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EVIDENCE FOR F-SHELL COVALENCY IN THE ACTINIDES

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December 5, 1950

ABSTRACT

A study has been made of the elution of Cm(III), Am(III), Pu(III), Pu(IV), Ac(III), Y(III), Ce(III), Eu(III), La(III), and Sr(II) with 3, 6, 9, and 12M hydrochloric acid solutions from Dowex-50 cation exchange resin columns. This work confirmed and extended previous observations that the elution rates of the actinides increase with increasing hydrochloric acid concentration, while the elution rates of the lanthanides pass through a maximum around 7M hydrochloric acid, and that the normal elution order of the actinides, Cm, Am, and Pu (as in citrate elutions or in hydrochloric acid solutions below 9M) is reversed in 12M hydrochloric acid. A possible explanation for this behavior is given in terms of complex ion formation involving 5f-orbital covalency in the actinides.

EVIDENCE FOR F-SHELL COVALENCY IN THE ACTINIDES

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INTRODUCTION

Previous work¹ had brought to light certain similarities and certain

(1) K. Street, Jr. and G. T. Seaborg, J. Am. Chem. Soc., 72, 2790 (1950).

important differences in the behavior of the actinide and lanthanide elements on elution with hydrochloric acid solutions of various concentrations from Dowex-50, hydrogen form, cation exchange resin columns, and an explanation was suggested involving complex ion formation using f-orbital hybridization. For example, it was observed that in going from 3 to 6M hydrochloric acid, the actinides and lanthanides moved up in their positions of elution, but that in going from 6 to 9 to 12M hydrochloric acid, the lanthanides lutecium, promethium, and cerium gradually moved back, that is, they showed slower and slower elution rates, while the actinides americium and curium always moved up, that is, their elution rates increased monotonically with increasing hydrochloric acid concentration. Furthermore, although lutecium, promethium, and cerium kept the same order in the various hydrochloric acid solutions and curium came off ahead of americium in 6M hydrochloric acid, all as would be expected from a comparison of their ionic radii, in 12M hydrochloric acid the order of elution of the actinides reversed and the americium moved up just ahead of curium.

A further study of the properties of the actinides and lanthanides on elution with hydrochloric acid solutions was undertaken in order to obtain additional evidence on this complex ion formation in the actinide elements.

EXPERIMENTAL

First, in order to establish that the maximum in the elution rate of the lanthanides is due to an actual minimum in the equilibrium distribution coefficients of the ions between the resin and the hydrochloric acid solution and not to some obscure column effect, a series of equilibrium distribution experiments were run at room temperature on Am^{241} and Pm^{147} . Known amounts of these ions in 5 ml. samples of various concentrations of hydrochloric acid were shaken with small amounts (0.0076 to 1.8013 grams) of oven dried resin (colloidal agglomerates of Dowex-50 resin, hydrogen form, wet graded to settle at ca. 0.5 cm./min.) and then 0.50 ml. aliquots were withdrawn for counting and titration. In this way, values of K, the distribution coefficient $\left[\frac{\text{counts/g. of resin}}{\text{counts/ml. of solution}} \right]$, were obtained for promethium and americium at various hydrochloric acid concentrations, giving the curves shown in Fig. 1. The results confirm the observations on column elutions; the graph of K vs. hydrochloric acid concentration for Am^{+++} shows a steady decrease, while that for Pm^{+++} decreases at first, passes through a minimum around 7M hydrochloric acid, and then increases. Plotting $\log K^{\text{Am}}/K^{\text{Pm}}$ against $\log \text{H}^+$ indicates that below 4N hydrochloric acid, Am^{+++} and Pm^{+++} have on the average the same number of chloride ions around them, but that at higher concentrations of hydrochloric acid the Am^{+++} has several more chloride ions than the Pm^{+++} .

Next, a series of column elutions with various ions using 3.2, 6.2, 9.3, and 12.2M hydrochloric acid solutions as eluting agents were begun and are still ^oin progress. Tracer amounts of trivalent Cm^{242} , Am^{241} , Pu^{239} , Y^{90} , $\text{Eu}^{152,154}$, Ce^{144} , La^{140} , of tetravalent Pu^{239} , and of divalent Sr^{90} have been studied so far.

The resin used was Dowex-50 spherical fines, hydrogen form, wet graded to settle at ca. 0.5 cm./min. The elutions were made at room temperature and at

flow rates of ca. $0.1 \text{ ml./cm.}^2/\text{min.}$ The procedure was to stir a solution of the tracers in 0.5M HClO_4 with a small amount of resin until the activity was essentially all on the resin, and then the resin was placed on the column bed and the elution begun. Two columns were used, one 10 cm. long by 1 mm. in diameter, and the other 10 cm. long by $1 \frac{1}{2}$ mm. in diameter; however, since the relative positions of the elements on elution should be the same for the two columns, the results obtained with the 10 cm. by $1 \frac{1}{2}$ mm. column have been normalized to the 10 cm. by 1 mm. column.

The elution of the tracers was followed by counting on standard Geiger-Müller and alpha particle counters, and the various isotopes were identified by their radiation characteristics and half-lives. Typical runs are illustrated in Figs. 2-5. 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 with the results shown in Figs. 6-8. The ordinate is given as counts/min./drop since in this type of experiment the actual number of atoms is unimportant. The abscissa, given in drops, is actually an arbitrary unit as the volume of solution necessary to elute a given element will vary somewhat with the particular "batch" of resin used and with the packing and the previous history of the resin in the column.

At first there was considerable ambiguity in the results of the plutonium experiments. Regardless of whether Pu(III) or Pu(IV) was put on the column, only a single peak eluted. In experiments in which plutonium was the only alpha activity used, the plutonium eluted was collected, and zirconium phosphate precipitated in the solution followed by a lanthanum fluoride precipitation. The zirconium phosphate precipitate carries Pu(IV), the lanthanum fluoride precipitate, Pu(III) and Pu(IV). From these experiments, as well as the position of the plutonium elution peak with respect to those of americium

and curium, the plutonium was shown to be eluting as Pu(III). Apparently the resin itself in the high hydrochloric acid concentrations was reducing Pu(IV) to Pu(III). To obtain data on Pu(IV), the various hydrochloric acid eluting solutions were made 0.02-0.05M in nitric acid, and this concentration of nitrate kept most of the plutonium in the (IV) oxidation state, seemingly without affecting the relative eluting rates of the ions.

The results of the runs on Cm(III), Am(III), Pu(III), Ac(III), Y(III), Ce(III), Eu(III), La(III), Pu(IV), and Sr(II) are shown in summary form in Fig. 9, normalized to the 10 cm. by 1 mm. column.

DISCUSSION OF RESULTS

The results shown in Figs. 6-8 and in Fig. 9 illustrate very well the reversal of position of the actinides in 12M hydrochloric acid, and the maximum in the elution rates of the lanthanides around 7M hydrochloric acid. The lanthanide behavior is very likely an effect, due not to the lanthanides, but to the resin, for at moderately high hydrochloric acid concentrations the resin starts to shrink, and above 9M hydrochloric acid this effect is quite noticeable, amounting to about 15% at 12M hydrochloric acid (and much more in the case of the colloidal agglomerates). This shrinkage of the resin causes an increase in the concentration of the active groups inside the resin, and hence shifts the ion equilibrium toward the resin and decreases the rate of elution. The behavior of the lanthanides is then the "normal" behavior, and it is the actinides that are unusual, as they do not show this minimum in the value of K around 7M hydrochloric acid, and furthermore have a reversal in their order of elution at 12M hydrochloric acid.

The cause of both these anomalies is probably due to the same factor, and that is the formation of a stronger complex ion of the actinide cation with chloride ion at high hydrochloric acid concentrations. The complexing more

than compensates for the tendency to shift the equilibrium toward the resin in high hydrochloric acid concentrations 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 $\text{Pu(III)} > \text{Am(III)} > \text{Cm(III)}$, the Pu(III) will move up faster than the Am(III) which in turn moves up faster than the Cm(III) , and this would explain the reversal in their elution order on going from $6M$ to $12M$ hydrochloric acid.

The Pu(IV) ion shows this complexing action with chloride ion to a much greater degree than the tripositive actinides, moving up in position a much greater distance, and this evidence of complex formation is corroborated by transference experiments² and anion exchange resin work,³ as the complex ion

(2) C. K. McLane, J. S. Dixon, and J. C. Hindman, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The Transuranium Elements: Research Papers," Paper No. 4.3 (McGraw-Hill Book Co., Inc., New York, 1949).

(3) D. A. Orth, unpublished work (1949).

is an anion.

The questions then arise as to why the actinides show this stronger complex ion formation than the lanthanides and why the strengths of the actinide complex ion vary in the order that they do. Since the actinides and lanthanides have comparable ionic radii, variations in the ability to form ionic complexes do not seem a likely cause for such differences in behavior.

A possible explanation is suggested by the differences in stability and size and shape of the 5f orbitals in the actinides and the 4f orbitals in the lanthanides, making possible the formation in the actinide series of covalent complex ions with chloride ion.¹ In the lanthanides the 4f orbitals are stable

with respect to the 6s and 5d around cerium; therefore, they may be available energetically for hybrid-bond formation. However, the 4f orbitals do not extend out very far with respect to the already filled 5s and 5p orbitals; that is, they are shielded from external influences and thus are not very useful orbitals for covalent bonding. In the actinide series, the 5f orbitals become stable with respect to the 7s and 6d somewhere between actinium and uranium. At actinium itself, they are still at too high an energy level and so there is little possibility of their use in bonding. Experimentally in its behavior in column elutions, actinium(III) shows a maximum in its elution rate around 6M hydrochloric acid just like the lanthanides and unlike plutonium(III), americium(III), and curium(III). However, after actinium the 5f orbitals, from the energy standpoint, are possible orbitals for hybridized bonds, and although they are shielded by the 6s and 6p electrons, they extend out somewhat farther relative to the 6s and 6p than the 4f in the lanthanides do relative to the 5s and 5p and so might be available for bonding. (Such 5f orbital bonding has been used as the possible explanation for the unusual behavior of uranyl, neptunyl, and plutonyl nitrates in various organic solvents containing oxygen, especially ethers,⁴ although there appears to be some discussion as to the

(4) E. Glueckauf and H. A. C. McKay, Nature, 165, 594 (1950).

validity of this argument.^{5,6)}

(5) L. I. Katzin, Nature, 166, 605 (1950).

(6) E. Glueckauf and H. A. C. McKay, ibid.

Furthermore, as Z, the atomic number, increases, the 5f orbitals are pulled in more and more by the increased nuclear charge and their availability for bonding decreases, and this would cause the plutonium, americium, curium reversal observed in the 12M hydrochloric acid elutions.

This work was performed under the auspices of the U. S. AEC.

LIST OF ILLUSTRATIONS

Figure

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- 3.-- 6.2M hydrochloric acid elution.
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- 5.-- 12.2M hydrochloric acid elution.
- 6.-- Breakdown of Cm(III), Am(III), Pu(III) peak in 6.2M hydrochloric acid elution from pulse analysis data.
- 7.-- Breakdown of Cm(III), Am(III), Pu(III) peak in 9.3M hydrochloric acid elution from pulse analysis data.
- 8.-- Breakdown of Cm(III), Am(III), Pu(III) peak in 12.2M hydrochloric acid elution from pulse analysis data.
- 9.-- Summary of positions of elution peaks.

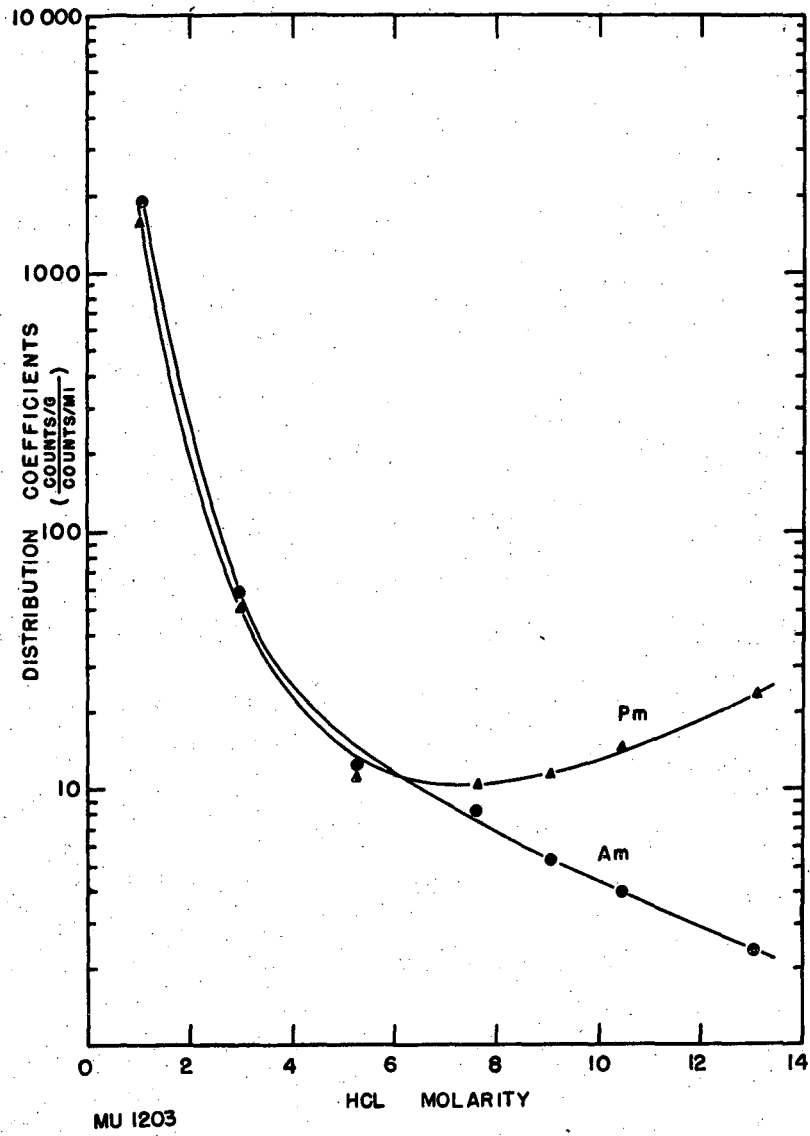


Fig. 1

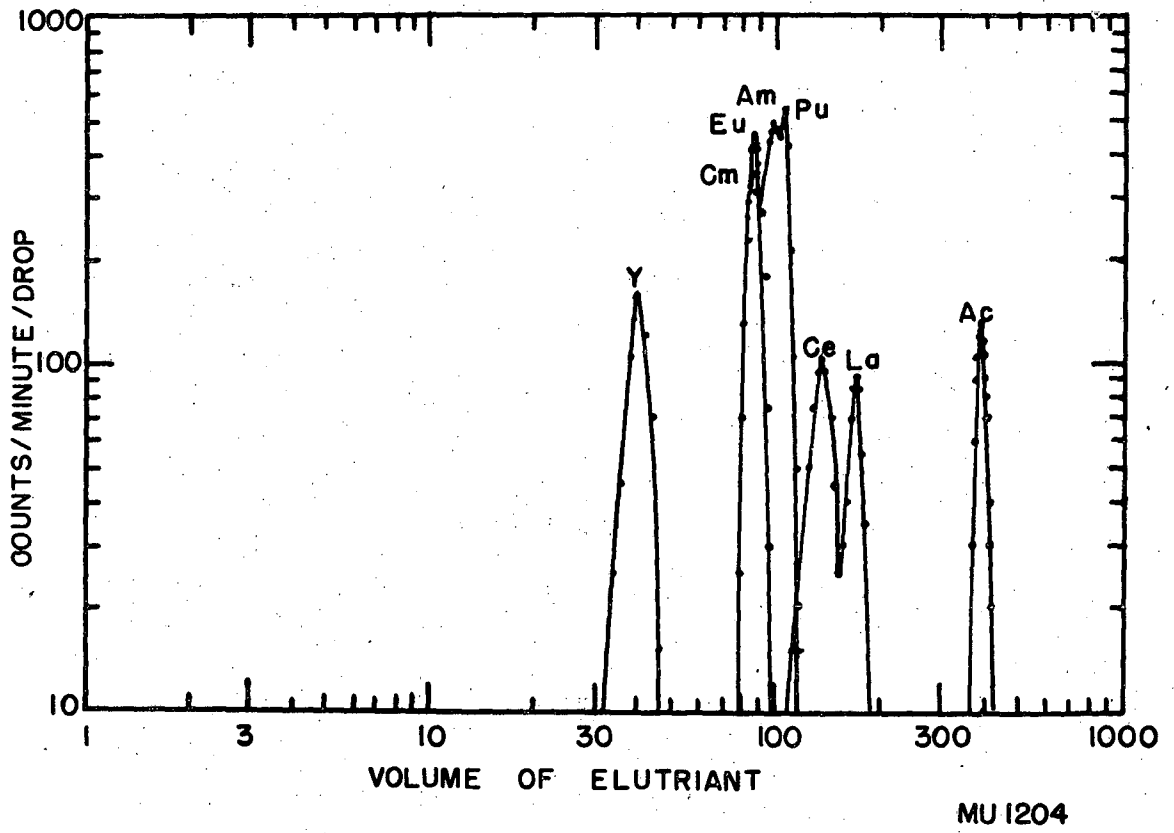


Fig. 2

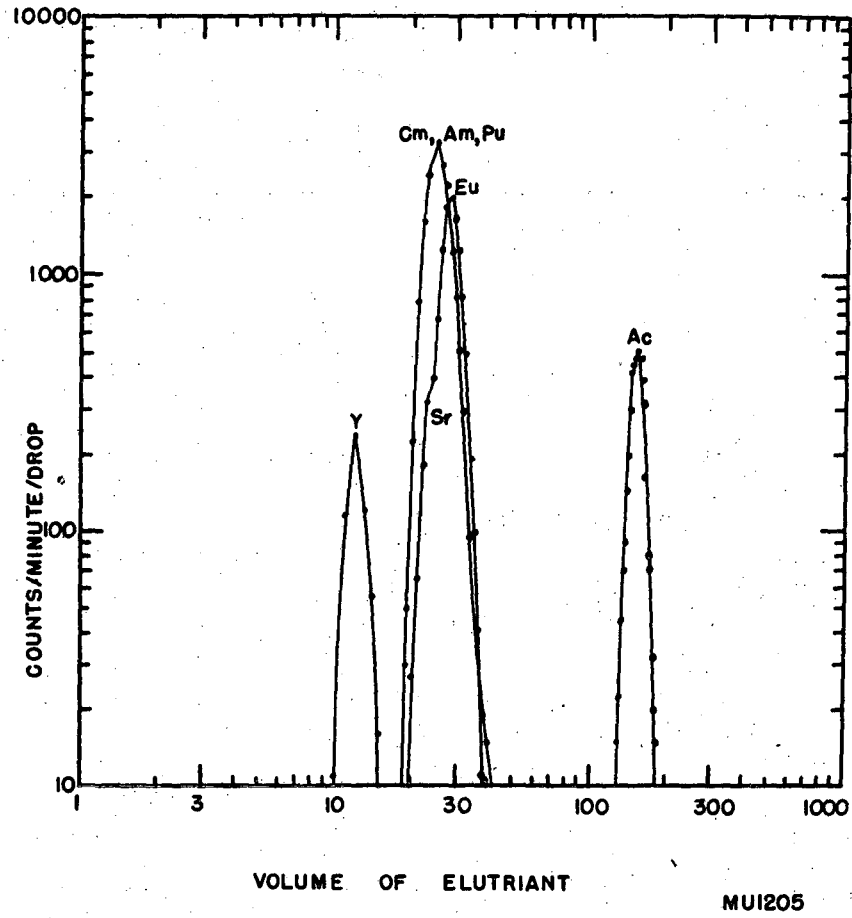


Fig. 3

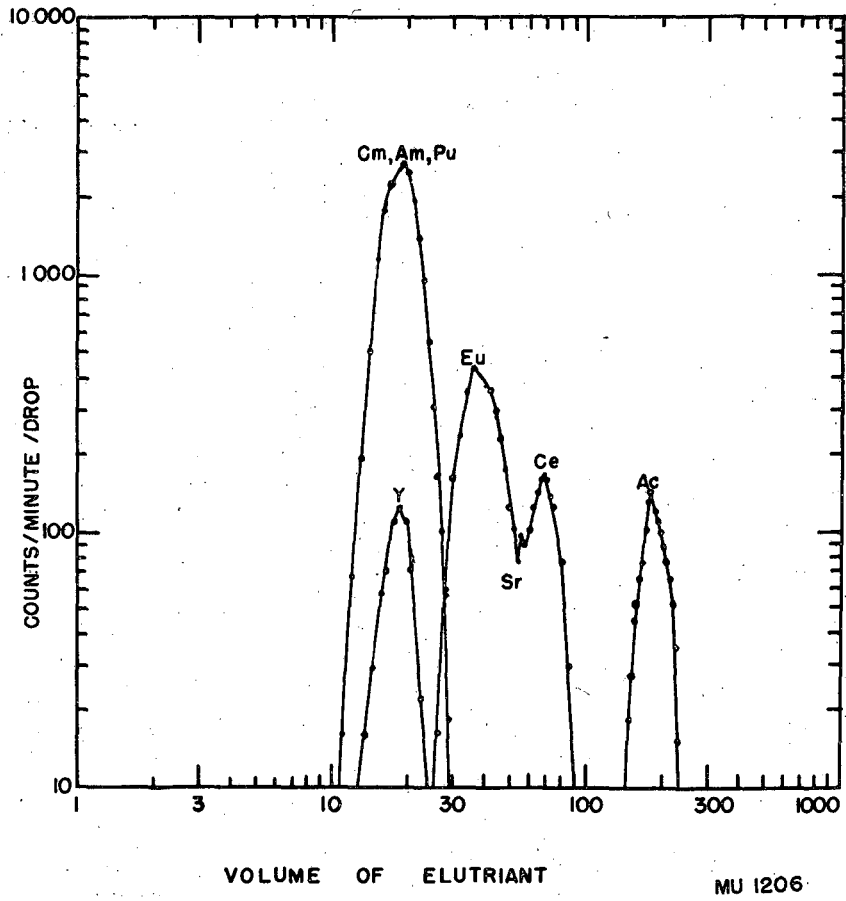


Fig. 4

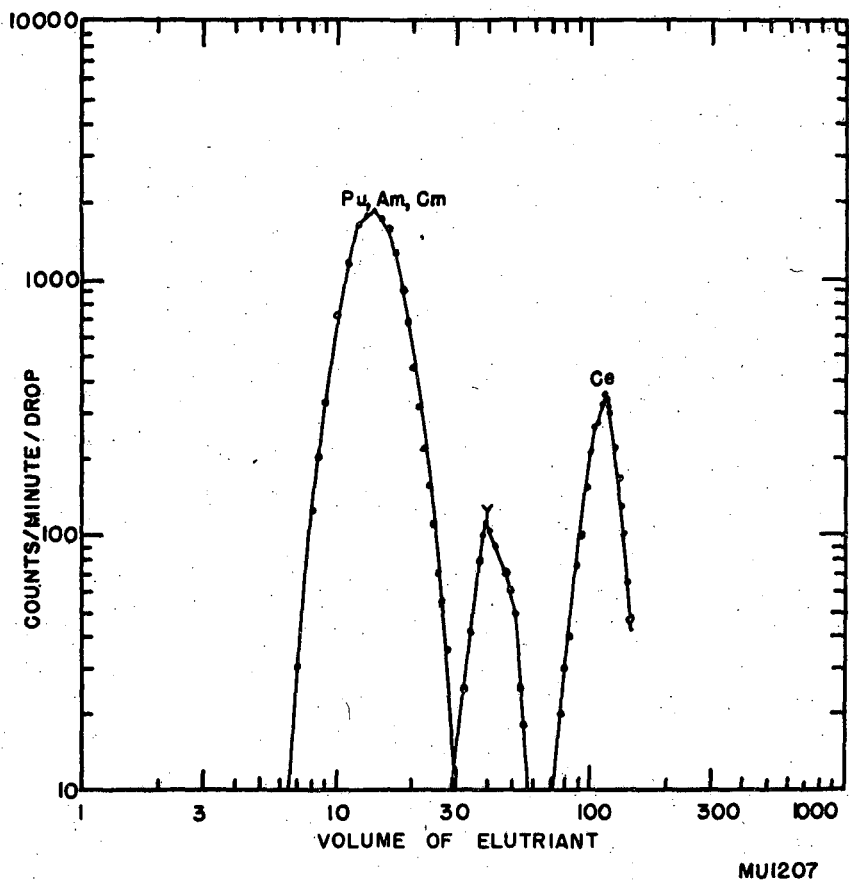


Fig. 5

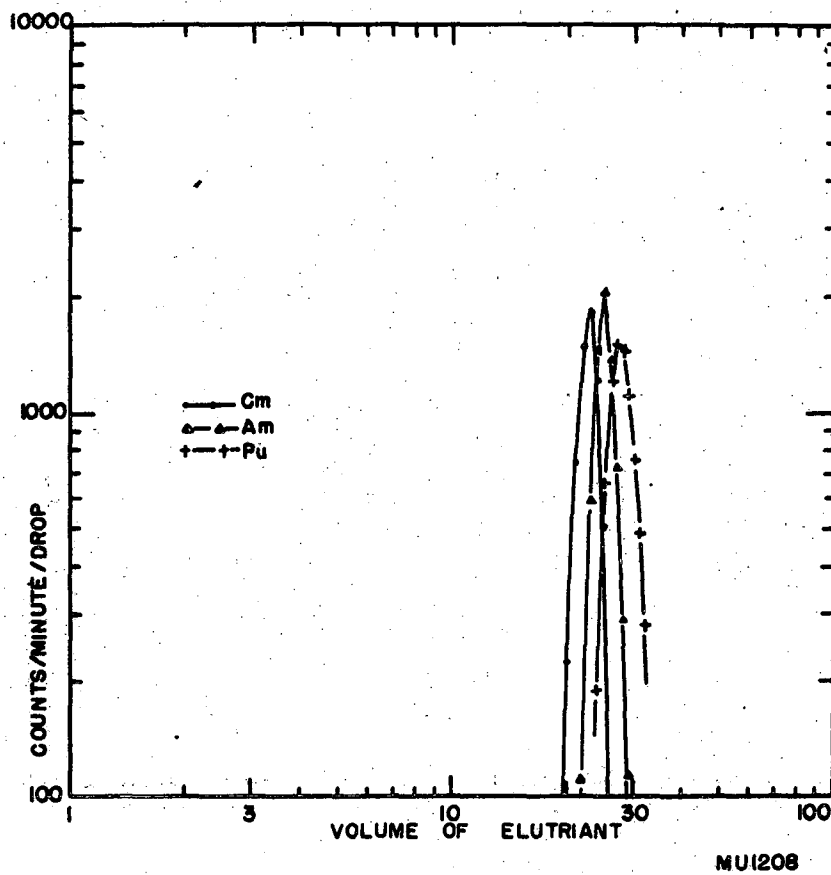


Fig. 6

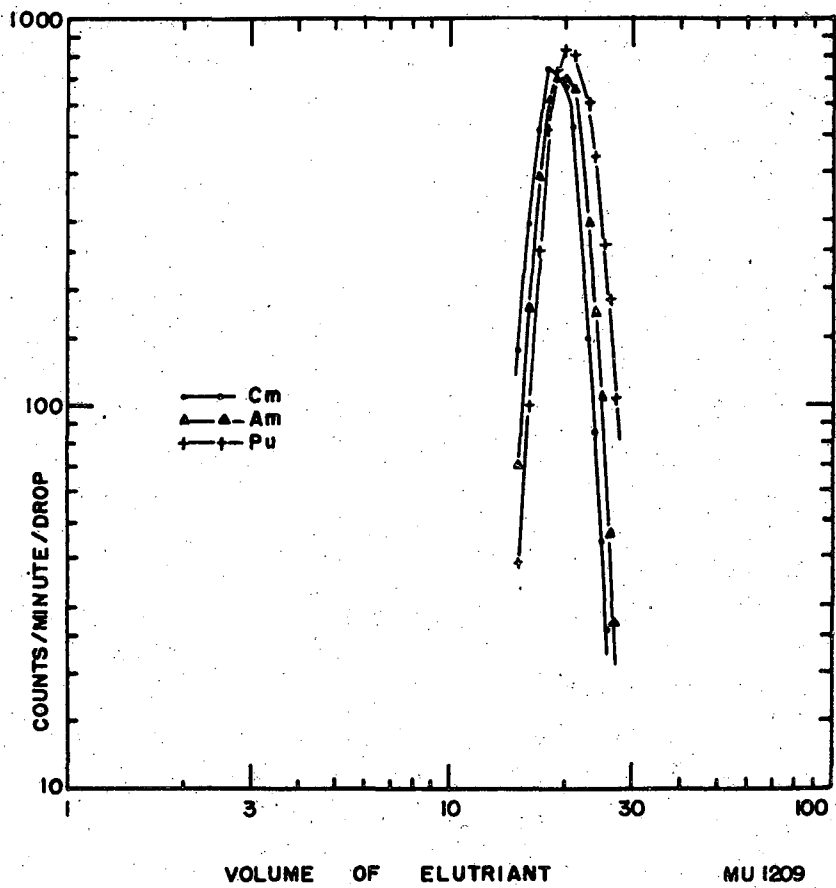


Fig. 7

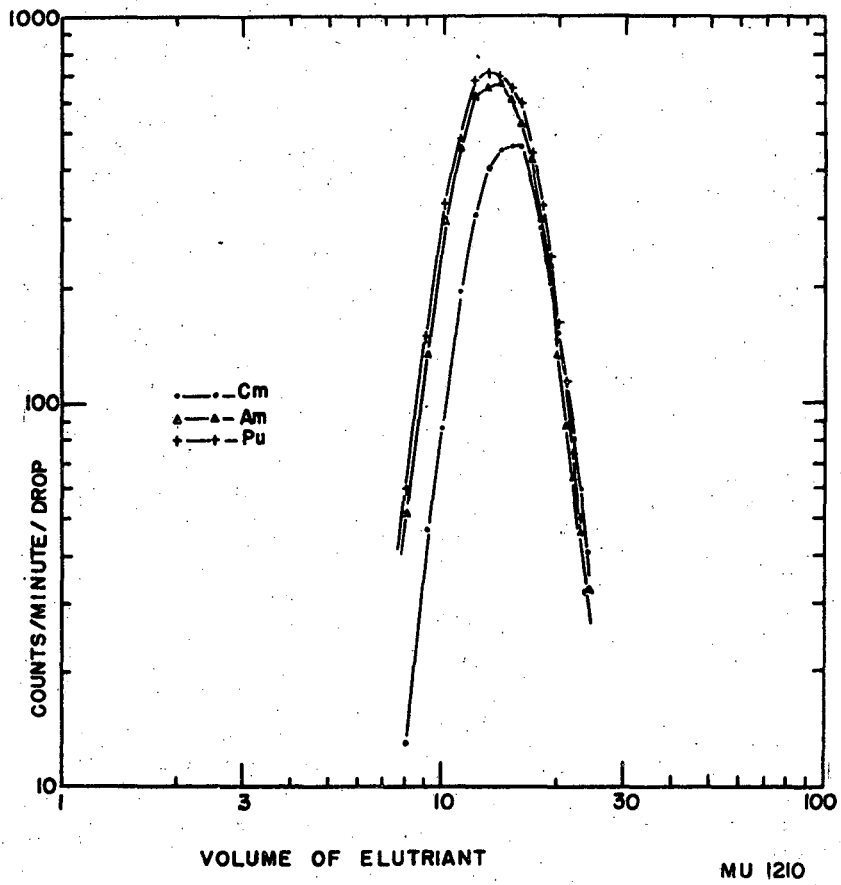


Fig. 8

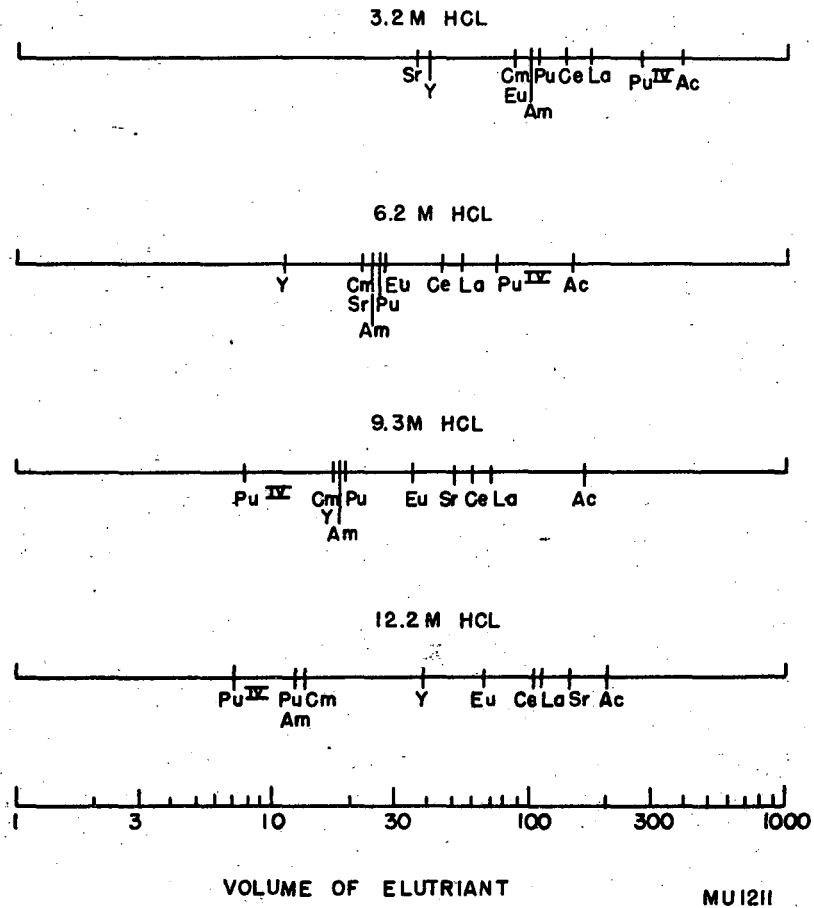


Fig. 9

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