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CHEMICAL PROPERTIES OF ELEMENTS 99 AND 100

S. G. Thompson, B. G. Harvey, G. R. Choppin and G. T. Seaborg

July 23, 1954

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S. G. Thompson, B. G. Harvey, G. R. Choppin and G. T. Seaborg
Department of Chemistry and Radiation Laboratory
University of California, Berkeley, California

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ABSTRACT

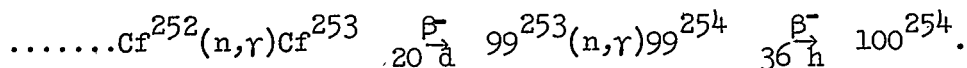
A description of some of the chemical properties and of the methods used in the separations of elements 99 and 100 is given. The new elements exhibit the properties expected for the tenth and eleventh actinide elements. Attempts to produce an oxidation state greater than III of element 99 have been unsuccessful. In normal aqueous media only the III state of element 100 appears to exist. The relative spacings of the elution peaks of the new elements in some separations with ion exchange resin columns are the same as the relative spacings of the homologous lanthanide elements. The results of experiments involving cation exchange resins with very concentrated hydrochloric acid eluant show that the new elements, like the earlier actinides, are more strongly complexed than the lanthanides. The new elements also exist partially as anions in concentrated hydrochloric acid, as do earlier actinide elements, and they may be partially separated from each other by means of ion exchange resins. With some eluants interesting reversals of elution positions are observed in the region Bk-Cf-99-100, indicating complex ion formation involving unusual factors.

CHEMICAL PROPERTIES OF ELEMENTS 99 AND 100

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Isotopes of elements 99 and 100 have been produced by neutron irradiation of Pu^{239} ; the final steps in their production are indicated by the following reaction sequence:¹⁻⁵



The properties of some of the isotopes thus produced are listed in Table I. These were the isotopes used for the present tracer studies of the chemical properties of the new elements.

Table I

Isotope	Radiations	Half-Life
${}_{99}^{253}$	6.68 Mev α	~20 days
${}_{99}^{254}$	1.1 Mev β^-	36 hours
${}_{100}^{254}$	7.22 Mev α	3.2 hours

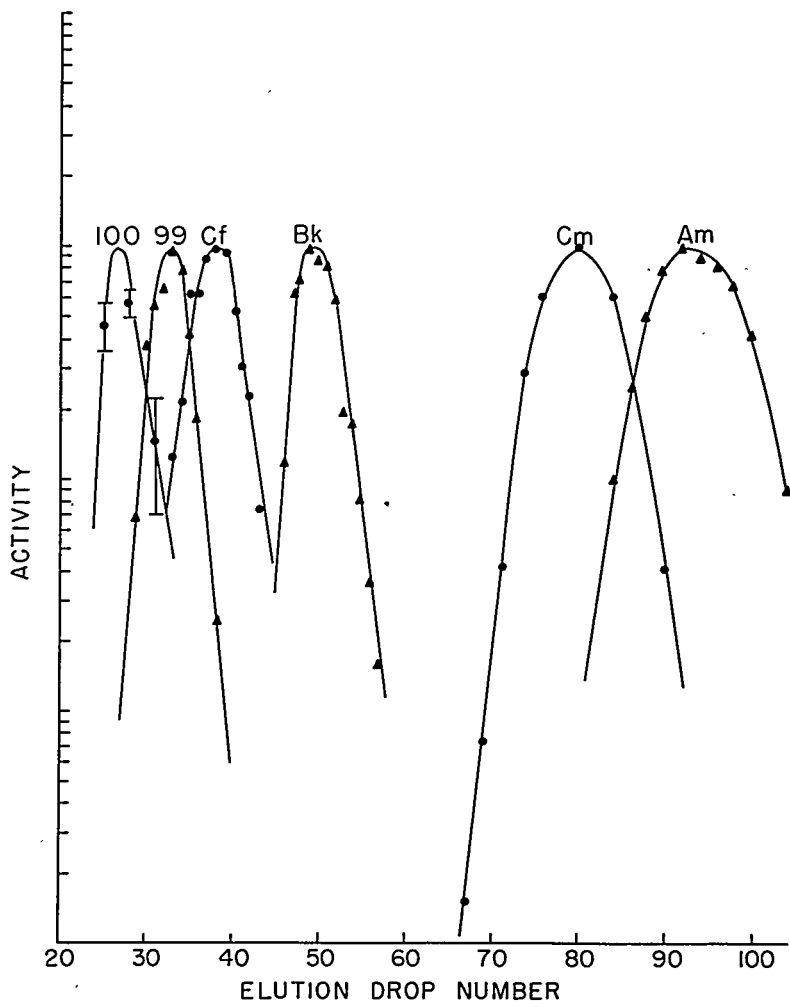
The first separation and identification of the new elements proved that prior expectations⁶ concerning the stability of their tripositive states, their precipitation properties and exchange column elution sequences were correct; in short, that they are chemically very similar to their actinide predecessors,^{7,8} differing in the manner to be expected for ions of somewhat smaller radius.

The results reported here were obtained in several instances in experiments which were primarily intended to separate and identify isotopes of the new elements rather than to obtain the maximum information concerning chemical properties. Since most of the experiments were essentially independent of each other, a separate introduction and discussion of each experiment is given in the section describing the experiment.

In the experiments to be described, the radioactivity of the isotopes of the new elements was normally measured by alpha particle pulse analysis of thin samples from the separated fractions. The sample deposits were made on platinum plates by the evaporation and ignition of the elutriant solutions from resin column experiments, and were usually essentially weightless. In the case of Bk²⁴⁹, the soft beta particles were counted in a windowless proportional counter (Nucleometer).

Ion Exchange Separations

1. Dowex 50 Resin - Ammonium Citrate Elution at 87° C. Since much of the prior work on separations of the heaviest elements has been done using this method,⁶⁻⁸ it seems worthwhile to show the relative positions of elements 99 and 100 in the citrate elution curves of Fig. 1. In this experiment some of the elements were present in rather low abundance, so that for convenience the heights of the peaks have been adjusted to a constant level without, of course, altering their shapes. The following deviations from the method of references 7 and 8 were employed: (1) The columns were shortened from 20 cm. to about 15 cm. (2) The pH of the ammonium citrate was changed to 3.35 ± 0.05 . These changes affect the



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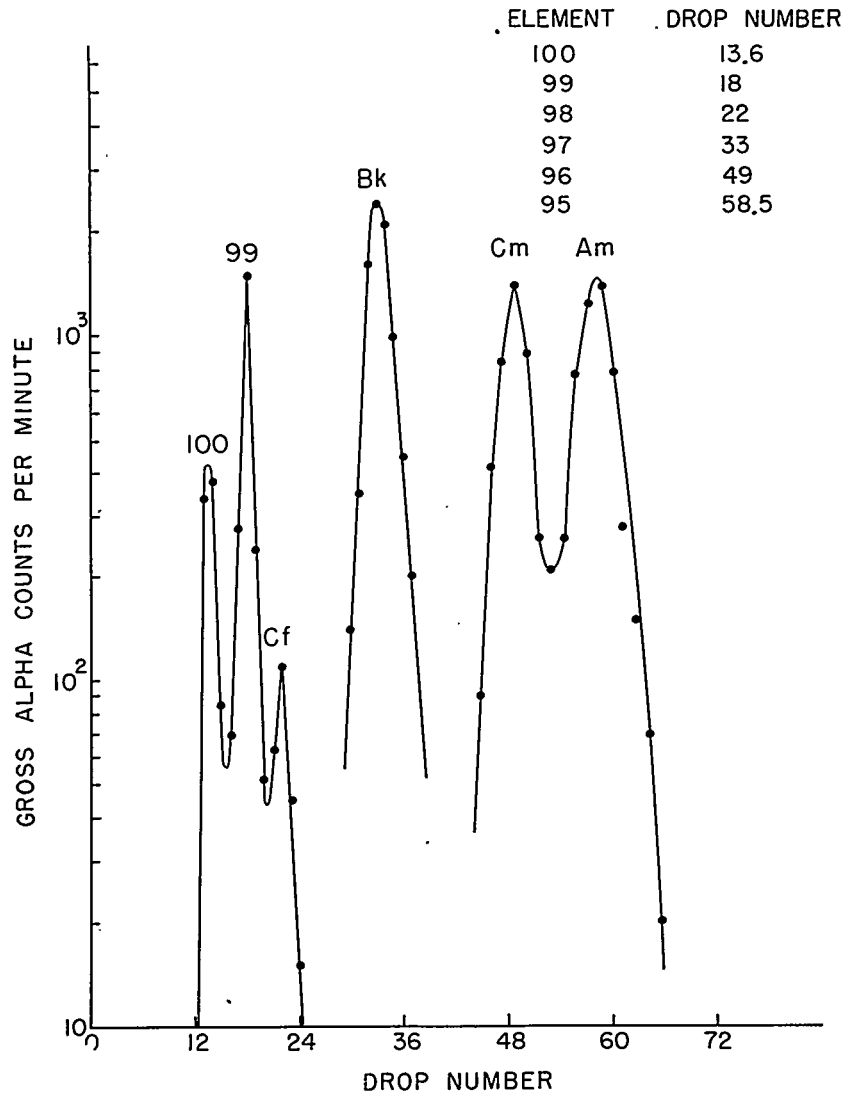
Fig. 1--Elution of tripositive actinides from Dowex 50 with ammonium citrate eluant.

actual elution position (drop number), but not the positions of either the actinide or lanthanide elements relative to each other.

2. Dowex 50 Resin - Ammonium Lactate Elution at 87° C. This method has been applied to americium-curium separations⁹ and to rare earth separations.^{10,11} Its application to the separation of the heaviest elements was found to give improved reproducibility and better separations of the individual actinides, particularly at more rapid flow rates, than had been obtained using ammonium citrate. Separation of the actinide elements from each other by this method was improved when the amounts of other elements present were minimized by previous separations. The results of experiments in which the elements americium through 100 were separated from each other are illustrated in Fig. 2a. The separation of homologous rare earths under identical conditions is shown (Fig. 2b) in order to emphasize the similarity in relative spacings between the rare earths and actinides. It should be noted that the actual drop numbers of the elution of the rare earths are multiplied by the factor 0.721 to facilitate comparison.

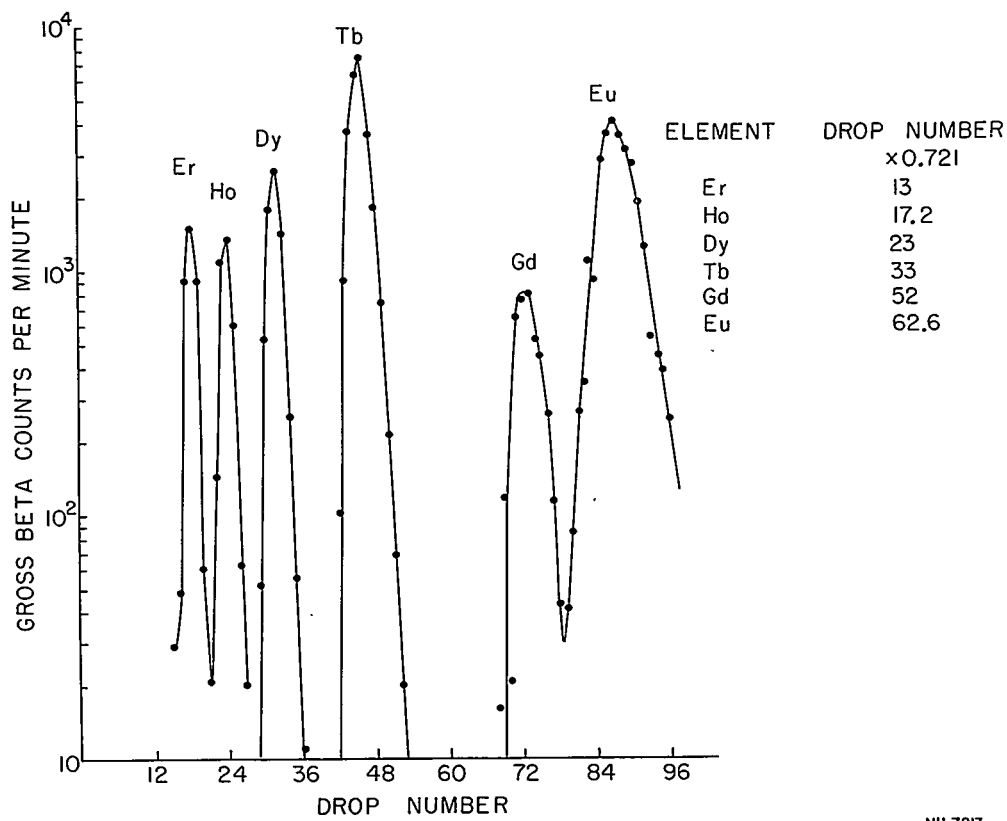
Experimental

Resin. Dowex 50 spherical resin, 200-400 mesh size, 12% cross linked, was graded (in the hydrogen form) by allowing it to settle from aqueous suspension. The fraction with a settling rate between 0.5 and 0.25 cm./min. was collected. It corresponded to the finer fraction of the ungraded material. The graded resin was washed alternately with 12 M hydrochloric acid and ammonium hydroxide. It was stored in the ammonium form until required.



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Fig. 2a--Elution of tripositive actinides from
Dowex 50 with ammonium lactate eluant
(~2 minutes per drop with 35λ drop size).



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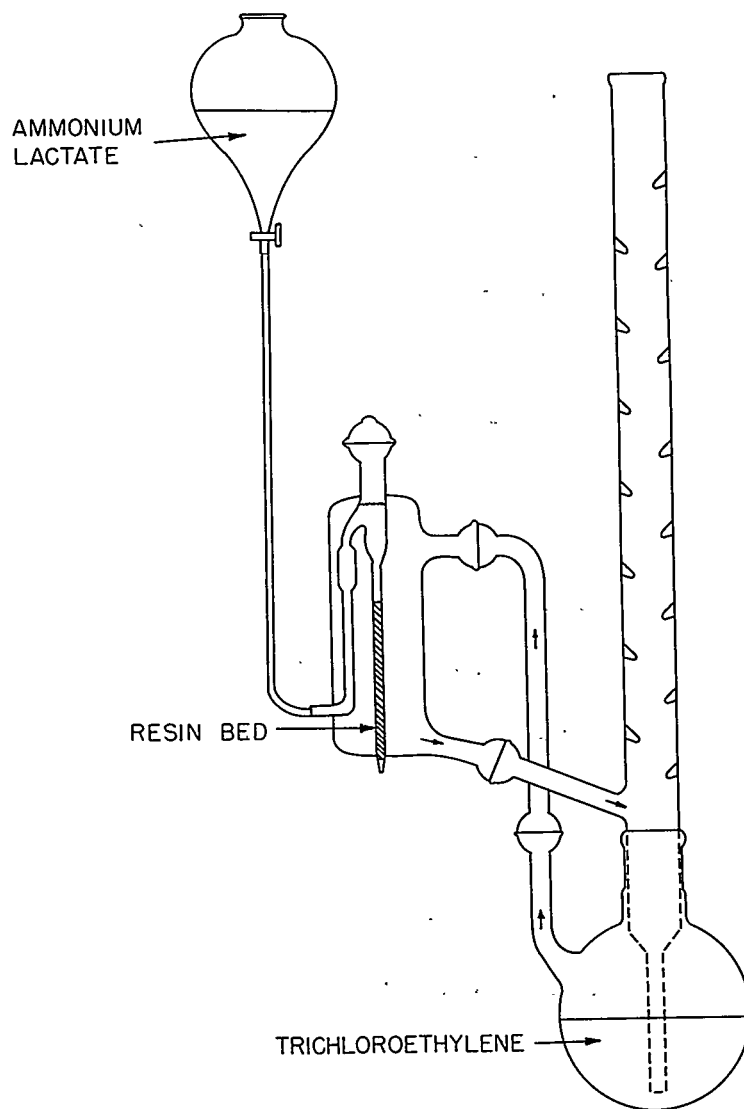
Fig. 2b--Elution of homologous lanthanides with ammonium lactate (conditions same as for actinides in Fig. 2a).

Ammonium Lactate. Reagent grade lactic acid was used to prepare a 0.4 M solution in conductivity water. The pH was adjusted to the required value (normally between 4.0 and 4.5) by the addition of conductivity water saturated with ammonia. The solution was finally made 0.01 M with respect to phenol to inhibit the growth of molds.

Column Apparatus. The column apparatus most frequently used is shown in Fig. 3. The diameter of the resin bed was usually 2 mm. (where essentially weightless materials were to be separated). The length was adjusted to give the degree and speed of separation required, but was normally 5 to 6 cm. These column dimensions were employed in the separations shown in Figs. 2a and 2b.

The resin was transferred to the column as an aqueous slurry. After the bed length had been adjusted, the column was heated to 87° C. by boiling the trichlorethylene and the eluant solution was allowed to flow through at a slow rate (roughly ~5 minutes per drop). The air bubbles which developed were removed by stirring the bed. As soon as bubbles stopped forming, the column could be used. However, if possible, the flow of the eluant was maintained for 24 hours to remove all soluble inorganic materials from the resin, thus reducing contamination of the actinide elements with impurities.

Column Operation. The flow of eluant was interrupted, and the ammonium lactate solution above the resin bed was removed. The space above the resin bed was washed carefully with hot (air-free) distilled water to remove traces of lactate. Finally, two drops of



MU-7814

Fig. 3--Column apparatus for separations
with lactate.

water were forced through the resin bed. This procedure was then repeated with hot 0.05 M hydrochloric acid, and two drops of the acid were forced through the resin bed. The remainder of the acid was removed from above the resin.

The mixture of actinide elements, dissolved in two drops of 0.05 M hydrochloric acid, was carefully transferred to the top of the resin bed and allowed to flow slowly through. The tube which contained the actinides was washed successively with two more drops of 0.05 M hydrochloric acid and then with two drops of water. These washings were allowed to wash down the space above the resin bed and to flow slowly through. The tube was finally washed with two drops of ammonium lactate solution which were transferred to the top of the column and allowed to flow slowly through the resin bed. The first drop to fall after the transfer of the ammonium lactate to the resin bed was collected as "drop number 1".

The space above the resin bed was then filled with hot ammonium lactate from the side-tube, the ground glass stopper inserted, the height of the reservoir adjusted to give the desired flow rate (measured in drops per minute).

Effect of Flow Rate. Increasing the flow rate of the eluant did not alter appreciably the volume required to elute a given ion. It did, however, increase the width of the bands into which the individual elements were separated. Hence, a compromise must be reached between the requirements of speed and completeness of separation. Normally, separations were so complete that there was little

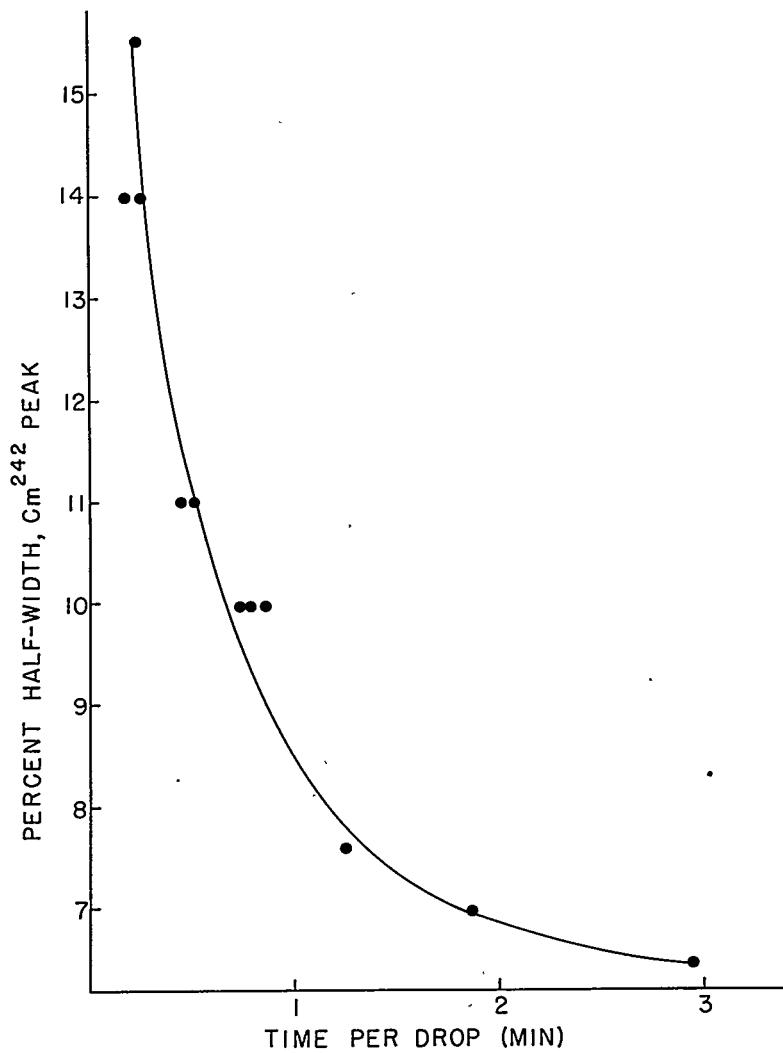
point in operating at flow rates of less than $0.5 \text{ ml./min./cm.}^2$. At flow rates greater than 4 ml./min./cm.^2 (i.e., 15 seconds per drop from a standard 2 mm. diameter resin bed), the samples accumulated faster than they could be conveniently dried, ignited, and analyzed.

Figure 4 shows the full-width at half-maximum (half-width) in drops as a percentage of the drop number of the peak which was obtained for the elution peak of curium at various flow rates. This relation is valid only for the conditions followed here. Obviously, the conditions could be varied to obtain fictitiously narrow half-widths (for example, if one increases the pH of the eluant during elution).

Effect of Eluant pH. One advantage of ammonium lactate (compared with ammonium citrate) is that the number of drops required to elute a given ion is not a very sharp function of the pH of the lactate solution (because the lactate ion concentration is large and changes slowly over the whole pH range normally used).

The number of drops of 0.4 M lactate of various pH values required to elute yttrium and curium from a 2 mm. diameter resin bed, 5 cm. long, is shown in Fig. 5.

For most purposes adequate separations were obtained with 0.4 M lactate at a pH of 4.5. The heaviest elements, californium, 99, and 100, however, eluted from 5 cm. of resin bed in a rather inconveniently small number of drops at this pH, and better separations were obtained (when the slight extra time was no disadvantage) by using lactate with a pH of 4.10 to 4.20.



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Fig. 4--Width of elution peaks versus drop rate with ammonium lactate eluant.

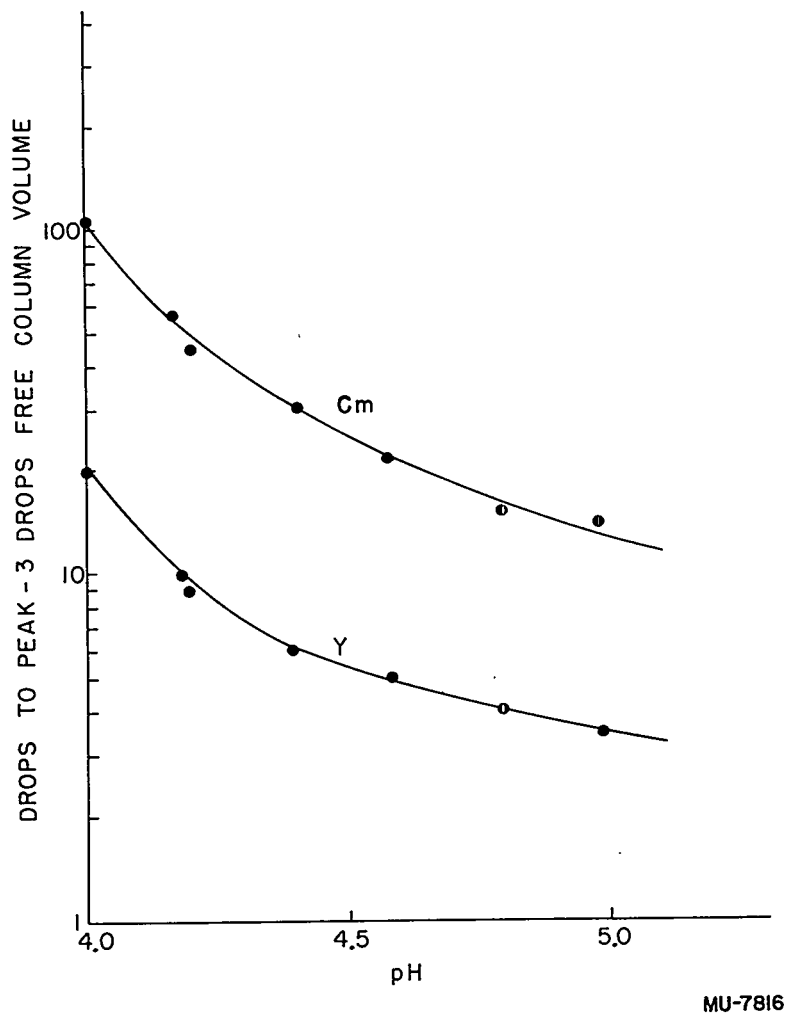
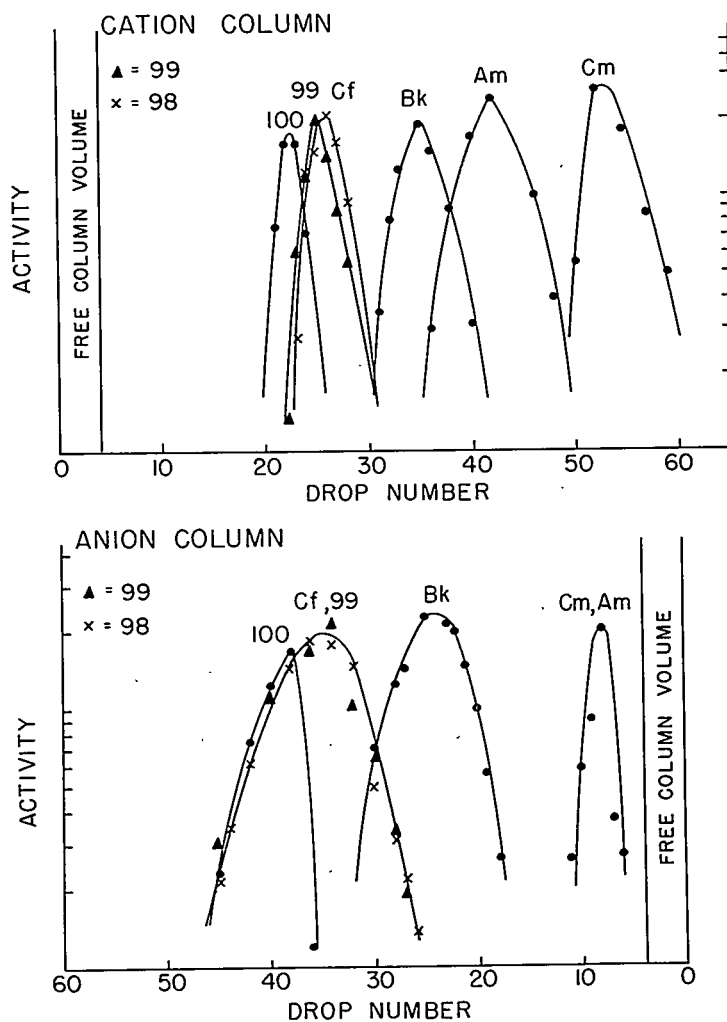


Fig. 5--Elution peak positions versus pH of lactate eluant.

3. Dowex 50 Resin - Concentrated Hydrochloric Acid Eluant. Group separations of lanthanides from the transplutonium elements have been commonly made by elution of the mixtures from Dowex 50 columns with 13 M hydrochloric acid.¹² The method has been improved recently by utilizing 20% ethyl alcohol saturated with hydrochloric acid as the eluting agent (first used by Street¹³) and also by using Dowex 50 colloidal 12% cross linked resin. The use of alcohol in the eluting agent has the effect of delaying elution both of actinides and of lanthanides, but with a greater effect upon the latter, and with resultant improved group separations. Use of the colloidal resin, as compared with spherical resin, gave sharper elution peaks, especially at more rapid flow rates. The improved method can also be used to make separations of some individual actinides, and is another means for comparison of elements 99 and 100 with their predecessors, as shown in Fig. 6a. The individual peaks in Fig. 6a have been adjusted by division with an appropriate number to give approximately equal peak heights. Americium was not present in the experiment shown in this figure but its elution position was calculated from data obtained in previous experiments. It is interesting to note that the elution positions are in order of atomic number except for the reversal of americium in preceding curium, which has been observed in several separate experiments in which americium and curium were both present.



MU-7817

Fig. 6a--Elution of actinides from Dowex 50 resin with 20% alcohol - 12.5 M hydrochloric acid.

Fig. 6b--Elution of actinides from Dowex 1 resin with 13 M hydrochloric acid.

Experimental

Resin. The cation resin (Dowex 50 X-12 colloidal) and the anion resin (Dowex 1 X-8) were washed alternately with ammonium hydroxide and hydrochloric acid several times. The fractions which had a settling rate from aqueous suspension of 0.50-0.75 cm./min. were used in these experiments.

Eluting Agent. A solution of 20% ethyl alcohol saturated with hydrogen chloride gas (12.5 M hydrochloric acid STP) was the eluting agent in these studies.

Operations. The columns were packed with the H^+ form of the resin so that the resin bed dimensions were normally 5 cm. length and 3 mm. diameter. After the resin had been washed with the eluting agent, the excess eluting agent was removed, and the tracer activities to be separated were transferred to the top of the resin column in one drop of eluting agent, which was allowed to flow into the resin. The operation was repeated with a second drop; then, to minimize the trailing edge of the activity peaks, the space above the resin bed was rinsed with several drops of the alcoholic hydrochloric acid solution. A sufficient amount of eluting agent was transferred to the column and pressure applied to obtain the desired flow rate.

To find optimum conditions for the actinide-lanthanide group separation, investigations of the effect of varying (a) alcohol and hydrochloric acid concentrations, and (b) flow rate, were made. A flow rate of one minute per drop, using 20% alcohol saturated with

hydrogen chloride gas proved to be the best practical conditions and produced half-widths (as defined in section 2) of 17%. Increased flow rates had the effect of increasing the half-widths; however, a rate of 20 seconds per drop provided satisfactory group separation when speed was necessary. The group separation of the actinides from the lanthanides was improved by maintenance of maximum hydrochloric acid concentrations, but was satisfactory when the concentration was in the range of 11.5 M to 12.5 M.

4. Dowex 1 Anion Resin - Hydrochloric Acid Eluant. In some early work¹⁴ involving rapid separations of Cf²⁴⁶ and Cm²⁴² from uranium, it was found that californium is delayed relative to curium in elution from columns of Dowex 1 anion resin when 13 M hydrochloric acid is used as the eluant. Further application of the method has shown that negatively charged chloride complex ions can be produced with all of the actinide elements ranging from americium through element 100. In 13 M hydrochloric acid solutions the existence of complex ions was barely detectable in americium and curium since these elements were only slightly adsorbed on anion resin as shown by very slightly delayed elution from anion resin columns. The apparent strength of the complex increases with increasing atomic number and the difference between the elements in certain cases is large enough so that the method is, in such cases, a practical and useful means of separation.

The elution positions of the elements ranging from Z = 95 through 100 are shown in Fig. 6b. (As in Fig. 6a, the peaks have been adjusted to similar heights by division of the height of some of the peaks by an

appropriate number.) The lanthanides were less adsorbed than curium and were readily separated from the transcurium elements. Comparison of Figs. 6a and 6b shows that the elution order of the actinides from Dowex 1 anion resin columns is the reverse of their elution order from Dowex 50 cation resin columns. The only exception to this occurs in the case of americium and curium. Separate experiments have shown that americium precedes curium in elution from a Dowex 1 anion resin column, which is the same as their elution order from a Dowex 50 cation resin column.

In both types of columns the peaks for elements 98 and 99 fall so close together that it is not possible to draw any conclusions as to which precedes the other.

The peculiar shape of the curve for element 100 in Fig. 6b is probably accounted for by the poor counting statistics - the amount of the element available at the time was very small.

Experimental

The anion resin used for all experiments reported here was Dowex 1, 8% cross linked. The preparation of the resin and the preparation and operation of the column followed the methods described in the previous section. Column dimensions of 5 cm. length and 3 mm. diameter were chosen for convenience. Flow rates less than about 0.15 ml./cm.²/min. seemed to be necessary in order to obtain satisfactory separations. (This rate corresponded to approximately one drop per three minutes from the standard column above.) Some separations were made using 20% alcohol saturated with hydrogen chloride gas, under which conditions the elution of

actinides is delayed as much as a factor of two as compared with the aqueous hydrochloric acid elution. Separations with Dowex 1 resin were also much more critically dependent on conditions of operation than were those with Dowex 50 cation resin. The separations were improved by using resin fines of the smallest particle size which would still permit a suitable flow of eluant. Even with such precautions elution peak half-widths were about 30%. The separations were highly dependent on the hydrochloric acid concentration. With 10 M hydrochloric acid, no delay in the elution of curium or californium could be observed. In the range 11-12 M hydrochloric acid some delay in elution became evident and a change from 12 to 13 M hydrochloric acid approximately doubled the drop number of the californium elution peak. The absence of delay in the elution of californium at hydrochloric acid concentrations less than 10 M enabled excellent separations of uranium and plutonium to be made when the latter were in oxidation states of VI and greater than III, respectively. In such cases a suitable range of hydrochloric acid concentrations was from 6 to 10 M whereupon complete adsorption of the uranium or plutonium was accomplished with no adsorption of elements 95 through 100 inclusive. In some cases it was convenient to ensure the presence of plutonium in the tetrapositive state by making the solution 0.1 M in ammonium nitrite. The plutonium was removed from the resin either by elution with 6 to 10 M hydrochloric acid containing HI at a concentration of about 0.1 M (the HI reduces the plutonium to the tripositive state), or by elution with 1 M

hydrochloric acid. The separation of many other elements with Dowex 1 resin and hydrochloric acid eluant has been described by Kraus, et al.¹⁵

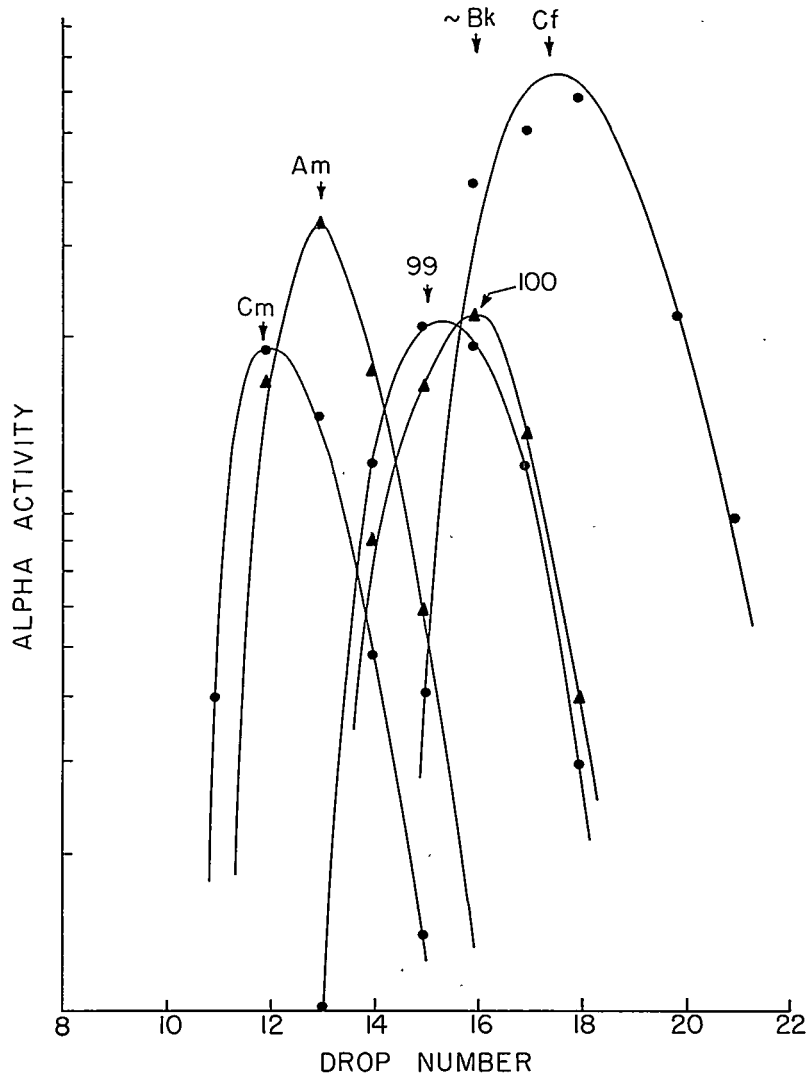
5. Other Ion Exchange Studies. An investigation of the behavior of some of the actinide elements in elution from columns of Dowex 1 anion resin using ammonium thiocyanate as eluant has been made.¹⁶ A jacketed column (described in section 2) was prepared and loaded by the techniques described in section 3. The elution was performed at 87° C., using 1.0 M ammonium thiocyanate. A flow rate of 0.2 ml./cm.²/min. was used.

A typical elution curve is shown in Fig. 7. Berkelium was absent in this experiment; its approximate elution position was obtained in separate experiments, and is indicated by a vertical line in Fig. 7.

Under these conditions, the rare earths precede curium in elution from the column.

Oxidation-Reduction Behavior

From the general trends of the oxidation potentials of the actinide elements it would not be expected that oxidation states other than III could be obtained of elements 99 and 100 in aqueous solutions.^{6,8} This postulate has been based to some extent on some unreported work with californium in which an unsuccessful attempt was made to produce a V oxidation state and to carry it with the compound $KAmO_3$. The conclusion of this experiment was that californium is more difficult to oxidize to the V state than is americium.¹⁷ It seems reasonable therefore that oxidation states greater than III will be even more difficult to obtain



MU-7818

Fig. 7--Elution of actinides from Dowex 1 resin with 1.0 M ammonium thiocyanate.

with the heavier elements. However, in the case of solid compounds such as the oxides, the increased stability produced by certain crystal structures may enable a IV oxidation state to be formed.

It is often difficult to interpret the results of a tracer experiment unless a comparison is made with another tracer element whose behavior is known. In the following experiment americium and curium tracer were present and the oxidation of the former to the VI state with simultaneous non-oxidation of the latter and the element 99 tracer permits the conclusion that element 99 is more difficult to oxidize to the VI state than americium under the same conditions. This method has been applied previously in the attempted oxidation of element 99¹⁸ with results the same as reported here.

Experimental

A mixture of the tracers Am²⁴¹, 99²⁵³ and Cm²⁴² was precipitated with 200 micrograms of lanthanum as the hydroxide by adding ammonium hydroxide. The precipitate was separated from the solution by centrifugation and was washed twice with water. The lanthanum hydroxide was dissolved in perchloric acid, the volume of the solution adjusted to 200 microliters and the pH adjusted to 1.5. The solution was heated for one hour at 90° C. and a few crystals of (NH₄)₂S₂O₈ were added approximately every 15 minutes. A small addition of ammonium hydroxide was made after about one-half hour to adjust the pH to ~3. The lanthanum was then precipitated as the fluoride by the addition of potassium fluoride solution which had been pretreated with (NH₄)₂S₂O₈. The solutions were chilled in an

ice bath just prior to and during precipitation. The LaF_3 was separated by centrifugation and was washed three times with water. The precipitate was transferred as a slurry to a platinum plate. It was then dried, ignited and subjected to alpha particle pulse analysis. A small amount of hydroxylamine hydrochloride and 200 micrograms of lanthanum were added to the supernatant and the solution heated at about 75° C. for 10 minutes. The lanthanum fluoride was subsequently treated in the same manner as the first lanthanum fluoride precipitate described above.

The activity of element 99 was distributed between the precipitate and the supernatant in exactly the same ratio as the curium; namely, approximately equal amounts in both fractions since the precipitation was not complete. Essentially all of the americium remained in the supernatant and was not carried in the first lanthanum fluoride precipitate.

Other Properties

The work performed in this laboratory in connection with separations of the new elements has involved primarily the use of combinations of precipitation and ion exchange methods. The latter have been described in preceding sections. It has been implied that the behavior of the new elements with carriers is the same as is observed with berkelium and californium.^{7,8} Nevertheless, it seems worthwhile to outline some of the general procedures involving carriers, and their combinations with ion exchange procedures which have been successfully used.

Experimental

It has been found that the precipitation of lanthanum hydroxide or ferric hydroxide in basic solutions ranging in pH from those generally obtained with buffered ammonia solutions (pH ~8.5) to those obtained with strong bases (pH ~14) resulted in complete carrying of elements 99 and 100 provided very high salt concentrations and the presence of organic complexing agents such as citrate or lactate were avoided. Elements 99 and 100 were well carried by rare earth fluorides precipitated from either nitric or hydrochloric acid solutions if the conditions produced the complete precipitation of the rare earths themselves. Alternation between hydrochloric and nitric acids in fluoride precipitations was effective in the separation of combinations of certain elements such as ruthenium, lead and magnesium. One useful method of dissolving fluoride precipitates was to use saturated boric acid together with hydrochloric or nitric acid, following which the hydroxides could be precipitated with ammonium hydroxide. The hydroxides were dissolved by blowing hydrogen chloride gas over them. The solution thus obtained could be transferred directly to an ion exchange column. In the operation of Dowex 50 cation resin columns, using alcoholic hydrochloric acid as eluant, to obtain a group separation of the actinide and lanthanide elements, it was frequently useful to place a 2mm. thick bed of Dowex 1 anion resin at the bottom of the Dowex 50 bed to remove those impurities which form strong anionic complexes (such as iron). Fractions of interest (usually obtained by combining

hydrochloric acid eluant fractions from a resin column) were conveniently reduced in volume by evaporation in a water bath with a moderate flow of air from an air jet above the liquid. Ammonium salts, when present in hydrochloric acid solutions, could be eliminated during evaporation by the occasional addition of nitric acid. In such cases the elimination of ammonium chloride prior to completion of the evaporation reduced losses of tracer activities. It was often necessary to combine fractions from a Dowex 50 column employing ammonium lactate eluant, to reduce the volume, and to separate interfering elements from the actinides by subsequent separations. To destroy the lactate in such cases, continuous fuming with nitric acid or aqua regia and eventual reduction to dryness was effective but time-consuming. Wet ashing with sulfuric and nitric acids in a platinum container followed by fuming to dryness was a much more rapid and effective procedure provided elements with insoluble sulfates (such as calcium) were absent. Direct evaporation to dryness and heating to a high temperature in platinum frequently presented difficulties in redissolving the activities. Best results were obtained by heating the residue on platinum with weak hydrofluoric acid in 10 M hydrochloric acid or 6 M nitric acid. Such difficulties were primarily dependent on the amount and composition of solid impurities which were present. It was also found that the new elements could be extracted from large volumes of solutions containing lactate by acidifying the solution to a pH of about 1 and then passing the solution slowly through a column packed

with H^+ form cation resin. The activities were then extracted by elution with a smaller volume of 13 M hydrochloric acid.

DISCUSSION

(a) Oxidation States. The evidence from the tracer experiments concerning the oxidation of elements 99 and 100 is consistent with the view that only the III states of these elements exist in aqueous solutions. The information concerning non-oxidation of element 99 was obtained under conditions resulting in oxidation of americium to the VI state; in the case of element 100 the only evidence stemmed from behavior typical of the III state when the previously described separations were made in aqueous solutions and in the absence of especially powerful oxidizing agents. These data, however, lend support to the view that oxidation states greater than III in aqueous solutions should not be stable for the remaining actinide elements 101, 102 and 103; the additional 5f electrons should be more strongly bound and, in this respect, an increasing resemblance to the lanthanide elements should be evident as the end of the series is approached. The increased resemblance may appear further in the existence of the II oxidation state in elements 102 and possibly 101.

(b) Ion Exchange Behavior. The elution positions of the elements from americium to 100 for various types of ion exchange columns and eluants are summarized in Fig. 8. All five types of elutions show certain common features which are discussed in detail below. It is remarkable that only from Dowex 50 resin with ammonium lactate (or citrate) as eluant do these elements fall in a simple order of atomic

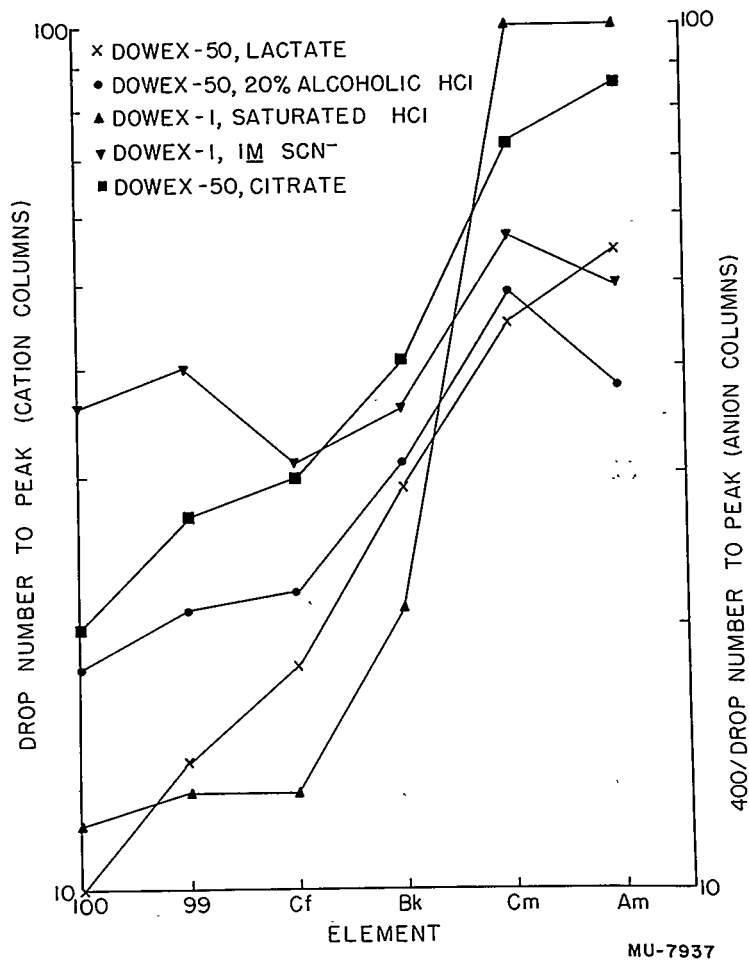


Fig. 8--Summary of elution positions of actinide elements as a function of Z.

number. From the known behavior of the lanthanide elements in this type of elution (with lactate or citrate), it is expected that the remaining actinide elements, 101, 102 and 103, will also elute in the inverse order of their atomic numbers with spacings between them which will be closely analogous to the homologous lanthanide elements (i.e., the separation between elements 102 and 103 will be small). In the other types of elutions shown in Fig. 8, it is apparent that there exists a variety of rather complicated situations, and obviously the elution positions are not determined solely by simple considerations of ionic radii (which would lead to a monotonic elution sequence). Some of the factors which may influence elution positions are listed below.

A study of Fig. 8 shows that departures from a "simple" elution sequence occur in two positions:

(1) Relative to curium, americium is more highly retained by anion resin and less highly retained by cation resin than would be expected. (This effect is just noticeable in the Dowex 50-lactate or citrate elution.) Presumably, therefore, americium has a tendency to form anionic complexes which are stronger or more negatively charged than would be expected from a study of the behavior of curium.

(2) Relative to berkelium and element 99, californium is more highly retained by anion resin, less by cation resin, than would be expected. (This effect also is just noticeable in the Dowex 50-lactate or citrate elution.) Presumably californium, like americium, tends to form complex ions which are stronger or more negatively

charged than would be expected from the behavior of its neighbors. In the elution with ammonium thiocyanate, in which this effect is most marked, berkelium also appears to be more strongly retained by the anion resin than might be expected from the behavior of curium and element 99. While the anomaly in the elution sequences is here attributed to californium, it must be remembered that a study of the properties of elements 101, 102 and 103 may later establish that there occurs, in the elements heavier than californium, a "reversal" in elution order with ammonium thiocyanate (in which element 99 would be "anomalous" in diverging from this reversed order). Thus if it should be established that the availability of 5f orbitals is important to the formation of complex ions in the heaviest actinides, the complex ions may decrease in strength at the end of the series due to the unavailability of 5f orbitals, leading to the elution of elements like 103 and 102 early in the sequence.

The first effect, the "reversal" of americium and curium, was reported earlier by Diamond, Street and Seaborg¹⁹ in studies of the elution sequence of these, and other, elements from Dowex 50 resin with various concentrations of hydrochloric acid. The concept of bond hybridization, utilizing the 5f orbitals, was used to explain the greater extent of chloride complex formation in the actinide elements as compared with the lanthanides. The "reversal" of americium and curium was interpreted as due to the greater tendency of americium to utilize 5f orbitals in the formation of chloride complexes. The shrinkage of the 5f orbitals in the neighborhood of curium makes them less available for bond hybridization. In the elements beyond curium, the progressive decrease in the ionic

radii might make the 5f orbitals again more available for bond hybridization, so that at least some of the following heavier actinide elements might again form complex ions more stable than those of curium. The smaller ionic radii would themselves increase the tendency of the heavier actinides to form complex ions.

It is more difficult to account for the reversal in elution positions in the neighborhood of californium, which is particularly evident in elutions from anion resin columns. It might, however, be useful to list some of the factors which could influence the elution position of an ion.

(1) The Ionic Radius. Small ions will be more tightly bound to cation resins, but will also be more liable to formation of complex ions.

(2) Degree of hydration. Small ions will have larger hydration shells, and will therefore be more sensitive to the influence of "dehydrating" eluant media such as strong solutions of hydrochloric acid. The importance of this phenomenon was shown by Diamond et al.,¹⁹ in the elution of radium, barium and strontium from Dowex 50 resin with strong hydrochloric acid.

(3) Bond hybridization. The importance of this phenomenon was mentioned above. A comparison of the behavior of the lanthanide and actinide elements will be illuminating in this context, since it seems probable that f orbital hybridization will be a much more important phenomenon in the actinide series than in the lanthanide. It is also possible that hybridization involving 7p orbitals might begin to occur toward the end of the actinide series.

(4) Stark effect. If surrounding ions or groups produce electric fields not of spherical symmetry around an actinide or lanthanide ion with unpaired electrons, the $(2J + 1)$ -fold degeneracy involving the spatial orientation of the total angular momentum vector J will be partially or completely broken up. The nature and extent of the splitting will depend upon the term value of the ion, and upon the symmetry and strength of the electric field. The splitting will be extremely small for the ions with electronic structure corresponding to the term $^8S_{7/2}$, i.e., Cm^{+++} and Gd^{+++} . If the magnitude of the Stark splitting is of the order of kT , the entropy of formation of the state in question may be altered significantly. The larger spatial extension of the $5f$ orbitals compared with $4f$ should make such effects greater in the actinide series than in the lanthanide series. Hence there may be differences between the two series, and between different elements within a series, in the entropy of formation of some complex ions.

It has been found that the formation of many organic complex ions causes a splitting of the absorption spectrum lines of praseodymium, neodymium and samarium.²⁰ Splitting of the order of kT (at room temperature) was observed for the citrate complex of praseodymium.

Measurements of the entropy change in the high temperature hydrolysis of the lanthanide trichlorides²¹ showed no differences which could be attributed to Stark splitting. The entropy of vaporization of PuF_3 is the same (within the limits of experimental error) as that of AmF_3 .²² Hence the difference in Stark splitting

between the solid and vapor forms of AmF_3 and PuF_3 must either be negligible or very similar for both compounds.

(5) Steric effects. It is possible that the formation of higher complexes might be slightly subject to a steric hindrance, which would be more noticeable with the smaller ions of the heaviest actinide elements. In this connection it may be significant that the crystal structures of the sesquioxides, fluorides, chlorides, bromides and oxychlorides of the lanthanides all show a change, with a reduction in coordination number, somewhere in the middle of the series.²³ The coordination number is usually 9 for the lighter lanthanide elements, but drops to as low as 6 for the heaviest lanthanides. A change of coordination number (from 9 to 8) has been observed at neptunium in the actinide tribromide series.²⁴

It is worth pointing out that the lanthanide and actinide elements provide an excellent opportunity for the investigation of some of the more subtle aspects of chemical behavior. Small effects may be detected which would be hidden by larger differences in the comparison of less closely similar series of elements.

The authors would like to re-emphasize the existence of unpublished information relevant to the discoveries of elements 99 and 100, as was stated in references 1 and 2. Under these conditions it seems inappropriate to suggest names for the new elements here.

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