the effluent to that in the feed solution goes on increasing and exceeds unity. This is because, while loading U-Th mixture initially both U(VI) and Th(IV) get loaded on the resin simultaneously, but at a later stage, Th(IV) starts displacing U(VI) from the resin due to its greater affinity to the resin. This results in higher U(VI) concentration in the effluent than in the feed solution.

It is seen from Table 9 (Run-1) that on washing with high concentration of  $\text{HNO}_3$ , recovery of U in effluent increases but at the same time contamination of Th also increases very much. Therefore, it was necessary to give more washing with 0.5M  $\text{HNO}_3$  only. Run-2 data indicate that on loading and washing of Amberlyst-15 with 45 and 50 bed volumes respectively though the contamination from Th is less (as compared when 55 bed volume feed was loaded), U recovery was only ~85%. It needs another 20 bed volumes of wash to get U recovery of ~90%.  $\beta$  values of Th/U for Dowex 50 x 8 (100-200 mesh) are reported to be high<sup>(7)</sup>. Therefore, it was decided to try to exploit this high affinity of Dowex 50 resin for Th. However, the use of Dowex 50 x 8 resin capsule did not give the desired decontamination from Th. This is because the effluent from main column when enters the Dowex capsule has 400-600 times more of U(VI) than Th(IV). Therefore, U(VI) competes fairly with Th(IV) for resin (Dowex) site, resulting in less Th(IV) absorption and more of U absorption.



this assumption is corroborated by the U(VI) recovery of only 52% (Table 9 Run 3) in effluent as compared to 58% in other column runs, without the Dowex 50 resin capsule. Results of increased flow rate and washing are presented in Table 9. These results indicate high Th(IV) amount in effluent which may be due to insufficient time of contact between influent and resin. Run 5 (Table 10) data suggests that Tulsion T-42 is a better resin for the separation of U from Th, as it gives recovery of U better than 92%, with Th contamination of 0.1% only.

## 10 CONCLUSION

Present studies indicate that it is possible to separate U(VI) from Th(IV) using these two macroporous cation exchange resins. Out of the two resins studied, Tulsion T-42 appears to be superior to Amberlyst-15 for the above purpose. Under the same conditions Tulsion T-42 gave product U containing only 0.1% of Th as compared to the product U containing 1% Th given by Amberlyst-15. Loading and washing rates used in this work are much higher (120 ml/hr) than those used for gel type of resins<sup>(7)</sup> (~40 ml/hr). But the disadvantage of using more volume of wash to recover >90% U is more than compensated by the use of high flow rates of loading/washing. Part of the U(VI) remaining on the column along with bulk of Th(IV) can be eluted along with Th(IV) and can be recycled for subsequent recovery. It indicates that there is a definite advantage of high throughput of U purification with macroporous resins as compared to the usual gel type resins.

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Table 1

**Distribution Coefficient of Thorium at  
Varying HNO<sub>3</sub> Concentration  
Resin - Amberlyst-15 (16-50 mesh)  
Volume (aq.) - 20 ml**

| HNO <sub>3</sub><br>(M) | Wt. of<br>resin | Initial<br>aqueous<br>Conc.<br>of Th<br>(mg/ml) | Equili-<br>brium<br>aqueous<br>Conc.<br>of Th<br>(mg/ml) | Equili-<br>brium<br>Th Conc.<br>in Resin<br>(mg/g) | Distribution<br>coefficient<br>(Kd) | Mean<br>(Kd) |
|-------------------------|-----------------|---|--|--|-------------------------------------|--------------|
| 0.3                     | 0.09935         | 0.990   | 0.195  | 160.0  | 821                                 | 839          |
|                         | 0.09888         | 0.990   | 0.189  | 162.0  | 857                                 |              |
|                         | 0.10188         | 1.485   | 0.609  | 172.0  | 282                                 | 281          |
|                         | 0.10203         | 1.485   | 0.612  | 171.0  | 279                                 |              |
|                         | 0.10078         | 2.475   | 1.569  | 179.8  | 115                                 | 117          |
|                         | 0.10475         | 2.475   | 1.532  | 180.0  | 118                                 |              |
|                         | 0.10298         | 3.713   | 2.580  | 220.0  | 85                                  | 83           |
|                         | 0.10400         | 3.713   | 2.610  | 184.0  | 81                                  |              |
| 0.5                     | 0.10211         | 0.990   | 0.231  | 148.7  | 643                                 | 630          |
|                         | 0.10300         | 0.990   | 0.231  | 146.2  | 616                                 |              |
|                         | 0.10094         | 1.485   | 0.669  | 161.7  | 241                                 | 237          |
|                         | 0.10044         | 1.485   | 0.680  | 159.2  | 233                                 |              |
|                         | 0.10044         | 2.475   | 1.604  | 173.4  | 108                                 | 108          |
|                         | 0.10036         | 2.475   | 1.608  | 173.4  | 108                                 |              |
|                         | 0.10532         | 3.713   | 2.782  | 176.6  | 63                                  | 64           |
|                         | 0.10535         | 3.713   | 2.769  | 177.2  | 65                                  |              |
| 1.0                     | 0.10300         | 0.990   | 0.409  | 112.8  | 276                                 | 281          |
|                         | 0.10219         | 0.990   | 0.402  | 115.1  | 286                                 |              |
|                         | 0.10127         | 1.485   | 0.809  | 133.5  | 165                                 | 167          |
|                         | 0.09979         | 1.485   | 0.805  | 136.3  | 169                                 |              |
|                         | 0.09969         | 1.980   | 1.257  | 145.1  | 115                                 | 114          |
|                         | 0.10162         | 1.980   | 1.257  | 142.3  | 113                                 |              |
|                         | 0.09957         | 3.713   | 2.515  | 240.6  | 96                                  | 96           |
|                         | 0.10033         | 3.713   | 2.512  | 239.4  | 95                                  |              |

Table 2

**Distribution Coefficient of Uranium at  
Varying HNO<sub>3</sub> Concentration**

Resin - Amberlyst-15 (16-50 mesh)

Volume (aq.) - 20 ml

| HNO <sub>3</sub><br>(M) | Wt. of<br>resin | Initial<br>aqueous<br>Conc.<br>of U<br>(mg/ml) | Equili-<br>brium<br>aqueous<br>Conc.<br>of U<br>(mg/ml) | Equili-<br>brium<br>U Conc.<br>in Resin<br>(mg/g) | Distribution<br>coefficient |              |
|-------------------------|-----------------|--|---|---|-----------------------------|--------------|
|                         |                 |  |   |   | (Kd)                        | Mean<br>(Kd) |
| 0.3                     | 0.09910         | 0.472  | 0.138   | 67.4  | 488                         | 491          |
|                         | 0.09903         | 0.472  | 0.137   | 67.6  | 494                         |              |
|                         | 0.09964         | 0.945  | 0.396   | 110.0   | 278                         | 274          |
|                         | 0.09958         | 0.945  | 0.404   | 108.7   | 269                         |              |
|                         | 0.10226         | 1.574  | 0.855   | 140.6   | 164                         | 164          |
|                         | 0.10340         | 1.574  | 0.855   | 139.1   | 163                         |              |
| 0.5                     | 0.09932         | 0.472  | 0.219   | 50.9  | 233                         | 235          |
|                         | 0.09922         | 0.472  | 0.222   | 50.4  | 237                         |              |
|                         | 0.10152         | 0.945  | 0.526   | 82.5  | 157                         | 156          |
|                         | 0.10100         | 0.945  | 0.530   | 82.2  | 155                         |              |
|                         | 0.10134         | 1.574  | 1.008   | 111.7   | 111                         | 110          |
|                         | 0.10100         | 1.574  | 1.015   | 110.7   | 109                         |              |
| 1.0                     | 0.10040         | 0.472  | 0.317   | 30.7  | 96                          | 97           |
|                         | 0.10150         | 0.472  | 0.316   | 30.7  | 97                          |              |
|                         | 0.10058         | 0.945  | 0.689   | 50.9  | 74                          | 75           |
|                         | 0.10142         | 0.945  | 0.685   | 51.3  | 75                          |              |
|                         | 0.10060         | 1.574  | 1.211   | 72.2  | 60                          | 58           |
|                         | 0.10020         | 1.574  | 1.235   | 67.7  | 55                          |              |

**Distribution Coefficient of Thorium at  
Varying HNO<sub>3</sub> Concentration**

**Resin - Tulsion T-42 (16-50 mesh)**

**Volume (aq.) - 20 ml**

| HNO <sub>3</sub><br>(M) | Wt. of<br>resin<br><br>(g) | Initial<br>aqueous<br>Conc.<br>of Th<br><br>(mg/ml) | Equili-<br>brium<br>aqueous<br>Conc.<br>of Th<br><br>(mg/ml) | Equili-<br>brium<br>Th Conc.<br>in Resin<br><br>(mg/g) | Distribution<br>coefficient |              |
|-------------------------|----------------------------|---|--|--|-----------------------------|--------------|
|                         |                            |   |  |  | (Kd)                        | Mean<br>(Kd) |
| 0.3                     | 0.10094                    | 0.990   | 0.149  | 166.6  | 1118                        | 1114         |
|                         | 0.10087                    | 0.990   | 0.150  | 166.6  | 1110                        |              |
|                         | 0.10201                    | 1.485   | 0.585  | 176.4  | 302                         | 297          |
|                         | 0.10191                    | 1.485   | 0.597  | 174.3  | 292                         |              |
|                         | 0.09914                    | 2.475   | 1.582  | 180.1  | 114                         | 115          |
|                         | 0.10103                    | 2.475   | 1.564  | 180.3  | 115                         |              |
|                         | 0.09967                    | 3.713   | 2.710  | 201.3  | 74                          | 75           |
|                         | 0.10253                    | 3.713   | 2.686  | 200.3  | 75                          |              |
| 0.5                     | 0.09954                    | 0.990   | 0.254  | 147.9  | 582                         | 574          |
|                         | 0.09940                    | 0.990   | 0.260  | 146.9  | 565                         |              |
|                         | 0.10277                    | 1.485   | 0.651  | 162.3  | 249                         | 249          |
|                         | 0.10126                    | 1.485   | 0.658  | 162.3  | 248                         |              |
|                         | 0.10269                    | 2.475   | 1.594  | 171.6  | 108                         | 108          |
|                         | 0.10137                    | 2.475   | 1.599  | 172.8  | 108                         |              |
|                         | 0.10316                    | 3.713   | 2.778  | 181.3  | 65                          | 64           |
|                         | 0.10227                    | 3.713   | 2.817  | 175.2  | 62                          |              |
| 1.0                     | 0.10068                    | 0.990   | 0.448  | 107.7  | 240                         | 245          |
|                         | 0.10074                    | 0.990   | 0.439  | 109.4  | 249                         |              |
|                         | 0.09944                    | 1.485   | 0.885  | 120.7  | 136                         | 140          |
|                         | 0.09915                    | 1.485   | 0.869  | 124.3  | 143                         |              |
|                         | 0.10217                    | 2.475   | 1.747  | 142.5  | 82                          | 80           |
|                         | 0.10180                    | 2.475   | 1.769  | 138.7  | 78                          |              |
|                         | 0.10308                    | 3.713   | 2.946  | 148.8  | 51                          | 51           |
|                         | 0.10373                    | 3.713   | 2.941  | 148.8  | 51                          |              |

Table 4

## Distribution Coefficient of Uranium at

Varying HNO<sub>3</sub> Concentration

Resin - Tulsion T-42 (16-50 mesh)

Volume (aq.) - 20 ml

| HNO <sub>3</sub><br>(M) | Wt. of<br>resin<br><br>(g) | Initial<br>aqueous<br>Conc.<br>of U<br><br>(mg/ml) | Equili-<br>brium<br>aqueous<br>Conc.<br>of U<br><br>(mg/ml) | Equili-<br>brium<br>U Conc.<br>in Resin<br><br>(mg/g) | Distribution<br>coefficient |              |
|-------------------------|----------------------------|--|---|---|-----------------------------|--------------|
|                         |                            |  |   |   | (Kd)                        | Mean<br>(Kd) |
| 0.3                     | 0.10043                    | 0.630  | 0.296   | 66.5  | 225                         | 227          |
|                         | 0.10102                    | 0.630  | 0.292   | 66.9  | 229                         |              |
|                         | 0.10062                    | 0.945  | 0.492   | 90.0  | 183                         | 180          |
|                         | 0.10082                    | 0.945  | 0.499   | 88.5  | 177                         |              |
|                         | 0.10284                    | 1.574  | 0.941   | 123.1   | 131                         | 135          |
|                         | 0.10300                    | 1.574  | 0.921   | 126.8   | 138                         |              |
| 0.5                     | 0.10144                    | 0.630  | 0.398   | 45.7  | 115                         | 116          |
|                         | 0.10152                    | 0.630  | 0.395   | 46.3  | 117                         |              |
|                         | 0.10068                    | 0.945  | 0.640   | 60.6  | 95                          | 94           |
|                         | 0.10045                    | 0.945  | 0.645   | 59.7  | 93                          |              |
|                         | 0.10235                    | 1.574  | 1.131   | 86.6  | 77                          | 73           |
|                         | 0.10203                    | 1.574  | 1.165   | 80.2  | 69                          |              |
| 1.0                     | 0.09978                    | 0.630  | 0.532   | 19.6  | 37                          | 40           |
|                         | 0.10003                    | 0.630  | 0.520   | 22.0  | 42                          |              |
|                         | 0.10021                    | 0.945  | 0.797   | 29.5  | 37                          | 36           |
|                         | 0.09985                    | 0.945  | 0.807   | 27.6  | 34                          |              |
|                         | 0.10130                    | 1.574  | 1.351   | 44.5  | 33                          | 32           |
|                         | 0.10095                    | 1.574  | 1.356   | 41.4  | 30                          |              |

Table 5

Column Breakthrough Capacity for Thorium

Resin Vol : 10 ml

Column : 9.5 mm x 140 mm

Medium : 0.5 M HNO<sub>3</sub>

| Resin used   | Feed Composition |              | Flow Rate<br>(ml/hr) | Capacity for 10%<br>breakthrough of<br>Th (mg/ml of<br>resin) |
|--------------|------------------|--------------|----------------------|---|
|              | Th<br>(mg/ml)    | U<br>(mg/ml) |                      |   |
| Amberlyst-15 | 1.01             | -            | 120                  | 65  |
|              | 1.01             | 1.02         | 120                  | 65  |
|              | 2.02             | 1.02         | 120                  | 58  |
| Tulsion T-42 | 1.01             | -            | 120                  | 76  |
|              | 1.01             | 1.02         | 120                  | 74  |
| Dowex 50 x 8 | 1.01             | -            | 120                  | 91  |
|              | 1.01             | 1.02         | 120                  | 91  |



Table 6

## Determination of Decontamination Factor of Uranium from Thorium

Resin : Amberlyst-15; Resin Volume : 10 ml; Column : 9.5 x 140 mm;  
 Flow rate : 5 minute/bed volume; Medium : 0.5 M HNO<sub>3</sub>;  
 Initial Th : U ratio (r<sub>1</sub>) = 0.994

| Column volumes | Volume (ml) | U (ng/ml) | Th (μg/ml) | Cumulative U (mg) | Cumulative Th (μg) | r <sub>2</sub> = $\frac{\text{Th}}{\text{U}}$ | DF = $\frac{r_1}{r_2}$ | % Th in U |
|----------------|-------------|-----------|------------|-------------------|--------------------|---|------------------------|-----------|
| 1-44           | 440         | 0.424     | 1.54       | 186.54            | 677.6              | 3.6 x 10 <sup>-3</sup>                        | 276                    | 0.36      |
| 45-49          | 50          | 1.296     | 2.14       | 251.33            | 784.6              | 3.12 x 10 <sup>-3</sup>                       | 319                    | 0.31      |
| 50-54          | 50          | 1.494     | 4.89       | 326.06            | 1029.1             | 3.15 x 10 <sup>-3</sup>                       | 315                    | 0.32      |
| 55-59          | 50          | 1.592     | 22.76      | 405.66            | 2167.1             | 5.34 x 10 <sup>-3</sup>                       | 186                    | 0.53      |
| 60-64          | 50          | 1.612     | 54.95      | 486.26            | 4914.6             | 10.10 x 10 <sup>-3</sup>                      | 98                     | 1.01      |
| 65-69          | 50          | 1.655     | 102.90     | 569.00            | 10059.6            | 17.68 x 10 <sup>-3</sup>                      | 56                     | 1.77      |
| 70-74          | 50          | 1.613     | 192.1      | 649.65            | 19664.6            | 30.27 x 10 <sup>-3</sup>                      | 33                     | 3.03      |
| 75-79          | 50          | 1.506     | 343.7      | 724.95            | 368849.6           | 50.83 x 10 <sup>-3</sup>                      | 20                     | 50.88     |

Table 7

Determination of Decontamination Factor of Uranium from Thorium

Resin : Amberlyst-15; Resin Volume : 10 ml; Column : 9.5 x 140 mm;  
 Flow rate : 5 minute/bed volume; Medium : 0.5 M HNO<sub>3</sub>;  
 Initial Th : U ratio (r<sub>1</sub>) = 1.98

| Column volumes | Volume (ml) | U (mg/ml) | Th (µg/ml) | Cumulative U (mg) | Cumulative Th (µg) | $r_2 = \frac{\text{Th}}{\text{U}}$ | $DF = \frac{r_1}{r_2}$ | % Th in U |
|----------------|-------------|-----------|------------|-------------------|--------------------|------------------------------------|------------------------|-----------|
| 1-20           | 200         | 0.107     | 1.75       | 21.5              | 350.0              | $16.28 \times 10^{-3}$             | 122                    | 1.63      |
| 21-25          | 50          | 0.726     | 26.82      | 57.77             | 1691.0             | $29.27 \times 10^{-3}$             | 68                     | 2.93      |
| 26-28          | 30          | 1.120     | 97.265     | 91.375            | 4608.8             | $50.44 \times 10^{-3}$             | 39                     | 5.04      |
| 29-31          | 30          | 1.344     | 195.3      | 131.71            | 10467.8            | $79.48 \times 10^{-3}$             | 25                     | 7.95      |
| 32-34          | 30          | 1.489     | 273.36     | 176.38            | 18668.6            | $105.84 \times 10^{-3}$            | 19                     | 10.58     |
| 35-37          | 30          | 1.564     | 581.18     | 223.30            | 36105.6            | $161.68 \times 10^{-3}$            | 12                     | 16.17     |
| 38-42          | 50          | 1.55      | 861.971    | 301.02            | 79202.5            | $263.10 \times 10^{-3}$            | 8                      | 26.31     |

Table 8

## Determination of Decontamination Factor of Uranium from Thorium

Resin : Tulsion T-42; Resin Volume : 10 ml; Column : 9.5 x 140 mm;  
 Flow rate : 5 minute/bed volume; Medium : 0.5 M HNO<sub>3</sub>;  
 Initial Th : U ratio (r<sub>1</sub>) = 0.995

| Column volumes | Volume (ml) | U (mg/ml) | Th (μg/ml) | Cumulative U (mg) | Cumulative Th (μg) | r <sub>2</sub> = $\frac{\text{Th}}{\text{U}}$ | DF = $\frac{r_1}{r_2}$ | % Th in U |
|----------------|-------------|-----------|------------|-------------------|--------------------|---|------------------------|-----------|
| 1-45           | 450         | 0.422     | 0.5        | 189.9             | 225.0              | $1.18 \times 10^{-3}$                         | 843                    | 0.11      |
| 46-55          | 50          | 1.177     | 1.19       | 307.6             | 344.0              | $1.12 \times 10^{-3}$                         | 888                    | 0.11      |
| 56-60          | 50          | 1.298     | 6.45       | 372.5             | 666.5              | $1.79 \times 10^{-3}$                         | 556                    | 0.18      |
| 61-65          | 50          | 1.344     | 15.65      | 439.7             | 1449.0             | $3.29 \times 10^{-3}$                         | 302                    | 0.33      |
| 66-70          | 50          | 1.381     | 37.08      | 508.7             | 3303.0             | $6.49 \times 10^{-3}$                         | 153                    | 0.64      |
| 71-75          | 50          | 1.400     | 64.39      | 578.7             | 6522.5             | $11.27 \times 10^{-3}$                        | 88                     | 1.13      |

Table 9

## Separation of Uranium from Thorium

Column : 9.5 x 140 mm; Flow Rate : 5 min/bed volume or  
2 min/bed volume

Feed Composition U - 1.02 mg/ml, Th - 1.01 mg/ml

Medium : 0.5 M HNO<sub>3</sub>;

Resin : AMBERLYST-15; Resin Volume : 10 ml

| Run No.                      | Feed vol. (ml) | Wash     |           | U Recovery(%) |         |            | Th Contamination (%) |
|------------------------------|----------------|----------|-----------|---------------|---------|------------|----------------------|
|                              |                | Molarity | Vol. (ml) | In effluent   | In wash | Cumulative |                      |
| FLOW RATE : 5 min/bed volume |                |          |           |               |         |            |                      |
| 1.A                          | 550            | 0.5      | 100       | 57.9          | 16.3    | 74.2       | 0.43                 |
| B                            | 550            | 1.0      | 100       | 58.4          | 27.7    | 86.1       | 4.58                 |
| C                            | 550            | 2.0      | 100       | 58.3          | 35.0    | 93.3       | 22.5                 |
| 2.A                          | 550            | 0.5      | 100       | 59.1          | 16.5    | 75.6       | 0.45                 |
|                              |                | 0.5      | 100       | -             | 6.8     | 82.4       | 0.54                 |
|                              |                | 0.5      | 100       | -             | 3.8     | 86.2       | 0.67                 |
|                              |                | 0.5      | 100       | -             | 2.8     | 89.0       | 0.94                 |
|                              |                | 0.5      | 100       | -             | 2.6     | 91.6       | 1.00                 |
| B                            | 450            | 0.5      | 100       | 41.6          | 18.2    | 59.8       | 0.27                 |
|                              |                | 0.5      | 100       | -             | 9.9     | 69.7       | 0.26                 |
|                              |                | 0.5      | 100       | -             | 6.6     | 76.3       | 0.27                 |
|                              |                | 0.5      | 100       | -             | 4.7     | 81.0       | 0.27                 |
|                              |                | 0.5      | 100       | -             | 3.9     | 84.9       | 0.27                 |
|                              |                | 0.5      | 200       | -             | 5.5     | 90.4       | 0.28                 |
| 3.A                          | 550            | 0.5      | 500       | 52.5          | 39.0    | 91.5       | 0.32                 |
| B                            | 550            | 1.0      | 300       | 51.2          | 42.7    | 93.9       | 3.85                 |
| FLOW RATE : 2 min/bed volume |                |          |           |               |         |            |                      |
| 4.                           | 550            | 0.5      | 500       | 68.5          | 21.5    | 90.0       | 9.31                 |

Table 10

**Separation of Uranium from Thorium**

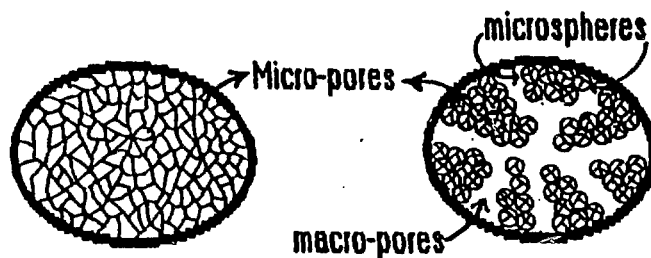
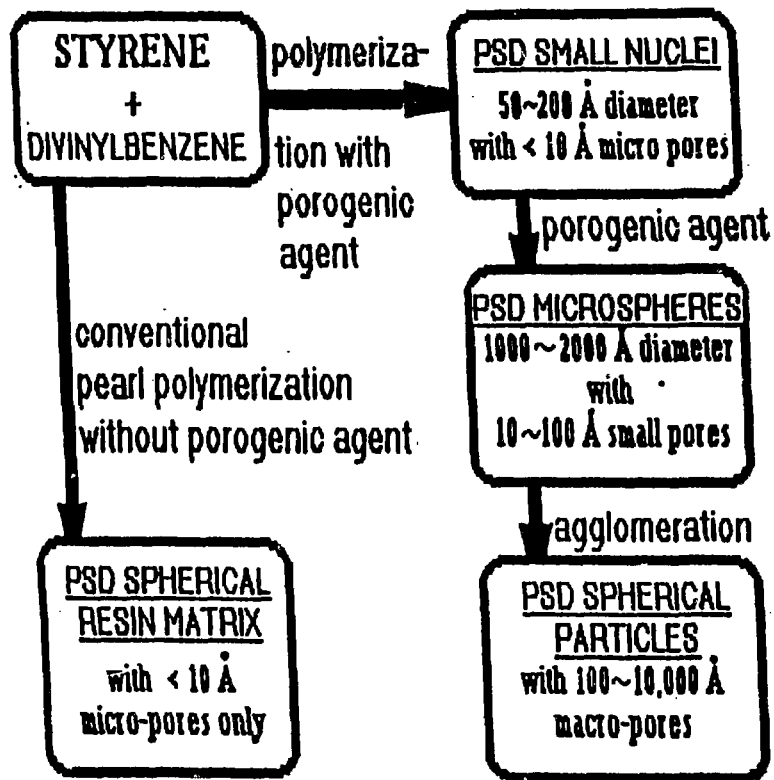
Column : 9.5 x 140 mm; Flow Rate : 5 min/bed volume

Feed Composition U - 1.02 mg/ml, Th - 1.01 mg/ml

Medium : 0.5 M HNO<sub>3</sub>;

Resin : TULSION T-42; Resin Volume : 10 ml

| Run No. | Feed vol. (ml) | Wash       |           | U Recovery(%) |         |              | Th Contamination (%) |
|---------|----------------|------------|-----------|---------------|---------|--------------|----------------------|
|         |                | Mola- rity | Vol. (ml) | In effluent   | In wash | Cumu- lative |                      |
| (i)     | 550            | 0.5        | 500       | 52.7          | 39.8    | 92.5         | 0.1                  |
| (ii)    | 550            | 0.5        | 500       | 55.1          | 36.7    | 91.8         | 0.1                  |



GEL-TYPE RESIN

MR-TYPE RESIN

**Fig. 1. Formation and Structure of Gel-Type<sup>(16)</sup>  
And Macroreticular Resins .**

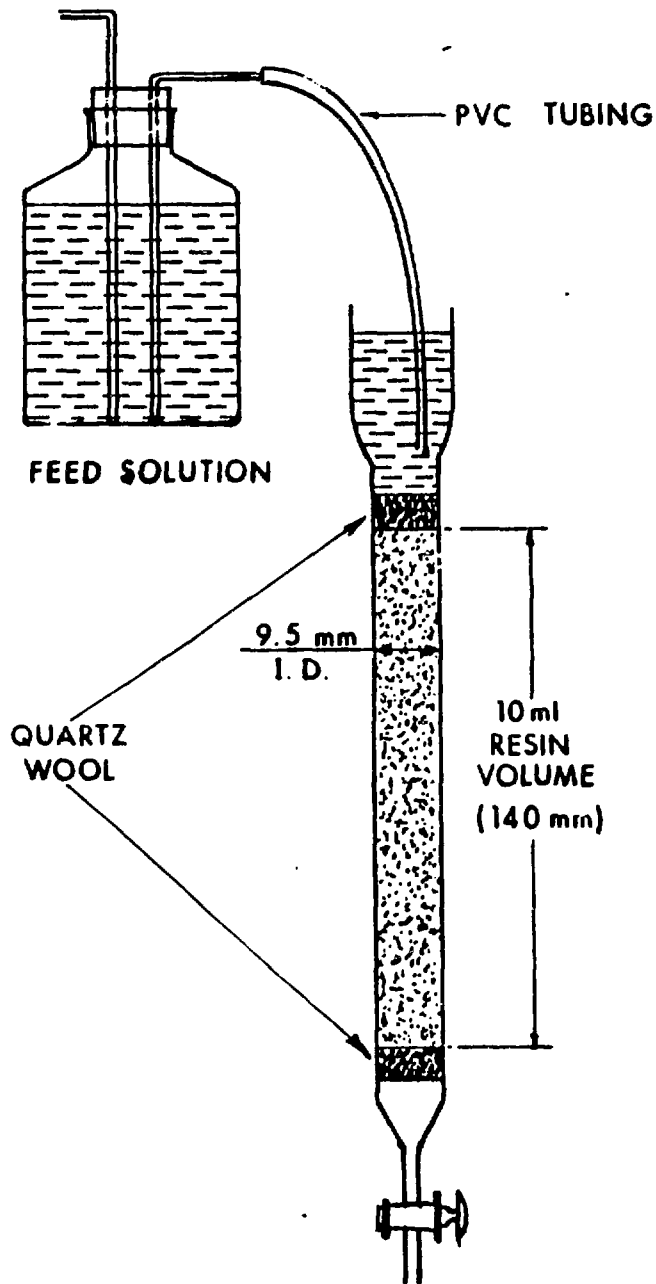


FIG. - 2. ION EXCHANGE COLUMN.

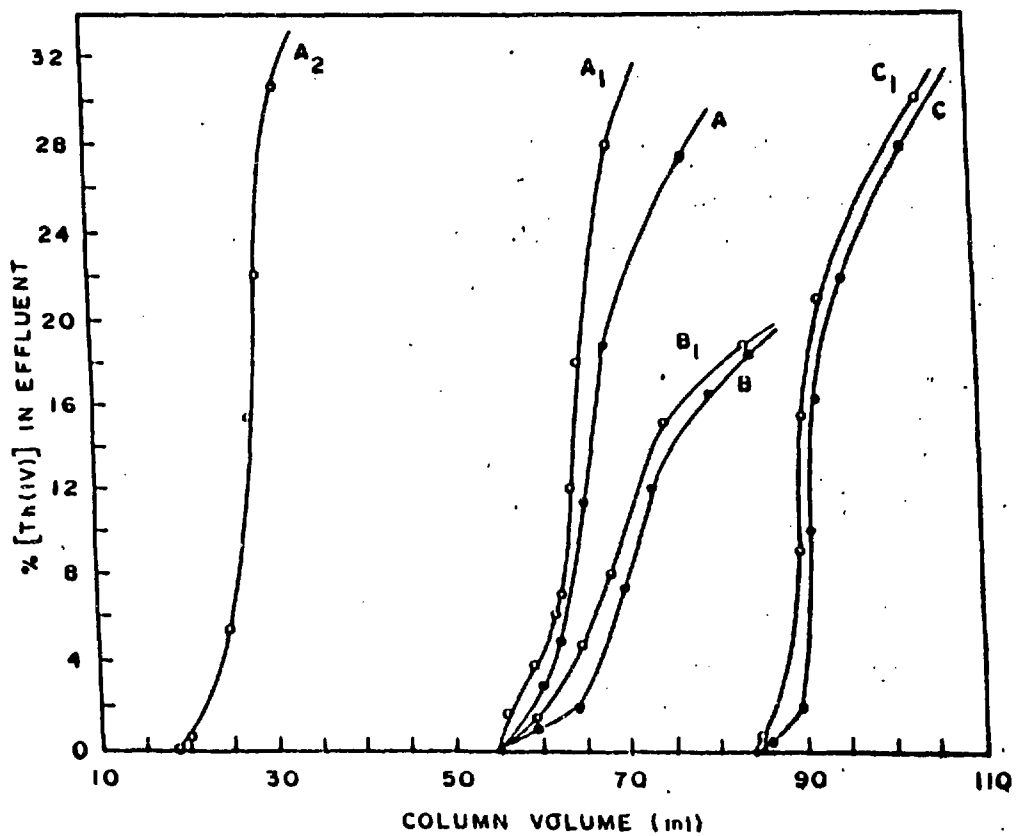


FIG. 3 BREAKTHROUGH CURVES:

Amberlyst-15 : A - Th alone, A<sub>1</sub> - Th:U = 1:1, A<sub>2</sub> - Th:U = 2:1  
 Tulsion T-42 : B - Th alone, B<sub>1</sub> - Th:U = 1:1  
 Dowex 50 x 8 : C - Th alone, C<sub>1</sub> - Th:U = 1:1



