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CHELATING AGENTS APPLIED TO ION EXCHANGE

SEPARATIONS OF AMERICIUM AND CURIUM[1]

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March 23, 1954

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(1) This work was performed under the auspices of the U.S.

Atomic Energy Commission.

(2) This note was abstracted from a portion of the thesis submitted

by R. A. Glass to the Graduate Division of the University of California,

Berkeley, in partial fulfillment of the requirements for the Degree of

Doctor of Philosophy.

Recent investigations of cation exchange column separations of

the rare earths have extended the original citrate elutions to include

elutions with a variety of chelating agents, such as lactate,[3,4] glycolate,[3]

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(3) S. W. Mayer and E. C. Freiling, J. Am. Chem. Soc., 75, 5647 (1953).

(4) E. C. Freiling and L. R. Bunney, ibid., 76, 1021 (1954).

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malate,[3] and ethylenediaminetetraacetic acid (EDTA).[3,5] At the same

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(5) F. H. Spedding, J. E. Powell, and E. J. Wheelwright,

ibid., 76, 612 (1954).

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time no comparable studies of elution of the trivalent actinides with other

than citrate solutions have been reported. The present report concerns

results on tartrate and lactate elutions of two actinides very difficult to

separate, namely, americium and curium, from investigations begun in

1950. Tartrate and citrate agents were selected on the basis of the

reported[6] large separation factors with the rare earths. It has also been

(6) E. R. Tompkins and S. W. Mayer, ibid., 69, 2859 (1947).

possible to compare the relative efficiencies of chelating agents

forming five- and six-membered rings from data obtained with

lactate and other related ions.

EXPERIMENTAL

The ion exchange column used for the separations (similar to

columns used for citrate elutions described elsewhere[7, 8]) was made

(7) K. Street, Jr., S. G. Thompson, and G. T. Seaborg, ibid., 72, 4832 (1950).

(8) S. G. Thompson, A. Ghiorso, and G. T. Seaborg, Phys. Rev., 80, 781 (1950).

by packing 2 mm. capillary tubing with 17 cm. of 250-500 mesh Dowex-50

resin (12% crosslinkage[9]), from which the fine and coarse particles had

(9) Dow Chemical Company, Midland, Michigan.

been carefully removed. The column could be operated at 87° by

circulating trichloroethylene vapor (B. P. 87° C.) in a surrounding jacket

in the standard manner.[8] The chelating agent solutions were prepared by

titrating solutions of the respective acids to the desired pH with

ammonium hydroxide using a Beckman pH meter.

The tracers eluted were the alpha-emitting Cm^{242} and Am^{241} and

the beta-emitting $Eu^{152, 154}$ and Pm^{147}. These were absorbed on

about 50 microliters of resin, placed on top of the column, and eluted

with the desired chelating solution. The actinide peaks were defined by
gross alpha counting and alpha pulse analysis of platinum plates on
which the drops of eluting solution from the column were collected,
evaporated, and flamed. The multi-channel alpha pulse analyzer[10]

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(10) A. Ghiorso, A. H. Jaffey, H. P. Robinson, and
B. B. Weissbourd, "The Transuranium Elements: Research Papers,"
McGraw-Hill Book Company, Inc., New York, N. Y., 1949,
Paper No. 16.8, National Nuclear Energy Series, Plutonium Project
Record, Vol. 14B.

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frequently enables one to detect fractions of a percent of one alpha-
emitting isotope in the presence of large amounts of another if the
alpha particles are of sufficiently different energy. Thus it is ideally
suited to the study of column separations of the alpha active actinides.
The rare earth peaks were defined by gross beta counting and absorption
curves of the same plates.

Equilibrium experiments were also made with americium in
order to determine the relative strengths of the various chelating ions
as well as to aid in the selection of optimum conditions for column
elutions. In these experiments, 10 to 20 ml. of the chelating solution
containing americium tracer were equilibrated at 25° or 87° C.
with 0.1 to 0.5 g. of the Dowex-50 resin in the ammonium form.
Alpha assays of the solution before and after equilibration were used
to determine the partition of americium between resin and solution
phases in terms of distribution coefficients.[6] The distribution
coefficient is defined as follows:

Distribution coefficient (Kd) $= \dfrac{(c./m./g.) \text{ Resin phase}}{(c./m./ml.) \text{ Solution phase}}$

where c./m. refers to the alpha counts per minute due to Am^{241}.

Since the ammonium ion concentration was not carefully measured

and it has a rather large effect on the equilibrium distribution, only

the relative magnitudes of the distribution coefficients are of significance

for the interpretation of the strengths of the chelate complexes.

RESULTS AND DISCUSSION

Two very satisfactory ion exchange methods of separating

the actinides resulted from these studies. The first employed 0.1 $\underline{M}$

tartaric acid adjusted with ammonium hydroxide to a pH of 4.0 and

used a flow rate of one drop per eight minutes (0.2 $cm.^3/cm.^2$-min.).

The column elutions were made at room temperature. A typical

elution curve using this tartrate solution is shown in Fig. 1. In this

elution, a separation factor (defined in the usual manner[3]) of 1.30

was obtained between americium and curium. The factor is calculated

by dividing the number of drops to the highest point of the americium

peak by the drops to the highest point of the curium peak, after sub-

tracting a free column volume of about eight drops in both cases, and

is equal to the ratio of the distribution coefficient of americium to that

of curium in the tartrate solution. Less than 0.2% by activity of

americium was found in samples corresponding to the curium peak,

from the front edge to the dip between the peaks. The contamination

of samples corresponding to the entire americium peak with curium

activity was likewise less than 0.2%. These room temperature tartrate

elutions represent the best one-step separations of americium and curium

yet reported. The only disadvantage of this method was in the long time

required for elution (ca. 16 hours).

A second method, capable of yielding americium-curium separations in a considerably shorter time (less than two hours), employed 0.4 $\underline{M}$ lactic acid adjusted with ammonium hydroxide to a pH of 4.6 and a flow rate of one drop per one to three minutes (1.5 - 0.5 cm.^{3}/cm.^{2}-min.). These elutions were carried out at 87° C. A typical example of the performance of this column is given in Fig. 2b. In this latter case, a separation factor of 1.19 was obtained between americium and curium, with a cross contamination (defined as before) this time of about 2%. For comparison of the effect of temperature, a room temperature elution with lactate solution using a column operated at a much slower flow rate (to insure equilibrium) of one drop every eight minutes is also shown in Fig. 2a. On the basis of the superior separations obtained with the lactate elution solutions, they have been rather extensively employed at this laboratory for actinide separations and were recently of use in demonstrating the existence, production, and separation of the recently reported new elements 99 and 100.[11]

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(11) B. G. Harvey, S. G. Thompson, A. Ghiorso, and G. R. Choppin, Phys. Rev., (in press, March 1, 1954).

In the course of trying to select the optimum conditions for elution and separations, some conclusions were made which bear on the nature of the effective chelating ions. When tartrate elutions were run at 87° C. the large separation factors observed at room temperature disappeared. For example, elution with 0.1 $\underline{M}$ tartaric acid adjusted

to pH 4.3 resulted in a separation factor between americium and

curium of only 1.07. However, increasing the ratio of singly ionized

to doubly ionized tartrate ions (which are the abundant species at pH 4)

by lowering the pH (simultaneously increasing the tartaric acid

concentration to maintain the previous elution time), caused the

separation factor to increase steadily to a value of 1.20 with 0.8 $\underline{M}$

tartaric acid at pH 2.8. Thus, the singly ionized tartrate ion is more

effective for separations even though it forms a weaker chelate complex.

The latter statement can be illustrated by the fact that the americium

distribution coefficient in 0.05 $\underline{M}$ tartaric acid adjusted to pH 4

(tartrate$^=$/tartrate$^-$ = 0.9) was found to be 20 times as large as the

distribution coefficient in 0.05 $\underline{M}$ adjusted to pH 5 (tartrate$^=$/tartrate$^-$ =

9.0). At both pH values the acid is almost completely dissociated, the

only difference being in the ratios of the ions. A similar conclusion

that the singly ionized chelate ion is more effective had also been reached

previously from the use of citric acid.[6]

A study of four related chelating acids was also made to determine

the relative efficiencies of five- and six-membered chelate rings on the

basis of the stability of the chelate formed as well as on the ability to

induce large separation factors. The data indicate that lactate ion

forms a stronger chelate (five-membered ring) with americium than does

the hydracrylate ion (six-membered ring). For purposes of comparison,

it will suffice to describe two distribution coefficient determinations.

Simple calculations show that 0.4 $\underline{M}$ lactic acid and 0.7 $\underline{M}$ hydracrylic

acid both adjusted to pH 5 have about the same dissociated ion

concentrations; yet the value of Kd for americium in the lactate

solution is 10 and that for the hydracrylate solution 2600, indicating that the formation constant for the americium-lactate chelate is much larger than that for the other chelate (assuming that the formula for the chelates is the same in both cases). At the same time, column elutions with both agents indicated that the lactate ion caused larger separation factors.

In the same way, the equilibrium experiments indicate that although α-alanine (five-membered ring) forms chelates with americium in solution above pH 6, β-alanine (six-membered ring) shows little tendency to do so. In this case, determinations of the values of Kd for americium as a function of pH in one molar solutions of the acids showed that the Kd with α-alanine dropped from 4000 at pH 6 to 100 at pH 9.5, whereas the values of Kd with β-alanine were at least above the upper limit of detection of 10,000 in this pH range. From this study of the four hydroxy and amino acids, it appears that the five-membered ring forms a more stable chelate and also causes larger separation factors. On this basis, the large separation factors obtained with tartrate ion (capable of forming two five-membered chelate rings) is to be expected. In the same manner, it might be predicted that the effective chelate formed with citrate ion employs the one five-membered ring available. The problem of the relative stabilities of five- and six-membered chelate rings has been discussed by Martell and Calvin.[12] The present results are in accord with the conclusions described there.

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(12) A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, Inc., New York, N. Y., 1952, p. 134.
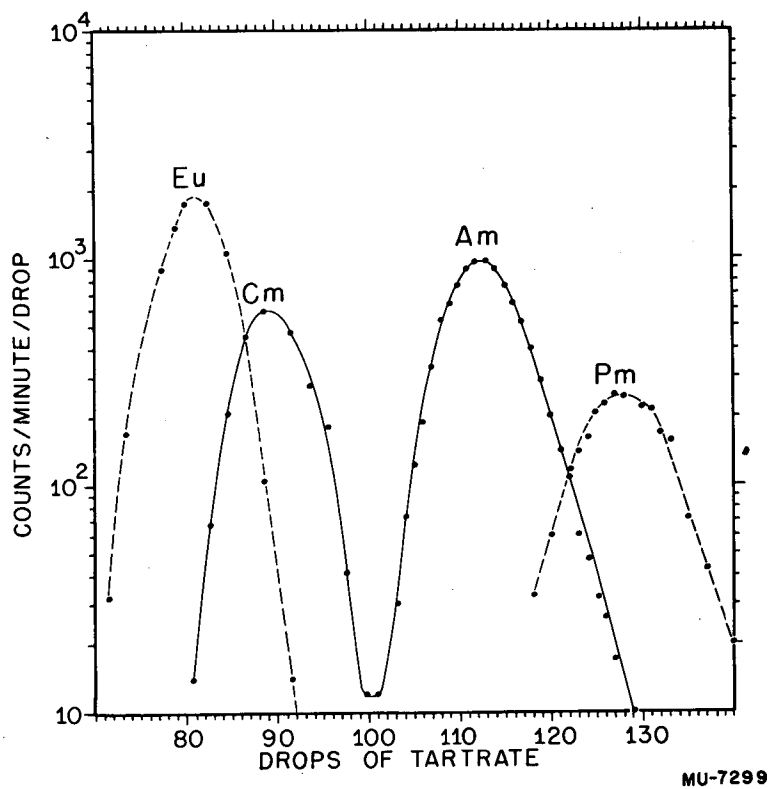

Fig. 1. Tartrate elution of actinide and rare earth tracers at room temperature: 0.10 $\underline{M}$ tartrate, pH 4.0, 1 drop/8 min: ---, beta counting; ——, alpha counting.
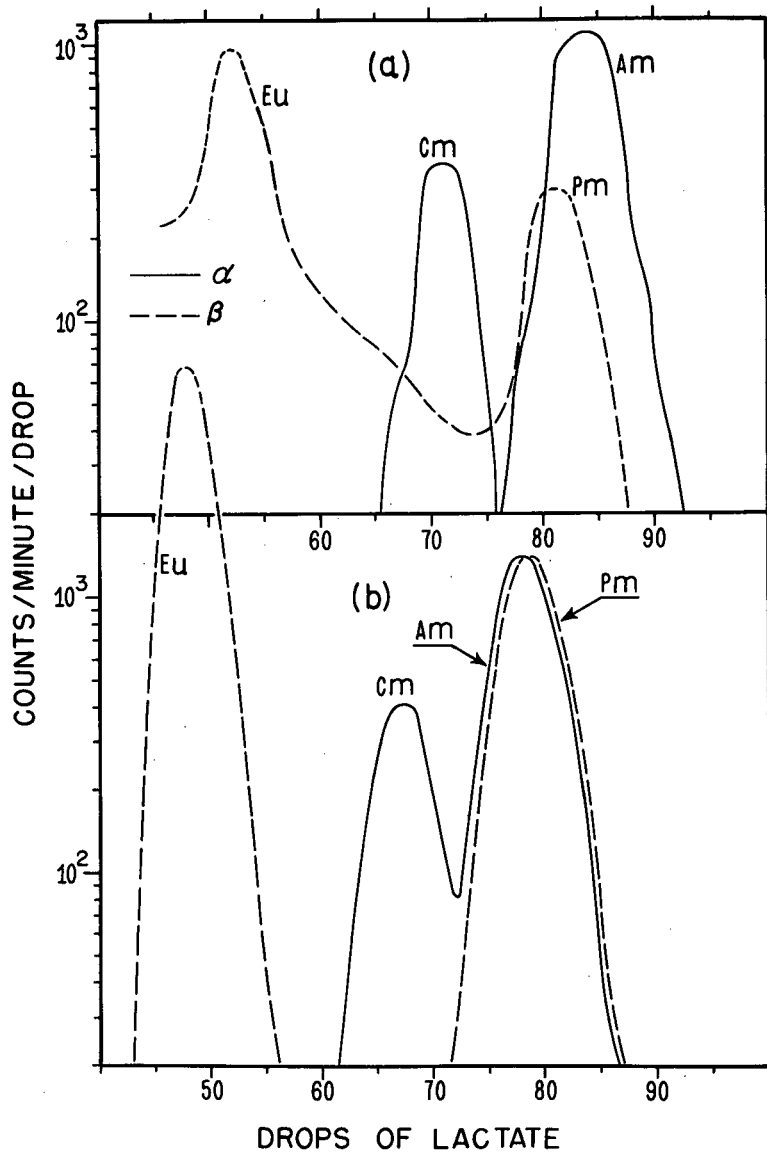
Fig. 2. Lactate elutions of actinide and rare earth tracers:

(a) 0.37 M lactate, pH 4.1, 1 drop/8 min., room temperature;

(b) 0.40 M lactate, pH 4.6, 1 drop/3 min., 87° C. : ---, beta

counting; ——, alpha counting.