SEPARATION OF URANIUM AND THORIUM FROM ORGANIC TBP SOLUTIONS BY CITRATE FORM ANION EXCHANGE RESIN

by 1264

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NOMENCLATURE

acceleration due to gravity	g
angström	Å
centimeter	cm
degrees Centigrade	^{o}C
electron volt	eV
gel liquid extraction	GLX
gram	g
height equivalent to a theoretical plate	H.E.T.P.
liter	l
milli	m
milligram	mg
milliliter	ml
millimeter	mm
millimicron	mμ
molar	*M*
normal	*N*
thorium	Th
tri-n-butyl phosphate	TBP
uranium	U

INTRODUCTION

The development of thermal power reactors has forced chemists and chemical engineers to develop means of obtaining and purifying chemical substances that were no more than scientific curiosities a few years ago.[1] Uranium has become an important source of energy and thorium is of interest as a breeder fuel. However, the fuel may be used for only a fraction of its useful life before the buildup of fission products makes the purification and recovery of the fuel necessary.

The Thorex Process is the basic process used in the reprocessing of uranium--thorium fuel elements. The fuel elements are dissolved in nitric acid. The feed solution is then contacted with tri-n-butyl phosphate (TBP) solution in a solvent extraction process. The separated and purified uranium is then concentrated by sorption on a cation exchange resin.

Small[2] developed a process he called "gel liquid extraction" (GLX). This process consists of contacting ion-exchange resins with organic instead of aqueous solutions in metal extraction. Nayak[3] followed Small's[4] general scheme for metal separation--first loading a solution of the metallic species in the organic solvent through a bed of aqueous gel, then eluting to obtain a separation of the sorbed species. However,

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[1]M. Benedict and T. H. Pigford, "Nuclear Chemical Engineering," McGraw-Hill Book Company, Inc., New York, 1957, p vii.

[2]H. Small, *J. Inorg, Nucl. Chem.*, 18, 232 (1961).

[3]M. N. Nayak, M.S. Thesis, Kansas State University, Manhattan, Kan., 1967.

[4]H. Small, *J. Inorg. Nucl. Chem.*, 19, 160 (1961).

Nayak used TBP with kerosene as the organic solvent instead of the TBP with perchloroethylene or TBP with toluene solutions Small used. Small[5] investigated a system that had the water swollen gel able to supply cations capable of exchanging with the metal ions in the organic phase. Nayak used a citrate form of an anionic exchange resin, Dowex 2-X8, instead of a cationic exchange resin.

Nayak studied the separation of uranium and thorium from 30% TBP--kerosene solution at a 21 millimolar total metal concentration. He also studied the effect of the uranium concentration in the TBP solution on the amount of uranium sorbed on the ion-exchange resin. This thesis is a study of the separation of uranium and thorium from 30% TBP--kerosene solution at a 40 millimolar total metal concentration and checks and extends the uranium concentration study.

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[5] *Ibid.*

TBP CHEMISTRY

Because of TBP's desirable properties, it is the extractant most often used in the United States[6] in solvent extraction of nuclear materials. TBP is a commercial plasticizer and is readily obtainable in large quantities, has a high flash point, is chemically stable with respect to concentrated nitric acid, and is only slightly miscible with water. The extracting power is so high that TBP's undesirable properties, high viscosity and a density similar to water, may be improved by diluting with other organic liquids which normally do not dissolve uranium.[7]

TBP - $(C_4H_9)_3PO_4$ - is a complexing agent[8] for the nitrate salts of the actinides. The nitrate complexes occur only as the neutral, unionized molecule, unhydrated, but with a definite number of TBP molecules. McKay[9] gives the formulas of typical complexes as:

$$M(NO_3)_3 \cdot 3TBP$$

$$M(NO_3)_4 \cdot 2TBP$$

$$MO_2(NO_3)_2 \cdot 2TBP$$

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[6]S. Peterson and R. G. Wymer, "Chemistry in Nuclear Technology," Addison-Wesley Publishing Company, Inc., Reading, Mass., 1963, p 159.

[7]H. A. C. McKay, "Tri-n-butyl Phosphate as an Extracting Agent for the Nitrates of the Actinide Elements," *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy*, United Nations, New York, N. Y., 1956, Vol. 7, p 314.

[8]B. Goldschmidt, P. Regnaut, and I. Prevot, "Solvent Extraction of Plutonium from Uranium Irradiated in Atomic Piles," *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy*, United Nations, New York, N. Y., 1956, Vol. 9, p 493.

[9]McKay, p 314.

Uranyl nitrate has the formula $UO_2(NO_3)_2 \cdot 6H_2O$, so it complexes with two molecules of TBP. Thorium nitrate has the formula $Th(NO_3)_4 \cdot 4H_2O$ and also complexes with two molecules of TBP. However, uranium and thorium are not the only elements whose nitrates complex with TBP. The fission products, particularly zirconium, niobium, ruthenium, and the rare earths, form extractable TBP complexes. Fission product decontamination is effected by prevention of the formation of the fission product--TBP complexes. This is achieved by using an acid deficient solution as the feed to the solvent extraction process.

THE THOREX PROCESS

Solvent extraction is the primary unit operation of the Thorex Process, as Figure 1 shows. Thorium and uranium are extracted into the organic phase by the formation of their TBP complexes in column I. A salting agent is present in both feed and scrub solutions to column I to increase the distribution coefficients of uranium and thorium. Benedict and Pigford[10] and Peterson and Wymer[11] list aluminum nitrate as the salting agent.

> However, the choice of a salting agent for a particular extraction-separation process depends on more than its salting strength (and its cost). The salting agent leaves the separation process with the highly radioactive fission-product wastes. Thus if a metal nitrate is used as a salting agent, its solubility limits the reduction in volume attainable by evaporation of the waste before storage. If nitric acid is used, it can be evaporated from the wastes and recovered for reuse. Also, the volume of highly radio-active waste to be stored is much less. Nitric acid, therefore, is the preferred salting agent when it is chemically unreactive with the solvent.[12]

Thorium enters the aqueous phase in column II and uranium enters the aqueous phase in column III. The thorium product may be concentrated by either evaporation or ion exchange; however, the uranium product is usually concentrated by sorption on a cation exchange resin, as shown in Figure 1.

The main disadvantage of the Thorex Process is TBP loss through emulsification and entrainment. TBP also is lost by decomposition due

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[10]Benedict and Pigford, p 339.

[11]Peterson and Wymer, p 238.

[12]*Ibid.*, p 159.

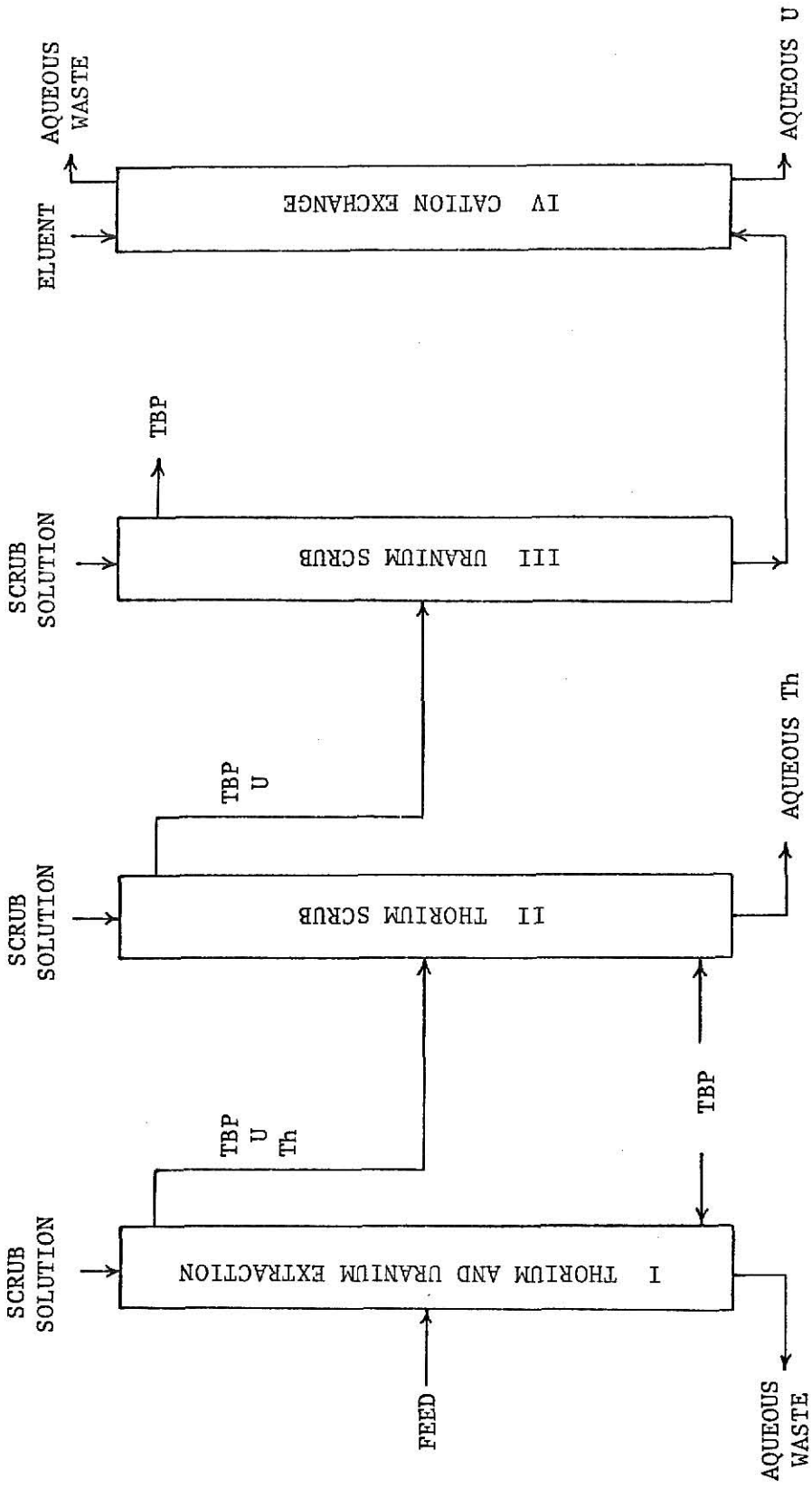

Figure 1. Thorex Process Flow Diagram

to radiation and hydrolysis. The mono and dibutyl phosphates formed during decomposition significantly increase the fission product extraction.[13] Therefore, the solvent must be washed before reuse, first with a sodium carbonate solution and then with dilute nitric acid.

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[13]F. R. Bruce, "Solvent Extraction Chemistry of the Fission Products," *Proceedings of the International Conference on the Peaceful Uses of Atomic Energy*, United Nations, New York, N. Y., 1956, Vol. 7, p 107.

THE GLX PROCESS

Copolymers of polystyrene-divinylbenzene swell in water and in several organic solvents forming a gel-like mass. Small investigated the suitability of both TBP swollen and water swollen gels for several separations in a process known as gel liquid extraction (GLX). The GLX process was found to be efficient due to the low height-equivalent-to-a-theoretical-plate (H.E.T.P.) values that are possible with ion exchange resins.

Small[14] initially studied TBP swollen gels and found that they were hydrophobic. He solved this problem by sulphonation of the resin beads. The sulphonated gels were then evaluated by measuring the gel's capacity to extract aqueous uranyl nitrate. Small then studied the separation of ferric nitrate from uranyl nitrate, thorium nitrate from yttrium nitrate, and uranyl nitrate from thorium nitrate by these gels. In later work, Small[15] reversed the organic and aqueous phases and used water swollen resin as the gel. However, he found that the thin film of water around the resin beads prevented efficient phase contact.

This experimentor used water swollen resin as the gel, but the resin was washed with pure 30% TBP solution to remove the water film before introducing the organic phase containing the metallic species.

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[14]Small, 18.

[15]Small, 19.

SYSTEM SELECTED FOR STUDY

Uranium and thorium both show a strong tendency to form complex compounds with the anions of nitrate, sulphate, fluoride, and chloride salts and with the anions of organic oxyacids such as oxalate, tartrate, and citrate. While both uranium and thorium can be recovered from the organic phase by the anionic complex formation, many other metal ions do not form such complexes and may be eliminated. Nayak determined that the citrate ion was the best choice for the complexing ion. However, since sodium citrate and citric acid are insoluble in TBP, he was forced to incorporate the citrate ion in the strong base anion exchange resin chosen, Dowex 2-X8. The resin properties are given in Appendix A.

While complex formation rarely occurs in the resin phase, uranium is believed to form anionic complexes in the resin. For example, when aqueous uranium is contacted with a sulphate form anion exchange resin, the uranyl ions are adsorbed from the solution by the formation of anionic sulphate complexes.

$$UO_2(SO_4) + SO_4^{-2}(\text{resin}) \rightleftharpoons UO_2(SO_4)_2^{-2}(\text{resin})$$

No similar example is known to exist for thorium.

Nayak hoped to prove that the GLX Process could be used to modify the Thorex Process. He stated that the TBP solution used in the Thorex Process was between 30% and 40% TBP in kerosene and chose to study the GLX Process using 30% TBP--kerosene solutions. According to Peterson and Wymer, the Thorex Process[16] uses a 42.5% TBP--kerosene solution and

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[16]Peterson and Wymer, p 238.

it is the Purex Process[17] that used 30% TBP--kerosene solutions. Since part of this work was to check Nayak's work, in particular the data given in Table I and the curve of Figure 2, 30% TBP in kerosene was again used as the organic phase.

[17] *Ibid.*, p 234.

CHEMICAL ANALYSIS

Nayak tried several methods for the determination of uranium and thorium before deciding to use gravimetric methods. Among the methods tried was spectrophotometric analysis. However, Nayak had access only to the Beckman DU Spectrophotometer Model 2400. The present work also had access to the EEL Model 140 Atomic Absorption Spectrophotometer and the Cary Model 14 Recording Spectrophotometer. Thorium solutions are clear if a coloring agent such as thorin (*p*-arsonic acid) is not present, but uranium solutions are yellow without coloring agents. Nayak tried adding the indicators thorin to thorium solutions and thiocyanate to uranium solutions but found that uranium may be determined directly by spectrophotometric analysis. However, Nayak felt that gravimetric methods were more precise.

The Cary Recording Spectrophotometer was used to check for absorbance peaks for both uranium and thorium. In scanning from 8000 Å to 3000 Å, it was found that uranium had a peak at 4150 Å in both aqueous and organic media. Aqueous thorium has no absorbance peaks in this range without the addition of coloring agents such as thorin. The Cary may lessen the work load of future investigators by enabling them to determine directly the amount of uranium sorbed from the uranium-TBP solution by scanning the organic solution.

Atomic Absorption

Atomic absorption was one of the methods tried in the search for a fast, easy way to determine uranium and thorium concentrations. However, it proved impractical. Atomic absorption spectroscopy was introduced by

Walsh[18] in 1955. It is one of the most sensitive analytical methods known since atomic absorption is based on the measurement of the amount of light of characteristic wavelength absorbed by ground state atoms. Although a flame is used to produce the atomic vapor, less than one per cent of the atoms are excited.

The equipment used was made by Evans Electroselenium Limited (EEL) of Halstead, England. It consisted of an EEL Model 140 spectrophotometer equipped with a nitrous oxide burner. A nitrous oxide--acetylene flame was used, along with neon filled hollow cathode reference lamps. The lamps were EEL type 22826 for uranium and EEL type 23028 for thorium.

There are two basic problems in the determination of uranium and thorium by atomic absorption spectroscopy. The monoxide dissociation energy of thorium is 8.7 eV[19] and the energy provided by the nitrous oxide--acetylene flame has an upper limit of 7.7 to 7.9 eV. Therefore, thorium cannot be determined by this method. However, uranium,with a monoxide dissociation energy of 7.8 eV, can be determined under the correct conditions, although it is difficult to achieve the proper conditions. The variables include the wavelength of the light, the source of the light, the fuel for the flame, the type of burner, the flame height, the degree of ionization, and the myriad variables introduced by the electronics and instrumentation. In short, the determination of uranium by atomic absorption spectroscopy "involves physics, chemistry, and voodoo, the latter playing the most important role."[20]

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[18]A. Walsh, *Spectrochim. Acta*, 7, 108 (1955).

[19]V. A. Fassel and D. W. Golightly, *Anal. Chem.*, 39, 446 (1967).

The EEL Model 140 was not designed as a research tool but rather as a reliable instrument for use in the routine analysis of the elements, such as magnesium, most easily analyzed by atomic absorption spectroscopy. Uranium could not be detected by atomic absorption spectroscopy due to the spectrophotometer's built-in lack of sensitivity and adaptability.

Uranium Determination

Uranium was determined by spectrophotometric analysis with the Beckman DU Spectrophotometer Model 2400. It was felt that it was possible to obtain accurate concentration determinations with at least the degree of precision Nayak reported. This, of course, depends on the accuracy and precision of the concentration curve. Dr. Walter Mayer made a standard solution of 0.10107 molar uranium in 0.1 normal nitric acid in 1967. The standard solution was made from a National Bureau of Standards standard sample, 950a, of uranium oxide (U_3O_8). This standard solution was used to produce a set of secondary solutions so that a concentration curve could be obtained.

The spectrophotometer was physically moved several times, each move making a new concentration curve mandatory. In addition, several concentration curves were made in the laboratory course - Nuclear Fuel Processing, NE 708. This work consumed part of the original standard and several of the secondary standards. However, new "standards" had been prepared by using the DU Spectrophotometer. A new concentration curve, Figure 11 in Appendix B, was made using the varied assortment of

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[20]J. W. Robinson, "Atomic Absorption Spectroscopy," Marcel Dekker, New York, N. Y., 1966, p 1.

standard solutions after the location of the DU Spectrophotometer had been fixed and the instrument was again operating. A detailed account of the method used for the uranium determination is given in Appendix B.

Thorium Determination

Nayak used a gravimetric method for the thorium determination; however, the fluoride method used by Nayak was not considered because of the possibility of interference by U(IV). The methods considered were those involving benzoic acid, *m*-cresoxyacetic acid, *p*-aminosalicylic acid, pyridine, fumaric acid, picrolinic acid, benzenephosphonic acid, hydroxylamine hydrochloride, and *m*-nitrobenzoic acid. The *m*-nitrobenzoic acid method was chosen because Ryabchikov said, "the method can be used for the estimation of milligram quantities of thorium in the presence of large quantities of uranium."[21] Ryabchikov also indicated that the nitrates of U(IV) are not precipitated and that about 98.5% of the thorium can be precipitated by this method. Indeed, thorin indicator showed that no thorium was present in the mother liquor after precipitation. A detailed account of the method used for the thorium determination is given in Appendix C.

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[21]D. I. Ryabchikov and E. K. Gol'braikh, "The Analytical Chemistry of Thorium," The Macmillan Company, New York, N. Y., 1963, p 38.

PROCEDURE

The first step in any work with ion exchange resins is placing the resin in the proper ionic form. The Dowex 2-X8 resin was supplied in chloride form and was converted to citrate form by simple ion exchange. A one-inch diameter glass column two feet long was two-thirds filled with chloride form resin. The resin was then washed with a two weight per cent solution of sodium citrate at a rate of less than 2 cm^3 per minute until the effluent showed no precipitate (silver chloride) when tested with silver nitrate. The resin was then washed several times with distilled water and stored under water. The resin was converted to citrate form two years before the actual experimentation began. Nine months before the resin was used, it was again washed with the sodium citrate solution to remove any chloride ions that had migrated out of the interior of the resin beads. This resin is called "unregenerated" resin.

The unregenerated resin was used in equilibrium experiments to determine the effect of uranium concentration in the uranium-TBP solution on the amount of uranium sorbed by the resin. The results, Figure 4 and Table II, were higher than those reported by Nayak, Figure 2 and Table I. It was decided to "regenerate" the resin and rerun the experiments. The regeneration was completed by placing the unregenerated resin in the glass column and slowly washing it with two liters of two weight per cent sodium chloride solution. The resin was then washed with two weight per cent sodium citrate solution until the resin was again in citrate form. Experimentation was postponed until all of the resin was regenerated to prevent inconsistancies in the data that might be caused by different levels of citrate ion concentration in the various batches of

TABLE I

Effect of TBP Solution Concentration on the Amount of Uranium Sorbed*

Weight of Wet Resin Used	Total Uranium Molarity in TBP Solution	Uranium Estimated in the Eluent mg/g Dry Resin		Uranium Estimated in Wash mg/g Dry Resin	
		Analysis I	Analysis II	Analysis I	Analysis II
4.96	10.5 mmolar	31.3	29.1	-	77
4.27	21 mmolar	30.7	29.8	-	100
5.14	42 mmolar	43.2	43.1	-	108

*M. N. Nayak, M.S. Thesis, Kansas State University, Manhattan, Kan., 1967, p 63.

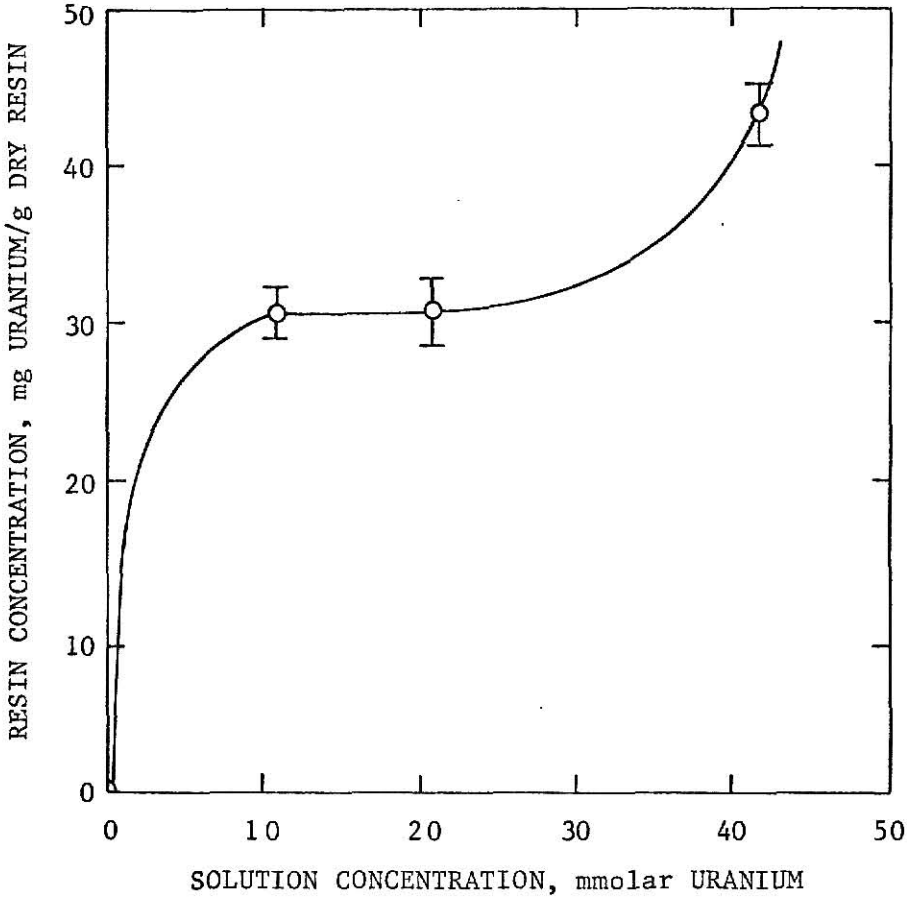

Figure 2. Effect of TBP Solution Concentration on the Amount of Uranium Sorbed*

*N. M. Nayak, M.S. Thesis, Kansas State University, Manhattan, Kan. 1967, p 28.

regenerated resin. The regenerated resin was the only resin used in the remainder of the experiments.

The second step in work with ion exchange resins is establishing a basis for reporting results. Since the data were to be reported on a dry resin basis, the weight ratio of dry to wet resin was determined. Seven to nine grams of citrate form resin (unregenerated) was washed into a cell. The cells are two centimeter diameter pyrex tubes about nine centimeters long with the walls collapsed around a stainless steel screen about two centimeters from the bottom of the cells as shown in Figure 3. The resin was shaken free of as much water as possible before placing the cells in a centrifuge which produces "approximately 300 g's."[22] The centrifuge was turned off and allowed to run down when a ten minute timer rang. The resin was shaken into preweighed weighting bottles and placed in a desiccator for transportation to the balance. The wet, centrifuged resin and weighting bottles were then weighed to determine the weight of the wet resin.

The resin was placed in an oven set at 102°C. The resin was removed from the oven after 24 hours and placed in the desiccator to cool for 30 minutes before weighing. The dry resin was returned to the oven after weighing and reweighed on the third and the sixth days after centrifugation. The resin did not reach a constant weight but continued to lose weight as the resin deteriorated. The dry weights obtained on the third day were used in the calculation of the dry to wet resin weight ratio. Four resin samples gave an average ratio of .5707 with an average

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[22]Nayak, p 23.

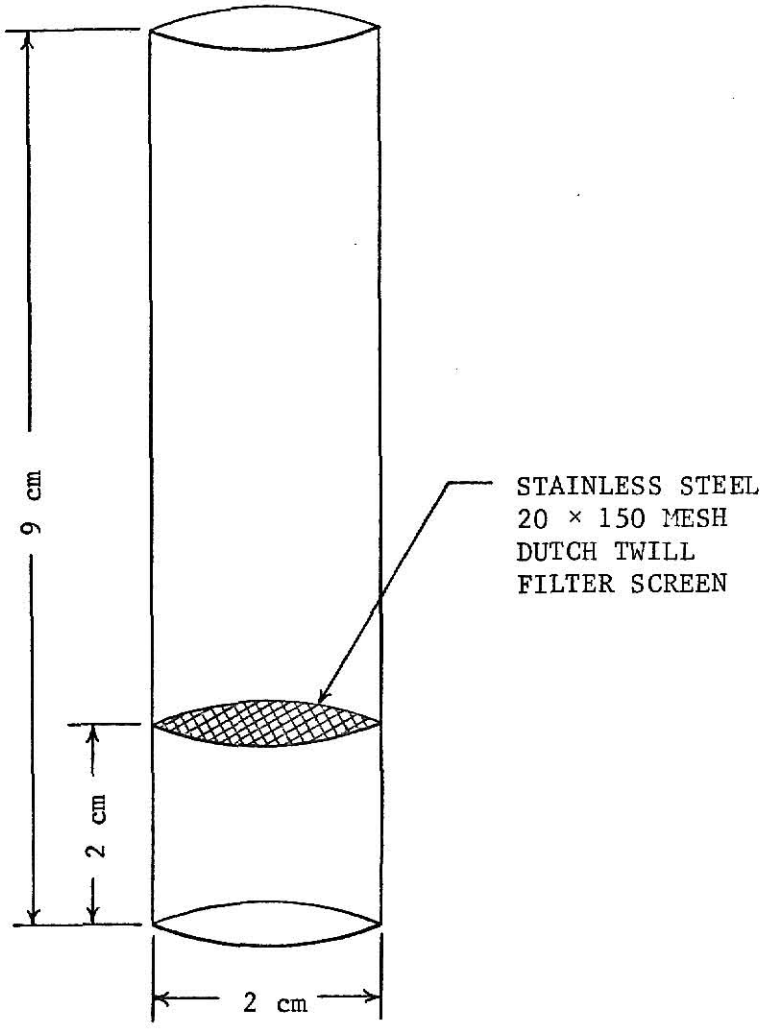

Figure 3. Equilibrium Cell

deviation of 0.45%. However, it was found that if the above procedure was not done quickly, the centrifuged resin would absorb water from the atmosphere and produce large deviations beweeen essentially identical samples.

The resin was centrifuged and weighed before it was washed into a clean cell for the experiments. The excess water was again shaken out and the resin centrifuged for about a minute. The cell was removed from the centrifuge and a rubber stopper was placed in the top of the cell. The cell was then inverted and the cell bottom filled with pure 30% TBP solution. A rubber stopper containing a stopcock was placed in the cell bottom and the air bubbles were worked out. The top of the cell was then filled with pure 30% TBP solution and the resin bed was stirred with a wire to remove the air bubbles. The cell was then connected to the 500 ml separatory funnel used as the solution reservoir. After removing any bubbles in the connection, the resin was washed with pure 30% TBP solution to remove the film of water around the resin beads. Water turns the TBP solution cloudy white.

Concentrated uranium- and thorium-TBP solutions were diluted to make up 500 ml of the desired molarity solution. The resin was again washed with pure 30% TBP solution before passing the 500 ml of uranium-thorium-TBP solution through the resin bed in six to seven hours. However, the flow rate slowed down as the resin swelled and often stopped during the night.

The concentrated uranium- and thorium-TBP solutions were made by contacting the pure 30% TBP solution with 0.1*N* HNO_3 uranium and thorium solutions of known concentrations. The concentrations of the aqueous

solutions were determined again after contact with the TBP solution. The uranium or thorium concentration in the TBP solution was then determined by measuring the volume of the aqueous and organic solutions. The aqueous and organic phases were contacted by shaking in a separatory funnel for one minute every ten minutes for a total contact time of thirty minutes. The concentrated uranium- and thorium-TBP solutions could then be diluted with the pure 30% TBP solution to obtain the desired uranium and thorium concentrations.

The apparatus was disconnected after the uranium-thorium-TBP solution had completely passed through the resin bed. A precipitate formed in the resin bed during this loading process. The cell with the resin was centrifuged for ten minutes to remove the interstitial organic solution. The remainder of the apparatus was rinsed free of the organic and thoroughly washed. The resin was then washed with distilled water to remove the uranium-thorium precipitate from the resin bed. The rubber stopper with the stopcock was used to regulate the water flow while the resin was stirred with a wire to dislodge all of the precipitate. After the precipitate was washed from the resin, the precipitate was vacuum filtered from the wash solution and dissolved in nitric acid.

The apparatus was assembled as before but with distilled water instead of the 30% TBP solution. Nayak found that 500 ml of 0.5 normal nitric acid (pH = 0.3) was sufficient to strip the uranium and thorium from the resin. Therefore, 500 ml of 0.5*N* HNO_3 were passed through the resin bed in four to five hours. The nitric acid was followed by 200 to 300 ml of distilled water if thorium was present. The wash solution was added to the eluent and the solution was evaporated to a volume of less

than 250 ml. The uranium and thorium content of both the wash and eluent and the precipitate solutions was then determined.

RESULTS

The experimental work consisted of: first, passing a uranium-thorium-TBP solution past water swollen citrate form anion exchange resin; second, washing precipitate from the resin bed; third, eluting the remaining metal from the resin. Then the amount of uranium and thorium sorbed on the resin was determined. The experimental work may be divided into two main sections: The experiments that involved uranium-TBP solutions only and the experiments that involved both uranium- and thorium-TBP solutions.

Uranium-TBP

Nayak[23] attempted "to determine the equilibrium amount of uranium adsorbed by the citrate type of resin from a 30 volume percent TBP Solution containing various concentrations of $UO_2(NO_3)_2$." His results are given in Figure 2 and Table I. It was decided to check his work because of the unusual curve (Figure 2) obtained from only three data points. Further study would also aid in understanding the mechanism involved. If the process of invasion[24] occurs, any undissociated electrolyte or complex present in the solution may be sorbed by the resin. The resin is merely acting like a sponge if the sorption process is absorption. However, if a specific attractive force exists between the sorbed species and the resin, the sorption process is physical adsorption or ion exclusion. The unregenerated resin produced the data shown in Figure 4 and

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[23]Nayak, p 27.

[24]F. Helfferich, "Ion Exchange," McGraw-Hill Book Company, Inc., New York, N. Y., 1962, p 217.

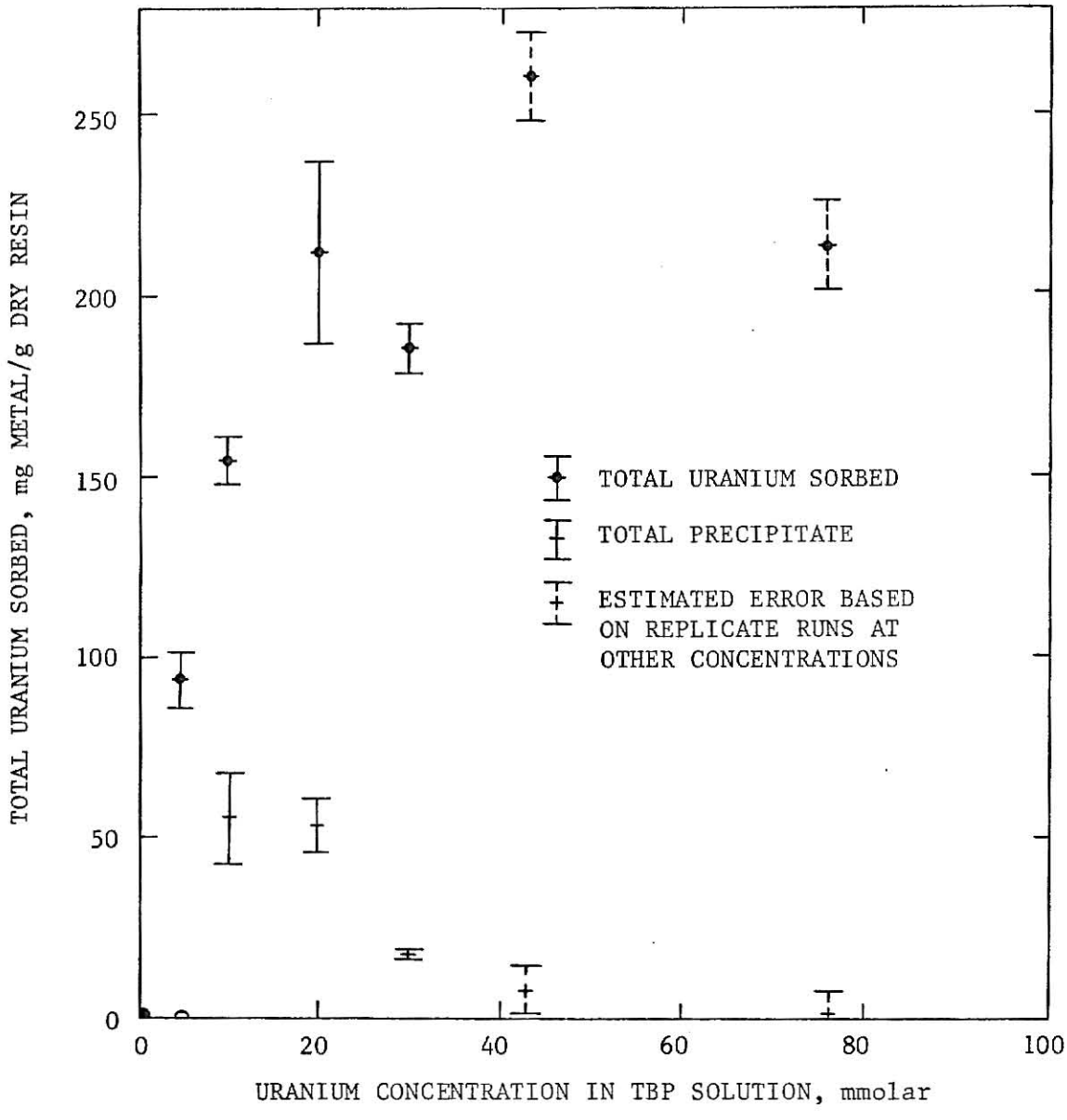

Figure 4. Effect of TBP Solution Concentration on Uranium Sorption by Unregenerated Citrate Form Dowex 2-X8 Resin

Table II. The resin was "regenerated" and the work was checked again because of the large difference between Nayak's results and those obtained in this work. The regenerated resin produced the data shown in Figure 5 and Table III.

The treatment of the precipitate is responsible for part of the large difference noted between Nayak's results and those obtained in this work. Nayak washed the resin free of precipitate but did not filter the precipitate from the wash solution. The precipitate was dissolved in the wash solution and the total was reported as the Wash. Nayak did not add the metal in the wash to the amount of metal obtained from the elutation of the washed resin and did not report the total metal sorbed by the resin. Figure 2 reported only the amount of metal obtained from the nonreproducible elutation of the washed resin. This work washed the precipitate from the resin and then filtered the precipitate from the wash solution. The wash solution was added to the eluent to give the total eluent. Both the precipitate and the total uranium (total eluent plus precipitate) sorbed are reported.

Nayak's results can be placed on a basis compatible with the results of this work, if the total uranium sorbed on the resin is calculated from Table I. Nayak's data is increased from 30, 30, and 43 mg/g dry resin to 107, 130, and 152 mg/g dry resin. The remaining difference between the results of this work and Nayak's results may be due to the washing of the resin with 30% TBP to remove the water film from the resin beads before loading the resin. This effectively gave a longer loading time. It also is possible that due to the process used to convert the resin to citrate form, the resin used in this work had more active sites than the resin Nayak used.

TABLE II

Effect of TBP Solution Concentration on Uranium Sorption by Unregenerated Citrate Form Dowex 2-X8 Resin

Uranium in TBP Solution Millimolar	Uranium in Precipitate mg/g Dry Resin		Total Uranium mg/g Dry Resin	
	Average of Experiments	Probable Error	Average of Experiments	Probable Error
5	0.0	-	94.2	7.52
10	56.2	12.5	153.	6.65
20	54.3	7.39	210.	24.8
30	18.6	1.05	184.	6.66
43	7.90	6.97[a]	258.	11.4[a]
76	1.38	6.97[a]	212.	11.4[a]

[a]Estimated error based on replicate runs at other concentrations.

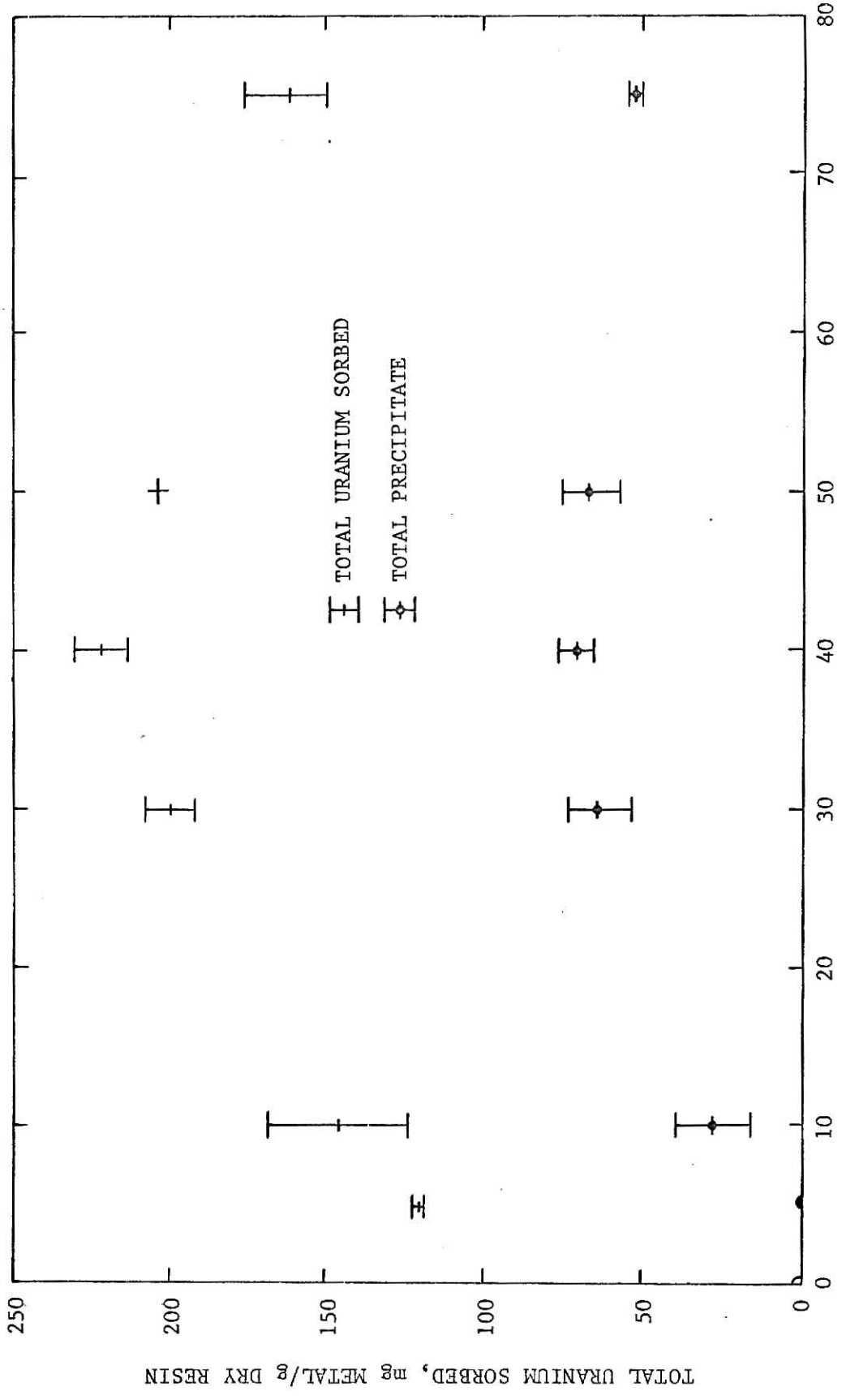

Figure 5. Effect of TBP Solution Concentration on Uranium Sorption by Regenerated Citrate Form Dowex 2-X8 Resin

TABLE III

Effect of TBP Solution Concentration on Uranium Sorption by Regenerated Citrate Form Dowex 2-X8 Resin

Uranium in TBP Solution Millimolar	Uranium in Precipitate mg/g Dry Resin		Total Uranium mg/g Dry Resin	
	Average of Experiments	Probable Error	Average of Experiments	Probable Error
5	0.0	-	121.	1.86
10	28.1	12.0	147.	22.6
30	64.2	10.0	200.	8.81
40	71.1	5.64	222.	7.61
50	66.0	8.80	203.	0.682
75	52.2	1.80	162.	12.6

Uranium-Thorium-TBP

Nayak also attempted to determine the equilibrium amount of uranium and thorium sorbed from 30% TBP solution at a 21 millimolar total metal concentration. Nayak again reported the amount of metal left on the resin after washing the precipitate from the resin bed instead of reporting the total metal sorbed by the resin. His results are given in Figure 6 and Tables IV and V.

This work used a 40 millimolar total metal concentration and reported both the precipitate and the total metal sorbed by the resin. Figure 7 and Table VI give the total uranium and total thorium sorbed by the resin. Figure 7 is a combination of Figure 8 which shows only the total uranium sorbed and Figure 9 which shows only the total thorium sorbed. The uranium and thorium are added together to give the total precipitate and the total metal sorbed. These data are given in Figure 10 and Table VII.

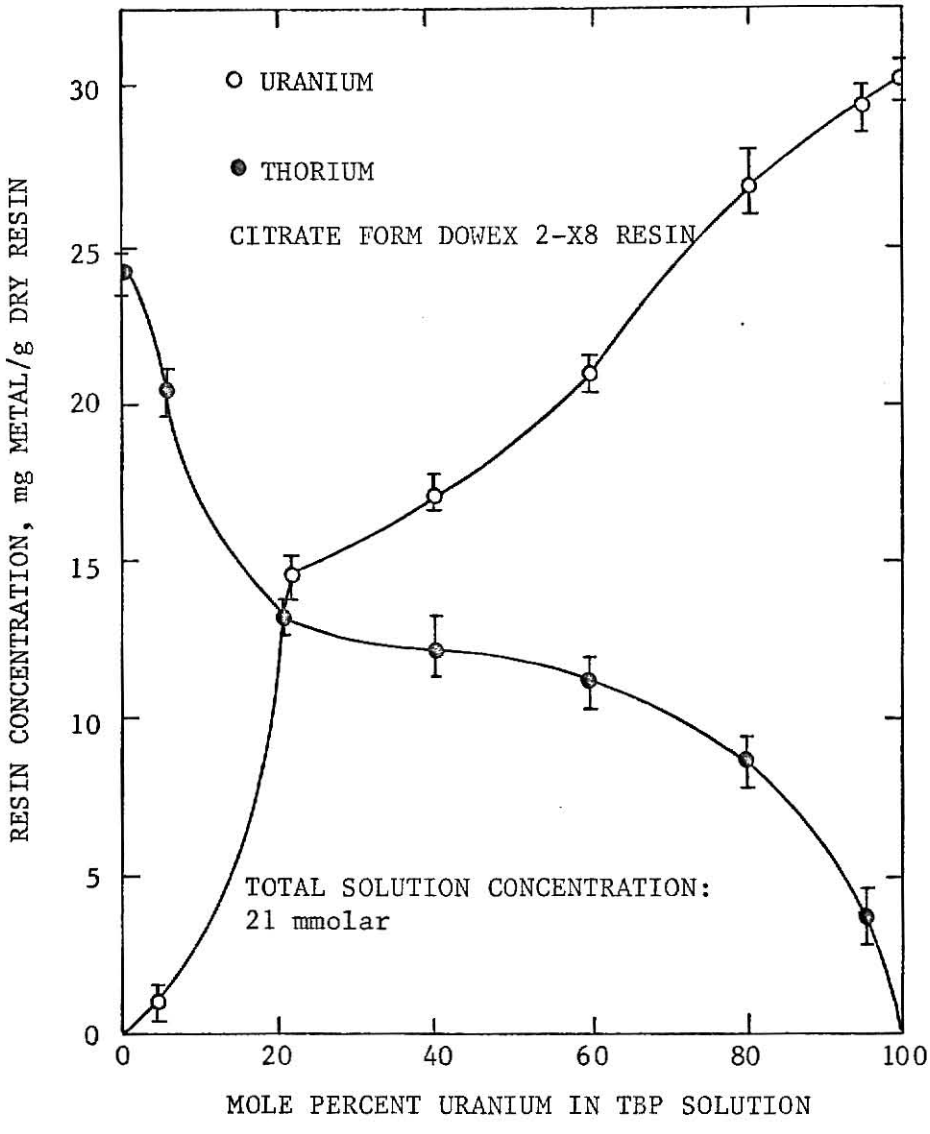

Figure 6. Uranium-Thorium-TBP-Dowex 2-X8 Equilibrium Curve*

*M. N. Nayak, M.S. Thesis, Kansas State University, Manhattan, Kan. 1967, p 30.

TABLE IV

Uranium in the Eluent*

Mole Percent Uranium in TBP§	Experiment 1 Uranium in mg/g Dry Resin		Experiment 2 Uranium in mg/g Dry Resin		Average of Two Experiments, Uranium in mg/g Dry Resin	Experimental Error, Percent Deviation from Average
	Average of Two Analyses	Analysis Error Percent Deviation from Average	Average of Two Analyses	Analysis Error Percent Deviation from Average		
0	-	-	-	-	-	-
5	1.1	-	-	-	1.1	-
20	14.8	2.7	-	-	14.8	-
40	17.1	4.7	17.6	5.7	17.4	5.2
60	20.8	1.9	30.0	0.8	20.4	2.6
80	28.1	0.8	26.4	0.9	27.3	3.6
95	30.2	5.0	-	-	30.2	-
100	31.2	3.8	29.8	3.4	30.5	3.6

*M. N. Nayak, M.S. Thesis, Kansas State University, Manhattan, Kan., 1967, p 34.

§Mole Percent in TBP Uranium-Thorium Solution, Total Concentration 21 mmolar.

TABLE V

Thorium in the Eluent*

Mole Percent Thorium in TBP§	Experiment 1 Thorium in mg/g Dry Resin		Experiment 2 Thorium in mg/g Dry Resin		Average of Two Experiments, Thorium in mg/g Dry Resin	Experimental Error, Percent Deviation from Average
	Average of Two Analyses	Analysis Error Percent Deviation from Average	Average of Two Analyses	Analysis Error Percent Deviation from Average		
0	-	-	-	-	-	-
5	3.66	2.1	-	-	3.66	-
20	9.14	1.0	7.60	1.3	8.37	9.2
40	10.0	0.8	8.42	3.2	9.22	8.6
60	11.1	1.1	13.3	0.8	12.2	9.0
80	13.0	-	12.2	2.8	12.6	2.9
95	20.4	1.9	-	-	20.4	1.9
100	23.2	2.4	25.4	2.2	24.3	4.5

*M. N. Nayak, M.S. Thesis, Kansas State University, Manhattan, Kan., 1967, p 35.

§Mole Percent in TBP Uranium-Thorium Solution, Total Concentration 21 mmolar.

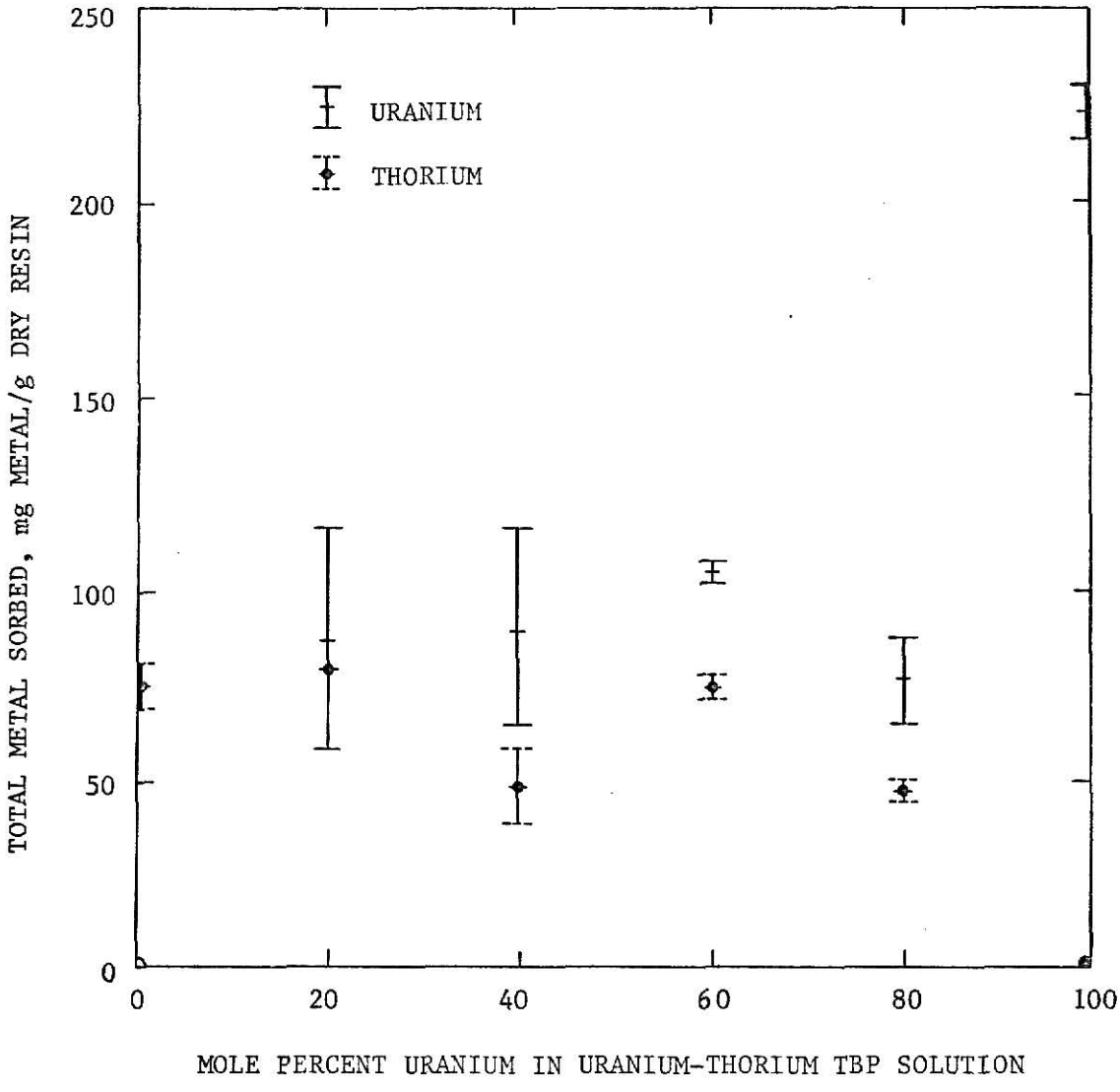

Figure 7. Total Uranium and Total Thorium Sorbed from 0.040*M* Uranium-Thorium-TBP Solution

TABLE VI

Uranium and Thorium Sorbed on Regenerated Citrate Form Dowex 2-X8 Resin from 0.040*M* TBP Solution

Mole Fraction Uranium	Total Uranium		Total Thorium		Mole Fraction Thorium
	Average of Experiments mg/g Dry Resin	Probable Error mg/g Dry Resin	Average of Experiments mg/g Dry Resin	Probable Error mg/g Dry Resin	
0	-	-	73.7	6.00	100
20	86.3	28.8	76.2	.112	80
40	88.2	26.3	48.0	10.0	60
60	103.	2.50	73.5	2.24	40
80	74.9	12.1	47.3	2.98	20
100	222.	7.61	-	-	0

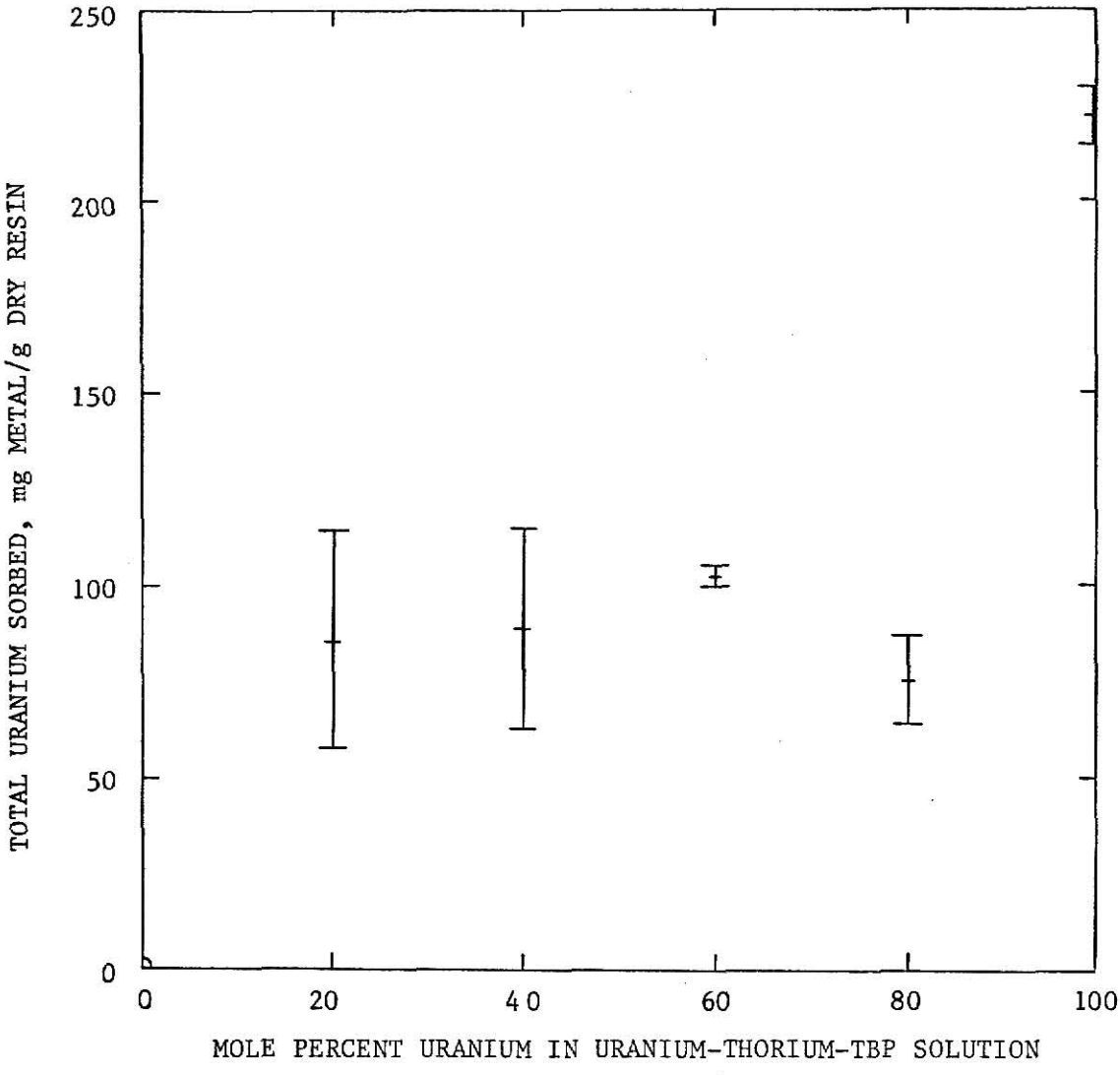

Figure 8. Total Uranium Sorbed from 0.040*M* Uranium-Thorium-TBP Solution

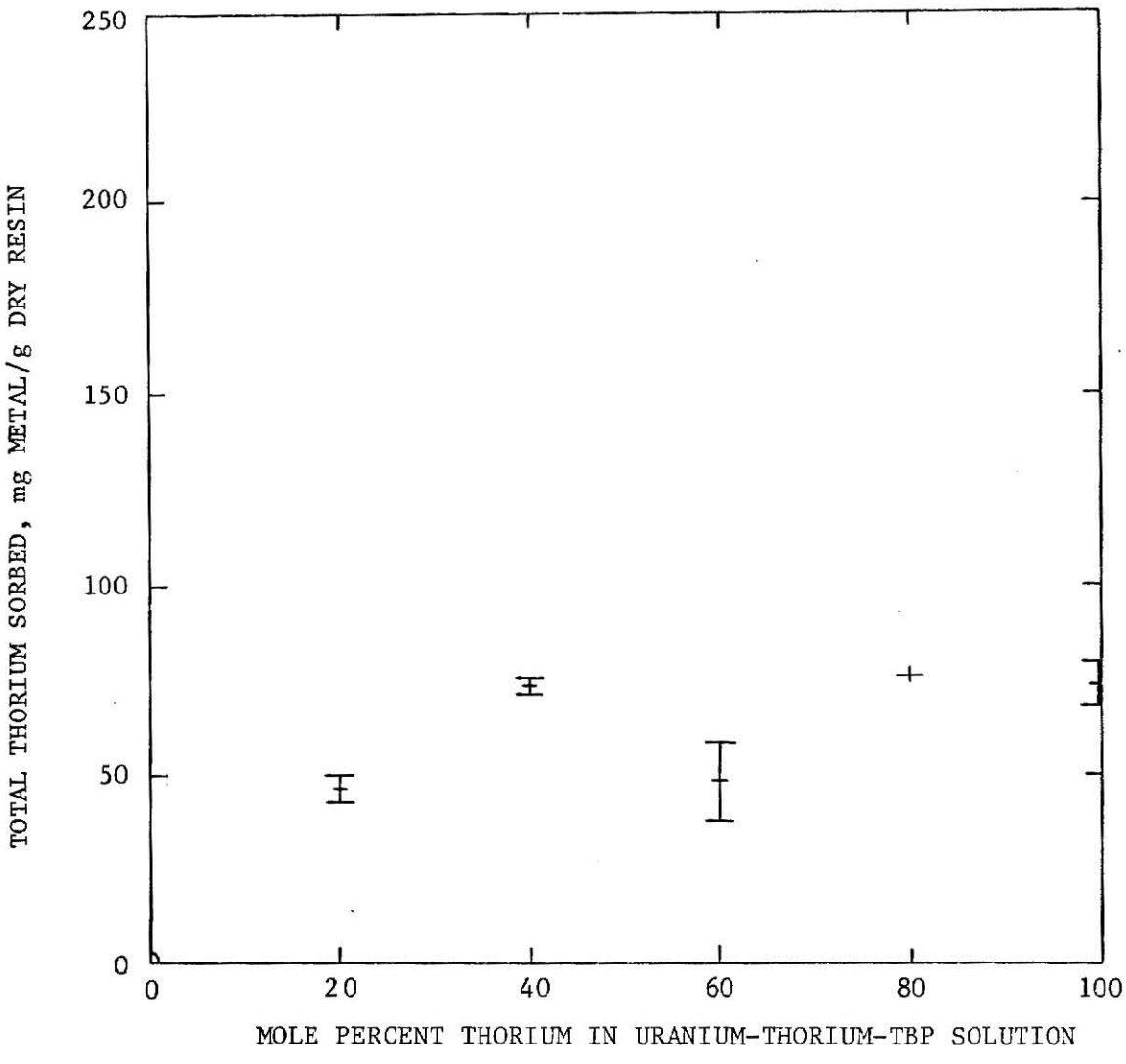

Figure 9. Total Thorium Sorbed from 0.040*M* Uranium-Thorium-TBP Solution

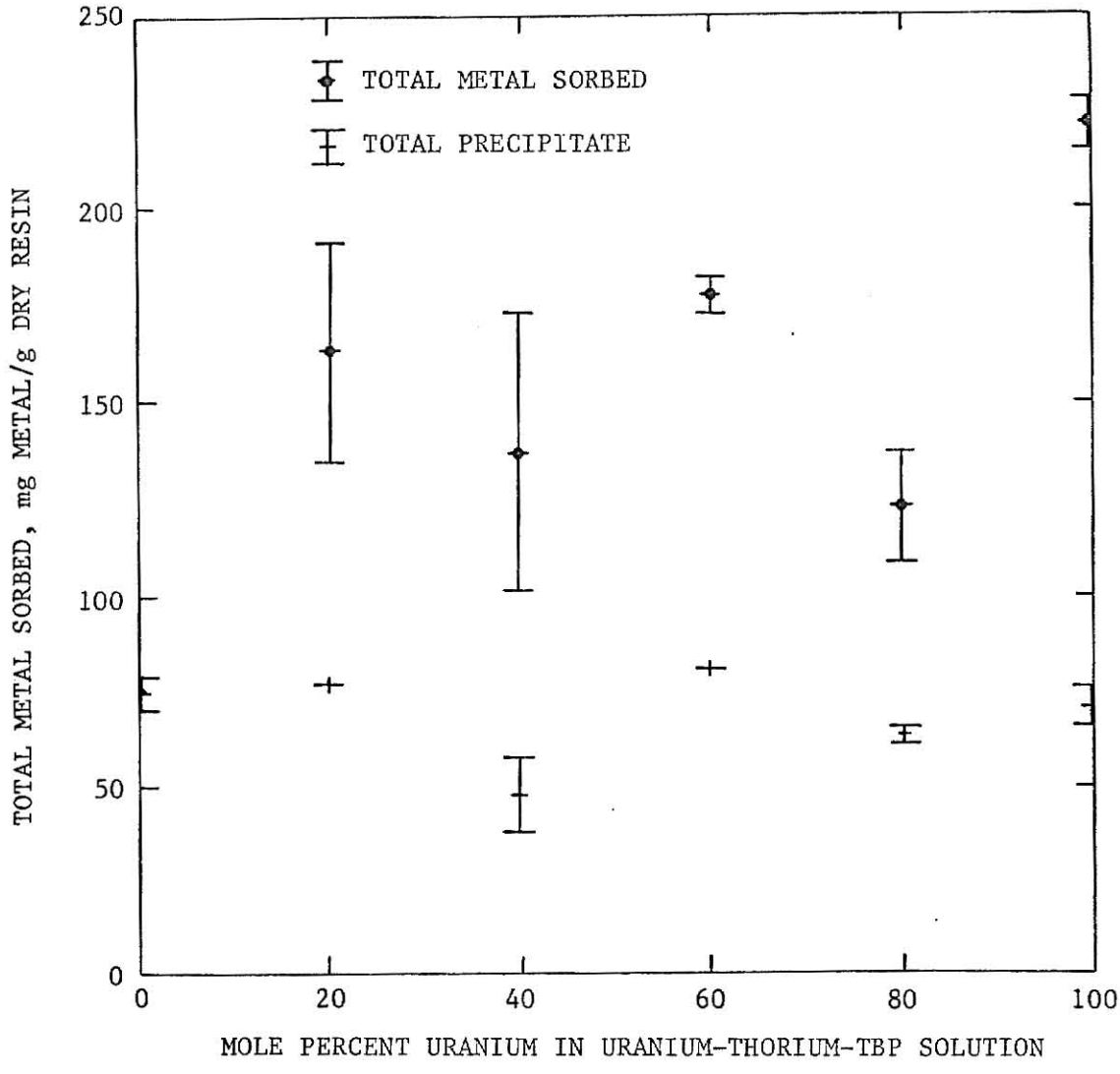

Figure 10. Total Precipitate and Total Metal Sorbed from 0.040*M* Uranium-Thorium-TBP Solution

TABLE VII

Total Metal Sorbed on Regenerated Citrate Form Dowex 2-X8 Resin from 0.040*M* TBP Solution

Mole Fraction Uranium	Metal in Precipitate mg/g Dry Resin		Metal in Wash & Eluent mg/g Dry Resin		Total Metal mg/g Dry Resin	
	Average of Experiments	Probable Error	Average of Experiments	Probable Error	Average of Experiments	Probable Error
0	72.9	5.19	0.848	0.808	73.7	6.00
20	75.8	0.073	86.7	28.8	163.	28.7
40	47.5	10.0	88.7	26.3	136.	36.3
60	79.3	0.545	97.6	5.28	177.	4.73
80	64.1	1.01	58.1	14.0	122.	15.0
100	71.1	5.64	151.	1.97	222.	7.61

DISCUSSION OF RESULTS

The data points in the figures show error bars based on the probable error calculated for the data (see error analysis). The large errors noted on Figures 4, 5, 7, 8, 9, and 10 are probably caused by differences in the length of time the resin was in contact with the organic phase containing the metallic species. It was observed that the longer the resin was in contact with the TBP solutions, the more uranium was sorbed by the resin. This increase in uranium sorbed appeared to be due to precipitate formation only - a process which apparently does not reach equilibrium in six hours. The figures also present precipitation data. Nayak assumed that the precipitate "formed at the surface of the resin"[25] only during the washing process. This work showed that precipitate accumulates in the resin bed during the loading phase when the metal concentration is high enough (greater than 5 millimolar). Both the accumulation of the precipitate and the swelling of the resin in the organic phase contributed to a decrease in the flow rate through the resin bed. The flow through the resin bed often stopped when the experiments were continued through the night. This increased the contact time and contributed to the large errors noted in the figures.

Precipitate formation is not a typical ion exchange phenomena. Precipitate formation seems to indicate that an adsorption process is present; sometime during the loading process the ion exchange resin ceases to act as a selective reagent and begins to act like a sponge. Nayak suggested that citrate complex formation could explain some of the

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[25]Nayak, p 29.

inconsistancies in the data; however, complexing tends to preclude precipitate formation. The resin probably acts as a weak base after the resin has been saturated and the citrate complexed. Dowex 2-X8 is a basic resin and in strong uranium solutions may cause the metal to form a stable precipitate that continues to build up on the resin surface.

Thorium collected in the resin bed as a precipitate only. It was found that even with the wash solution added to the eluent, thorium was not present in large enough amounts to be quantitatively determined. This would bear out Nayak's theory that only one thorium-citrate complex is formed, if complex formation were the controlling factor in thorium sorption. Figure 9 seems to show that the resin has a definite capacity for thorium. Again, this indicates a physical adsorption process.

The precipitate would cause problems in adaptation of this process for use on a commercial basis. The uranium concentration would have to be kept low enough to avoid precipitate formation and thorium could not be present. The precipitate would be difficult to remove if the metal concentrations were high enough to cause precipitation. It was found that while nitric acid did dissolve the precipitate, the thorium precipitate dissolved very slowly.

The Thorex Process could be changed to use the modified GLX Process if either the uranium concentration was kept low enough to avoid precipitate formation or the flow through the column was stopped before precipitate formation began. The Thorex Process modification would consist of removing the last solvent extraction column (column III in Figure 1) and using the modified GLX Process in the ion exchange column. The proposed modification, however, might not be practical. If the resin would

be allowed to sorb only 100 mg uranium/g dry resin, 25 liters of citrate form Dowex 2-X8 resin would be required to sorb one kilogram of uranium.

It is recommended that any future work include a kinetics study of precipitate formation. This study should determine exactly how and why precipitate forms and determine the role the resin plays in precipitate formation. Future work should also determine the amount of uranium sorbed before precipitate formation begins and should use both different uranium-TBP solution concentrations and resin of different crosslinkages. It is not recommended that the modified GLX Process be used to modify the Thorex Process unless both the kinetics studies and an economic analysis show the modification to be practical.

ERROR ANALYSIS

Nayak considered two types of errors, "(1) errors in chemical analysis and (2) experimental errors which would include the analysis as well as other errors."[26] Both types of errors are reported in Tables IV and V. The errors were estimated by doing each analysis and experiment twice. Nayak reported that the experimental error was never "greater than 10 percent; the average experimental error was less than 4.5 percent."[27] In chemical analysis, "the average error in carrying out thorium analysis was 1.8 percent while the average uranium analytical error was 3 percent."[28]

This experimentor considered only the experimental error or the probable error, q[29], which is .674 times the standard deviation. S_i is

$$q = .674 \sqrt{\frac{1}{N-1} \sum_i (S_i - m)^2} \qquad (1)$$

$$m = \frac{1}{N} \sum_i S_i \qquad (2)$$

the experimental reading, N is the number of readings, and m is the arithmetic mean. The average of experiments is the arithmetic mean of the results. The probable error was calculated using equation 1.

The errors in chemical analysis are submerged in the larger errors in the experiments. If the probable error is converted to percentage,

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[26]Nayak, p 43.

[27]*Ibid.*

[28]*Ibid.*

[29]R. Livingston, "Physico Chemical Experiments," The Macmillan Co., New York, N. Y., 1953, p 15.

the average probable error for uranium is less than 10% and the average probable error for thorium is less than 8%. The deviation from the average corrected transmittance in uranium analysis was usually much less than 0.3% and the average error in converting the transmittance reading to concentration was on the order of 1%. The deviation from the average in the thorium analysis ranged from 11% to less than 1% with the usual analysis having a deviation of less than 4%.

The differences in resin loading times are believed to be the major source of experimental error, but the experimental errors could be enlarged by the variation in the weight of the resin used and any variance in the resin capacity. These variations could introduce irregularities in the loading, washing, and eluting procedures and contribute to the experimental error.

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APPENDIX A: Properties of Dowex 2-X8 Resin[30]

Nature - Strongly Basic Anion Exchanger

Active Group - Dimethyl Ethanol Benzyl Ammonium

Crosslinkage - 8%

Ionic Form as Shipped - Cl^-

Physical Form - Spheres

Mesh Size (Wet) - 20-50 U.S. Standard Screen Size

Shipping Density (lb/ft^3) - 44

Moisture Content (%) - 37

Volume Change (%) - $Cl^- \rightarrow OH^-$ = +14%

Effective pH Range - 0 to 14

Selectivity - Cl^-/OH^- = Approximately 1.5

Order of Selectivity for Ions - $I > NO_3 > Br > Cl > OH >$ Acetate $> F$

Total Exchange Capacity - (Cl^- Form)

Kg as $CaCO_3/ft^3$ - 29.0

Meq/g Dry Resin - 3.5

Meq/ml Wet Resin - 1.33

Sphericity (%) - >85

Bed Expansion - 50% Maximum at 2 gpm/ft^2 at 25°C

Pressure Drop - Approximately 0.5 $lb/(in^2\ ft)$ at 5 gpm/ft^2

Stability - (Cl^- Form)

Thermal - Good up to 150°C

Solvent - Very Good

Oxidation - Slow Solution in Hot 15% HNO_3

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[30] "Dowex :: Ion Exchange," The Dow Chemical Company, Midland, Mich., 1964, p 76.

Reduction - Breakdown in presence of some sulfur containing reducing agents

APPENDIX B: Uranium Determination

This appendix provides a step-by-step guide for the use of the Beckman DU Spectrophotometer Model 2400 in the determination of uranium concentrations. It is intended to supplement, not replace, the Instruction Manual. It is assumed that the concentration curve shown in Figure 11 is still valid, or that a current concentration curve is available. It is further assumed that all aqueous uranium solutions are set at .1 normal nitric acid (pH = 1.0) before the concentrations are determined and that cell number one always contains 0.1*N* HNO_3.

Steps

1. The Beckman DU Power Supply should NEVER be turned off or covered. If it has been turned off, set the control settings as follows and let the unit warm up for 24 hours.

SENSITIVITY	3	ZERO SUPPRESSION	OFF
H_2 LAMP	OFF	SCREEN BIAS	4
POWER	ON	LAMP SELECTOR	H_2

The Model 2400 should never be turned off, instead, the Selector Switch should always be left in the CHECK position.

2. Check the Shutter Switch to be sure that it is OFF. Pull the Phototube Positioning Knob all the way out, then turn on the Tungsten Lamp Switch (on the Lamp House Backplate). Make sure that the Mirror Positioning Knob is turned so that the red dot is at 2 o'clock. Turn on the cooling water and set the Wavelength Selector to 420 mμ and the Slit to 0.04 mm. The Resistor Switch should be in position 1 and the Filter Slide should be all the way in. Let the spectrophotometer warm up for

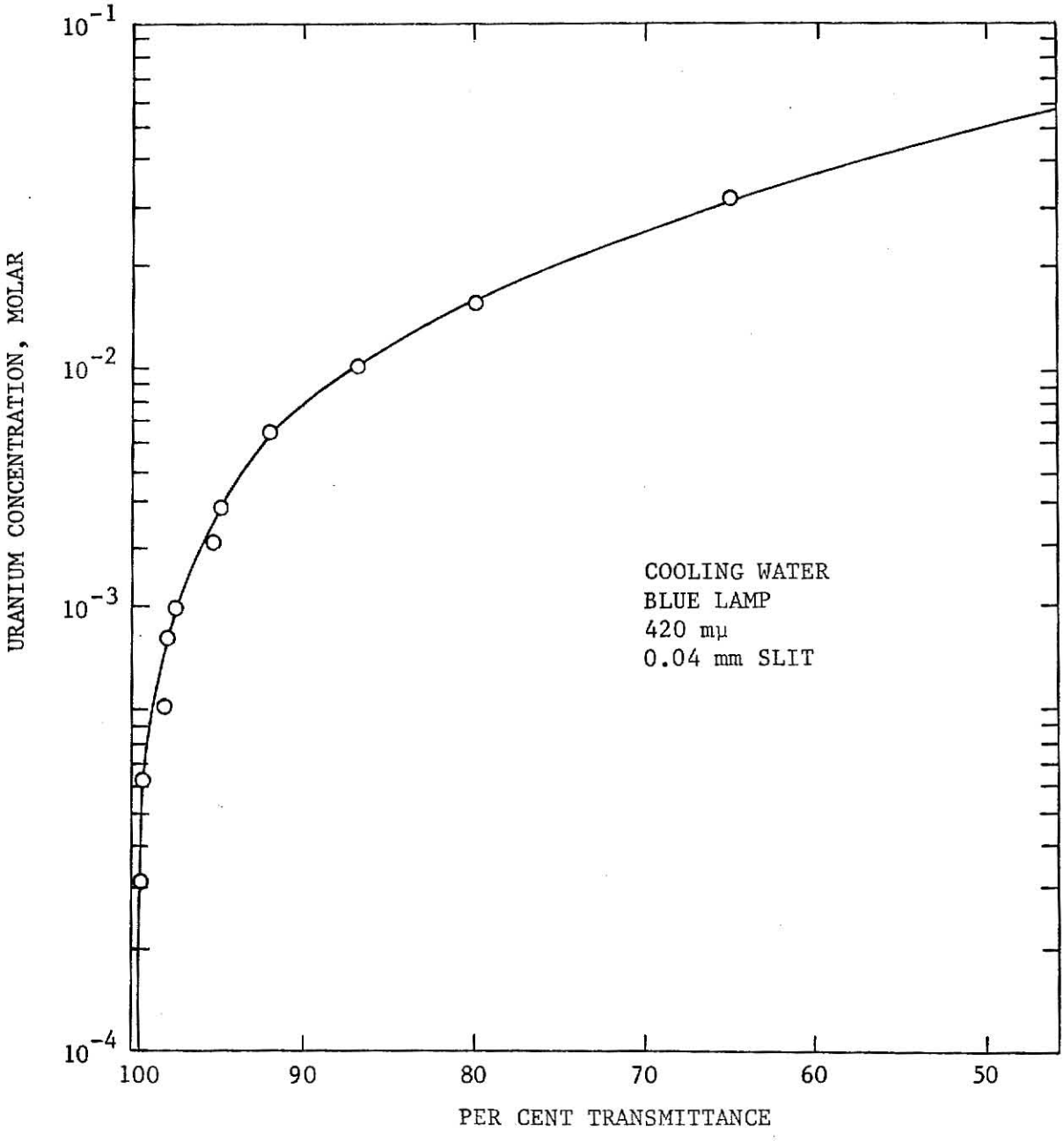

Figure 11. Spectrophotometric Uranium Concentration Curve

at least an hour.

3. Obtain:

_____a. a clean 3 ml pipet and a pipet bulb

_____b. a small beaker of 0.1*N* HNO_3

_____c. paper towels

_____d. a box of lint-free paper towels (Kaydry)

_____e. beakers for the unknowns

_____f. a wash bottle of distilled water

_____g. slop jars for the radioactive waste

_____h. a notebook and a pen

4. Take the spectrophotometer cells out of the cleaning solution they are stored in and rinse them with distilled water. Be careful to touch only the frosted sides of the cells. Place them upside down on paper towels and let them drain dry (about 20 minutes).

5. Turn the Cell Holder so that the numbers on it are readable. Number each cell with a pencil and carefully place each in the Cell Holder with the pencil numbers to the left.

6. Pipet 3 ml of 0.1*N* HNO_3 into each of the cells. Be careful not to contaminate the outside of the cells. Place the pipet on a paper towel to drain dry.

7. Be sure the Shutter Switch is OFF before opening the Cell Compartment. Place the Cell Holder on the slide in the Cell Compartment so that the numbers on the Cell Holder are to the right. Replace the Cell Compartment Cover and let the temperature of the cells and solutions stabilize for 20 to 30 minutes.

8. Take off the rubber apron if one was worn.

9. Check that the controls are still set as instructed in steps 1 and 2. Do not touch the Phototube Positioning Knob! Push the Sample Positioning Knob all the way in and adjust the Dark Current so that the Null Meter is zeroed.

10. GENTLY turn the Shutter Switch ON. Now adjust the Sensitivity Control until the Null Meter is zeroed. It helps to concentrate on the needle alone.

11. Repeat steps 9 and 10 until the Null Meter remains zeroed with the Shutter Switch in either the ON or OFF position. This step will be repeated throughout the determinations as needed to keep the Null Meter zeroed. Always use the standard cell (number one) to zero the Null Meter and always have the Selector Switch on CHECK.

12. Pull the Sample Positioning Knob out to the first position (cell number two) and turn the Selector Switch from CHECK to 1.

13. Rotate the Transmittance Control to zero the Null Meter.

14. Push the Sample Positioning Knob in and turn the Selector Switch to CHECK. If the Null Meter returns to zero, record the value of the transmittance (101.3, 98.7, ...). If the Null Meter does not return to zero, repeat steps 11 to 14.

15. Repeat steps 12 to 14 for cells three and four.

16. Rezero the Null Meter with the Shutter Switch OFF, then with it ON. Obtain a second set of readings, ie., repeat steps 9 to 15.

17. The two values of transmittance recorded for each of the cells should be within one-tenth of a unit, ie., 97.6 and 97.5. If they are not within one-tenth of a unit, repeat step 16 until agreement is reached.

18. Check to be sure that the Shutter Switch if OFF and the Selector Switch is on CHECK before opening the Cell Compartment. Remove the Cell Holder and take it back to the laboratory after replacing the Cell Compartment Cover.

19. Empty the cells into a slop jar with a quick flip of the wrist. Be careful not to touch the cell faces or to spash any liquid on them. If the cell faces are contaminated, the cells must be cleaned again and the calibration procedure repeated.

20. Blot the excess liquid from the mouth of the cells with a Kaydry while the cells are inverted.

21. Carefully pipet 3 ml of 0.1*N* HNO_3 into cell number one.

22. Blot the excess nitric acid from the pipet. Fill the pipet with the uranium solution and drain into the slop jar three to five times.

23. Carefully pipet 3 ml of the uranium solution into each of the cells. Thoroughly rinse the pipet with distilled water and place it on a paper towel to drain.

24. Repeat step 7.

25. While waiting for temperature equilibrium, determine the correction factors for the cells by taking the average of the two (or more) readings and dividing into 1. This gives a multiplication factor for each cell (0.9872, 1.0132, ...).

26. When the temperature of the uranium solutions has stabilized (15 to 20 minutes), repeat steps 9 to 20.

27. Fill the sample cells (not cell number one) with distilled water and repeat steps 19 and 20.

28. The samples should be run in order of increasing concentration and only three samples may be run without cleaning and recalibrating the

cells.

29. Take the average of the corrected, averaged readings, discarding if necessary any one cell's corrected readings. Look up the uranium concentration on the concentration curve (Figure 11).

30. Turn off the Tungsten Lamp Switch and the cooling water. Be sure that the Shutter Switch is OFF and the Selector Switch is on CHECK.

APPENDIX C: Thorium Determination

This appendix provides a step-by-step guide for the gravimetric determination of thorium with *m*-nitrobenzoic acid. It is recommended that the samples contain 0.1 to 0.2 grams of thorium, although the method was used successfully with samples as small as 0.005 grams of thorium. However, at this low concentration it is necessary to use thorin indicator and a spot plate to determine when precipitation is complete. Ayres[31] was used as a guide in laboratory procedures.

Steps

1. The following equipment is needed:

_____ three 1000 ml beakers

_____ two 3000 ml beakers

_____ one blast burner with rubber tubing

_____ two empty acid bottles

_____ two indicator (dropper) bottles

_____ two stoppered reagent bottles

_____ one buret brush

_____ one test tube brush

_____ two bunsen burners with rubber tubing

_____ one 100 ml buret and small funnel

_____ one buret holder

_____ two buret stands

_____ one platinum crucible with lid

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[31]G. H. Ayres, "Quantitative Chemical Analysis," Harper & Row, Publishers, New York, N. Y., 1958, p 571.

_____ one measuring cup

_____ one combination hot plate and magnetic stirrer

_____ matches or a lighter

_____ one box of 15 cm Whatman filter paper No. 44

_____ one 2000 ml Erlenmeyer flast with stopper

_____ one 1000 ml Florence flask with stopper

_____ three long-stem funnels

_____ asbestos center wire gauze

_____ 50-, 100-, and 250-ml graduated cylinders with guards

_____ bottle of ammonium hydroxide

_____ methyl orange indicator

_____ *m*-nitrobenzoic acid

_____ bottle of nitric acid

_____ thorin indicator

_____ two ring clamps (to hold the funnels)

_____ one 12-hole spot plate (white)

_____ one stand to hold a triangle over the blast burner

_____ two three-legged stands to fit over the bunsen burners

_____ four magnet stirring bars

_____ three stirring rods with rubber policemen

_____ stopcock grease

_____ crucible tongs

_____ flask tongs

_____ silica pipe covered triangles

_____ wash bottles

_____ notebook and pen

2. Make up a 20% solution of *m*-nitrobenzoic acid in absolute ethanol in the 1000 ml Florence flask.

3. Fill an acid bottle with 1:5 nitric acid.

4. Fill an acid bottle with 1:3 ammonium hydroxide.

5. Make up a reagent bottle each of 1% thorin indicator and 1% methyl orange indicator and fill the indicator bottles.

6. Place the combination hot plate and magnetic stirrer on a buret stand and place the buret in the buret clamp. The buret should be placed so that it can be rotated over the 1000 ml beaker on the hot plate. Fill the buret with 1:3 ammonium hydroxide.

7. Put a magnet in the 2000 ml Erlenmeyer flask and nearly fill it (1960 ml) with distilled water. Heat the water (60 to 80°C) on the hot plate (set at 3) and add 40 ml of the 20% *m*-nitrobenzoic acid solution. Stir until dissolution is complete.

8. Fill a 3000 ml beaker with distilled water and place it on a stand over a bunsen burner. Heat to steaming.

9. Place a thorium aliquot in a 1000 ml beaker containing a stirring magnet. Then put the beaker on the hot plate in place of the hot 0.4% *m*-nitrobenzoic acid.

10. Add one drop of methyl orange indicator, then slowly add, while stirring, ammonium hydroxide from the buret. Stop when yellow spots form in the solution and do not immediately dissolve.

11. Slowly add, while stirring, 250 ml of the hot 0.4% *m*-nitrobenzoic acid. A large quantity of white precipitate should form.

12. Turn off the magnetic stirrer and let the solution heat until the precipitate floats to the top of the solution.

13. Put a ring clamp on the remaining buret stand so that when a funnel is in the ring the ground tip of the stem touches the side of the 3000 ml beaker below.

14. Take a circle of Whatman No. 44 filter paper. Fold the circle in half so that the turned edge curves to the outside of the fold. Fold in quarters. Tear the single outside thickness of paper diagonally down to the fold starting about 2 cm away from the first fold. Open the paper on the opposite quadrant to form a cone with the torn segment folded across the fold.

15. Put the cone in the funnel and wet it with distilled water. Smooth the paper down and work out any bubbles. Be careful not to tear the paper. Fill the funnel with distilled water and let the funnel stem fill. A new piece of filter paper or a clean funnel may be needed if the funnel stem will not fill.

16. Pour the hot solution from the beaker down a stirring rod into the funnel. Do not fill the funnel to more than 3 mm from the top edge of the filter paper. Repeat until the beaker is empty.

17. Wash the precipitate out of the beaker into the funnel with hot distilled water. Be careful not to wash the magnet into the funnel.

18. Put 5 ml of the hot 0.4% *m*-nitrobenzoic acid in the 100 ml graduated cylinder and fill with the hot distilled water (use the measuring cup as a dipper). Use this 0.02% *m*-nitrobenzoic acid solution to wash out the beaker; scrub the walls with the rubber policeman.

19. Put 50 to 100 ml of the 1:5 nitric acid into the original 1000 ml beaker and put it on the hot plate. Wash the stirring rod off and remove it; then turn the hot plate on LOW.

20. Carefully take the filter paper and precipitate out of the funnel and place in the 1000 ml beaker. Turn on the magnetic stirrer and let it beat the filter paper until only small peices of filter paper are left.

21. Turn the stirrer down and add three drops of methyl orange indicator. Add 100 to 150 ml of hot 0.4% *m*-nitrobenzoic acid before causing precipitation with the 1:3 ammonium hydroxide (use the buret).

22. Repeat steps 12 to 18. Be sure to wash all of the precipitate onto the filter paper. Distilled water may be used as needed since the precipitate, $Th(C_6H_4NO_2COO)_4$, is practically insoluble in water.

23. Carefully fold the filter paper with the precipitate inside and place in the platinum crucible. Put the crucible on a triangle over the blast burner in the hood. Slowly heat until the precipitate is dry.

24. Smoke off the filter paper. Be careful not to let the paper catch on fire; use the crucible lid as needed.

25. Tilt the crucible on the triangle and place the lid on it so that oxygen can get in. Turn the blast burner on full.

26. Turn off the burner when the last of the black ash has burned and the residue is white and light. Cover the crucible while it is cooling.

27. Pick up the crucible with the crucible tongs and take it to the balance. Let the crucible cool until a weight change is no longer detectable. Record the weight.

28. Dump the thorium oxide in the dry radioactive waste can and wipe out the inside of the crucible with a lint free paper towel.

29. Put the crucible on the triangle and heat until it is cherry red. Play a bunsen burner over the inside of the crucible.

30. Repeat step 27.

31. Find the weight difference and multiply by the repeated decimal $0.878787\ldots$ to determine the amount of thorium in the aliquot.

32. Repeat the thorium determination until there is less than 10 milligrams difference in the thorium oxide weight. Average and report the results.

33. Wash the dirty glassware.

SEPARATION OF URANIUM AND THORIUM FROM ORGANIC TBP SOLUTIONS BY CITRATE FORM ANION EXCHANGE RESIN

by

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ABSTRACT

Water swollen citrate form Dowex 2-X8 ion exchange resin was contacted with organic solutions containing uranium and thorium to determine the amount of metal sorbed by the resin from the organic solution. The organic solution was 30% tri-n-butyl phosphate (TBP) in kerosene. The metal in the resin bed was removed and the amount of uranium and thorium determined. Uranium was determined by spectrophotometric analysis and thorium was determined by gravimetric analysis.

The studies with uranium used uranium-TBP solutions of various concentrations from 0 to 76 millimolar. The amount of uranium sorbed varied from 0 to 258 mg/g dry resin. The studies using both uranium and thorium were performed at a 40 millimolar total metal concentration. The mole fraction uranium was varied and the amount of uranium sorbed ranged from 0 to 222 mg/g dry resin. The amount of thorium sorbed over the same range varied from 74 to 0 mg/g dry resin.

It was found that a precipitate formed in the resin bed during the loading phase if the uranium-TBP solution concentration were greater than 5 millimolar uranium. Thorium collected in the resin bed as a precipitate only. It is recommended that any future work include a kinetics study of precipitate formation to determine exactly how and why precipitate forms.