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AN ION EXCHANGE STUDY OF POSSIBLE HYBRIDIZED 5f BONDING IN THE ACTINIDES

R. M. Diamond, K. Street, Jr., and G. T. Seaborg

August 28, 1951

Berkeley, California

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ABSTRACT

A study has been made of the elution behavior of curium(III), americium(III), plutonium(III), actinium(III), plutonium(IV), neptunium(IV), uranium(IV), thorium(IV), neptunium(V), plutonium(VI), uranium(VI), lanthanum(III), cerium(III), europium(III), ytterbium(III), ytterium(III), strontium(II), barium(II), radium(II), cesium(I) with 3.2 $\underline{M}$, 6.2 $\underline{M}$, 9.3 $\underline{M}$, and 12.2 $\underline{M}$ HCl solutions from Dowex-50 cation exchange resin columns. These elutions show that in high concentrations of hydrochloric acid the actinides form complex ions with chloride ion to a much greater extent than the lanthanides. The strengths of the tripositive actinide complex ions apparently go in the order plutonium > americium > curium, although their ionic radii also decrease in this same order. To explain these results, a partial covalent character may be ascribed to the bonding in the transuranium complex ions. It is shown that a reasonable structure for such covalent bonding involves hybridization of the 5f orbitals in the actinide elements.

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I. INTRODUCTION

A study of the physical and chemical properties of the transuranium elements has revealed similarities and regularities in their behavior analogous to those in the properties of the rare earth elements, and, in fact, great similarity with the rare earth series itself. Much evidence, chemical, crystallographic, spectroscopic, from magnetic susceptibility measurements, that is, from a variety of data, now leads to the view that the 5f electron shell is being filled in the transuranium elements, similarly to the filling of the 4f shell in the rare earths.[1]

The ion exchange resin elution of the tripositive ions furnish a very interesting and striking piece of chemical evidence for the similarity of the lanthanides and actinides. The two series on elution with 0.25 $\underline{M}$ ammonium citrate solution, pH 3.5 at a temperature of 87° C, are very similar even to the spacings between the ions with 6, 7, 8, and 9 f electrons; europium, gadolinium, terbium, dysprosium, and the corresponding heavy elements americium, curium, berkelium, and californium. This is shown[2] in Figure 1.

The use of such analogies with the elution behavior of the lanthanide ions permitted the accurate prediction of the elution peak positions of elements 97 and 98 from ion exchange columns, and hence their rapid separation
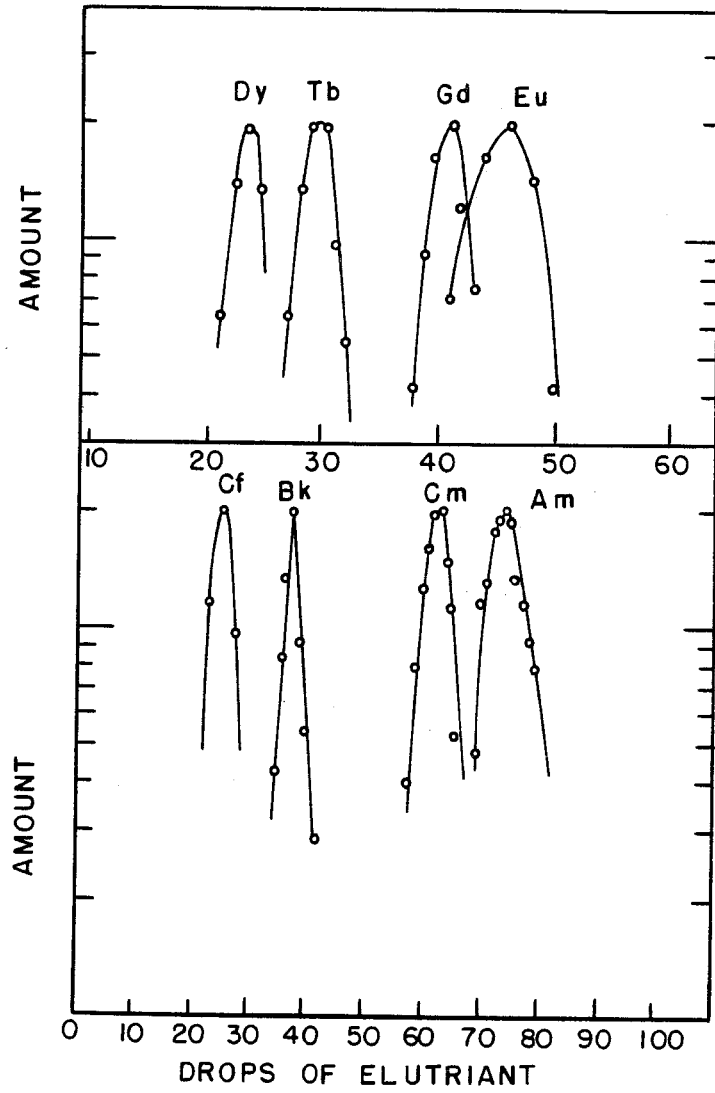
MU 391

Fig. 1

from the other actinide elements present.[3,4] The half-lives being short, time was valuable, so this was an important item in their successful preparation.

However, some previous work[5] in this laboratory brought to light certain important differences in the behavior of the actinide and lanthanide elements on elution from Dowex-50 cation exchange resin columns with hydrochloric acid solutions of various concentrations. It was observed that in varying the concentration of the hydrochloric acid solutions from 3 $\underline{M}$ to 6 $\underline{M}$ HCl, the actinides and lanthanides moved up in their positions of elution, but that in going from 6 $\underline{M}$ to 9 $\underline{M}$ to 12 $\underline{M}$ HCl solutions, the lanthanides lutetium, promethium, and cerium gradually moved back, that is, they showed slower and slower elution rates, while the actinides americium and curium always moved up, their elution rates increasing monotonically with increasing hydrochloric acid concentration. Also, although lutetium, promethium, and cerium kept the same order with the various hydrochloric acid solutions, and curium came off ahead of americium with 3 $\underline{M}$ and 6 $\underline{M}$ HCl, as in the citrate elutions, and as would be expected from a comparison of their ionic radii, with 12 $\underline{M}$ HCl the order of elution of americium and curium reversed, and americium moved up just ahead of curium. An explanation was suggested involving complex ion formation of the actinides with chloride ion in the high concentrations of hydrochloric acid.

In order to confirm these results and to obtain additional evidence on the nature of this complex ion formation in the transuranium elements, this study of the properties of the actinides and lanthanides and certain other ions on elution with hydrochloric acid solutions was undertaken.

Since the interpretation of the results of this work will require a
little knowledge of the factors influencing ion exchange equilibria, the most
important conclusions about ion exchange affinities can be summarized in the
following two empirical rules:

1. The degree of adsorption of cations on a resin depends upon the
   charge on the ion, being greater the higher the charge.

2. The degree of adsorption depends on the effective size of the
   ion, being greater the smaller the hydrated radius.

II. EXPERIMENTAL WORK

First, in order to establish that the previously observed[5] maximum in
the elution rates of the lanthanide ions cerium(III), promethium(III), and
lutetium(III) from Dowex-50 cation columns with hydrochloric acid solutions
of varying concentrations, is due to an actual minimum in the equilibrium dis-
tribution coefficients of the ions and not to some obscure column effect, and
similarly, that with the same range of concentration of hydrochloric acid so-
lutions the apparent nonexistence of such a maximum in the column elution rates
of the actinide ions americium(III) and curium(III) is a real equilibrium
effect, a series of equilibrium distribution experiments were performed at
room temperature on tracer amounts of Am^{241} and Pm^{147}. The resin used was
Dowex-50 colloidal agglomerates, hydrogen form, wet graded to settle at
ca. 0.5 cm/minute, and then oven dried at 95 - 105° C overnight. Known
amounts of the radioactive ions in 5.00 ml samples of solutions of hydrochloric
acid varying in concentration from 1.12 $\underline{M}$ to 13.1 $\underline{M}$ were shaken with small
amounts (0.0076 to 1.8013 grams) of resin, about 30 minutes being allowed for

attainment of equilibrium. (Equilibrium is attained quite rapidly for most ions with Dowex-50.) Then the 5 ml volumetric flasks containing the resin and solution were centrifuged, and 0.50 ml aliquots of the supernatant solutions were withdrawn for counting of the tracers and for titration to determine the acid concentration.

From the experimental data shown in columns 2 to 6 of Table 1, values of K_d, the equilibrium distribution coefficient, were obtained for promethium and americium at various hydrochloric acid concentrations, and are listed in the last two columns.

$$K_d = \frac{1 - F_S}{F_S} \frac{V_S}{W_R} = \frac{(\text{counts/g of resin})}{(\text{counts/ml of solution})}$$

F_S is the fraction of activity in the solution phase

W_R is the weight of resin taken, and

V_S is the volume of solution used.

The values of K_d are plotted against the corresponding hydrochloric acid concentration in Figure 2, and the results confirm the observations on column elutions. The plot of K_d versus hydrochloric acid concentration for americium(III) shows a steady decrease, while that for promethium(III) decreases at first, passes through a minimum around 7 $\underline{M}$ HCl, and then increases.

In order to determine whether the explanation already advanced,[5] i.e. covalent complex ion formation with the tripositive actinides, would be consistent with more complete data, a series of column elutions of various actinide and lanthanide ions using 3.2 $\underline{M}$, 6.2 $\underline{M}$, 9.3 $\underline{M}$, and 12.2 $\underline{M}$ HCl solutions as eluting agents were performed. The elution behavior of tracer amounts of tripositive Cm^{242}, Am^{241}, Pu^{239}, $Eu^{152,154}$, Ce^{144}, Y^{90}, and of tetrapositive Pu^{239}

Table I

Equilibrium Distribution Data for Americium and Promethium

Expt.	Resin weight	Solution volume	Solution normality	α counts/min/ml $\times 10^{-2}$	β counts/min/ml $\times 10^{-2}$
1	0.0000 g	5.0 ml	1.12	44.7	40.6
2	0.0076	4.0 ml	1.12	10.0	10.3
3	0.0468	5.0 ml	3.02	28.9	28.0
4	0.0825	4.5 ml	3.02	22.2	21.4
5	0.4771	5.0 ml	5.30	20.4	19.15
6	0.6697	5.0 ml	7.61	21.1	16.8
7	1.1800	5.0 ml	10.44	22.8	9.02
8	0.0061	10.0 ml	1.12	20.4	20.2
9	0.6863	5.0 ml	9.04	25.8	15.5
10	1.8013	5.0 ml	13.06	24.1	4.25

Expt.	Solution normality	K_d of Am	K_d of Pm
2	1.12	1.8×10^3	1.6×10^3
3	3.02	58.5	48.3
4	3.02	60.0	52.8
5	5.30	12.5	11.7
6	7.61	8.36	10.6
7	10.44	4.06	14.6
8	1.12	1.9×10^3	1.7×10^3
9	9.04	5.33	11.4
10	13.06	2.37	23.7
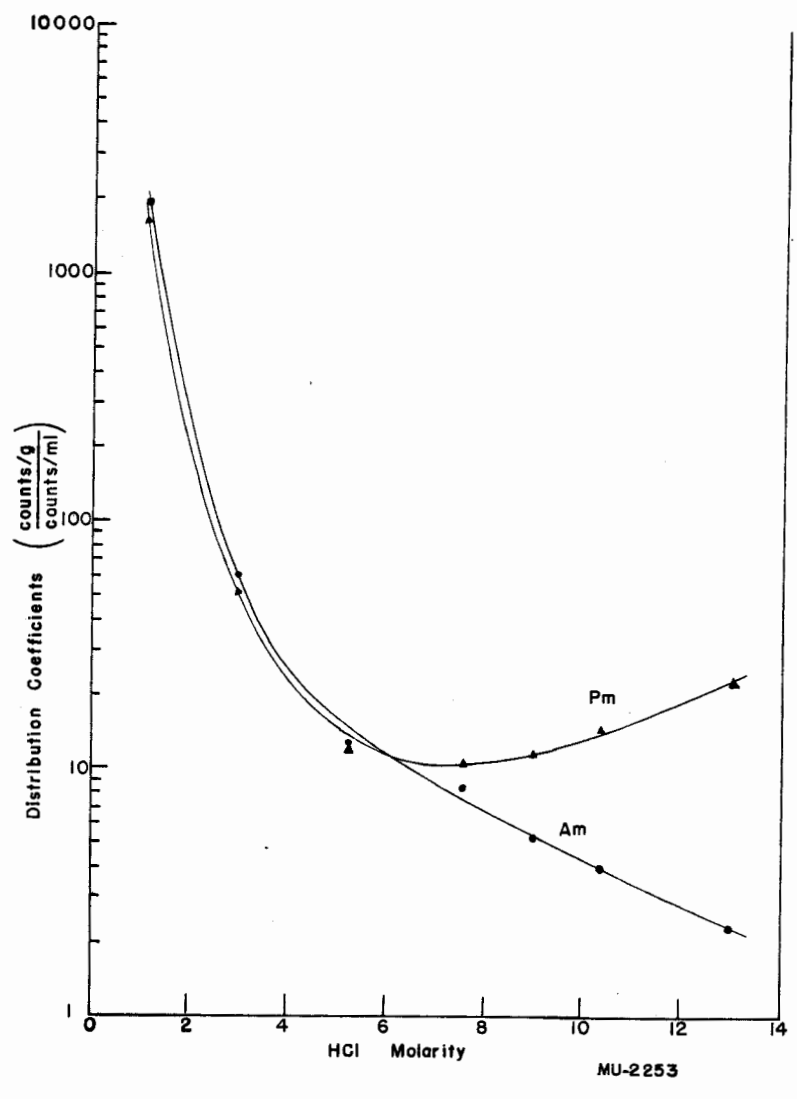
Fig. 2

was studied, and then, for reasons given in the discusion, the behavior
of tripositive La^{140}, Yb^{169}, of tetrapositive Np^{237}, Th^{230}, U^{233}, of diposi-
tive Ra^{226}, Ba^{140}, Sr^{90}, of pentapositive Np^{237}, of hexapositive U^{233}, Np^{237},
Pu^{239}, and of monopositive Cs^{134} was also obtained.

The resin used was Dowex-50, hydrogen form, 250 - 500 mesh, wet graded
to settle at ca. 0.5 cm/minute. Two columns were used, one 10 cm long by
1 mm in diameter, and the other 10 cm long by 1 1/2 mm in diamter. The 10 cm
long resin bed was contained in a pyrex capillary tube pulled to a tip at
the bottom end and joined at the top to a short piece of ordinary pyrex
tubing fitted with a side arm as shown in Figure 3. A small piece of tygon
tubing on the top of the column can be closed with a screw clamp during an
elution and can be removed for loading the column bed. The side arm was
connected by tygon tubing to the reservoir of eluting solution (a 50 ml
separatory funnel) which was large enough so that there was little change in
the hydrostatic head forcing the solution through the column bed during the
elution. Thus a practically constant flow rate was approximated; the linear
flow rate was ca. 0.1 cm/minute. Before an elution the resin column was
rinsed overnight with the hydrochloric acid solution to be used as the eluting
agent. To preserve reducing conditions in the 10 cm by 1 mm column, a drop
of hydriodic acid was also added to this rinse solution, and a drop or two
of nitric acid was added in the case of the 10 cm by 1 1/2 mm column to main-
tain oxidizing conditions. In this manner different oxidation states of the
transuranium elements could be studied, and the low concentration of hy-
driodic or nitric acid used apparently did not affect the relative elution
rates of other ions. This can be seen by comparing relative positions of

SCREW CLAMP ON SHORT PIECE
OF TYGON TUBING

TYGON TUBING TO
SOLUTION RESERVOIF

10 CM RESIN BED

GLASS WOOL PLUG
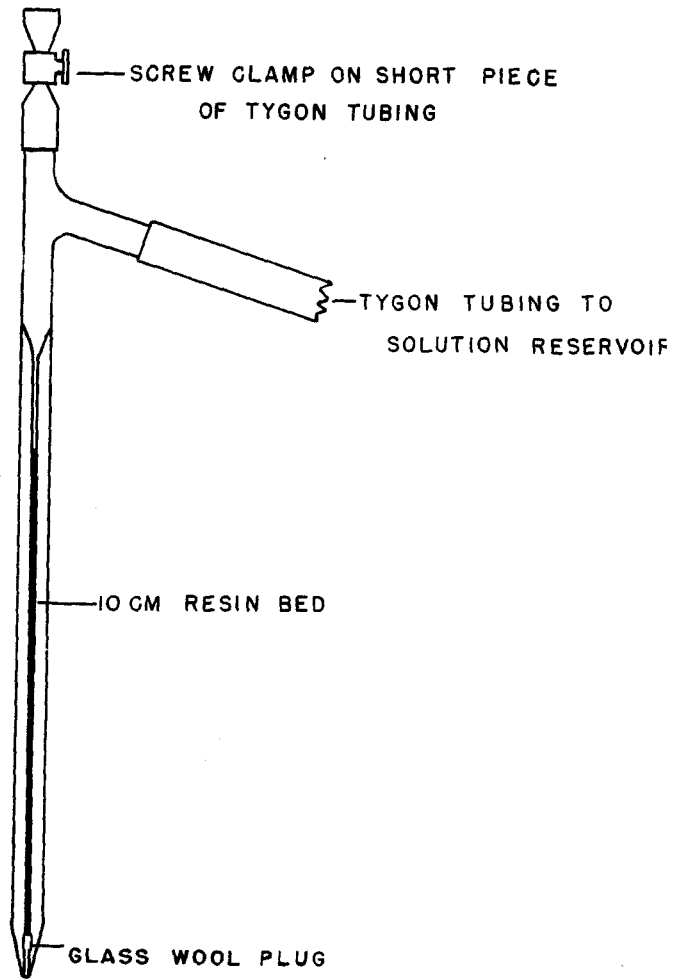
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Fig. 3

ions in runs with one or the other acid present. See tables 3 - 6. Whenever the concentration of the eluting solution was changed, going from one experiment to another, the resin bed was backwashed with water, and then allowed to repack with the new hydrochloric acid solution.

The elutions were performed at room temperature without any thermostatting of the system, as some rough equilibrium distribution coefficient determinations over a range of temperature from 15° C to 80° C showed a small temperature coefficient for hydrochloric acid elutions in contrast to the situation with citrate solutions. Due to the slow flow rate used, days, even weeks, were required for some of the elutions, and so variations in the temperature up to $15 - 20^{\circ}$ C during a long elution were possible and probably contributed to the scattering of the results for the elution peak position of an ion in different experiments with hydrochloric acid solutions of the same concentration. Another possible contributing factor to such scattering of the experimental data is the gradual decrease in concentration of the 9.3 $\underline{M}$ and 12.2 $\underline{M}$ HCl solutions during a long elution.

Two alternative procedures were used to get the ions in a narrow band at the top of the resin column.. Usually, a solution of the tracers in 0.5 $\underline{M}$ HClO$_4$ was stirred with a small amount of resin until the activity was essentially all on the resin. Two or three minutes were sufficient, the mixture being warmed in a water bath when there was no fear of changing the oxidation states of the ions in the process. Afterwards the resin was centrifuged away from the solution, placed on the top of the column bed with a drop of 0.5 $\underline{M}$ HClO$_4$, allowed to settle, and then the elution was begun, that is, the flow of hydrochloric acid solution through the column was started. In

the case of certain ions, namely neptunium(V), plutonium(VI), uranium(VI),
and cesium(I), which had little tendency to be adsorbed on the resin, that
is, very small K_d's, the above method could not be used. When studying such
ions the minimum possible volume of the solution of tracers itself (15 - 30
microliters) was placed on the top of the column bed, and after it had passed
into the resin, the elution was begun.

The elution of the tracer ions was followed by counting the plates on
standard alpha particle and end-window G.M. counters. Whenever necessary,
the various nuclides were identified by their radiation characteristics and
half-lives. Typical runs are illustrated in Figures 4 - 8. In the case of
the close curium, americium, plutonium triad, resolution of the total alpha
particle peak was made using the 48 channel pulse analyzer[6] with the results
shown in Figures 9 - 11. The ordinate is given as counts/minute/drop since
in this type of experiment the actual number of atoms is unimportant. The
abscissa, given in drops, is really an arbitrary unit, as the volume of solu-
tion necessary to elute a given element, even under the near equilibrium con-
ditions employed in this work, will vary somewhat with the particular "batch"
of resin used and with the packing and previous history of the resin in the
column.

Sodium dichromate was used to oxidize neptunium and plutonium to the hexa-
positive state, but in the 9 M and 12 M HCl elutions the dichromate was reduced
during the experiment and eluted in the first few drops as the green chromic
chloride complex. However, enough plutonium remained in the (VI) state to give
results in agreement with predictions based on the behavior of uranium(VI).
The results for neptunium(VI) in 9 M and 12 M HCl are very ambiguous, as the
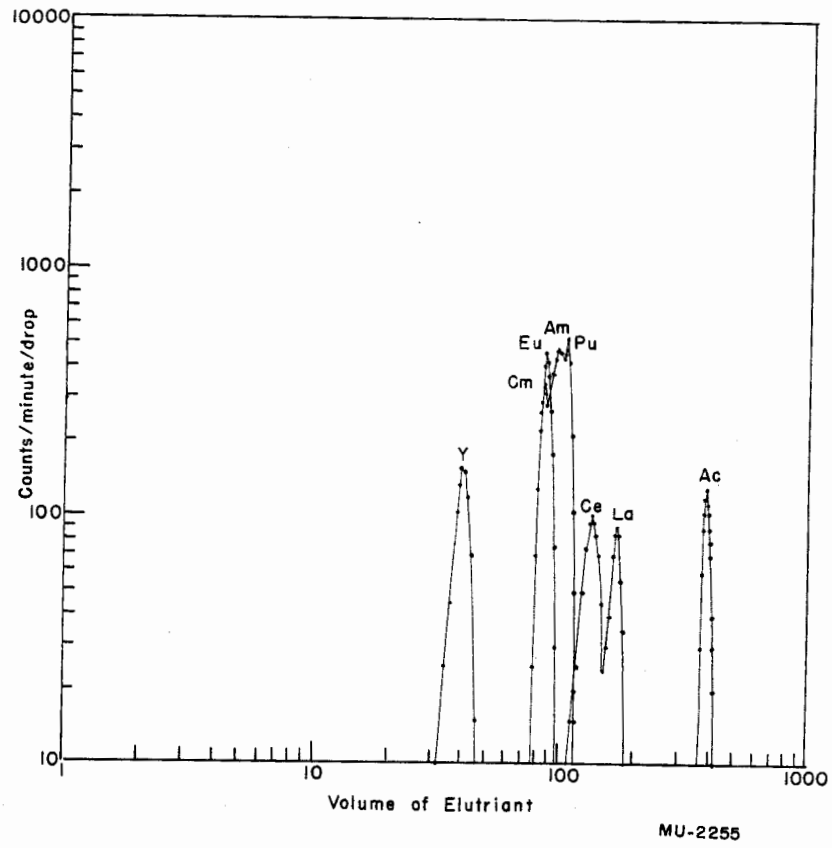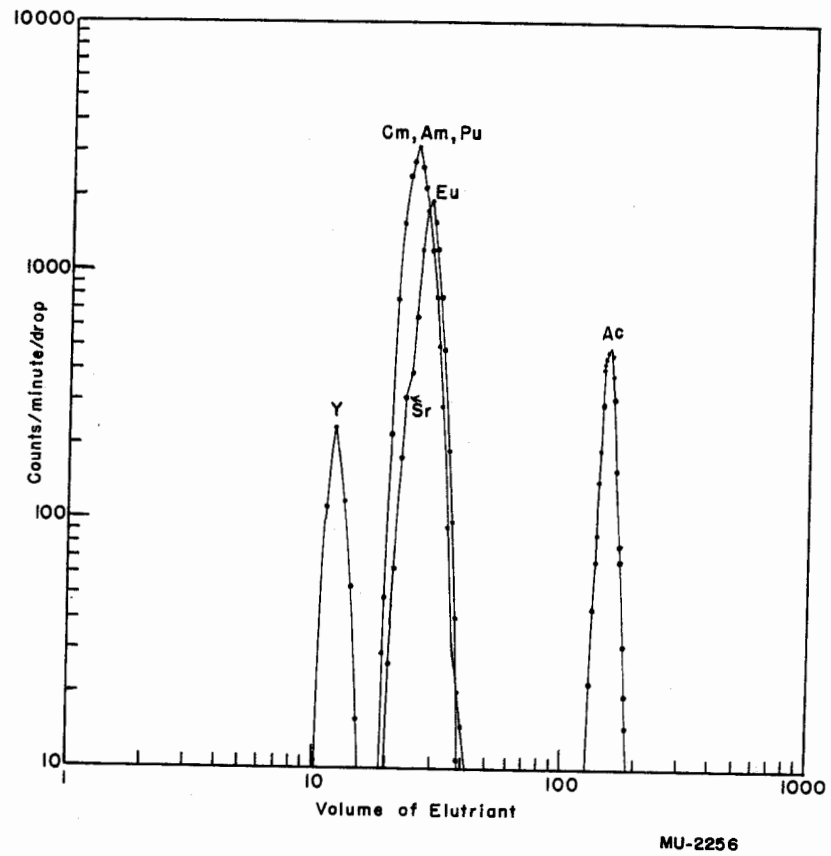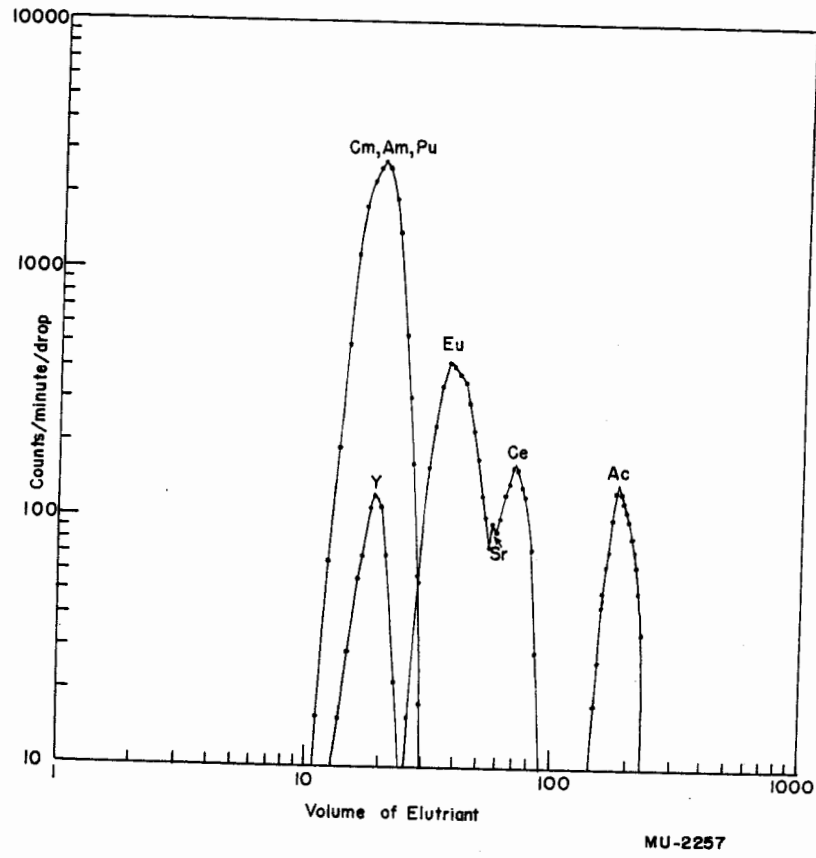
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Fig. 4

Fig. 5

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Fig. 6

Fig. 7

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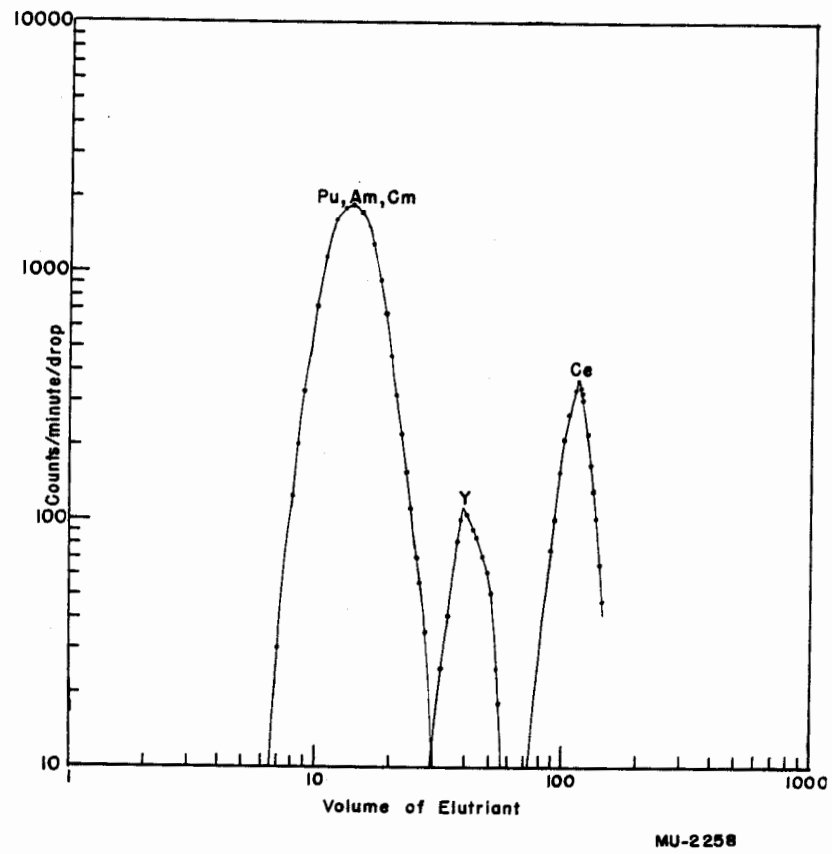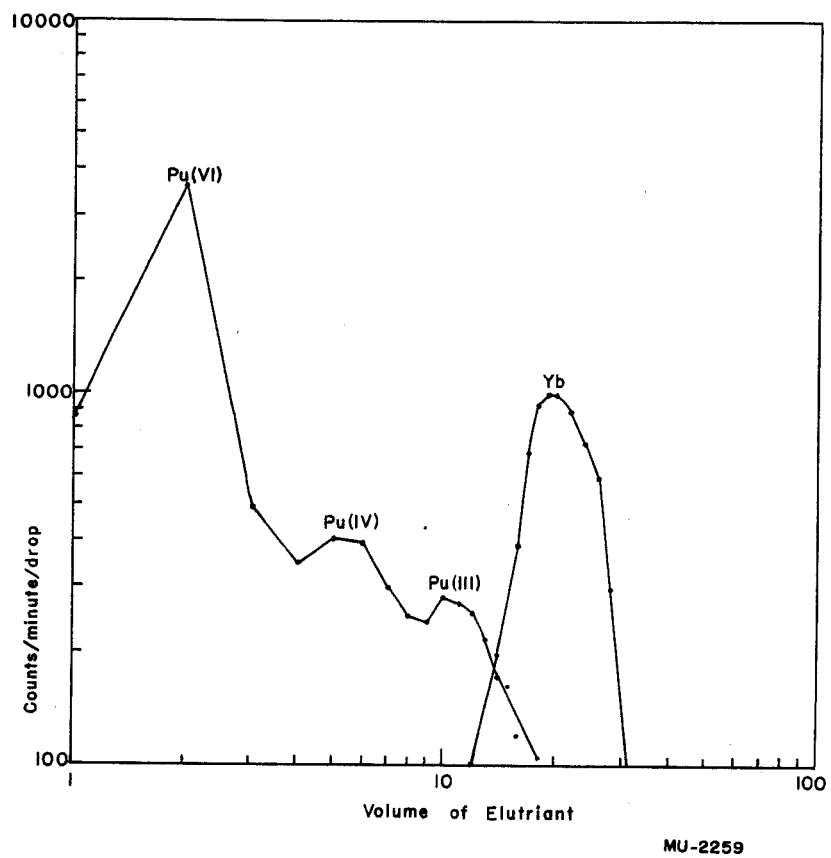
Fig. 8
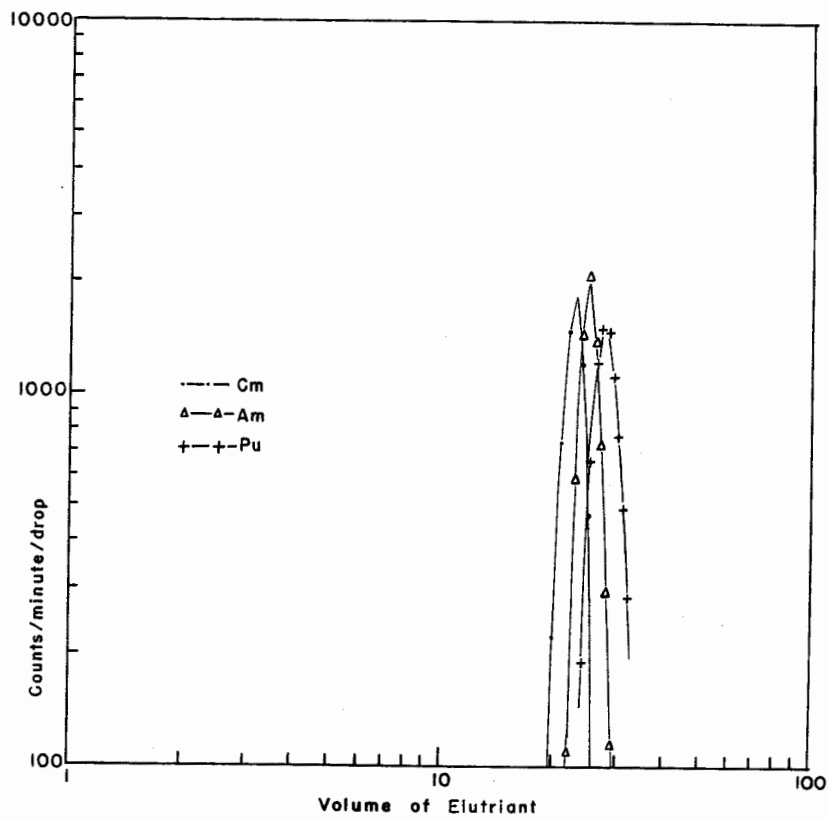
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Fig. 9

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Fig. 10

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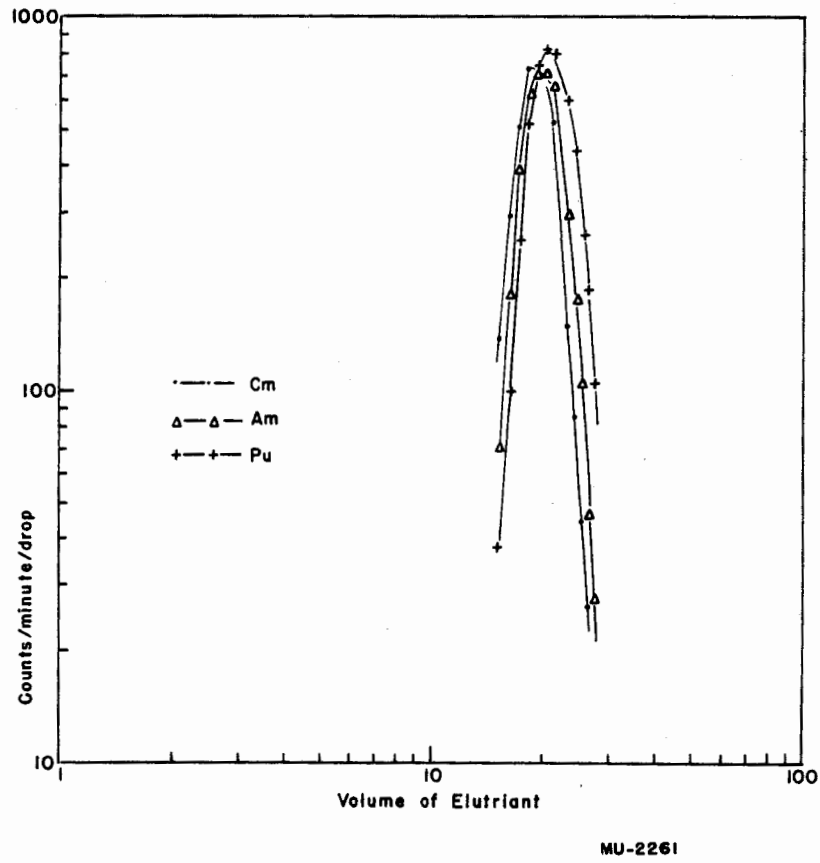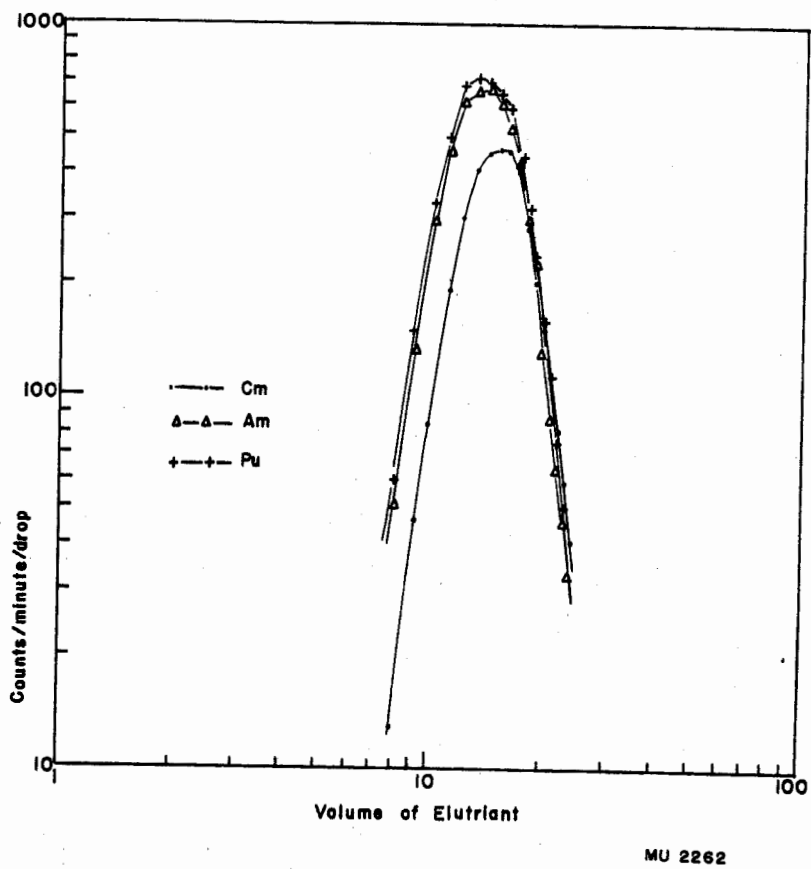
Fig. 11

(V) and (VI) states should elute in about the same place, namely in the first
column volume, and furthermore, it has been observed[7] that neptunium(VI) is
unstable in strong hydrochloric acid solutions. Most likely no neptunium(VI)
remained in these elutions at 9 $\underline{M}$ and 12 $\underline{M}$ HCl, although the presence of nep-
tunium(VI) is quite definite at 3 $\underline{M}$ HCl.

An attempt was made to determine the elution peak position of thorium
in 6 $\underline{M}$ and in 12 $\underline{M}$ HCl using only a few hundred counts/minute of Th^{230} mixed
with much larger amounts of Th^{232}. At both these hydrochloric acid concen-
trations the value of the K_d for thorium is quite large, and so it elutes
quite late. Two weeks and one week were required for the 6 $\underline{M}$ HCl and 12 $\underline{M}$ HCl
elutions respectively, and the peaks were too broad and had too low a counting
rate for any accuracy, so that it was decided to determine the K_d's for
thorium by equilibrium distribution experiments with europium ion as a stan-
dard. The method was the same as that described previously; 2.00 ml samples
of hydrochloric acid solutions containing known amounts of the thorium and
europium tracers were equilibrated with known weights of resin, and then
0.40 ml aliquots of the solution were withdrawn for counting. The accuracy
in this set of experiments was not as good as had been hoped for, mainly be-
cause of the low activity of the thorium tracer, and because the great differ-
ences in the K_d's of the two ions did not permit a compromise in the amount
of resin used so as to approximate a 50 - 50 distribution of each activity be-
tween the solution and resin phases. However, the ratio of the K_d's of thorium
and europium from the same equilibration should be more accurate than the ab-
solute value of the equilibrium distribution coefficients themselves, and it
is only the ratio that is necessary to fix the position of thorium relative to

europium in an elution. (Table 2.) Even so the elution peak positions for
thorium calculated with these ratios and the known peak positions for europium
do not agree too well with the two thorium elutions actually performed.

To determine the elution peak positions of uranium(IV), a tracer solu-
tion was prepared by reducing a solution of U^{233} in 0.5 $\underline{M}$ HCl or $HClO_4$ by
stirring for 15 - 60 minutes with a small piece of metallic U^{238}. At the
hydrogen ion concentration employed, the metallic uranium apparently does
not react rapidly with hydrogen ion but does react with the uranium(VI) ions,
providing a solution of tetrapositive U^{233} and containing not too much U^{238}
to seriously load the column.

A summary of what were considered successful elutions, i.e., those
that were not disturbed mechanically by factors beyond control, bubbles in
the resin bed, overly great temperature fluctuations, etc., are given in
Tables 3 through 6. Again a drop is the elution unit volume. Although two
columns of different diameter were used, the relative positions of the ions
on elution should be the same, so the results have been normalized to the
10 cm by 1 mm column by adjusting the relative positions of the ions to that
of an ion chosen as a standard. The peak positions so chosen are underlined
in the Tables. The symbols given after the trial number have the following
significance: R means that the eluting solutions was ~0.001 $\underline{M}$ in hydriodic
acid; O means that the eluting solution was ~0.02 $\underline{M}$ in nitric acid; (U) means
that uranium metal was used to reduce the tracers;

Table 2

Equilibrium Distribution Data for Thorium and Europium

Expt.	Resin weight	Solution volume	Solution normality	β counts/min/0.4 ml	α counts/min/0.4 ml
1		2.0 ml	11.6	2325	866
2	.0356 g	2.0 ml	11.6	1781	290
3		2.0 ml	11.6	2376	863
4	.0356 g	2.0 ml	11.6	1730	248
5	.0308 g	2.0 ml	8.8	1983	203
6	.0308 g	2.0 ml	8.8	1971	178
7		2.0 ml	5.9	2389	795
8	.0375 g	2.0 ml	5.9	1939	91
9		2.0 ml	5.9	2420	770
10	.0375 g	2.0 ml	5.9	2105	91

Expt.	Solution normality	Eu K_d	Th K_d	Ratio Th K_d/Eu K_d
2	11.6	17.1	111	6.5
4	11.6	21.0	139	6.6
5	8.8	11.2	212	18.9
6	8.8	13.3	250	18.8
8	5.9	10.4	412	39.6
10	5.9	8.7	398	45.7

(D) means that sodium dichromate was used to oxidize the tracers. The average value of the elution peak positions from the various trials is shown graphically in summary form in Figure 12.

Table 3

Elution Peak Positions with 3 M HCl Solutions

	Np(V)	U(VI)	Np(VI)	Pu(VI)	Cs	Yb	Sr	Y	Eu	Cm	Am	Pu(III)	Ba	Ce	La	Ra	Pu(IV)	Ac
1.	R					28.5	36.5	40	81	82	97	103	135	138	172	212		
2.	R						36	40	85.5	85	98	106		134	170			384
3.	R											105						
4.	R											105						
5.	R											104						
6.	R									90	99	105		~140				
7.	O					30.5					100		134		177	198	370	
8.	O								87		100						~275	
9.	O	2			18		37	41						135				
10.	O				18		36	39						135			>500	
11.	O(D)	4.5		10		29												
12.	O(D)	4		10														
13.	O(D)				8-9													
14.	O		12.5-13				37	40										

R means an elution with a drop of hydriodic acid present in the eluting solution; O means eluting solution is 0.02 M in nitric acid; (U) means uranium metal used to reduce the tracers; (D) means sodium dichromate used to oxidize the tracers.

Table 4

Elution Peak Positions with 6 M HCl Solutions

	Np(V)	U(VI)	Np(VI)	Pu(VI)	Cs	Yb	Y	Sr	Cm	Am	Pu(III)	Eu	Ce	La	Ba	Pu(IV)	Ra	Np(IV)	U(IV)	Ac	Th
1. R(U)		3.5			5		12	22.5					40						116–126		
2. R(U)		3.5			5.5		12	23					40						~130–135		
3. R		3			5		10.5	20.5				25	40					97		124	
4. R(U)		3			5.5		12	23.5					40					62–63			
5. R					5		11	20.5					40					91			
6. R	2				5.5		12.5	22.5					40					~95			
7. R							10	~19	19	20.5	22.5	22.5	40							~125	
8. R							10		18.5	20.5	22.5	22.5	40								
9. R									19.5	21.5	23.5		40								
10. O	1.5	3			5.5		10	20.5		21.5		~23	40			72		89–92	119		
11. O	1.5				6		11	21.5		22		25	40					91			
12. O							10.5	22		23.5			40	49		~67			138		
13. O						7.5	10	20.5		22.5				49	56.5		72	~90			
14. R						6.5	10.5	22		24				50	57		68	~82			

Table 4 continued

	Np(V)	U(VI)	Np(VI)	Pu(VI)	Cs	Yb	Y	Sr	Cm	Am	Pu(III)	Eu	Ce	La	Ba	Pu(IV)	Ra	Np(IV)	U(IV)	Ac	Th
15.	0											23.5				71					
16.	0									21		23.5				64					
17.	0									22		23.5				72					~1000
18. O(D)	2.5	2.5?				7															
19. O(D)	1.5	1.5?					10	21.5													
20. O(D)	1.5			2.5		7						22				39					
21.	1.5	1.5?		2.5								23				68					
22. R(U)							12	21									20		140		
23.	2						10.5	21.5									20				

Table 5

Elution Peak Positions with 9 $\underline{M}$ HCl Solutions

	Np(V) Cs	U(VI)	Np(VI)	Pu(VI)	Pu(IV) Yb	Np(IV)	Y	Cm(III)	Am	Pu(III)	U(IV)	Eu	Sr	Ce	Ra	La	Ba	Ac	Th
1. R	3						15		18.5				49	60		69			
2. R	3.5						16		19				50.5	59		71		160.5	
3. R	3						17		18				~50.5	60		~67		160	
4. R							~16.5	15	16	17		31.5	49	60				153-4	
5. R							17.5	17	18	19			~50	60					
6. R							15.5	15	16	17		30.5		60					
7. R						23	16.5						50						
8. R						14.5	14.5					30.5	50		56			156	
9. R					9		16		16.5				50		58.5	~71	~71		
10. R(U)		2.5									29	31							
11. R(U)	3	2					14.5				31		50						
12. R(U)	3.5					~15	15						50						
13. O		2.5			9.5 ~16		16					31	50		59			153	
14. O				7					16										

Table 5 continued

	Np(V)	Cs	U(VI)	Np(VI)	Pu(VI)	Pu(IV)	Yb	Np(IV)	Y	Cm(III)	Am	Pu(III)	U(IV)	Eu	Sr	Ce	Ra	La	Ba	Ac	Th
15. O					6.5						16										
16. O(D)				1.5	5									31							
17. O				2	8									31							
18. O				1.5?								~20									
19. O				1.5										31							
20. O				2	6.5		8.5							31							
21. O(D)				2?			8														
22. R		3.5							16.5						50						
23. R		3.5							18						50						
24. O									18						50	55					
25. R	1.5	4						20.5	15					34	50						
26. O									15					31	50	70					
27. R		3.5							16.5					31	50	~58					
28. R		3							16.5						50						

Table 6

Elution Peak Positions with 12 M HCl Solutions

	Np(V)	Cs	U(VI)	Np(VI)	Pu(VI)	Pu(IV)	Np(IV)	Pu(III)	Am	Cm	U(IV)	Yb	Y	Ra	Eu	Ba	Ce	La	Sr	Ac	Th
1. O							6.5					21.5	40	39	67.5				125	~207.5	
2. R			2									20	41	41	67.5		~105		~118		
3. R												22	41	34	67.5				123	~225	
4. O							6.5		13.5			20	39	43	67.5	72		~92	119		
5. O(D)				2?			5.5					20			67.5						
6. O(D)					2	5.5		11.5													
7. O					2	5.5						20									
8. O									12			20									
9. O					2	5.5		12				20									
10. O(D)					2	6.5		12													
11. O					2	6.5		11				20			67.5						
12. O							6.5								67.5						
13. O						5 →															
14. O						7.5 →			12.5												
15. O						7 →				13.5											
16. R(U)		3	2								15		39.5				~108				
17. R(U)							7.5 →					20							~128		

Table 6 continued

	Np(V)	Cs	U(VI)	Np(VI)	Pu(VI)	Pu(IV)	Np(IV)	Pu(III)	Am	Cm	U(IV)	Yb	Y	Ra	Eu	Ba	Ce	La	Sr	Ac	Th
18. R(U)							7.5 →					20									
19. R							6					20									
20. R									11				~39.5		67.5		~104	~205			
21. R								13.5	14	15			39				114				
22. R								11	11.5	12.5			39.5		67.5		~116	~217			
23. R							6		12				39		74		114				
24. R									11								111	115			
25. R									11				38.5		68		~109				
26. R									11.5				39.5		~68			~204	~550		
27. O		2							12.5				39.5				106	113	~148		
28. O									11.5								~111	~119			
29. R	3												40	35	67.5			127.5	200		
30. R(U)		2-2.5									18		39.5					148			
31. O(D)		4.5			3.5	8							42	37	67.5			153			
32. O													39.5	39.5							

3.2 M HCl

Np(V) Pu(VI) U(VI) Cs Yb Sr Y Cm Pu Ce La Ra Ac
                                    Eu   Ba
       Np(VI)   Am

6.2 M HCl

Np(V) U(VI) Cs Yb Y Cm Pu(III) Ce La Ba Ra Ac
       Pu(VI)   Sr Eu   U(IV)
                     Am   Pu(IV) Np(IV)

9.3 M HCl

Np(V) Cs Pu(IV) Yb Y Cm Pu(III) Eu Sr Ce La Ac
U(VI)   Np(IV)
Pu(VI)   Am   U(IV)

12.2 M HCl

Np(V) Cs Pu(IV) Np(IV) Am Cm Yb Ra Y Eu Ba Ce La Sr Ac
U(VI)   Pu(III)
Pu(VI)

1   10   100   1000

Volume of Elutriant

MU 2263
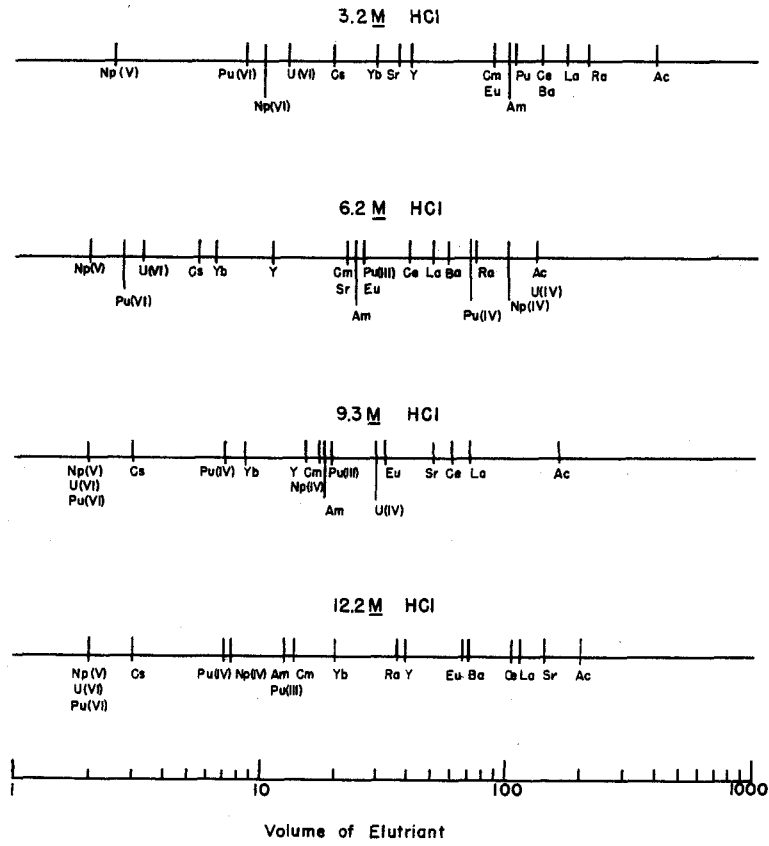
Fig. 12

III. RESULTS AND DISCUSSION

The results of the equilibrium distribution experiments on americium
and promethium in hydrochloric acid solutions of various concentrations,
Figure 2, illustrate very well the minimum in the K_d for the lanthanides
around 7 $\underline{M}$ HCl, and the continuous decrease in K_d with increasing hydrochloric
acid concentrations for the actinide ions. The lanthanide behavior is very
likely an effect, due not to the lanthanides, but to the resin. Increasing
the hydrochloric acid concentration in the contacting solution causes the
resin to shrink, and this shrinkage of the resin causes an increase in the
concentration of the functional groups inside the resin, hence shifting the
ion equilibrium toward the resin and decreasing the rate of elution. The
behavior of the lanthanides is then the normal behavior, and it is the acti-
nides that are unusual, as they do not show this minimum in the value of K_d
around 7 $\underline{M}$ HCl.

Furthermore, as is shown in Figures 9 - 11, the actinide ions curium(III),
americium(III), and plutonium(III) reverse their order of elution from 3 $\underline{M}$ HCl
to 12 $\underline{M}$ HCl, that is, in 3 $\underline{M}$ and 6 $\underline{M}$ HCl they show the order, curium, americium,
plutonium, as would be expected from the empirical rules for ion exchange
affinities given earlier and the order of their hydrated ionic radii,
curium > americium > plutonium, but by 12 $\underline{M}$ HCl, they elute in the order
plutonium, americium, curium. The cause of both these anomalies is probably
due to the same factor, and that is the formation by the actinide cation of
a complex with chloride ion at high hydrochloric acid concentration. This
complex ion formation more than compensates for the tendency to shift the
equilibrium toward the resin due to the resin shrinkage, and so the actinides

continue to move up, that is, show faster and faster elution rates, as the hydrochloric acid concentration is increased. Then if the strengths of the complex ions vary as plutonium(III) > americium(III) > curium(III), the plutonium(III) will move up faster than the americium(III), which in turn will move up faster than the curium(III), and this would explain the reversal in their elution order on going from 6 $\underline{M}$ to 12 $\underline{M}$ HCl solutions.

The questions then arise as to why the actinides show this complex ion formation while the lanthanides do not, and why the strengths of the actinide complex ions vary in the order plutonium(III) > americium(III) > curium(III). Since, as a group, the actinides have comparable ionic radii to the lanthanides, (see Table 7) in fact, slightly larger values, ionic complexes do not seem a likely cause for such differences in behavior. Especially, since among the actinides the ionic radii go as plutonium(III) > americium(III) > curium(III), so that the strengths of ionic complexes should go in the reverse order, the smaller ion forming the stronger complex. Solutions of ionic complex forming agents would then enhance the natural elution order of the resin, curium, americium, plutonium, instead of reversing it.

Table 7

Ionic Radii of Actinide and Lanthanide Elements[8]

Lanthanide Series		Actinide Series	
Element	Radius, Å	Element	Radius, Å
1. La(III)	1.04	Ac(III)	1.11
2. Ce(III)	1.02	---	---
3. Pr(III)	1.00	---	---
4. Nd(III)	0.99	U(III)	1.04
5. Pm(III)	(0.98)	Np(III)	1.02
6. Sm(III)	0.97	Pu(III)	1.01
7. Eu(III)	0.97	Am(III)	1.00

Since ionic complex ion formation cannot account for the observed behavior of the ions, covalent bonding must be considered, and this does lead, in fact, to a possible explanation, suggested by the differences in stability and size of the 5f eigenfunctions in the actinides and the 4f functions in the lanthanides.[5] M. G. Mayer has shown on theoretical grounds that the f eigenfunctions have a unique behavior compared to the s, p, or d functions,[9] that is, they undergo a sudden change in spatial extent and energy at certain atomic numbers. The effective potential energy of an f electron in the field of the residual atom has two negative regions after a minimum Z (about 47) and at first the outer potential minimum is dominating so the 4f eigenfunctions have a maximum there and are "outside" functions, that is, they extend out spatially as far as, or beyond, the 5d and 6s orbitals. The 4f orbitals, however, are at a higher energy level than the 5d or 6s, so these latter fill in first. With increasing atomic number, the inner potential minimum gets deeper very rapidly so that it comes to dominate the nature of the 4f function and in a small range of Z the shape of the function changes abruptly to that of an "inner" orbit. The rapidly decreasing potential also brings the energy down so that the 4f level begins to fill at cerium, Z = 58, and at this point the 4f functions are already "inside" the 5s and 5p electron shells. This can be seen by the negligible effect of the 4f electrons on the valence properties of the atoms, the rare earths all having a common tripositive state, and by the very sharp absorption lines shown by the lanthanides. These lines are due to (forbidden) f to f transitions, and so are shielded from external influences.

Because the 4f eigenfunctions have already shrunk at cerium, they are
not very useful for covalent bonding in the lanthanide elements, as, for
such bonding, orbitals must be available spatially as well as energetically,
that is, they must extend out far enough to have sufficient overlap with
the bonding orbitals of the other atom or atoms. However, at a lower
atomic number than that of cerium, the 4f eigenfunctions, although at a
higher energy, are appreciable beyond the 5s and 5p shell maxima, and so,
if more energy can be gained by using them in hybridized covalent bonding
than is lost in promoting or placing electrons in these higher levels, the
4f orbitals may become bonding orbitals. It has been noted that TeF_6
hydrolyzes readily in water in contrast to the inert behavior of SeF_6 and
SF_6, and the explanation offered involves such a use of 4f orbitals.[10]

The 5f eigenfunctions go through a transformation similar to that of the
4f after the completion of the rare earth series. At first they are "out-
side" functions, but again, as the atomic number increases, a critical
region of Z is reached at which the eigenfunctions shrink and become "inner"
functions and their energy level falls so that the 5f shell starts to fill.
In this actinide series, however, the 5f orbitals either do not shrink as
rapidly as in the 4f series, or they have a greater spatial extension relative
to the 6s and 6p orbitals than the 4f orbitals have relative to the 5s and
5p functions. In either case the result is a lower shielding of the 5f elec-
trons.

Moreover, the nearness of the 5f and 6d levels over a region of several
atomic numbers makes it difficult to determine where they cross, that is,
at what Z the first 5f electron fills in, and the lower shielding of the 5f

orbitals compared to the 4f, makes it possible that, at the beginning of

the 5f series, the levels change positions depending on the chemical binding

of the element or on its degree of ionization. Thus, the gaseous atom may

have a different electronic configuration than the metallic atom, and the

electronic configuration of the ion may differ from compound to compound

in solids and in solution. These small energy differences are evident also in

the spectroscopic data; for example, spectroscopic evidence seems to show that

the ground state of the neutral thorium atom has a $7s^2 6d^2$ configuration[11]

(although x-ray data indicate the presence of a 5f electron)[12] but the

ground state of the triply ionized atom has a single 5f electron.[13]

The fact that the first members of the actinide series have higher

oxidation states than the characteristic tripositive state, i.e. protac-

tinium(V), uranium(IV), uranium(VI), neptunium(IV), neptunium(V),

neptunium(VI), plutonium(IV), plutonium(V), plutonium(VI), in contrast to

the beginning of the lanthanide series, shows that the first 5f electrons

are not bound as tightly as the 4f electrons and that they are more easily

affected by external influences, although the gradual uniform stabilization

of the tripositive state indicates the presence of a regular f series, analo-

gous to the rare earths.

The comparable binding energy, at the beginning of the actinide series,

of the 5f, 6d, and 7s levels for a range of several atomic numbers, is a

favorable condition for their use in hybridized bonds. Furthermore the

greater spatial extension of the 5f orbitals relative to the 4f and their

slower shrinkage, might make them more available for such hybridization closer

to the atomic number where the levels start to fill, rather than several

numbers earlier as with the 4f orbitals. Thus such hybridization involv-
ing 5f orbitals seems reasonable to account for the results reported in the
present paper.

Consideration of the type of coordination compounds formed by the
actinides may throw light on the possibility of such covalent bonding.
Plutonium(IV) forms an insoluble crystalline compound with 8-hydroxyquinoline
of the formula PuR_4,[14] and so is probably eight coordinated, as compounds of
8-hydroxyquinoline with metallic cations have two linkages from each organic
radical to the central atom. Similarly, it forms an acetylacetonate com-
pound[15] with the structure PuR_4, again indicating eight coordination.
Thorium, zirconium, hafnium, cerium, and uranium also form such acetylacetone
compounds, but the elements that can form eight coordinated compounds or
complexes are quite few, in fact are limited practically to those in the
above mentioned acetylacetonates and to ruthenium (as RuO_4), osmium (as
OsO_4 and OsF_8), tantalum (as TaF_8^{-3}), molybdenum (as $Mo(CN)_8^{-4}$, and
$Mo(CN)_8^{-3}$), tungsten (as $W(CN)_8^{-4}$), and certain other complex ions of
tetrapositive tin and lead.

It has been shown from group theoretical arguments[16] that a symmetrical
eight coordinated compound or complex, that is, one with the eight groups
at the corners of a cube, must contain an f orbital, in fact, involve
d^3fsp^3 or d^3f^4s hybridizations, and so it has been suggested that this is
the arrangement in the $Mo(CN)_8^{-4}$ complex, although the 4f orbitals do not
fill until sixteen atomic numbers later at cerium, $Z = 58$. This structure
for the $Mo(CN)_8^{-4}$ complex is wrong, however, as shown by the x-ray
crystallographic work of Hoard and Nordsieck[17] who found a lower symmetry

arrangement than cubic in the complex, in fact a dodecahedron obtainable from d^4sp^3 bonding,[10] a much more reasonable result at this point in the periodic table. Hoard and Nordsieck point out that $W(CN)_8^{-4}$, would have the same type structure and Kimball[10] suggests that OsF_8 and TaF_8^{-3} might be d^5sp^2 hybridization. Possibly RuO_4 and OsO_4 have this structure also.

None of these structures would involve f orbitals as the possible f levels, whether 4f or 5f as the case may be, are at too high an energy at the elements mentioned. As we have already seen, however, 4f levels may be used for bonding at tellurium (Z = 52) and they possibly are involved at iodine in the molecules IF_7 and IF_5.[18] They also may be taking part in the eight coordination of cerium acetylacetonate, just as the 5f orbitals may be involved in the acetylacetonates of thorium, uranium, and plutonium, and necessarily so if these structures are cubic.

Along another experimental line Glueckauf and McKay have pointed out a series of facts about the chemistry of uranyl nitrate that, taken altogether, indicate, they say, the use of 5f orbitals in complexes formed by this salt.[19]

The fact that no known structures have as yet been definitely established to involve f orbital hybridization does not mean that f orbitals are inherently nonbonding; apparently insufficient work has been done studying complexes in the narrow regions of the periodic table where f orbitals may be possible bonding eigenfunctions. These regions, between about antimony and cerium for the 4f functions between possibly polonium and californium for the 5f functions, are narrow because of the necessity of a compromise between atomic numbers large enough so that the actual energy level is not too high

and atomic numbers low enough so that the f eigenfunction has not already undergone its drastic spatial shrinkage and change from an "outer" bonding to an "inner" shielded function. In these regions there is no reason why the f orbitals cannot take part in all types of hybridization. For example, tetrahedral bonding, the usual sp^3 hybridization of carbon, can be formed from sf^3, f^4, fp^3, or fd^3 hybridizations, as can be shown by a group theoretical treatment. The common six coordination complex, the symmetrical octahedral arrangement, is usually a d^2sp^3 hybridization, but d^2sf^3 hybridization can give the same structure.

With these considerations in mind, the experimental results of the ion exchange studies may now be interpreted. As has already been mentioned, the difference in the behavior of the tripositive lanthanides and actinides in going from elutions with 6 $\underline{M}$ HCl to elutions with 12 $\underline{M}$ HCl can be explained by the formation to a much greater extent by the actinides of covalent complex ions with chloride ion. They are, therefore, pulled off the resin the faster, the higher the chloride activity in solution, while the lanthanides, which complex to a much smaller degree, actually are pulled back more on the resin in hydrochloric acid solutions of higher concentration due to the shrinkage of the resin and consequent increase in concentration of its active points. The actinides also feel the greater attraction by the resin at higher hydrochloric acid concentrations, but the complex ion formation more than offsets this. The results of the elutions with the tripositive ions of lanthanum, cerium, europium, ytterbium, actinium, plutonium, americium, curium are summarized in Figure 13. Yttrium(III) is also included because it acts as a pseudo lanthanide, but with no possibility of f orbital bonding.
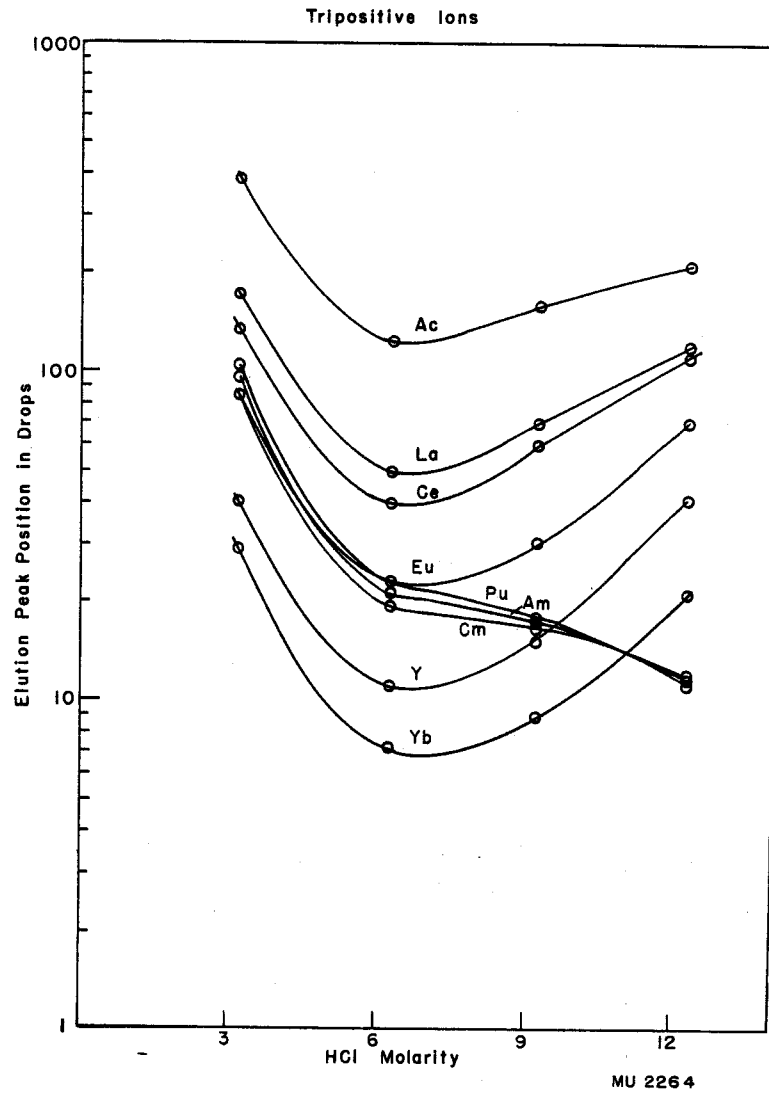
Fig. 13

The molarity of the eluting hydrochloric acid solution is plotted as abscissa, and the elution peak position in drops, normalized to the 10 cm by 1 mm column is plotted as ordinate. The elution peak position is directly related to the equilibrium distribution coefficient of the ion, its K_d, and so this method of plotting is comparable to Figure 2.

Certain features in Figure 13 are clear. The difference in behavior of curium, americium, and plutonium on the one hand, and ytterbium, yttrium, europium, cerium, lanthanum, and actinium on the other, stand out. In solutions of hydrochloric acid above 6 $\underline{M}$ in concentration the actinide ions show much greater complex ion formation than the others. This complex formation with chloride ion is borne out by other types of data. Absorption spectra measurements on plutonium(III) show that changes in the spectrum indicative of complex ion formation occur in hydrochloric acid solutions above 6 $\underline{M}$ in concentration.[20] Transference experiments on plutonium(III) in hydrochloric acid solutions indicate that a small but appreciable fraction of the plutonium migrates to the anode in 1 $\underline{M}$ HCl, and that a somewhat larger amount[21] does so in 10 $\underline{M}$ HCl. This fact suggests that the actinides can form negative complex ions with chloride ion, and some careful anion exchange work with europium and americium in 12 $\underline{M}$ HCl does indeed show a small delay in the elution peak position of americium(III) compared to europium(III), while similar experiments in 5 $\underline{M}$ HCl show no such differentiation.[22]

If these tripositive actinide complex ions with chloride ion do have some covalent character, then the use of a stronger covalent complexing agent should increase the relative amount of complex ion formed.

Again, it would seem most likely that covalent complex ions are being dealt

with, and that the differences in the behavior of the actinide and lanthanide

ions can be ascribed to differences in the bonding eigenfunctions available

in the two series. The s and p functions must be similar in the lanthanides

and actinides, that is the 6s and 6p, and the 7s and 7p, respectively, so

the change in ability to form complex ions results from the differences in

the 4f and 5d functions in the one case and the 5f and 6d in the other. Both

the d and f orbitals probably contribute, but for the reasons already dis-

cussed, the difference between the 4f and 5f eigenfunctions is very likely

a predominating factor. Evidence that this is so is furnished by the data

on yttrium(III), which has a comparable radius to the lanthanides and elutes

with them, and has plenty of d orbitals available, but has so low an atomic

number that the 4f orbitals are still at too high an energy level to be

available for bonding. In Figure 13 the curve for yttrium(III) rises more

steeply from 6 $\underline{M}$ to 12 $\underline{M}$ HCl than that of any of the lanthanide ions, indi-

cating even less complex ion formation in this range of hydrochloric acid

concentration than the lanthanide ions show. This is in agreement with the idea presented that f orbitals play a significant part in this complex ion formation.

If such is the case, the greatest tendency for complex ion formation among the rare earths should occur at the beginning of the series where the 4f functions have their maximum extension, and an examination of Figure 13. shows that, in fact, the lanthanide curves do flatten out between ytterbium and lanthanum in going from 6 $\underline{M}$ to 12 $\underline{M}$ HCl eluting solutions, indicating a slight, but increasing, tendency toward complex ion formation with chloride.

Examination also shows that actinium(III) resembles the lanthanides much more closely in its elution behavior than it does plutonium(III), americium(III), and curium(III), that is, its tendency toward complex ion formation is much weaker than in the case of the latter ions. The curve for actinium(III), however, is flatter between 6 $\underline{M}$ and 12 $\underline{M}$ HCl than that of any of the lanthanides, corresponding to a somewhat greater complex ion forming tendency than that of even lanthanum, which forms the strongest complex ion with chloride of the rare earth ions.

Since the atomic number for which the 4f orbitals are at an optimum for bonding in a tripositive ion is apparently below $Z = 57$, lanthanum, it was thought worthwhile to look at $Z = 56$, barium. However, as barium is a dipositive ion its behavior cannot be compared with the tripositive ions already studied, so strontium and radium elutions were also performed. It was felt that strontium(II) should show little tendency to complex with chloride ion, as it does not have f orbitals available, but that barium(II) might very well complex in high hydrochloric acid concentrations due to the

availability of 4f orbitals for hybridized bonds, and that radium(II) might

also form complex ions with chloride ions due to the possibility of using

5f orbitals. The results of the experiments, as shown in Figure 14, are

most satisfying from this point of view. (The ordinate and abscissa are

the same as in Figure 13, i.e., elution peak position and hydrochloric acid

molarity, respectively.) The curve for strontium(II) passes through a

minimum around 6 M HCl exactly as in the case of the rare earth elements,

showing that it is indeed not complexed greatly by chloride ion. The slope

of the curve from 6 M to 12 M HCl is not the same as for the tripositive

ions, but it should not be expected that the shrinkage of the resin would

affect ions of different charge in the same manner, or that their activi-

ties in 6 M and 12 M HCl would have the same ratios. As was thought pro-

bable, barium(II) showed complex ion formation, indicated by a flatter

curve from 6 M to 12 M HCl. Radium(II) showed complex ion formation to even

a greater extent, and, although this was not expected, due to the behavior

of actinium(III), it is not altogether surprising, as dipositive ions might

very well have a different optimum atomic number for 5f orbital hybridiza-

tion than tripositive ions, and since actinium(II), thorium(II), and uran-

ium(II) cannot be studied, there is no way of knowing that these latter might

not form stronger complexes with chloride ion than does radium(II).

Thus the series of ions, strontium(II), barium(II), and radium(II),

offers additional evidence that f orbitals play an important part in covalent

complex ion formation at the beginning of the lanthanide and actinide series.

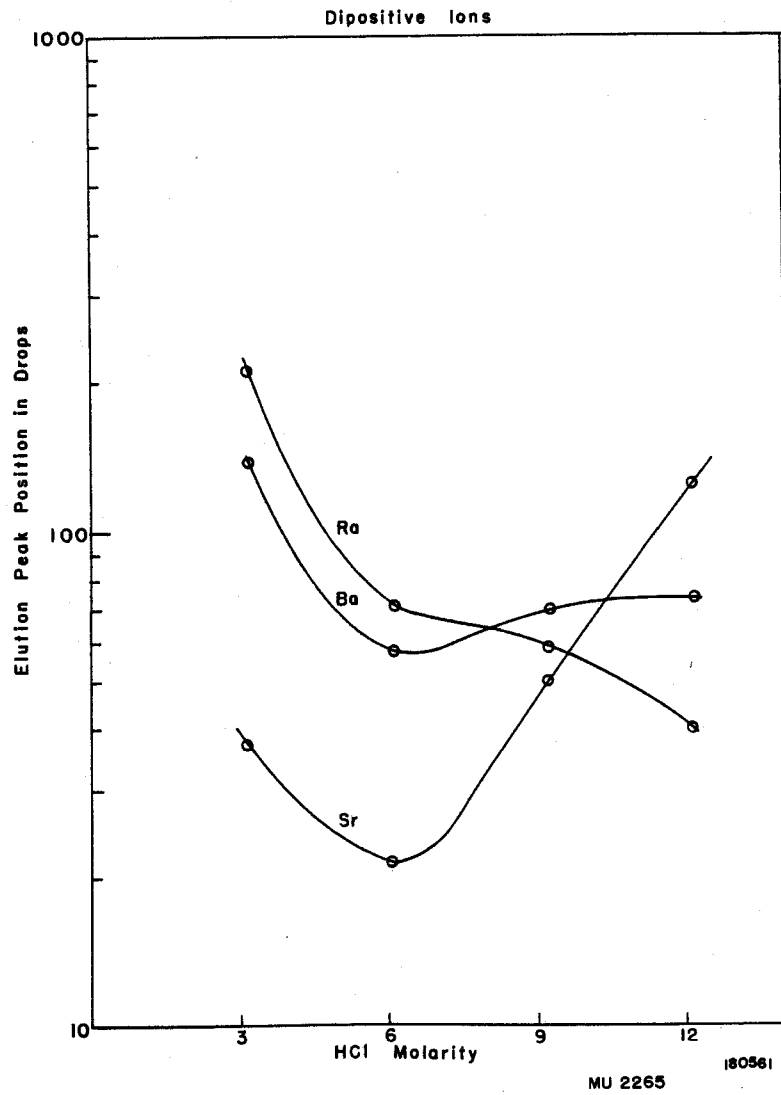Strontium ion with the smallest ionic radius and with vacant and available

Fig. 14

d orbitals just like barium and radium, has, however, no f orbitals, and its almost negligible tendency to form a complex with chloride ion can be correlated with this fact, just as in the case of yttrium(III).

The hexapositive states of uranium, neptunium, and plutonium were also studied. These are oxygenated to form the UO_2^{++}, NpO_2^{++}, and PuO_2^{++} ions, which are often considered as large dipositive cations. The results can be seen in Figure 12. Already at 6 $\underline{M}$ HCl these ions pour right through the resin column and come off in the first column volume, indicating strong complex ion formation with chloride ion, and, as might be expected for a large dipositive cation, little binding to the resin. Evidence for the formation of such complex ions with chloride is already in the literature from transference experiments[21] and spectroscopic studies.[20] In these complex ions it is very likely that ionic binding plays a large part, but resonance with the covalent forms (possible if there is no change in multiplicity, that is, in the number of unpaired electrons) strengthens the binding even more.

Similar to these ions is neptunium(V) which exists in the form NpO_2^+, and washes right through the resin column even in 3 $\underline{M}$ HCl. Since cesium(I), a typical monopositive ion, is held up a bit on the resin column in hydrochloric acid solutions of such concentration, the rapid elution of NpO_2^+ signifies that appreciable complex ion formation occurs with the neptunium(V) in 3 $\underline{M}$ HCl.

Still another series of ions can be considered in the actinides: the tetrapositive states of thorium, uranium, neptunium, and plutonium. The results for these are summarized in Figure 15 where again elution peak
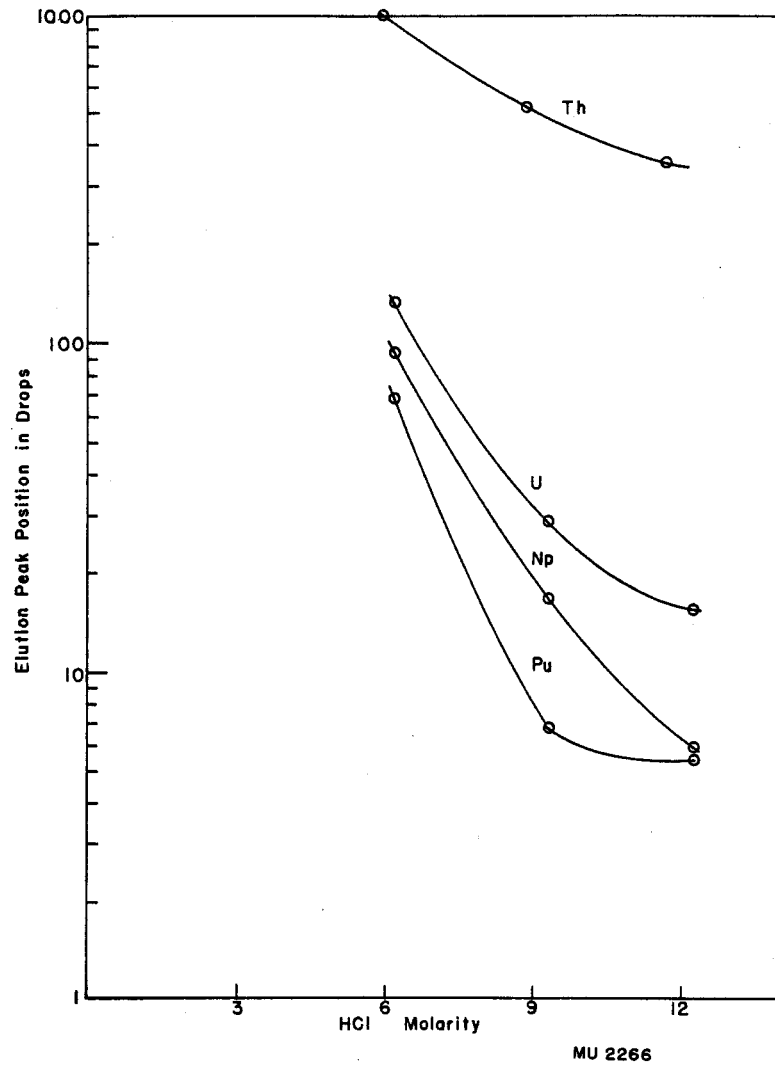
Fig. 15

position is the ordinate and hydrochloric acid molarity is the abscissa.
All these ions are presumably bare ions, that is, are not oxygenated,
and so due to their high charge should be strongly adsorbed on the resin
in the absence of complexing agents. However, the same high charges should
cause these ions to be strongly bound in ionic complexes, and, if there is
a possibility of resonance with covalent forms, the resulting complex will
be even stronger. No data are shown for 3 $\underline{M}$ HCl solutions, as the ions are
all bound so tightly to the resin at this hydrochloric acid concentration
that no elution can be conveniently observed. With the 6 $\underline{M}$, 9 $\underline{M}$, and
12 $\underline{M}$ HCl solutions, the tetrapositive ions elute in the sequence plutonium,
neptunium, uranium, and then thorium, which is the order expected from their
radii, neglecting complex ion formation. As the hydrochloric acid concentra-
tion is increased, these ions elute more and more rapidly, showing a tre-
mendous variation in the value of K_d, and indicating strong complex ion for-
mation, particularly for plutonium, neptunium, and uranium.

As these tetrapositive ions are relative-
ly small and highly charged, and since the complex ion formation does not
change, but enhances, their natural elution order from the resin, it seems
most probable that electrostatic attraction, that is ionic bonding, is the
major factor in their complex ion formation with chloride ion.

However, in the ions with a lower charge density, covalent bonding may
play a larger role. The reversals of the elution peak positions in 12 $\underline{M}$ HCl

of the tripositive actinide elements and of the alkaline earths, seem to
require such an explanation, although greater polarizability of the acti-
nide ions with their more densely packed electrons is also a possibility.
It should be mentioned that even though enough s, p, and d orbitals may be
available in the ions of these elements to account for the coordination in
the complex ions formed, stronger bonds might be formed by hybridization of
f orbitals and only incomplete use of the d orbitals, and the discussion
presented in this paper makes such a structure a reasonable model to explain
the differences in the elution behavior of the actinides and lanthanides
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