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NOTES FOR CHEMISTRY LECTURE

G. R. Choppin

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I. Introduction

The purpose of this lecture is to discuss some of the chemistry studies which are in progress at present in our laboratory in Berkeley. In the efforts to better the methods of chemical purification and isolation of the actinide elements, results have been obtained which are of sufficient interest to lead to the initiation of chemical studies for themselves apart from the practical separation techniques. Since most of our separations involve ion exchange resin column elutions, it is natural that the majority of these investigations should deal with resin column studies.

II. Ammonium Chloride

Before proceeding to the elution work, a study of distinct practical importance should be mentioned. It had been felt for some time that an appreciable fraction of the activity in a solution might be lost on the evaporation of the solution should NH_4Cl be present. To check this, varying amounts of NH_4Cl from a 100 $\mu g/\lambda$ stock solution was put into a 5 ml cone, curium tracer was added and the total volume was brought to 2 ml with 6 $\underline{M}$ HCl. The evaporation was done in a boiling water bath with an air jet adjusted so that the time needed for evaporation was 35 to 40 minutes. The tube was then rinsed three times and the rinses were plated and counted. The curve (Fig. 1) shows the results.

No. 1. NH_4 was destroyed by addition of HNO_3 during evaporation.

No. 2. 2000 µg NH_4Cl evaporated directly on a platinum plate. Dotted

line represents standard amount of curium added each time.

III. Column Elutions

A. <u>HCl.</u> --There are two types of column elutions of main interest in

the separation chemistry of the actinides. In the first type the actinides

are separated as a family from the lanthanides as a family. This has been

traditionally done by use of concentrated HCl as the eluant in Dowex-50

cation exchange resin columns. In addition to the group separations, the

secondary separations within the group have attracted some interest.

Diamond, Street, and Seaborg studied the relative elution positions of

plutonium, americium, curium, and the rare earths at various concentra-

tions of HCl and found that the order is curium, americium, plutonium with

the lanthanides quite close up to 10 $\underline{M}$HCl after which the order is pluton-

ium-americium, curium and the lanthanides progressively farther behind.

This reversal and separation has been explained by the theory of 5f bond

hybridization in the actinides causing greater complexing in these elements

compared to the lanthanides. By this argument, the probability of this

hybridization is a maximum at plutonium and americium and falls off

going to curium which explains the reversal of americium-plutonium and

curium.

More recent work with such a system using americium through 99

tracers has expanded our knowledge of this reversal. From a study of
                    (see Fig. 2)
the curve/it is evident that curium is abnormal compared with the others.

If the 5f hybridization concept is held to, it is necessary to postulate a
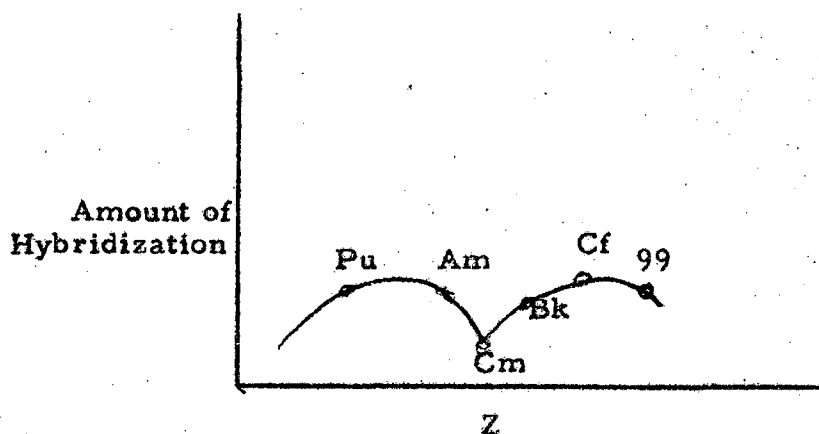
hybridization curve such as that above. The data is insufficient at this time to either prove or disprove such a possibility. Other considerations which shall be mentioned later in relation to other elution work might be applied with equal validity here. Some light might be shed on the situation here by using HBr and/or HF as the eluant and considering the effect which the variation in anion size might have on the complex. However, preliminary studies have indicated these do not lend themselves readily to our present column techniques. For example, rough relatives K_d's for HCl and HBr are ($K_D Cm_{HCl} = 1$).

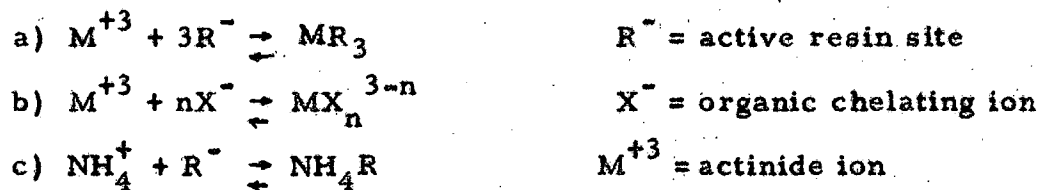|	Cm	Lu
13.3 $\underline{M}$ HCl	1	1.2
13.7 $\underline{M}$ HBr	10	45

Preliminary studies of the relative elution positions of the lanthanides from a Dowex-50 cation resin column at various HCl concentrations have failed to show any "reversals" but a concentration effect is quite evident. See Fig. 3.

B. <u>Anion Resin Columns</u>. --Elution of the actinide elements from Dowex-1 anion exchange resin with 1 $\underline{M}$ NH_4SCN solution as the eluant has also shown an "abnormal" order with respect to Z. See Fig. 4. Elution from Dowex-1 resin with 13 $\underline{M}$ HCl fails to show any reversals and is, as expected, the reverse of the Dowex-50 cation elution order except for the americium-curium reversal in the latter (Fig. 5).

The chemistry group at the Livermore site has studied concentrated LiCl as an eluting agent for anion resin. Their results are shown in Fig. 6.

C. <u>Hot Columns</u>.--The second type of column used in the actinide separation chemistry employs Dowex-50 cation resin and a solution of the ammonium salt of an organic acid complexing agent. The individual actinides are isolated by such a column. Better separations are obtained by operating the column at an elevated temperature (87° C). The equilibria involved are:

a) $M^{+3} + 3R^- \rightleftharpoons MR_3$ R^- = active resin site

b) $M^{+3} + nX^- \rightleftharpoons MX_n^{3-n}$ X^- = organic chelating ion

c) $NH_4^+ + R^- \rightleftharpoons NH_4R$ M^{+3} = actinide ion

R. Glass demonstrated the superiority of ammonium lactate over the older ammonium citrate in actinide separations, especially americium and curium, while ammonium tartrate elutions at room temperature gave the best americium-curium separations. A study of 5 and 6 membered chelate rings of hydroxy and amino acids showed the 5 membered hydroxy chelates to be best.

Studies had been made with ammonium glycolate and ammonium lactate as eluting agents. From the positions of californium and americium relative to curium, lactate was seen to give larger separations. The difference between the two ions

Glycolate   Lactate

would seem to be an increase in the negativity of the hydroxy oxygen atom due to the inductive effect of the methyl group. Such an increase in the electron density of the oxygen atom should increase the strength of the chelate and therefore affect the elution positions. The positions of all the actinides would be expected to move forward (elute earlier) with the lactate with relative position changes among the individual elements being a secondary effect. In fact, there is little difference in the curium position for the two eluants while the relative differences are much greater (using curium as the standard), the reverse of what would be expected.

There is an increasing body of evidence which points to the existence of a Stark effect in the actinide ions when a non-centrosymmetric electric field (such as anions in a complex might produce) is present. Such an effect would contribute to the entropy and hence to the elution position. The term values argue a minimum Stark effect at the beginning, middle (curium) and end of the 5f series. In the stronger field of the lactate ion, the splitting would be greater than in that of the glycolate ion. Therefore, the position of curium would be unchanged by the Stark effect while the separation of the other actinides relative to curium would be affected.

It should be possible then to obtain better eluants by using molecules with stronger electron donating inductive effects. The first tried was α-hydroxy isobutyric acid

$$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{OH}{|}}{C}}-C\overset{OH}{\underset{O}{\diagdown}}$$
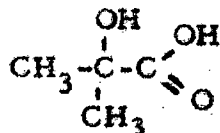
with satisfactory results. Figures 7 and 8. Others which are intended for trials are pyruvic acid ($CH_3-\overset{O}{\overset{||}{C}}-C\overset{OH}{\underset{O}{\diagdown}}$), α-hydroxy n-butyric acid (which is expected to behave as lactic acid) and similar acids. Use of the lanthanides makes possible use of a whole series whose behavior is analogous to that of the actinides in these systems.

IV. Absorption Spectra of Rare Earth Ions in Solution

Following some suggestions by B. B. Cunningham, a program has been started to investigate the occurrence and importance of Stark effects in solutions of rare earth ions. This phenomenon, also known as the "inner Stark effect," was treated theoretically by Bethe as early as 1929. He showed that in non-centrosymmetric fields, such as those existing in crystals, the degeneracy in the atomic levels could be partly or wholly removed, depending on the symmetry of atomic arrangement. Such effects have been observed repeatedly in the solid state and more recently in solution. The very recent work of Holleck and co-workers and unpublished work of the Radiation Laboratories have further shown that not only the magnitudes of the splitting but also the level patterns in the perturbed state are dependent on the nature of the ligands surrounding the metal ion. Preliminary

calculations have indicated splittings of the order of kT may be expected in solution, and consequently, chemical effects amounting to several kcal/mol may be produced.

The theoretical treatment of the Stark effect on the rare earths indicates that the magnitude of the splitting should be greatest at about the 1/4 and 3/4 filled 4f shell. Lanthanum, gadolinium, and lutetium should not split at all since they are in S states. In the remaining rare earths the magnitude of the splitting is a function of the J values for the unperturbed ion. In addition to this dependence on J, there may be other effects such as an odd-even atomic number dependence (due to the Kramer's degeneracy) in the less symmetrical fields and a rather pronounced effect exactly at the 1/4 and 3/4 filled shell due to the inversion of the split levels. Samarium and europium may also show anomalous behavior due to the presence of other levels close to the ground state in the unperturbed ion.

In order to investigate these phenomena, the absorption spectra of a number of rare earth ions in various solutions are being measured. Neodymium spectra have been taken in perchlorate, nitrate, thiocyanate, and chloride solutions. Profound differences in the level patterns which can probably be attributed to the spatial arrangement of the ligands about the central ion have been observed. Solutions of neodymium in saturated HCl show particularly striking effects, the multiplet at 570 mμ being spread over 25 to 30 mμ.

The present program involves the study of the spectra in saturated HCl over the temperature range $-24°$ to $30°$ C. It is hoped to extend these measurements considerably toward lower temperatures by working with supercooled solutions and thus to establish the ground state level pattern of the

ions.   In addition, the spectra of rare earth solutions containing a number

of different complexing agents are being examined for correlation with the

observed behavior of the rare earths in elutions from ion exchange columns.

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

Energy Commission.

APPENDIX TO CHEMISTRY LECTURE

Recently Dowex-1 anion resin columns with hydrochloric acid as the eluant have been run at a temperature of 87° C. Lead leaked through the column at room temperature, 5 $\underline{M}$ HCl, when the drop rate was faster than 1 minute per drop off a 3 mm x 5 cm column. At 87° C, a 2 mm x 5 cm column and 10 seconds per drop, lead was held up past drop 15. This was necessary to be sure of the elimination of Po^{214}. While no intensive study has been undertaken yet, it is almost certain that operation of the anion resin columns at 87° C considerably improves the kinetics of the column and allows faster and more complete separations.

To study further the possible break-through of Po^{214} in the bombardment chemistry an a-hydroxy isobutyrate column was run (0.4 $\underline{M}$, pH 3.8) and the lead peak eluted in about the same position as element 100 would. This indicates the necessity of eliminating lead in an anion column.

ELECTROPLATING PROCEDURE FOR HEAVY ELEMENTS

I. _Electrolyte._ ~0.1 $\underline{M}H_2SO_4$ adjusted to pH ~3.5 by addition of concentrated ammonia.

II. _Current density._ ~0.3 amp/cm^2 of cathode surface.

III. _Cells._

    a. For large cathode. The apparatus is shown in Figure 9.

    A carefully ground lower end to the glass cell chimney seals satisfactorily provided that a thin card is placed under the annealed platinum cathode. No grease or gasket is required. The anode is rotated at ~300 rpm.

    b. For small cathode.

    For electroplating onto an area 1/4 inch x 1/32 inch (for 60-inch cyclotron targets), a smaller cell is used to reduce the volume of electrolyte required. The glass chimney is made by cutting off the tip of a 15-ml centrifuge cone and flattening the end of the cone to an eliptical cross section about 1/2 inch x 1/8 inch (internal). The glass is finally ground flat, and the top of the cone is cut off to make a chimney about 2 inches long.

    The platinum cathode is painted with 4A varnish, leaving the required clear area in the center. The varnish is allowed to air dry for a few minutes and then baked at ~160° C until it is a clear golden color (~30 minutes).

    The anode is similar to that shown in the figure, but is not rotated.

IV. Procedure. Evaporate the sample to complete dryness with a few drops
of 8 M nitric acid. Transfer the sample to the cell with three portions
of the ammonium sulfate electrolyte. The final volume should be
sufficient to produce a liquid depth of ~1/2 inch in the large cell, but
only three drops are used in the small cyclotron target cell.

Plate for 1 1/2 to 2 1/2 hours. After ~1 hour, rinse down the cell walls
with a few drops of electrolyte from the cell. Repeat 1/2 hour later.
If necessary, add distilled water to make up losses by evaporation.
Check progress by counting aliquots.

After deposition is complete, add a few drops of 0.5 M ammonia to
the electrolyte. After 30 seconds, stop the current, remove the solu-
tion and wash out the cell twice with distilled water. Take out the
plate, rinse with methyl alcohol, dry, and flame.

The 4A plastic burns away without leaving a residue.

Yields of 85 to 95 percent may be obtained with large cathodes,
80 to 90 percent with 1/4 inch x 1/32 inch cyclotron targets. The
deposit (using tracer amounts of material) should be completely
invisible on large cathodes. On the 1/4 inch x 1/32 inch area, a very
faint dark stain can usually be seen.

The procedure has been tested with curium and element 99. It would
probably fail with plutonium because the sample would be rather com-
pletely hydrolyzed and adsorbed on the glass tube during the transfer
to the cell. In this case, it might be better to transfer the plutonium
in 0.1 M H_2SO_4 and neutralize with ammonia in the cell using methyl red
indicator.

V. Reference. This procedure is a modification of that used by

Tracerlab in Berkeley.

FIGURE CAPTIONS

Fig. 1.   Evaporation losses.

Fig. 2.   Elution curves.

Fig. 3.   HCl-rare earth system (normalized vertically to light rare earths).

Fig. 4.   Elution of actinides from Dowex-1 resin with 13 $\underline{M}$ hydrochloric acid.

Fig. 5.   Elution of actinides from Dowex-1 resin with 1.0 $\underline{M}$ ammonium thiocyanate.

Fig. 6.   Elution curve--LiCl ~14 $\underline{M}$ - 15 $\underline{M}$, 87° C.

Fig. 7.   Elution curve for actinides--0.4 $\underline{M}$ α-hydroxy isobutyrate, pH 4.2.

Fig. 8.   Relative elution positions based on curium standards.

Fig. 9.   Electroplating cell.

EVAPORATION LOSSES

Fig. 1

MU-8934

Am ———
Bk —·—·—
Cm ━━━
Cf – – – –
99 ——— ———

MOLARITY HCl

Fig 2

23100-1
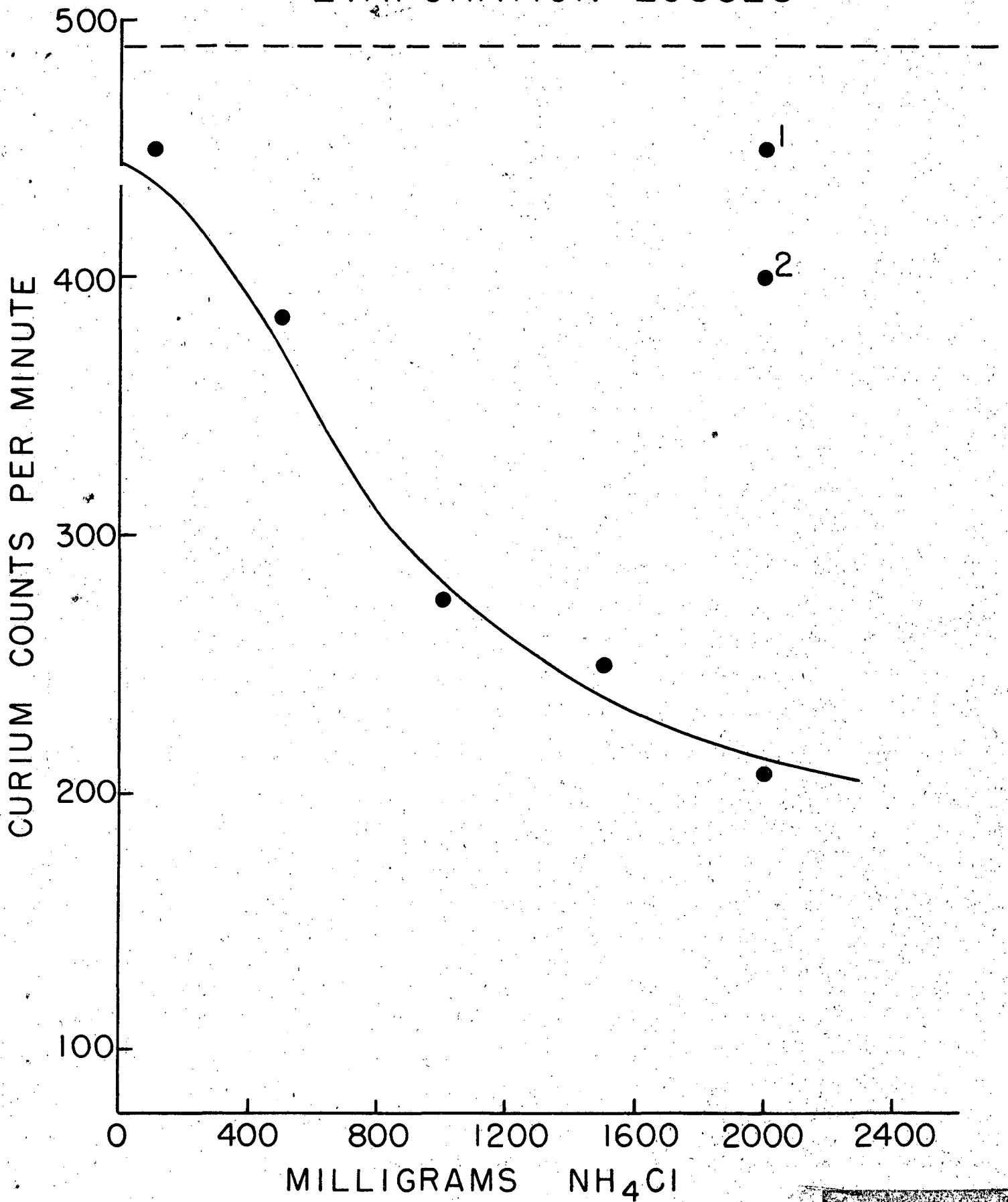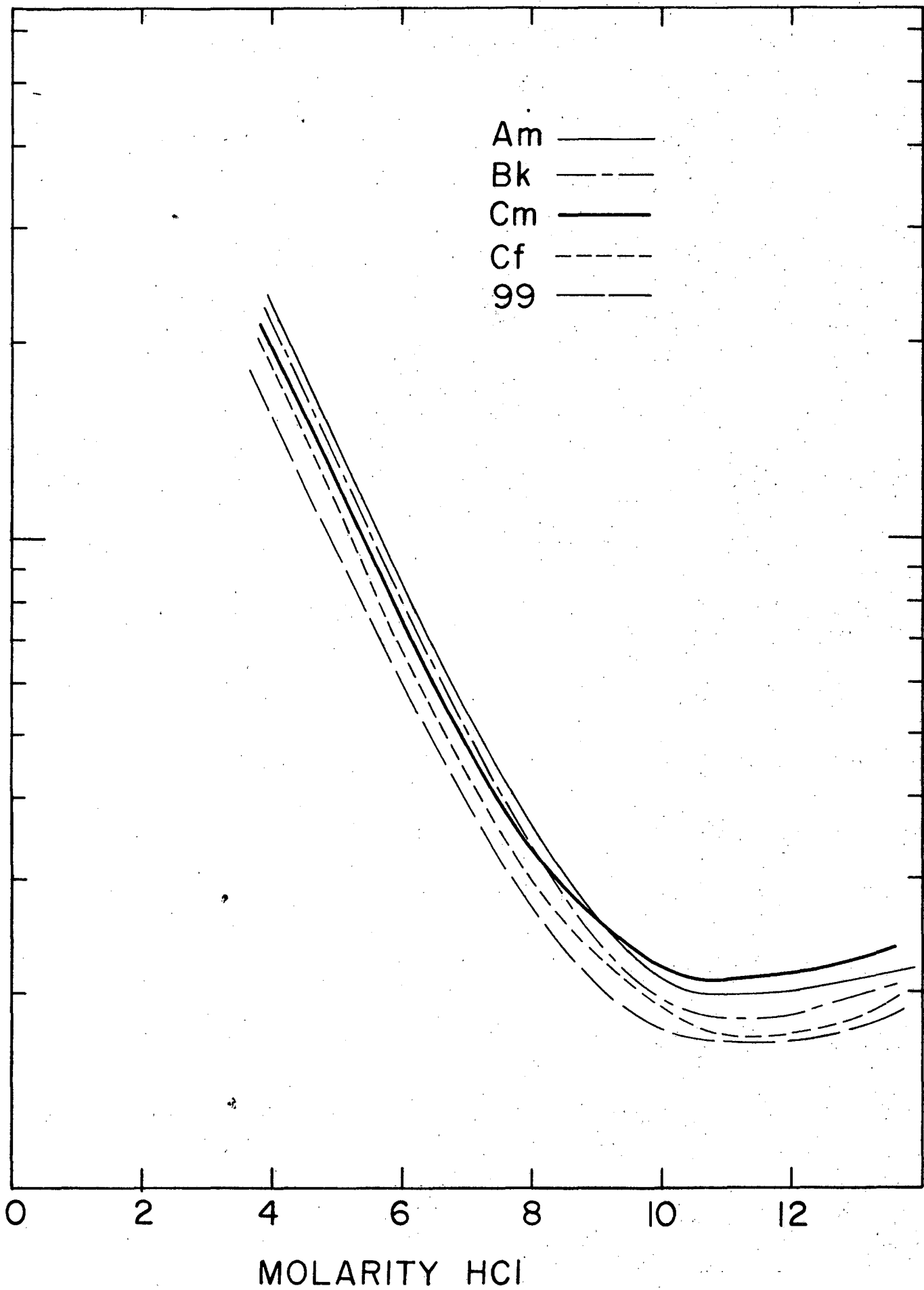
HCl – RARE EARTH SYSTEM
(NORMALIZED VERTICALLY TO LIGHT RARE EARTHS)

ACTIVITY

● 3 M HCl
▲ 6 M HCl
▼ 9 M HCl

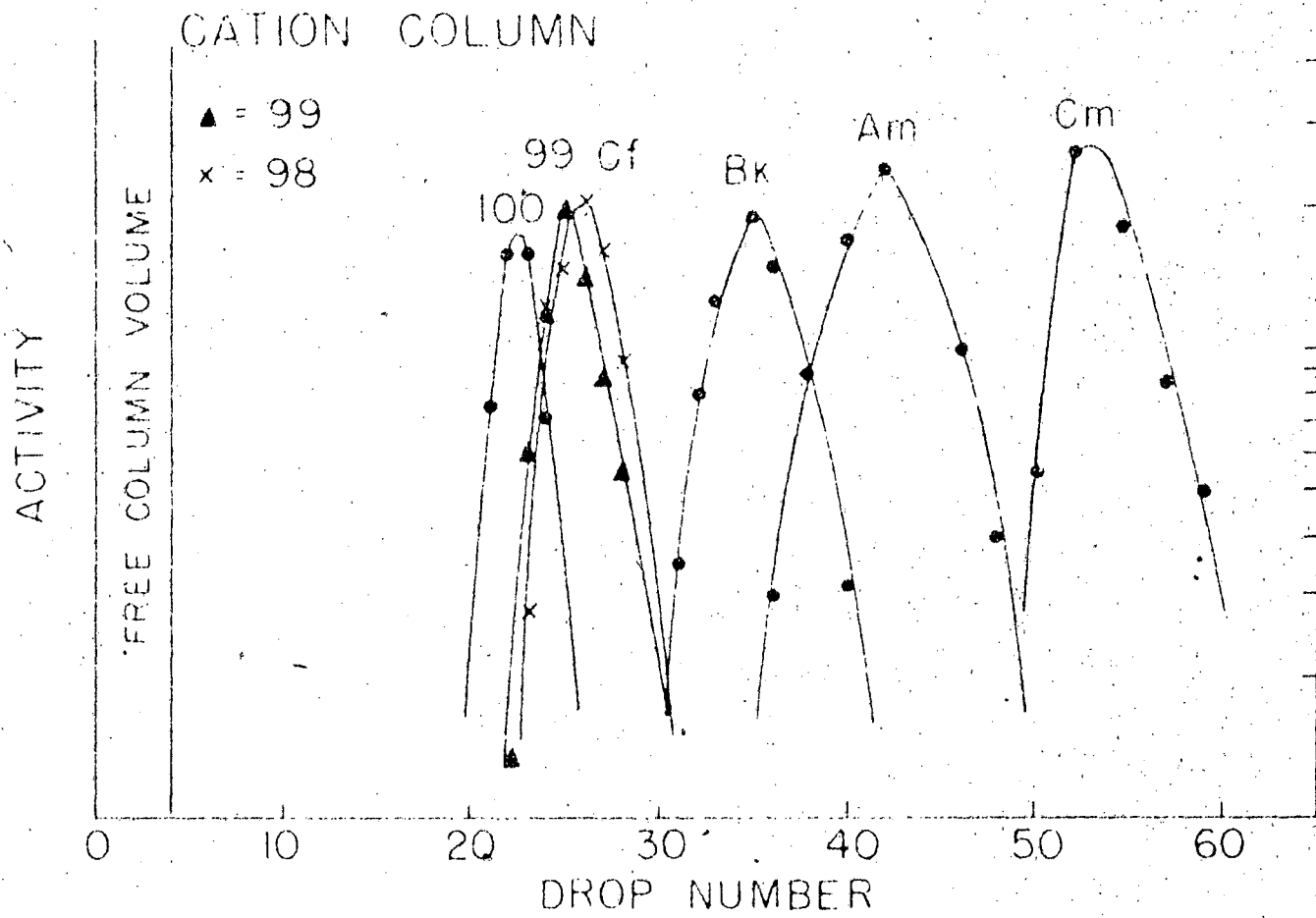Lu Yb Tm Er Ho Dy Tb Gd Eu Sm Pm Nd Pr Ce La
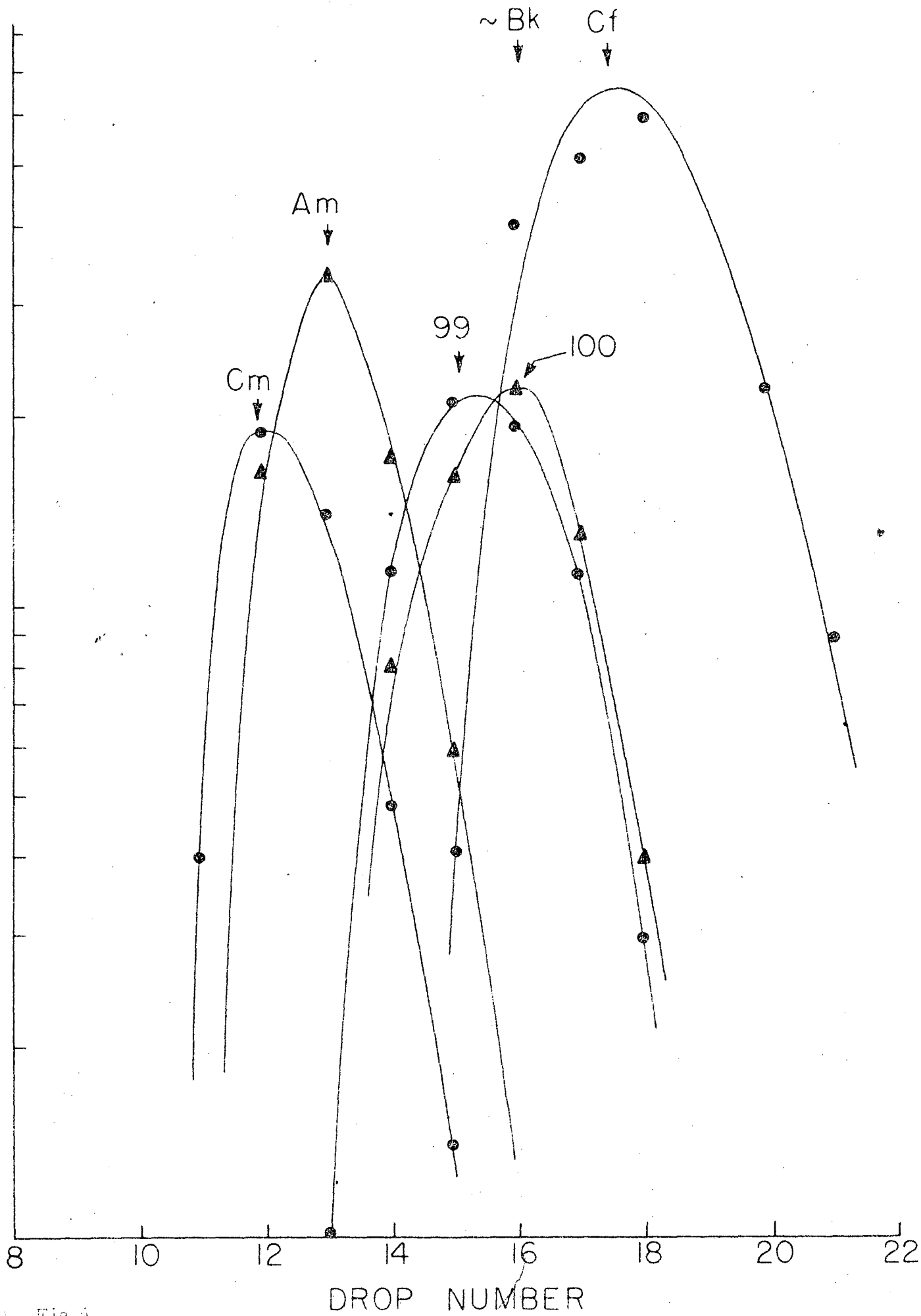
ELEMENT

Fig. 3

MU-8933

Fig 4

Fig 3

225441
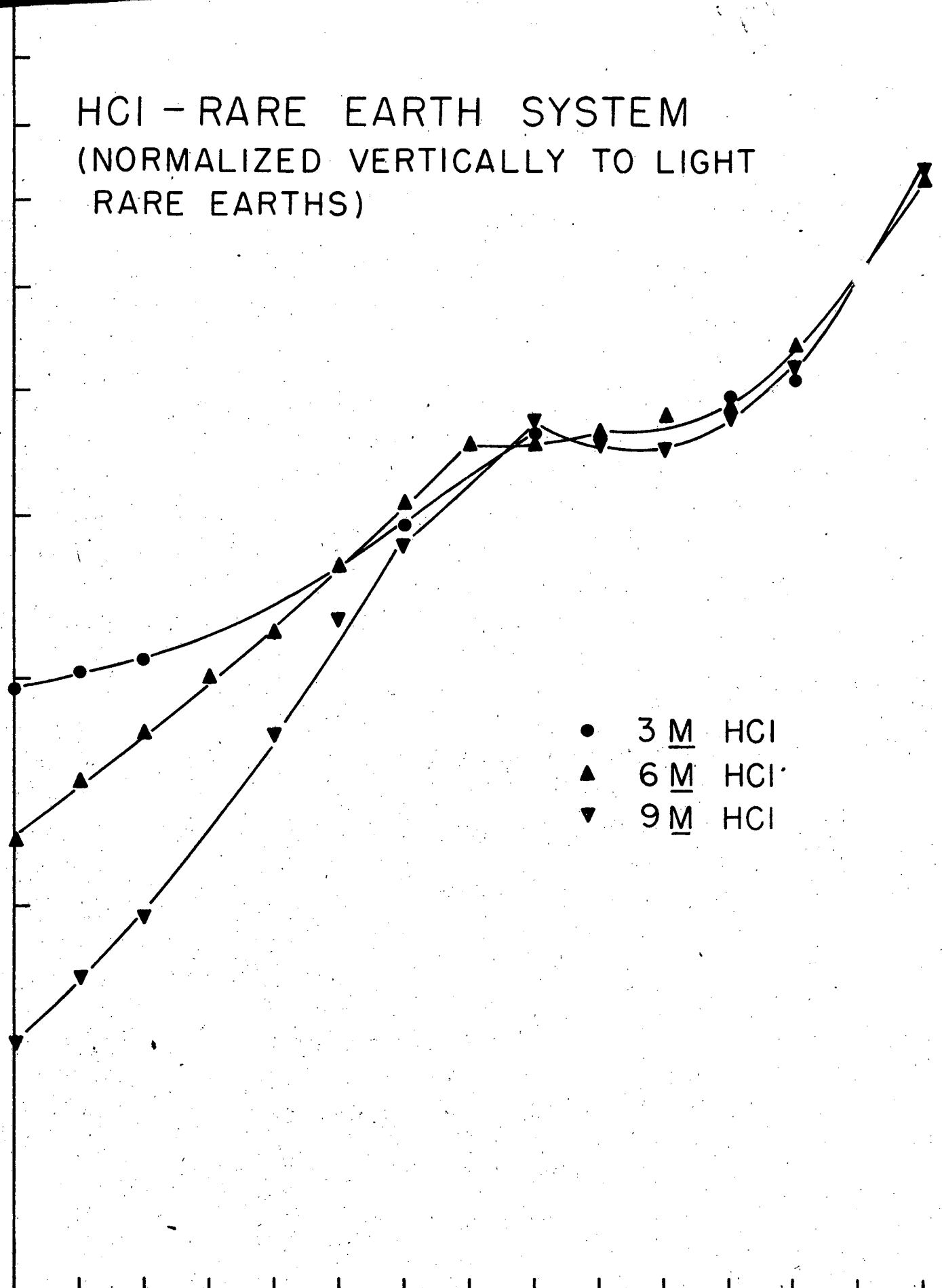
ELUTION CURVE

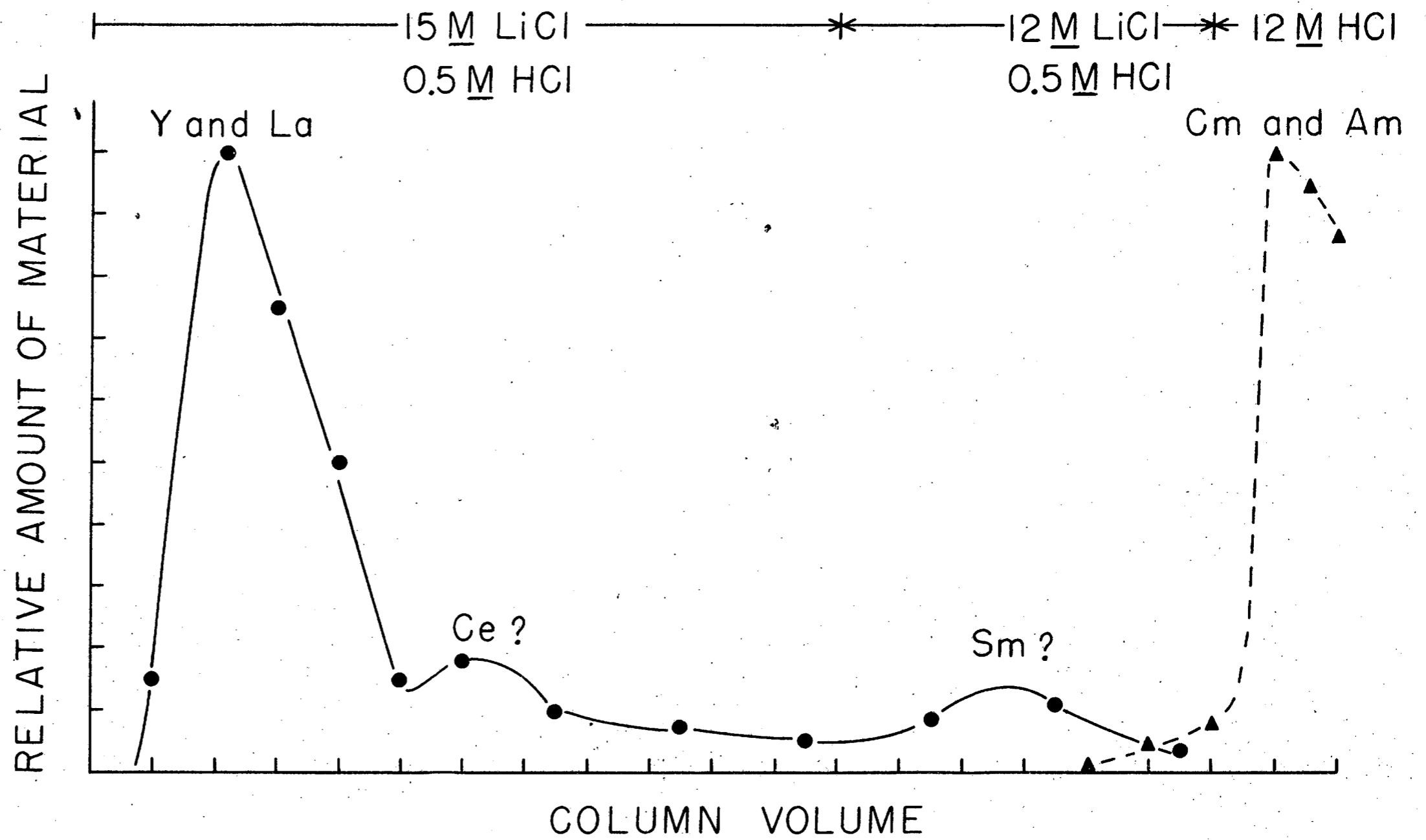LiCl ~14M - 15M, 87°C

Fig. 6

ELUTION CURVE FOR ACTINIDES
0.4 M α-HYDROXY ISOBUTYRATE
pH 4.2

Am

Cm

Bk

Cf

99

ACTIVITY

DROP NUMBER
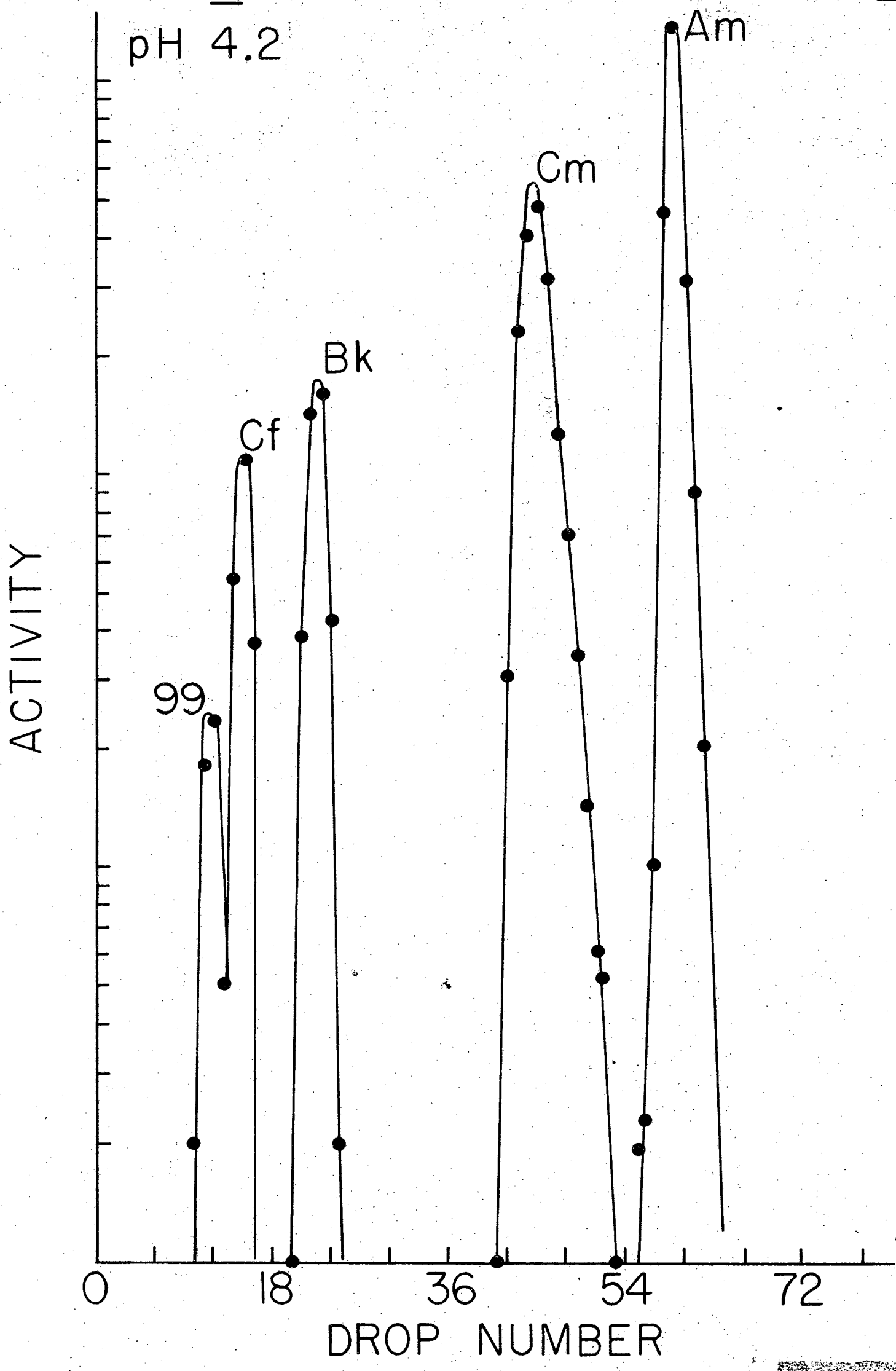
Fig. 7

RELATIVE ELUTION POSITIONS
BASED ON CURIUM STANDARDS

0.4 M GLYCOLATE (pH 4.5)

Cf   Cm   Am

0.4 M LACTATE (pH 4.5)

99 Cf   Bk   Cm   Am

0.4 M α-HYDROXY ISOBUTYRATE (pH 4.2)

99 Cf   Bk   Cm   Am

MU-8932

Fig. 8

RUBBER PADS

GLASS CELL
    CHIMNEY

PLATINUM
WIRE ANODE

SOLUTION
    LEVEL

4"

PLATINUM COUNTING
    PLATE (CATHODE)

THIN CARDBOARD

PLATINUM FOIL
    CONTACT

Fig. 9

23099-1