acetate reagent. From the shade of the spot a suggestion as to the position of hydroxyl groups may be obtained.

Chrysophanol gives a very high Rf-value, whereas emodin, having one more hydroxyl group in the 7-position, gives a lower value and compounds such as endocrocin (emodin-3-carboxylic acid), rhein and aloe-emodin, which have carboxyl or carbinol groups in their molecules, show very little movement. Quinizarin which possesses two hydroxyl groups in the 1,4-positions moves relatively more easily than emodin; alizarin, containing 1,2-hydroxyl groups in its molecule, gives a very low rate of movement. Methylation of the hydroxyl in the 7-position of emodin shifted its spot toward that of crysophanol.

Estimation of the purgative anthraquinone crude drugs by this method is now in progress.

PHARMACEUTICAL INSTITUTE
MEDICAL FACULTY
UNIVERSITY OF TOKYO

RECEIVED DECEMBER 7, 1949

The Separation of Americium and Curium from the Rare Earth Elements

BY KENNETH STREET, JR., AND GLENN T. SEABORG

Introduction

In connection with the general problem of determining the nuclear and chemical properties of the elements americium and curium, it is very desirable to have fast and efficient methods of isolating them from the other elements. The separation of americium and curium from the rare earth elements presents one of the most difficult problems encountered in this work, and consequently considerable time has been devoted to achieving a satisfactory separation procedure.

As is the case for the rare earth elements, the only thermodynamically stable oxidation state of americium and curium in aqueous solution is the tripositive; and since their crystal radii overlap those of the light rare earth elements, being about the same as neodymium, the solubilities of their compounds are very similar to those of the rare earths. The only reasonably satisfactory group separation of americium and curium from the rare earths known when the present work was undertaken was the procedure known as "the fluosilicate precipitation."[1,2] This procedure, which involves partial precipitation of lanthanum fluoride carrier, has the serious drawback of only giving fractionation of the lanthanides and actinides and hence requires numerous repetitions of a relatively low yield step to achieve even a moderately satisfactory separation.

For many of the nuclear experiments contemplated a good yield and a very complete separation of americium and curium from rare earth fission products and from each other was necessary, but because of the relatively long half-lives of the isotopes involved, time was not a major consideration. For work with isotopes of short half-life a method which would give a very rapid and complete separation from the rare earths and some fractionation of americium and curium had to be found. Because a promising method of attack was at hand, a solution to the first problem was sought first, and very fortunately in the course of its solution the direction of a satisfactory solution to the second problem was indicated.

The very successful separation of the rare earth elements from each other by selective elution from columns of cation exchange resins with ammonium citrate solutions[3] led Cunningham and co-workers[4] to try this method for the separation of americium and curium with equally good results. Because of this success the elution with citrate was taken as a starting point for further investigation.

Experimental

In order to establish the elution behavior of americium and curium and the rare earth elements under our experimental conditions a run was made at room temperature using 0.25 *M* citric acid solution adjusted to *p*H 3.05 with concentrated ammonium hydroxide. The elution curve is shown in Fig. 1.

In this experiment and all those described below tracer amounts were used and the isotopes employed, namely, Am^{241}, Cm^{242}, Ce^{144}, Pm^{147} and Lu^{172}, were identified by their radiation characteristics. In this and the following figures the ordinate is given as counts per minute per drop, where the counting was done with a Geiger counter for all except americium and curium whose alpha particles were counted. The data are given in this direct manner since in tracer experiments of this type the relative amounts are unimportant and no purpose is served by calculating the number of atoms on an absolute basis through the use of the half-lives and counting efficiencies of the isotopes concerned. The abscissas are given in arbitrary units since the actual volume of solution necessary to elute a given element will vary with the particular "batch" of resin used as well as with the column size. With our resin and columns 1 unit is about 0.030 cc. It will be noted that americium is eluted at the same rate as promethium so that separation from this fission product is not obtained by this method.

There was no *a priori* reason to believe that equally good separation of americium and curium could not be effected with eluting solutions other than ammonium citrate. In addition the possibility existed that due to more subtle differences between the actinides and the rare earth elements, the relative rate of elution of americium and curium with respect to the rare earths might be shifted so that with a different eluting solution a rare earth other than promethium would be eluted at the same rate as americium. Thus, although the time required might be long, a complete decontamination of americium and curium from the rare earths might be effected by eluting with one solution and then placing the material on another column and eluting with a different solution.

---

[1] S. G. Thompson, R. A. James, L. O. Morgan and I. Perlman, National Nuclear Energy Series, Plutonium Project Record, Vol. 14B, "The Transuranium Elements: Research Papers," Paper No. 19.1 (McGraw-Hill Book Co., Inc., New York, N. Y., 1949).

[2] R. A. James, Ph.D. Thesis, University of California, 1948.

[3] The history of the development of ion exchange separations of the rare earth elements within the Manhattan Project is given by W. C. Johnson, L. L. Quill and F. Daniels, *Chem. Eng. News*, **25**, 2494 (1947).

[4] B. B. Cunningham, E. R. Tompkins and L. B. Asprey, unpublished work.

Elution with 0.25 M ammonium citrate (pH 3.0).

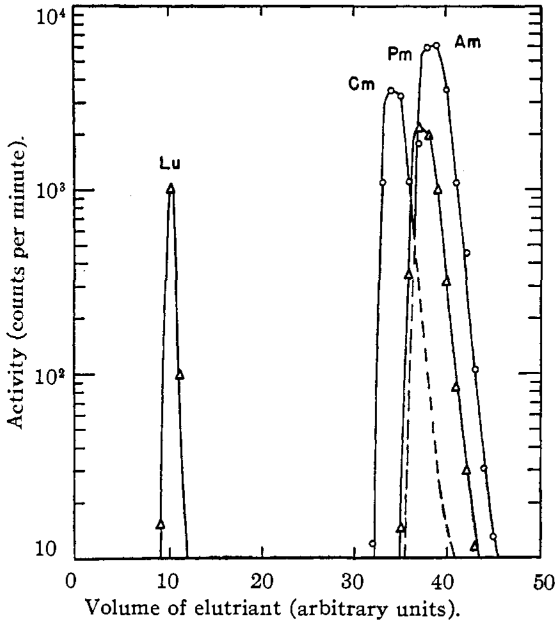

Fig. 1.—Elution of Am, Cm, Lu and Pm tracers with 0.25 M citric acid solution adjusted to pH 3.05 with ammonium hydroxide. The column used was 1 mm. in diameter, 10 cm. long, and packed with colloidal agglomerates of Dowex-50 cation exchange resin (ammonium form).

With this in mind a series of column experiments was run in order to test various eluting solutions. The columns (10 cm. long and 1 mm. diameter) were packed with colloidal agglomerates of "Dowex-50" cation exchange resin (hydrogen form) wet graded to settle at *ca.* 0.5 cm./min. The runs were made at room temperature and at flow rates of *ca.* 0.3 ml./sq. cm./min. A solution of the tracers in 0.1 M hydrochloric acid was placed in contact with a small amount of resin until the activity was essentially all on the resin, then the resin was placed on the column bed and eluted with the desired solution.

Elution with 6 M HCl.

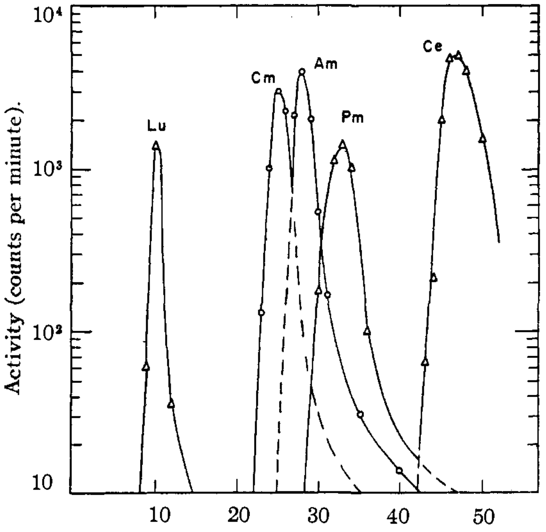

Fig. 2.—Elution of Am, Cm, Lu, Pm and Ce tracers with 6 M hydrochloric acid. The column used was the same as in Fig. 1.

Elution with 9 M HCl.

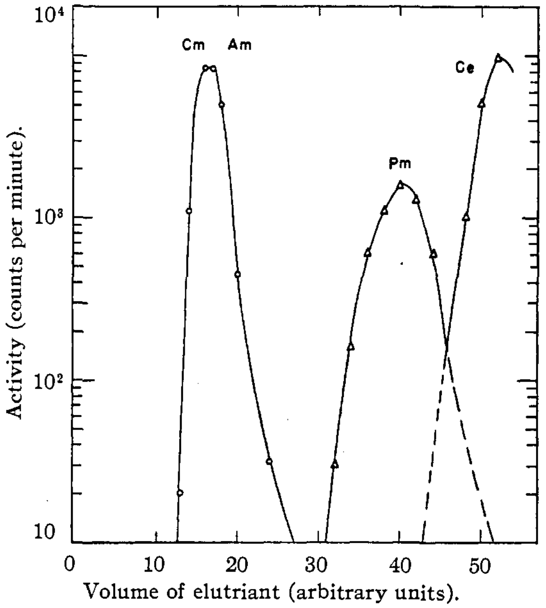

Fig. 3.—Elution of Am, Cm, Pm and Ce with 9 M hydrochloric acid. The column used was the same as in Fig. 1.

Elution with 13.3 M HCl.

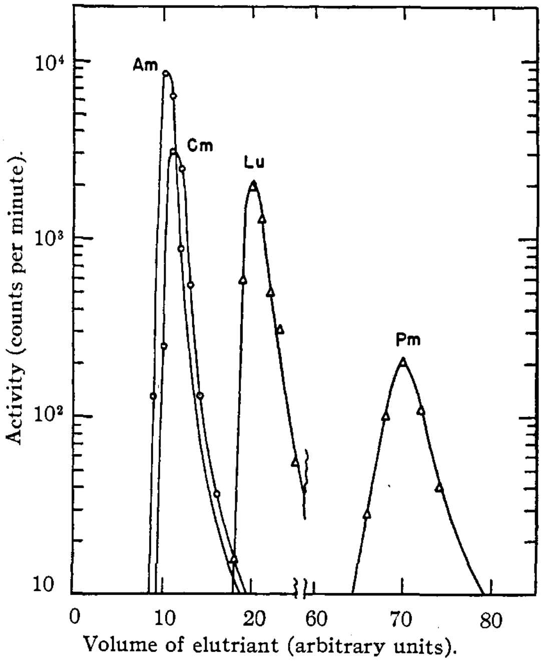

Fig. 4.—Elution of Am, Cm, Lu and Pm with 13.3 M hydrochloric acid. The column used was the same as in Fig. 1.

Experiments were performed in which eluting solutions such as 2 M ammonium nitrate and various concentrations of hydrochloric acid, hydrobromic acid and perchloric acid were employed. With all of these eluting agents the separation of tracer amounts of americium and curium is essentially the same as with citrate. Figure 2 shows an elution with 6 *M* hydrochloric acid run with the same column as that used for the citrate run whose results are shown in Fig. 1. It is apparent that there has been a shift in the relative rate of elution of the two actinide elements with respect to the rare earths. Elution with solutions of still higher hydrochloric acid concentration shows the very marked effect of hydrochloric acid concentration on the time of elution of americium and curium with respect to the rare earths. This is illustrated in Figs. 3 and 4 which show elutions with 9 and 13.3 *M* hydrochloric acid, respectively. It will be noted that with 9 *M* hydrochloric acid americium and curium are eluted with the heavy rare earths while with 13.3 *M* hydrochloric acid they have moved out well ahead of all the rare earths.

Examination of Figs. 2, 3 and 4 will also reveal another striking fact. It will be noted that with 6 *M* hydrochloric acid americium and curium are eluted in their normal order, that is, curium is eluted before americium in the order that would be predicted from the size of their ions and the order of elution of the rare earths. In 9 *M* hydrochloric acid the americium and curium are eluted together while in 13.3 *M* hydrochloric acid the order of elution is reversed, the americium coming off slightly ahead of the curium while the rare earths maintain their normal order throughout the whole range of hydrochloric acid concentrations.

Discussion of Results

The effects found were of a much greater magnitude than anything anticipated when the experiments were undertaken. Thus a single elution with 13.3 *M* hydrochloric acid separates americium and curium from all the rare earth elements. The relatively large differences in the rate of elution of americium and curium and the first rare earth element makes rapid elution possible. By using columns 5 cm. long and flow rates of 2 ml./sq. cm./min. a separated americium–curium fraction can be obtained in about twenty minutes. Although the separation of curium from americium is not good, some fractionation does occur and this is very useful in attempting to identify short-lived isotopes of these elements.

In addition to the very useful nature of this result as an analytical tool, the anomalous behavior of americium and curium suggests some very interesting speculation in regard to its explanation.

On elution with solutions of hydrochloric acid of increasing concentration, americium and curium behave as though at high hydrochloric acid concentration there are on the average several more chloride ions in the complex ions involving americium and curium than in those of the rare earth elements. In view of the similarity in size and charge of the americium and curium and the rare earth ions, this suggests that in addition to the interactions which the rare earths show with chloride ion perhaps americium and curium form weak covalent coördination complexes involving large numbers (say 6) of chloride ions.

One of the most obvious differences between the actinide and the lanthanide elements is the relative stability of the f orbitals. Thus in the actinide transition series the 5f have probably just become stable with respect to the 6d orbitals at uranium and are only a little more stable at americium and curium. On the other hand, in the rare earth elements the 4f are already quite stable with respect to the 5d orbitals at cerium. This suggests that perhaps the 5f orbitals of some of the actinides can contribute to hybridized covalent bond orbitals, while in the rare earths the very stable and more deeply buried 4f orbitals are not available. Thus if the covalent complex ion of americium were slightly more stable than that of curium, elution with increasing concentrations of hydrochloric acid would result in both americium and curium moving up with respect to the rare earths, but americium moving slightly faster, as is observed to be the case.

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

DEPARTMENT OF CHEMISTRY AND RADIATION LABORATORY
UNIVERSITY OF CALIFORNIA
BERKELEY, CALIF.

RECEIVED APRIL 12, 1950

The Reaction of Tributylacetyl Chloride and Anhydrous Cuprous Cyanide

BY NATHAN SPERBER AND ROSEMARIE FRICANO

As part of a related problem, tributylacetyl cyanide was required as an intermediate. Acyl cyanides have been prepared by the reaction of an acid chloride with anhydrous cuprous cyanide[1] or silver cyanide.[2] When tributylacetyl chloride was treated with dry cuprous cyanide, a product was obtained which contained no nitrogen[3] or chlorine, decolorized bromine water and had a lower boiling point and viscosity than did tributylacetyl chloride. On the basis of the qualitative tests and quantitative analysis, it appeared that rupture of the acyl chloride group occurred at the quaternary carbon with the formation of an olefin. The latter was identified as 5-butylnonene-4 by comparison with an authentic sample prepared[4] by the dehydration of tributylcarbinol. On catalytic reduction, the olefin absorbed one mole of hydrogen to yield 5-butylnonane.[5] In contrast, when trimethylacetyl chloride was refluxed with cuprous cyanide, trimethylacetyl cyanide was isolated.[6]

Experimental

Tributylacetyl Chloride was prepared by the reaction of tributylacetic acid[7] and thionyl chloride; yield 90%, b. p.

---

[1] Tschelinzeff and Schmidt, *Ber.*, **62**, 2210 (1929).

[2] Hüber, *Ann.*, **120**, 330 (1861); Moritz, *J. Chem. Soc.*, **39**, 13 (1881).

[3] In one experiment, the tributylacetyl cyanide was apparently obtained. *Anal.* Calcd. for $C_{15}H_{27}ON$: N, 5.91. Found: N, 6.01. This product could not be obtained in subsequent experiments.

[4] Whitmore and Woodburn, THIS JOURNAL, **55**, 361 (1933); Church, Whitmore and McGrew, *ibid.*, **56**, 176 (1934).

[5] Ivanov, *Bull. soc. chim.*, [4] **37**, 287 (1925).

[6] Trimethylacetyl chloride decomposes in the presence of aluminum chloride to yield carbon dioxide, hydrogen chloride and the olefin polymer (Böeseken, *Rec. trav. chim.*, **29**, 94 (1910). The same reaction occurs when an acyl chloride is passed over heated nickel (Mailhe, *Compt. rend.*, **180**, 111 (1925)).

[7] Whitmore, *et al.*, THIS JOURNAL, **63**, 643 (1941); Sperber, Papa and Schwenk, *ibid.*, **70**, 3091 (1948).