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K. Street, Jr.
S. G. Thompson
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CHEMICAL PROPERTIES OF CALIFORNIUM*

By K. Street, Jr., S. G. Thompson, and G. T. Seaborg

ABSTRACT

Some evidence as to the chemical nature of the new element californium is presented. The chemical separation and identification of the new element was accomplished through the use of ion-exchange adsorption methods employing the resin Dowex-50. Californium appears in the eka-dysprosium position on elution curves containing berkelium and curium as reference points—that is, it precedes berkelium and curium off the column as dysprosium precedes terbium and gadolinium. The experiments so far have revealed only the tripositive oxidation state of eka-dysprosium character and suggest either that higher oxidation states are not stable in aqueous solution or that the rates of oxidation are slow.

INTRODUCTION

In the course of the production and identification of a radioactive isotope of californium[1] (atomic number 98), some evidence as to the chemical nature of this transuranium element was obtained. This isotope was prepared by the bombardment of Cm^{242} with 35-Mev helium ions in the 60-in. cyclotron of the Crocker Radiation Laboratory, and it is believed to have the mass number 244. The Cf^{244} has a half-life of about 45 min and decays at least partially by the emission of alpha particles of 7.1 Mev energy.

It should be pointed out that the first successful identification of the new element depended on the quite accurate prediction of some of its nuclear and chemical properties. The anticipation of the nuclear properties (principally half-life and radiation characteristics) was necessary in order to design adequate chemical procedures of sufficiently short duration and to use suitable instruments for the detection of its radiations. The prediction of the nuclear properties of isotopes of element 98 will be discussed more completely in another report;[2] however, it should be mentioned that the isotope expected to be most easily detected in the bombardments contemplated was Cf^{244} with an anticipated half-life of from 30 min to several hours and emitting alpha particles with an energy in the range 7.0 to 7.3 Mev, and it was on this basis that the chemical procedure was designed.

The necessity for predicting some of the chemical properties arises principally because of the large amount of radioactivity associated with the Cm^{242} target material. The few micrograms of Cm^{242} available for the target emitted approximately 10^{10} alpha particles per minute. With the yields expected for the isotopes of element 98 that could be produced by helium-ion bombardment, one could hope to make only a few hundred disintegrations per minute of the new element. Thus it is obvious that after bombardment a very substantial chemical separation from the target material had to be made before any attempt to detect the new element could possibly be successful.

These problems are of the same type as those encountered in the first production and isolation of berkelium[3,4] using Am^{241} as the target material. The smaller amount of Cm^{242} and its higher specific activity (about 1000 times that of Am^{241}) made the problem of isolation from the target material more difficult. On the other hand, the additional data furnished by the chemical properties of berkelium made the prediction of the chemical properties of element 98 much more certain.

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Since berkelium had taken its place as the eighth member of the actinide transition series of elements, there was every reason to believe that element 98 should be an "eka-dysprosium." The fact that the Bk(III)-Bk(IV) couple had a potential of approximately -1.6 volts made it extremely likely that element 98 would have a stable plus three oxidation state in aqueous solution and that higher states would be attained with difficulty if at all. Thus element 98 should follow the rare-earth elements in its precipitation chemistry.

The most satisfactory method up to the present of separating the heavy actinide elements from each other consists in selectively eluting them from a column of cation-exchange resin with ammonium citrate solution,[4,5] and hence it was necessary to anticipate the position of elution of element 98. That element 98 should elute ahead of berkelium was obvious from the behavior of the rare earths* and the preceding actinides, but it was necessary to make a more quantitative estimate of its position of elution relative to the other actinides in order to devise the most efficient chemical procedure possible. A comparison of relative rates of elution of the lanthanide triad europium-gadolinium-terbium with the actinide triad americium-curium-berkelium[4] had disclosed a remarkable similarity in the change in ionic size (and consequently rate of elution) on filling in the 4f and 5f electrons. The break in change of radius which is encountered after the half-filling of the 4f shell and which results in the large separation of terbium from gadolinium on elution with ammonium citrate solution occurs again at the half-filling of the 5f shell and results in the large separation of berkelium from curium. The most obvious difference between the lanthanide and actinide elements is the more rapid change in ionic radius and consequent greater differences in rate of elution of the actinides. Thus, although the relative spacing in the triad americium-curium-berkelium is very similar to that of europium-gadolinium-terbium, the separation between adjacent actinides is about 1.2 times that of the analogous rare earths. Using this relation between the actinides and the rare earths, one felt quite confident that the position of elution of element 98 could be predicted quite accurately from the position of dysprosium in relation to terbium. The top half of Fig. 2 shows the relative rates of elution of the rare-earth elements europium, gadolinium, terbium, and dysprosium. This figure was constructed by combining data from several different sources.[4,7-9] Through the use of this information it was predicted that element 98 would be eluted at about 1.4 times the rate of elution of berkelium.

EXPERIMENTAL

With these nuclear and chemical predictions in mind, a bombardment was made in which the chemistry was designed to allow the detection of long-range alpha particles of half-life as short as 20 min. The chemical procedure consisted essentially in dissolving the curium oxide target in 6M HNO_3, adding 200 μg of La^{+3} carrier, and precipitating the lanthanum hydroxide with ammonium hydroxide. Lanthanum hydroxide carries the heavy actinides and many fission products. The hydroxide precipitate was dissolved in 0.5M perchloric acid, adsorbed on a small amount of ammonium-form Dowex-50 cation-exchange resin, and placed on top of a column 2 mm in diameter and 17 cm long packed with the same resin. The eluting agent was ammonium citrate buffered with citric acid to a pH of 3.5 (total citrate concentration 0.25M). In order to decrease the time of separation, the elution was carried out at an elevated temperature of 87°C. The flow rate of the eluting agent was held at one drop (approximately 0.030 cm^3) about every 2 min. In this elution experiment 7.1-Mev alpha particles were found very close to the expected position (drop numbers 24 to 28) of elution of element 98. At this same elution position there were approximately 10^4 alpha disintegrations per minute of Cm^{242} which came from column break through of some of the large amount of activity in the curium elution peak; under these conditions a maximum decontamination factor from curium of about 10^6 can be obtained. The high-energy alpha particles were detected in the presence of the Cm^{242} alpha particles by means of a 48-channel differential pulse analyzer, and decay of these alpha particles was followed by taking successive pulse analyses. The 7.1-Mev alpha particles decayed with a half-life of about 45 min. This single experiment probably offers sufficient evidence for the discovery of element 98. The possible exception to this conclusion is that the activity could conceivably be another isotope of berkelium if the position of elution had been miscalculated, since the Cm^{242} breakthrough prevented the location of the known Bk^{243} activity (formed by deuteron contamination in the alpha-particle beam) at its expected position.

*See W. C. Johnson, L. L. Quill, and F. Daniels[6] for references.

In order to eliminate this latter possibility, in a later bombardment the length of the column was shortened to about 15 cm, and instead of attempting to locate elements 97 and 98 immediately, all the fractions up to and including approximately 10^6 c/m of Cm^{242} were combined. This combined fraction which should have contained element 98 and berkelium, as well as part of the curium, was acidified with hydrochloric acid, readsorbed on a small volume of resin, placed on another column, and eluted again under the same conditions. The results of this elution are shown in Fig. 1. Three distinct peaks, labeled californium, berkelium, and curium, are evident. Pulse analysis of the activity in the californium peak showed the 7.1-Mev alpha particles, and these decayed with a 45-min half-life. The berkelium peak was identified by the 4.6-hr half-life of the electron and electromagnetic radiation and the three characteristic alpha-particle groups[3] of Bk^{243}. The first peak is due to beta-particle-emitting fission product yttrium which would not have been separated up to this point. This elution demonstrates conclusively that the new alpha emitter is not an isotope of berkelium.

ADDITIONAL CHEMICAL EXPERIMENTS

In subsequent bombardments small amounts (approximately 50 c/m) of the new alpha emitter were isolated, and further tracer chemical experiments were performed in order to characterize somewhat more closely its chemical properties. It is interesting to note that the amount of californium (approximately 50 c/m) which it has been possible to produce for these experiments corresponds to only a few thousand atoms of the element. In these experiments the activity was first separated by carrying on lanthanum fluoride and lanthanum hydroxide and by the use of ion-exchange columns as described above. Because of the small amount of activity produced and the short half-life, only a few chemical experiments could be performed after each bombardment. The results of these tracer experiments are given below. In all cases the course of the californium in the experiments was followed by performing pulse analyses for the 7.1-Mev alpha particle.

A small amount of the californium tracer (with 10^4 alpha counts per minute Cm^{242}) was placed on a cation-exchange column packed with hydrogen-form Dowex-50 resin and eluted with 13M hydrochloric acid solution. The californium was eluted at essentially the same position as the curium, as are the other heavy actinides,[4,10] americium and berkelium, and well ahead of the rare-earth elements.

Several attempts were made to oxidize Cf(III) to a higher oxidation state. Carrying with zirconium phosphate was used as a test for oxidation to the Cf(IV) state, and lack of carrying on lanthanum fluoride was used as a test for Cf(VI), on the basis of analogy with the behavior of other actinide elements in tracer experiments.

Experiments performed after oxidation with 0.2M ammonium persulfate for 10 min at 70°C in a solution 1M in nitric acid and 0.2M in sulfate showed less than 10 per cent carrying on zirconium phosphate and greater than 80 per cent carrying on lanthanum fluoride precipitated by adding La^{+3} and making the supernatant 1M in hydrofluoric acid.

Similar experiments after oxidation with sodium bismuthate for 5 min at 60°C in 5M nitric acid also showed less than 10 per cent carrying on zirconium phosphate and greater than 80 per cent carrying on lanthanum fluoride from the supernatant made 3M in hydrochloric acid.

Although the uncertainties in the tracer experiments are largely due to the small amount of californium available, it can be concluded that the oxidation of Cf(III) to the Cf(IV) or Cf(VI) states in aqueous solution even with these strong oxidizing agents is not possible or that the oxidation is slow.

DISCUSSION

The chemical properties of californium all indicate that it fits in well as the ninth actinide element. Perhaps the best evidence for this is a comparison of the relative rates of elution with ammonium citrate of the actinide elements californium-berkelium-curium-americium and their rare-earth homologs dysprosium-terbium-gadolinium-europium. To facilitate this comparison the elution data for the rare earths and actinides are plotted together in Fig. 2. Here the ordinates are normalized to show equal amounts of activity. The relative spacing for californium, berkelium, curium, and americium were taken

from Fig. 1 and from an elution experiment in which berkelium, curium, and americium were present. The curves for the rare earths were taken from the previously mentioned sources.

A remarkable analogy between these two groups of elements is apparent, indicating that the same sequence of changes in ionic radius is encountered on filling in the 5f electrons as occurs on filling the 4f shell. It seems quite clear that curium represents the midway point in the actinide transition series of elements in view of its position analogous to gadolinium. The most obvious difference between the two groups is the larger magnitude of the contraction found in the actinides. That this should be the case is quite reasonable when one considers that the more loosely bound 5f electrons of the actinides would certainly be less effective as shielding electrons.

The experiments with respect to oxidation of californium above the (III) state are incomplete, and further work is necessary in order to establish whether such states can exist in aqueous solution. The difficulty of oxidizing berkelium to the (IV) state[4] indicates that such higher oxidation states may not be expected. However, as the second element beyond the midpoint of this transition series, the possibility of oxidation to a (V) state (CfO_2^+) must be borne in mind, particularly in view of the great stabilizing influence of the two oxygen atoms found in these elements for the MO_2^+ (and Mo_2^{++}) type of ions.

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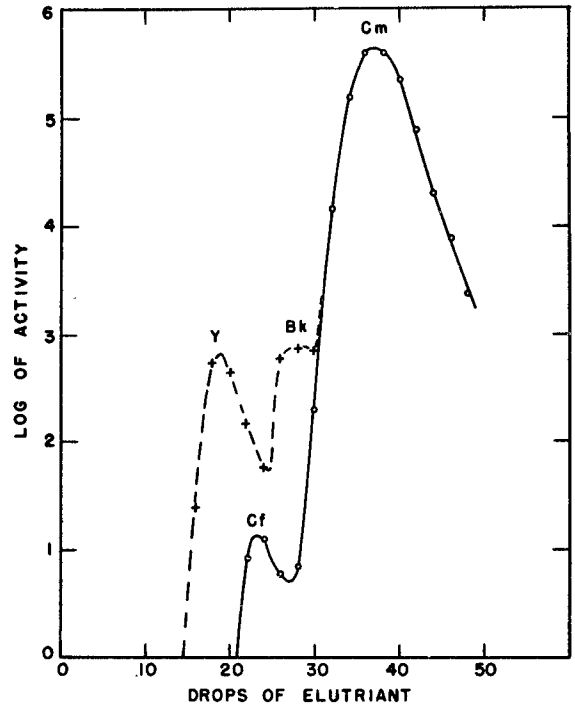

Fig. 1—Elution of combined curium, berkelium, and californium fraction with ammonium citrate. Solid curve indicates alpha-particle counts per minute; dashed curve, Auger and conversion electrons and beta-particles (and alpha-particles).

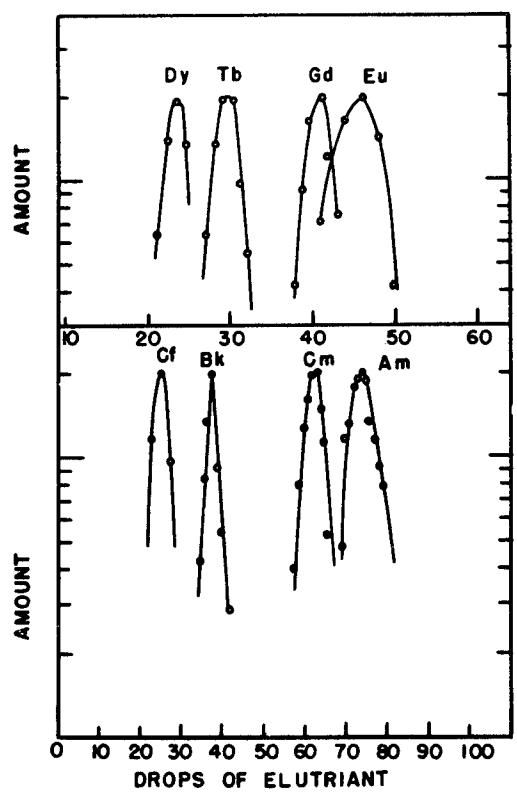

Fig. 2—Comparison of the rates of elution of californium, berkelium, curium, and americium with their homologues dysprosium, terbium, gadolinium, and europium. One free column volume has been subtracted.

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